STUDIES OF STRUCTURE AND PROPERTIES OF LIQUID CRYSTALS

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY (SCIENCE) OF THE UNIVERSITY OF NORTH BENGAL.
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This is to certify that the research work reported in this thesis entitled " Studies of structure and properties of liquid crystals" by Mrs. Aparna Nath has been carried out under joint supervision and guidance of myself and Dr. Basana Chaudhury, Lecturer, R. E. College, Silchar. She has fulfilled all the requirements for the Ph.D degree of the University of North Bengal. Some part of the research work presented in this dissertation has been performed in collaboration with others. However, major work has been performed by her and her contribution is very substantial. In character and disposition Mrs. Aparna Nath is fit to submit the thesis for Ph.D degree.

Sukla Paul

(Sukla Paul)

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(Aparna Nath.)

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CHAPTER 1

Introduction

INTRODUCTION :

Anisotropic fluid or liquid crystals are mysterious in their properties and are extremely useful, thus providing scientists and engineers with one of the most active and fascinating fields of scientific and industrial research.

The liquid crystalline state had been discovered in 1888 by Austrian botanist Reinitzer[1,2] and Lehman[3,4,5] while investigating the properties of some easters of cholesterol.The properties of liquid crystalline phases are intermediate between those of crystalline solids and isotropic liquids, so they are referred to as mesophases or mesomorphic phases by Friedel[6,7]. Nowadays thousands of organic chemicals are known to form mesophases[8,9,10]. Few organo-metallic and some inorganic chemicals also show liquid crystalline properties.

Liquid crystals have some-what asymmetric shape of molecules. The molecules in the form of rods are held together by highly anisotropic forces due to dipole and quadrupole interactions. These anisotropic intermolecular forces, taken together with the asymmetric shape of the molecules can give a turbid mobile liquid, exhibiting some degree of long range orientational or translational ordering of the molecules not present in an ordinary isotropic liquid. Many excellent books and review articals on liquid crystals regarding detail molecular structures and physical properties of mesogenic compounds have already been published and only a few of them[11-23] have been listed.

CHARACTERISTICS OF MOLECULES WHICH FORM LIQUID CRYSTALS.

The molecular features of compounds which form thermotropic liquid crystals may be described as follows :

1. The molecules will be long relative to its width.
2. The molecules will have some rigidity along the axis.
3. The molecules may have simultaneous existence of strong dipoles

and easily polarizable groups. The most pronounced liquid crystalline effect is most likely to occur if the strong dipole is on the molecular axis.

4. The molecule may have weak polar groups at its extremities. This property appears to have sub-ordinate importance.

These general characteristics serve only as guide lines and that some molecules without them, or may be only some of them, will form liquid crystal systems.

Along with the architecture of the molecule, one is interested in molecular interactions which produce the liquid crystalline state. Some of these interactions are as follows :

(1) Dipole-dipole interactions.

(2) Ion-dipole interactions.

(3) Induced dipole interactions.

(4) Hydrogen bonding in large molecules.

1. CLASSIFICATION OF LIQUID CRYSTALS.

Liquid crystals can be divided into two distinct types, known as lyotropic and thermotropic liquid crystals.

1.1 Lyotropic mesophase.

The lyotropic liquid crystals[24-30] are prepared by mixing two or more compounds, one of which has a rather large polar character. A typical system of this type is soap and water system where mesomorphic phase appears as a function of either concentration or temperature. In this soap water system, the polar water molecules penetrates between the layers of the polar groups of the soap molecules and accomplish the weakening of the attractive forces between them to cause transition from the solid phase to the liquid crystal phase. This solid - liquid system behaves as a mobile liquid and show many of the anisotropic physical properties chacteristics of the solid phase. However no technical application

of lyotropic system for display devices are known as yet[31]. Since this dissertation is concerned only with thermotropic liquid crystals, I will not discuss this lyotropic phase in detail.

1.2 Thermotropic mesophase :

Thermotropic liquid crystals are those where phase transitions occur due to the change of temperature. Now these thermotropic mesogens are divided into three classes distinguished by their different degrees of orientational and translational orders. Friedel[32] recognized three main classes of thermotropic liquid crystals known as nematic, smectic and cholesteric. A diagrammatic representation of the molecular structure in each of these is shown in figure 1.1.

1.2a Nematic mesophase

The nematic mesophase consists of elongated molecules and have long range orientational order. The centres of the molecules are distributed at random but their long axis tends to be parallel to one particular direction, the director. This phase is uniaxial with respect to all physical properties but a biaxial modification has been discovered recently. It is very easy to deform the aligned nematic liquid crystals by external agents. Nematics are able to translate weak external signals (electrical, magnetic, mechanical) into visible optical effects. This has made them very useful for certain display applications.

X-ray studies[34,35] indicate that some nematics possess a lamellar type of short-range order i.e.,they consists of clusters of molecules called cybotactic groups[36]- the molecular centres in each clusters arranged in layers. The cybotactic nematics may be either normal or skewed depending on the condition whether the molecules in the cybotactic group are arranged orthogonal to or tilted with respect to the layers. Those phases which are neither

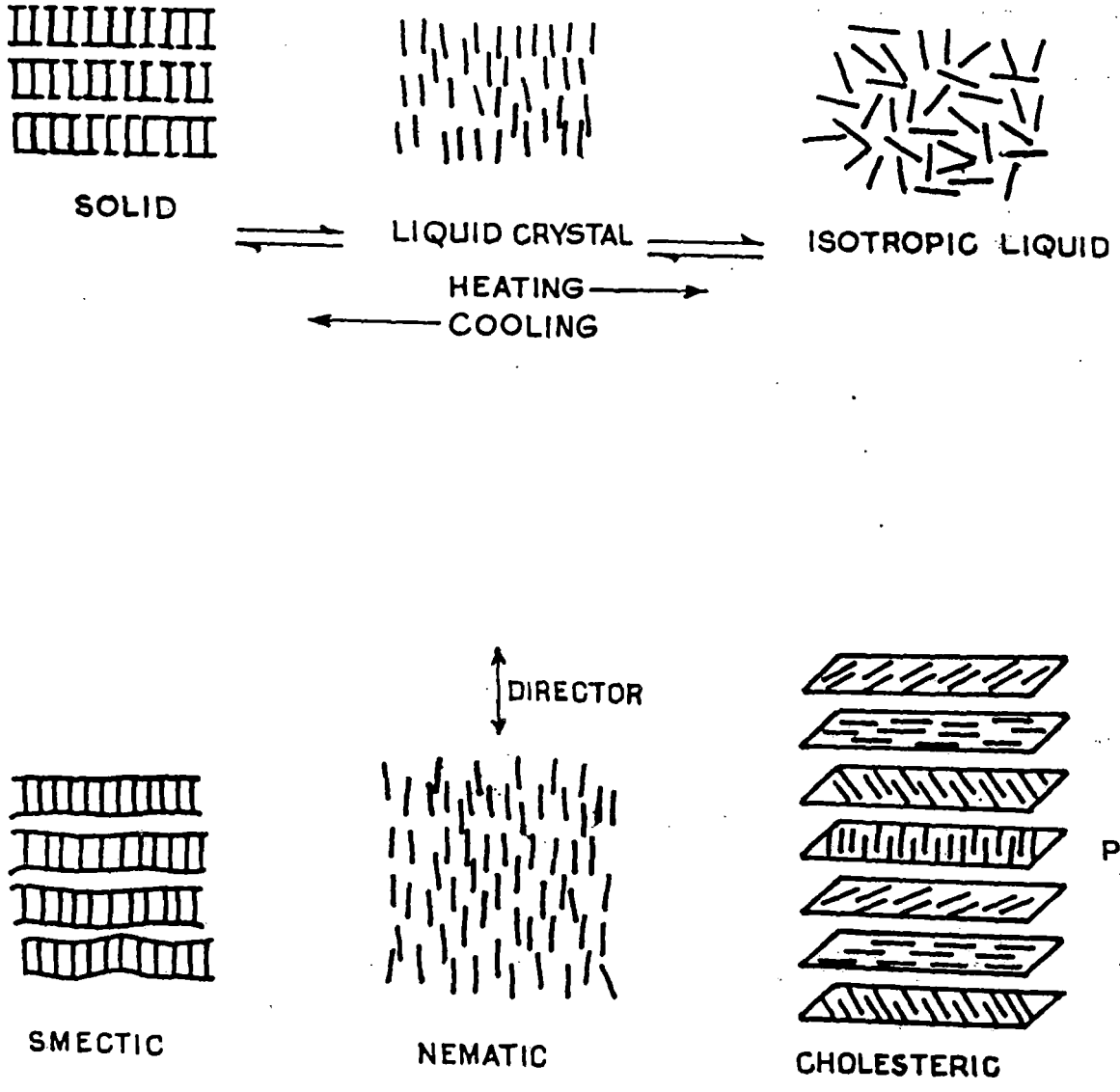


Figure 1.1 : Molecular arrangement in various type of liquid crystals.

distinctly cybotactic nor completly normal nematic, have been placed in a group known as intermediate nematic.

1.2b Cholesteric or chiral nematic phase

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules. Indeed, it can be said that a nematic is simply a cholesteric with an infinite helical pitch. Cholesteric phase has an inherent chirality associated with them. This causes them to pack with a sense of helical twist imparted to the preferred direction of molecular alignment giving rise to a natural repeat or pitch in the structure[37-40] which is characteristic of the pure cholesteric material. Typical values of this natural pitch are in the range 0.2 to 1μm for pure material and many of them exhibit diffraction colours since they selectively reflect one sense of circularly polarised light. Due to this colour effect, cholesterics are used in liquid crystal thermometers. Cholesterics of low pitch less than about 0.5μm exhibit what are known as blue phases. These phases exist over a small temperature range (~1^{o}C) between the liquid crystal phase and the isotropic liquid.

1.2c Smectic mesophase.

The smectic phase represents a higher state of order and have always layer structures. A variety of molecular arrangement is possible within each layer. Molecules may be upright in the layer or may be inclined with respect to the normals to the layers. Some of them have three dimensional long range positional order as in a crystal, while some others, referred to as hexatic phases, have three dimensional long-range "bond orientational" order, but without any long range positional order. The interlayer attractions are weaker than the lateral forces between the molecules and hence the layers can slide over one another thus showing fluid behaviour.

A large number of smectic polymorphs have been indentified[41-50]

S_A, S_B, S_C, S_D, S_E, S_F, S_G, S_H, S_I, S_J, S_K, S_L

The main features of the smectic are presented in table 1.1

TABLE - 1.1

Sm. Phase type	Molecular orientation	Molecular packing	Orientational ordering	Positional ordering	Optical activity
A	Orthogonal	random	short range	short range	uniaxial
C	Tilted	random	short range	short range	biaxial
$B_{(hexatic)}$	Ortho-gonal.	hexagonal	long range	short range	uniaxial
I	Tilt to apex of hexagon	pseudo-hexagonal	long range	short range	biaxial
F	Tilt to side of hexagon	pseudo-hexagonal	long range	short range	uniaxial
$L_{(B\ crys)}$	Orthogonal	hexagonal	long range	long range	uniaxial or biaxial
J (G')	Tilt to apex of hexagon	pseudo-hexagonal	long range	long range	biaxial
G	Tilt to side of hexagon	pseudo-hexagonal	long range	long range	biaxial
E	Orthogonal	Orthorho-mbic.	long range	long range	uniaxial or biaxial
K (H')	Tilted to side a	Monoclinic	long range	long range	biaxial
H	Tilted to side b	Monoclinic	long range	long range	biaxial

The compounds which have been studied by me have mainly nematic phases, except one which has got SmecticA phase over very small range of temperature.

SmecticA phase :

In the classical smecticA, the layer spacing (d) is approximately equal to molecular length (l). However, if the molecules have strong longitudinal dipole moment, there will be near neighbour antiparallel correlations and this can result in subtle changes[51,52] in the structure of smecticA. Recent works[53-59] have revealed that smecticA phase can be subdivided into several distinct phases such as monolayer smectic A_1, bilayer smectic A_2, partially bilayer smectic A_d, and smectic antiphase smectic A. Details regarding this polymorphism on smecticA are given in references[60-68].

1.3 NEW LIQUID CRYSTALLINE PHASES

1.3a. Discotic Phase.

Thermotropic mesomorphism has also been observed[69] in pure compounds consisting of simple disc like molecules and is termed as discotic liquid crystals. Structurally, most of them fall into two distinct categories, the columnar and the nematic. In columnar phase discs are stacked one on top of the other aperiodically to form liquid-like columns, the different columns constituing a two dimensional lattice. A number of variants of this structure have been identified : hexagonal, rectangular, tilted etc. The nematic phase has an orientationally ordered arrangement of the disc without any long range translational order. This phase is optically negative. A cholesteric phase has also been identified. In recent years significant amount of research have been performed with disc like molecules[70-74].

1.3b Re-entrant nematic and injected smectic phase.

Re-entrant nematic phase is a phenomenon first observed by Cladis[75-77] in a binary mixture of two strongly polar cyano-compounds. Over a range of composition, the sequence of transition on the mixture from the isotropic phase was as follows

Iso ———> N ———> SmA ———> N_R ———> Solid

where N stands for the usual nematic and N_R for a second nematic, called the re-entrant nematic phase, which appears at a lower temperature. In certain polar compounds this behaviour is readily induced either by the application of elevated pressure or by making appropriate binary mixtures[78]. Based on the molecular point of view, S. Chandrasekhar[79] has discussed qualitatively the re-entrant phenomenon.

One of the fascinating features of binary liquid crystal mixture is the formation of so-called injected (or induced) smectic phases from components which show only nematic phases in their pure states[80,81]. Induced smectic phases are often formed in binary mixtures of one compound having a strong terminal polar group and another compound having non-polar terminal group. Evidently, dipole-induced dipole interactions play a major part in this phase stabilization. A molecular model of the induced smectic phase has been discussed by de Jeu et al.[82]

1.3c Ferroelectric liquid crystal.

All smectic phases with tilted structure derived from chiral compounds exhibit ferroelectric properties.[83] The seven liquid crystal classes (C, I ,F, G, H, J, and K) are characterised by a tilt between the director and normal to the smectic layer. If additionaly the constituent molecules are optically active, these smectic phases are denoted by C^*, I^*, F^*, G^*, H^*, J^* and K^* and they show ferroelectric properties. By virtue of their symmetry, ferroelectric smectics are piezoelectric (polarization can be

induced by mechanical shear). The study of ferroelectric liquid crystals have become important for their variety of application such as in display devices.

An anti-ferroelectric smectic phase has been identified recently.The structure is expected to have an interlayer herringbone arrangement.

1.3d Polymer liquid crystal.

Thermotropic liquid crystalline phases are also exhibited by some polymers and this is the subject of much recent research nowa -days. The polymeric liquid crystals usually reveal a wider range of mesophase than the corresponding monomeric ones. The polymers show a high thermal resistance and chemical stability. Biphenylcarboxylic esters of polysiloxanes constitute a large group of liquid crystal polymers.

1.4 APLLICATIONS :

Liquid crystals have got a wide range of scientific applications. Nematic and cholesteric liquid crystals have already found wide applications in display devices, as many of their physical properties such as birefringence , optical activity ect. are sensitive to weak external perturbations. The remarkable electro-optic effects have rendered it possible to prepare liquid crystal displays whose main advantage over the other types is that they do not require emission of light and so consume very low power.

Although liquid crystalline materials have been known for 100 years, large scale applications of the materials in the form of electronic displays did not occur until the mid 1970 when compact, attractive calculators and watches with liquid crystal displays (LCD) reached market and soon became household items. The applications for liquid crystal displays are rapidly moving well beyond the early simple watches and calculators to a new level of

sophistication, which is far more demanding and therefore is forcing rapid advances in the technology. Nowadays liquid crystals are used in optical computing, nonlinear optics, decorative and visual arts, spectroscopy , chromatography and others indicating that there is a relatively broad future potential for this technology.

Recently ferro-electric liquid crystals (Sm C^*) have been used for a new generation of fast versatile liquid crystal devices. Polymer dispersed liquid crystals[84] (PDLC) form a relatively new class of materials which are used in many types of displays, switchable windows and other light shutter devices.

1.5 OBJECTIVE AND SCOPE OF THIS WORK.

The subject of liquid crystals has grown enormously to become a fascinating interdisciplinary field of study. A variety of new thermotropic phases have been discovered including over a dozen of different smectic modifications, discotic, biaxial nematics which have opened up new field of research for the condensed matter physicists. Technological advances are also spectacular. In view of these, study of the physical properties of some liquid crystals by different experimental techniques have been undertaken by me.

It is well known that stuctures of the rigid core of liquid crystal molecules strongly affect their physical properties. It has been found that the introduction of a double bond at specific side chain positions also markedly affect the material properties of liquid crystals. I have undertaken the study of six alkenyl liquid crystalline compounds which have nematic phase over a wide range of temperature. Order-parameter determination is very important from both theoretical and technical consideration, because efficiency of liquid crystal material in display devices depends on its order paranmeter values. By means of small-angle x-ray diffraction studies the compounds have been characterised, order parameters

have been determined from aligned samples. Order parameters have also been determined by optical birefringence study.

The investigation of the crystal stucture of mesogenic compounds may provide clues for the formation and stability of liquid crystalline phases. If certain interactions or properties play an important role in the liquid crystalline as well as in the crystalline state, an investigation of the crystal structure may lead to a better understanding of the packing of molecules in the liquid crystalline phase. In view of this I have undertaken the study of crystal structure analysis of some nematogens and successfully solved two crystal structures by direct method.

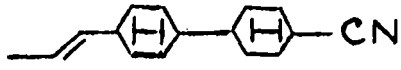
Experimental determination of dipole moments of polar liquid crystalline samples dissolved in non-polar p-xylene solution has been done by me. These experimental values are compared with the dipole moments calculated from atomic charge distribution.

STRUCTURE OF THE LIQUID CRYSTALS STUDIED.

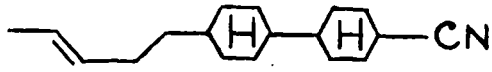
The liquid crystals studied in the present investigations were obtained from Hoffman - La Roche, Bassel , Switzerland as gift. These samples were used fresh from the package without further purification.

A list of the liquid crystals and their structural formula is given below :

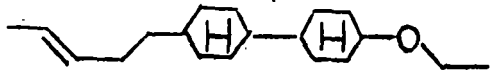
(1) $C_3H_5-C_6H_{10}-C_6H_{10}-CN$



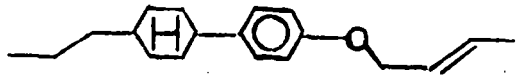
(2) $C_5H_9-C_6H_{10}-C_6H_{10}-CN$



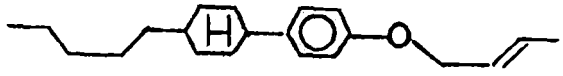
(3) $C_5H_9-C_6H_{10}-C_6H_{10}-OC_2H_5$



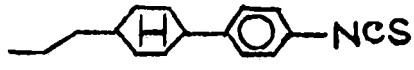
(4) $C_3H_7-C_6H_{10}-C_6H_6-OC_4H_7$



(5) $C_5H_{11}-C_6H_{10}-C_6H_6-OC_4H_7$



(6) $C_3H_7-C_6H_{10}-C_6H_6-NCS$



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CHAPTER 2

Determination of crystal structures by x-ray diffraction methods: Theoretical backgrounds and experimental technique.

2.1. INTRODUCTION.

The structure determination of the crystalline state seems to be one way to obtain general information about conformation and packing of the molecules in the crystalline state. The interactions as well as the steric conditions, which are menifested in the crystal structure can sometimes explain the formation of the LC states as temperature changes.

A large scale of systematic investigation is needed to obtain detailed knowledge in this field of liquid crystal research. Although in the past 15 years, a large number of papers are published on this subject, the available data are not yet sufficient for the derivation of general ideas or laws. A prelimimary survey of the present knowledge of the solid-mesophase relationships has been given by Bryan[1]. The transformation from the solid to the nematic phase is characterised by the breakdown of the positional order of the molecules but not of the orientational order. But Leadbetter[2] has, however, pointed out that although this is true of at least the majority of the cases so far known, it is a generalisation which must at this stage be treated with caution. Hence we find it very promising to undertake the project of determining the crystal and molecular structure of a number of alkenyl nematogenic compounds, the properties of which have been studied in liquid crystalline phase. I have successfully solved two structures. One of the structures have already been published[3] in MCLC and the other one is communicated.

2.2. X-RAY DIFFRACTION BY CRYSTALS.

In the analysis of crystal structures by x-ray diffraction, the dimensions of the unit cell are determined by observing the positions and intensities of the diffraction maxima. To locate the positions of individual atoms in the unit cell, the intensities must be measured and analysed. Most important equation relating the

positions of the atoms to the structure factor is given by,

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp 2\pi i \, (hx_j + ky_j + lz_j) \qquad (2.1)$$

Where f_j is the scattering factor or form factor of the j^{th} atom and x_j , y_j and z_j are the fractional co-ordinates of the j^{th} atom in a unit cell containing N atoms. The observable quantity I is proportional to $|F|^2$.

Now the atoms in the unit cell are the positions of the high electron density $\rho(x,y,z)$, so $\bar{F}_{hkl}$ can be expressed as

$$\bar{F}_{hkl} = \int_V \rho \, (x,y,z) \exp 2\pi i \, (hx + ky + lz) dv \qquad (2.2)$$

where V is the volume of the unit cell. Then by Fourier transform we have ,

$$\rho \, (x, y, z,) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp -2\pi i \, (hx + ky + lz) \qquad (2.3)$$

We could have directly derived the crystal structure by making a Fourier summation, if F_{hkl} values could be determined from diffraction experiment. From experiments we can have structure amplitude $|F_{hkl}|$, but not the phases and this lack of information constitutes the phase problem in crystallography.

In general there are four methods to overcome the phase problem, e.g. (1) Patterson function, (2) Direct method, (3) Isomorphous replacement technique and (4) Anomalous scattering method.

Since we have determined the structure of two compounds using Direct methods, only this method will be described in detail.

2.3 INTENSITY DATA COLLECTION

All the intensity data have been collected with an ENRAF - NONIUS CAD4 automatic single crystal diffractometer using CuK_α radiation monocromated by a graphite monochromator. The intensity data is collected by $\omega - 2\theta$ scan mode. The measured value of the intensity is given by,

$$I_{raw} = \frac{A}{n} (C - R.B) \qquad (2.4)$$

where A = attenuation factor (26.55 for CuK_α).

n = an integer varying from 8 to 24 as mentioned earlier.

C = Total count.

R = Ratio of scan time to background counting time.

B = Total background count.

The standard deviation $\sigma(I)$ calculated on the basis of counting statistics is given by

$$\sigma(I_{raw}) = \frac{20.166}{n} A (C + R^2 B)^{1/2} \qquad (2.5)$$

2.4 Intensity Data Reduction

The relationship between $|F_o|$ and $I^{1/2}$ depends on a number of factors, primarily geometric which relates to the individual reflection and to the apparatus used to measure the intensity. The proportionality can be written as

$$|F_{(hkl)}| = \left(\frac{KI_{hkl}}{L_p}\right)^{1/2} \qquad (2.6)$$

K is called the scale factor, which is normally constant for a given set of measurements and is usually obtained at a later stage.

In our case the incident beam is partially polarized during monochromatization by reflection from the basal plane of a graphite crystal and P takes the form,

$$P_{hkl} = P_{erf}\frac{\cos^2 2\theta_m + \cos^2 2\theta_{hkl}}{1 + \cos^2 2\theta_m} + (1 - P_{erf})\frac{\cos^2 2\theta_m + \cos^2 2\theta_m}{1 + \cos^2 2\theta_m}$$

---- (2.7)

Where P_{erf} = Constant depending on the crystal used in the monochromator (0.5 in our experiment).

θ_m = Bragg angle of reflection from the monochromator crystal.

The Lorentz factor[4-6] L depends on the precise measurement technique used and for our diffraction data it is given by,

$$L_{hkl} = \frac{1}{\sin 2\theta_{hkl}} \qquad (2.8)$$

Temperature Factor

It has been shown theoretically and practically that the change in scattering power of the atoms in a crystal due to thermal vibrations can be given by the expression,

$$f_o^{-B(\sin^2\theta)/\lambda^2}$$

where B is related to the mean-square amplitude ($\bar{u}^2$) of atomic vibration by,

$$B = 8\pi\bar{u}^2$$

By using the method introduced by A.G.C. Wilson[7] one can obtain an overall value of B and at the same time, places all the observed intensities on an approximately absolute basis.

Wilson showed that average absolute structure factor depends only on what is in the cell and not where the atoms are located and hence for a random distribution of N atoms in the unit cell,

$$\langle |F|^2 \rangle = \sum_{j=1} f_j^2 \qquad (2.9)$$

Dividing entire reciprocal space observed into annular zones of equal S^2 ($S = \sin\theta/\lambda$), $\langle|F_{obs}|^2\rangle$ is determined for each of them and $\sum_{j=1}^{N} f^2_{obs}(S_{mid})$ is calculated using the mean value of S^2 for each zone. Since $|F_{obs}|^2$ is usually known on an arbitrary scale, we may write

$$\langle|F_{obs}|^2\rangle = K \langle|F|^2\rangle \qquad (2.10)$$

where $\langle|F|\rangle$ is the average absolute structure factor. To separate out thermal motion in the crystal, we write,

$$\langle|F|\rangle^2 = \sum_{j=1}^{N} f_j^2 = \sum_{j=1}^{N} f_{oj}^2 \exp(-2B_j S^2) \qquad (2.11)$$

Assuming B same for all atoms,

$$\langle|F|^2\rangle = \exp(-2BS^2) \sum_{j=1}^{N} f_{oj}^2 \qquad (2.12)$$

Substituing the equation (2.12) in equation (2.10) we get,

$$\langle|F_{obs}|^2\rangle = K \exp(-2BS^2) \sum_{j=1}^{N} f_{oj}^2$$

$$\ln \frac{\langle|F_{obs}|^2\rangle}{\sum_{j=1}^{N} f_{oj}^2} = \ln K - \frac{2B\sin^2\theta}{\lambda^2} \qquad (2.13)$$

The plot of $\ln\langle|F_{obs}|^2\rangle / \sum_{j=1}^{N} f_{oj}^2$ against $\sin^2\theta/\lambda^2$ called the wilson plot is, therefore, a straight line except for the scattering due

to experimental errors and furnishes us with intercept of ln K and a slope of -2B.

When instead of random distribution of atoms, groups of atoms with known geometry (such as benzene ring) are present in the structure, they may be included in the expression for average intensity even knowing nothing about their positions and orientations. When G groups of known geometry are present, the K^{th} of which contains M_k atoms, we may write using the scattering formula of Debye[8],

$$\langle |F|^2 \rangle = \sum_{k=1}^{G} \sum_{i=1}^{M_k} \sum_{j=1}^{M_G} f_i f_j \frac{\sin 2\pi r_{ij} S}{2\pi r_{ij} S} + \sum_{j=1}^{N} f_j^2 \qquad (2.14)$$

Where r_{ij} is the distance between the i^{th} and j^{th} atoms of the k^{th} group and $S = S_{mid}$ as before. The plot in this case is known as Debye plot and gives a better straight line fit for obtaining B and K.

It is often advantageous to use a k-curve. For this purpose, $K(S_{mid})$ is computed for each zone of S^2 mentioned above, as

$$K(S_{mid}) = \frac{\sum \varepsilon \sum_{j=1}^{N} f_{oj}(S)}{\sum |F_o|^2 (S)} \qquad (2.15)$$

where ε is a small integer depending on the space group[9]. A least squares procedure is used to fit a best smooth analytical function usually $\ln K = A + B^c$ to experimental points. When c = 2.0, the curve is the same as Wilson's plot.

After scaling the data and estimating the temperature factors we try to postulate a trial structure by direct methods.

2.5 DETERMINATION OF TRIAL STRUCTURE BY DIRECT METHOD.

The crystal structure of relatively small molecules of up to 100 independent atoms are readily determined from the diffraction intensities by means of Direct-Method techniques.[10-14]

From a diffraction experiment it is possible to derive the amplitude of a complex quantity, the structure factor, which may be written as,

$$F(\bar{h}) = |F(\bar{h})| \exp\{i\phi(\bar{h})\} \qquad (2.16)$$

If the positions of the atoms in the unit cell were known then the values of the structure factors could be found from,

$$F(\bar{h}) = \sum_{j=1}^{N} f_j \exp 2\pi i \bar{h}.r_j \qquad (2.17)$$

where f_j is the scattering factor for the j^{th} atom. The problem in structural crystallography is that of finding the atomic positions when usual experiments only give $|F_{\bar{h}}|$. If stucture factors were known in both amplitude and phase then the electron density could be calculated at all points of the unit cell from ,

$$\rho(\bar{r}) = 1/v \sum_{h} |F(\bar{h})| \mathrm{Cos}(2\pi \bar{h}.\bar{r} - \phi_h) \qquad (2.18)$$

Direct methods of solving crystal structures are those methods which attempt to find the phases directly by mathematical processes from the measured x-ray intensities.

2.6 Unitary and Normalised Structure Factors

For direct methods it is an advantage to work with unitary structure factors for which the fall off with increasing scattering angle has been removed. The unitary structure factor is defined as,

$$U(\bar{h}) = \frac{F(\bar{h})}{\sum_{j=1}^{N} f_j} \quad \text{so that } |U(h)| \leq 1$$

Writing the unitary scattering factor as

$$n_j = \frac{f_j}{\sum_{j=1}^{N} f_j}$$

We may write,

$$U(\bar{h}) = \sum_{j=1}^{N} n_j \exp 2\pi i \, (\bar{h}.\bar{r}_j) \qquad (2.19)$$

Another corrected structure factor of great theoretical importance is the normalized structure factor given by,

$$|E(\bar{h})|^2 = \frac{|F(\bar{h})|^2}{\varepsilon(h) \sum_{j=1}^{N} f_j^2}$$

Where $\varepsilon(h)$ takes into account the effect of space group symmetry. Now if f be the common shape for all atoms then $f_j = Z_j f$.

$$E(\bar{h}) = \varepsilon(\bar{h})^{-1/2} \frac{F(\bar{h})}{\left(\sum_{j=1}^{N} Z_j^2 f^2\right)^{1/2}} = \varepsilon(\bar{h})^{-1/2} \sum_{j=1}^{N} \left(\frac{Z_j}{\sigma_2^{1/2}}\right) \exp 2\pi i (\bar{h}.r_j)$$

----(2.20)

where $\sigma_m = \sum Z_j^m$. $E(\bar{h})$ is called the normalised structure factors because of its property $\langle |E(h)|^2 \rangle = 1$. This relationship shows

that the average of E^2 can be carried out regardless of θ. The same is not true, however, of either $|F(h)|^2$ or $|U(h)|^2$ and this simplification is one of the main reasons why E's are preferred for use in direct method.

2.7 SOME RELATIONS INVOLVING THE MAGNITUDES AND THE PHASES.

Harker-Kasper Inequalities.

In 1948 Harker and Kasper[15] using Cauchy inequality relation derived the following inequality relation between magnitudes and phases of unitary structure factors,

$$U(\bar{h})^2 \leq 1/2\ [1 + U(2\bar{h})] \qquad (2.21)$$

If we denote the sign of $U(\bar{h})$ by $S(\bar{h})$ which can have the values either +1 or -1, then this relationship can be written as

$$S(\bar{h})\ S(\bar{h}')\ S(\bar{h} + \bar{h}') = 1 \qquad (2.22)$$

A development made by Karle and Hauptman[16] in the form of an inequality does depend on the non-negativity of electron density. For a centro-symmetric structure where $U(\bar{h}) = U(-\bar{h})$ gives,

$$1 - U(\bar{h})^2 - U(\bar{k})^2 - U(\bar{h}-\bar{k})^2 + 2U(\bar{h})U(\bar{k})U(\bar{h}-\bar{k}) \geq 0$$

from which, if the U's are sufficiently large, it may be shown that,

$$S(\bar{h})\ S(\bar{k})\ S(\bar{h} - \bar{K}) = 1 \qquad (2.23)$$

A significant step in the development of direct methods was done by Sayre[17].

The electron density is given by the summation,

$$\rho(\bar{r}) = 1/v \sum_{\bar{h}} F(\bar{h}) \exp -2\pi i(\bar{h}.\bar{r})$$

and we may write,

$$\rho(\bar{r})^2 = 1/v \sum_{\bar{h}} G(\bar{h}) \exp -2\pi i(\bar{h}.\bar{r}) \qquad (2.24)$$

where $G(\bar{h})$ is the Fourier coefficient of the squared density.

If the structure consists of equal resolved atoms, then both $\rho(\bar{r})$ and $\rho(\bar{r})^2$ will show equal resolved peaks. If the scattering factors of the squared atoms is represented by g and that of the normal atoms by f then,

$$F(\bar{h}) = \frac{f}{gv} \sum_{h} F(\bar{h}') F(\bar{h} - \bar{h}') \qquad (2.25)$$

This is Sayre's equation, and is an exact relation-ship between structure factors for equal and resolved atoms.

For a centro-symmetric structure it might be assumed that a large product on the right hand side of equation (2.25) was likely to have the same sign as $F(\bar{h})$. This leads to the relation-ship that for large structure factors

$$S(\bar{h})\ S(\bar{h}')\ S(\bar{h} - \bar{h}') = +1 \qquad (2.26)$$

This was the sign relationship given in the papers by Cochran[18] and Zachariason[19]. Expression for probability of equation(23) was given Cochran and Woolfson[20]. This is for an equal atom structure.

For non-centrosymmetric crystals, the main phase determining formula are the sum of angles formula,

$$\phi_3(\bar{h},\bar{k}) = \phi(\bar{h}) - \phi(\bar{k}) - \phi(\bar{h} - \bar{k}) = 0 \quad (\text{modulo } 2\pi) \qquad (2.27)$$

and the tangent formula,

$$\tan\phi(\bar{h}) = \frac{\sum_{k} K(\bar{h},\bar{k})\ \text{Sin}\ [\phi\ (\bar{h}-\bar{k}) + \phi\ (\bar{k})]}{\sum_{k} K(\bar{h},\bar{k})\ \text{Cos}\ [\phi\ (\bar{h}-\bar{k}) + \phi\ (\bar{k})]} \qquad (2.28)$$

Structure Invariant and Semi-Invariant.

A structure invariant is defined as a quantity which is independent of the choice of origin in the unit cell.

The intensities of reflections, $|F(\bar{h})|^2$s are structure invariants. However, the structure factor itself is not structure invariant, otherwise the phase problem would not exist in crystallography. The structure factor $F(\bar{h})$ is given by,

$$F(\bar{h}) = |F(\bar{h})| \exp i\phi(\bar{h}) = \sum_{j=1}^{N} f_j \exp 2\pi i (\bar{h}.\bar{r}_j) \qquad (2.29)$$

With shift Δr of the origin, the equation(2.29) changes to

$$F'(\bar{h}) = \sum f_j \exp 2\pi i [\bar{h}. (\bar{r}_j - \Delta\bar{r})$$

$$= |F(\bar{h})| \exp -2\pi i (\bar{h}.\Delta\bar{r}) \exp i\phi(\bar{h}) \qquad (2.30)$$

Thus we see that the phase changes by $-2\pi i(\bar{h}.\Delta\bar{r})$ while the amplitude is invariant.

In a similar way it can be shown that $|F(h)|^2$ is structure invariant.

Individual phases depends on the structure and choice of origin, some combinations of them is a structure is a structure invariant. For example if $h_1 + h_2 + h_3 = 0$, then $\phi(h_1) + \phi(h_2) + \phi(h_3)$ is a structure invariant for every space group. It follows directly from the fact that $F(\bar{h})\ F(\bar{k})\ F(-\bar{h}-\bar{k})$ is an invariant,

$$F'(\bar{h})F'(\bar{k})F'(-\bar{h}-\bar{k}) = F(\bar{h}) \exp -2\pi i(\bar{h}.\Delta\bar{r})\ F(\bar{k}) \exp -2\pi i(\bar{k}.\Delta\bar{r}).$$
$$F(-\bar{h}-\bar{k}) \exp 2\pi i[(\bar{h}.\Delta\bar{r})+(\bar{k}.\Delta\bar{r})]$$
$$= F(\bar{h})\ F(\bar{k})\ F(-\bar{h}-\bar{k}) \qquad (2.31)$$

Since the moduli of the structure factors are invariant themselves, the angular part of $F(h)\ F(k)\ F(-h-k)$ is also an

invariant i.e.. $\phi(h) + \phi(k) + \phi(-h-k)$ is an invariant or $\phi_3 = \phi(h) + \phi(k) + \phi(-h-k)$ is an invariant.

Knowledge of the actual values of ϕ_3 or reliable estimates of ϕ_3 would strengthen direct method procedures enormously. Direct methods mostly use $|\phi_3| = 0$ for large values of $E_3 = N - 1/2|E(h)\ E(k)\ E(-h-k)|$.

The quartet structure invariant relationship is given by

$$\phi_4 = \phi_H + \phi_K + \phi_L + \phi_{-H-K-L} \qquad (2.32)$$

The value of ϕ_4 is not only dependent on $E_4 = N^{-1}|E_H E_K E_L E_{-H-K-L}|$ but also on the cross term $|E_{H+K}|, |E_{H+L}|$ and $|E_{K+L}|$. In case the cross terms are large $\phi_4 = 0$.

The structure semi-invariants are quantities which do not change value by transfer from one special origin to another. The structure semi-invariants originate from space group symmetry. In any space - group any structure invariant is also a structure semi-invariant, but in general the converse is not true. A complete theory concerning this subject is given in a series of papers by Hauptman and Karle[21-23] and by Schenk[24,25].

We have solved crystal structures of two different compounds. The first one belongs to centro-symmetric space group and its structure was determined by using the program SIMPEL. The program SIMPEL estimates phases using symbolic addition procedure. It is a complete direct method system, which may enter with $|F|$ and may produce an E-map of the structures. The unique part of SIMPEL is formed by a series of routines, successively gathering the relationships and determining a starting set, carrying out a symbolic addition, finding the correct numerical values for the symbols and finally executing a numerical phase extension and refinement.

The symbolic-addition method starts with collecting n phase relationships for m unknown phases where $m << n$. Then origin

defining phases are selected and a number of other unknown phases is given a symbolic phase. These starting reflections are choosen such, that in principle all other phases can be reached from this set via the phase relationship. Then a phase propagation is carried out, using throughout the symbolic phases. With the extended phase set as basis, the numerical values of the symbols are then determined through Figures of Merit. In most cases an additional tangent extension is carried out, folowed by a Fourier summation, which is expected to show the structures.

2.8 Starting Set Determination.

The determination of the starting set begins with a convergence procedure similar to that deviced by Germain, Main and Woolfson[26]. This procedure searches for that reflection which is the weakest linked to the other reflections by means of the phase relations and then this reflection is removed from the set of reflections. At the same time all its phase relations are removed from the collection of phase relationships. This process is repeated until no reflections are left in the set. Any time the reflection is removed without having phase relationships linking it with other phases, this reflection has taken to be starting set. Since a starting set reflections with large $|E|$ are preferred, the use of triplets and quartets generally leads to very good starting set. The second set is a few cycles of symbolic addition using quartets and triplets, employing very strict acceptance criteria, and not allowing relations among the symbolic phases. This leads to a much larger starting set.

The next step is the extension of starting set. This is done in SIMPEL using triplet relations only. It is very essential that no errors are included during this process and therefore, the criteria used to accept a symbolic phase for a reflection are very strict, in particular in the beginning. In, general, no single indication

will be accepted unless it belongs to the ten to fifteen strongest triplet relationships. For multiple indications giving rise to the symbolic phase, high acceptance limits are applied. In general, this precautions make sure that the resulting set of symbolic phases contains the correct solution.

Figures of Merit.

With the extended group of phased reflections as input numerical values for the symbols are calculated using a number of figures of merit (FOM's).

Apart from the separate FOM's also a combined FOM is calculated, which mostly discriminates the correct solution without difficulties.

After determining the symbols all symbolically phased relations can get numerical phase. These phases are then used as starting point for numerical phase extension, because in general the number of phased reflections is yet insufficient to calculate a good E-map. In the centrosymmetric case this is achieved by means of a $\sum_2$ refinement and extension.

Thus SIMPEL produces a set of E-values with phases, which can be fed into an E-map calculating program with subsequent interpretation.

Eventually the atomic positions can be tested and be refined by a fast diagonal least squares program.

2.9 Refinement of the structure :

The trial structure thus obtained is, however, an approximate one. The positional and thermal parameters describing the model along with the scale factor for reducing the observed structure factors, have to be refined. An agreement between the calculated structures factors F_c and those observed, F_o, indicates the degree of refinement. The most common method of assesssing the agreement

is calculating the residual or reliability index of the form,

$$R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \qquad (2.33)$$

the summation being over all the reflections.

Another form of the residue of common use is

$$R_w = \left[\Sigma w \left(|F_o| - |F_c| \right) / \Sigma w |F_o|^2 \right]^{1/2} \qquad (2.34)$$

where the weight,

$$W = \frac{1}{\sigma^2(F_o)}$$

$\sigma(F_o)$ being the standard deviation of F_o.

Generally for refinement of a crystal structure we adopt following three methods, e.g., (i) Fourier synthesis, (ii) Difference fourier synthesis and (iii) Least square refinement. The fourier synthesis gives the refined co-ordinates of the atoms and also tends to reveal the position of any atom which is not included in computing the structure factors. The difference fourier map is very useful for locating H-atoms towards the final stages of refinement procedure. Difference fourier synthesis is free from series termination effect which arises due to limitation in the amount of data being collected.

The method of least square :

An analytical method of refinement of great power and generality is that based on the principle of least squares. In this case the quantity most commonly minimised is

$$D = \sum_{hkl} W_{hkl} \left(|F_o| - |KF_c| \right)^2 \qquad (2.35)$$

where W_{hkl} is the weight of the observations and Σ_{hkl} indicates summation over all the observed reflections. To obtain the least

square fit, it will be necessary to consider the parameters P as variables which may be adjusted to minimise D. This is a straight forward minimization problem which is treated by differentiating the right side of equation (2.35) with respect to each of the parameters in turn and setting the derivation equal to zero. This gives, a equation of the type,

$$\sum_{r=1}^{m} W_r \left(f_{or} - f_{cr} \right) \frac{\delta f_{cr}}{\delta p_j} = 0 \qquad (2.36)$$

A set of n equations in n unknowns called the normal equations. Solutions of these n equations gives directly the best values of the parameters p_j in the least-squares sense.

The second compound belongs to a noncentro-symmetric space group $P2_12_12_1$. Phases for this structure were estimated by generalised tangent procedures using the program GENTAN of XTAL system. GENTAN uses triplet and/or quartet structure invariant relationships in a general tangent formula to propagate and refine structure factor phases.

The first step in the GENTAN calculation is to specify sufficient phases to uniquely define the origin. The specification of phases to fix the cell origin may be done automatically or may be selected by the user. GENTAN provides for a wide range of starting and refinement options. From these phases additional values are determined through the application of the tangent formula to connect invariant relationship. When the space group is non-centrosymmetric this procedure is also used to specify the phases for fixing the enantiomorphic form of the structure.

Multiple phase sets may be initialised with permuted, magic integer or random starting phases. The extension and refinement of phases is simultaneous in the tangent process. There are two different methods for propagating phases in Gentan ; CASCADE and

BLOCK. Tangent weighting schemes include probalistic[27], Hull-Irwin[28] statistical and Modified H-I Statistical weights. Refined phase sets are examined for correctness in terms of a variety of figures of merit. A combined figure-of-merit CFOM and an absolute measure of success parameters AMOS are used to sort the best phase sets. Caculation of the E-maps, interpretation of the structure and refinement are done in the usual methods.

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CHAPTER 3

Crystal and molecular structure of 4(3" - Pentenyl) - 4'(cyano) 1,1' bicyclohexane.

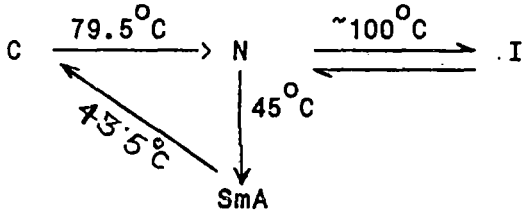
3.1 INTRODUCTION

In this chapter I describe the crystal and molecular structure of 4(3'' - Pentenyl)4' (cyano)1,1' bicyclohexane both in the crystalline and mesomorphic state and try to explain the mesomorphic organization in relation to its solid state packing and molecular interactions. Compounds with alkenyl end chains belong to different structural classes[1]. Their common features are low viscosities as well as low optical anisotropies. The alkenyl compounds differ from each other in many of their properties with respect to the systematic changes made in the position of the alkenyl double bond. The molecular arrangement in the crystalline state is one of the factors which sometimes predetermines the properties in the liquid crystalline state. The structure of the compound CCH5 (trans, trans - 4' pentyl bicyclohexyl - 4 carbonitrile) has already been determined by Haase et al.[2].

3.2 EXPERIMENTAL

Under a crossed polarizing microscope (150X) a marbled texture of nematic phase has been observed both during heating and cooling. The transition is found to be monotropic. A fan-shaped texture of Smectic A phase was observed over a very short range of temperature during cooling. X-ray diffraction photographs were taken in the whole of the mesomorphic range.

The transition temperatures of different phases as determined by X-ray diffraction and texture studies are given below:



3.2.1 Crystal data

Transparent plate shaped crystals were obtained by means of slow evaporation from a solution of acetone. The crystal belongs to centrosymmetric monoclinic system. Lattice parameters and space groups were determined by taking oscillation, rotation and weissenberg photographs along a and b axes. Some photographs are given in figure 3.1 - 3.3. From the systematic absences of h0l with h+l odd and 0k0 with k odd, the space group was determined to be $P2_1/n$. Accurate cell parameters was determined by a least squares fit of $Sin\theta$ values of 23 reflections having θ values $40^{o}<\theta<42^{o}$, measured on an Enraf Nonius CAD-4 diffractometer using $CuK\alpha$ radiation and a graphite monochromator. A total of 3381 reflections were measured on $\omega - 2\theta$ scan mode, of which 2326 were treated as observed with $I > 2.5\ \sigma(I)$. The data were corrected for Lorentz and Polarization factors and no absorption correction was necessary. The crystal data are given in Table 3.1.

3.3. STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by means of direct method program SIMPEL-83 of Kiers and Schenk[3]. The normalisation process used is based on a Wilson plot procedure. This approach provides an estimate of the overall temperature factor U and overall scale factor K which was found to be 0.068241 and 0.2196 respectively. The strongest 300 reflections were phased using 4 symbols. Phase set with best combined figure of merit was used for E map calculation which is shown in figure 3.4. The positions of all the non-hydrogen atoms could be located from E-map and the trial structure was obtained. These positions are given in Table 3.2. Five cycles of least squares with individual isotropic temperature brought down the R-value from 0.47 in the 1st cycle to 0.19. Introduction of individual anisotropic temperature factors reduced the R value to 0.13. From the difference Fourier we could not determine the positions of the

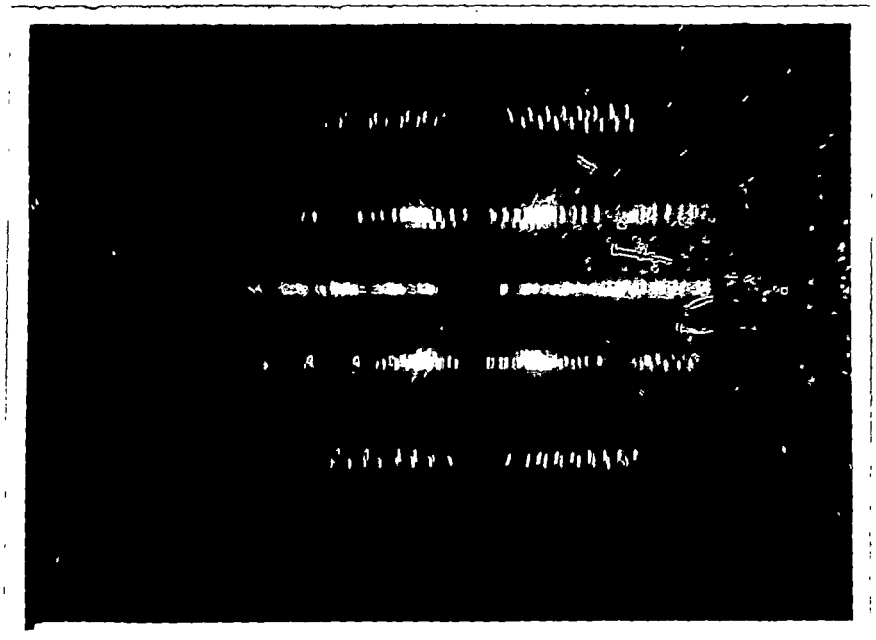


Figure 3.1 : Rotation photograph about a-axis.

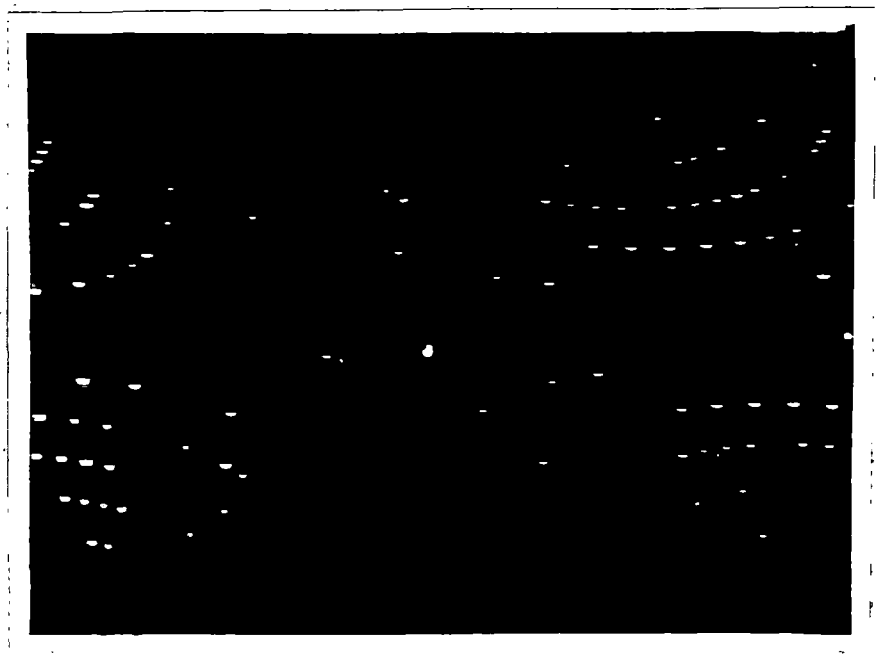


Figure 3.2 : Zero-layer Weissenberg photograph about a-axis.

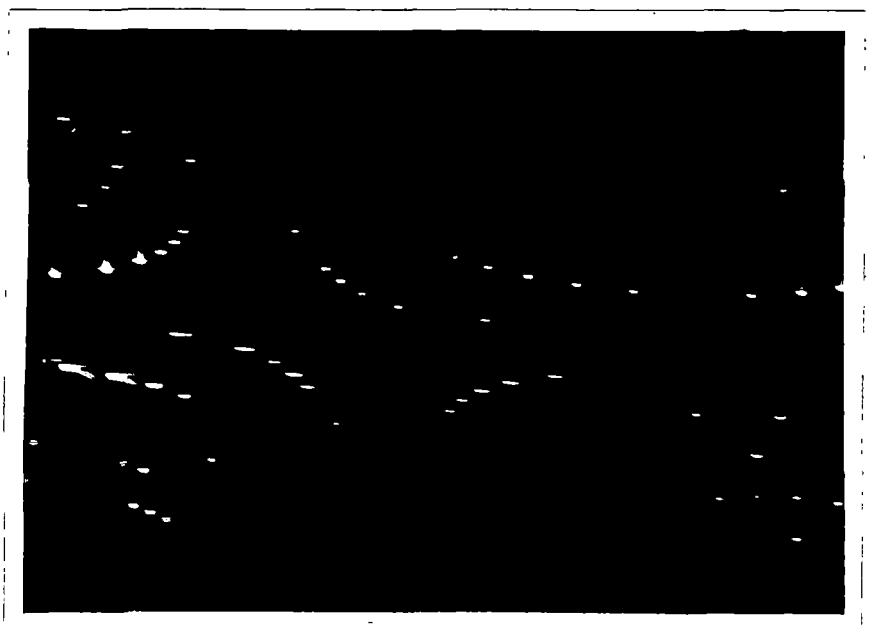


Figure 3.3 : 1st layer Weissenberg photograph about a-axis.

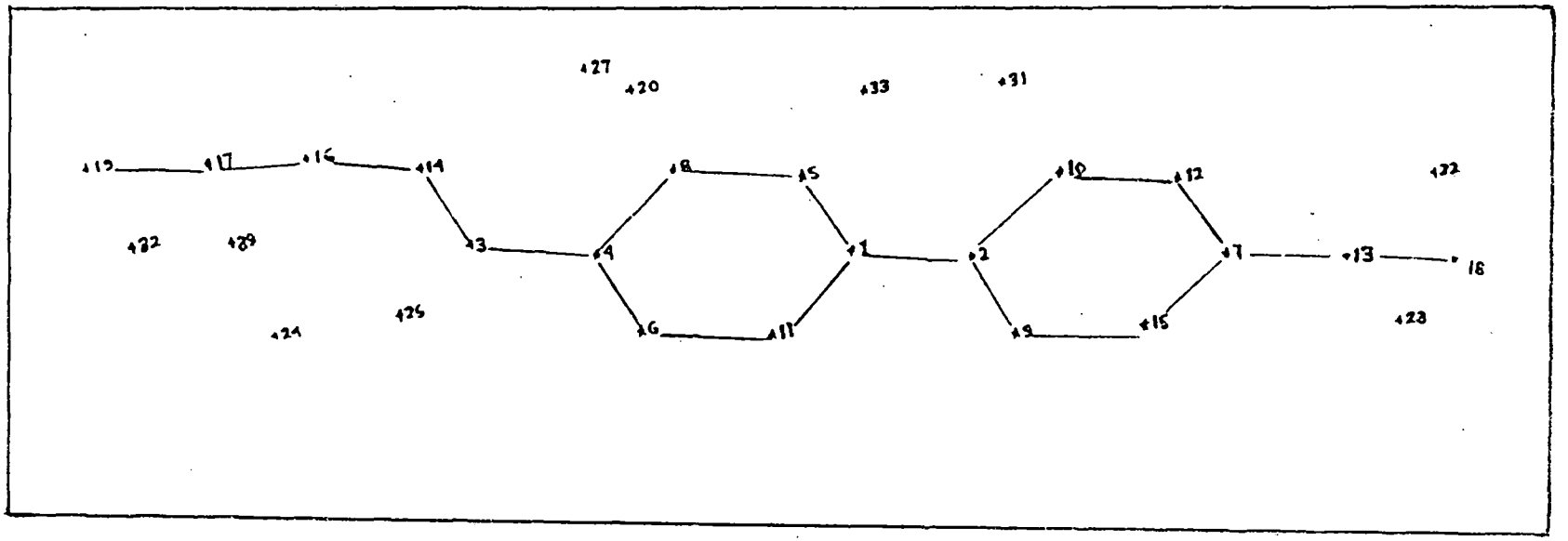


Figure 3.4 : E-map of 4(3''-Pentenyl)4'(cyano) 1,1' bicyclohexane

TABLE 3.1

Summary of Crystallographic data

Molecular formula	$C_{18}H_{29}N$
Molecular weight	259.422 gm/mol.
Crystal system	Monoclinic
Space group	$P2_1/n$
Form/habit	Plate shaped
a = 5.609(1) Å	
b = 31.390(2) Å	
c = 9.562(1) Å	
β = 98.89(9)°	
V_c = 1663.43 Å^3	
D_c = 1.084 gm/cm^{-3}	
Z = 4	
λ(CuKα) = 1.542 Å	
Number of independent reflections	3381
Number of observed reflections	2326

TABLE 3.2

Atom name	Positional co-ordinates		
	X	Y	Z
C1	0.5000	0.6023	0.2887
C2	0.3008	0.6338	0.3048
C3	0.8811	0.4842	0.1902
C4	0.6713	0.5159	0.2086
C5	0.5008	0.5633	0.3803
C6	0.6803	0.5542	0.1151
C7	0.1209	0.7202	0.3822
C8	0.7153	0.5319	0.3638
C9	0.3113	0.6725	0.2125
C10	0.3453	0.6515	0.4636
C11	0.4719	0.5860	0.1314
C12	0.1300	0.6820	0.4809
C13	- 0.0763	0.7500	0.4000
C14	0.8803	0.4451	0.2714
C15	0.0899	0.7028	0.2296
C16	1.0649	0.4124	0.2551
C17	1.0298	0.3722	0.1958
C18	1.2168	0.3407	0.1740
N1	- 0.2674	0.7696	0.4016

large number of hydrogen atoms present in the molecule. We tried to generate the co-ordinates of hydrogen atoms applying known geometry of the molecule, but the structure did not refine. These were then located from energy optimisation using the program Sybyl[4]. The structure was refined by block diagonal least squares method to a final R = 0.065 (Rw = 0.081), the hydrogen atoms being allowed to vibrate isotropically and non-hydrogen to vibrate anisotropically. The scattering factors were taken from Cromer and Mann[5]. All the calculations were done using XTAL[6] and PC version of the NRCVAX[7] package utilities.

3.4 RESULTS AND DISCUSSIONS

3.4.1 Molecular conformation

The perspective view of the molecule is shown in figure 3.5. Final positions and thermal parameters of the atoms are listed in Tables 3.3 - 3.5 using the atomic numbering scheme shown in figure 3.5. Bond lengths and bond angles are given in Table 3.6. It has been seen that alkenyl chain is in the trans conformation. The average C-C bond length in the cyclohexane ring is 1.535(8) Å. These values are consistent with our previous observations and have expected values. Carbon-carbon distances both for single and double bonds are found to be as expected. The $C_{18} - N_1$ distance and bond angle $C_{15} - C_{18} - N_1$ compare well with other results[8,9].

It is being found that the hydrogen atoms have large temperature factors, specially the atoms in the methyl group. As was mentioned earlier I could not locate the positions of these large number of hydrogen atoms from difference fourier or from known geometry. There might be disordering in their positions. But it is difficult to obtain appropriate geometry because of their small scattering value.

ORTEP drawing with the thermal ellipsoids for the non-hydrogen atoms are shown in figure 3.6.

The molecule is not planar . The cyclohexane rings are in chair

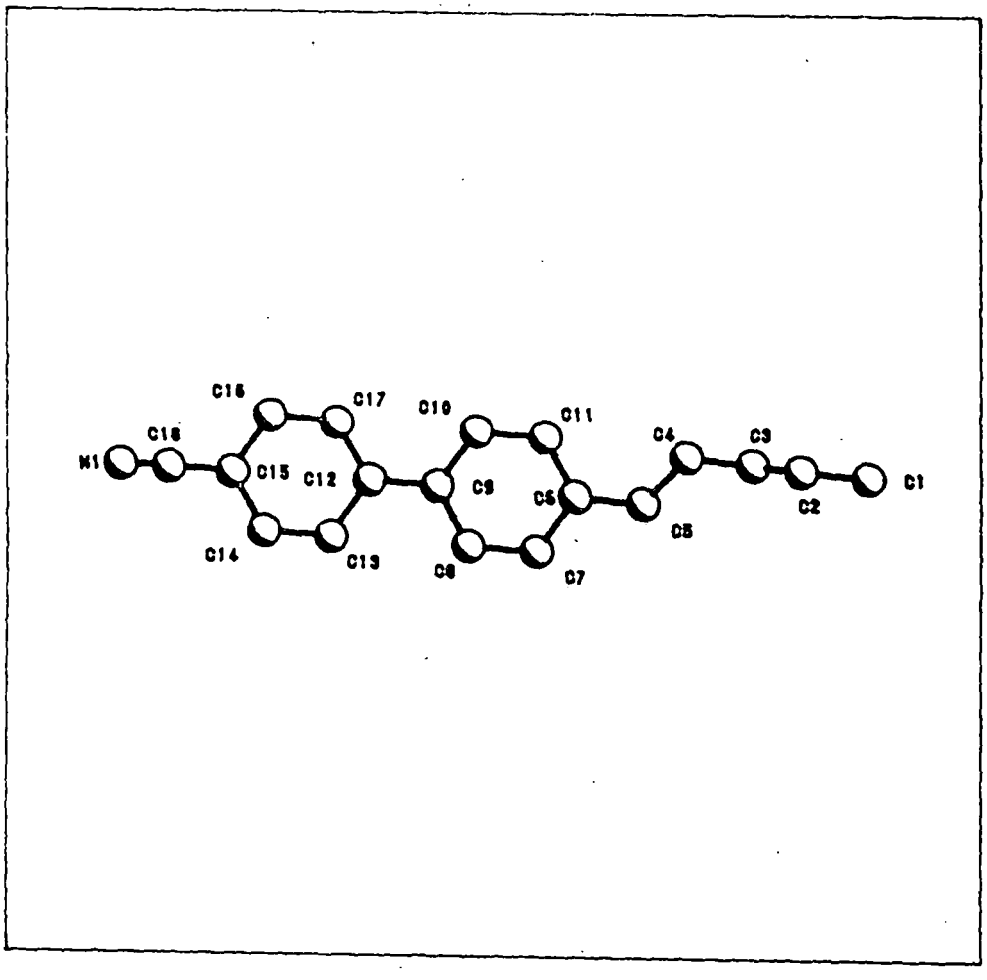


Figure 3.5 : The perspective view of the PCBCH molecule showing the atomic numbering scheme.

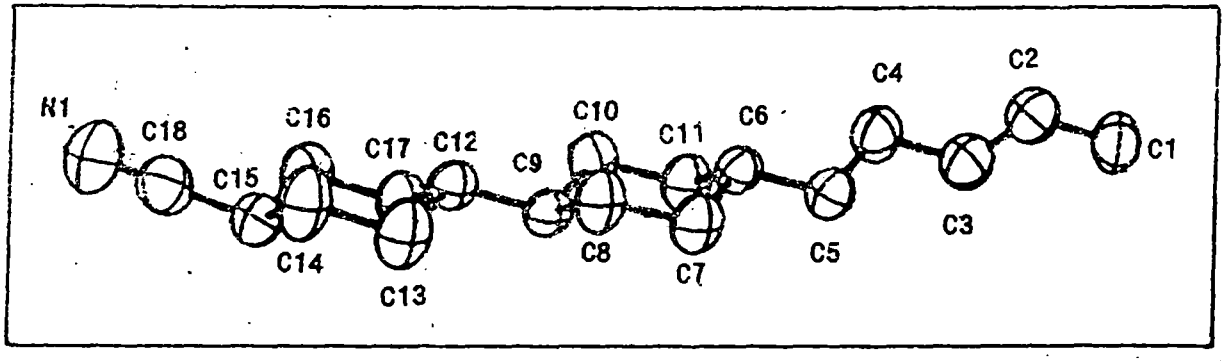


Figure 3.6 : ORTEP drawing of the PCBCH molecule with the thermal ellipsoids for the non-hydrogen atoms.

conformation, the angle between them is 34°. The angle between chain part and cyclohexane ring is found to be 27°. Because the molecules are flexible, during the process of crystallisation they twist themselves for favourable packing.

3.4.2 Molecular packing .

Figure 3.7 is a projection along the short crystallographic a-axis. The molecules related by inversion centre of symmetry lie collinear to each other. They are arranged in layers parallel to bc plane and layers are stacked along a-axis. The direction cosines of the molecular long axis, defined as best fitted line through C_5 to N_1 are .5598, -.8055 and -.1945 which shows that the molecule makes an angle of 36° with b-axis. In figure 3.8 the projection along c-axis is presented. The long axis of the molecules makes an angle 74° with one another, thus resulting in a herringbone - like pattern. This type of packing is mostly observed in crystals which gives rise to smectic phase on melting. In the present case the long chains from adjacent layers are deeply interdigitated. The terminal dipole-dipole interaction between CN groups of the neighbouring molecules in the adjacent layers hinders the formation of layer like structure of smectic.

The length of the molecule in the crystalline state is 16.1 Å whereas the theoretical length is at a maximum 16.3 Å, indicating that the molecule is in its most extended conformation. The intermolecular distances smaller than 4 Å are given in Table 3.7. A dipole - dipole short contact of less than 3.5 Å exists in most cyano compounds. This is not found in the list of intermolecular distances mentioned above. But a spacing less than 4 Å between anti-parallel molecules may be interpreted as a weak dipole - induced dipole interaction forming pairs of molecule related through a centre of symmetry. The apparent molecular length in the nematic phase was also found to be almost 30 Å from x-ray diffraction study.

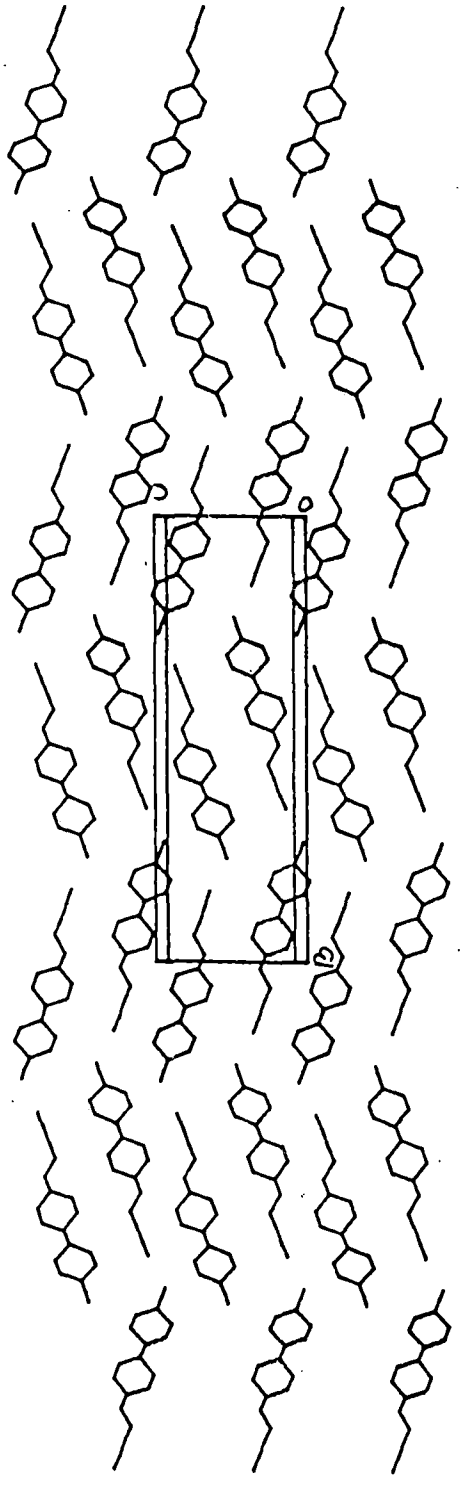


Figure 3.7 : Molecular packing projected along [100].

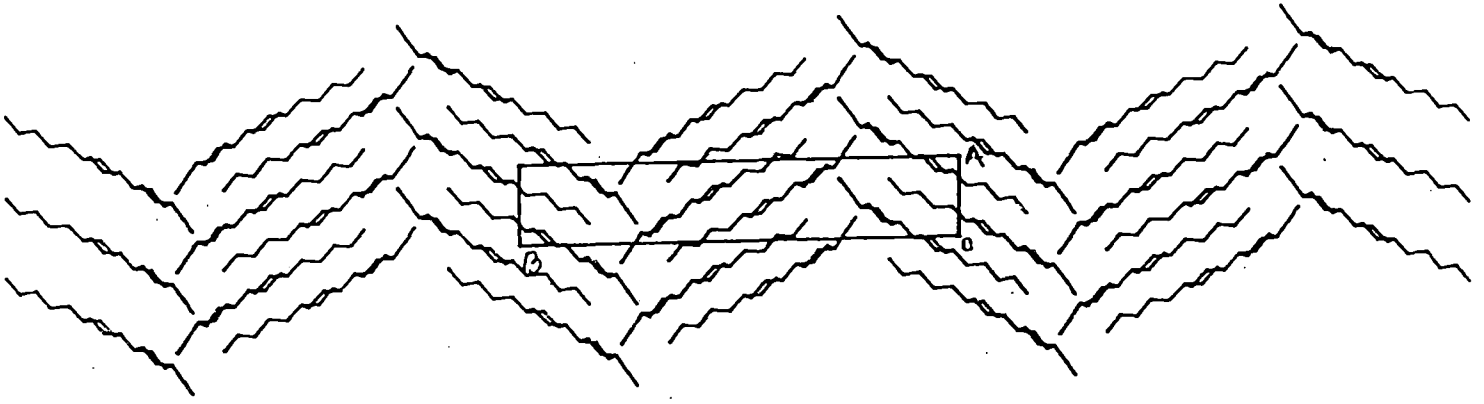


Figure 3.8 : Molecular packing projected along [001].

TABLE 3.3

Fractional co-ordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms with e.s.d.'s in parentheses.

$U_{eq} = 1/3(U_{11}a^2a^{*2} + U_{22}b^2b^{*2} + U_{33}c^2c^{*2} + U_{13}aa^*cc^*Cos\beta)$.

Atom	x(σ)	y(σ)	z(σ)	U_{eq}
C1	1.2349(1)	0.3423(2)	0.1708(9)	0.0886(3)
C2	1.0351(1)	0.3726(2)	0.1932(8)	0.0830(2)
C3	1.0574(1)	0.4106(2)	0.2382(8)	0.0761(2)
C4	0.8573(1)	0.4411(2)	0.2633(8)	0.0753(2)
C5	0.8723(1)	0.4833(2)	0.1883(7)	0.0675(2)
C6	0.6790(1)	0.5158(2)	0.2138(7)	0.0583(2)
C7	0.6787(1)	0.5539(2)	0.1162(7)	0.0686(2)
C8	0.4883(1)	0.5872(2)	0.1371(6)	0.0692(2)
C9	0.5116(1)	0.6029(2)	0.2917(6)	0.0534(2)
C10	0.5165(1)	0.5643(2)	0.3908(7)	0.0674(2)
C11	0.7101(1)	0.5313(2)	0.3683(7)	0.0701(2)
C12	0.3108(1)	0.6348(2)	0.3134(6)	0.0565(2)
C13	0.2919(1)	0.6719(2)	0.2085(7)	0.0809(2)
C14	0.0881(1)	0.7025(2)	0.2277(7)	0.1202(2)
C15	0.1221(1)	0.7196(2)	0.3812(7)	0.0704(2)
C16	0.1436(1)	0.6835(2)	0.4881(7)	0.0753(2)
C17	0.3445(1)	0.6530(2)	0.4650(7)	0.0722(2)
C18	-0.0859(1)	0.7476(2)	0.3967(8)	0.0772(2)
N1	-0.2504(1)	0.7684(2)	0.4037(8)	0.1051(2)

TABLE 3.4

Fractional co-ordinates and isotropic thermal parameters of the hydrogen atoms with e.s.d.'s in parentheses. Atoms are numbered according to the heavy atoms to which they are attached.

Atom	x(σ)	y(σ)	z(σ)	U
H11	1.1747(1)	0.3195(1)	0.1280(1)	0.2572(4)
H12	1.3165(1)	0.3360(1)	0.2454(1)	0.2856(4)
H13	1.3151(2)	0.3495(1)	0.1171(1)	0.2954(4)
H21	0.8674(2)	0.3617(2)	0.1861(1)	0.1592(5)
H31	1.2420(2)	0.4239(2)	0.2594(1)	0.1393(3)
H41	0.7026(2)	0.4270(1)	0.2276(1)	0.1103(5)
H42	0.8660(1)	0.4472(1)	0.3726(1)	0.0986(5)
H51	1.0451(1)	0.4978(1)	0.2263(1)	0.0975(5)
H52	0.8561(2)	0.4773(1)	0.0825(1)	0.0960(5)
H61	0.5061(2)	0.5005(1)	0.1869(1)	0.0753(6)
H71	0.6518(1)	0.5424(1)	0.0108(1)	0.0944(5)
H72	0.8451(1)	0.5662(1)	0.1397(1)	0.0852(6)
H81	0.5008(2)	0.6146(1)	0.0758(1)	0.0883(7)
H82	0.3187(1)	0.5723(1)	0.1131(1)	0.0943(4)
H91	0.6624(1)	0.6202(1)	0.3113(1)	0.0828(6)
H101	0.3446(1)	0.5508(1)	0.3680(1)	0.0942(5)
H102	0.5342(1)	0.5748(1)	0.4957(1)	0.0884(5)
H111	0.8899(1)	0.5464(1)	0.3959(1)	0.0988(5)
H112	0.7004(1)	0.5052(1)	0.4380(1)	0.0868(4)
H121	0.1540(1)	0.6162(1)	0.2913(1)	0.0815(4)
H131	0.2702(1)	0.6590(1)	0.1070(1)	0.0923(6)
H132	0.4586(1)	0.6858(1)	0.2261(1)	0.1131(7)
H141	0.0780(1)	0.7299(1)	0.1549(1)	0.1127(8)
H142	-0.0838(1)	0.6844(1)	0.2020(1)	0.1136(7)
H151	0.2877(1)	0.7374(1)	0.4158(1)	0.1235(7)
H161	-0.0121(1)	0.6696(1)	0.4755(1)	0.1029(7)
H162	0.1721(1)	0.6970(1)	0.5940(1)	0.1084(5)
H171	0.5061(1)	0.6697(1)	0.4825(1)	0.0877(6)
H172	0.3414(1)	0.6284(1)	0.5363(1)	0.0808(6)

TABLE 3.5

Anisotropic thermal parameters of the non-hydrogen atoms with the e.s.d.'s in parentheses. The temperature factor is of the form

$$\mathrm{Exp}[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*].$$

Atom	$U_{11}(\alpha)$	$U_{22}(\alpha)$	$U_{33}(\alpha)$	$U_{12}(\alpha)$	$U_{13}(\alpha)$	$U_{23}(\alpha)$
C1	0.0833(5)	0.0813(5)	0.0942(6)	0.0146(4)	0.0152(5)	-0.0102(5)
C2	0.0818(6)	0.0856(5)	0.0795(5)	-0.0018(4)	0.0220(4)	-0.0016(4)
C3	0.0786(5)	0.0797(5)	0.0764(5)	0.0004(4)	0.0187(4)	-0.0010(4)
C4	0.0815(5)	0.0752(5)	0.0742(5)	0.0054(4)	0.0253(4)	-0.0018(4)
C5	0.0636(4)	0.0687(4)	0.0669(4)	-0.0017(3)	0.0201(3)	-0.0061(3)
C6	0.0554(4)	0.0649(4)	0.0586(4)	-0.0055(3)	0.0172(3)	-0.0084(3)
C7	0.0795(5)	0.0806(5)	0.0523(4)	0.0044(4)	0.0239(3)	-0.0029(3)
C8	0.0848(5)	0.0768(5)	0.0480(3)	0.0114(4)	0.0196(3)	-0.0031(3)
C9	0.0559(4)	0.0644(4)	0.0488(3)	-0.0057(3)	0.0149(3)	-0.0056(3)
C10	0.0820(5)	0.0713(4)	0.0529(4)	0.0041(4)	0.0231(3)	0.0009(3)
C11	0.0815(5)	0.0750(5)	0.0555(4)	0.0090(4)	0.0199(3)	0.0004(3)
C12	0.0584(4)	0.0634(4)	0.0489(3)	-0.0034(3)	0.0163(3)	-0.0040(3)
C13	0.0968(6)	0.0889(5)	0.0595(4)	0.0214(5)	0.0303(4)	0.0112(4)
C14	0.1011(5)	0.0927(5)	0.0611(5)	0.0293(4)	0.0282(4)	0.0048(4)
C15	0.0692(5)	0.0649(4)	0.0797(5)	-0.0011(3)	0.0254(4)	-0.0069(3)
C16	0.0918(5)	0.0769(5)	0.0554(4)	0.0055(4)	0.0251(4)	-0.0052(3)
C17	0.0877(5)	0.0738(5)	0.0531(4)	0.0079(4)	0.0160(3)	-0.0088(3)
C18	0.0908(5)	0.0750(5)	0.0756(5)	-0.0073(4)	0.0267(4)	-0.0130(4)
N1	0.1006(5)	0.1038(5)	0.1091(5)	0.0218(4)	0.0341(4)	-0.0136(4)

TABLE 3.6

Bond distances (Å) of the non-hydrogen atoms with standard deviations in parentheses.

C1 - C2	1.51(8)	C10 - C11	1.54(8)
C2 - C3	1.27(8)	C12 - C15	1.53(8)
C3 - C4	1.52(8)	C12 - C17	1.54(8)
C4 - C5	1.51(8)	C13 - C14	1.53(8)
C5 - C6	1.54(8)	C14 - C15	1.55(8)
C6 - C7	1.52(8)	C15 - C16	1.52(8)
C6 - C11	1.54(8)	C15 - C18	1.49(8)
C7 - C8	1.53(8)	C16 - C17	1.52(8)
C8 - C9	1.54(8)	C18 - N1	1.14(8)
C9 - C10	1.54(8)		
C9 - C12	1.54(8)		

Bond angles (°) of the non-hydrogen atoms with standard deviations in parentheses.

C1 - C2 - C3	127(5)	C10 - C9 - C12	111(4)
C2 - C3 - C4	127(5)	C9 - C10 - C11	112(4)
C3 - C4 - C5	112(5)	C6 - C11 - C10	111(4)
C4 - C5 - C6	114(5)	C9 - C12 - C13	112(4)
C5 - C6 - C7	111(4)	C9 - C12 - C17	112(4)
C5 - C6 - C11	112(4)	C13 - C12 - C17	108(4)
C7 - C6 - C11	109(4)	C12 - C13 - C14	112(4)
C6 - C7 - C8	113(5)	C13 - C14 - C15	110(4)
C7 - C8 - C9	112(4)	C14 - C15 - C16	111(4)
C8 - C9 - C10	109(4)	C14 - C15 - C18	108(4)
C8 - C9 - C12	112(4)	C16 - C15 - C18	110(5)
		C15 - C16 - C17	110(4)
		C12 - C17 - C16	112(4)
		C15 - C18 - N1	177(6)

TABLE 3.7

Intermolecular contact distances less than 4 Å (involving non-hydrogen atoms)

C2 - C5[a]	3.589
C2 - C16[b]	3.787
C3 - C6[a]	3.911
C16 - C2[c]	3.787
N1 - C2[d]	3.696
N1 - C13[a]	3.443
N1 - C14[a]	3.481
N1 - C15[e]	3.813

a (1/2+x)-1, (1/2-y)+1, 1/2+z

b 1/2-x, 1/2+y, (1/2-z)+1

c 1-x, 1-y, 1-z

d 1/2-x, 1/2+y, 1/2-z

e x-1, y, z

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CHAPTER 4

Crystal and molecular structure of 4(3" - Pentenyl) - 4' (Ethoxy) 1,1' bicyclohexane

4.1 INTRODUCTION :

Since liquid crystals may possess long range one-dimensional or quasilong range two-dimensional translational symmetry, one expects that the molecular arrangement in the crystalline state will predetermine the molecular arrangement in the mesomorphic state[1-4]. In this context, the crystal and molecular structure of one polar alkenyl compound PCBCH was reported by us[5] and described in chapter 3. In this chapter, I describe the crystal and molecular structure of one non-polar alkenyl compound 4(3"-pentenyl) -4'-(ethoxy)-1,1' -bicyclohexane [PEBCH in short] and discuss the change in the molecular packing which accompanies the solid to nematic phase transition.

4.2 EXPERIMENTAL DETAILS :

4.2.1 Crystal data

The compound was obtained from Hoffmann-La Roche and Co., Basel, Switzerland. Single crystal, suitable for x-ray analysis, was obtained from an acetone solution by slow evaporation. Lattice parameters and space group were determined by oscillation and weissenberg photographs which were not of sufficiently good quality to be reproduced here.The crystal belongs to the orthorhombic system. From the systematic absences of h00 with h odd, 0k0 with k odd and 00l with l odd, the space group was uniquely determined to be P $2_12_12_1$. Accurate cell parameters was determined by a least squares fit of Sinθ values of 23 reflections having θ values $39 < \theta < 43$, measured on an Enraf Nonius CAD-4 diffractometer using CuK_α radiation and a graphite monochromator. A total of 2136 reflections were measured on $\omega - 2\theta$ scan mode, of which 1855 were treated as observed with $I > 2.5\sigma(I)$. The data were collected at -45^oC and corrected for Lorentz and Polarization factors but no absorption correction was made. Important crystallographic data are listed in table 4.1.

Table - 4.1

Summary of crystallographic data

Molecular formula	$C_{19}H_{34}O$
Molecular weight/g*mol^{-1}	278.426
Crystal system	Orthorhombic
Lattice type	Non-centrosymmetric
Space group	$P\ 2_12_12_1$
a/Å	4.7095 (10)
b/Å	17.8195 (2)
c/Å	21.1616 (19)
α,β,γ/^{o}	90
V/Å^3	1775.901
D_c/g*cm^{-3}	1.042
Z	4
λ (CuK_α)/Å	1.5418
No. of independent reflection	2136
No. of observed reflection	1855

4.3 STRUCTURE DETERMINATION AND REFINEMENT.

Since the structure is non-centrosymmetric, phases were estimated using generalised tangent procedures using the programe GENTAN of XTAL systems[9]. Multiple phase sets were initialized using magic integer procedure. Phase extension was performed by cascade technique. Hall-Irwin statistical weighting scheme was used for tangent formula. E-map was calculated from the phase set 1 having CFOM 0.85 and AMOS 98%. 300 strong reflections were phased through the application of tangent formula using triplet and quartet structure invariant relationship. E-map is shown in figure 4.1. From the E-map we could locate eighteen non-hydrogen atoms. With the help of Fourrier and difference Fourrier map the other two atoms could be located. The structure thus obtained was refined and initially five cycles of full matrix least squares with individual isotropic temperature factor brought the R-value to 0.20. Introduction of individual anisotropic temperature factors reduced the R-value to 0.15. At this point it was observed that the bond lengths and angles involving the double bond of the alkenyl chain have large values, the thermal vibrations were also found to be very large. A difference Fourrier map was computed and the atoms were relocated. But subsequent refinement did not show any improvement in the structure. Attempts were also made to refine the structure by varying the occupancy of those atoms but no better result was obtained. The positions of hydrogen atoms were then calculated from the known geometry around the carbon atoms and these positions were subsequently confirmed on a difference Fourrier map. The hydrogen atoms were given isotropic temperature factors of the parent carbon atoms. Then the structure was refined through several cycles by full matrix, first keeping hydrogen atoms fixed, allowing non-hydrogen atoms to vibrate anisotropically and then with hydrogen atoms vibrating isotropically and non-hydrogen atoms fixed. This resulted in an R-value of 0.119. From structure factor tables three

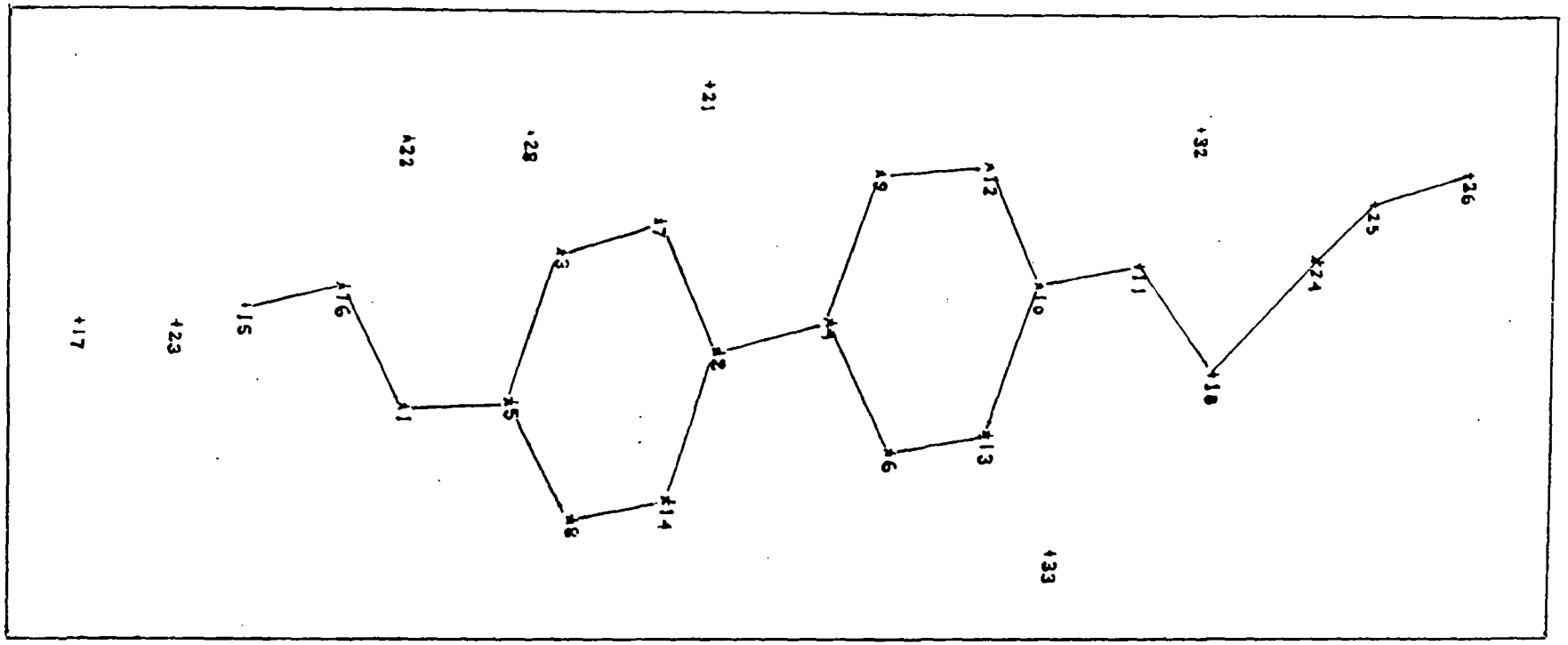


Figure 4.1 : E-map of 4(3′′-pentenyl)-4′-(ethoxy)-1,1′-bicyclohexane.

reflections 021, 200 and 101 were found to have secondary extinction effects. These reflections were excluded. Finally six cycles of refinement was carried out keeping all the hydrogen atoms fixed and non-hydrogen atoms to vibrate anisotropically. The final R-value was 0.077 and R_w = 0.077 . A difference Fourrier map at this stage showed no electron density greater than 0.42 e/A^{03}. Therefore, the large bond lengths and angles in the alkenyl chain may be due to disordering in that part of the molecule.

All the calculations were done using PC version of the NRCVAX package utilties [10].

4.4 RESULTS AND DISCUSSIONS

4.4.1 Molecular Structure

Final positional and thermal parameters of the non-hydrogen and hydrogen atoms are given in tables 4.2 - 4.4. The molecular structure of PEBCH is presented in figure 4.2 indicating the atom numbering scheme. It also shows that both the cyclohexyl rings are in chair conformation. The length of the molecule in the crystalline state (C1- C19) is 17.28 A^{O} whereas the model length is found to be 17.4 A^{O}. Thus the molecules are in most extended form with all trans - conformation of both the pentenyl and ethoxy groups as is also observed in figure 4.2. Bond lengths and bond angles involving non-hydrogen atoms are given in table 4.5 The average C - C bond lengths in the two cyclohexyl rings A and B (figure 4.2) is 1.529 A^{O} and 1.534 A^{O} respectively. The value of the C - O bond distance is 1.393 A^{O}. The maximum and minimum bond angles are respectively 112.4^{O} and 108.7^{O} in ring A, 112.9^{O} and 108.9^{O} in ring B. All these distances and angles are normal and comparable with PCBCH[5] and other reported values[8-10]. However the length of the double bond C17-C18 is 1.077 A^{O} and the angle C17-C18-C19 is 145.7^{O} which differ from normal values to a large extent. Atoms C17 and C18 in the chain have large temperature factors. There may be some conformational disorder

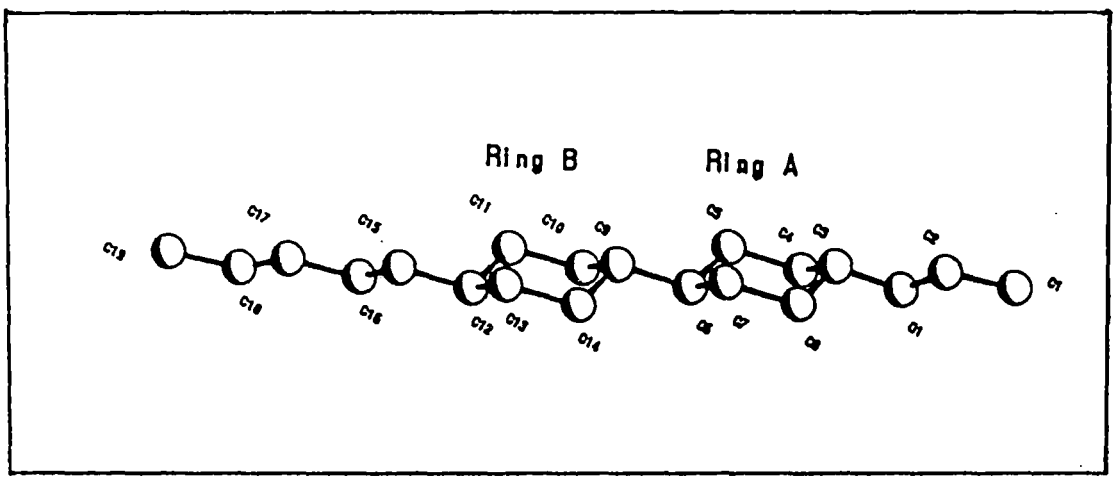


Figure 4.2 : The perspective view of the PEBCH molecule depicting the chair conformation of the cyclohexyl rings and the atom numbering scheme.

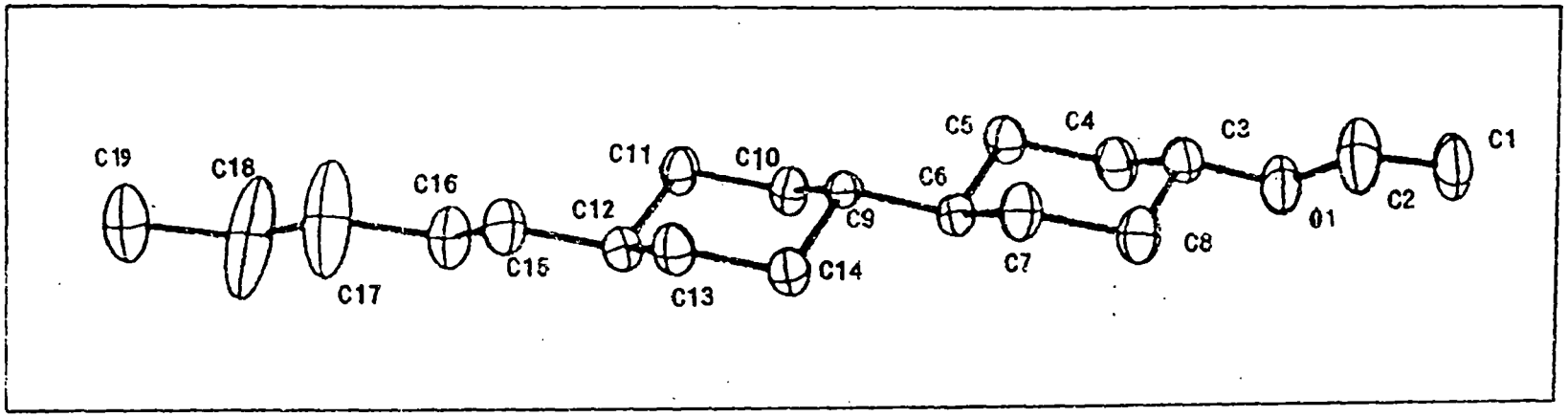


Figure 4.3 : ORTEP drawing of the PEBCH molecule showing the thermal ellipsoids of the non-hydrogen atoms.

in the molecular structure around the double bond. It was difficult to obtain appropriate geometries for these disordered atoms. In liquid crystals such conformational disorder has been reported earlier [9,11,12].

ORTEP drawing showing the thermal ellipsoids of the non-hydrogen atoms is given in figure 4.3. Two disordered atoms in the chain have large thermal displacements in the direction perpendicular to the long molecular axis thereby resulting in an abnormal value of the C17 - C18 double bond.

4.4.2 Molecular Packing

In order to describe the molecular packing we have given the a, b and c-axis projection of the structure in figures 4.4 - 4.6 . In describing the packing we have to keep in mind that the compound crystallized in non-centrosymmetric orthorhombic cell with four molecules in the unit cell. The figures clearly depicts that the molecules are packed parallel to the crystallographic c-axis with a tilt angle of about 5^{o}. The symmetrically related molecules are also parallel to each other in head-tail or head-head manner. These parallel molecules are packed in an imbricated mode. This type of packing is normally observed where transition occurs from crystalline to nematic phase where the molecules possess no positional correlation but have only orientational ordering about a director. Also we note from figure 4.4 that the bulky cyclohexane groups overlap with either less bulky alkenyl or ethoxy group.

We calculated the interatomic distances between the neighbouring molecules and no such distance was found which is less than the sum of the van der Waals' radii of the atoms involved. So in PEBCH no molecular "association" , as a result of van der Waals' type of interaction, occurs in the crystalline state. On trasition to nematic phase the picture does not alter as is evident from the fact that the average length of the molecules, obtained from x-ray

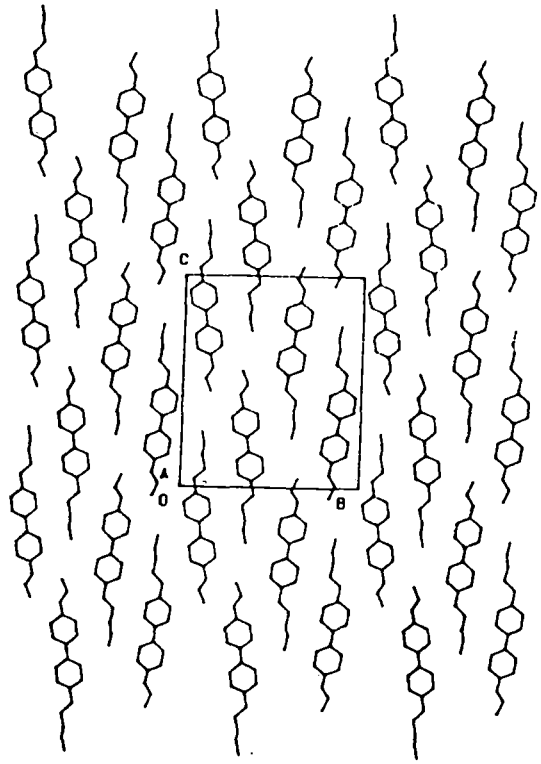


Figure 4.4 : Molecular packing projected along [100].

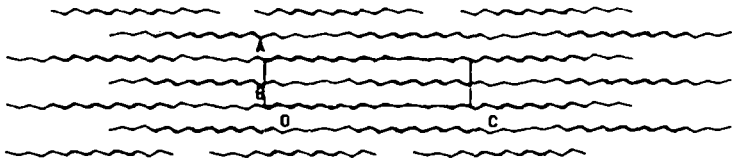


Figure 4.5 : Molecular packing projected along [010].

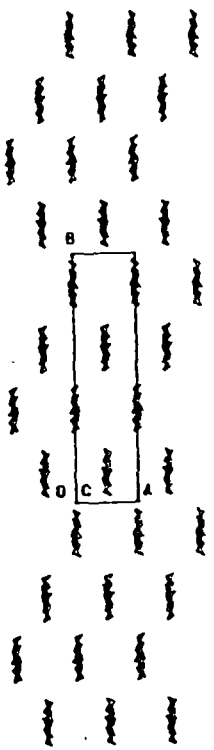


Figure 4.6 : Molecular packing projected along [001].

diffraction study[13], in the nematic phase is 17.0 Å, almost equals to the length of a single molecule.

It would be of interest to compare at this point the phase sequences and molecular packing of two related compounds[5,8,13,14] CCH5 and PCBCH with the present compound PEBCH. Relevent data are given in table 4.6.

The only structural difference between CCH5 and PCBCH is that in PCBCH a double bond has been introduced at a specific position of the alkyl chain whereas the structural difference between PCBCH and PEBCH is that, in PEBCH a non-polar ethoxy group has been introduced at the position of the polar cyano group. Introduction of the double bond in CCH5 causes suppression of smectic phase and increase of both the C-N and N-I transition temperatures but the nematic range does not increase. On other hand introduction of the ethoxy group in PCBCH considerably reduces the C-N transition temperature as well as widens the nematic range.

If we look into the crystal structures of the compounds, we observe that various types of molecular overlapping is present in the compounds. In CCH5 bulky central cyclohexyl rings of neighbouring molecules overlap in head to tail manner[8]. While in PCBCH and PEBCH no overlapping of the core cyclohexyl rings is observed. In both smectic and nematic phases of CCH5 and PCBCH "bimolecular association" is observed but in the crystalline state of CCH5 evidence of such association is not found whereas in PCBCH a very weak association is observed. On the other hand, PEBCH shows no evidence of molecular association both in nematic and crystalline states.

Moreover, in crystalline state, both CCH5 and PCBCH have layered structure and within the layers the molecules are tilted with respect to the normal to the layer. These type of packing may be precursor to the tilted smectic phase but not to the observed orthogonal SmB or SmA phases wherein the molecules are parallel to

the smectic layer normals. The parallel imbricated type of packing of PEBCH , however, corresponds to the observed nematic phase. Qualitatively it can also be inferred that the lateral interaction between the molecules is strong in all cases. But in CCH5 the terminal interaction is sufficient to maintain the layer structure so that it melts to smectic phase, in PCBCH it is not sufficient to maintain the layer structure on melting (it shows SmA monotropi -cally, that too within a very small temperature range) and in PEBCH this terminal interaction is negligible so that from imbricated packing it melts to nematic phase. However, we can not give any quantitative explanation only from crystal structure analysis.

Tables - 4.2

Atomic Parameters x,y,z and Biso. E.S.Ds. refer to the last digit printed. Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.

Atom	x	y	z	Biso
C1	.4800(16)	.1608 (3)	.45152(19)	4.8 (3)
C2	.5739(15)	.1285 (3)	.51364(21)	5.0 (3)
O1	.4403(8)	.16667(18)	.56278(12)	3.75(14)
C3	.5525(10)	.15078(23)	.62387(17)	2.79(16)
C4	.4568(12)	.21378(22)	.66654(18)	3.19(18)
C5	.5585(12)	.20269(20)	.73501(17)	2.71(16)
C6	.4560(10)	.12660(19)	.76197(16)	2.05(14)
C7	.5560(12)	.06388(21)	.71804(17)	2.83(17)
C8	.4571(11)	.07555(22)	.64982(17)	3.03(17)
C9	.5588(9)	.11564(19)	.83087(16)	1.91(13)
C10	.4637(11)	.17999(19)	.87428(16)	2.51(16)
C11	.5518(11)	.16835(20)	.94315(16)	2.52(15)
C12	.4471(10)	.09390(19)	.97018(16)	2.10(14)
C13	.5436(11)	.02927(19)	.92736(17)	2.60(16)
C14	.4521(11)	.04045(18)	.85873(16)	2.35(15)
C15	.5408(11)	.08059(21)	1.03844(17)	2.75(16)
C16	.4246(12)	.13959(23)	1.08544(18)	3.42(20)
C17	.5114(21)	.1234 (3)	1.15212(21)	7.5 (4)
C18	.4534(20)	.1318 (4)	1.20081(22)	7.9 (4)
C19	.5283(16)	.11659(25)	1.26745(19)	4.3 (3)

Tables - 4.3

Anisotropic thermal parameters u(i,j) values *100.

E.S.Ds. refer to the last digit printed.

	u11	u22	u33	u12	u13	u23
C1	9.5 (5)	6.0 (3)	2.84(21)	-1.4 (4)	.2 (3)	.28(20)
C2	7.9 (4)	7.9 (3)	3.37(22)	2.4 (4)	.3 (3)	-.78(23)
O1	4.69(19)	6.74(20)	2.83(14)	1.61(20)	.05(16)	.29(14)
C3	3.20(22)	4.77(22)	2.64(18)	.15(23)	.13(20)	.62(16)
C4	5.5 (3)	3.55(20)	3.05(19)	.1 (3)	.21(24)	.84(16)
C5	4.6 (3)	2.64(18)	3.01(18)	-.34(22)	.05(22)	.51(15)
C6	2.72(20)	2.48(17)	2.58(17)	.31(19)	-.07(18)	.10(13)
C7	4.9 (3)	3.16(19)	2.73(18)	1.06(23)	-.03(22)	-.28(15)
C8	4.8 (3)	3.76(20)	2.90(19)	.70(25)	.08(22)	-.51(16)
C9	2.18(19)	2.52(17)	2.55(16)	-.03(17)	-.12(18)	.29(13)
C10	4.5 (3)	2.36(16)	2.72(18)	-.10(21)	-.24(21)	.13(14)
C11	4.24(24)	2.83(18)	2.52(17)	-.15(21)	-.09(20)	-.22(14)
C12	2.98(21)	2.55(17)	2.44(16)	.35(18)	.17(18)	.07(13)
C13	4.38(25)	2.41(16)	3.09(18)	-.02(21)	.05(21)	.25(14)
C14	4.11(24)	2.02(16)	2.79(17)	-.26(20)	.10(20)	-.06(13)
C15	4.3 (3)	3.43(19)	2.77(17)	.87(22)	.08(21)	.19(15)
C16	6.0 (3)	4.20(23)	2.82(19)	.8 (3)	-.13(24)	-.13(17)
C17	17.1 (9)	8.5 (4)	2.88(22)	7.1 (6)	-.2 (4)	-.19(24)
C18	16.6 (9)	10.3 (5)	3.20(23)	9.9 (6)	-1.7 (4)	-1.0 (3)
C19	9.0 (5)	4.40(24)	2.91(20)	1.0 (3)	.0 (3)	.19(17)

Table - 4.4

Atomic Parameters x,y,z and Biso of the hydrogen atoms

Biso is the mean of principle axis of the thermal ellipsoid

Atom	x	y	z	Biso
H1A	.584	.129	.414	3.3
H1B	.250	.150	.447	5.7
H1C	.524	.218	.448	5.7
H2A	.802	.137	.518	5.6
H2B	.529	.070	.517	5.6
H3	.779	.151	.621	3.3
H4A	.548	.266	.649	3.9
H4B	.231	.217	.666	3.9
H5A	.787	.206	.737	3.6
H5B	.470	.248	.764	3.6
H6	.228	.127	.761	2.8
H7A	.469	.011	.734	3.7
H7B	.784	.061	.719	3.7
H8A	.552	.032	.621	3.7
H8B	.232	.072	.648	3.7
H9	.785	.114	.830	2.6
H10A	.240	.187	.872	3.1
H10B	.569	.231	.858	3.1
H11A	.776	.171	.947	3.3
H11B	.453	.213	.971	3.3
H12	.220	.094	.969	2.7
H13A	.446	-.022	.944	3.2
H13B	.770	.024	.929	3.2
H14A	.545	-.005	.831	3.0
H14B	.226	.038	.856	3.0
H15A	.768	.080	1.041	3.3
H15B	.459	.026	1.053	3.3
H16A	.198	.140	1.083	4.2
H16B	.507	.194	1.072	4.2
H17	.711	.093	1.151	7.3
H18	.269	.169	1.202	8.5
H19A	.379	.145	1.299	3.3
H19B	.522	.058	1.276	4.8
H19C	.741	.138	1.278	4.8

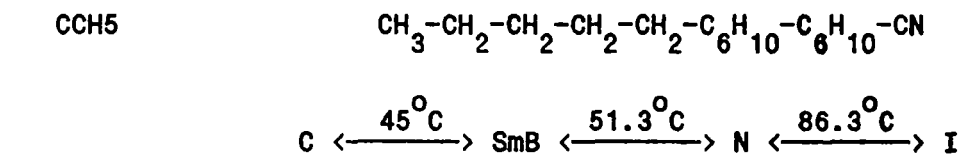
Tables - 4.5

Bond distances (Å) and angles (^{o}) with e.s.d's in parenthesis.

C(1)-C(2)	1.502(7)	C(9)-C(14)	1.548(5)
C(2)-O(1)	1.393(6)	C(10)-C(11)	1.529(5)
O(1)-C(3)	1.425(5)	C(11)-C(12)	1.527(5)
C(3)-C(4)	1.510(6)	C(12)-C(13)	1.534(5)
C(3)-C(8)	1.517(6)	C(12)-C(15)	1.529(5)
C(4)-C(5)	1.539(6)	C(13)-C(14)	1.528(5)
C(5)-C(6)	1.548(5)	C(15)-C(16)	1.547(6)
C(6)-C(7)	1.528(5)	C(16)-C(17)	1.497(6)
C(6)-C(9)	1.548(5)	C(17)-C(18)	1.077(7)
C(7)-C(8)	1.531(5)	C(18)-C(19)	1.479(6)
C(9)-C(10)	1.536(5)		
C(1)-C(2)-O(1)	109.5(5)	C(6)-C(9)-C(14)	111.5(3)
C(2)-O(1)-C(3)	114.4(4)	C(10)-C(9)-C(14)	108.9(3)
O(1)-C(3)-C(4)	106.5(3)	C(9)-C(10)-C(11)	112.9(3)
O(1)-C(3)-C(8)	113.2(4)	C(10)-C(11)-C(12)	112.8(3)
C(4)-C(3)-C(8)	110.6(3)	C(11)-C(12)-C(13)	109.6(3)
C(3)-C(4)-C(5)	112.0(4)	C(11)-C(12)-C(15)	113.3(3)
C(4)-C(5)-C(6)	111.2(3)	C(13)-C(12)-C(15)	110.8(3)
C(5)-C(6)-C(7)	108.7(3)	C(12)-C(13)-C(14)	112.3(3)
C(5)-C(6)-C(9)	111.1(3)	C(9)-C(14)-C(13)	112.6(3)
C(7)-C(6)-C(9)	112.6(3)	C(12)-C(15)-C(16)	113.6(3)
C(6)-C(7)-C(8)	112.4(3)	C(15)-C(16)-C(17)	112.2(4)
C(3)-C(8)-C(7)	111.8(4)	C(16)-C(17)-C(18)	143.7(8)
C(6)-C(9)-C(10)	112.2(3)	C(17)-C(18)-C(19)	145.7(8)

Table - 4.6

CCH5

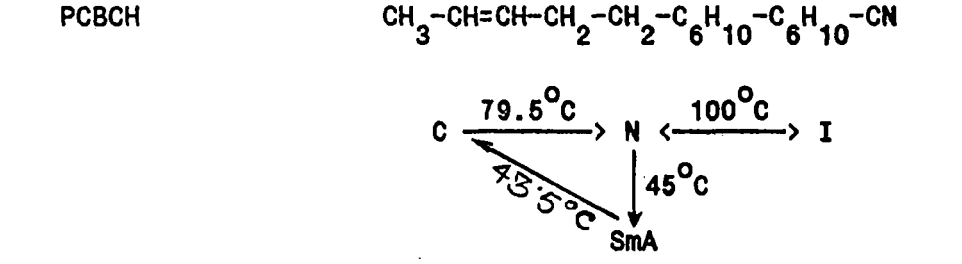


Single molecule model length = 16.5 Å

Smectic layer spacing = 31.2 Å

Molecular length in nematic phase = 27.2 Å

PCBCH

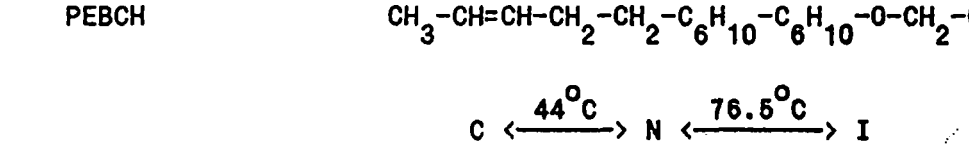


Single molecule model length = 16.3 Å

Smectic layer spacing = 24.0 Å

Molecular length in nematic phase = 30.0 Å

PEBCH



Single molecule model length = 17.4 Å

Molecular length in nematic phase = 17.0 Å

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CHAPTER 5

Physical properties of liquid crystals : Theory and experimental methods.

5.1 THEORIES OF LIQUID CRYSTALLINE PHASES :

The study of liquid crystalline behaviour provides a major challenge for contemporary theoretians. To some extent liquid crystals can be understood on the basis of the simplest of theories. The early work of Maier and Saupe[1] provided a convenient molecular field rationale for the existence of the nematic phase which depends on anisotropic dispersion forces. Landau-de Gennes theory on the other hand treats liquid crystalline behaviour as perturbation of the isotropic phase by expanding the free energy density in terms of the order parameter and its spatial derivatives[2,3]. Prior to this Onsager had predicted that a system of hard rods could exhibit a first order transition from an isotropic liquid to an orientatioally ordered phase without the need for attractive forces[4].In this case the driving force for molecular alignment is provided by the orientational entropy. Despite the success of these theories, the need still remains for a more detailed description of liquid crystalline phase behaviour.

The theories of liquid crystalline phases have been described in detail in several books[5-8]. The salient features of the mean field theories of nematic and smecticA phases in a nutshell as developed by Maier-Saupe[1] and Mc Millan[9,10] are given below.

5.1.a Maier-Saupe theory for nematic phase :

The rod like molecules of a liquid crystalline substance tend to align their long axis along a preffered direction, called the director $\hat{n}$, in a mesophase. The distribution of the molecular long axes about the director is given by an orientational distribution function $f(\cos\theta)$ asssuming cylindrical symmetry of the mesophase, where θ is the angle between the director the molecular long axes. If the molecules have no head to tail asymmetry, than $\hat{n} = -\hat{n}$, and $f(\cos\theta)$ is an even function of $\cos\theta$. The distribution function can also be written as[11]:

$$f(\cos\theta) = \sum_{L \text{ even}} \left(2L + 1 \right) / 2 \langle P_L(\cos\theta) \rangle P_L \cos\theta \qquad (5.1)$$

Where $P_L(\cos\theta)$ are the L^{th} even order Legendre polynomials, and $\langle P_L(\cos\theta) \rangle$ are the statistical average given by

$$\langle P_L(\cos\theta) \rangle = \int_0^1 P_L(\cos\theta)\, f(\cos\theta)\, d(\cos\theta) \Big/ \int_0^1 f(\cos\theta)\, d(\cos\theta) \qquad (5.2)$$

$\langle P_L \rangle$ are called the orientational order parameters of which the first member, i.e., $\langle P_2 \rangle$ is commonly called the order parameter. $\langle P_2 \rangle$ is equal to one for perfectly oriented sample and is equal to zero for randomly oriented i.e., isotropic liquid.

The angular part of the generalised mean-field potential as felt by a rigid rod like molecule can be written as,

$$V(\cos\theta) = \sum_{L \text{ even}} u_L \langle P_L \rangle P_L(\cos\theta) \qquad (5.3)$$

Where U_L are functions of distance between the central molecule and its neighbours only. Maier and Saupe assumed that the potential can be taken to be the leading term only of the sereis (5.3) i.e.,

$$V(\cos\theta) = -V \langle P_2 \rangle P_2(\cos\theta) \qquad (5.4)$$

Hence, the orientational distribution function $f(\cos\theta)$ and the partition function Z are given by

$$f(\cos\theta) = Z^{-1} \exp \left[- V (\cos\theta) / K T \right] \qquad (5.5)$$

(K being the Boltzmann constant).

$$Z = \int_0^1 \exp\left[- V(\mathrm{Cos}\theta) \,/\, K\,T \right] d(\mathrm{Cos}\theta) \qquad (5.6)$$

Substituting the value of $f(\mathrm{Cos}\theta)$ as in equation (5.5) to equation (5.2), we get for L = 2

$$\langle P_2 \rangle = Z^{-1} \int_0^1 P_2(\mathrm{Cos}\theta) \exp\left[\langle P_2 \rangle \, P_2(\mathrm{Cos}\theta) / \, T^* \right] d(\mathrm{Cos}\theta) \qquad (5.7)$$

Where $T^* = V/KT$

$\langle P_2 \rangle$ at different temperatures can be determined by solving this self consistent equation. For many liquid crystals the Maier-Saupe $\langle P_2 \rangle$ values agree quite well with those found experimentally.

5.1.b Mc Millan's theory for SmecticA phase.

In SmecticA phase, there is a periodic density variation along the layer normal (Z -direction) in addition to the orientational distribution of the molecular axes. Hence the normalised distribution function can be written, in this case, as,

$$f(\,\mathrm{Cos}\theta, z\,) = \sum_{L \text{ even}} \sum_{n} A_{L,n} \, P_L(\mathrm{Cos}\theta) \, \mathrm{Cos}(2\pi n z/d) \qquad (5.8)$$

$$\text{with} \quad \int_{-1}^{1} \int_{0}^{d} f(\,\mathrm{Cos}\theta, z\,) \, dz\, d(\mathrm{Cos}\theta) = 1 \qquad (5.9)$$

as normalising condition, d being layer thickness.

McMillan [9,10] following Kobayashi [12,13] assumed a model potential of the following form,

$$V_m(\text{Cos}\theta,z) = -V\left[\delta\alpha\tau\ \text{Cos}(2\pi z/d) + \{\eta + \alpha\sigma\ \text{Cos}(2\pi z/d)\}\ P_2(\text{Cos}\theta)\right] \tag{5.10}$$

Where α and δ are constants which depends on the characteristics of the molecules.

$\eta = \langle P_2(\text{Cos}\theta)\rangle$, $\tau = \langle \text{Cos}\theta(2\pi z/d)\rangle$ and $\sigma = \langle P_2(\text{cos}\theta)\text{Cos}(2\pi z/d)\rangle$ are the orientational, transitional and mixed order parameters respectively, and $\langle\ \rangle$ denotes statistical average of the quantities inside.

The distribution function can be written as

$$f_M(\text{Cos}\theta,z) = Z^{-1} \exp\left[-V_M\ (\text{Cos}\theta,z)\ /\ KT\right] \tag{5.11}$$

where the partition function

$$Z = \int_0^1 \int_0^d \exp\left[-V_M\ (\text{Cos}\theta,z)/\ KT\right] d(\text{Cos}\theta)\ dz \tag{5.12}$$

Once again, three self consistency equation containing η, τ and σ can be written and solved iteratively.

Out of several solutions, the equilibrium state is identified by the minimum value of free energy.

In general, we get the following three cases :

Case I : $\eta = 0$, $\tau = 0$, $\delta = 0$, isotropic liquid.

Case II : $\eta \neq 0$, $\tau = 0$, $\delta = 0$, nematic liquid crystal

Case III : $\eta \neq 0$, $\tau \neq 0$, $\delta \neq 0$, smectic liquid crystal.

5.2 Experimetal Observation :

5.2a Texture Studies :

The texture are the complex optical patterns of liquid crystalline samples observed microscopically, usually in polarised light. These are nothing but the defects of the phase structure

which are generated by the combined action of the phase structure and the surrounding glass plates. Change in texture at particular temperature indicates the occurance of phase transition. For the determination of transition temperatures and the identification of different mesomorphic phases, observation of textures is an important tool for the scientists dealing with liquid crystals. Again for a given structure, different textures can exist, depending on the spacial conditions in preparation of the sample.

It is seen that, homeotropic textures are observed only in phases of nematic, smecticA and smecticB (both orthogonal smectic phases). In smecticC, smecticF and smecticI phases (all tilted smectic phases) broken focal conic texture are observed. The inlayer ordered smectic phases show mosaic texture. Classification of different liquid crystalline phases by the texture study alone is often ambiguous, and therefore other methods are needed to support it.

5.2b X-ray diffaction from mesophases :

X-ray diffraction from mesomorphic phases has been reviewed by many workers[14-20], specially by Vainshtein and Leadbetter.

The x-ray diffraction patterns of the nematic and smectic mesophase are shown in figure 5.1 (a) & (b). In the nematic phase, the diffraction pattern consists of two different rings. The inner ring at small Bragg angle, appears along $\hat{n}$, and outer ring corresponding to the average intermolecular distance D appears along the direction perpendicular to $\hat{n}$. The diffuse rings of unoriented nematic change into cresent-shaped spots in aligned samples as shown in figure 5.1. In the smectic phases, the diffuse inner x-ray diffraction spot changes into a sharp reflection, demonstrating that these phases posses one dimensional transitional order. However, the diffraction peaks are not infinitely sharp delta function characteristics of true crystalline structure.

The angular distribution of the x-ray intensity around the outer

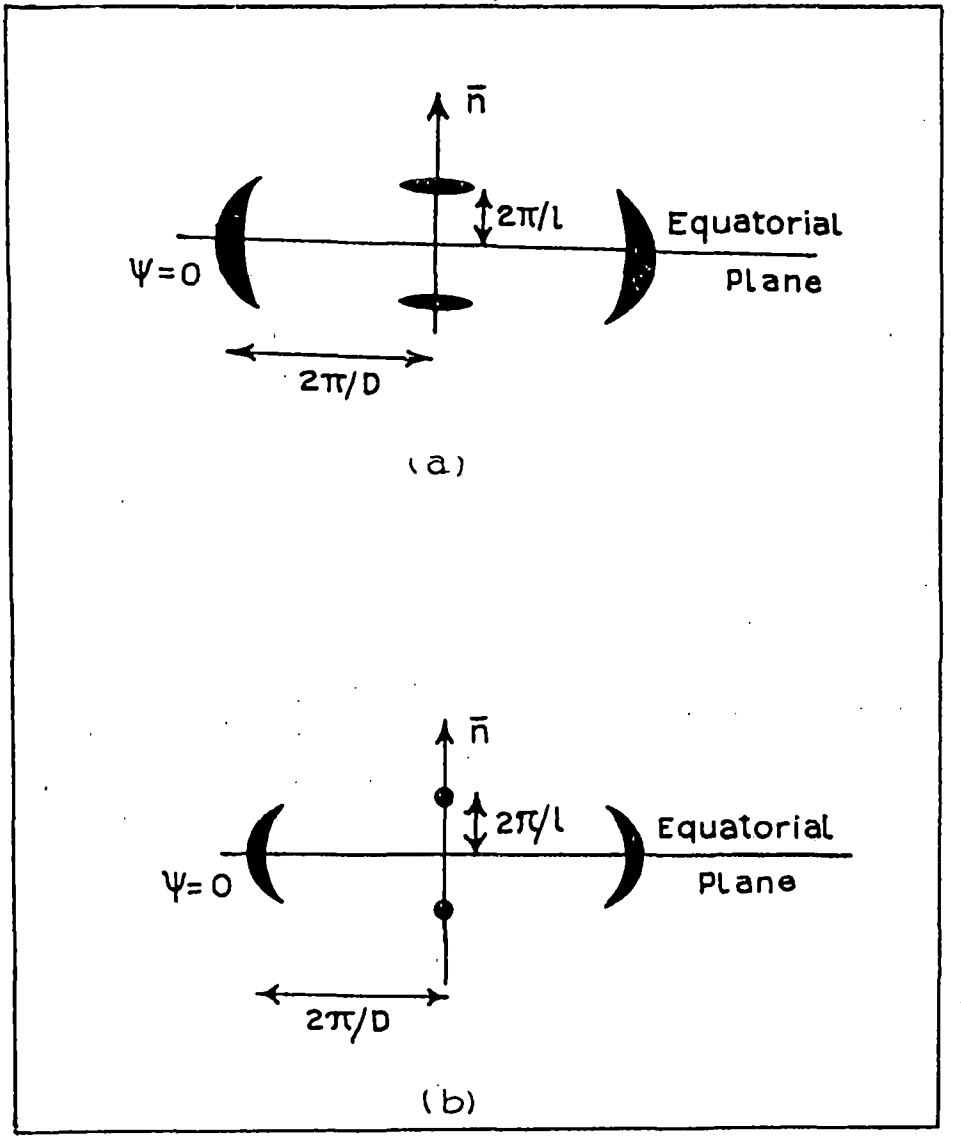

Figure 5.1 : Schematic representation of x-ray diffraction patterns of the (a) Nematic and (b) Smectic A phase.

halo (figure 5.1) also gives the orientational distribution function $f(\mathrm{Cos}\beta)$ and order parameters $\langle P_2 \rangle$.

Orientational Distribution Functions and Order Parameters :

For a system of cylindrically symmetric molecules one can define an orientational distribution function $f(\beta)$, which gives an average state of orientation of the long axis of the molecules relative to the director[14]. From the x-ray diffraction photographs we get intensities averaged over a relatively long time and over a macroscopic volume so that it can be assumed that the molecules have an averaged cylindrical symmetry even if they do not rotate about their long axis[15]. The order parameters $\langle P_L \rangle$ for a system of rigid rods in a uniaxial phase as defined in section 5.1a can be written as,

$$\langle P_L \rangle = \frac{\int_0^{\pi/2} P_L(\mathrm{Cos}\beta)\, f(\beta)\, \mathrm{Sin}\beta\, d\beta}{\int_0^{\pi/2} f(\beta)\, \mathrm{Sin}\beta\, d\beta} \qquad (5.13)$$

Where $P_L(\mathrm{Cos}\beta)$ is well known Legendre polynomial of order L. Putting L = 2 and L = 4 we get $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from equation (5.13). In relating the x-ray intensities $I(\psi)$ around the diffuse equatorial arc (Fig. 5.1) with the orientational distribution function, Leadbetter and Norries[15] assumed the molecules as rigid rods perfectly aligned in clusters of a small number of molecules and obtained

$$I(\psi) = C \int_{\beta=\psi}^{\pi/2} f_d(\beta)\, \sec^2\psi \left[\tan^2\beta - \tan^2\psi \right]^{-1/2} \mathrm{Sin}\beta\, d\beta \qquad (5.14)$$

where $f_d(\beta)$ describes the distribution function of the clusters in which the molecules are perfectly aligned. Moreover, they assumed that for a perfectly aligned sample $\left[f_d(\beta)=\delta(\beta)\right]$, the scattering is zero except for the directions of the scattering vector perpendicular to the cluster axis. They have calculated the effects showning that the deviations are negligible except for highly ordered phases ($\langle P_2 \rangle \geq 0.8$). Comparing the values of $f_d(\beta)$ with $f(\beta)$ of the same sample obtained by other methods it has been seen that $f_d(\beta)$ can be replaced by $f(\beta)$ values, the true distribution function. Because of centro-symmetric molecular distribution in nematic phase, the orientational distribution function can be expanded in the form

$$I(\psi) = \sum_{n=0}^{r} a_{2n} \, \mathrm{Cos}^{2n}\psi \qquad (5.15)$$

$$f(\beta) = \sum_{n=0}^{r} b_{2n} \, \mathrm{Cos}^{2n}\beta \qquad (5.16)$$

Substituting $\mathrm{Sin}\alpha = \mathrm{Cos}\beta \, \mathrm{Sec}\psi$ in equation (5.14) we get

$$I(\psi) = C \int_0^{\pi/2} f_1(\alpha) \, \mathrm{Sin}\alpha \, d\alpha \qquad (5.17)$$

From equations (5.15), (5.16) and (5.17) we have

$$\sum a_{2n} \, \mathrm{Cos}^{2n}\psi = \int_0^{\pi/2} \sum_{n=0}^{r} b_{2n} \, \mathrm{Cos}^{2n}\psi \, \mathrm{Sin}^{2n+1}\alpha \, d\alpha$$

$$= \sum_{n=0}^{r} b_{2n} \, \mathrm{Cos}^{2n}\psi \int_0^{\pi/2} \mathrm{Sin}^{2n+1}\alpha \, d\alpha \qquad (5.18)$$

Since ψ is arbitrary, the coefficient of $\mathrm{Cos}^{2n}\psi$ must be equal. Now,

$$\int_0^{\pi/2} \mathrm{Sin}^{2n+1}\alpha \, d\alpha = \frac{2^{2n}\,(n\,!)^2}{(2n+1)\,!}$$

and so

$$b_{2n} = a_{2n} \frac{(2n+1)\,!}{2^{2n}\,(n!)^2} \qquad (5.19)$$

The series in equations (5.15) and (5.16) converge rapidly. Retaining eight terms in the truncated series, a least square fitting was made to obtain the coefficients from equations(5.15) with corrected intensity values. The calculated intensity values in all cases were found to be in good agreement with the observed intensities. This values of a_{2n} were then used to calculate the coefficients of b_{2n}. Then, $f(\beta)$ values were calculated using eight terms in the series in equation (5.16).

By calculating the integral,

$$\int_0^{\pi/2} f(\beta)\, \mathrm{Sin}\beta \, d\beta = A \quad \text{(say)},$$

and then dividing all the b_{2n} values by A we obtained the normalised values of the orientational distribution function.

Substituting equation (5.16) in equation (5.13) we get

$$\langle P_2 \rangle = 1/2 \; \frac{\int_0^1 \left(3\,\mathrm{Cos}^2\beta - 1 \right) \sum_{n=0}^{r} b_{2n}\, \mathrm{Cos}^{2n}\beta \, d(\mathrm{Cos}\beta)}{\int_0^1 \sum_{n=0}^{r} b_{2n}\, \mathrm{Cos}^{2n}\beta \, d(\mathrm{Cos}\beta)} \qquad (5.20)$$

This can be written in the form of standard integrals and $\langle P_2 \rangle$

can be calculated. Similarly, $\langle P_4 \rangle$ can also be calculated. Vainshtein obtained a fairly good approximation for the order parameter by replacing $f(\beta)$ values with $I(\psi)$ values at a certain Bragg angle in equation (5.13).

Molecular parameters for x-ray studies :

The average lateral distance between the neighbouring molecules (D) was calculated from the x-ray diffraction photographs by a formula given by[21]

$$2D \sin\theta = K\lambda \qquad (5.21)$$

K is a constant which comes from the cylindrical symmetry of the system. Recent calculations[22] have shown that the value of K depends on the order parameter of the sample under consideration. For perfectly ordered state K = 1.117 as given by de Vries[23]. However, since the variation of K with $\langle P_2 \rangle$ is small, we have used the value K = 1.117 for all our calculations.

For both oriented and unoriented samples the Bragg equation was used ($2d\sin\theta = \lambda$) to calculate the apparent molecular length or layer thickness, where θ is the Bragg angle for inner diffraction maxima.

Experimental technique and data analysis :

X-ray diffraction photographs were obtained with the apparatus described below using nickel filtered CuKα radiation in the transimission geometry on a film, using a flat plate camera designed in our laboratory by Jha et al[24].(Figure 5.2). X-ray diffraction photographs were taken at different temperatures in the presence of a magnetic field. The sample was taken in thin walled lithium glass capillary of 1mm diameter. The capillary containing sample was placed in a brass block. The temperature of the block was controlled within $\pm 0.5^{\circ}C$ by a temperature controller (Indotherm MD 401). The sample was first heated to the isotropic phase and magnetic field

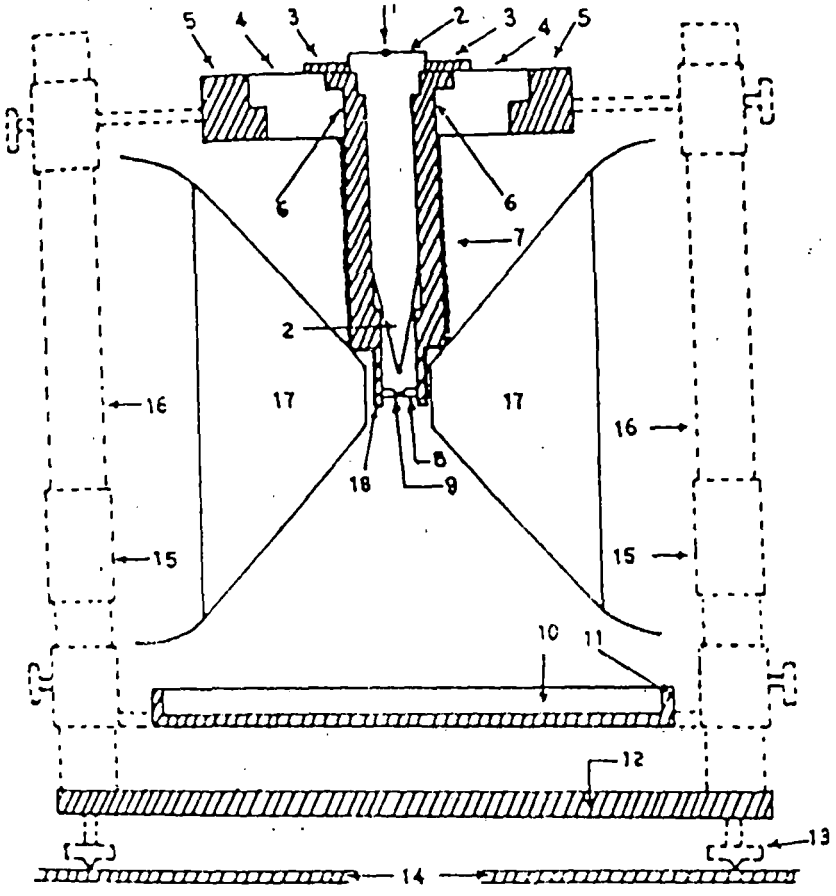

Figure 5.2 : Sectional diagram of the x-ray diffraction camera. 1 - X-ray, 2 - Collimator, 3 - Brass ring, 4 - Ring of sindanyo board, 5 - Brass ring, 6 - Cylindrical brass chamber, 7 - Asbestos insulation and heater winding, 8 - Specimen holder and thermocouple, 9 - Sample, 10 - Film cassette, 11 - Film cassette holder, 12 - Base plate, 13 - Levelling screw, 14 - Brass plates over the coils of the electromagnet, 15 - Removable spacer, 16 - Supporting brass stand, 17 - Pole pieces, 18 - Asbestos insulation.

was applied parallel to the capillary axis. The substance was allowed to cool to the desired temperature in presence of the magnetic field. The strength of the magnetic field was measured previously by a gaussmeter (ECIL model GH867). X-ray beam was collimated by a collimater of aperture 0.8mm. A Ni-filter of thickness 0.009mm was used to obtain predominant CuKα radiation of wavelength 1.542Å. When the temperature reached equilibrium then the x-ray tube was switched on. Photographs were taken at various constant temperatures. In case of the determination of orientational order parameters the sample to film distance was maintained at about 7cm.

For the determination of the exact distance between the sample and the film, an aluminium photograph was taken. Measuring the diameter of the diffraction rings corresponding (111) and (200) reflections and values of Bragg angles, the actual distance between sample and the film can be calculated.

(a) Conversion of optical density to x-ray intensity :

The optical density of the x-ray photographs were measured by microdensitometer (Carl Zeiss MD 100) which has a potentiometric recording (K200) facility for linear scanning. X-ray intensity values are then obtained from the conversion of the corresponding optical density values from a graph as shown in figure 5.3 .Using multiple film technique as given by Klug and Alexander[25] an intensity scale was prepared for this purpose.

(b) Circular Scaning of X-ray Photographs.

A rotating stage was fabricated in our laboratory to facilitate 360° scanning of the photographs. Photographs were scanned to measure the angular intensity distribution $I(\theta)$ which was used to calculate the orientational distribution function $f(\beta)$ and order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The circular scans of the outer diffraction arc taken from $\psi = 0$ to $\psi = 360^{\circ}$ at about 1° intervals

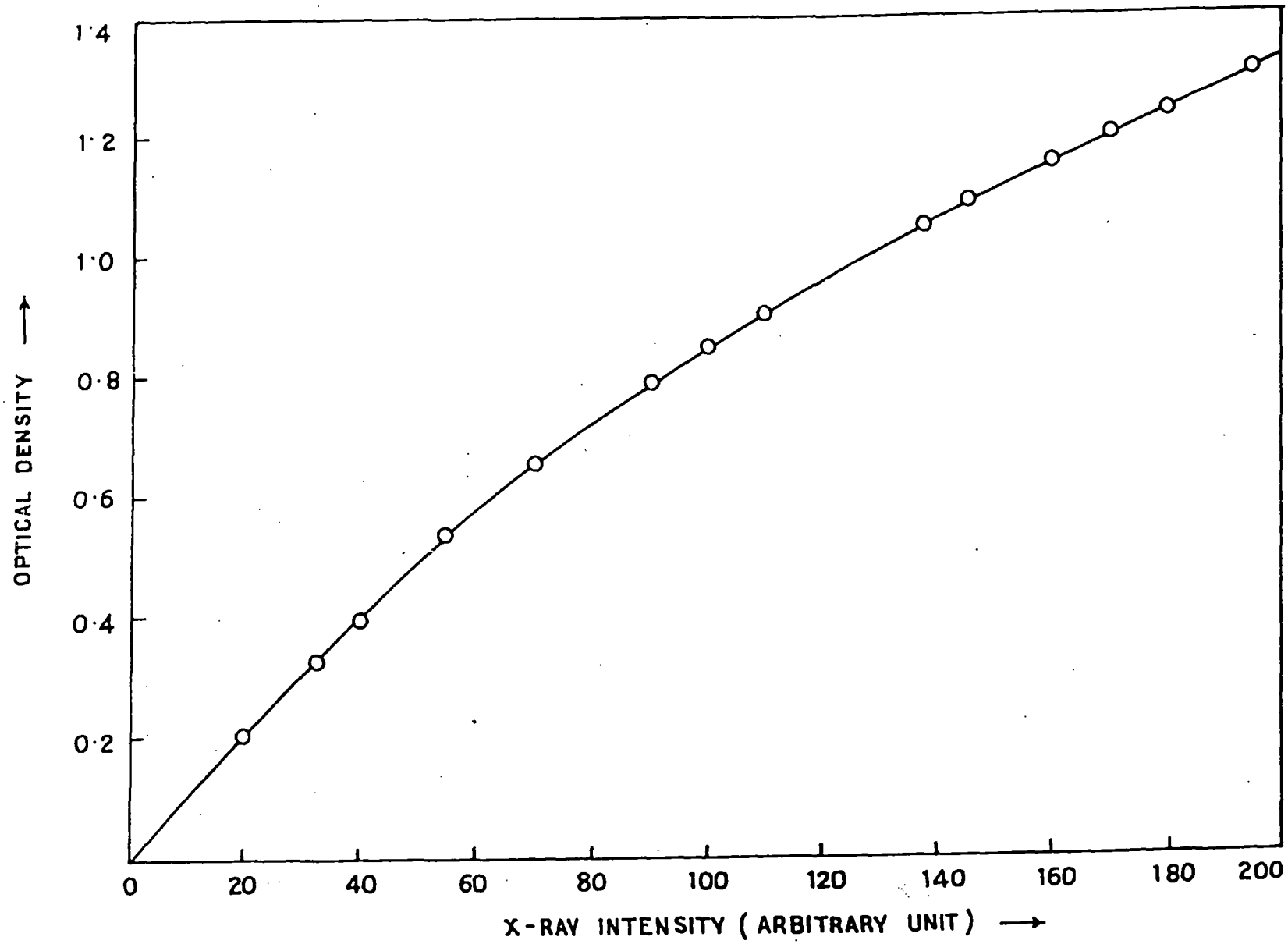

Figure 5.3 : Optical density vs. x-ray intensity curve used for calibration.

near the peak and at larger intervals elsewhere. The optical density values obtained from the densitometric circular scan where converted to x-ray intensity with the help of calibration curve. Intensity values were then corrected for background values arising due to the air scattering. The peak intensity position which corresponds to ψ = 0 was determined from angle vs intensity curve (figure 5.4). Taking nineteen $I(\psi)$ values from $\psi = 0$ to $\psi = 90^{o}$ at 5^{o} intervals from the smoothed $I(\psi)$ vs ψ curve, $f(\beta)$, $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were calculated by using Leadbetter's expression. A computer program has been developed for these calculations.

(c) Linear Scaning of X-ray Photographs.

The diameter of the diffraction rings were determined from the peak positions obtained by linear scanning using a chart drive and corresponding values were calculated.

5.2c OPTICAL BIREFRINGENCE STUDY.

Theoretical considerations :

The birefringence of liquid crystals is the visible manifestation of their long-range order and it is defined only for a uniformly ordered domain. In a uniaxial liquid crystal, the ordinary refractive index n_o is perpendicular to the optic axis or director and represented as $n_\perp$ and extra-ordinary refractive index n_e is parallel to the director which is denoted as $n_\parallel$. From the measurement of n_o and n_e , we can estimate ordering in the liquid crystal at different temperatures.

In a liquid crystal the polarisation $\bar{P}$ is given by,

$$\bar{P} = N \langle \alpha . E_l \rangle \qquad (5.22)$$

where the brackets denote the average over the orientations of all molecules. $\bar{\alpha}$ is the molecular polarizability. N is the number of

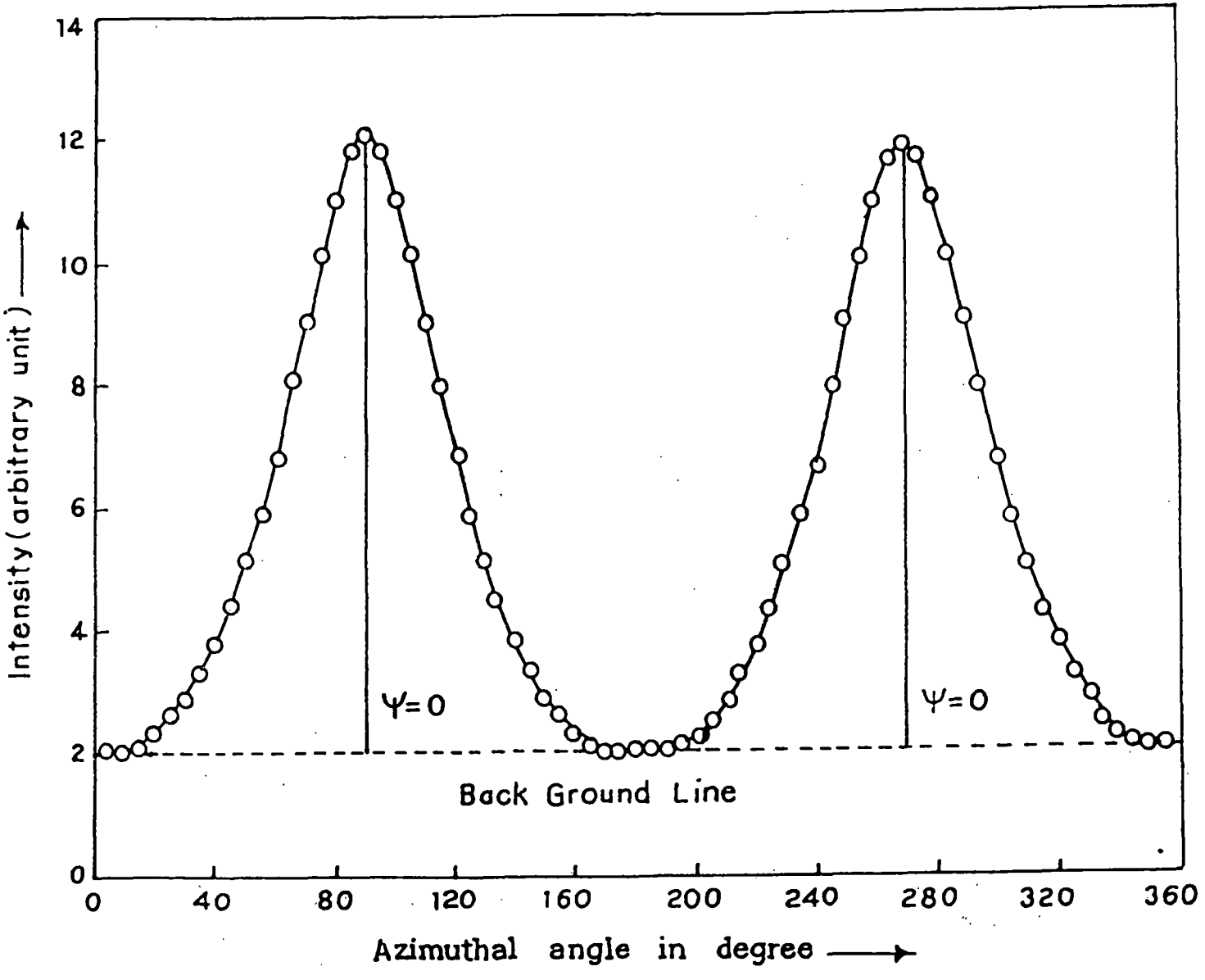

Figure 5.4 : Average intensity I(ψ) vs. azimuthal angle (ψ).

molecules per unit volume and E_i is the internal field, the average field that acts on a molecule.

The internal field is a linear function of the macroscopic field and can be represented by

$$E_i = \bar{K} \cdot E \qquad (5.23)$$

Where $\bar{K}$ is an ordinary second rank tensor. The introduction of this tensor makes it possible to write $\bar{P} = N < \bar{\alpha}.\bar{K} >E$.

Refractive index is related to polarizability by the following relation

$$n_{\parallel}^2 - n_{\perp}^2 = N \left(< \bar{\alpha}.\bar{K} >_{\parallel} - <\bar{\alpha} .\bar{K} >_{\perp} \right) \qquad (5.24)$$

So if we want to calculate molecular polarizability we must know the internal field tensor $\bar{K}$ which was ususually valid for isotropic medium.Because of anisotropy of the internal field, Lorentz-Lorentz formula can not be applied to liquid crystals. We follow, therefore, Neugebauer's relation or Vuk's formula to calculate the polarizabilities. Saupe and Maier also applied a more elaborate form of internal field suggested by Neugebauer.

(a) Neugebauer's method :

Neugabauer[26] extended Lorentz-Lorentz equations for an isotropic system to an anisotropic system. The effective polarizabilities α_e and α_o of the liquid crystals are given by

$$n_e^2 - 1 = 4\pi N \alpha_e \left(1 - N \alpha_e \gamma_e \right)^{-1} \qquad (5.25)$$

$$n_o^2 - 1 = 4\pi N \alpha_o \left(1 - N \alpha_o \gamma_o \right)^{-1} \qquad (5.26)$$

Where N is the number of molecules per cc and γ_i's are internal field constants, n_e and n_o the extra-ordinary and ordinary refractive indices respectively. The equations for calculating the

α_o and α_e obtained from equations (5.25) and (5.26) are

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{n_e^2 + 2}{n_e^2 - 1}\right] + \left[\frac{2(n_o^2 + 2)}{n_o^2 - 1}\right] \qquad (5.27)$$

and $$\alpha_e + 2\alpha_o = \frac{9}{4\pi N}\left[\frac{n^2 - 1}{n^2 + 2}\right] \qquad (5.28)$$

where, $n^2 = 1/3\ (n_e^2 + 2n_o^2)$

Solving equations (5.27) and (5.28) α_o and α_e can be obtained.

(b) Vuk's method.

Vuks[27] has derived another formula for polarizabilities associated with anisotropic organic molecules. The principal polarizabilities and refractive indices can be expressed as,

$$\frac{n_i^2 - 1}{n^2 + 2} = \frac{4\pi N}{3}\alpha_i , \quad i = x,y,z \qquad (5.29)$$

where $n^2 = 1/3 \sum_i n_i^2$

So we find, $$\frac{n_o^2 - 1}{n^2 + 2} = \frac{4\pi N}{3}\alpha_o \qquad (5.30)$$

$$\frac{n_e^2 - 1}{n^2 + 2} = \frac{4\pi N}{3}\alpha_e \qquad (5.31)$$

where $n^2 = 1/3\ (2n_o^2 + n_e^2)$; n being mean refractive index. α_e and α_o can be calculated directly from the refractive index values.

Additive Rule of Bond Polarizability.

Denbigh - Le Fevre[28] established a simple sum rules for the

calculation of molecular polarizability in terms of mean bond polarizability. Molecular polarizabilities for all the substances have been calculated from this additive rule and compared with the values obtained from Vuk's and Neugebauer's methods.

Calculation of order parameters from polarizabilities :

The principal polarisabilities (α_o,α_e) have been calculated by using Vuk's (isotropic model)and Neugabauer's relations (anisotropic model). It can be shown that

$$\alpha_e = \bar{\alpha} + 2/3\ \alpha_a \langle P_2 \rangle \qquad (5.32)$$

$$\alpha_o = \bar{\alpha} - 1/3\ \alpha_a \langle P_2 \rangle \qquad (5.33)$$

Where $\bar{\alpha} = (2\alpha_o + \alpha_e)/3$ is the mean polarizability. $\alpha_a = (\alpha_{\parallel} - \alpha_{\perp})$ is the molecular polarizability anisotropy where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal polarizabilities, parallel and perpendicular to the long axes of the molecules in the crystalline state.

To get the values of $(\alpha_{\parallel} - \alpha_{\perp})$, when solid phase data is not available, the widely used method of Haller[29] et. al was adopted. A graph was plotted with $\log(\alpha_e - \alpha_o)$ vs $\log.(T_c - T)$, where T_c corresponded to the nematic isotropic transition temperature. The plot which is found to be a straight line is extrapolated to $T=0$, giving $(\alpha_e - \alpha_o)_{T=0} = (\alpha_{\parallel} - \alpha_{\perp})$. For each case a set of values of α_e, α_o and $(\alpha_{\parallel} - \alpha_{\perp})$ were obtained (figure 5.5) and then from the relation

$$\langle P_2 \rangle = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \qquad (5.34)$$

Order parameter $\langle P_2 \rangle$ was calculated.

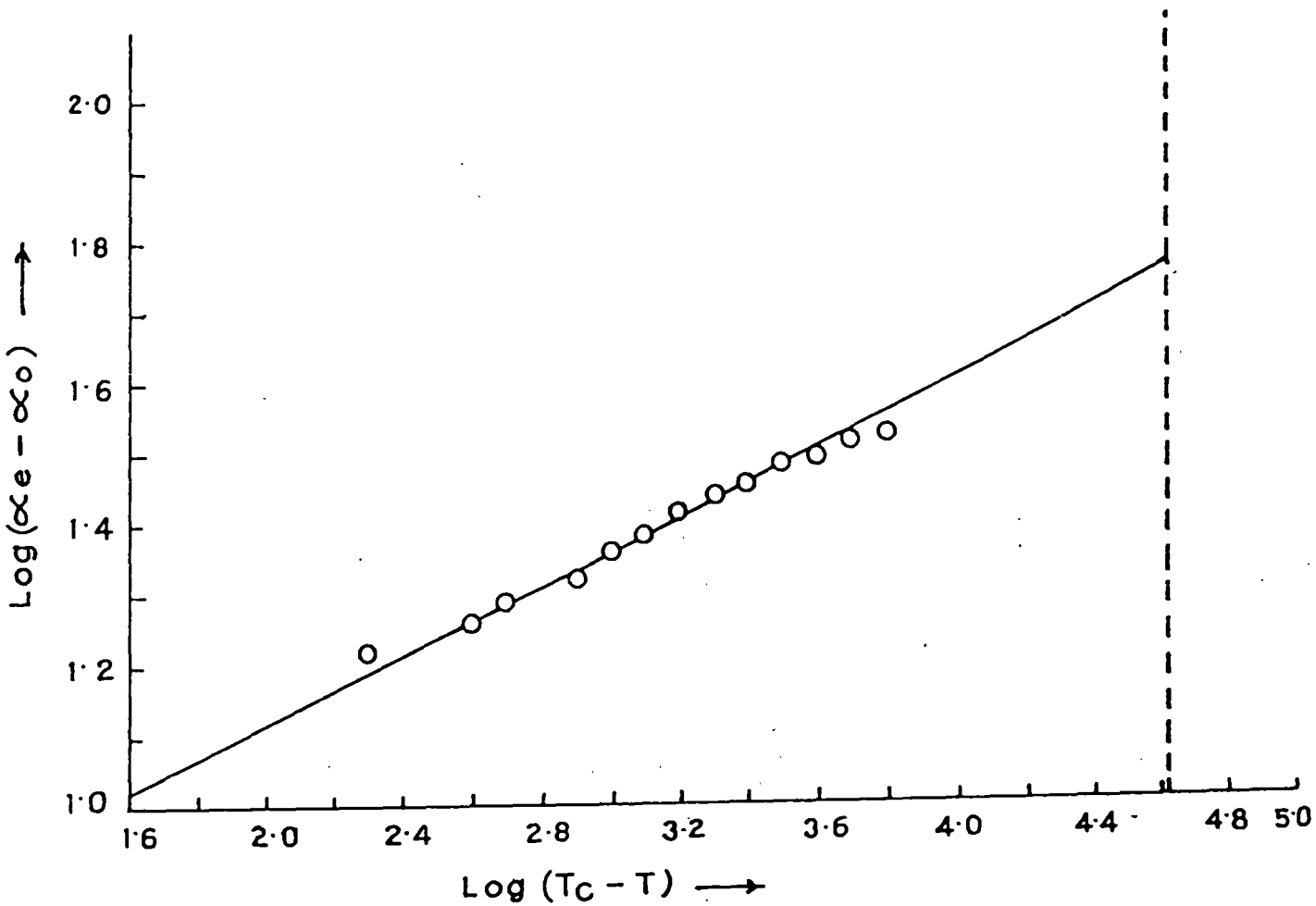

Figure 5.5 : Typical $\log(\alpha_e - \alpha_o)$ vs. $\log(T_c - T)$ curve
(Sample - 1d(1)CC, Chapter - 6).

Measurement of refractive indices :

The refractive indices n_e and n_o fo extra-ordinary and ordinary ray were measured by a thin prims technique. The refracting angle of the prism was less than 2^o. The details of the preparation of the prism and the experimental procedure have already been reported by Zeminder et al[30]. For the preparation of a prism two clean optically plane glass plates were used. One surface of each of the glass plates was rubbed parallel to the direction of one of their edges. The plates were then treated with a dilute solution of polyvinyl alcohol and then dried. The prefered direction on the substrate can be obtained by rubbing the same surface in the same direction again by a tissue paper. The prism was then formed by placing the treated surfaces inside and the rubbing direction parallel to the refracting edge of the prism. The sides of the prism were sealed with a high temperature adhesive. Now the liquid crystal sample was allowed to flow inside the prism by melting a few crystals at the top. The sample was heated to the isotropic state and then cooled down very slowly to the desired temperature. This process was repeated several times. No magnatic field was applied. Repeated heating and cooling produced a homogeneous namatic sample with optic axis parallel to the refracting edge of the prism. The prism was then placed in a brass chamber, whose temperature could be maintained by a temperature controller (Indotherm model 401) at any desired value to an accuracy of $\pm$ 0.5^{o}C by means of an electric heater. The refractive indices were measured for three wave-lengths (λ = 6907Å , 5890Å , 5461Å) from a murcury lamp by means of a precision spectrometer, a wavelength selector and a Nicol prism.

5.2d Measurement of Densities :

The densities of the liquid crystals were measured with the help a dilatometer of the capillary type. A weighed sample of the liquid crystal was introduced inside the capillary tube of the

dilatometer and it was placed in a thermostated water bath. Sufficient time was allowed for equilibrium at the desired temperature before taking each reading. The length of the liquid crystal column was measured at different temperatures with a travelling microscope. The densities were calculated after correction for the expansion of the glass. The accuracy of the measurement of the densities were within 0.1%.

5.2e. THEORETICAL CALCULATION OF ELECTRIC DIPOLE MOMENT.

Guggenheim[31] showed a simpler way of calculating electric dipole moment of a polar solute dissolved in a non-polar solvent at a temperature T. Provided the solution is suffficiently dilute for mutual interaction between solute molecules to be negligible, partial molar volume V_1 of solvent and partial molar volume V_2 of solute are constants. According to Debye the basic formulae for the determination of electric dipole moment μ from the measurements of ε and n are

$$\frac{\varepsilon - 1}{\varepsilon + 2}\,\bar{V} = \frac{\varepsilon_o - 1}{\varepsilon_o + 2} V_1(1 - x) + \frac{4\pi N}{3}\left(\gamma_e + \gamma_a + \frac{\mu^2}{3KT}\right) x \qquad (5.35)$$

$$\frac{n^2 - 1}{n^2 + 2}\,\bar{V} = \frac{n_o^2 - 1}{n_o^2 + 2} V_1(1 - x) + \frac{4\pi N}{3}\gamma_e x \qquad (5.36)$$

The notations used in the above equations are,

x = Mole fraction of solute.

C = Concentration of solute expressed as moles/volume

$\bar{V}$ = Mean molar volume.

ε = Dielectric constant of solution.

ε_o = Dielectric constant of pure solvent.

n = Refractive index of solution.

n_o = Refractive index of pure solvent.

γ_e = Electronic contribution to polarizability of solute molecule

γ_a = Atomic contribution to polarizability of solute molecule.

K = Boltzmann's constant

N = Avogadro's number.

V_1 and V_2 are related with $\bar{V}$ as

$\bar{V} = (1 - x)V_1 + x V_2$ and $C = x/V$

From equation (1) and (2) we can write,

$$\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right]\bar{V} = \left[\frac{\varepsilon_o - 1}{\varepsilon_o + 2} - \frac{n_o^2 - 1}{n_o^2 + 2}\right]V_1(1 - x) + \frac{4\pi N}{3}\left[\gamma_a + \frac{\mu^2}{3KT}\right]x \qquad (5.37)$$

For no atomic contribution to the polarizability of either solvent or solute molecules , we can write $\varepsilon_o = n_o^2$ and $\gamma_a = 0$ and equation (5.37) can be written as,

$$\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] = \frac{4\pi N}{3}\frac{\mu^2}{3KT}C \qquad (5.38)$$

According to equation (5.38) if the experimental quantity,

$$\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] = \frac{3(\varepsilon - n^2)}{(\varepsilon+2)(n^2+2)} \qquad (5.39)$$

were plotted against C , then a straight line is obtained through the origin having a slope equal to $4\pi N\mu^2/9KT$.

But due to the atomic polarizability of the solvent, $\varepsilon_o = n_o^2$. Guggenheim then defined a fictitious atomic polarizability γ'_a expressed by the equation,

$$\frac{4\pi N}{3}\gamma'_a = \left[\frac{\varepsilon_o - 1}{\varepsilon_o + 2} - \frac{n_o^2 - 1}{n_o^2 + 2}\right]\frac{V_2}{V_1} \qquad (5.40)$$

Now from equations (5.37) and (5.40) we obtain ,

$$\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] = \left[\frac{\varepsilon_o - 1}{\varepsilon_o + 2} - \frac{n_o^2 - 1}{n_o^2 + 2}\right] + \frac{4\pi N}{3}\left[\gamma_a - \gamma'_a + \frac{\mu^2}{3KT}\right]C \qquad (5.41)$$

According to equation (5.41), if the experimental quantity $3(\varepsilon-n^2)/(\varepsilon+2)(n^2+2)$ is plotted against C , the curve has an

initial height $\left[\frac{\varepsilon_o - 1}{\varepsilon_o + 2} - \frac{n_o^2-1}{n_o^2+2}\right] = \frac{3(\varepsilon_o - n_o^2)}{(\varepsilon_o+2)(n_o^2+2)}$ (5.42)

and an initial slope $\frac{4\pi N}{3}\left[\gamma_a - \gamma'_a + \frac{\mu^2}{3KT}\right]$.

Since it is only the initial slope that is of interest so it was further simplified by equating the denominator of equations (5.39) and (5.42) we then have

$$3(\varepsilon - n^2) = 3(\varepsilon_o - n_o^2) + \frac{4\pi N}{3}(\varepsilon_o+2)(n_o^2+2)\left[\gamma_a - \gamma'_a - \frac{\mu^2}{3KT}\right]C$$

$$\text{or, } (\varepsilon - n^2) - (\varepsilon_o - n_o^2) = \frac{4\pi N}{9}(\varepsilon_o+2)(n_o^2+2)\left[\gamma_a - \gamma'_a - \frac{\mu^2}{3KT}\right]C \qquad (5.43)$$

Thus plotting the experimental quantity $(\varepsilon-n^2)$ against C , a curve is obtained having an initial height $(\varepsilon_o-n_o^2)$ and an

initial slope,

$$\frac{(\varepsilon_o+2)(n_o^2+2)}{3}\,\frac{4\pi N}{3}\left[\gamma_a-\gamma'_a-\frac{\mu^2}{3KT}\right]$$

For polar solute molecules , at least those having μ greater than one debye, γ_e is itself usually small compared with $\mu^2/3KT$. It is found that γ_a is always less than one-tenth of γ_e. Hence an accurate estimate of γ_a is not needed. Under these circumstances, the simplest assumption can be made as $\gamma_a = \gamma'_a$.

Thus equation (5.44) can be written as,

$$(\varepsilon - n^2) - (\varepsilon_o - n_o^2) = \frac{(\varepsilon_o + 2)\,(n_o^2 + 2)}{3} \cdot \frac{4\pi N}{3} \cdot \frac{\mu^2}{3KT}\, C$$

$$\text{or,}\quad \mu^2 = \frac{27KT\left[(\varepsilon - n^2)-(\varepsilon_o - n_o^2)\right]}{4\pi NC\,(\varepsilon_o + 2)(n_o^2 + 2)} \qquad \text{----------(5.45)}$$

This simplified equation was used for the determination of dipole moments of polar compounds which is given in detail in chapter 8.

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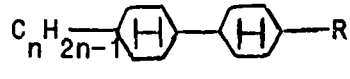
CHAPTER 6

Study of mesomorphic properties of three alkenyl liquid crystalline compounds.

6.1 INTRODUCTION

As the complexity and diversity of the liquid crystal display technology increases, demands for new liquid crystal materials with wide band-width of material properties also increases. New type of polar and non-polar bicyclohexane liquid crystals containing alkenyl side chains were reported in this context[1-4]. These compounds have low optical anisotropy, low viscosity but high elastic constants, so can be used in display devices as materials of short response times. Properties of these compounds changes markedly with respect to the position of the double bond in the alkenyl chain. Since the end chains in nematics are usually quite short, double bonds are close to the core and steric interactions between the core and the double bonds are certainly important. In view of these I have undertaken the study of some alkenyl liquid crystalline compounds which have nematic phase over a wide range.

In this chapter the experimental result of x-ray diffraction and optical studies on three compounds having the following structures have been discussed,



(I) n=3, R=CN, 4(1″-propenyl)4′(cyano)1,1′ bicyclohexane.
[1d(1)CC].

(II) n=5, R=CN, 4(3″-pentenyl)4′(cyano)1,1′ bicyclohexane
[1d(3)CC].

(III) n=5, R=OC_2H_5, 4(3″-pentenyl)4′(ethoxy)1,1′ bicyclohexane.
[1d(3)CCO2]

The crystal structure for the compounds 1d(3)CC and 1d(3)CCO2 has already been solved[5,6] and discussed in chapter 3 and chapter 4.

6.2 EXPERIMENTAL DETAILS

6.2.1 Texture Study

The phase transition of the three compounds were studied by observing textures under crossed polarizers with a polarising microscope of magnification 150x. The transition temperatures agree well with the literature values, except that we get supercooling in all three compounds and for 1d(3)CC we observed smecticA phase for a very short range of temperature during cooling. The compounds 1d(1)CC and 1d(3)CCO2 showed marbled textures, both during heating and cooling, which are often found in the nematic phase. The compound 1d(3)CC showed a fan shaped texture of SmecticA phase and a nematic marbled texture. The existence of these phases were also confirmed from x-ray studies.

6.2.2 X-ray diffration study

A detailed description of the experimental method for x-ray diffraction study is given in chapter 5. The alkenyl bicyclohexanes under investigation have very small magnetic anisotropy, virtually zero[4] and these could not be aligned by usual magnetic field. By heating the sample slowly to the isotropic state and then cooling it down to the desired temperature well aligned samples were obtained. Diffraction photographs were taken at regular intervals during cooling from isotropic phase.

In order to determine the various parameters, the photographs were scanned, both linearly and circularly, by an optical micro densitometer (VEB Carl Zeiss Jena, Model MD 100) equiped with an automatic recording facility. The measured optical densities were converted to x-ray intensity values with the help of a calibration curve following Klug and Alexander[7].

To obtain better accuracy in the layer thickness measurement, x-ray diffraction photographs of inner rings were taken, increasing the sample to film distance about 9cm with a Carl Zeiss Universal

Camera (Model 90486) for the compound 1d(3)CC. The same measurements could not be done for the compound 1d(1)CC due to shut down of the x-ray generator.

6.2.3 Optical study :

Birefringence measurements were made using the technique of thin prism and the experimental procedures were described in chapter 5. A precision spectrometer and a nicol prism were used to measure the refractive indices (n_o,n_e) within experimental error $\pm$.001 for three different wavelengths.

6.2.4 Density measurement :

The densities of the sample were determined by a dilatometer of capillary type. Temperature during the experiment was controlled to about $\pm 0.5^{o}C$ by a temperature controller. The experimental uncertainty of density measurement is 1%.

6.3 RESULTS AND DISCUSSIONS

From texture study, the three compounds are found to have the following mesophase behaviour,

(I) 1d(1)CC $\quad C \underset{47.5^{o}C}{\overset{65.5^{o}C}{\rightleftharpoons}} N \underset{\longleftarrow}{\overset{100.5^{o}C}{\longrightarrow}} I$

(II) 1d(3)CC $\quad C \xrightarrow{79.5^{o}C} N \underset{\longleftarrow}{\overset{100.5^{o}C}{\longrightarrow}} I$, $N \xrightarrow{43.5^{o}C} SmA$

(III) 1d(3)CCO2 $\quad C \underset{29.5^{o}C}{\overset{44^{o}C}{\rightleftharpoons}} N \underset{\longleftarrow}{\overset{76.5^{o}C}{\longrightarrow}} I$

6.3.1 Refractive index measurements

Variations of density measurements with temperatures for the

samples are given in figure 6.1. The density graph for the compound 1d(3)CC shows a first order phase transition at 45°c in the supercooled state. The phase was identified to be SmA by our x-ray and texture studies. Figures 6.2 - 6.4 indicate the variation of (n_o,n_e) with temperature of the three samples. The refractive indices (n_o,n_e) and the densities of the three samples at different temperatures for the three wave-lengths are arranged in tables 6.1 - 6.3.

It is found that the value of birefringence(Δn) is very low for these compounds. This low anisotropy may be due to the influence of the π-electron in -c=c- double bond of the alkenyl side chain which for all the three compounds are in even position making angles with the long axis of the molecule. Over and above this, the cyclohexane cores are less polarizable compared to the biphenyl cores. It will be interesting to study the optical anisotropy of compounds having double bonds in the odd positions.

From the values of the refractive indices the molecular polarizabilities (α_o,α_e) were calculated using Vuks[8] isotropic (1966) and Neugebauer's (1954) anisotropic[9] internal field models. The values of effective polarizabilities α_o and α_e obtained from Vuk's and Neugebauer's method are given in tables 6.4 - 6.6 and 6.7 - 6.9 respectively. From these polarizabily anisotropy values at different temperatures we calculated the orientational order parameter $\langle P_2 \rangle$ for all the three compounds. The values of order parameters $\langle P_2 \rangle$ at different temperatures obtained from the three different wavelengths and their average values have been included in tables 6.10 - 6.12 and 6.13 - 6.15. Due to lack of refractive index data in the crystalline state tho values of $\alpha_\parallel$ and $\alpha_\perp$ could not be calculated directly. In order to obtain ($\alpha_\parallel - \alpha_\perp$) we took help of Haller's extrapolation procedure.

Estimation of the polarizabilities of the molecules was also carried out using the additive rule of bond polarizability proposed

by Le Fevre[10] (1965). This molar polarizability is approximated as a sum of bond polarizabilities

$$a = \sum a_k$$

the summation extending over all covalent bonds k in the molecule. Assuming rotational symmetry[11] around the bonds, a_k is specified by its longitudinal component ($\alpha_{\parallel}$) its transverse component ($\alpha_{\perp}$) and the orientations of the bond. The bond polarizability values were taken from Le Fevre.

Table 1.16 shows the experimental and calculated values of mean

TABLE - 6.16

Comparison of experimental and calculated polarizability values.

Compounds.	α		$\Delta\alpha$		
	Calculated	Expt.	Calculated	Experimental.	
				Vuks	Neug.
1d(1)CC	27.96	22.14	8.31	6.89	5.81
1d(3)CC	31.54	24.53	10.52	9.92	8.49
1d(3)CCO2	33.57	27.32	8.04	9.97	8.76

α and $\Delta\alpha$ are in 10^{-24} cm^3 unit.

polarizability α and molecular polarizability anisotropy $\Delta\alpha$. Since α_o and α_e values at different wavelengths are quite close we have given values for λ=5780Å only.

It cannot be said that the experimental values of α agree well with calculated values. But it is observed that as the experimental values of α increases, the calculated values also increases. The calculated value of $\Delta\alpha$ for the compound 1d(1)CC and 1d(3)CC agree better with Vuk's values. For the third non-polar compound the

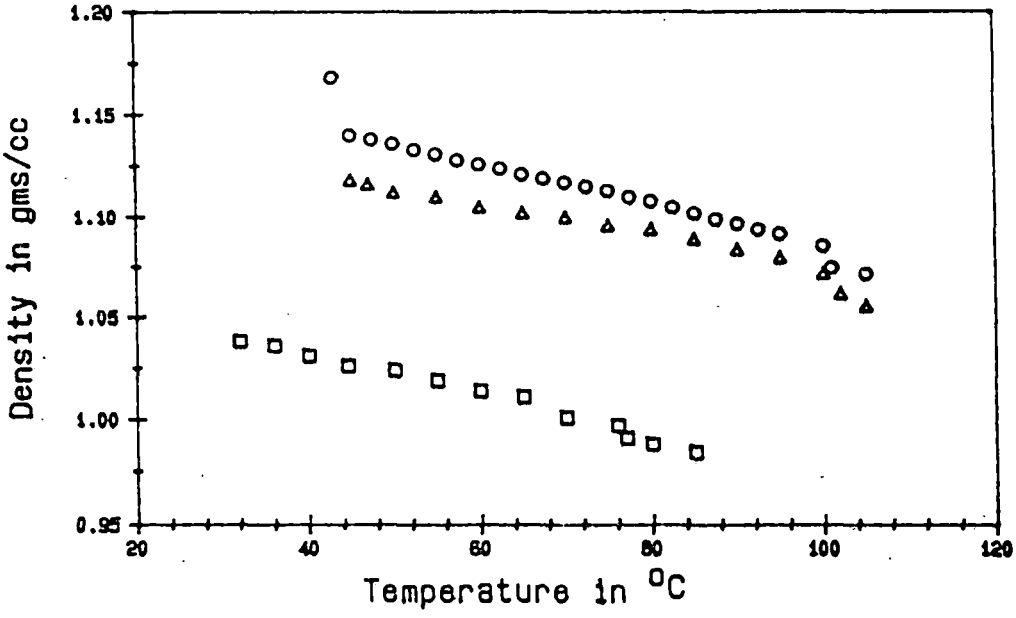


Figure 6.1 : Variation of density with temperature.
o - 1d(3)CC, Δ - 1d(1)CC, □ - 1d(3)CCO2.

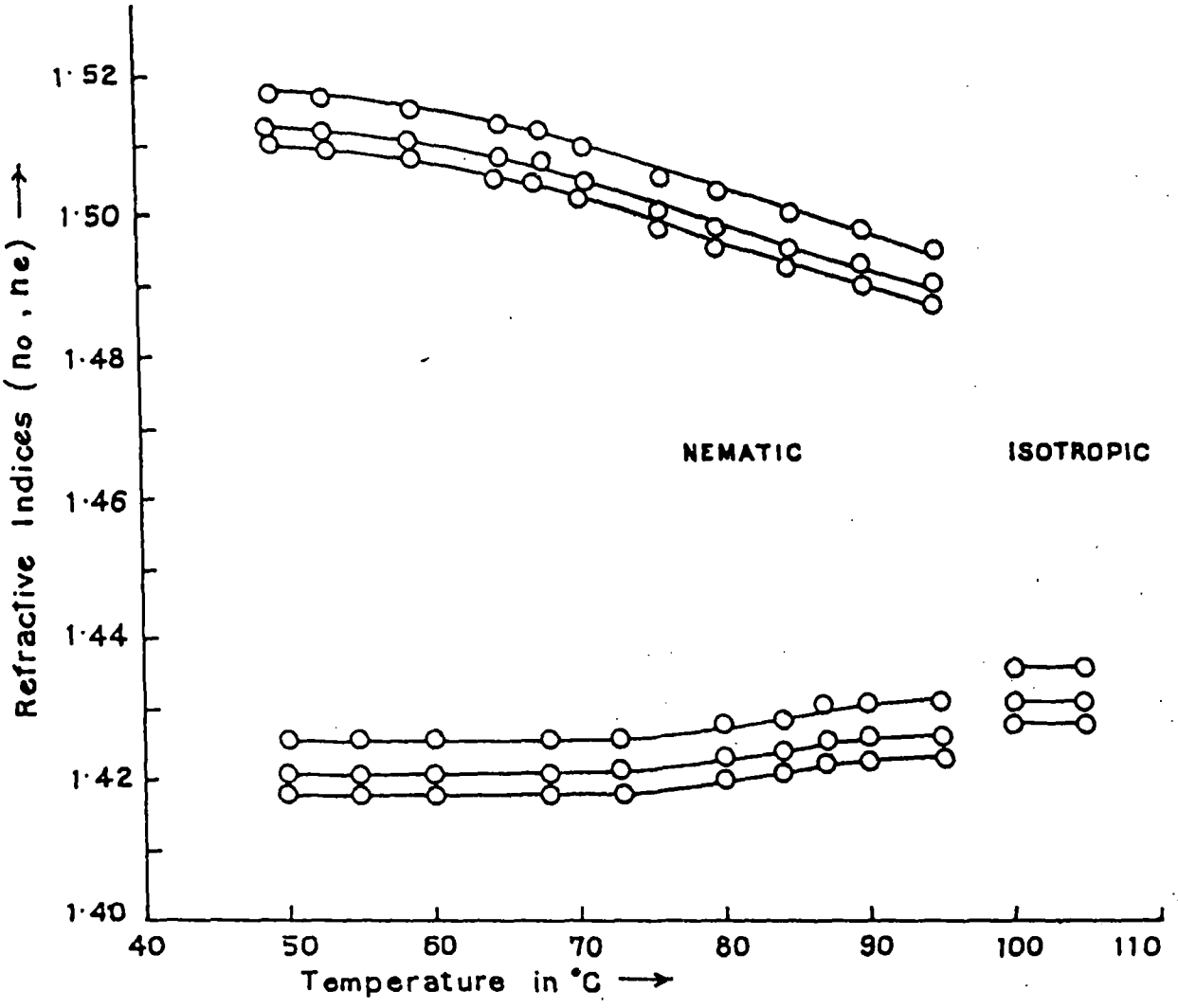


Figure 6.2 : Variation of refractive indices (n_o,n_e) at different temperatures of compound 1d(1)CC. Upper curve for λ = 5461 Å, middle curve for λ = 5780 Å, and lower curve for λ = 6907 Å.

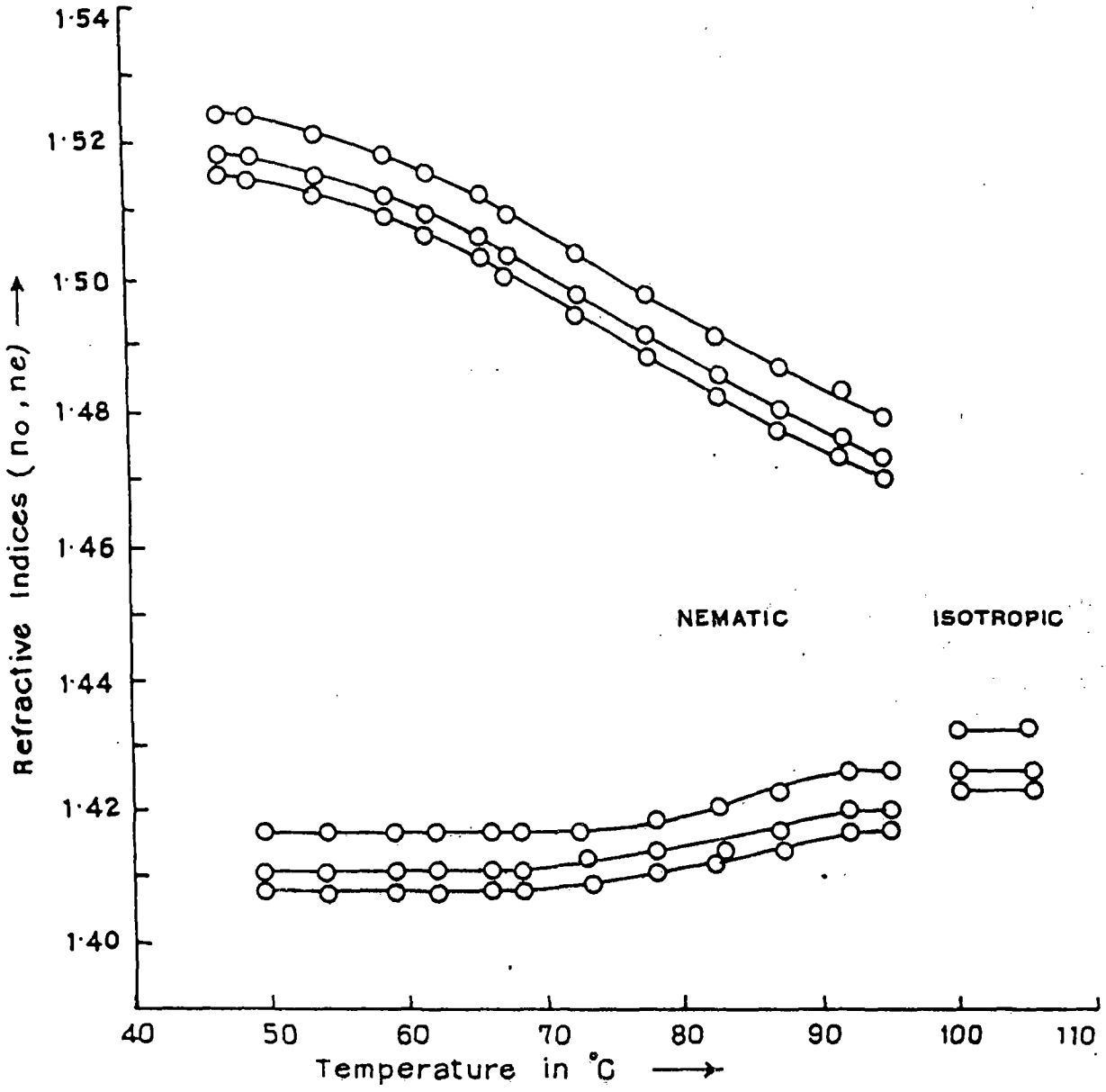


Figure 6.3 : Variation of refractive indices (n_o,n_e) at different temperatures of compound 1d(3)CC. Upper curve for λ = 5461 Å, middle curve for λ = 5780 Å, and lower curve for λ = 6907 Å.

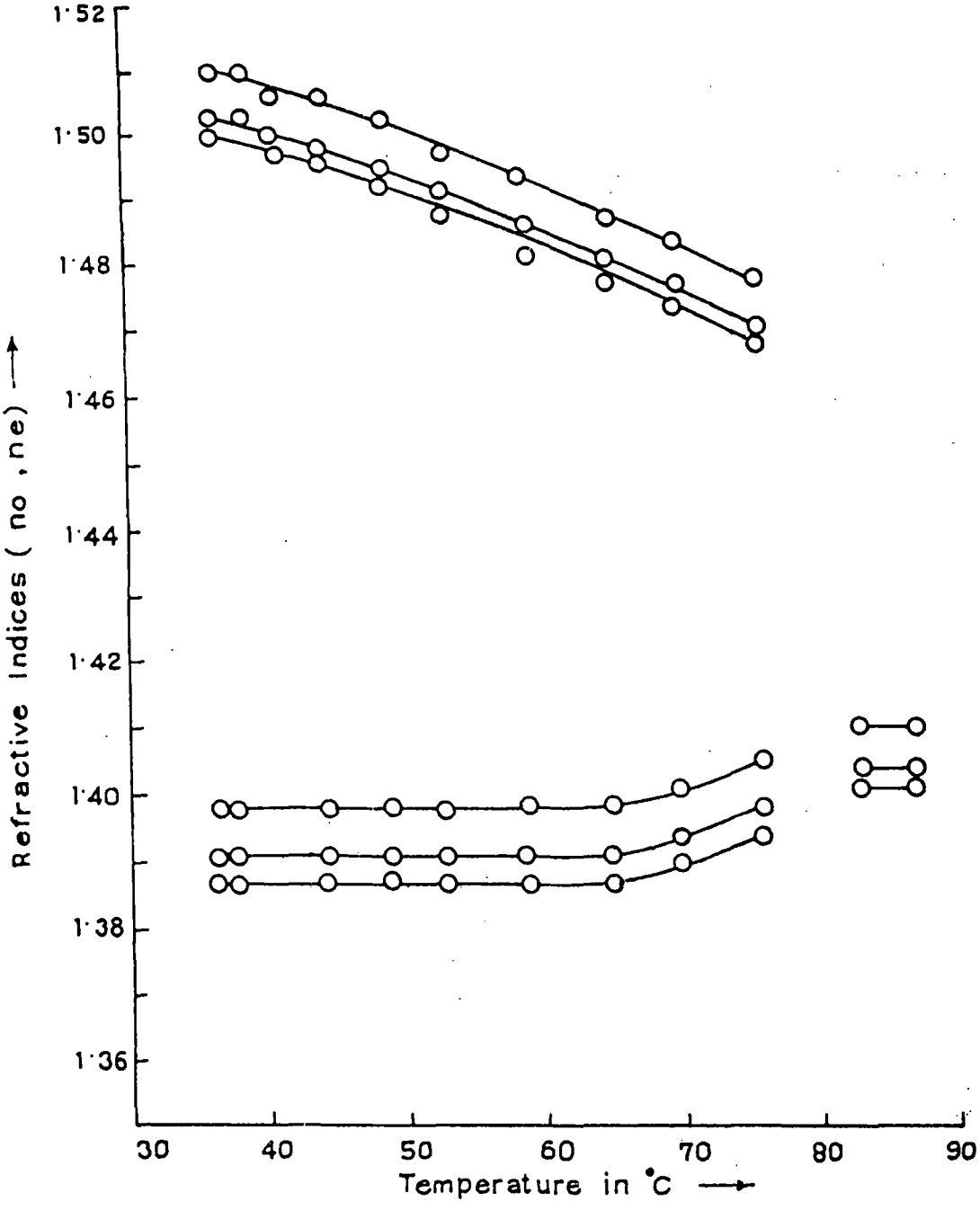


Figure 6.4 : Variation of refractive indices (n_o,n_e) at different temperatures of compound 1d(3)CCO2 Upper curve for λ = 5461 Å, middle curve for λ = 5780 Å, and lower curve for λ = 6907 Å.

agreement is better with Neugebauer's. I could not arrive at any definite conclusion for this type of results, because all the three compounds do not belong to the same homologous series. Moreover, both additive rule of bond polarizability and Haller's extrapolation procedure is not free from limitations. Probably best results could have been obtained if experimental values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ were available in the solid phase and then from comparison it could have been said definitely whether the extrapolation procedure is justified or not.

6.3.2 Parameters from x-ray diffraction study.

X-ray diffraction photographs of the three compounds at different temperatures are given in figures 6.5 - 6.10. From the x-ray diffraction photographs, fluctuation wave lengths[12] parallel and perpendicular to the director and correlation lengths for all the compounds have been calculated. X-ray intensity data from linear scanning of outer halo were fitted to a gaussian form[13] with a background varying linearly with the scattering vector q as follows,

$$I(q) = a + \exp\{-b(q-c)^2\} + d + eq$$

The best fitted values of q_o, the peak position, give the value of intermolecular distance D using the relation $D = 2\pi(1.117/q_o)$. The intensity vs q-values graph at temperature 50°C for the compound 1d(3)CC is shown in the figure 6.11. The D values are found to be temperature independent for all the compounds. From the the best fitted value of Δq we calculated the correlation length and it has been found that the local director is random beyond five molecular diameters.

Fluctuation wavelength l parallel to the director are obtained from scattering about the meridional direction. using Bragg's formula. For 1d(3)CC this pseudo layer spacings in the nematic phase is about 1.8 times the molecular length (16Å). Antiparallel

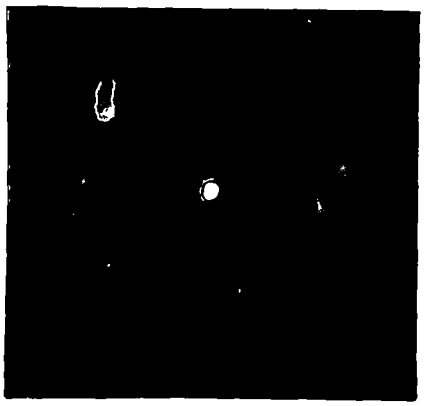


Figure 6.5 : X-ray diffraction photograph of oriented sample 1d(1)CC at 77°C

Figure 6.6 : X-ray diffraction photograph of oriented sample 1d(1)CC at 85°C.

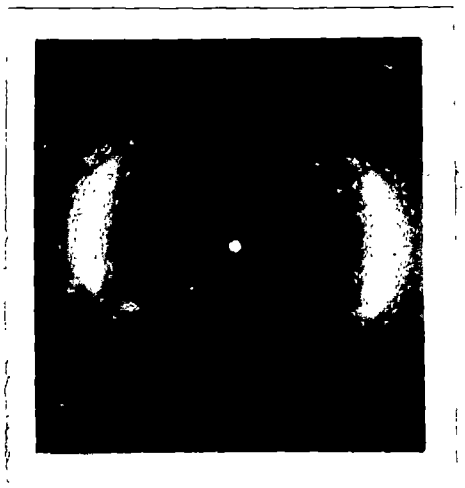


Figure 6.7 : X-ray diffraction photograph of oriented sample 1d(3)CC at 60^{o}C.

Figure 6.8 : X-ray diffraction photograph of oriented sample 1d(3)CC at 45^{o}C. (Smectic phase)

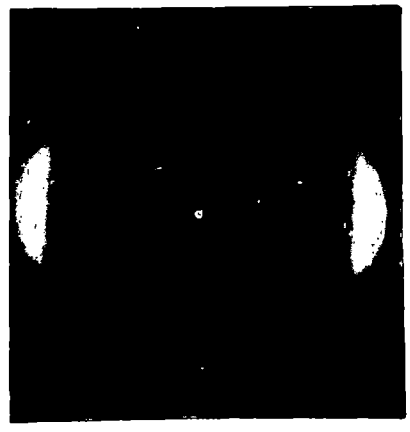


Figure 6.9 : X-ray diffraction photograph of oriented sample 1d(3)CCO2 at 35°C.

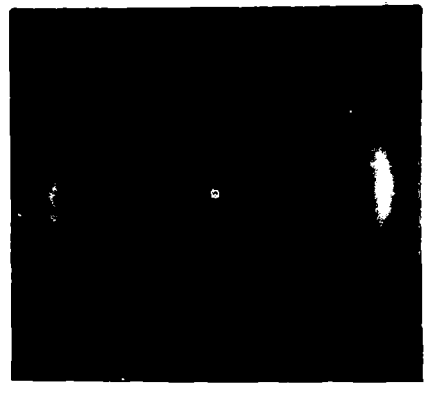


Figure 6.10 : X-ray diffraction photograph of oriented sample 1d(3)CCO2 at 60°C.

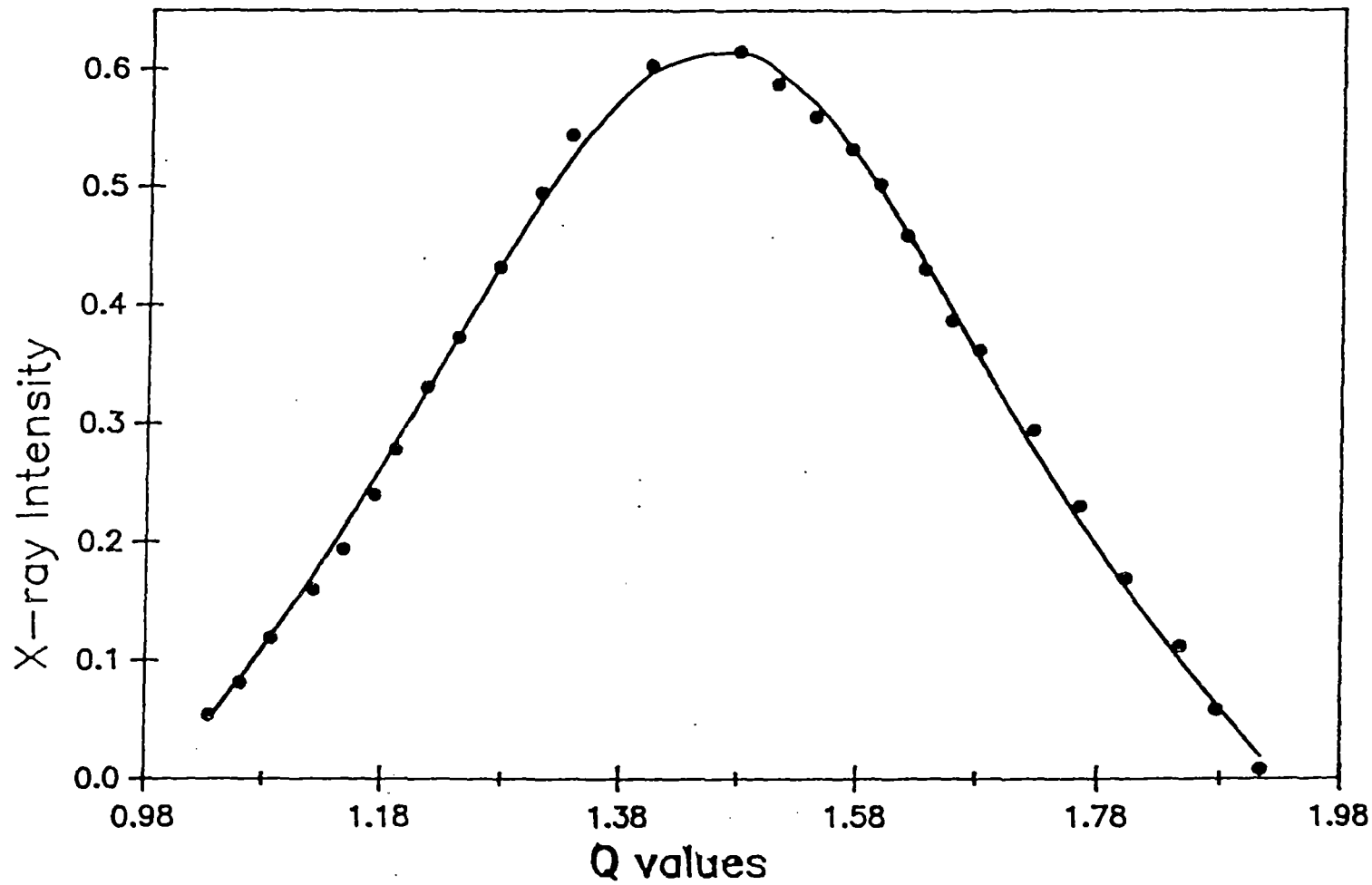


Figure 6.11 : Q vs intensity graph of sample 1d(3)CC at $50^{o}C$, o experimental points, —— fitted curve through calculated values.

molecules have dipole - dipole interaction forming dimers. The length (L), of the compound 1d(1)CC, measured from stereo-model unit was found to be 13.8 Å. I could not determine the pseudo layer spacing from x-ray diffraction photographs in the nematic phase. Probably this polar cyano compound also form dimers in the mesomorphic state, resulting in an increase in apparent value of l. Compound 1d(3)CCO2 is weakly polar and the layer spacing is found to be almost same as the molecular length (17.0 Å). Vander Waals type of interactions are involved in mesophase stability in this compound.

The compound 1d(3)CC exhibits a monotropic SmA phase with two collinear but incommensurate density modulation of periodicity 14.94Å which is almost the same as the molecular length and the other periodicity is 24.01Å, which is between l and 2l. This type of SmA phase is never been observed so far for pure compounds. We could not explain the existence of this smectic phase from the structural studies in the solid phase. Different kind of intermolecular interaction are responsible for this phase formation.

6.3.3 Orientational order parameters :

The mean intensity values of the four quardrants are given in tables 6.17 - 6.19 for the three compounds. The procedure for the determination of normalised orientational distribution function $f(\beta)$ values using Leadbetter's formula were described in chapter 5. Tables 6.20 - 6.22 give the normalised distribution function $f(\beta)$ values at angles of 5^{o} intervals, calculated by an even power series of $\cos\beta$. Appearance of some negative values are due to the truncation errors. $f(\beta)$ versus β at different temperature are given in figures 6.12 - 6.14. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for the three compounds calculated from distribution function at different temperature are listed in table 6.23. Variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperatures are shown in figures 6.15 - 6.17.

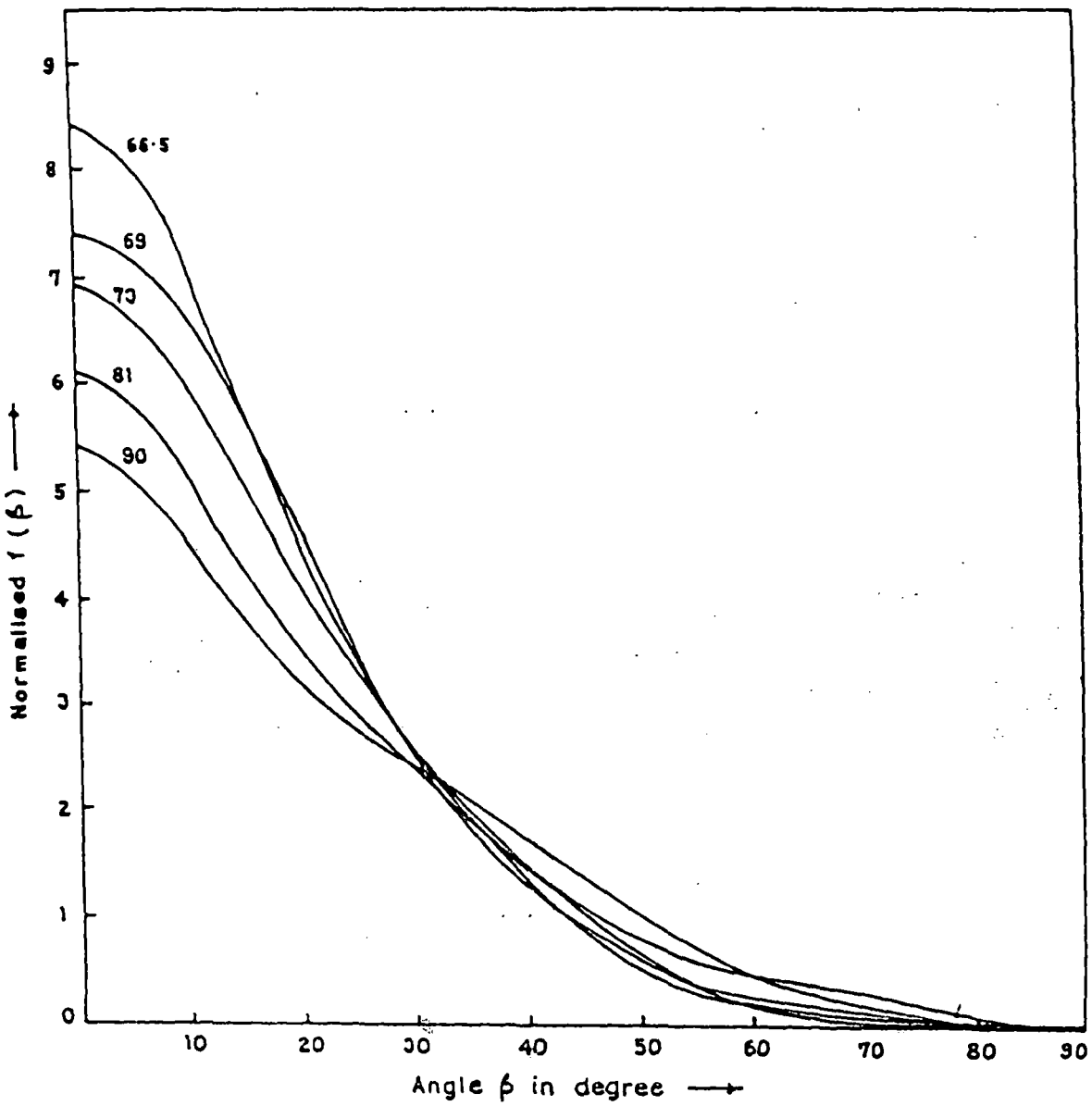


Figure 6.12 : Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temperatures of the sample 1d(1)CC.

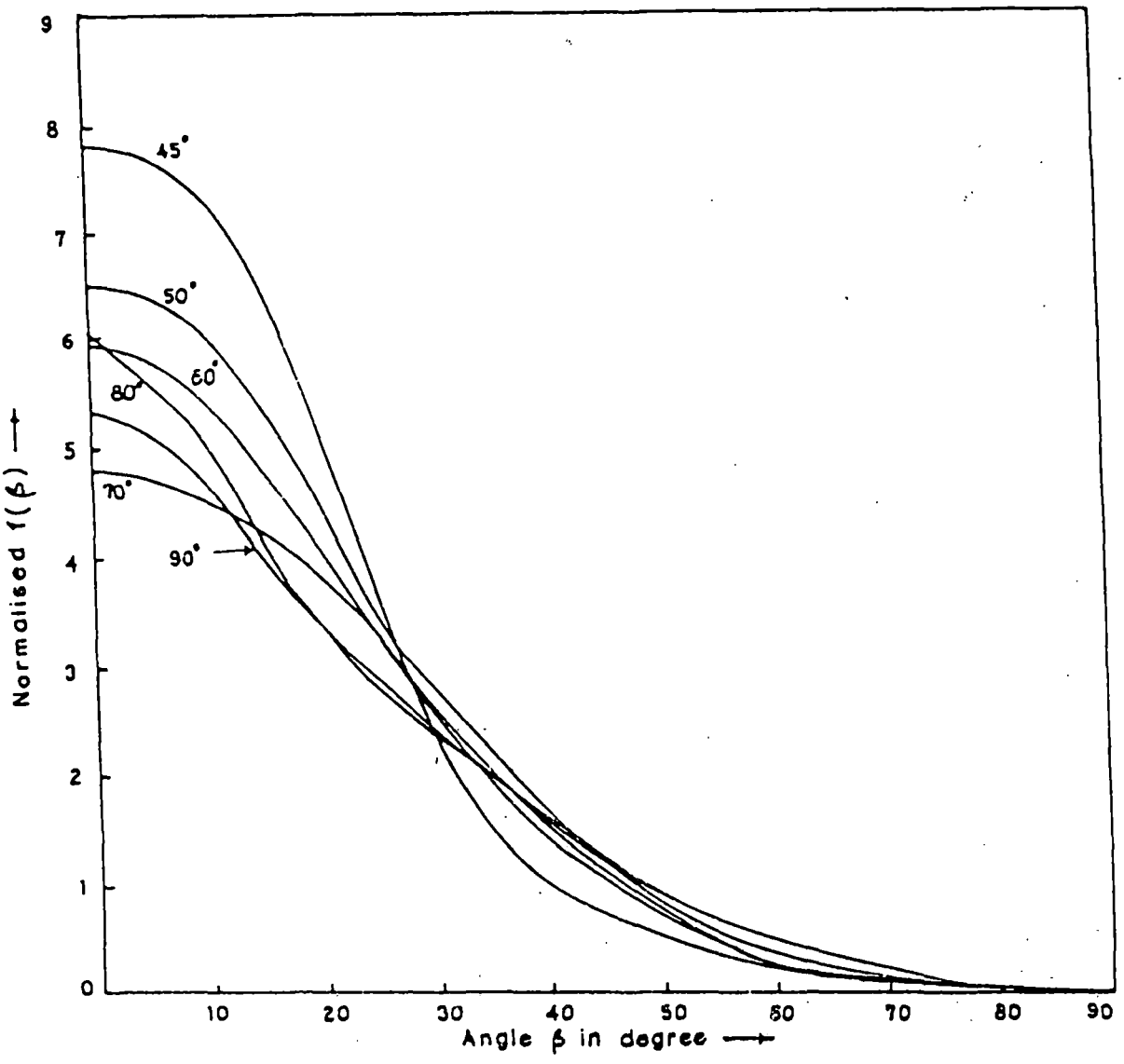


Figure 6.13 : Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temperatures of the sample 1d(3)CC.

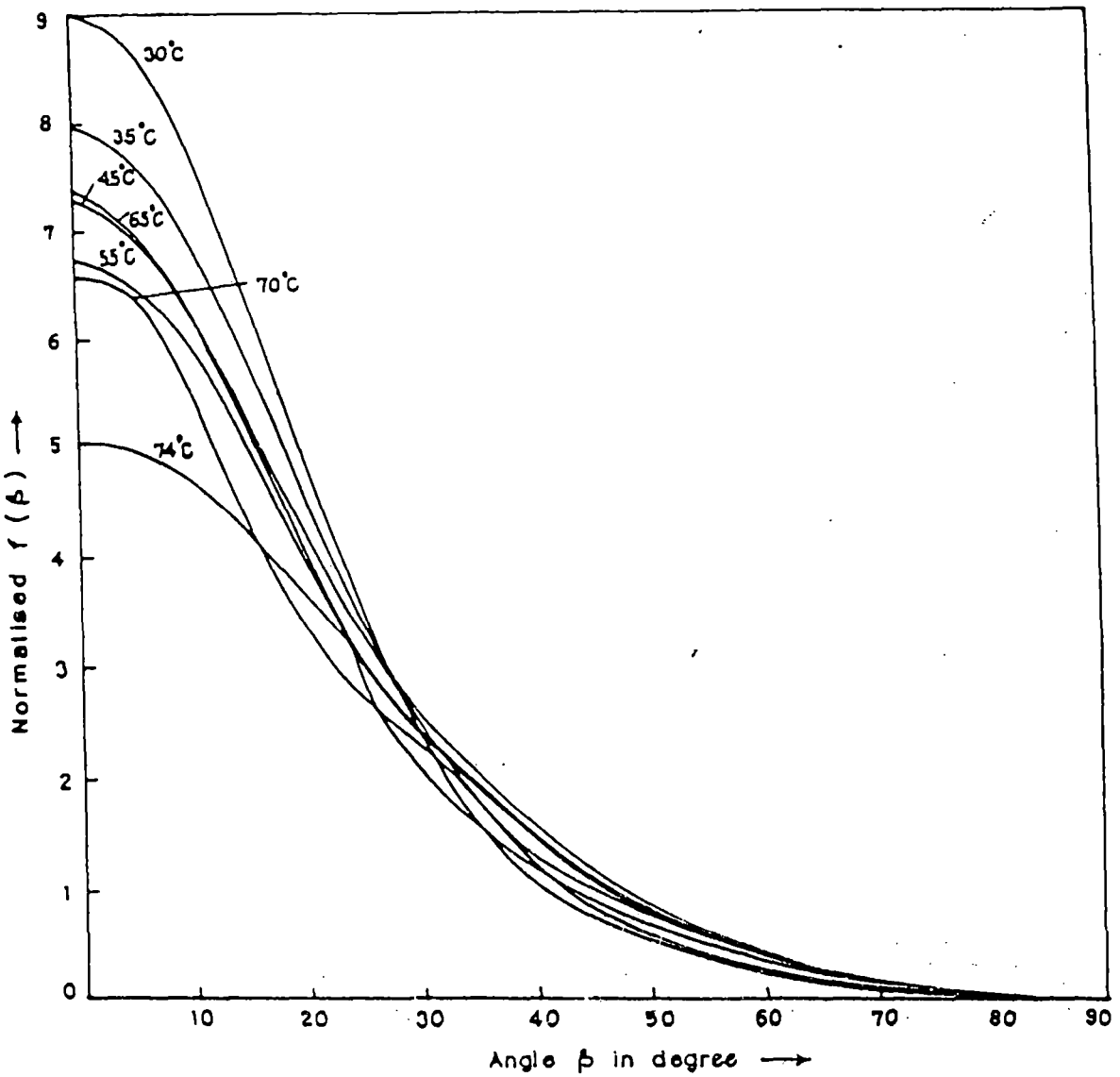


Figure 6.14 : Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temperatures of the sample 1d(3)CCO2.

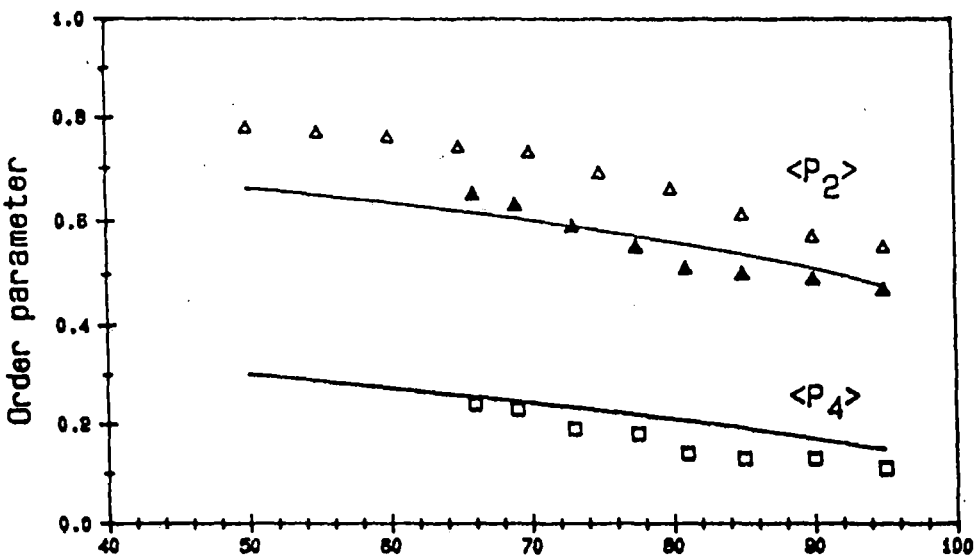


Figure 6.15 : Variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for the compound 1d(1)CC.

- optical data, - x-ray $\langle P_2 \rangle$ data

□ - x-ray $\langle P_4 \rangle$ data, —— MS theoretical values.

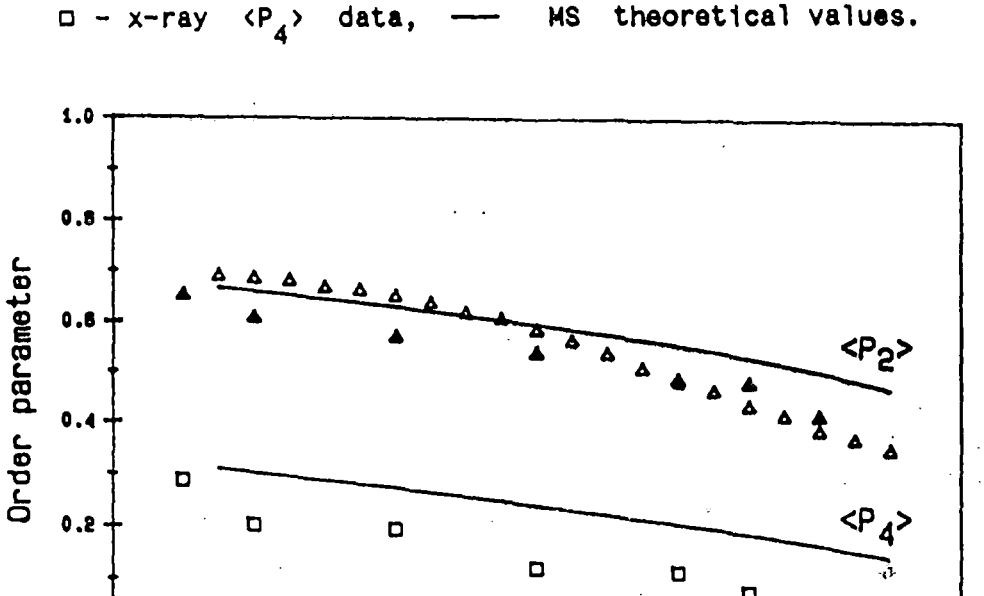


Figure 6.16 : Variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for the compound 1d(3)CC.

- optical data, - x-ray $\langle P_2 \rangle$ data

□ - x-ray $\langle P_4 \rangle$ data, —— MS theoretical values

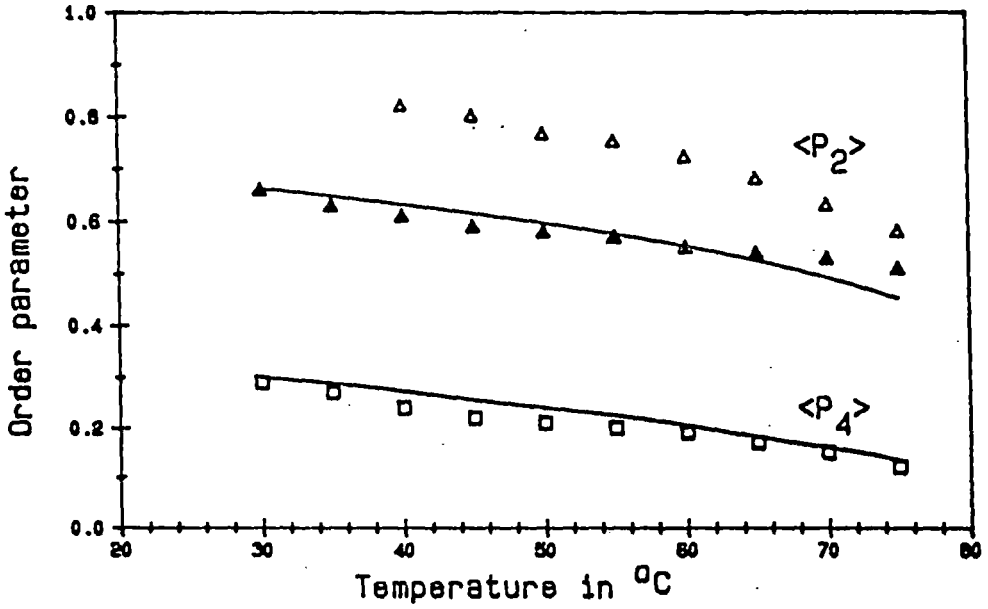


Figure 6.17 : Variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for the compound 1d(3)CCO2.

△ - optical data, ▲ - x-ray $\langle P_2 \rangle$ data

□ - x-ray $\langle P_4 \rangle$ data, —— MS theoretical values

Some peculiarity was observed in the behaviour of 1d(1)CC. I could find supercooling in texture and birefringence study whereas in case of x-ray diffraction study no supercooling was observed. So order papameters from x-ray diffraction study could not be calculated for this particualr compound in the supercooled region.

The experimental uncertainties in both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are estimated to be ± 0.02. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ determined from x-ray data agree reasonably well with the MS theoretical curve for 1d(1)CC and 1d(3)CCO2. For the compound 1d(3)CC the $\langle P_2 \rangle$ values are in agreement whereas the $\langle P_4 \rangle$ values are less than calculated values. $\langle P_2 \rangle$ values determined from birefringence measurements for the compound 1d(3)CC are in good agreement with the theories apart from the fluctuations at high temperatures[14,15].

Surface treatment produced highly ordered molecules for compounds 1d(1)CC and 1d(3)CCO2, resulting in high value of order parameters determined by optical studies. The anisotropy of the alkenyl compound depends on the position of the double bond, the distance of the double bond from the core, the molecular structure and the specific steric conformation of the side chains. More studies on the physical properties of this type of alkenyl compounds are needed to give a quantitative explanation of the large discripancy between MS theoretical values and the experimental values.

TABLE - 6.1

Density (ρ) and refractive indices (n_o,n_e) at different temperatures of compound - 1d(1)CC.

Temp. in ^oC	Density(ρ) in gm/cm^3	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
		n_o	n_e	n_o	n_e	n_o	n_e
50.0	1.114	1.418	1.511	1.421	1.513	1.426	1.519
52.5	1.112	1.418	1.510	1.421	1.513	1.426	1.518
55.0	1.110	1.418	1.509	1.421	1.512	1.426	1.517
57.5	1.108	1.418	1.509	1.421	1.511	1.426	1.516
60.0	1.107	1.418	1.508	1.421	1.510	1.426	1.516
62.5	1.105	1.418	1.507	1.421	1.509	1.426	1.515
65.0	1.104	1.418	1.506	1.421	1.508	1.426	1.514
67.5	1.102	1.418	1.504	1.421	1.507	1.426	1.512
70.0	1.100	1.418	1.503	1.421	1.506	1.426	1.511
72.5	1.099	1.418	1.502	1.421	1.504	1.426	1.509
75.0	1.097	1.419	1.500	1.422	1.502	1.426	1.508
77.5	1.095	1.419	1.498	1.422	1.500	1.426	1.506
80.0	1.093	1.420	1.496	1.423	1.499	1.427	1.504
82.5	1.091	1.421	1.495	1.424	1.497	1.428	1.502
85.0	1.089	1.422	1.493	1.424	1.495	1.429	1.501
87.5	1.087	1.422	1.492	1.425	1.494	1.430	1.499
90.0	1.085	1.423	1.490	1.426	1.492	1.431	1.497
92.5	1.083	1.423	1.489	1.426	1.491	1.432	1.496
95.0	1.080	1.424	1.487	1.426	1.489	1.432	1.494
100(iso)	1.072	1.428	1.428	1.431	1.431	1.436	1.436
102.5	1.062	1.428	1.428	1.431	1.431	1.436	1.436

TABLE - 6.2

Density (ρ) and refractive indices (n_o,n_e) at different temperatures of compound - 1d(3)CC.

Temp. in ^oC	Density(ρ) in gm/cm^3	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
		n_o	n_e	n_o	n_e	n_o	n_e
47.5	1.138	1.408	1.515	1.411	1.518	1.417	1.524
50.0	1.136	1.408	1.514	1.411	1.517	1.417	1.524
52.5	1.133	1.408	1.513	1.411	1.516	1.417	1.522
55.0	1.131	1.408	1.512	1.411	1.514	1.417	1.521
57.5	1.128	1.408	1.510	1.411	1.513	1.417	1.519
60.0	1.126	1.408	1.508	1.411	1.511	1.417	1.517
62.5	1.124	1.408	1.506	1.411	1.509	1.417	1.515
65.0	1.121	1.408	1.504	1.411	1.506	1.417	1.513
67.5	1.119	1.408	1.501	1.411	1.504	1.417	1.510
70.0	1.117	1.409	1.498	1.412	1.501	1.418	1.507
72.5	1.115	1.409	1.495	1.412	1.498	1.418	1.504
75.0	1.113	1.410	1.492	1.413	1.495	1.419	1.501
77.5	1.110	1.411	1.489	1.414	1.491	1.419	1.498
80.0	1.108	1.412	1.486	1.415	1.488	1.420	1.495
82.5	1.105	1.413	1.483	1.416	1.486	1.421	1.492
85.0	1.102	1.414	1.480	1.417	1.483	1.422	1.489
87.5	1.099	1.415	1.478	1.418	1.481	1.424	1.487
90.0	1.097	1.416	1.475	1.420	1.478	1.425	1.484
92.5	1.094	1.417	1.473	1.420	1.476	1.426	1.481
95.0	1.092	1.417	1.470	1.420	1.473	1.426	1.479
100(iso)	1.082	1.423	1.423	1.426	1.426	1.432	1.432

TABLE - 6.3

Density (ρ) and refractive indices (n_o,n_e) at different temperatures of compound - 1d(3)CCO2.

Temp. in ^oC	Density(ρ) in gm/cm^3	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
		n_o	n_e	n_o	n_e	n_o	n_e
37.5	1.035	1.387	1.500	1.391	1.502	1.398	1.510
40.0	1.033	1.387	1.499	1.391	1.501	1.398	1.509
42.5	1.031	1.387	1.497	1.391	1.500	1.398	1.507
45.0	1.029	1.387	1.495	1.391	1.498	1.398	1.505
47.5	1.027	1.387	1.494	1.391	1.496	1.398	1.503
50.0	1.024	1.387	1.492	1.391	1.494	1.398	1.502
52.5	1.022.	1.387	1.489	1.391	1.493	1.398	1.500
55.0	1.019	1.387	1.487	1.391	1.490	1.398	1.497
57.5	1.017	1.387	1.485	1.391	1.488	1.398	1.495
60.0	1.015	1.387	1.483	1.391	1.486	1.398	1.493
62.5	1.012	1.387	1.480	1.392	1.483	1.398	1.490
65.0	1.009	1.387	1.478	1.392	1.481	1.398	1.488
67.5	1.007	1.388	1.476	1.393	1.479	1.400	1.486
70.0	1.004	1.390	1.474	1.394	1.477	1.401	1.483
72.5	1.001	1.392	1.471	1.396	1.474	1.403	1.481
75.0	0.998	1.394	1.469	1.397	1.472	1.405	1.478
80.0	0.988	1.401	1.401	1.404	1.404	1.410	1.410

TABLE - 6.4

Polarizabilities (α_o,α_e) at different temperatures of compound - 1d(1)CC by Vuks' method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
50.0	20.29	25.73	20.42	25.83	20.63	26.07
52.5	20.33	25.75	20.46	25.85	20.67	26.09
55.0	20.37	25.74	20.50	25.87	20.71	26.08
57.5	20.41	25.76	20.54	25.86	20.75	26.10
60.0	20.43	25.73	20.56	25.83	20.77	26.07
62.5	20.47	25.72	20.61	25.82	20.82	26.08
65.0	20.51	25.70	20.64	25.80	20.85	26.04
67.5	20.54	25.65	20.67	25.78	20.89	25.99
70.0	20.59	25.64	20.72	25.74	20.93	25.96
72.5	20.61	25.58	20.74	25.68	20.96	25.90
75.0	20.68	25.54	20.82	25.62	21.00	25.86
77.5	20.75	25.47	20.89	25.55	21.06	25.83
80.0	20.83	25.40	20.98	25.53	21.14	25.76
82.5	20.92	25.38	21.05	25.46	21.23	25.68
85.0	21.01	25.31	21.13	25.39	21.33	25.63
87.5	21.10	25.26	21.22	25.34	20.12	25.90
90.0	21.18	25.21	21.32	25.29	21.54	25.51
92.5	21.24	25.18	21.36	25.25	21.61	25.47
95.0	21.32	25.16	21.43	25.24	21.70	25.45
100(iso)	22.01	22.01	22.14	22.14	22.35	22.35

TABLE - 6.5

Polarizabilities (α_o,α_e) at different temperatures of compound -1d(3)CC by Vuks' method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
47.5	21.72	28.64	21.86	28.78	22.14	29.06
50.0	21.77	28.63	21.91	28.77	22.18	29.08
52.5	21.83	28.64	21.97	28.78	22.25	29.06
55.0	21.87	28.63	22.02	28.71	22.30	29.06
57.5	21.94	28.59	22.08	28.73	23.38	28.89
60.0	21.99	28.52	22.13	28.66	23.42	28.94
62.5	22.04	28.45	22.18	28.59	23.47	28.87
65.0	22.11	28.40	22.26	28.49	23.54	28.83
67.5	22.17	28.27	22.31	28.41	23.60	28.70
70.0	22.25	28.13	22.39	28.28	22.68	28.56
72.5	22.33	27.99	22.48	28.14	22.76	28.42
75.0	22.44	27.85	22.59	27.99	22.85	28.29
77.5	22.57	27.73	22.70	27.82	22.95	28.17
80.0	22.66	27.59	22.81	27.67	23.07	28.03
82.5	22.79	25.47	22.94	27.61	23.20	27.91
85.0	22.92	27.34	23.10	27.48	23.33	27.79
87.5	23.08	27.28	23.23	27.42	23.52	27.71
90.0	23.19	27.13	23.37	27.27	23.63	27.57
92.5	23.32	27.07	23.47	27.21	23.77	27.45
95.0	23.38	26.93	23.53	27.08	23.82	27.37
100(iso)	24.38	24.38	24.53	24.53	24.82	24.82

TABLE - 6.6

Polarizabilities (α_o,α_e) at different temperatures of compound - 1d(3)CCO2 by Vuks' method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
37.5	24.43	33.06	24.67	33.14	25.05	33.60
40.0	24.48	33.05	24.72	33.13	25.11	33.56
42.5	24.54	32.97	24.78	33.09	25.17	33.52
45.0	24.61	32.91	24.85	33.06	25.24	33.45
47.5	24.67	32.86	24.91	32.98	25.30	33.38
50.0	24.74	32.80	24.98	32.92	25.37	33.35
52.5	24.81	32.69	25.04	32.88	25.43	33.27
55.0	24.89	32.64	25.13	32.79	25.53	33.19
57.5	24.95	32.56	25.19	32.71	25.59	33.11
60.0	25.03	32.49	25.26	32.65	25.67	33.01
62.5	25.11	32.36	25.38	32.51	25.75	32.91
65.0	25.20	32.31	25.50	32.45	25.84	32.87
67.5	25.32	32.21	25.59	32.36	26.00	32.73
70.0	25.54	32.13	25.78	32.25	26.19	32.62
72.5	25.73	31.99	25.97	32.14	26.41	32.54
75.0	25.95	31.91	26.16	32.07	26.64	32.39
80.0(Iso)	27.14	27.14	27.32	27.32	27.68	27.68

TABLE - 6.7

Polarizabilities (α_o,α_e) at different temperatures of compound - 1d(1)CC by Neugebauer's method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
50.0	20.56	25.19	20.69	25.29	20.90	25.52
52.5	20.60	25.21	20.73	25.31	20.94	26.54
55.0	20.63	25.21	20.76	25.33	20.98	26.54
57.5	20.67	25.23	20.80	25.33	20.02	26.56
60.0	20.69	25.20	20.82	25.31	20.04	26.54
62.5	20.73	25.20	20.86	25.30	20.08	26.55
65.0	20.76	25.19	20.89	25.29	20.11	26.52
67.5	20.79	25.15	20.92	25.27	21.14	25.48
70.0	20.83	25.15	20.97	25.25	20.18	25.46
72.5	20.85	25.10	20.99	25.20	20.21	25.41
75.0	20.92	25.06	20.05	25.14	21.25	25.38
77.5	20.98	25.01	21.12	25.09	21.30	25.35
80.0	21.05	24.95	21.20	25.08	21.37	25.30
82.5	21.14	24.94	21.27	25.02	21.45	25.24
85.0	21.22	24.89	21.34	24.97	21.54	25.21
87.5	21.30	24.85	21.42	24.93	20.40	25.35
90.0	21.38	24.82	21.51	24.90	21.73	25.11
92.5	21.43	24.79	21.56	24.87	21.80	25.08
95.0	21.51	24.78	21.62	24.87	21.89	25.08
100(iso)	22.01	22.01	22.14	22.14	22.35	22.35

TABLE - 6.8

Polarizabilities (α_o,α_e) at different temperatures of compound - 1d(3)CC by Neugebauer's method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
47.5	22.06	27.96	22.20	28.10	22.49	28.37
50.0	22.10	27.96	22.24	28.09	22.53	28.39
52.5	22.16	27.98	22.31	28.11	22.59	28.39
55.0	22.20	27.97	22.35	28.06	22.63	28.38
57.5	22.27	27.94	22.41	28.08	22.70	28.25
60.0	22.31	27.88	22.45	28.02	22.74	28.30
62.5	22.35	27.83	22.50	27.96	22.79	28.24
65.0	22.42	27.79	22.56	27.88	22.85	28.21
67.5	22.46	27.68	22.61	27.82	22.90	28.10
70.0	22.53	27.57	22.68	27.71	22.97	27.98
72.5	22.61	27.45	22.75	27.59	23.04	27.87
75.0	22.70	27.33	22.85	27.47	23.12	27.75
77.5	22.82	27.23	22.95	27.32	23.21	27.66
80.0	22.90	27.12	23.04	27.20	23.31	27.54
82.5	23.01	27.02	23.16	27.16	23.43	27.45
85.0	23.14	26.92	23.31	27.06	23.55	27.35
87.5	23.28	26.88	23.43	27.02	23.72	27.31
90.0	23.38	26.75	23.55	26.89	23.82	27.19
92.5	23.50	26.71	23.65	26.86	23.95	27.09
95.0	23.55	26.59	23.70	26.74	24.00	27.03
100(iso)	24.38	24.38	24.53	24.53	24.82	24.82

TABLE - 6.9

Polarizabilities (α_o,α_e) at different temperatures of compound - 1d(3)CCO2 by Neugebauer's method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
37.5	24.84	32.25	25.07	32.34	25.46	32.78
40.0	24.89	32.24	25.12	32.34	25.51	32.75
42.5	24.94	32.18	25.17	32.30	25.57	32.71
45.0	25.00	32.13	25.23	32.29	25.63	32.67
47.5	25.05	32.10	25.29	32.22	25.69	32.60
50.0	25.12	32.05	25.35	32.17	25.75	32.59
52.5	25.17	31.95	25.41	32.14	25.81	32.52
55.0	25.25	31.92	25.49	32.07	25.89	32.46
57.5	25.31	31.85	25.54	32.01	25.95	32.40
60.0	25.37	31.80	25.61	31.96	26.02	32.32
62.5	25.44	31.69	25.71	31.84	26.09	32.24
65.0	25.52	31.65	25.82	31.80	26.17	32.20
67.5	25.64	31.57	25.91	31.73	26.32	32.09
70.0	25.84	31.52	26.08	31.65	26.49	32.01
72.5	26.02	31.41	26.26	31.57	26.70	31.96
75.0	26.23	31.36	26.43	31.52	26.91	31.85
80.0(Iso)	27.14	27.14	27.32	27.32	27.68	27.68

TABLE - 6.10

Order parameter $\langle P_2 \rangle$ of compound - 1d(1)CC at different temperature by Vuks' method.

$(\alpha_{\parallel} - \alpha_{\perp}) = 6.89$ in 10^{-24} cm^3 unit.

Temp. in ^{o}C	λ = 6907 Å	λ = 5780 Å	λ = 5461 Å	Average
	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$
50.0	0.7817	0.7852	0.7896	0.7855
52.5	0.7788	0.7823	0.7866	0.7826
55.0	0.7717	0.7793	0.7794	0.7768
57.5	0.7688	0.7721	0.7765	0.7725
60.0	0.7602	0.7634	0.7678	0.7638
62.5	0.7529	0.7562	0.7634	0.7575
65.0	0.7458	0.7489	0.7533	0.7493
67.5	0.7343	0.7417	0.7417	0.7392
70.0	0.7271	0.7300	0.7300	0.7290
72.5	0.7142	0.7170	0.7170	0.7161
75.0	0.6983	0.6967	0.7054	0.7001
77.5	0.6783	0.6763	0.6923	0.6823
80.0	0.6581	0.6604	0.6705	0.6620
82.5	0.6409	0.6386	0.6459	0.6418
85.0	0.6165	0.6183	0.6241	0.6196
87.5	0.5978	0.5980	0.5951	0.5969
90.0	0.5791	0.5762	0.5762	0.5772
92.5	0.5662	0.5646	0.5602	0.5636
95.0	0.5518	0.5530	0.5443	0.5497

TABLE - 6.11

Order parameter $\langle P_2 \rangle$ of compound - 1d(3)CC at different temperature by Vuks' method.

$(\alpha_{\parallel} - \alpha_{\perp}) = 9.924$ in 10^{-24} cm^3 unit.

Temp. in ^{o}C	λ = 6907 Å	λ = 5780 Å	λ = 5461 Å	Average
	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$
47.5	0.7076	0.6963	0.6997	0.7012
50.0	0.7014	0.6913	0.6977	0.6968
52.5	0.6963	0.6862	0.6896	0.6907
55.0	0.6912	0.6741	0.6845	0.6832
57.5	0.6799	0.6701	0.6592	0.6697
60.0	0.6677	0.6580	0.6613	0.6623
62.5	0.6554	0.6459	0.6491	0.6501
65.0	0.6431	0.6278	0.6369	0.6359
67.5	0.6237	0.6146	0.6177	0.6186
70.0	0.6012	0.5925	0.5954	0.5964
72.5	0.5787	0.5703	0.5732	0.5741
75.0	0.5532	0.5441	0.5508	0.5494
77.5	0.5266	0.5159	0.5286	0.5237
80.0	0.5041	0.4897	0.5023	0.4990
82.5	0.4785	0.4705	0.4769	0.4753
85.0	0.4519	0.4423	0.4506	0.4483
87.5	0.4294	0.4232	0.4253	0.4259
90.0	0.4029	0.3929	0.3989	0.3982
92.5	0.3824	0.3768	0.3726	0.3772
95.0	0.3629	0.3577	0.3595	0.3600

TABLE - 6.12

Order parameter $\langle P_2 \rangle$ of compound - 1d(3)CCO2 at different temperature by Vuks' method.

$(\alpha_{\parallel} - \alpha_{\perp}) = 9.974$ in 10^{-24} cm^3 unit.

Temp. in ^{o}C	λ = 6907 Å	λ = 5780 Å	λ = 5461 Å	Average
	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$
37.5	0.8566	0.8492	0.8572	0.8543
40.0	0.8507	0.8432	0.8472	0.8470
42.5	0.8368	0.8332	0.8372	0.8357
45.0	0.8229	0.8241	0.8231	0.8233
47.5	0.8130	0.8101	0.8101	0.8111
50.0	0.8001	0.7961	0.8001	0.7987
52.5	0.7822	0.7860	0.7860	0.7847
55.0	0.7683	0.7690	0.7690	0.7687
57.5	0.7544	0.7539	0.7540	0.7541
60.0	0.7405	0.7409	0.7369	0.7394
62.5	0.7197	0.7148	0.7189	0.7178
65.0	0.7057	0.6968	0.7048	0.7024
67.5	0.6839	0.6787	0.6748	0.6791
70.0	0.6542	0.6486	0.6447	0.6491
72.5	0.6204	0.6186	0.6146	0.6178
75.0	0.5906	0.5925	0.5775	0.5868

TABLE - 6.13

Order parameter $\langle P_2 \rangle$ of compound - 1d(1)CC at different temperature by Neugebauer's method.

$(\alpha_{\parallel} - \alpha_{\perp}) = 5.812$ in 10^{-24} cm^3 unit.

Temp. in ^{o}C	λ = 6907 Å	λ = 5780 Å	λ = 5461 Å	Average
	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$
50.0	0.7966	0.7915	0.7908	0.7929
52.5	0.7849	0.7897	0.7874	0.7873
55.0	0.7863	0.7863	0.7806	0.7844
57.5	0.7846	0.7794	0.7771	0.7804
60.0	0.7760	0.7708	0.7703	0.7723
62.5	0.7691	0.7639	0.7652	0.7661
65.0	0.7605	0.7553	0.7549	0.7569
67.5	0.7502	0.7485	0.7429	0.7472
70.0	0.7416	0.7364	0.7309	0.7363
72.5	0.7295	0.7244	0.7189	0.7242
75.0	0.7140	0.7037	0.7069	0.7082
77.5	0.6934	0.6831	0.6950	0.6905
80.0	0.6727	0.6676	0.6727	0.6710
82.5	0.6555	0.6452	0.6488	0.6498
85.0	0.6297	0.6245	0.6265	0.6269
87.5	0.6108	0.6039	0.5991	0.6046
90.0	0.5919	0.5833	0.5786	0.5846
92.5	0.5781	0.5712	0.5632	0.5708
95.0	0.5643	0.5592	0.5460	0.5565

TABLE - 6.14

Order parameter $\langle P_2 \rangle$ of compound - 1d(3)CC at different temperature by Neugebauer's method.

$(\alpha_{\parallel} - \alpha_{\perp}) = 8.499$ in 10^{-24} cm^3 unit.

Temp. in ^{o}C	λ = 6907 Å	λ = 5780 Å	λ = 5461 Å	Average
	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$
47.5	0.7011	0.6930	0.7058	0.6999
50.0	0.6964	0.6883	0.7034	0.6960
52.5	0.6916	0.6836	0.6962	0.6905
55.0	0.6856	0.6718	0.6902	0.6825
57.5	0.6749	0.6671	0.6662	0.6694
60.0	0.6619	0.6553	0.6674	0.6615
62.5	0.6500	0.6436	0.6542	0.6492
65.0	0.6393	0.6247	0.6434	0.6358
67.5	0.6203	0.6130	0.6242	0.6192
70.0	0.5977	0.5918	0.6014	0.5969
72.5	0.5752	0.5694	0.5797	0.5747
75.0	0.5502	0.5436	0.5569	0.5502
77.5	0.5240	0.5153	0.5341	0.5244
80.0	0.5015	0.4894	0.5077	0.4995
82.5	0.4753	0.4706	0.4825	0.4761
85.0	0.4504	0.4412	0.4561	0.4492
87.5	0.4278	0.4224	0.4297	0.4266
90.0	0.4005	0.3929	0.4033	0.3989
92.5	0.3815	0.3776	0.3769	0.3786
95.0	0.3613	0.3576	0.3637	0.3608

TABLE - 6.15

Order parameter $\langle P_2 \rangle$ of compound - 1d(3)CCO2 at different temperature by Neugebauer's method.

$(\alpha_{\parallel} - \alpha_{\perp}) = 8.758$ in 10^{-24} cm^3 unit.

Temp. in ^{o}C	λ = 6907 Å	λ = 5780 Å	λ = 5461 Å	Average
	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$	$\langle P_2 \rangle$
37.5	0.8631	0.8301	0.8686	0.8539
40.0	0.8573	0.8244	0.8592	0.8469
42.5	0.8433	0.8141	0.8497	0.8357
45.0	0.8305	0.8050	0.8354	0.8236
47.5	0.8200	0.7913	0.8223	0.8112
50.0	0.8072	0.7787	0.8116	0.7991
52.5	0.7897	0.7684	0.7986	0.7855
55.0	0.7758	0.7525	0.7807	0.7696
57.5	0.7618	0.7388	0.7665	0.7557
60.0	0.7490	0.7251	0.7487	0.7409
62.5	0.7268	0.6999	0.7308	0.7191
65.0	0.7140	0.6828	0.7178	0.7048
67.5	0.6919	0.6645	0.6868	0.6810
70.0	0.6616	0.6360	0.6559	0.6511
72.5	0.6278	0.6063	0.6262	0.6201
75.0	0.5975	0.5812	0.5870	0.5885

TABLE - 6.17

Mean experimental intensity values I(ψ), in arbitrary units, of compound - 1d(1)CC after background correction.

ψ (degree)	I(ψ) values at different temperatures in ^{o} C							
	66.5	69	73	77	81	85	90	95
0	37.5	36.0	37.5	29.0	22.0	34.0	37.0	30.0
5	36.0	35.0	36.5	28.5	20.5	33.5	35.5	29.0
10	32.0	32.0	34.0	26.0	19.0	31.0	32.5	27.0
15	27.0	28.0	29.0	23.0	17.0	27.0	30.0	25.0
20	23.0	23.0	25.0	19.5	15.0	23.0	26.5	22.0
25	18.0	18.5	21.0	16.5	13.0	18.0	24.0	19.0
30	14.0	14.0	17.0	13.0	10.5	14.0	21.0	16.0
35	10.0	9.5	13.0	10.5	9.0	10.5	18.0	13.0
40	7.5	8.5	10.0	8.5	7.0	8.0	14.5	11.0
45	5.0	5.5	7.0	6.0	5.5	6.0	11.5	9.0
50	3.5	4.0	5.0	5.0	4.5	5.0	10.5	7.5
55	2.5	2.5	3.5	4.0	3.5	4.0	6.5	6.0
60	1.5	1.5	2.2	3.0	3.0	3.0	4.5	5.0
65	1.2	1.0	1.5	2.0	2.0	2.0	3.0	3.5
70	1.0	0.8	1.0	1.8	1.5	1.5	2.0	3.0
75	0.8	0.5	0.8	1.0	1.0	1.0	1.0	2.0
80	0.5	0.3	0.5	0.5	0.5	0.5	0.5	1.5
85	0.2	0.1	0.1	0.2	0.2	0.2	0.1	1.0
90	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE - 6.18

Mean experimental intensity values $I(\psi)$, in arbitrary units, of compound - 1d(3)CC after background correction.

ψ (degree)	$I(\psi)$ values at different temperatures in ^{o} C					
	45	50	60	70	80	90
0	73.0	67.0	70.0	58.5	35.0	39.0
5	71.0	66.0	69.0	58.0	33.5	38.0
10	65.0	63.0	65.0	56.0	31.0	35.0
15	57.0	55.0	58.0	51.0	28.0	32.0
20	46.0	46.0	50.0	46.5	24.0	29.0
25	32.0	37.0	42.0	40.0	20.5	25.0
30	23.0	29.0	34.0	34.0	18.0	21.0
35	16.0	23.0	26.5	26.5	15.5	18.0
40	12.0	17.0	21.0	20.0	12.3	15.0
45	9.0	12.0	15.5	15.0	9.5	11.0
50	7.0	8.0	11.0	11.0	7.5	9.0
55	5.0	6.0	8.0	7.5	6.0	7.0
60	4.0	4.0	5.5	5.0	4.5	5.0
65	2.0	2.0	4.0	4.0	3.0	4.0
70	1.5	1.0	2.0	2.5	1.8	2.5
75	1.0	0.5	1.5	1.5	1.0	1.5
80	0.0	0.0	0.5	1.0	0.5	1.0
85	0.0	0.0	0.0	0.0	0.0	0.0
90	0.0	0.0	0.0	0.0	0.0	0.0

TABLE - 6.19

Mean experimental intensity values $I(\psi)$, in arbitrary units, of compound - 1d(3)CCO2 after background correction.

ψ (degree)	$I(\psi)$ values at different temperatures in ^{o} C					
	30	35	40	45	50	55
0	65.0	53.2	43.0	44.0	47.0	54.5
5	63.0	51.5	42.0	43.0	46.0	53.0
10	56.0	47.5	38.0	39.5	43.0	49.0
15	46.5	40.0	33.0	34.0	38.0	42.5
20	38.0	33.0	28.0	28.0	32.0	36.0
25	28.0	26.0	22.0	23.0	26.5	30.0
30	20.0	20.0	16.5	18.0	21.0	24.0
35	14.5	14.0	11.5	14.0	16.0	19.5
40	11.0	10.0	8.5	10.0	13.0	16.0
45	8.0	7.5	6.5	8.0	9.5	12.0
50	6.0	5.5	5.0	6.5	7.0	9.0
55	4.0	4.0	4.0	5.0	5.0	6.0
60	2.5	2.5	3.0	3.0	3.5	4.0
65	1.5	2.0	2.5	2.5	2.0	2.5
70	1.0	1.0	1.5	1.5	1.0	1.5
75	0.5	0.8	1.0	1.0	0.5	1.0
80	0.2	0.5	0.5	0.5	0.2	0.5
85	0.1	0.2	0.2	0.0	0.1	0.2
90	0.0	0.0	0.0	0.0	0.0	0.0

(continued)

TABLE - 6.19

Mean experimental intensity values I(ψ), in arbitrary units, of compound - 1d(3)CCO2 after background correction.

ψ (degree)	I(ψ) values at different temperatures in ^{o} C			
	60	65	70	74
0	53.2	46.5	44.0	34.0
5	51.0	44.5	42.5	33.0
10	46.5	40.5	38.0	31.0
15	40.0	35.0	32.5	28.0
20	32.0	28.0	28.0	26.0
25	26.0	22.0	24.5	22.0
30	21.0	18.0	21.0	18.0
35	17.0	15.0	17.0	15.0
40	14.5	13.0	13.0	12.0
45	11.2	10.5	11.5	9.5
50	9.0	8.5	9.0	7.0
55	7.0	6.5	7.0	5.0
60	5.5	5.0	6.0	3.5
65	4.0	3.0	4.5	2.5
70	2.8	2.5	3.5	2.0
75	1.5	1.5	2.0	1.5
80	1.0	1.0	1.5	1.0
85	0.5	0.5	1.0	0.5
90	0.0	0.0	0.0	0.0

TABLE - 6.20

Normalised distribution function f(β) values at different temperatures of compound - 1d(1)CC.

β (degree)	f(β) values at temperatures in ^{o} C					
	66.5	69	73	77	81	85
0	8.42	7.39	6.93	6.46	6.06	6.72
5	8.03	7.19	6.66	6.23	5.79	6.55
10	7.01	6.61	5.95	5.61	5.09	6.06
15	5.69	5.71	5.01	4.77	4.25	5.29
20	4.42	4.60	4.08	3.89	3.48	4.37
25	3.37	3.48	3.27	3.10	2.89	3.38
30	2.55	2.52	2.60	2.42	2.40	2.48
35	1.88	1.79	2.02	1.86	1.94	1.74
40	1.31	1.29	1.49	1.39	1.49	1.21
45	0.85	0.93	1.05	1.02	1.10	0.86
50	0.52	0.63	0.69	0.74	0.81	0.65
55	0.32	0.40	0.44	0.55	0.63	0.51
60	0.22	0.23	0.29	0.42	0.51	0.39
65	0.16	0.14	0.19	0.32	0.39	0.29
70	0.12	0.09	0.12	0.22	0.27	0.19
75	0.07	0.05	0.07	0.14	0.16	0.11
80	0.04	0.03	0.04	0.06	0.07	0.05
85	0.02	0.01	0.01	0.02	0.02	0.02
90	0.01	0.003	0.008	0.005	0.01	0.01

(continued)

TABLE - 6.20

Normalised distribution function f(β) values at different temperatures of compound - 1d(1)CC.

β (degree)	f(β) values at temperatures in ^{o} C	
	90	95
0	5.35	4.98
5	5.12	4.85
10	4.52	4.50
15	3.80	3.99
20	3.17	3.41
25	2.72	2.83
30	2.38	2.29
35	2.05	1.83
40	1.71	1.45
45	1.35	1.13
50	1.03	0.89
55	0.77	0.71
60	0.54	0.56
65	0.35	0.44
70	0.20	0.33
75	0.09	0.22
80	0.03	0.13
85	0.01	0.06
90	0.008	0.04

TABLE - 6.21

Normalised distribution function $f(\beta)$ values at different temperatures of compound - 1d(3)CC.

β (degree)	$f(\beta)$ values at temperatures in ^{o} C					
	45	50	60	70	80	90
0	7.76	6.46	5.89	4.77	5.98	5.29
5	7.67	6.35	5.76	4.70	5.72	5.11
10	7.32	6.00	5.37	4.51	5.03	4.61
15	6.51	5.36	4.78	4.21	4.18	3.98
20	5.22	4.48	4.06	3.80	3.41	3.38
25	3.71	3.49	3.30	3.32	2.81	2.87
30	2.37	2.59	2.59	2.77	2.36	2.44
35	1.45	1.90	1.99	2.20	1.96	2.02
40	0.95	1.39	1.49	1.65	1.58	1.61
45	0.71	1.02	1.09	1.17	1.22	1.23
50	0.55	0.71	0.77	0.80	0.92	0.91
55	0.40	0.45	0.53	0.54	0.69	0.68
60	0.26	0.27	0.35	0.36	0.51	0.51
65	0.16	0.15	0.23	0.25	0.36	0.37
70	0.10	0.08	0.14	0.16	0.23	0.25
75	0.06	0.05	0.08	0.09	0.12	0.15
80	0.03	0.02	0.04	0.05	0.05	0.07
85	0.001	-0.002	0.006	0.01	0.00	0.02
90	-0.011	-0.010	-0.005	0.00	0.00	0.001

TABLE - 6.22

Normalised distribution function f(β) values at different temperatures of compound - 1d(3)CCO2.

β (degree)	f(β) values at temperatures in ^{o} C					
	30	35	40	45	50	55
0	9.081	7.979	7.399	7.263	6.457	6.724
5	8.729	7.690	7.124	6.997	6.288	6.496
10	7.756	6.902	6.374	6.277	5.807	5.862
15	6.372	5.806	5.344	5.288	5.082	4.964
20	4.857	4.618	4.256	4.236	4.219	3.988
25	3.464	3.503	3.278	3.267	3.337	3.099
30	2.357	2.547	2.482	2.447	2.541	2.393
35	1.578	1.780	1.860	1.788	1.892	1.871
40	1.077	1.203	1.374	1.284	1.400	1.475
45	0.760	0.802	0.988	0.921	1.036	1.141
50	0.544	0.543	0.684	0.674	0.758	0.836
55	0.377	0.382	0.456	0.505	0.536	0.567
60	0.244	0.271	0.297	0.376	0.354	0.356
65	0.144	0.182	0.191	0.262	0.212	0.213
70	0.075	0.110	0.121	0.163	0.112	0.125
75	0.035	0.057	0.072	0.086	0.050	0.072
80	0.014	0.026	0.036	0.036	0.018	0.036
85	0.006	0.013	0.013	0.011	0.004	0.012
90	0.004	0.010	0.005	0.004	0.001	0.004

(continued)

TABLE - 6.22

Normalised distribution function f(β) values at different temperatures of compound - 1d(3)CCO2.

β (degree)	f(β) values at temperatures in ^{o} C			
	60	65	70	74
0	7.431	7.347	6.858	5.095
5	7.124	7.069	6.468	4.983
10	6.286	6.290	5.483	4.664
15	5.135	5.165	4.320	4.188
20	3.935	3.929	3.353	3.627
25	2.903	2.829	2.703	3.054
30	2.139	2.027	2.262	2.519
35	1.630	1.542	1.869	2.039
40	1.289	1.272	1.459	1.606
45	1.029	1.079	1.079	1.216
50	0.803	0.877	0.798	0.877
55	0.604	0.659	0.628	0.607
60	0.442	0.462	0.520	0.415
65	0.319	0.314	0.418	0.289
70	0.224	0.213	0.303	0.203
75	0.143	0.138	0.188	0.136
80	0.074	0.076	0.099	0.079
85	0.024	0.031	0.047	0.038
90	0.006	0.013	0.003	0.023

TABLE - 6.23

Order parameter values at different temperatures of compounds - 1d(1)CC, 1d(3)CC and 1d(3)CCO2 from x-ray diffraction study.

sample - 1d(1)CC			sample - 1d(3)CC			sample - 1d(3)CCO2		
Temp. in ^{o}C	$\langle P_2 \rangle$	$\langle P_4 \rangle$	Temp. in ^{o}C	$\langle P_2 \rangle$	$\langle P_4 \rangle$	Temp. in ^{o}C	$\langle P_2 \rangle$	$\langle P_4 \rangle$
66.5	0.65	0.25	45.0	0.66	0.29	30.0	0.66	0.29
69.0	0.63	0.23	50.0	0.61	0.20	35.0	0.63	0.27
73.0	0.59	0.19	60.0	0.57	0.19	40.0	0.61	0.24
77.0	0.55	0.18	70.0	0.55	0.12	45.0	0.59	0.22
81.0	0.51	0.14	80.0	0.49	0.11	50.0	0.58	0.21
85.0	0.50	0.13	85.0	0.48	0.08	55.0	0.57	0.20
90.0	0.49	0.12	90.0	0.42	0.05	60.0	0.55	0.19
95.0	0.47	0.11				65.0	0.54	0.17
						70.0	0.53	0.15
						74.0	0.52	0.12

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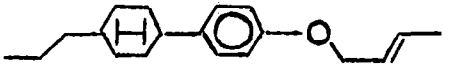
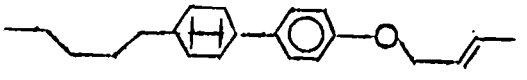
CHAPTER 7

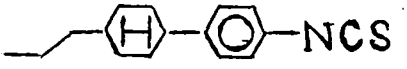
Study of physical properties of three mesogenic phenyl cyclohexane compounds.

7.1 INTRODUCTION

In continuation of my study of mesogenic alkenyl compounds[1], here I have reported the mesomorphic behaviour of two alkenyl non-polar phenyl cyclohexane compounds and one alkyl compound having their polar substituent. The molecular structure of the compounds are as follows :

[1] 3CPOd(3)1 

[2] 5CPOd(3)1 

[3] 3CPS 

Small angle x-ray diffraction analysis for magnetically alinged samples has been performed to determine the molecular and orientational order parameters. Densities and optical birefringence of these compounds at different temperatures have also been measured. Polarizability anisotropy and orientational order parameters have been calculated from these value.

Schadt et al[2-5] have reported the optical anisotropy and elastic constants of the compound 3CPOd(3)1.

7.2 EXPERIMENTAL DETAILS

7.2.1 Texture study :

The transition temperatures as determined by texture study of the compounds are given below :

(1) 3CPOd(3)1 $\quad \text{Solid} \xrightarrow[\xleftarrow{25.5^{o}C}]{43^{o}C} \text{Nematic} \xrightarrow{58^{o}C} \text{I}$

(2) 5CPOd(3)1 $\quad \text{Solid} \xrightarrow[\xleftarrow{22.8^{o}C}]{32^{o}C} \text{Nematic} \xrightarrow{67^{o}C} \text{I}$

(3) 3CPS $\quad$ Solid $\underset{34^{o}C}{\overset{39^{o}C}{\rightleftharpoons}}$ Nematic $\xrightarrow{42^{o}C}$ I

These temperatures agree with those given in the literature except that supercooling is observed in all the compounds. The compound 3CPOd(3)1 showed schlieren texture and the other two compounds 5CPOd(3)1 and 3CPS showed threaded texture which are very often found in nematic phase.

7.2.2 Density measurements :

Densities were measured with the help of a dilatometer of capillary type as described in chapter 5. Variation of density with temperature for the three compounds are shown in figures 7.1 - 7.3.

7.2.3 Refractive index measurement :

The ordinary and extraordinary refractive indices (n_o,n_e) were measured having an accuracy of $\pm$0.001 by thin prism method (refracting angle < 2^{o}) for the three wave-lengths (λ = 6907$\mathring{A}$, 5780 $\mathring{A}$ and 5461 $\mathring{A}$) of mercury vapour lamp. Details of the experimental technique used has been described in chapter 5.

Order parameter $\langle P_2 \rangle$ at different temperature have been calculated from α_o and α_e adopting the usual procedure. In this case also Haller's extrapolation procedure[6] is used to calculate ($\alpha_{\parallel}$ - $\alpha_{\perp}$), in the absence of any solid phase data. Estimation of the polarizabilities of the molecule was also carried out using the additive rule of bond polarizability proposed by Le Fevre[7].

7.2.4 X-ray diffraction study :

Flat plate x-ray diffraction photographs using CuKα radiation were taken at different temperatures. Temperature was controlled by a temperature controller (Indotherm model IT 401D). Samples were

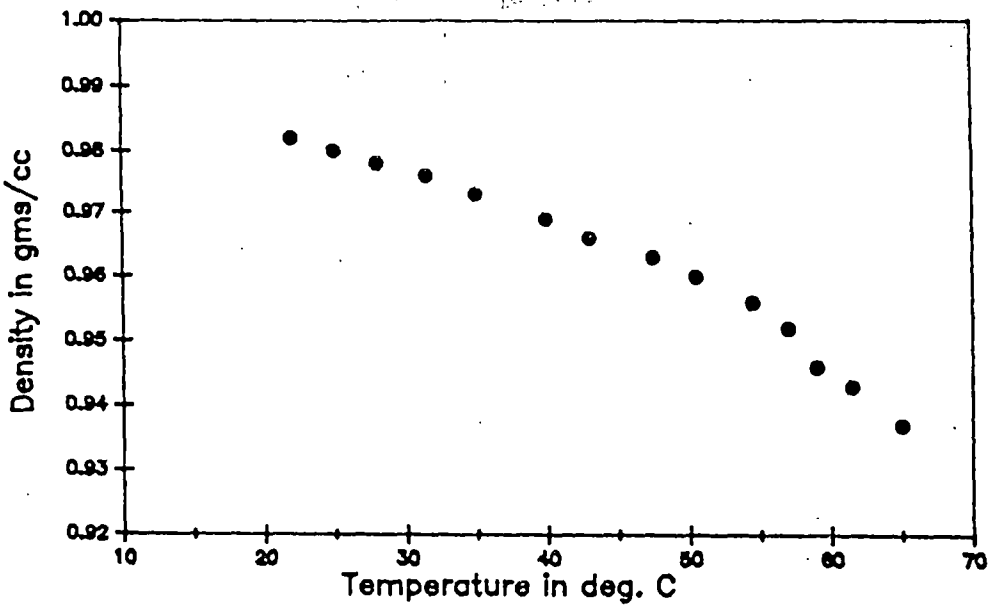


Figure 7.1 : Variation of density with temperature for the compound 3CPOd(3)1.

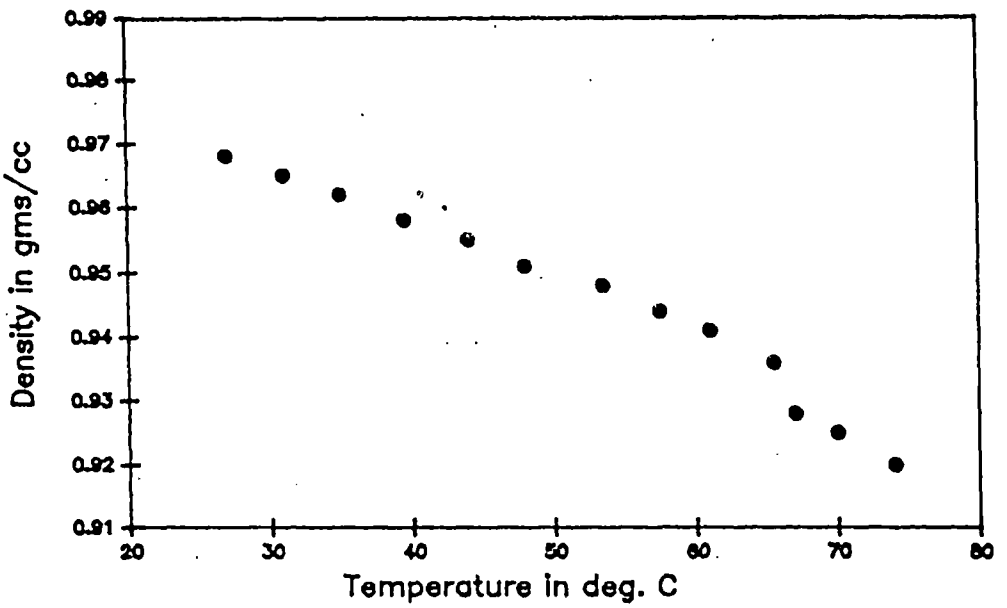


Figure 7.2 : Variation of density with temperature for the compound 5CPOd(3)1.

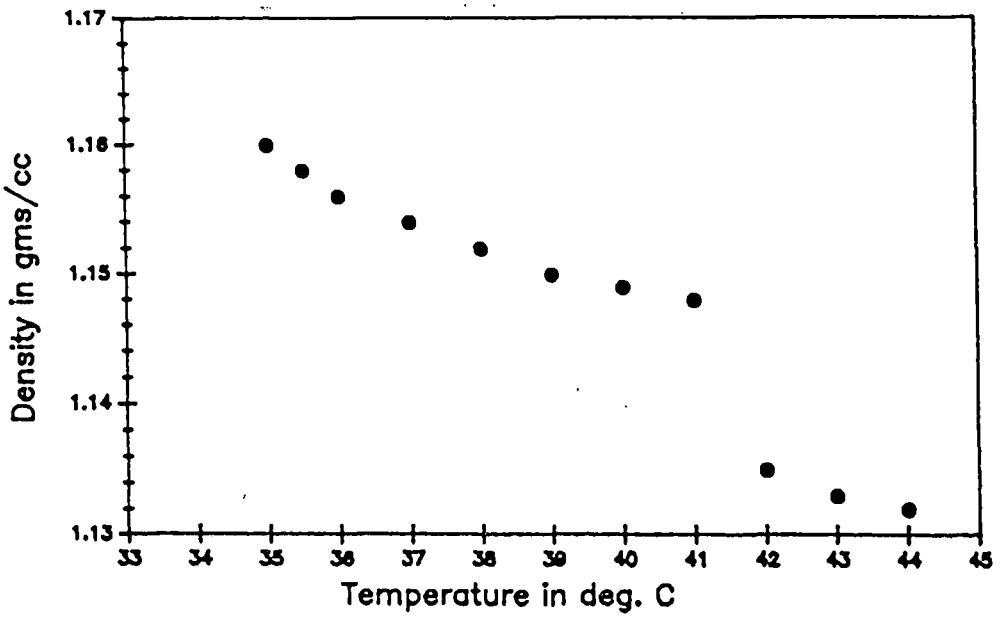


Figure 7.3 : Variation of density with temperature for the compound 3CPS.

aligned by cooling from the isotropic phase to the desired temperature in the presence of a magnetic field of about 1 K gauss.

The orientational distribution function $f(\beta)$ was calculated from the measured intensity distribution along the arc of the equatorial reflection and the orientational order parameters were calculated from respective statistical averages[8].

In order to determine the various parameters, the photographs were scanned, both linearly and circularly, by an optical microdensitometer (VEB Car Zeiss Jena, Model MD 100) equipped with autorecording facility.

7.3 RESULTS AND DISCUSSIONS :

7.3.1 Refractive index study:

Figures 7.4 - 7.6 indicate the variation of (n_o,n_e) with temperature of the three compounds. The refractive indices (n_o,n_e) and the densities of the three compounds at different temperatures for the three wave lengths are arranged in tables 7.1 - 7.3. From refractive index data (n_o,n_e), the molecular polarizabilities (α_o, α_e) were calculated using Vuks isotropic[9] and Neugebaur's aniso -tropic[10] internal field model. The values of effective polarizabilities α_o and α_e obtained from Vuk's and Neugebauer's method are given in tables 7.4 - 7.5 respectively. The values of order parameters $\langle P_2 \rangle$ at different temperatures obtained from three different wave lengths and their average values have also been included in tables 7.6 and 7.7.

Since α_o and α_e values at different wavelengths are quite close, in table 7.8, we have given values for λ = 5780 Å only. Table 7.8 shows that the agreement between the calculated and experimental value of $\Delta\alpha$ is better for Vuks' model.

The polarizability anisotropy $\Delta\alpha$ mainly comes from the central core, the side chain, on the other hand contributes more to the average polarizability than to the anisotropy[11]. But our

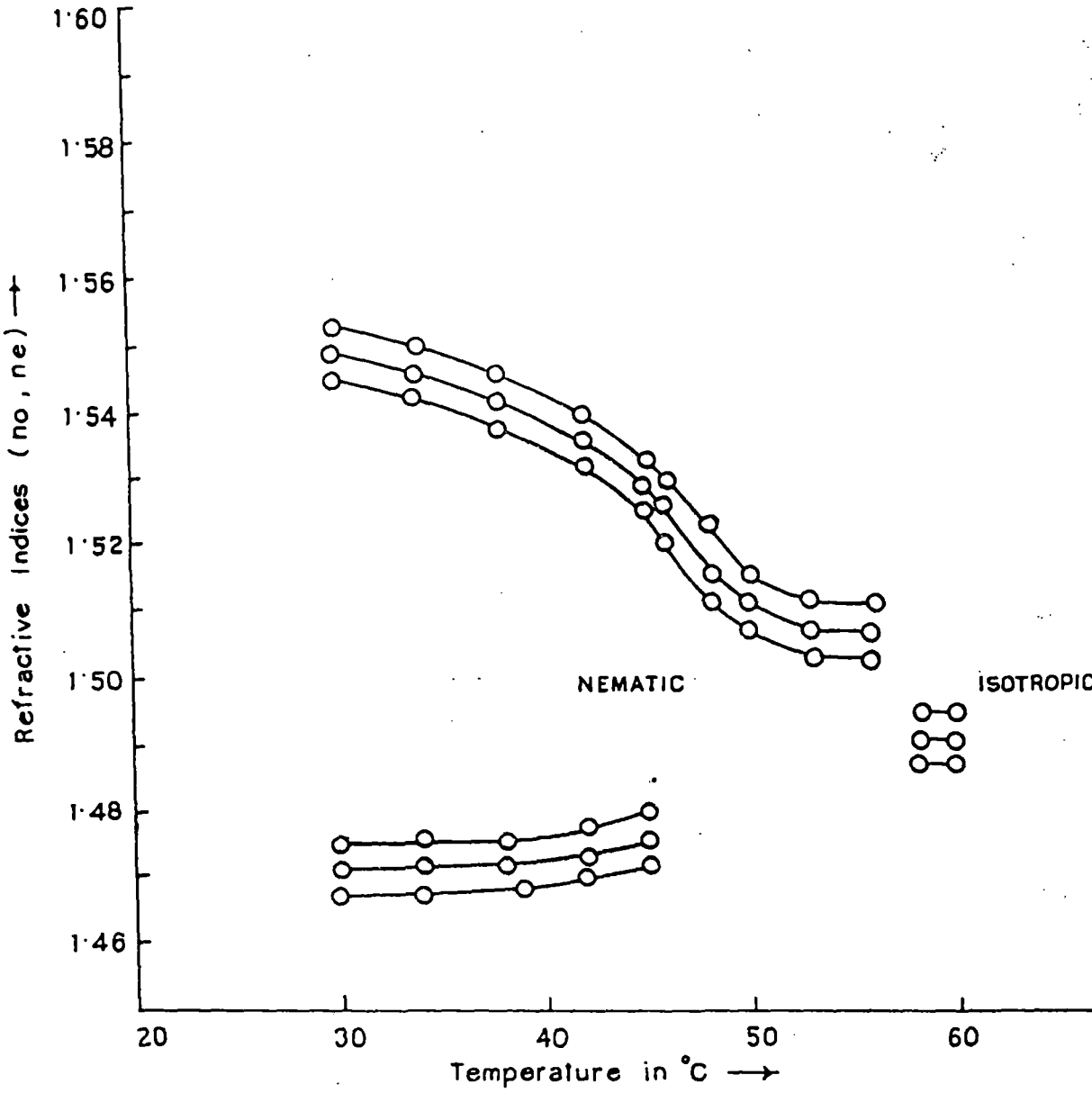


Figure 7.4 : Variation of refractive indices (n_o,n_e) at different temperatures of compound 3CPOd(3)1. Upper curve for λ = 5461 Å, middle curve for λ = 5780 Å, and lower curve for λ = 6907 Å.

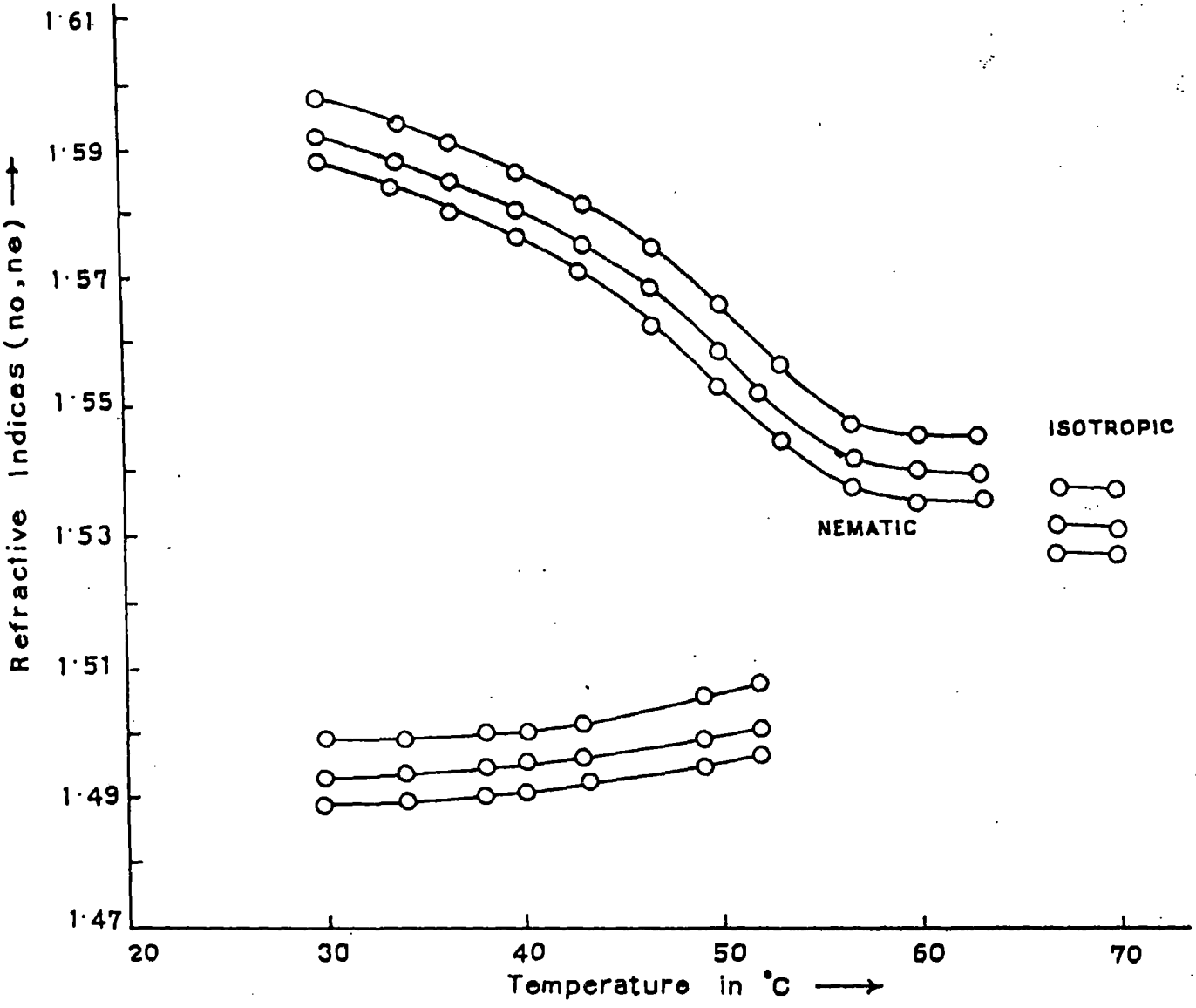


Figure 7.5 : Variation of refractive indices (n_o,n_e) at different temperatures of compound 5CPOd(3)1. Upper curve for λ = 5461 Å, middle curve for λ = 5780 Å, and lower curve for λ = 6907 Å.

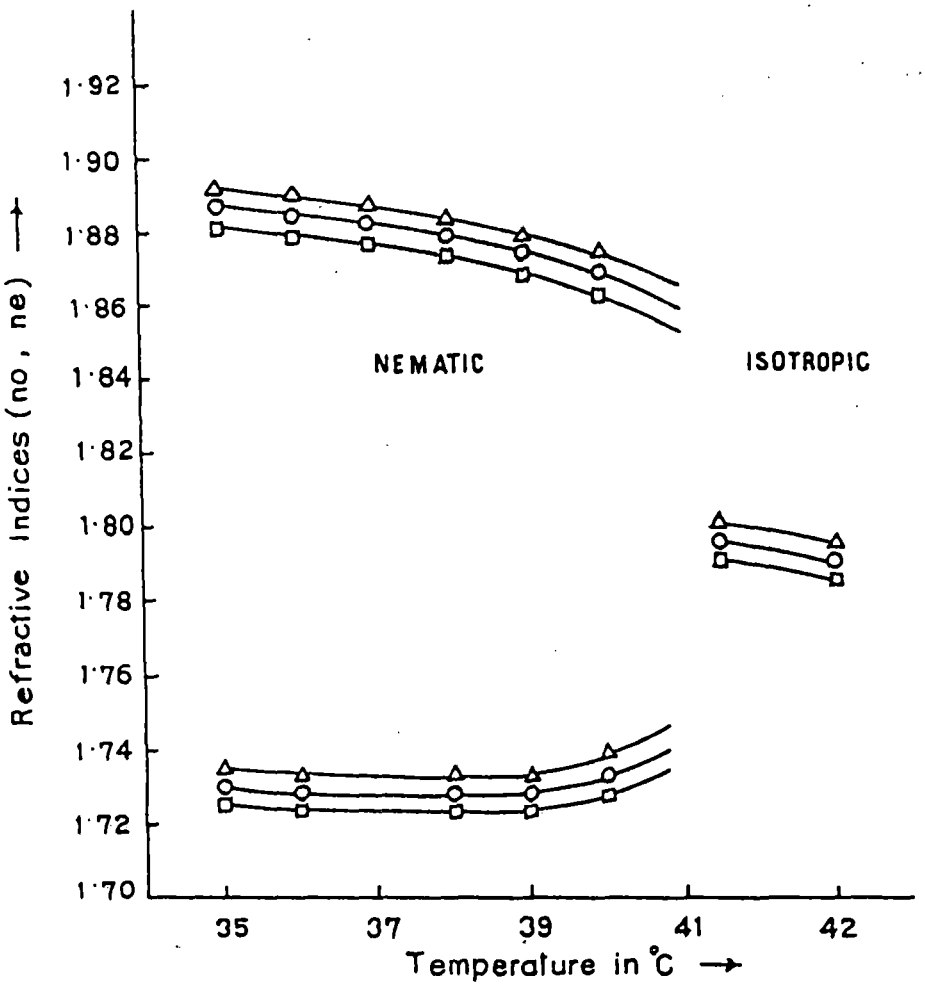


Figure 7.6 : Variation of refractive indices (n_o,n_e) at different temperatures of compound 3CPS. Upper curve for λ = 5461 Å, middle curve for λ = 5780 Å, and lower curve for λ = 6907 Å.

experimental observation do not confirm this. The Δn value at $T=T_m$ for compounds 3CPOd(3)1, 5CPOd(3)1 and 3CPS are 0.068, 0.097 and 0.143 respectively. As in our previous paper[1] we find that the double bond at the even position in the side chain, making an angle with the long axis of the molecule, lowers the Δn value. The polar compound on the other hand having no double bond in the side chain has a rather large Δn value.

Table - 7.8

Compound	α		$\Delta\alpha$		
	Calculated	Expt.	Calculated	Experimental Vuks	Neug.
3CPOd(3)1	33.92	33.10	14.02	11.47	9.68
5CPOd(3)1	37.50	39.71	14.74	15.18	12.68
3CPS	29.12	38.35	13.64	14.15	10.91

α and $\Delta\alpha$ are in 10^{-24} cm^3 unit.

For the compound 3CPOd(3)1 and 5CPOd(3)1, beyond the temperatures 45^oC and 52^oC respectively, birefringence could not be measured, because the ordinary rays (n_o) were not visible. The orientational order parameter $\langle P_2 \rangle$ at these temperatures drops to a very low value. It seems that there might be a phase transition at this temperature. Density versus temperature graphs also show a somewhat first order phase transition at this particular temperatures. But no such transition could be observed in the texture.

7.3.2 Parameters from x-ray diffraction study :

Aligned diffraction photographs for the three compounds at different temperatures are given in figures 7.7 - 7.11. X-ray intensity data from linear scanning of outer halos were fitted to a

Figure 7.7 : x-ray diffraction photograph of magnetically aligned sample 3CPOd(3)1 at 41°C.

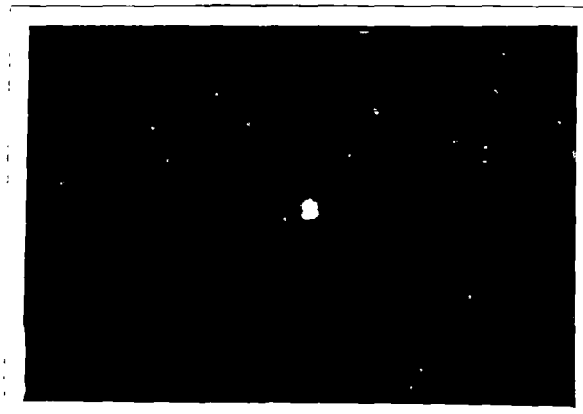


Figure 7.8 : x-ray diffraction photograph of magnetically aligned sample 3CPOd(3)1 at 49°C.

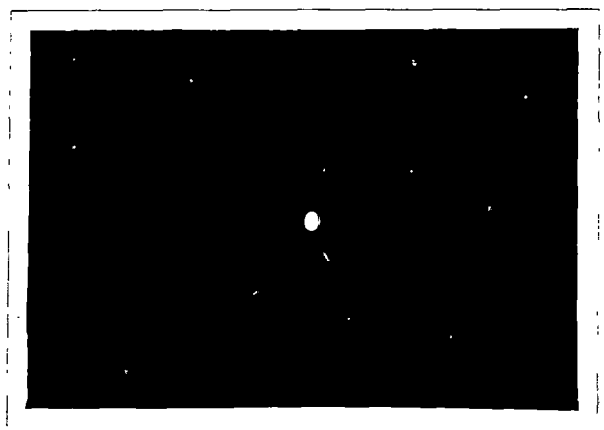


Figure 7.9 : x-ray diffraction photograph of magnetically aligned sample 5CPOd(3)1 at 50^{o}C.

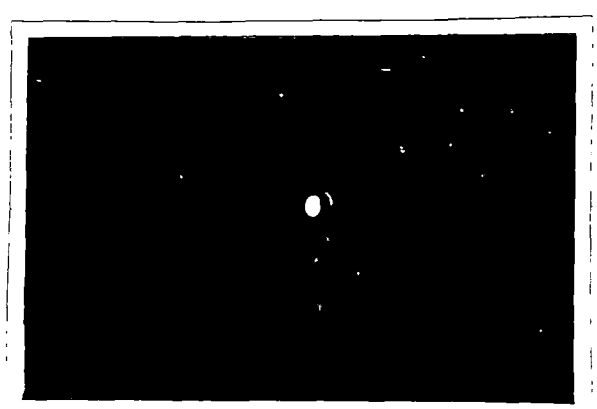


Figure 7.10 : x-ray diffraction photograph of magnetically aligned sample 5CPOd(3)1 at 60^{o}C.

Figure 7.11 : x-ray diffraction photograph of magnetically aligned sample 3CPS at 39^{o}C.

gaussian form[12] with a background varying linearly with the scattering vector q. The best fitted values of q_o give the value of intermolecular distances D using the relation $D = 2\pi(1.117/q_o)$. The intensity versus q-values graph at temperature 37^oC for the compound 3CPOd(3)1 is shown in the figure 7.12. The average value of intermolecular distances are approximately 4.72 Å, 4.73 Å and 4.56 Å for the compounds 3CPOd(3)1, 5CPOd(3)1 and 3CPS respectively and are almost temperature independent within our experimental uncertainty of $\pm$0.05. We have also calculated correlation lengths from the value of Δq using Hosemann's paracrystalline model[13]. In all the compounds, correlation number is found to be approximately 5 which is normally found in most nematic liquid crystals.

For the two non-polar compound apparent molecular length l values are found to be 16.8 Å and 19.1 Å respectively and they do not vary significantly with temperature. Lengths (L) measured from the streo-model unit are found to be 17.1 Å for 3CPOd(3)1 and 19.0 Å for 5CPOd(3)1. Thus the molecules are in fully extended form in the liquid crystalline phase and there is no dimer formation. Vander Waals type of interactions are responsible for the stability of mesophases of these two non-polar compounds. From stereo-model unit L is found to be 15.1 Å for the polar compound 3CPS. Probably this polar compound in the liquid crystalline phase form dimer due to dipole - dipole or dipole -induced dipole interactions resulting in a large value of apparent molecular length (l) and low value of Bragg scattering angle. We are not able to measure this low angle with our present experimental set up.

The mean intensity values of the four quadrants are given in tables 7.9, 7.11 and 7.13 for the three compounds. The procedure for the determination of normalised orientational distribution function $f(\beta)$ values were described in chapter 5. Tables 7.10, 7.12 and 7.14 give the normalised distribution function $f(\beta)$ values at angles of 5^o intervals. $f(\beta)$ versus β at different temperatures are given in

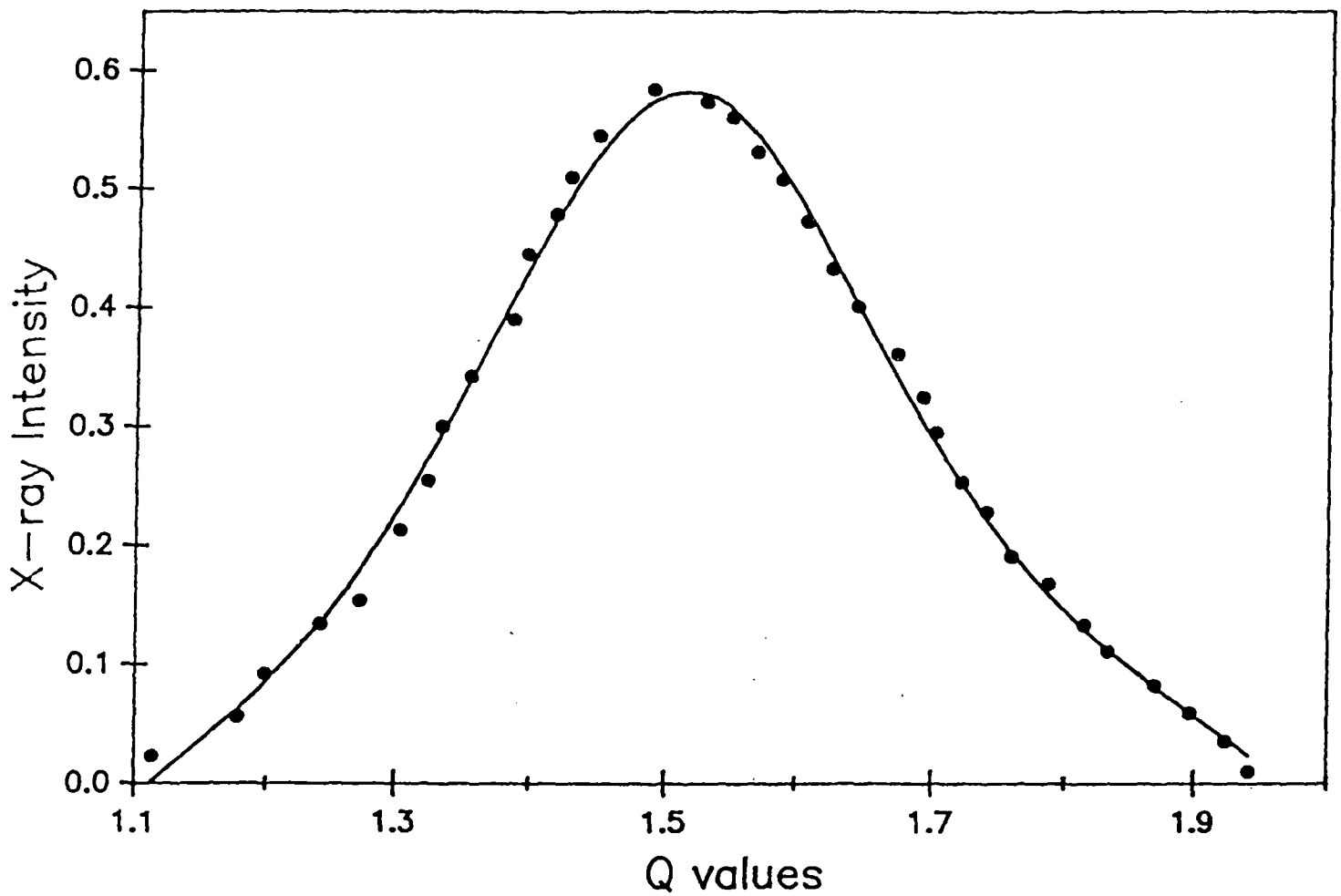


Figure 7.12 : Q vs intensity graph of sample 3CPOd(3)1 at $37^{o}C$, o experimental points, —— fitted curve through calculated values.

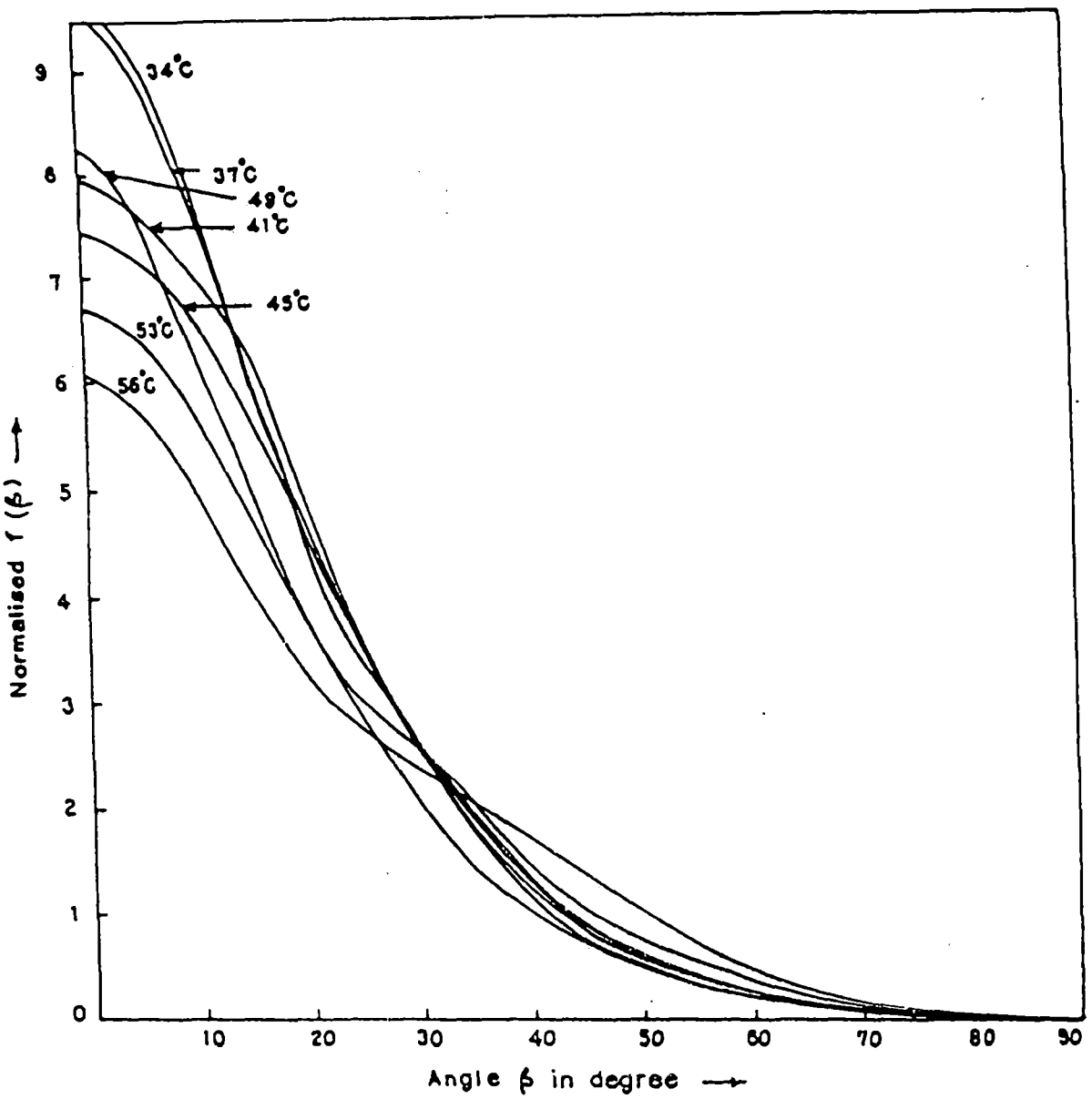


Figure 7.13 : Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temperature of the sample 3CPOd(3)1.

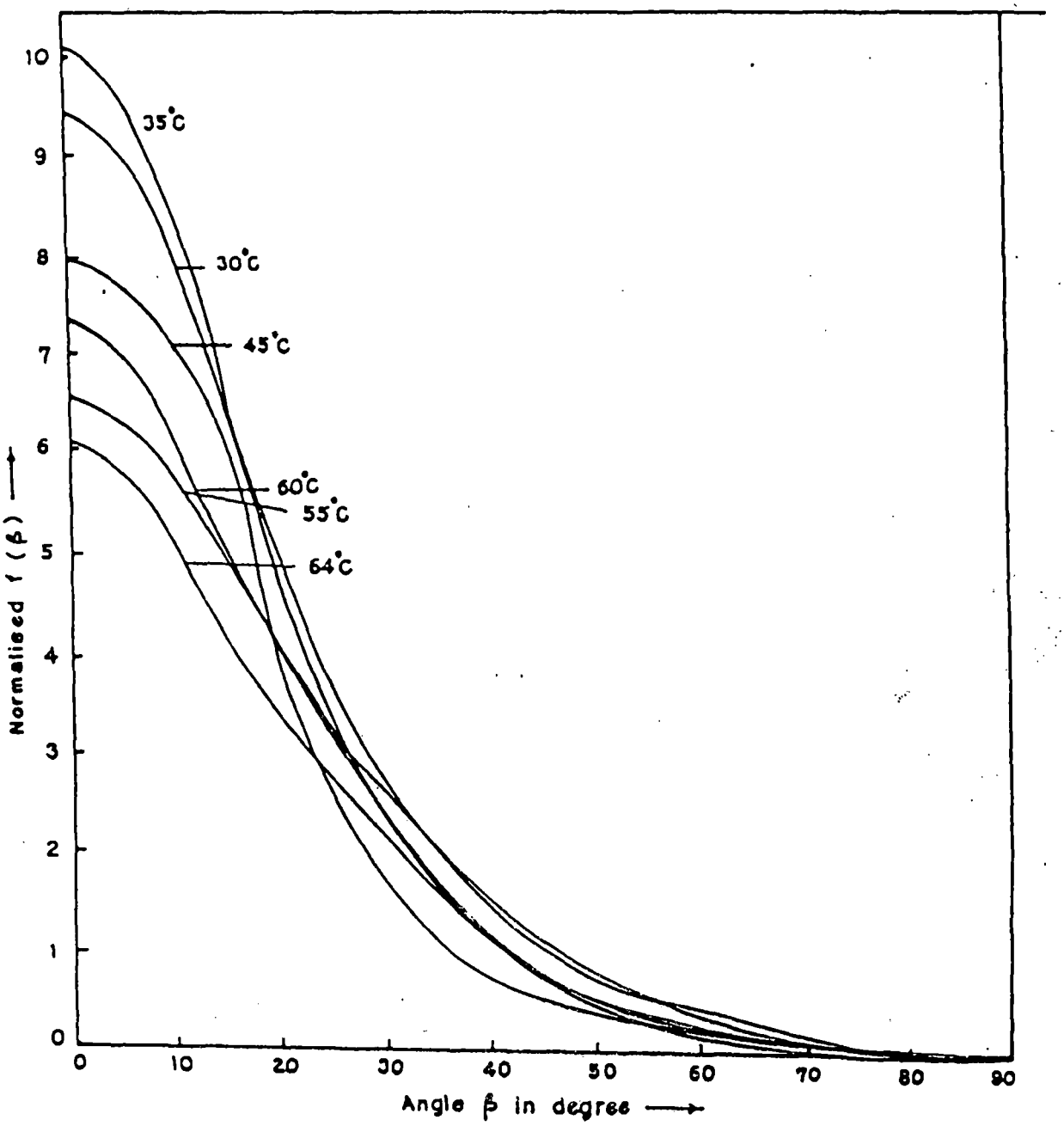


Figure 7.14 : Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temperature of the sample 5CPOd(3)1.

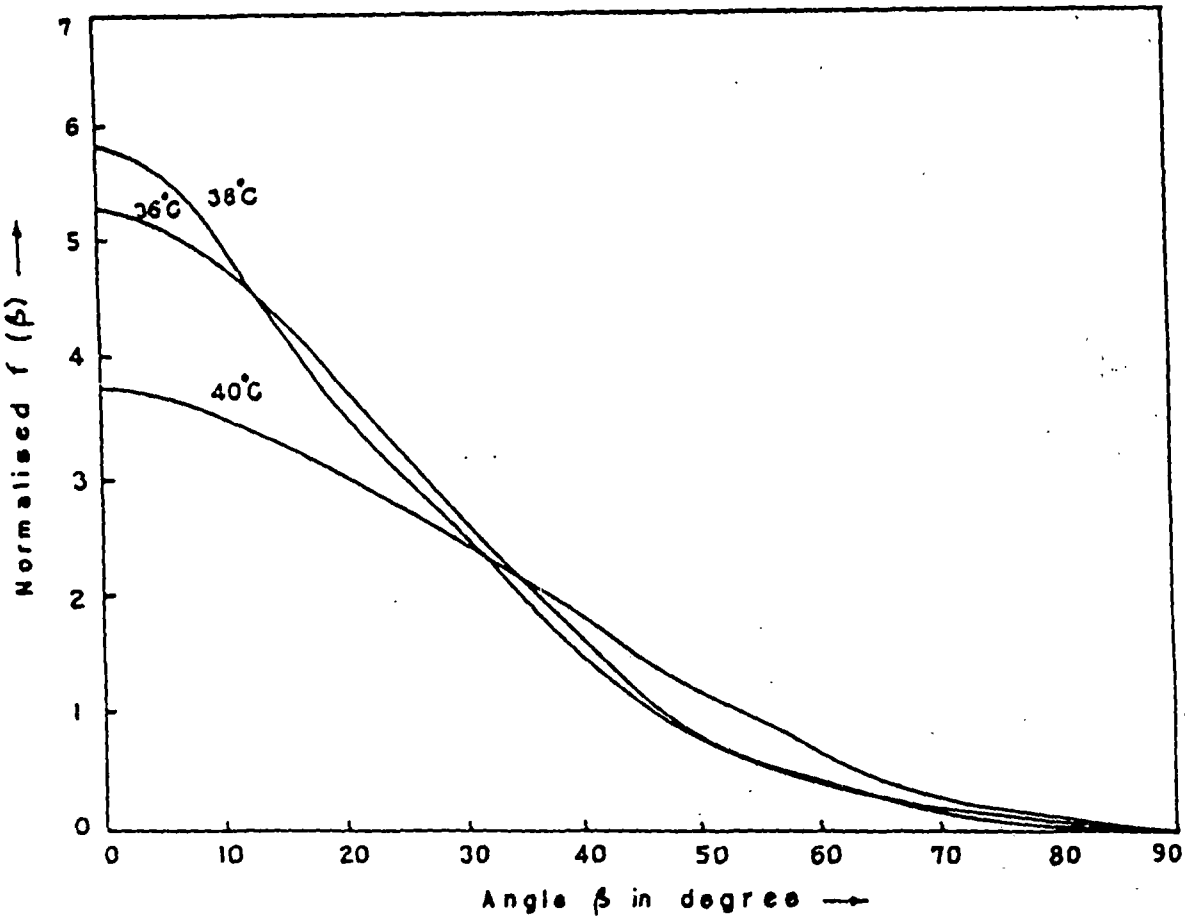


Figure 7.15 : Normalised orientational distribution function $f(\beta)$ plotted against the angle β at different temperature of the sample 3CPS.

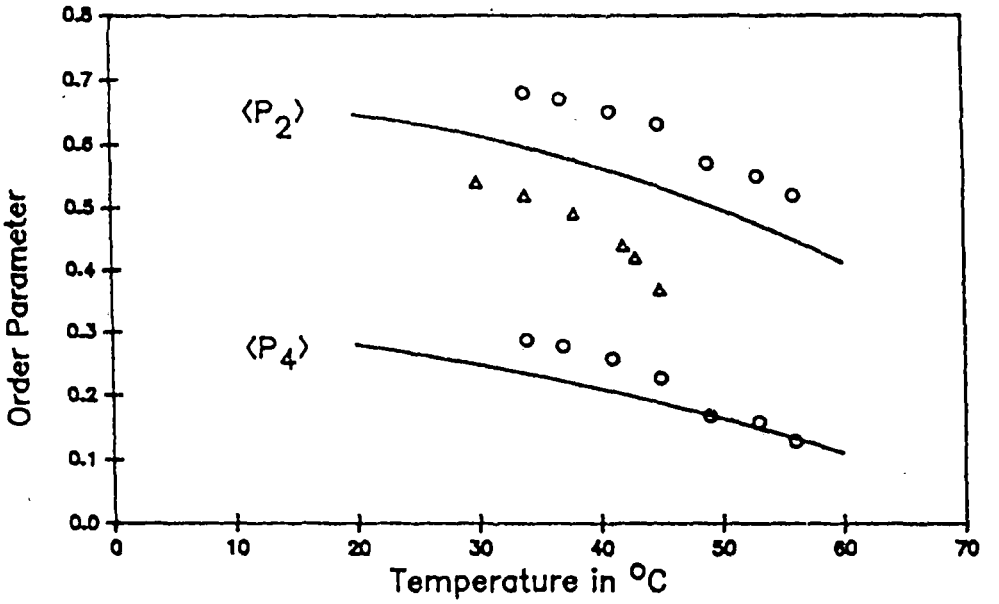


Figure 7.16 : Variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for the compound 3CPOd(3)1.

Δ - optical data, o - x-ray data, —— MS theoretical values.

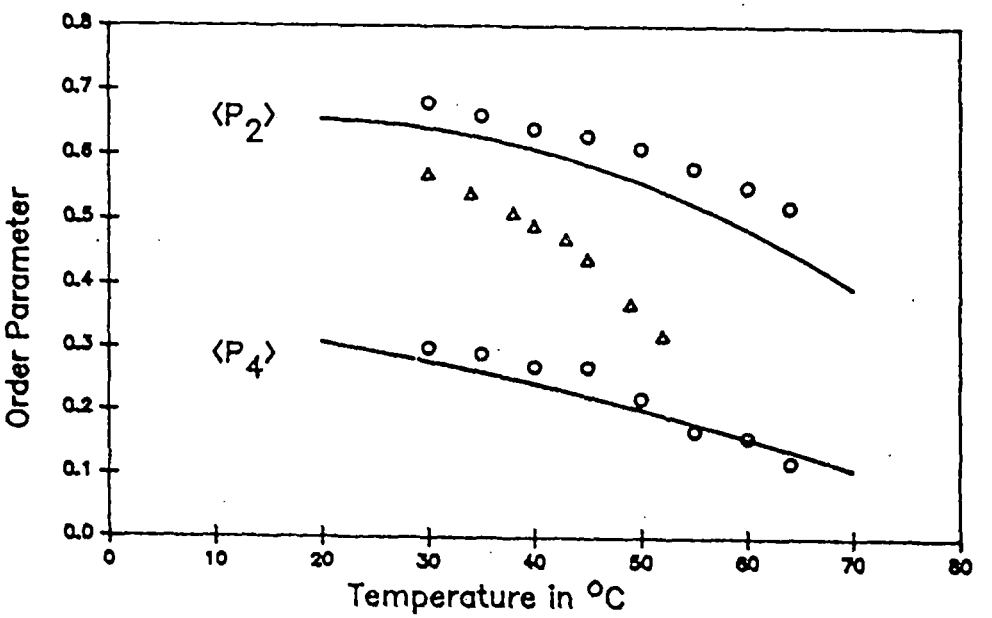


Figure 7.17 : Variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for the compound 5CPOd(3)1.

△- optical data, o - x-ray data, —— MS theoretical values.

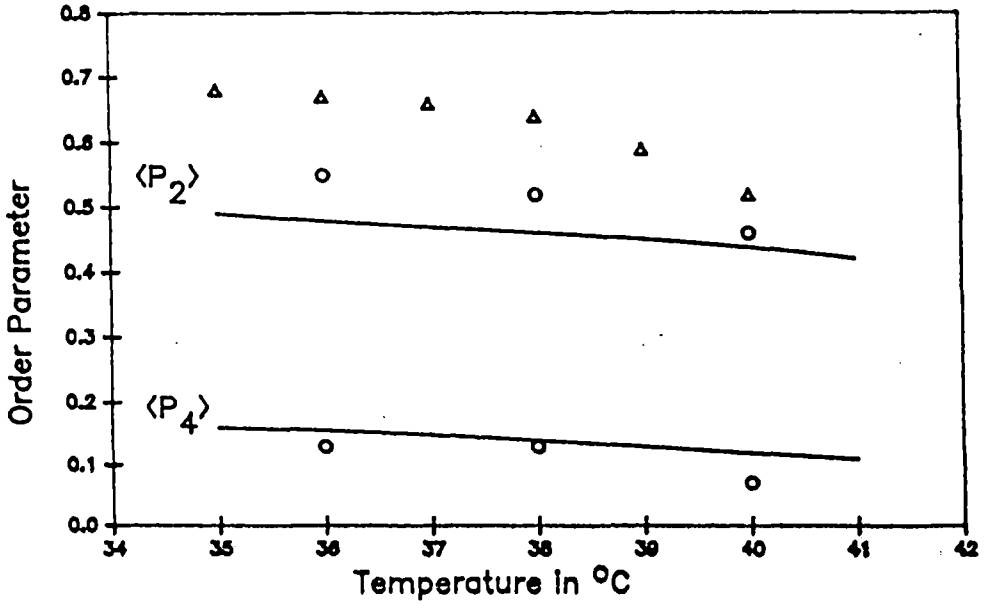


Figure 7.18 : Variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for the compound 3CPS.

Δ - optical data, o - x-ray data, ——— MS theoretical values.

figures 7.13 - 7.15. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for the three compounds calculated at different temperatures are listed in table 7.15. Temperature variation of order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ calculated from x-ray and optical data are shown in figures 7.16 - 7.18. The average order parameter $\langle P_2 \rangle$ as well as $\langle P_4 \rangle$ decreases with increasing temperature. These values are compared with theoretical values based on the Maier-Saupe model. $\langle P_2 \rangle$ values determined from x-ray data are higher than the Maier-Saupe values. It is well known that the orientational behaviour of the nematic phase may be distinguished in two parts : a long range order and a short range order. Whereas the Maier-Saupe model reflects long range ordering in the liquid crystalline phase, a short range local ordering due to intermolecular interactions also exists[14]. This short range interaction causes an increase in the orientational order parameter $\langle P_2 \rangle$ of the compounds. $\langle P_2 \rangle$ values obtained from two methods differs considerably and such behaviours were reported in our previous papers[15,16]. This may be due to the difference in the technique of alignment and difference in the averaging involved. We can not depend too much on the value of $\langle P_2 \rangle$ determined from optical studies, because there are much approximation in the the solid phase data of $(\alpha_{\parallel} - \alpha_{\perp})$ determined either by Haller's method or by bond additivity rule.

From the nature of temperature variation of $\langle P_2 \rangle$ (from x-ray data) in fig.7.16, it seems that there is a phase transition near the temperature 45^{o}C. Similar abnormal behaviour were observed in optical studies for both the non-polar compounds. X-ray photographs at these temperatures show that these phases are nematic, that means there may be nematic to nematic phase transition. This nematic phase is not cybotactic, because the inner rings do not split into four discrete spots in these aligned photographs, as is found in most cases. Cybotactic to ordinary nematic transitions were observed by Mandal et al.[17], but unlike them, the intensity of the inner ring is

not greater than the outer ring in this observation. Differential thermal analysis could have given us some insight. Since we do not have this facility in our laboratory, I am unable to explain this anomaly.

Table - 7.1

Density (ρ) and Refractive index (n_o,n_e) at different temperature of the compound 3CPOd(3)1.

Temp. in (^oC)	Density (ρ) in gm/cm^3	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
		n_o	n_e	n_o	n_e	n_o	n_e
30.0	0.977	1.467	1.545	1.471	1.549	1.475	1.553
34.0	0.974	1.467	1.542	1.471	1.546	1.475	1.550
38.0	0.971	1.467	1.538	1.471	1.542	1.475	1.546
42.0	0.968	1.469	1.532	1.473	1.536	1.477	1.540
43.0	0.967	1.470	1.530	1.474	1.534	1.478	1.538
45.0	0.965	1.472	1.524	1.476	1.529	1.480	1.533
46.0	0.964		1.520		1.527		1.530
48.0	0.963		1.512		1.516		1.523
50.0	0.961		1.507		1.511		1.516
54.0	0.956		1.503		1.507		1.511
56.0	0.954		1.503		1.507		1.511
58.5	0.947 (iso)	1.487		1.491		1.495	
60.0	0.945 (iso)	1.487		1.491		1.495	

Table - 7.2

Density (ρ) and Refractive index (n_o,n_e) at different temperature of the compound 5CPOd(3)1.

Temp. in (^oC)	Density (ρ) in gm/cm^3	λ = 6907 Å		λ = 6780 Å		λ = 5461 Å	
		n_o	n_e	n_o	n_e	n_o	n_e
30.0	0.966	1.489	1.588	1.493	1.592	1.499	1.598
34.0	0.964	1.489	1.584	1.493	1.588	1.499	1.594
38.0	0.961	1.489	1.579	1.493	1.583	1.499	1.591
40.0	0.959	1.491	1.576	1.495	1.580	1.501	1.586
43.0	0.957	1.492	1.571	1.496	1.575	1.502	1.582
45.0	0.955	1.493	1.567	1.497	1.571	1.503	1.578
49.0	0.951	1.495	1.556	1.499	1.562	1.505	1.568
52.0	0.949	1.497	1.546	1.501	1.552	1.507	1.560
53.0	0.948		1.543		1.549		1.556
57.0	0.945		1.537		1.541		1.547
60.0	0.942		1.535		1.539		1.545
64.0	0.937		1.535		1.539		1.545
67.0	0.928 (iso)	1.527		1.531		1.537	
69.0	0.926 (iso)	1.527		1.531		1.537	

Table - 7.3

Density (ρ) and Refractive index (n_o,n_e) at different temperature of the compound 3CPS.

Temp. in (^oC)	Density (ρ) in gm/cm^3	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
		n_o	n_e	n_o	n_e	n_o	n_e
35.0	1.160	1.724	1.879	1.728	1.884	1.733	1.889
36.0	1.157	1.724	1.876	1.728	1.882	1.733	1.887
37.0	1.154	1.724	1.874	1.728	1.879	1.733	1.883
38.0	1.152	1.724	1.868	1.728	1.874	1.733	1.880
39.0	1.150	1.728	1.863	1.733	1.868	1.739	1.874
40.0	1.149	1.736	1.854	1.740	1.860	1.748	1.866
42.0	1.138	1.790	1.790	1.794	1.794	1.800	1.800

Table - 7.4

Polarizabilities (α_o,α_e) at different temperatures of compounds 3CPOd(3)1 , 5CPOd(3)1 and 3CPS by Vuk's method.

Temp. in ^oC	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
			3CPOd(3)1			
30.0	30.10	36.24	30.32	36.46	30.54	36.68
34.0	30.21	36.13	30.43	36.35	30.66	36.57
38.0	30.34	35.95	30.56	36.18	30.78	36.40
42.0	30.60	35.60	30.82	35.82	31.05	36.04
43.0	30.71	35.47	30.93	35.70	31.16	35.92
45.0	30.95	35.08	31.16	35.37	31.39	35.60
58.0	32.86		33.10		33.33	
			5CPOd(3)1			
30.0	34.75	43.44	34.99	43.68	35.35	44.04
34.0	34.85	43.21	35.09	43.45	35.46	43.81
38.0	35.00	42.94	35.25	43.19	35.59	43.71
40.0	35.24	42.75	35.49	43.00	35.85	43.36
43.0	35.43	42.42	35.67	42.66	36.03	43.11
45.0	35.61	42.17	35.85	42.41	36.21	42.86
49.0	35.99	41.42	36.22	41.82	36.59	42.19
52.0	36.30	40.66	36.53	41.07	36.88	41.60
67.0	39.45		39.71		40.08	
			3CPS			
35.0	33.84	43.42	33.97	43.61	34.15	43.78
36.0	33.96	43.39	34.09	43.63	34.27	43.81
38.0	34.16	43.12	34.29	43.37	34.46	43.60
39.0	34.44	42.85	34.62	43.02	34.84	43.23
40.0	34.90	42.24	35.03	42.49	35.33	42.66
42.0	38.21		38.35		38.85	

Table - 7.5

Polarizabilities (α_o,α_e) at different temperatures of compounds 3CPOd(3)1 , 5CPOd(3)1 and 3CPS by Neugebauer's method.

Temp. in °C	λ = 6907 Å		λ = 5780 Å		λ = 5461 Å	
	α_o	α_e	α_o	α_e	α_o	α_e
			3CPOd(3)1			
30.0	30.43	35.58	30.65	35.79	30.87	36.01
34.0	30.53	35.50	30.75	35.71	30.98	35.93
38.0	30.64	35.35	30.86	35.57	31.09	35.79
42.0	30.87	35.07	31.09	35.28	31.32	35.50
43.0	30.96	34.97	31.19	35.19	31.42	35.40
45.0	31.17	34.64	31.39	34.92	31.61	35.14
58.0	32.86		33.10		33.33	
			5CPOd(3)1			
30.0	35.24	42.46	35.48	42.69	35.85	43.04
34.0	35.32	42.27	35.57	42.50	35.94	42.85
38.0	35.45	42.05	35.70	42.29	36.06	42.78
40.0	35.66	41.91	35.91	42.14	36.28	42.50
43.0	35.82	41.63	36.07	41.87	36.43	42.30
45.0	35.97	41.43	36.22	41.67	36.59	42.10
49.0	36.30	40.81	36.54	41.19	36.91	41.55
52.0	36.54	40.18	36.78	40.56	37.15	41.06
67.0	39.45		39.71		40.08	
			3CPS			
35.0	34.61	41.87	34.75	42.04	34.94	42.21
36.0	34.72	41.86	34.86	42.08	35.05	42.25
38.0	34.88	41.68	35.02	41.90	35.20	42.11
39.0	35.12	41.49	35.30	41.66	35.52	41.87
40.0	35.49	41.06	35.63	41.28	35.93	41.47
42.0	38.21		38.35		38.65	

Table - 7.6

Order parameter values of compound 3CPOd(3)1, 5CPOd(3)1 and 3CPS for different wavelengths by Vuk's method.

Temp. in ^{o}C	λ = 6907 Å $\langle P_2 \rangle$	λ = 5780 Å $\langle P_2 \rangle$	λ = 5461 Å $\langle P_2 \rangle$	Average $\langle P_2 \rangle$
		3CPOd(3)1		
30.0	0.535	0.535	0.535	0.535
34.0	0.516	0.516	0.516	0.516
38.0	0.489	0.489	0.489	0.489
42.0	0.436	0.436	0.435	0.436
43.0	0.415	0.415	0.415	0.415
45.0	0.359	0.367	0.367	0.364
		5CPOD(3)1		
30.0	0.573	0.572	0.572	0.572
34.0	0.551	0.551	0.550	0.551
38.0	0.523	0.523	0.534	0.527
40.0	0.495	0.495	0.495	0.495
43.0	0.461	0.461	0.466	0.463
45.0	0.432	0.432	0.438	0.434
49.0	0.357	0.369	0.369	0.365
52.0	0.297	0.299	0.311	0.302
		3CPS		
35.0	0.677	0.681	0.680	0.679
36.0	0.666	0.674	0.674	0.671
37.0	0.658	0.662	0.658	0.659
38.0	0.633	0.642	0.646	0.640
39.0	0.594	0.593	0.593	0.593
40.0	0.518	0.527	0.518	0.521

Table 7.7

Order parameter values of compound 3CPOd(3)1, 5CPOd(3)1 and 3CPS for different wavelengths by Neugebauer's method.

Temp. in ^{o}C	λ = 6907 Å $\langle P_2 \rangle$	λ = 5780 Å $\langle P_2 \rangle$	λ = 5461 Å $\langle P_2 \rangle$	Average $\langle P_2 \rangle$
		3CPOd(3)1		
30.0	0.532	0.531	0.530	0.531
34.0	0.513	0.512	0.511	0.512
38.0	0.488	0.487	0.486	0.487
42.0	0.434	0.433	0.433	0.433
43.0	0.413	0.413	0.412	0.413
45.0	0.358	0.366	0.365	0.363
		5CPOd(3)1		
30.0	0.569	0.568	0.567	0.568
34.0	0.547	0.547	0.545	0.546
38.0	0.521	0.520	0.530	0.524
40.0	0.492	0.491	0.491	0.491
43.0	0.458	0.457	0.462	0.459
45.0	0.431	0.430	0.435	0.432
49.0	0.356	0.368	0.367	0.364
52.0	0.297	0.298	0.309	0.301
		3CPS		
35.0	0.665	0.668	0.666	0.667
36.0	0.654	0.661	0.659	0.658
37.0	0.646	0.651	0.641	0.646
38.0	0.623	0.630	0.633	0.628
39.0	0.584	0.583	0.581	0.682
40.0	0.510	0.518	0.507	0.511

Table 7.9

Mean experimental intensity values $I(\psi)$, in arbitrary units, of compound - 3CPOd(3)1 after background correction.

ψ (degree)	$I(\psi)$ values at different temperatures ^{o} C						
	34	37	41	45	49	53	56
0	58.0	43.0	45.0	39.0	37.0	32.0	12.5
5	56.0	41.5	44.0	38.0	35.0	31.0	11.0
10	49.5	36.0	40.0	35.0	30.5	27.5	10.3
15	40.0	30.0	35.0	30.5	26.0	24.5	9.0
20	34.0	25.0	28.0	25.5	22.0	21.5	8.0
25	25.0	19.0	22.0	20.0	18.0	18.0	7.0
30	18.5	15.0	16.0	16.0	15.0	14.0	6.2
35	13.0	11.0	12.0	11.0	12.0	11.5	5.2
40	9.0	7.5	8.5	8.0	9.3	9.0	4.5
45	6.0	5.0	6.5	6.0	7.5	7.0	3.3
50	4.0	3.0	4.0	4.5	6.0	5.5	2.2
55	2.5	2.0	2.8	3.0	4.5	4.5	1.8
60	1.5	1.0	1.5	2.0	3.0	3.0	1.3
65	1.0	0.5	0.8	0.8	2.0	2.5	0.8
70	0.3	0.2	0.4	0.4	1.0	1.5	0.4
75	0.0	0.0	0.2	0.2	0.5	1.0	0.1
80	0.0	0.0	0.0	0.0	0.0	0.5	0.0
85	0.0	0.0	0.0	0.0	0.0	0.0	0.0
90	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 7.10

Normalised distribution function values $f(\beta)$ of compound - 3CPOd(3)1 at different temperatures.

β (degree)	$f(\beta)$ values at different temperatures °C						
	34	37	41	45	49	53	56
0	9.649	9.569	7.906	7.387	8.228	6.693	6.042
5	9.183	9.051	7.684	7.159	7.738	6.048	5.736
10	7.954	7.712	7.035	6.528	6.493	5.664	4.978
15	6.367	6.053	6.034	5.627	5.008	4.719	4.065
20	4.822	4.547	4.825	4.604	3.749	3.817	3.282
25	3.542	3.407	3.602	3.583	2.883	3.063	2.744
30	2.546	2.578	2.547	2.649	2.308	2.438	2.389
35	1.769	1.913	1.755	1.864	1.843	1.890	2.083
40	1.163	1.327	1.216	1.265	1.409	1.407	1.745
45	0.721	0.837	0.854	0.857	1.036	1.019	1.364
50	0.439	0.489	0.587	0.601	0.769	0.749	1.002
55	0.279	0.282	0.376	0.431	0.594	0.576	0.699
60	0.184	0.168	0.214	0.293	0.452	0.451	0.465
65	0.109	0.094	0.107	0.168	0.303	0.333	0.290
70	0.047	0.038	0.047	0.068	0.158	0.216	0.163
75	0.006	0.003	0.019	0.009	0.053	0.117	0.076
80	-0.006	-0.007	0.007	-0.007	0.006	0.049	0.023
85	-0.001	-0.001	0.001	0.001	0.000	0.014	-0.004
90	0.003	0.003	-0.001	0.006	0.003	0.004	-0.001

Table 7.11

Mean experimental intensity values $I(\psi)$, in arbitrary units, of compound - 5CPOd(3)1 after background correction.

ψ (degree)	$I(\psi)$ values at different temperatures ^{o}C							
	30	35	40	45	50	55	60	64
0	38.0	34.0	25.5	35.0	25.0	20.5	19.0	11.5
5	37.0	33.0	24.5	34.0	24.0	19.5	17.5	11.0
10	33.0	28.0	21.5	31.0	21.5	18.0	16.0	10.0
15	28.0	23.5	17.5	27.0	19.0	16.0	14.0	9.0
20	21.5	18.5	13.0	22.0	16.0	14.0	12.0	8.0
25	17.0	13.5	10.0	16.5	13.0	12.0	10.5	7.0
30	12.5	10.0	8.0	12.0	10.5	9.0	8.5	6.0
35	9.0	7.5	6.0	8.5	7.5	7.0	6.5	5.2
40	6.0	5.5	5.0	6.0	5.5	6.0	5.5	4.5
45	4.0	4.0	4.0	4.5	4.0	4.0	4.0	3.5
50	2.0	3.0	3.0	3.0	3.0	3.0	3.0	2.2
55	1.5	2.2	2.0	2.5	2.0	2.5	2.0	1.8
60	0.8	1.5	1.0	2.0	1.0	1.5	1.2	1.3
65	0.5	1.0	0.5	1.5	0.5	1.0	0.5	0.8
70	0.2	0.5	0.2	1.0	0.2	0.5	0.2	0.4
75	0.0	0.2	0.0	0.5	0.0	0.3	0.0	0.1
80	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
85	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
90	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 7.12

Normalised distribution function values $f(\beta)$ of compound - 5CPOd(3)1 at different temperatures.

β (degree)	$f(\beta)$ values at different temperatures °C				
	30	35	40	45	50
0	9.372	10.066	10.032	7.909	7.654
5	8.964	9.552	9.511	7.692	7.328
10	7.869	8.189	8.115	7.062	6.476
15	6.399	6.412	6.262	6.087	5.389
20	4.897	4.680	4.434	4.894	4.337
25	3.596	3.277	2.983	3.655	3.436
30	2.573	2.263	2.029	2.539	2.668
35	1.796	1.563	1.490	1.665	1.986
40	1.206	1.079	1.189	1.064	1.396
45	0.762	0.746	0.968	0.696	0.939
50	0.445	0.525	0.744	0.484	0.631
55	0.241	0.379	0.511	0.357	0.436
60	0.125	0.270	0.301	0.270	0.292
65	0.066	0.176	0.144	0.199	0.163
70	0.037	0.094	0.050	0.136	0.056
75	0.019	0.037	0.008	0.079	- 0.006
80	0.006	0.008	- 0.003	0.033	- 0.017
85	- 0.002	- 0.001	- 0.001	0.001	- 0.001
90	- 0.005	- 0.001	0.001	- 0.011	0.009

(continued)

Table 7.12

Normalised distribution function values $f(\beta)$ of compound - 5CPOd(3)1 at different temperatures.

β (degree)	$f(\beta)$ values at different temperatures °C		
	55	60	64
0	6.499	7.275	6.033
5	6.269	6.899	5.736
10	5.664	5.944	4.978
15	4.865	4.796	4.065
20	4.047	3.799	3.282
25	3.294	3.073	2.744
30	2.608	2.532	2.389
35	1.984	2.047	2.083
40	1.443	1.572	1.741
45	1.024	1.147	1.364
50	0.734	0.817	1.002
55	0.539	0.576	0.699
60	0.388	0.383	0.465
65	0.251	0.211	0.290
70	0.133	0.074	0.163
75	0.051	- 0.004	0.076
80	0.011	- 0.019	0.023
85	0.001	- 0.001	- 0.004
90	0.001	0.011	- 0.011

Table 7.13

Mean experimental intensity values I(ψ), in arbitrary units, of compound - 3CPS after background correction.

ψ (degree)	I(ψ) values at different temperatures (^{0}C)		
	36	38	40
0	15.5	15.5	12.0
5	15.0	14.5	11.5
10	14.0	13.5	11.0
15	13.0	12.2	10.5
20	11.8	11.2	10.0
25	10.0	9.0	9.0
30	8.0	8.0	8.0
35	7.0	6.0	7.0
40	5.0	5.0	5.5
45	4.0	4.0	5.0
50	2.0	3.0	4.0
55	1.5	2.5	3.0
60	1.0	2.0	2.0
65	0.5	1.5	1.0
70	0.0	1.0	0.5
75	0.0	0.5	0.3
80	0.0	0.0	0.1
85	0.0	0.0	0.0
90	0.0	0.0	0.0

Table 7.14

Normalised distribution function values $f(\beta)$ of compound - 3CPS at different temperatures.

β (degree)	$f(\beta)$ values at different temperatures °C		
	36	38	40
0	5.287	5.788	3.842
5	5.152	5.561	3.752
10	4.792	4.978	3.525
15	4.306	4.261	3.257
20	3.776	3.593	3.007
25	3.235	3.024	2.759
30	2.679	2.501	2.467
35	2.119	1.976	2.119
40	1.598	1.476	1.757
45	1.169	1.069	1.437
50	0.849	0.800	1.172
55	0.616	0.639	0.929
60	0.431	0.522	0.673
65	0.271	0.397	0.411
70	0.140	0.261	0.189
75	0.052	0.136	0.051
80	0.008	0.048	0.003
85	- 0.005	0.002	0.006
90	- 0.006	- 0.012	0.015

Table 7.15

Order parameter values at different temperatures of compounds - 3CPOd(3)1, 5CPOd(3)1 and 3CPS from x-ray diffraction study.

compound - 3CPOd(3)1			compound - 5CPOd(3)1			compound - 3CPS		
Temp. in °C	$\langle P_2 \rangle$	$\langle P_4 \rangle$	Temp. in °C	$\langle P_2 \rangle$	$\langle P_4 \rangle$	Temp. in °C	$\langle P_2 \rangle$	$\langle P_4 \rangle$
34	0.683	0.298	30	0.686	0.297	36	0.550	0.130
37	0.672	0.375	35	0.661	0.295	38	0.520	0.120
41	0.654	0.258	40	0.644	0.267	40	0.460	0.070
45	0.634	0.232	45	0.643	0.270			
49	0.574	0.176	50	0.628	0.217			
53	0.550	0.166	55	0.580	0.173			
56	0.523	0.130	60	0.550	0.165			
			64	0.523	0.103			

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CHAPTER 8

Determination of molecular properties of some polar mesogenic compounds.

8.1 INTRODUCTION

For a molecule to exhibit a liquid crystalline phase, it must satisfy certain structural requirements. But it is often very difficult to predict the effect of changes in the molecular structure on the stability and properties of liquid crystals. In reality the situation is very complicated, because, in addition to molecular structure, intermolecular interactions must be considered. Dipole-dipole interactions and steric factors play a major role in stabilizing liquid crystal phases[1]. Knowledge of dipole moments of mesogenic molecules is, therefore, very useful. In this chapter I have reported the results of dipole moment determination of some polar compounds. I have also calculated the molecular parameters, such as mean polarizability (α) and polarizability anisotropy ($\Delta\alpha$) by bond additivity scheme. Dipole moments calculated from crystallographic data for two compounds have been compared with experimental values.

The molecular formula and transition temperatures (^{o}C) of the compounds are given in Table 8.1.

TABLE - 8.1

	STRUCTURES	ABBREVIATION	NEMATIC RANGE
(1)	C_3H_5-⟨H⟩-⟨H⟩-CN	1d(1)CC	65.0°C - 100°C
(2)	C_5H_9-⟨H⟩-⟨H⟩-CN	1d(3)CC	79.5°C - 100°C
(3)	C_3H_7-⟨H⟩-⟨O⟩-NCS	3CPS	39.0°C - 42.0°C
(4)	C_5H_{11}-⟨O⟩-⟨O⟩-CN	5CB	22.5°C - 35.3°C
(5)	C_7H_{15}-⟨O⟩-COO-⟨O⟩-CN	CPHB	44.2°C - 56.5°C

8.2 EXPERIMENTAL DETAILS

The liquid crystalline compounds under investigation were extensively studied by small angle x-ray diffraction and by optical methods[2-5].

Molecular dipole moments were determined[6] by measuring the dielectric constants and refractive indices of solutions of the compounds in a non-polar solvent p-xylene at different concentrations of the solute. Dielectric constants was measured using a digital LCR bridge at 1 KHz. A cell was constructed by means of two plane parallel conducting glass plates separated by a thin glass spacer. After each measurement the cell was cleaned by benzene and dried. Refractive index was measured by Abbe's refractometer. All the measurements were done at room temperature.

The dipole moment (μ) is calculated using the Guggenheim[7] equation,

$$\mu^2 = \frac{27KT}{4\pi N \left(\varepsilon_o + 2\right)\left(n_o^2 + 2\right)} \frac{\left(\varepsilon - n^2\right) - \left(\varepsilon_o - n_o^2\right)}{C}$$

where N = Avogadro's number

K = Boltzman's constant

ε_o = Dielectric constant of the solvent (p-xylene)

ε = Dielectric constant of the solution.

n_o = Refractive index of the solvent (p-xylene).

n = Refractive index of the solution.

C = Molar concentration.

The dipole moments evaluated at different concentrations are plotted as a function of concentration (weight percent of the solute). The value of μ is obtained on extrapolation to infinite dilution.

8.3 SEMI-EMPIRICAL METHOD OF DIPOLE MOMENT CALCULATION :

The molecular dipole momemt depends on the conformation of the rings in the molecules and also on the partial charges on the constituent atoms. Electro-static point charges on the atoms in a molecule can be calculated by a number of semi-empirical quantum mechanical methods. In these methods partial atomic charges are obtained from ab initio LCAO MO calculations using crystallographic data and geometry optimization. Structural analysis have been done by us[8,9] for 1d(3)CC and CPHB. For these two compounds atomic charge distribution and dipole moments were calculated by different methods using molecular orbital theory[10] with the help of package program SYBYL[11].

The Huckel molecular orbital (HMO) method is a simple quantum method applicable to π electron systems.

The molecular π-orbitals are defined as

$$\psi_j = \sum_{i=1}^{N} C_{ij} \phi_i$$

Where N = the number of atoms in the π electron systems.

ψ = molecular orbital (MO).

ϕ_i = orbital of the i^{th} atom (AO).

C_{ij} = coefficient in the j^{th} MO for i^{th} AO.

To find the best set of values for the coefficients that gives the best value for the energy E of the molecular orbital the following system of secular equations is solved by the Jacobi diagonalization

$$\sum_{i=1}^{N} \left(H_{ij} - S_{ij}E \right) C_i \qquad \text{for } j = 1,2 \quad N$$

The term H_{ii} are called Coulomb integrals.

The terms H_{ij} for $i \neq j$ are called the resonance or bond intregrals. When atoms i and j are not bonded, the interaction is likely to be

small and H_{ij} is taken to be equal to zero. For bonded atoms the terms H_{ij} are called the resonance intregral and have finite values. The overlap intregral S_{ij} is zero for $i \neq j$ and is equal to one for $i=j$.

The tatal electron density at any atom q_i is the sum of electron densities contributed by each electron in each MO,

$$q_i = \sum_{i}^{N} n_i C_{ij}^2$$

C_{ij} is the coefficient of atom i in the j^{th} MO, which is occupied by n_j electrons. The sum is taken over all of the MO's.

The net atomic charge Q_i due to π electrons is then calculated by

$$Q_i = m_i - \sum_{j=1}^{N} n_j C_{ij}^2$$

where m_i is the number of π electrons by atom i. n_j is the number of electrons on the j^{th} molecular orbital.

The method of Pullman is a combination of two methods ; the Del Re method to calculate the σ component of the atomic charge and Huckel method to calculate the π component of the atomic charge. The total charge is the sum of the charges calculated by the two methods.

According to Del Re the atomic charges Q_i are calculated from the equation

$$Q_i = Q_i^o + \sum_{j=\text{bonded}} q_{ij}$$

Where Q_i^o is formal charge on atom i.

$\sum q_{ij}$ is the total electron densities contributed by each electron in each atomic orbital bonded to the i^{th} atom.

The Del Re method is applicable to molecules containing σ bonds only.

The method of Gast-Huck is a combination of two other charge

computation methods, the Gasteiger Marsili method to calculate the σ component of the atomic charge and the Huckel method to calculate the π component of the atomic charge. The total charge is the sum of the charges calculated by the two methods. Formal charges on atoms included in the π system are assumed to be delocalised over the entire π-system. For this reason the Huckel portion of the charges is calculated first and these charges are used as the basis for the Gasteiger-Marsili σ charge calculation. The method is based on the following relationship between orbital electronegativity and atomic charge.

$$X_A = b_A Q + C_A Q^2$$

The orbital electronegativity X_A is represented as a function of the total charge Q residing on the given atom. The necessary values of coefficients b and c are calculated on the basis of electronegativity values of anionic , neutral and cationic state of a given atom type. Electronegativity values calculated by the method of Hinze & Jaffe[12,13].

8.4 RESULTS AND DISCUSSIONS :

The variation of refractive index, dielectric constants and dipole moment with concentration are given in table 8.2 - 8.6. The variation of dipole moments with concentration for the five compounds are shown in Fig.8.1 - 8.5 . Best fitted least square curve are drawn through experimental points. As is expected the value of the dipole moment increases as concentration decreases or dilution increases. The dipole moment increases slowly at first and then quite rapidly for concentration less than 10%. The value of the dipole moment of 5CB, determined by me agrees well with that obtained by Dunmur et al[14], the only literature value available for the compounds under investigation. Values for various molecular

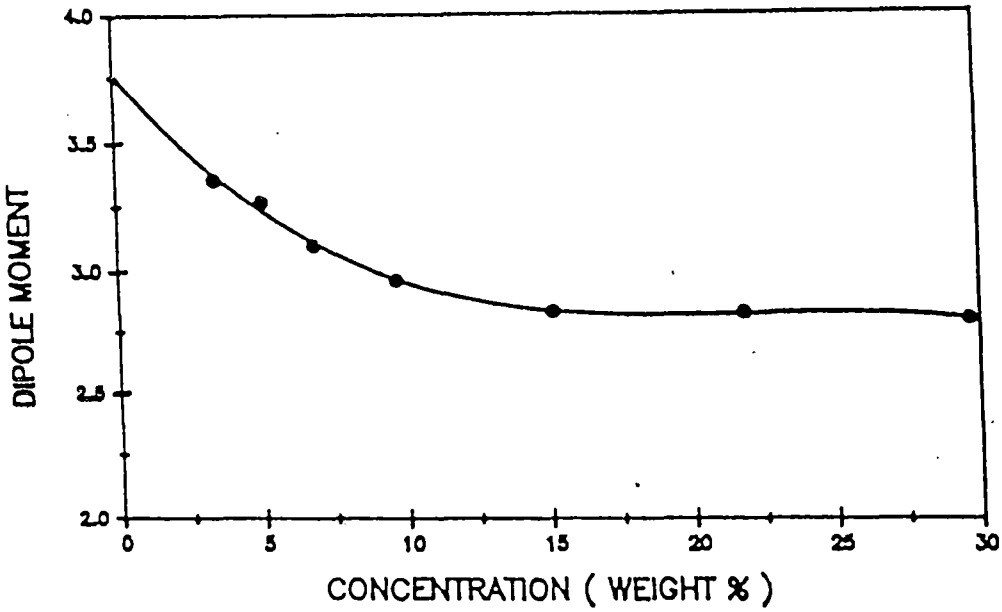

Figure 8.1 : The dipole moment of 1d(1)CC in p-xylene solution as a function of concentration.

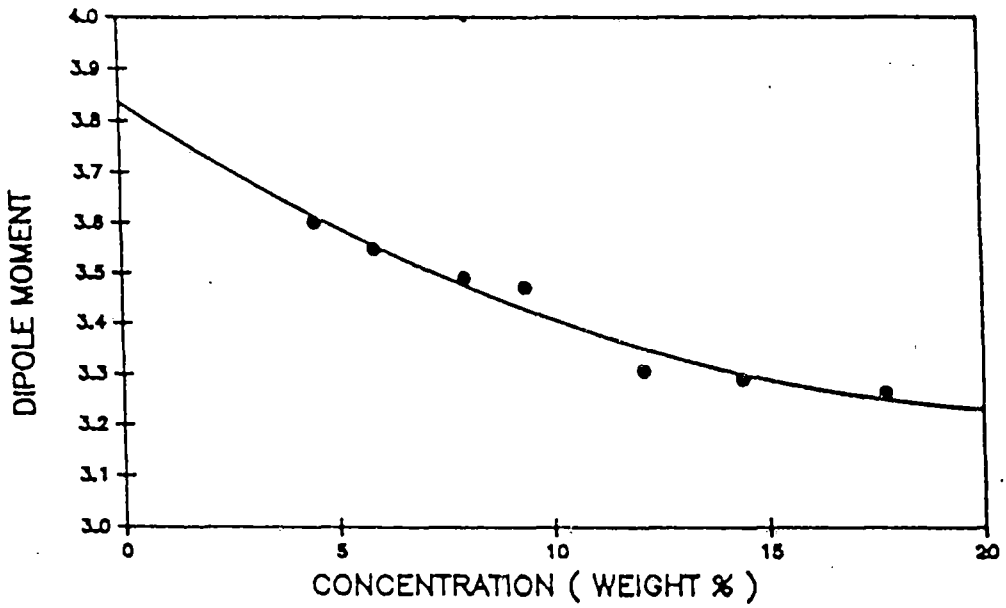

Figure 8.2 : The dipole moment of 1d(3)CC in p-xylene solution as a function of concentration.

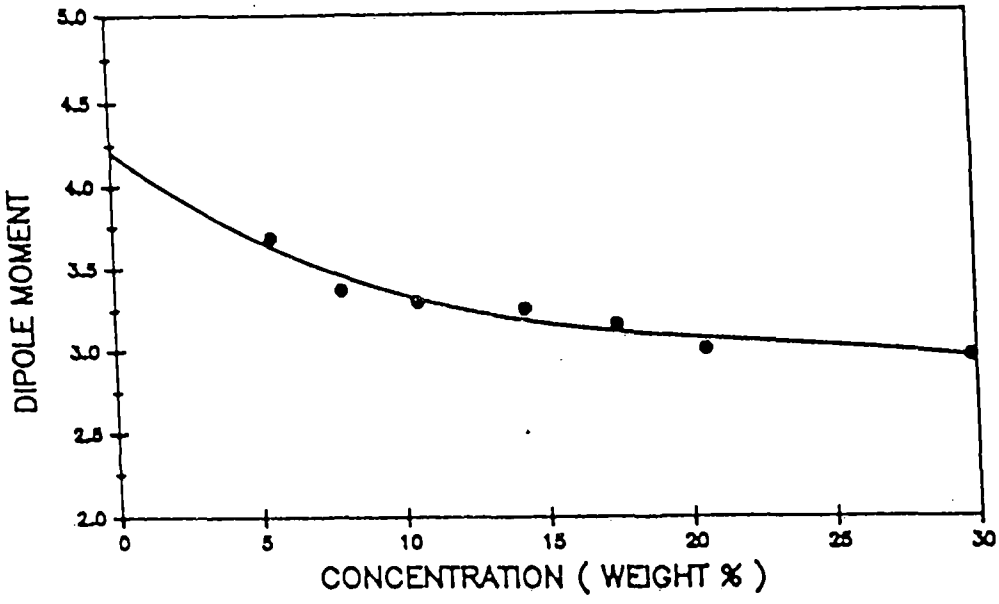

Figure 8.3 : The dipole moment of 3CPS in p-xylene solution as a function of concentration.

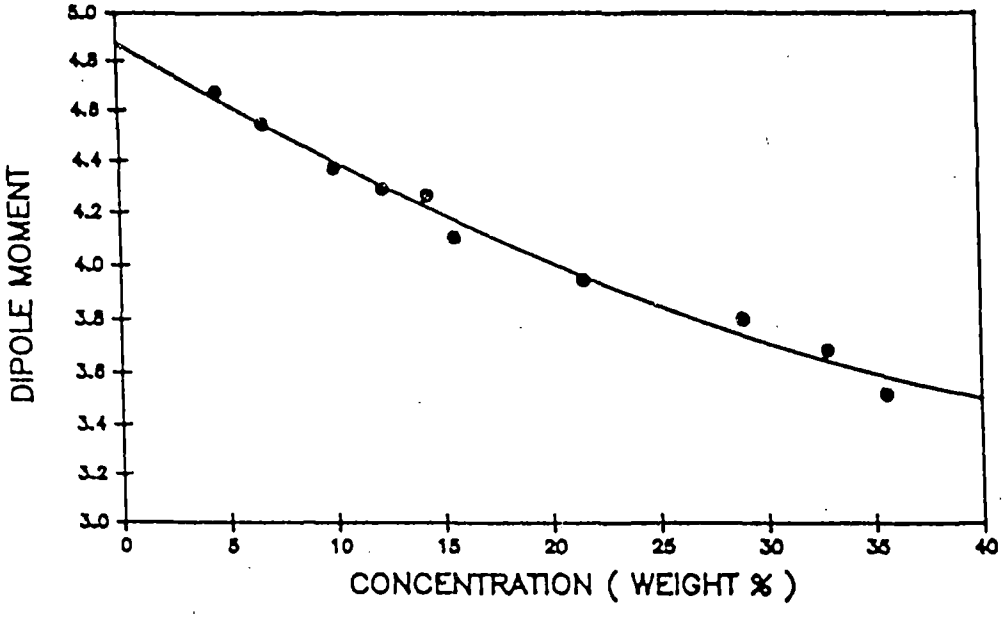

Figure 8.4 : The dipole moment of 5CB in p-xylene solution as a function of concentration.

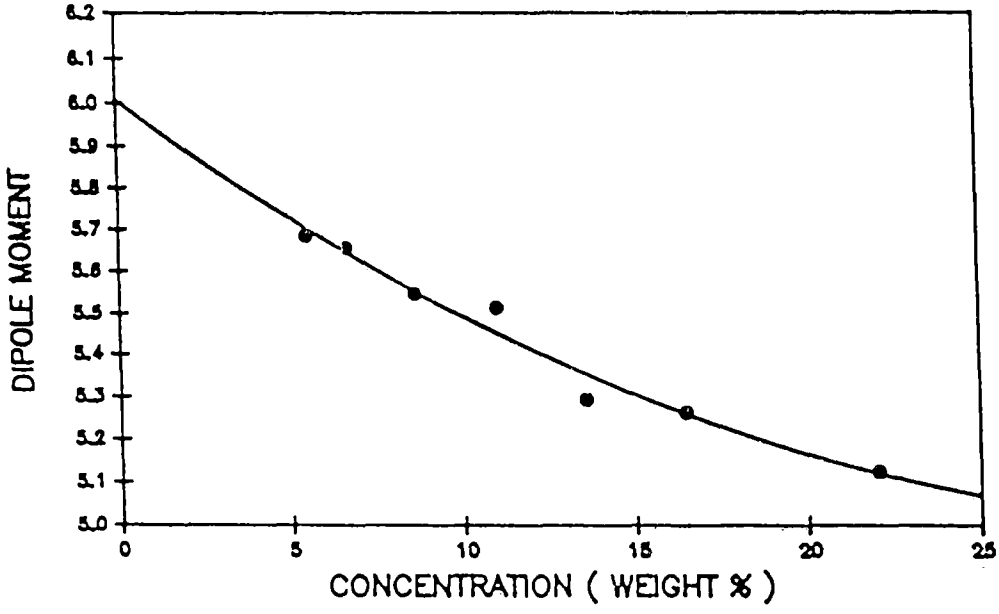

Figure 8.5 : The dipole moment of CPHB in p-xylene solution as a function of concentration.

Table - 8.2

The refractive index, dielectric constant and dipole moment of 1d(1)CC in p-xylene solution at different concentration.

concentration in percentage	refractive index (n)	dielectric constant(ε)	dipole moment (μ)
29.64	1.490	3.791	2.763
21.82	1.490	3.275	2.829
15.14	1.490	2.932	2.873
9.72	1.490	2.693	2.965
6.85	1.490	2.574	3.100
5.09	1.490	2.528	3.268
3.45	1.490	2.451	3.356

Table - 8.3

The refractive index, dielectric constant and dipole moment of 1d(3)CC in p-xylene solution at different concentration.

concentration in percentage	refractive index (n)	dielectric constant(ε)	dipole moment (μ)
17.73	1.489	3.186	3.265
14.40	1.489	2.999	3.293
12.10	1.489	2.871	3.309
9.38	1.490	2.772	3.475
7.97	1.490	2.693	3.493
5.88	1.490	2.585	3.550
4.51	1.490	2.516	3.602

Table - 8.4

The refractive index, dielectric constant and dipole moment of 3CPS in p-xylene solution at different concentration.

concentration in percentage	refractive index (n)	dielectric constant(ε)	dipole moment (μ)
29.82	1.514	3.933	2.948
20.58	1.509	3.252	2.997
17.52	1.505	3.153	3.148
14.30	1.502	3.004	3.247
10.56	1.499	2.806	3.295
7.91	1.496	2.677	3.367
5.51	1.494	2.598	3.685

Table - 8.5

The refractive index, dielectric constant and dipole moment of 5CB in p-xylene solution at different concentration.

concentration in percentage	refractive index (n)	dielectric constant(ε)	dipole moment (μ)
35.59	1.522	5.243	3.515
32.88	1.517	4.866	3.683
28.97	1.515	4.824	3.800
21.57	1.508	4.126	3.944
15.59	1.504	3.624	4.102
14.37	1.502	3.590	4.263
12.29	1.499	3.373	4.290
10.03	1.497	3.173	4.370
6.76	1.495	2.905	4.543
4.61	1.493	2.716	4.670

Table - 8.6

The refractive index, dielectric constant and dipole moment of 5CB in p-xylene solution at different concentration.

concentration in percentage	refractive index (n)	dielectric constant(ε)	dipole moment (μ)
22.05	1.501	4.691	5.125
16.46	1.497	4.046	5.264
13.57	1.495	3.649	5.294
11.01	1.494	3.490	5.515
8.63	1.493	3.213	5.548
6.66	1.492	3.004	5.655
5.50	1.492	2.875	5.683

parameters obtained for the mesogens, I have studied, are listed in Table 8.7.

Table - 8.7

Compounds	Mean Polarizability (α) (in $10^{-24} cm^3$)	Polarizability Anisotropy ($\Delta\alpha$) (in $10^{-24} cm^3$)	Dipole Moment (μ) (in Debye)
1d(1)CC	27.96	8.31	3.76
1d(3)CC	31.54	10.52	3.83
3CPS	29.12	13.64	4.21
5CB	29.78	21.88	4.87 4.76*
CPHB	36.26	23.74	6.00

* value obtained by Dunmur et al.

The molecular polarizability anisotropy ($\Delta\alpha$) strongly depends on the structural features of the molecules. The degree to which a given molecule displays anisotropy of polarizability is sensitively connected with structure, conformation, and also with electronic polarization of a given molecule[15,16]. We observe from the table 8.7 that as the calculated value of $\Delta\alpha$ for different compounds increases the dipole moment (μ) of the respective compound also increases.

The dipole moment of the compounds (1d(1)CC and 1d(3)CC) having bicyclohexane as core is less than the dipole moment of the compounds (5CB and CPHB) having two phenyl rings in the core. For the compound 3CPS we got a intermediate value of dipole moment which have phenyl and cyclohexane as core. The large value of dipole moment of CPHB may be due to different core structure . The anisotropy $\Delta\alpha$ mainly comes from the central core, the alkyl chain on the other hand contributes more to the mean polarizability than to

the anisotropy[17]. As can be seen, for the two homologous compounds 1d(1)CC and 1d(3)CC , increase in chain length does not change the dipole moment significantly.

Values of these calculated dipole moments and the direction of its major components, along with our experimental value are given in Table 8.8.

Table - 8.8

Name of molecular orbital theory	CPHB				1d(3)CC			
	x	y	z	μ	x	y	z	μ
Huckel	-3.94	0.25	5.34	6.64	1.50	-0.96	-0.10	1.78
Gust-Huck	-4.51	-0.24	6.60	7.99	2.90	-2.01	-0.32	3.54
Pullman	-4.11	-0.15	6.12	7.37	2.43	-1.57	-0.21	2.89
Experimental value				6.00				3.83

The experimental value of μ for CPHB agrees best with the calculation using Huckel's model, which considers π electrons only.

For 1d(3)CC the calculated value of Gust-Huck agrees with our experimental data. This method is a combination of charge computation by Gasteiger - Marsellis' method for σ electrons and Huckels method for π electrons. The experimental values for both the compounds do not agree with the calculated value from the model of Pullman which also considers both σ and π electrons, although both the compounds have contributions from π and σ electrons. Biphenyls have delocalised π electrons, double bonds have π electrons where as alkyl chain and bicyclohexanes have contributions from σ electrons. The experimental dipole moment was determined for a molecule in solution which may have different geometrical configuration from the one in the crystalline state. This may be a reason for discrepancy between the observed and calculated values.

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CHAPTER 9

Summary and conclusion.

In the present dissertation I have discussed the crystal structures of one polar and one non-polar liquid crystalline compounds. X-ray diffraction, optical birefringence study of some alkenyl liquid crystalline compounds and determination of dipole moments of polar liquid crystalline samples dissolved in non-polar p-xylene at different concentrations have also been undertaken by me.

In chapter 1, I have given a brief introduction to liquid crystals and in chapter 2 I have described in somewhat detail the theoretical background and experimental technique of crystal structure analysis.

The molecular arrangement in the crystalline state is one of the factors which sometimes predetermines the properties in the liquid crystalline state. Of the six compounds studied by me, single crystal structures for only two compounds such as PCBCH or 1d(3)CC and PEBCH or 1d(3)CCO2 could be determined. These structures are described in chapter 3 and chapter 4. For other compounds I could not grow good quality single crystal.

The crystal of the compound PCBCH belongs to the monoclinic system with space group $P2_1/n$ with four molecules in the unit cell. The structure has been solved by direct method program SIMPEL. Least squares refinement produced a R-value of .065 for 2326 observed reflections. The bond lengths and angles in the molecule are found to be comsistent with previous observations. Molecules related through the centre of symmetry are bound together by weak dipole induced dipole interaction between the chain part and polar cyano groups. The length of the pair is 30.03 Å . Apparent molecular length in the nematic phase shows the presence of this association. At C-N transition temperature these molecules gain sufficient energy to move within the layers and undergo rotation about axes other than the long molecular axis.

The second compound PEBCH crystallizes in non-centrosymmetric

orthorhombic space group $P2_12_12_1$ and four molecules in the unit cell. The structure was solved by direct method program GENTAN. Least squares refinement produced a R-value of .077 for 1855 observed reflections. The double bond length in the pentenyl chain differ from normal value to a large extent. Thermal parameters of the two carbon atoms of the double bond are also very large compared to other atoms. So there may be some conformational disorder in the molecular structure around the double bond. Parallel imbricated type of molecular arrangement is observed in the crystalline state as a precursor to the nematic phase. Molecular packing and phase structures have been compared with two related mesogenic compounds.

Chapter 5 deals with the theoretical back-ground and experimental technique of optical birefringence and x-ray diffraction study and dipole moment determination.

In chapter 6 and chapter 7 I have reported the x-ray diffraction and optical birefringence study of some alkenyl liquid crystalline compounds. The physical properties e.g. density, optical anisotropy and molecular parameters are strongly affected by the positional changes of the double bond. I have measured the refractive indices (n_o,n_e) of all the compounds, for three different wave-lengths and calculated the molecular polarizability values (α_o,α_e) at different temperatures. Optical birefringence Δn are found to be very low for all the alkenyl compounds. Polarizability anisotropy ($\Delta\alpha$) and molecular polarizability (α_o,α_e) are also calculated from bond additivity scheme and compared with our experimental values.

The compound 3CPOd(3)1 and 5CPOd(3)1, beyond the temperatures 45^oC and 52^oC respectively, birefringence could not be measured, because the ordinary rays (n_o) were not visible. The orientational order parameter $\langle P_2 \rangle$ at these temperatures drops to a very low value. It seems that there might be a phase transition at this temperature. Density versus temperature graphs also show a somewhat first order phase transition at this particular temperatures. But no

such transition could be observed in the texture and x-ray photographs.

X-ray diffraction photographs were analysed to obtain apparent molecular length (l) and average intermolecular distance (D) in the mesophase. The apparent molecular length (l) of the polar cyano compounds are found to increase in the mesophase, due to dipole - dipole or dipole - induced dipole interactions forming dimers. On the other hand, the molecular length (l) of the non-polar compounds are almost same in both solid and mesomorphic phases. Van der waal's type of interactions are responsible for the mesophase stability of these compounds.

The compound 1d(3)CC exhibits a monotropic smecticA phase with two colinear but incommensurate density modulation of periodicity 14.94 Å , which is almost same as the molecular length and the other periodicity is 24.01 Å which is between 1 and 2l. The existence of this type of smecticA phase could not be explained from the structural studies in the solid phase. Different kinds of intermolecular interactions are responsible for this phase formation.

Order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are calculated by analysing x-ray diffraction photographs. Temperature variation of order parameters calculated from x-ray and optical data have been compared with Maier-Saupe theoretical values. Sometimes the $\langle P_2 \rangle$ values determined experimentally are found to be higher than Maier-Saupe values. The orientational behaviour of the nematic phase may be distinguished in two parts : a long range order and a short range order. Whereas Maier-Saupe model reflects only long range ordering in the liquid crystalline phase, but a short range local ordering due to intermolecular interactions also exists. This short range interaction causes an increase in the orientational order parameter $\langle P_2 \rangle$.

$\langle P_2 \rangle$ values obtained from optical birefringence differ

considerably with $\langle P_2 \rangle$ values obtained from x-ray data. This anomaly may be due to the errors inherent in determining $\alpha_{\parallel}$ and $\alpha_{\perp}$ in the solid phase by extrapolation procedure and rules of bond additivity. Moreover order parameter values obtained from x-ray data involve different types of approximations and averaging than those obtained from refractive index data.

Molecular dipole moments of five polar liquid crystalline compounds have been determined by measuring the dielectric constants and refractive indices of solutions of the compounds in a non-polar solvent p-xylene. Dipole moment of an isolated molecule is evaluated by extrapolation to infinite dilution. Molecular parameters such as mean polarizability and polarizability anisotropy were also calculated from bond additivity rule. From the crystal structure data, atomic charge distributions for two of the five compounds were calculated by different empirical methods using molecular orbital theory. The calculated values of dipole moments were compared with our experimental data. This is described in detail in chapter 8.

LIST OF PUBLICATION

1. Study of mesomorphic properties of a number of alkenyl liquid crystalline compounds.

   A. Nath, B. Chaudhury and S. Paul, Mol. Cryst. Liq. Cryst., 265, page, 699 - 711, (1995).

2. Structure and properties of an alkenyl liquid crystalline compound.

   S. Gupta, A. Nath, S. Paul, H. Schenk and K. Goubitz, Mol. Cryst. Liq. Cryst., 1994. [In Press].

3. Structural analysis by x-ray diffraction of a non-polar alkenyl liquid crystalline compound.

   A. Nath, S. Gupta, P. Mandal, S. Paul and H. Schenk, Communicated to Liquid Crystals.

4. Determination of molecular properties of some polar mesogenic compounds.

   A. Nath, P. Mandal, B. Chaudhury and S. Paul, communicated to Mol. Cryst. Liq. Cryst.

The following papers have been presented at the National Solid State Physics Symposium and International Conferences.

1. Structure and properties of an alkenyl liquid crystalline compound.

   S. Gupta, A. Nath, S. Paul, Solid State Physics Sym., S.V.U., Tirupati (INDIA) Dec.28, 1992 - Jan.1, 1993.

2. Structure and properties of an alkenyl liquid crystalline compound.

   S. Gupta, A. Nath, S. Paul, presented at IUC$_r$ XVI, Beijing. 21 - 29 August, 1993.

3. Study of mesomorphic properties of an alkenyl cyano compound.

   A. Nath, S. Gupta, B. Chaudhury and S. Paul, Indian Liquid Crystal Conference, Mysore, 18 - 20 Oct. 1993.

4. Study of mesomorphic properties of a number of alkenyl liquid

crystalline compounds.

A. Nath, B. Chaudhury and S. Paul, 15th International Liquid Crystal Conference, 3 - 8 July. Budapest. 1994.

5. Optical studies of two mesogenic phenyl cyclohexane alkenyls.

S.Gupta, A. Nath and S. Paul, 15th ILCC, 3-8 July.1994, Budapest.

Appendix

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-6, 0, 1			5	23	23	1155	4	41	42	1097		-5, 9, 1				-5, 22, 1			8	99	99	734
4	20	19	1635	6	16	14	1482	5	25	25	1586	2	27	27	1510	1	20	29	1285	10	56	56	655
6	43	45	798		-6, 11, 1			6	34	35	1193	3	25	28	1611	3	12	10	2288		-4, 4, 1		
	-6, 1, 1			1	18	24	1618	7	23	20	1522	4	63	69	826	5	47	50	685	1	227	218	581
1	53	50	817	3	22	27	1415		-5, 3, 1			5	34	33	1219	6	38	42	691	2	187	194	599
2	13	13	2426		-6, 12, 1			1	43	42	1149	6	21	19	1632		-5, 23, 1			3	16	13	2389
3	28	25	1244	1	22	22	1303	3	15	3	2344	9	11	12	1828	1	18	18	1495	4	38	43	1153
4	25	25	1334	2	12	13	2393	4	33	35	1210		-5, 10, 1			4	11	14	2132	6	68	68	789
6	28	32	1048	3	74	81	632	5	35	34	1124	1	26	26	1349	5	10	11	2023	7	64	62	822
	-6, 2, 1			4	16	12	1723	6	33	38	1244	2	39	41	1131		-5, 24, 1			8	56	55	862
1	60	57	846	5	26	27	1069	7	22	22	1626	3	42	43	1050	2	20	22	1275	9	105	105	637
2	39	44	1023		-6, 13, 1			8	37	38	896	4	71	76	781	4	12	11	1787	10	44	45	732
3	14	13	2551	1	14	15	1746		-5, 4, 1			6	23	18	1435		-5, 25, 1				-4, 5, 1		
4	46	48	857	2	31	29	1046	2	60	64	897	8	19	17	1403	2	30	31	821	1	51	54	852
	-6, 3, 1			5	32	34	875	5	95	102	730		-5, 11, 1			3	13	13	1652	2	68	64	749
1	78	79	732	6	11	12	1779	6	14	15	2607	2	16	20	2166		-5, 26, 1			3	70	80	757
2	43	43	1011		-6, 14, 1			7	101	106	691	3	53	58	907	1	13	15	1665	4	93	95	697
3	29	31	1326	1	36	40	843	8	34	30	987	4	53	53	874	2	48	53	617	5	38	37	1113
4	28	31	1300	2	33	35	931		-5, 5, 1			5	37	35	1066	4	21	23	844	6	20	20	2048
5	34	35	938	3	42	41	813	1	32	35	1248	6	26	29	1225		-5, 27, 1			8	38	37	1160
7	14	20	1591	4	38	35	801	2	15	17	2343		-5, 12, 1			1	25	26	868	9	49	47	828
	-6, 4, 1			5	40	41	725	3	16	20	2541	3	23	25	1689	2	28	30	757	10	26	27	1036
1	57	50	816		-6, 15, 1			4	22	20	1840	4	21	20	1782	3	15	13	1150		-4, 6, 1		
3	13	10	2365	4	52	54	628	5	88	89	735	5	51	50	913		-4, 0, 1			1	29	33	1246
4	16	15	1960	5	13	13	1633	6	26	28	1560	6	23	19	1524	2	90	86	667	2	34	37	1204
5	18	24	1559		-6, 16, 1			7	83	82	707		-5, 13, 1			4	91	92	696	5	92	101	754
	-6, 5, 1			1	12	9	1827	9	61	66	579	5	41	40	917	8	43	38	1042	6	59	62	911
2	37	43	1041	4	14	15	1597		-5, 6, 1			7	12	8	2181		-4, 1, 1			7	49	52	980
3	24	24	1424	5	11	18	1885	1	19	21	1890	8	11	12	2114	1	30	39	1279	9	14	11	2162
5	12	13	2284		-6, 17, 1			2	31	34	1282		-5, 14, 1			2	33	22	1195		-4, 7, 1		
6	14	6	1826	2	11	10	2052	3	39	44	1142	3	14	13	2400	3	32	41	1157	1	38	35	1092
7	16	14	1329		-6, 18, 1			4	42	44	1064	7	11	9	2195	5	66	65	829	2	13	16	2523
	-6, 6, 1			3	10	8	2013	5	59	68	866		-5, 16, 1			6	61	61	872	3	89	90	704
1	20	21	1695	4	21	21	957	6	72	78	766	2	18	18	1815	7	71	68	809	4	51	61	971
2	31	34	1235		-6, 19, 1			7	68	69	754	4	29	23	1150	8	94	96	734	5	20	13	1977
3	20	23	1685	2	13	12	1468	8	54	57	734	6	12	4	2096	9	51	51	835	6	146	155	671
6	13	11	2039		-5, 0, 1			9	88	91	524	7	13	15	1828	10	18	16	1477	7	46	44	945
7	20	17	1149	1	125	126	710		-5, 7, 1				-5, 17, 1				-4, 2, 1			9	20	21	1522
	-6, 7, 1			3	150	145	682	2	28	36	1409	2	34	31	1130	1	109	100	641		-4, 8, 1		
3	16	13	1845	5	22	23	1775	3	20	23	2002	3	17	16	1952	3	96	88	656	1	37	38	1127
5	15	10	1808	7	21	17	1715	4	90	99	729	5	12	19	2307	4	25	24	1592	2	40	38	1054
6	37	35	814	9	11	11	2080	5	37	35	1143		-5, 18, 1			6	21	25	1684	3	39	45	1128
7	11	14	1864		-5, 1, 1			6	30	35	1295	1	18	14	1688	7	53	56	921	4	143	152	671
	-6, 8, 1			1	201	190	662	7	17	14	1925	4	20	14	1542	8	147	146	661	5	16	24	2430
1	13	15	2311	2	172	175	672	8	68	67	640		-5, 19, 1			9	19	16	1691	6	116	117	733
6	45	45	697	3	19	23	2152	9	48	48	648	4	19	14	1469	10	38	39	803	7	76	83	790
7	25	28	930	4	39	33	1148		-5, 8, 1			7	17	15	1241		-4, 3, 1			9	22	20	1361
	-6, 9, 1			5	43	45	1011	2	21	28	1920		-5, 20, 1			1	304	307	569		-4, 9, 1		
3	23	25	1328	6	31	30	1169	3	36	40	1233	5	16	17	1697	2	139	156	617	1	39	42	1085
5	18	19	1524	8	31	31	1003	5	13	5	2526	6	38	38	791	3	121	124	649	2	51	56	915
6	18	22	1413	9	23	22	1068	7	29	27	1226	7	59	64	497	4	66	66	789	3	16	18	2262
7	39	39	613		-5, 2, 1			8	28	25	1063		-5, 21, 1			5	47	46	1001	4	59	60	934
	-6, 10, 1			1	46	45	1167		-5, 9, 1			2	14	11	1954	6	31	36	1302	5	212	222	645
3	12	11	2249	3	38	39	1185	1	17	14	2047	5	32	37	934	7	42	43	1053	7	55	56	847

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-4, 9, 1			6	15	19	2199	3	39	38	966		-3, 3, 1				-3, 9, 1			10	47	48	698
8	18	23	1847	7	32	30	1102	5	35	40	935	8	109	114	692	1	253	227	496		-3, 15, 1		
9	14	15	2011		-4, 17, 1			6	54	53	674	9	28	30	1287	2	55	55	671	2	19	13	1724
10	13	14	1787	4	23	25	1512	7	40	35	612	10	18	16	1785	3	52	53	758	4	95	96	677
	-4, 10, 1			6	24	25	1470		-4, 26, 1			11	17	20	1456	4	19	16	1780	5	68	72	825
1	50	57	862	7	35	35	977	4	35	39	913		-3, 4, 1			5	73	77	726	6	87	92	769
3	84	91	734		-4, 18, 1				-4, 27, 1			1	146	147	467	6	66	68	829	7	124	125	705
4	30	30	1428	2	34	44	1166	2	23	19	1348	2	37	36	855	7	48	45	1019	8	63	66	797
5	132	143	673	3	46	55	975	3	35	30	895	3	87	94	549	9	30	31	1120	9	14	13	1946
6	13	2	2667	5	13	12	2525	6	20	20	1069	4	135	135	557	10	13	5	2164	10	49	49	650
7	15	12	2274	6	51	47	897		-4, 28, 1			5	84	88	660		-3, 10, 1				-3, 16, 1		
8	27	21	1222	7	15	15	1949	1	22	25	1268	7	33	29	1177	1	207	197	506	1	56	60	785
	-4, 11, 1			8	15	18	1731	4	23	22	1076	8	17	18	2109	2	34	31	960	2	31	30	1191
2	22	22	1631	9	11	7	1672		-4, 29, 1			9	13	6	2476	3	16	20	1910	3	66	73	776
3	48	54	956		-4, 19, 1			2	28	26	949	10	18	20	1756	5	182	194	612	4	24	32	1697
4	20	20	1997	1	28	27	1448		-4, 31, 1				-3, 5, 1			6	21	22	1853	6	29	29	1372
5	14	10	2488	2	27	32	1317	1	21	22	1090	1	29	29	994	7	107	110	710	7	133	130	677
8	23	22	1359	3	14	0	2532	3	31	27	728	2	232	221	473	8	32	28	1215	10	32	34	781
9	17	21	1691	5	14	13	2375		-3, 0, 1			3	118	116	528		-3, 11, 1				-3, 17, 1		
10	12	16	1656	6	42	41	958	1	103	114	482	4	62	64	688	1	53	46	782	1	35	31	1104
	-4, 12, 1			8	20	22	1160	3	14	9	1654	5	19	17	1665	2	94	109	612	2	48	50	886
1	21	19	1775		-4, 20, 1			5	97	101	622	6	73	71	707	3	20	13	1469	3	29	36	1382
2	32	30	1151	1	26	31	1523	7	189	193	639	7	21	18	1639	4	57	57	811	4	29	27	1332
3	40	41	1072	2	35	37	1140	9	255	255	641	9	18	19	1786	5	205	209	617	5	44	42	1000
5	22	26	1641	4	16	9	2078	11	13	9	1800	10	16	14	1857	6	181	184	664	6	49	51	916
6	26	30	1500	6	21	26	1450		-3, 1, 1			11	16	15	1418	7	70	66	828	7	24	28	1567
9	38	34	852	8	20	26	1184	1	39	44	762		-3, 6, 1			8	36	34	1071	8	13	14	2451
10	17	16	1107		-4, 21, 1			2	34	30	830	1	221	226	479	9	22	18	1476	9	78	83	638
	-4, 13, 1			1	51	48	934	3	31	21	843	2	369	366	472		-3, 12, 1				-3, 18, 1		
1	58	58	868	2	31	40	1260	4	19	21	1403	3	131	130	528	1	191	183	531	1	54	52	886
2	21	37	1782	7	23	25	1230	5	19	13	1575	4	88	90	598	2	22	38	1435	2	49	51	901
3	24	26	1653		-4, 22, 1			6	28	29	1365	5	63	68	733	4	116	126	636	3	29	22	1313
4	20	15	1814	1	67	69	762	7	55	58	932	8	30	29	1332	5	128	130	661	4	31	32	1275
5	22	20	1611	2	52	46	885	8	78	80	803	9	22	23	1592	6	253	257	636	5	68	65	782
6	14	3	2250	3	57	60	857	9	15	7	2749		-3, 7, 1			7	27	30	1503	6	22	3	1601
9	31	35	969	4	15	10	1997	10	17	16	1876	1	391	392	2370	9	32	36	1059	9	25	22	1163
	-4, 14, 1			6	13	7	2262		-3, 2, 1			2	190	196	499	10	26	27	1088	10	35	37	646
2	28	23	1392	7	15	14	1675	1	64	64	567	3	51	42	728		-3, 13, 1				-3, 19, 1		
6	26	23	1291	8	17	14	1150	2	77	79	554	4	51	50	744	1	18	6	1760	1	103	111	679
7	18	11	1709		-4, 23, 1			4	72	66	609	5	30	31	1212	2	73	73	676	2	89	100	748
8	17	22	1655	1	62	62	792	5	44	41	844	7	17	18	2067	3	75	69	701	3	142	139	663
	-4, 15, 1			3	94	93	707	6	58	56	802	8	49	48	902	4	223	232	596	4	25	21	1586
1	18	17	2154	4	22	18	1464	7	79	82	766	9	17	16	2036	5	17	16	2428	8	37	39	935
4	28	24	1289	6	20	18	1520	8	132	132	674	11	24	29	973	6	56	63	942	9	15	13	1634
5	34	26	1173	7	19	12	1289	9	50	47	891		-3, 8, 1			8	42	42	978		-3, 20, 1		
6	20	20	1707		-4, 24, 1			10	62	60	763	1	186	198	495	9	29	28	1154	1	59	55	868
8	14	12	2180	1	34	37	1130		-3, 3, 1			2	19	25	1579	10	16	14	1503	2	184	197	651
9	16	14	1394	2	26	20	1352	1	61	72	608	3	16	18	1806		-3, 14, 1			3	106	122	698
	-4, 16, 1			3	71	80	732	2	59	67	610	4	42	45	864	1	30	21	1112	4	101	108	703
1	23	21	1521	5	26	27	1168	3	26	36	1126	5	39	35	1028	3	24	19	1499	5	33	29	1204
2	38	34	1051	6	60	58	654	4	25	23	1176	7	33	29	1082	4	98	109	681	7	18	17	1900
3	28	25	1280	7	18	18	1356	5	65	67	731	8	22	24	1582	5	137	141	648	8	12	13	2149
4	16	7	2181		-4, 25, 1			6	27	21	1305	9	55	57	832	6	29	25	1361		-3, 21, 1		
5	27	26	1477	2	35	44	1024	7	34	36	1157	11	26	28	905	8	15	10	2359	1	30	34	1289

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-3, 21, 1			4	14	9	1810	8	113	121	705		-2, 10, 1			10	15	14	1733	4	59	57	852
2	82	75	749	5	43	38	664	9	47	48	917	2	486	477	2116		-2, 15, 1			5	63	63	839
3	88	91	758	6	37	29	611	10	22	21	1514	3	81	87	516	2	318	328	492	6	62	56	861
4	51	50	972		-3, 32, 1				-2, 5, 1			4	52	49	671	3	69	73	657	8	14	15	2022
5	24	27	1665	1	13	12	1983	2	136	139	390	5	100	94	605	4	90	94	642	9	19	15	1546
8	15	13	1825	5	13	12	1488	3	195	186	413	6	38	39	979	5	242	245	600	10	63	65	544
	-3, 22, 1				-3, 33, 1			4	45	29	654	7	39	38	1088	6	45	43	1025		-2, 21, 1		
1	76	77	757	1	27	25	923	5	35	32	883	8	34	33	1184	7	136	134	689	1	18	14	1874
2	120	134	701		-3, 34, 1			6	13	9	2340	9	43	42	960	8	66	66	846	2	89	89	701
3	81	88	767	1	12	9	1898	7	32	37	1260	10	22	22	1420	9	16	14	2033	3	42	46	981
4	127	130	666		-3, 35, 1			8	17	19	2071	11	25	28	1002		-2, 16, 1			4	77	73	783
	-3, 23, 1			2	14	11	1257	9	73	75	772		-2, 11, 1			1	113	113	555	5	62	65	856
1	51	58	953		-2, 0, 1			11	15	13	1551	1	115	106	466	2	165	161	540	6	107	102	699
2	72	78	804	2	29	7	656		-2, 6, 1			2	134	128	457	3	110	113	584	8	59	58	745
4	18	16	2218	4	85	81	474	1	249	229	367	3	87	88	533	4	167	159	597	9	12	15	2263
5	26	23	1415	6	60	59	706	2	173	158	388	4	104	109	540	5	236	237	604		-2, 22, 1		
6	13	7	2383	8	20	33	1785	3	52	67	561	5	73	76	676	6	86	83	750	2	64	69	823
	-3, 24, 1				-2, 1, 1			4	60	49	584	6	139	142	637	7	35	37	1157	3	44	46	958
2	16	14	2254	2	133	114	373	5	21	20	1365	7	140	132	677	8	59	61	844	6	22	11	1589
3	30	17	1341	3	38	39	586	6	32	39	1078	9	23	27	1586	9	24	27	1425	9	50	50	681
4	41	41	1043	4	33	31	771	7	90	95	715	10	18	14	1532	10	13	15	1936		-2, 23, 1		
6	17	15	1905	5	13	14	1771	8	22	25	1606	11	22	23	1058		-2, 17, 1			1	102	105	696
8	13	12	1782	6	45	50	786	9	50	54	945		-2, 12, 1			1	250	250	522	2	18	27	1913
	-3, 25, 1			7	13	13	2382	10	23	25	1408	1	48	35	635	2	62	53	716	3	70	72	808
2	15	16	2277	9	41	39	1068		-2, 7, 1			2	65	68	567	3	221	225	550	4	44	44	1017
4	30	31	1213	10	27	23	1353	1	16	6	1319	3	48	56	703	4	181	183	594	5	32	26	1268
5	35	29	1085		-2, 2, 1			2	51	32	554	4	12	11	2279	5	33	37	1226	9	29	31	878
7	13	12	2059	1	38	41	569	3	123	110	444	5	24	18	1455	6	39	32	1116		-2, 24, 1		
	-3, 26, 1			2	13	9	1368	4	142	145	474	6	56	57	921	7	53	54	913	1	60	61	863
3	21	20	1595	3	82	65	446	5	95	89	553	7	139	143	693	8	27	24	1368	2	52	57	918
8	16	17	1197	4	35	33	737	6	70	73	704	8	95	96	746	9	58	57	729	3	99	106	715
	-3, 27, 1			5	36	32	814	7	33	35	1240	9	30	25	1169		-2, 18, 1			4	26	25	1353
1	17	18	1945	6	12	6	2399	8	50	53	890	10	16	13	1894	1	27	32	1184	5	29	27	1381
2	18	21	1830	7	44	47	892	10	29	29	1195	11	15	12	1421	2	22	21	1371	8	16	17	1813
3	19	26	1636	8	53	54	918		-2, 8, 1				-2, 13, 1			3	237	253	571	9	46	41	608
7	23	22	1074	9	66	71	801	1	588	555	1928	1	195	191	456	4	42	39	1025		-2, 25, 1		
	-3, 28, 1			10	61	60	780	2	61	68	518	2	30	29	913	5	45	48	1036	1	56	55	870
4	16	12	1666		-2, 3, 1			3	14	30	1529	3	68	72	602	6	15	18	2293	2	62	57	860
5	18	16	1632	1	27	33	772	4	73	68	543	4	58	59	694	7	43	45	1033	3	132	136	677
6	13	14	1901	2	149	146	375	5	28	28	1057	6	352	356	598	9	51	48	773	5	15	13	2207
7	34	30	734	4	92	86	472	6	58	62	802	7	59	55	903	10	19	22	1284	8	18	16	1448
	-3, 29, 1			5	43	38	746	7	43	41	964	8	174	168	657		-2, 19, 1			9	24	18	855
1	15	20	1945	6	27	25	1229	11	52	53	654	9	42	45	915	1	29	25	1194		-2, 26, 1		
2	21	20	1544	7	40	45	982		-2, 9, 1			10	19	17	1490	2	69	71	717	1	108	106	701
3	15	10	2042	8	111	118	675	1	434	399	1998	11	33	35	721	3	166	170	607	2	54	62	914
4	24	27	1265	10	48	50	916	2	346	333	2069		-2, 14, 1			4	78	77	727	3	69	67	843
5	18	13	1473		-2, 4, 1			3	299	290	435	1	42	48	719	5	136	132	665	4	54	55	883
6	42	39	709	1	191	178	357	4	67	63	577	2	12	14	2245	7	49	49	874	5	20	18	1653
	-3, 30, 1			2	15	18	1274	5	127	133	560	3	94	86	583	9	53	55	741	6	25	23	1306
2	17	12	1779	3	25	20	802	6	17	14	1926	4	147	155	571	10	52	50	614		-2, 27, 1		
3	12	13	2278	4	99	107	470	9	36	37	1042	5	253	250	583		-2, 20, 1			1	30	30	1344
4	36	30	920	5	21	24	1173	11	11	5	1989	6	141	140	675	1	25	24	1298	2	71	80	816
6	27	26	906	6	36	32	924		-2, 10, 1			7	101	92	747	2	54	59	823	3	44	40	1000
	-3, 31, 1			7	22	24	1622	1	336	307	2082	8	67	66	846	3	55	62	853	4	20	12	1694

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-2, 27, 1			2	172	183	292	4	134	121	428		-1, 12, 1			3	68	63	649	6	58	49	877
5	43	35	898	3	163	149	340	6	133	139	575	11	17	14	1330	4	138	132	589	7	22	23	1503
	-2, 28, 1			4	239	218	385	7	89	87	694		-1, 13, 1			5	102	101	698	8	13	9	1944
1	29	24	1230	5	104	82	478	9	28	30	1254	1	413	391	1975	6	193	192	652	9	37	38	733
2	18	21	1967	6	74	60	597	10	28	33	1186	2	222	233	417	7	42	38	1058		-1, 25, 1		
3	16	15	2128	8	14	7	2495		-1, 8, 1			3	442	437	2209	10	22	18	1156	1	49	47	859
5	54	46	815	11	13	8	1980	2	78	55	409	4	94	96	569		-1, 19, 1			2	41	40	1043
6	27	21	1114		-1, 3, 1			3	78	81	441	6	19	27	1770	1	86	84	576	4	52	58	861
7	33	26	897	1	921	1028	1275	4	167	164	432	9	19	24	1924	4	135	139	603	5	20	24	1732
	-2, 29, 1			2	100	101	324	5	142	153	495	10	24	19	1253	5	80	74	719	6	37	24	995
1	30	31	1302	3	198	191	338	6	197	192	547		-1, 14, 1			6	72	73	796	7	21	18	1476
2	15	17	2233	4	413	402	1937	7	27	14	1431	1	263	259	418	7	43	34	1024	8	17	25	1711
3	14	12	1994	5	52	31	617	8	162	168	654	2	367	384	2157	8	16	10	1965		-1, 26, 1		
6	28	21	1067	6	97	85	580	9	14	12	2573	3	216	223	470	9	71	71	693	1	45	46	959
7	36	27	761	7	41	37	907		-1, 9, 1			4	283	278	501	10	63	60	602	2	74	76	768
	-2, 30, 1			8	33	30	1189	1	115	121	352	5	110	103	607		-1, 20, 1			3	28	29	1407
1	13	13	2493	11	47	50	778	2	267	266	355	6	50	49	857	1	19	25	1469	4	74	73	780
3	14	18	2165		-1, 4, 1			3	78	84	445	7	23	14	1687	2	102	97	580	5	14	17	2502
5	16	12	1726	1	986	1177	1325	4	35	43	736	8	40	46	1001	3	43	45	900	8	35	32	851
	-2, 31, 1			2	234	231	1487	5	162	155	501	9	26	25	1365	4	20	26	1774		-1, 27, 1		
1	15	13	2021	3	79	82	389	6	61	67	716	10	39	36	888	5	82	81	721	1	23	24	1562
	-2, 32, 1			4	18	14	1069	7	222	218	614	11	22	25	956	6	28	23	1456	2	82	84	758
1	21	20	1517	5	91	80	509	8	110	100	728		-1, 15, 1			8	25	29	1356	3	51	50	966
2	14	21	2184	6	53	53	679	10	17	24	1813	1	77	82	499	9	32	28	1085	4	87	85	755
3	15	12	1681	7	23	33	1456	11	14	16	1787	2	258	252	445	10	59	58	596	5	17	13	1976
4	13	6	1948	8	51	43	852		-1, 10, 1			3	60	57	642		-1, 21, 1			8	15	8	1433
	-2, 33, 1			10	44	42	962	1	38	42	552	4	291	290	515	1	47	44	781		-1, 28, 1		
1	17	19	1711	11	44	44	770	2	175	166	380	7	96	96	734	2	33	32	1060	1	16	21	2258
2	27	27	1139		-1, 5, 1			3	31	20	713	8	48	42	922	3	64	69	756	2	133	135	702
3	13	8	1983	1	530	533	1372	4	197	208	450	9	33	31	1150	4	30	38	1200	4	70	67	790
	-2, 34, 1			2	28	31	649	5	101	98	560	11	19	17	1048	5	64	62	812		-1, 29, 1		
1	18	20	1412	3	71	63	410	7	300	308	612		-1, 16, 1			6	38	43	1053	1	86	88	725
	-2, 36, 1			4	219	216	401	8	93	92	716	1	135	145	466	9	21	21	1400	2	99	100	712
2	13	12	1531	5	36	21	735	9	102	97	709	2	44	43	725		-1, 22, 1			3	49	48	962
	-1, 0, 1			6	34	33	900		-1, 11, 1			3	149	148	520	2	26	31	1309	5	25	19	1325
1	71	56	295	7	55	47	823	1	139	122	381	4	157	148	544	3	50	42	875		-1, 30, 1		
3	558	550	1630	8	38	42	1031	2	409	413	1909	5	111	120	625	4	71	72	764	1	86	94	755
5	414	390	2211	9	22	20	1633	3	155	150	434	6	89	89	748	6	20	18	1818	2	45	42	958
7	41	41	890	10	21	20	1607	4	155	143	478	7	80	84	775	7	35	32	1065	3	103	107	679
9	15	12	2295	11	27	29	1128	5	37	23	866	8	22	22	1586	8	24	21	1288	4	24	21	1272
11	15	13	1811		-1, 6, 1			6	29	24	1239	9	30	30	1103	9	32	31	968	5	19	15	1593
	-1, 1, 1			1	484	496	1436	7	139	137	657		-1, 17, 1				-1, 23, 1			6	15	10	178
1	88	80	280	2	107	114	343	8	31	26	1287	1	108	106	511	1	41	37	923	7	17	13	1383
2	365	349	1393	3	21	13	907	9	101	98	705	2	45	49	719	3	17	14	1968		-1, 31, 1		
3	276	261	1657	4	144	150	422	11	19	17	1245	4	50	60	796	4	36	29	1095	1	39	34	97
4	337	313	1919	5	84	81	521		-1, 12, 1			5	175	175	610	6	38	39	1049	3	16	20	221
5	182	167	455	6	50	52	747	2	206	173	406	6	210	211	628	7	45	45	955	5	15	10	178
6	137	115	531	7	98	92	662	3	211	191	440	7	49	49	909	9	62	62	608	7	13	9	159
7	21	24	1556	8	27	36	1432	4	29	33	975	8	18	19	1864		-1, 24, 1				-1, 32, 1		
8	34	34	1145	9	43	46	1021	5	62	62	691	9	33	33	1041	1	73	75	714	2	45	50	84
9	20	20	1739		-1, 7, 1			6	112	107	626	10	33	30	904	2	30	28	1241	3	17	16	186
10	19	15	1590	1	353	363	1508	8	25	24	1596		-1, 18, 1			3	23	22	1496	4	22	18	129
	-1, 2, 1			2	295	288	1645	9	36	32	1145	1	13	20	1854	4	59	50	819		-1, 33, 1		
1	556	573	1226	3	93	91	397	10	28	29	1119	2	15	10	1705	5	59	59	834	1	17	15	179

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-1, 33, 1			11	26	28	1143	5	182	175	484		0, 14, 1			6	85	90	780	0	142	148	653
3	13	13	2210		0, 4, 1			6	94	85	625	0	82	84	426	7	83	80	741	1	63	72	817
6	13	9	1487	0	86	87	219	7	17	5	2057	1	76	83	451	8	24	25	1302	2	136	142	668
	-1, 34, 1			1	129	132	235	8	197	185	650	2	93	90	455	10	15	15	1541	4	21	17	1706
2	22	24	1442	2	266	278	1376	9	26	26	1503	3	47	41	640		0, 20, 1			6	20	19	1563
5	14	12	1495	3	700	728	1641	10	28	25	1218	4	54	50	675	0	25	27	1064	7	16	14	1751
	-1, 35, 1			4	377	369	1944	11	14	15	1673	5	29	28	1169	1	17	16	1591		0, 27, 1		
1	18	16	1455	5	461	442	2250		0, 9, 1			6	13	20	2388	2	14	14	2007	1	97	100	725
2	12	10	2002	6	196	183	537	1	195	209	312	7	39	41	1115	3	28	32	1229	2	64	68	830
4	18	17	1291	7	80	83	709	2	667	720	1679	9	27	27	1263	4	40	41	974	3	58	58	845
	-1, 36, 1			8	100	93	741	3	206	201	385	10	18	22	1654	5	90	91	705	4	17	15	2036
1	13	14	1870	9	16	14	2242	4	185	173	444		0, 15, 1			6	57	61	856	5	46	45	914
2	24	23	1064	11	19	18	1404	5	33	36	900	1	69	71	491	7	75	81	815	6	43	44	934
	-1, 37, 1				0, 5, 1			6	34	27	1001	2	98	103	465	8	13	17	2389	8	23	23	979
2	13	14	1777	1	153	161	244	8	32	27	1378	5	32	31	1089	9	16	12	1746		0, 28, 1		
	-1, 38, 1			2	99	95	317	11	11	7	1990	6	22	14	1637	10	17	17	1259	0	78	83	738
1	19	14	1118	3	380	394	1684		0, 10, 1			7	17	9	1840		0, 21, 1			1	48	52	927
2	10	7	1851	4	291	280	391	0	285	307	1585	9	17	12	1908	1	23	21	1278	2	73	80	791
	0, 0, 1			5	327	306	455	1	75	70	386		0, 16, 1			4	40	41	1007	5	39	40	1004
2	926	1105	1258	6	247	228	532	2	369	363	1766	0	53	46	560	5	142	162	671	8	16	14	1256
4	96	97	408	7	262	251	580	3	253	252	390	1	33	26	714	7	58	66	802		0, 29, 1		
6	32	34	916	8	101	98	733	4	349	329	2204	2	19	15	1136	8	31	29	1142	1	52	52	864
8	97	99	710	9	41	34	1066	5	19	21	1490	3	16	18	1520		0, 22, 1			3	118	119	699
10	84	89	712	11	14	12	1889	6	15	7	2128	4	74	63	630	1	18	16	1517	4	29	30	1285
	0, 1, 1				0, 6, 1			7	45	45	912	5	33	17	1113	2	22	27	1458		0, 30, 1		
1	96	87	196	0	22	2	597	8	22	17	1656	6	43	41	967	3	20	23	1738	0	25	27	1410
2	776	862	1259	1	390	415	1275	9	16	20	2081	7	18	15	2018	5	74	66	777	1	65	66	809
3	474	480	1571	2	12	18	1324	11	22	25	1125	9	19	21	1643	6	43	40	1043	2	41	41	1067
4	112	103	406	3	214	210	352		0, 11, 1			10	52	50	688	8	20	17	1485	3	88	86	715
5	124	118	465	4	446	421	2004	1	53	43	456		0, 17, 1			9	16	15	1575	5	44	41	852
6	25	11	1148	5	134	115	489	2	23	31	887	1	19	26	1238		0, 23, 1				0, 31, 1		
7	68	63	710	6	244	258	538	3	361	354	2029	2	26	27	995	1	29	27	1124	1	30	30	1264
8	35	25	1109	7	132	135	641	4	251	233	457	4	26	12	1150	2	26	30	1313	3	54	56	873
	0, 2, 1			8	160	146	659	5	47	48	744	5	45	44	924	4	23	20	1479	4	24	23	1375
0	199	198	683	9	70	60	813	6	25	20	1312	8	14	12	2160	6	55	64	872		0, 32, 1		
1	484	515	944	10	17	13	1955	7	24	25	1566	9	22	23	1405	9	22	20	1189	0	47	49	957
2	546	567	1276	11	26	29	1075	11	37	39	723	10	36	35	839		0, 24, 1			1	23	26	1614
3	426	417	1585		0, 7, 1				0, 12, 1				0, 18, 1			0	89	82	693	2	40	40	990
4	55	40	511	1	14	9	1011	0	240	244	350	0	19	33	1211	1	38	39	1037	3	54	54	814
5	78	67	518	2	238	244	1561	1	224	242	360	1	73	67	558	2	16	21	2007	4	47	42	838
6	39	21	912	3	256	260	1795	2	57	43	479	2	19	11	1320	3	19	21	1793	5	12	13	2200
7	23	24	1433	4	254	233	409	3	329	326	2101	3	23	36	1328	4	29	29	1349		0, 33, 1		
8	32	28	1207	5	73	73	581	4	82	79	545	4	30	24	1149	5	55	59	893	1	39	39	972
9	27	21	1313	6	155	157	558	5	118	108	543	5	14	8	2529	9	20	23	1088	2	86	81	671
11	83	80	600	7	53	53	886	6	18	11	1676	6	57	56	843		0, 25, 1			4	26	24	1101
	0, 3, 1			8	209	205	654	10	12	5	2253	7	19	23	1864	1	52	61	867		0, 34, 1		
1	296	319	1021	9	33	33	1180		0, 13, 1			9	15	7	1864	2	82	81	718	0	17	18	1816
2	238	235	1338	11	31	28	929	1	123	119	401	10	21	15	1233	3	45	50	960	1	17	20	1781
3	407	414	1612		0, 8, 1			2	12	5	1500		0, 19, 1			4	31	27	1154	2	20	20	1486
4	443	429	1908	0	115	122	298	3	231	221	434	1	13	7	1936	5	28	29	1425	3	39	41	924
5	193	180	459	1	93	104	332	4	118	103	511	2	35	46	848	6	20	20	1670	5	16	12	1422
6	291	282	511	2	143	148	343	5	45	32	784	3	34	32	969	7	14	9	2276		0, 35, 1		
8	27	26	1445	3	77	79	419	7	39	41	1095	4	36	25	1033	9	20	19	1011	1	26	26	1187
10	22	19	1488	4	102	98	452	10	18	19	1600	5	24	19	1539		0, 26, 1			2	13	5	2044

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig
	0, 35, 1		
3	18	15	1559
4	28	25	994
5	13	13	1515
	0, 36, 1		
1	12	10	2080
3	13	9	1829
4	38	34	758
	0, 37, 1		
3	28	28	874
	0, 38, 1		
1	11	11	1875
	1, 0, 1		
1	9	7	1655
3	84	74	397
5	187	197	482
7	253	282	601
9	14	8	2081
11	12	10	1969
	1, 1, 1		
0	238	219	1171
1	550	565	1292
2	203	201	309
3	87	79	403
4	229	234	412
5	119	127	500
6	49	52	814
7	108	122	703
8	29	30	1384
9	35	38	1084
10	20	22	1456
11	18	18	1303
	1, 2, 1		
0	430	414	1182
1	1017	1099	1325
2	33	33	566
3	222	202	359
4	229	243	415
5	100	100	519
6	78	77	636
7	33	33	1229
8	66	66	806
9	35	45	1083
10	16	16	1895
11	51	57	639
	1, 3, 1		
0	254	248	1239
2	81	85	361
3	130	111	382
4	224	230	422
5	12	2	1949
6	92	92	618
7	147	161	634
8	127	141	702
9	32	40	1203
10	18	16	1592
11	34	39	773
	1, 4, 1		
0	788	822	1282
1	601	595	1389
2	142	135	336
3	193	191	371
4	83	71	470
5	93	106	546
6	22	14	1378
7	127	130	672
8	75	81	768
9	51	61	912
10	21	27	1549
11	15	20	1463
	1, 5, 1		
0	575	582	1338
1	384	372	1443
2	148	153	339
4	74	77	513
5	43	39	763
6	72	72	664
7	108	113	681
9	75	77	777
10	30	32	1067
	1, 6, 1		
0	121	129	308
1	130	122	319
2	102	94	369
3	264	250	381
4	92	76	497
5	157	149	514
6	84	82	663
7	29	38	1288
9	34	37	1100
11	25	27	963
	1, 7, 1		
0	111	93	327
1	193	174	315
2	49	67	480
3	412	381	1953
4	359	354	2222
5	83	88	586
6	238	243	567
7	31	24	1224
10	22	22	1395
11	10	9	1955
	1, 8, 1		
0	317	310	1556
1	155	150	333
2	119	112	384
3	85	67	475
4	382	395	2263
5	265	256	511
6	87	85	665
7	18	12	1912
9	29	32	1240
10	15	18	1797
	1, 9, 1		
0	256	244	1649
1	114	95	362
2	352	324	1858
3	198	180	414
4	338	312	461
5	190	193	529
7	39	38	995
8	22	26	1595
9	35	39	1126
	1, 10, 1		
0	66	54	432
1	123	120	377
2	109	116	420
3	206	192	430
4	157	145	485
5	48	45	786
6	24	22	1403
7	53	53	901
10	15	15	1786
	1, 11, 1		
0	93	90	398
1	74	73	430
2	99	80	423
3	23	17	1045
4	86	84	559
5	62	68	687
7	21	13	1672
8	39	40	1010
9	34	34	1010
	1, 12, 1		
0	278	249	374
1	143	136	398
3	98	108	495
4	18	12	1581
5	25	29	1220
6	32	31	1127
8	21	20	1671
9	36	45	1021
10	12	11	2072
	1, 13, 1		
0	127	122	419
1	61	70	488
2	37	32	682
3	57	57	610
4	39	43	835
5	54	60	780
6	37	35	1115
7	15	17	2384
	1, 13, 1		
8	16	16	2143
10	23	21	1130
	1, 14, 1		
0	17	12	1143
1	45	32	583
2	53	72	594
3	54	53	631
4	68	66	639
5	55	56	796
8	32	32	1205
	1, 15, 1		
0	108	99	448
1	55	51	563
2	67	68	544
3	24	13	1169
4	32	39	1011
5	35	30	1077
6	19	19	1761
9	17	14	1711
	1, 16, 1		
0	21	29	1109
1	115	125	477
2	17	16	1570
3	62	70	673
4	44	43	850
5	15	15	2117
	1, 17, 1		
0	20	21	1238
1	13	13	1836
2	169	165	513
4	20	18	1432
6	23	23	1520
7	21	24	1680
	1, 18, 1		
0	151	156	497
1	27	20	1046
2	60	54	655
3	26	22	1146
4	27	36	1252
6	60	76	813
7	14	16	2106
	1, 19, 1		
0	91	88	572
1	67	59	629
2	50	48	765
3	30	31	1161
4	38	42	1043
5	22	25	1594
6	67	82	803
8	23	30	1404
	1, 20, 1		
0	38	38	892
3	22	34	1547
4	33	32	1122
5	39	42	1000
6	38	43	1052
7	43	50	962
	1, 21, 1		
0	25	20	1199
1	48	42	857
2	96	94	642
4	28	31	1377
6	29	32	1231
8	22	27	1267
	1, 22, 1		
1	142	140	591
2	100	103	650
3	51	51	888
4	14	14	2454
5	17	20	2080
6	31	35	1239
7	31	39	1086
8	12	15	2163
	1, 23, 1		
0	65	67	760
1	182	183	613
3	86	87	737
5	27	31	1302
6	60	71	836
8	12	15	1916
9	18	22	1086
	1, 24, 1		
0	74	74	756
1	165	167	638
2	120	119	662
3	109	110	717
4	24	25	1482
5	25	32	1417
6	44	51	911
	1, 25, 1		
0	30	29	1249
1	66	65	829
2	141	145	672
3	100	105	712
4	56	59	870
5	43	45	987
6	21	24	1453
7	14	21	1999
	1, 26, 1		
0	50	48	940
1	18	14	1966
2	80	83	774
3	24	22	1482
4	14	14	2590
5	39	44	953
	1, 27, 1		
0	40	37	1005
2	28	31	1296
3	18	19	1987
4	20	20	1674
6	28	35	1174
8	15	17	1249
	1, 28, 1		
0	14	8	2281
1	49	50	909
2	32	27	1240
5	26	26	1286
6	16	14	1645
	1, 29, 1		
0	47	48	952
1	40	39	990
4	20	19	1564
7	15	22	1413
	1, 30, 1		
1	30	26	1285
4	31	36	1172
6	15	18	1560
7	12	11	1517
	1, 31, 1		
1	53	56	852
2	40	44	997
4	31	36	1054
	1, 32, 1		
1	14	14	2233
2	23	24	1314
4	37	44	955
	1, 33, 1		
0	14	16	2050
2	55	56	740
3	28	28	1208
4	64	70	643
5	24	25	1087
	1, 34, 1		
0	15	14	1746
2	37	39	913
3	37	38	945
4	19	15	1381
5	44	43	638
	1, 35, 1		
2	25	31	1143
3	48	49	714
4	40	42	709
	1, 36, 1		
1	29	31	998
3	34	36	767
4	14	18	1386
	1, 37, 1		
1	29	28	915
2	12	17	1731
	1, 38, 1		
2	17	21	1088

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig
	2, 0, 1		
0	192	193	345
2	147	143	403
4	66	75	603
6	111	115	639
8	57	64	913
	2, 1, 1		
0	47	44	485
1	51	40	493
2	89	94	433
3	33	31	789
4	50	49	688
5	16	9	1802
6	36	40	1089
7	111	115	712
8	94	104	742
9	46	52	867
	2, 2, 1		
0	145	119	355
1	10	12	1630
2	91	89	427
3	125	140	451
5	39	45	934
7	48	47	922
	2, 3, 1		
0	35	21	600
1	60	51	459
2	129	130	419
3	102	103	472
4	43	46	694
5	45	47	821
6	90	97	702
8	72	83	790
	2, 4, 1		
0	328	300	1770
1	122	107	384
2	162	137	409
4	29	21	951
5	18	11	1722
6	56	65	855
7	51	54	869
8	20	18	1736
10	15	17	1560
	2, 5, 1		
0	549	511	1793
1	138	121	387
2	245	231	409
3	50	40	600
4	22	33	1155
5	18	16	1734
7	16	24	2251
8	13	6	2242
	2, 6, 1		
0	571	542	1831

l	kFo	Fc	Sig
1	50	49	537
2	273	266	416
3	91	105	518
5	59	64	765
6	47	50	954
7	28	36	1264
8	18	27	1899
9	14	11	2027
10	13	14	1832
	2, 7, 1		
0	469	445	1878
1	352	329	1979
2	76	75	505
3	70	69	557
4	47	53	758
5	60	62	760
6	34	33	1100
7	14	11	2227
8	33	35	1141
10	19	22	1257
	2, 8, 1		
0	24	31	1023
1	108	104	446
2	93	91	481
3	150	147	486
4	29	27	1047
5	60	61	789
8	13	13	2592
	2, 9, 1		
0	75	86	485
1	135	131	437
2	81	74	520
4	21	26	1451
5	94	93	671
7	41	45	970
9	18	16	1617
10	14	14	1507
	2, 10, 1		
0	465	445	2052
1	97	74	472
2	18	11	1273
3	45	36	731
4	41	46	863
5	227	231	600
6	26	17	1490
7	62	65	864
8	17	19	1959
	2, 11, 1		
0	400	384	2122
1	35	38	758
3	165	150	517
4	82	80	651
5	226	233	602
6	74	78	760

l	kFo	Fc	Sig
7	24	25	1479
8	23	23	1578
	2, 12, 1		
0	58	53	601
1	165	166	467
2	57	59	641
3	189	187	520
4	170	169	570
5	18	10	2202
6	28	36	1428
8	36	38	1091
10	19	18	1148
	2, 13, 1		
0	86	80	517
1	101	98	514
2	104	103	552
3	104	109	598
4	128	129	617
5	48	50	938
7	32	34	1248
8	24	26	1403
10	16	20	1167
	2, 14, 1		
0	20	32	1283
1	87	94	543
2	70	75	618
3	143	131	570
5	28	23	1319
6	83	91	750
7	15	2	2307
8	26	27	1277
9	22	19	1177
	2, 15, 1		
0	49	44	713
1	88	91	571
2	28	33	1079
3	99	98	619
4	93	100	661
5	88	94	723
6	42	45	1070
7	61	67	838
8	15	15	1906
	2, 16, 1		
0	76	85	597
1	22	28	1372
2	77	82	628
3	39	43	1005
4	28	28	1270
5	79	93	772
6	64	66	839
7	58	66	865
8	21	30	1469
9	26	31	1044
	2, 17, 1		

l	kFo	Fc	Sig
	2, 17, 1		
1	58	53	710
2	41	44	913
3	32	34	1163
4	60	62	825
5	81	86	757
6	46	52	955
7	46	53	961
8	14	21	2229
9	21	26	1159
	2, 18, 1		
0	67	67	671
1	134	136	576
2	56	58	761
3	24	25	1431
4	15	12	2279
5	14	11	2542
6	33	37	1191
7	57	65	815
8	32	36	1031
9	12	14	1859
	2, 19, 1		
0	170	182	566
1	111	109	639
2	126	131	625
3	116	119	663
4	33	40	1174
9	14	13	1386
	2, 20, 1		
0	81	74	671
1	71	71	736
2	187	190	631
5	33	37	1072
	2, 21, 1		
0	98	99	663
1	52	51	909
2	279	282	617
4	53	55	930
6	20	19	1625
	2, 22, 1		
0	13	6	2412
1	183	185	625
2	40	48	1257
3	92	92	762
4	47	50	956
6	29	29	1193
	2, 23, 1		
0	111	111	678
1	32	34	1334
2	16	10	2229
3	112	114	713
4	22	21	1592
8	11	17	1734
	2, 24, 1		

l	kFo	Fc	Sig
0	45	46	947
1	97	96	721
2	25	26	1413
5	18	18	1844
	2, 25, 1		
0	23	23	1507
2	32	31	1238
3	40	42	1100
4	19	18	1821
6	17	18	1686
7	18	22	1401
	2, 26, 1		
0	34	31	1187
1	19	25	1866
3	14	18	2573
5	28	28	1145
	2, 27, 1		
0	20	12	1593
2	38	33	1042
	2, 28, 1		
0	18	15	2004
2	35	33	1088
4	14	12	2068
5	16	21	1666
	2, 29, 1		
1	20	10	1691
5	12	10	2192
6	18	23	1280
	2, 30, 1		
3	26	25	1179
4	42	46	847
5	12	14	1978
6	12	14	1690
	2, 31, 1		
0	17	21	1968
1	15	14	1992
3	27	26	1164
4	21	19	1404
5	29	25	892
	2, 32, 1		
0	30	29	1047
2	13	13	2264
5	27	27	882
	2, 33, 1		
0	13	18	2144
3	12	13	2039
	2, 34, 1		
3	14	18	1612
	2, 35, 1		
3	25	30	903
	3, 0, 1		
1	27	27	999
3	44	54	799
7	16	18	2145

l	kFo	Fc	Sig
9	28	35	962
	3, 1, 1		
0	15	21	1351
1	42	61	705
2	15	14	1671
3	42	54	830
4	18	24	1857
5	22	24	1732
6	16	19	1906
7	19	23	1857
	3, 2, 1		
1	12	10	1895
2	42	37	722
4	13	13	2490
5	28	35	1353
7	39	40	992
8	22	23	1462
	3, 3, 1		
0	15	27	1597
1	48	46	633
2	50	56	723
3	17	14	1546
4	44	47	928
6	13	13	2462
7	13	16	2352
8	38	40	946
	3, 4, 1		
0	50	48	620
1	12	8	1994
2	33	33	959
4	19	23	1739
6	28	25	1295
8	32	33	1092
	3, 5, 1		
0	61	52	595
1	33	35	787
2	26	27	1098
3	24	13	1218
4	63	65	778
6	24	26	1460
7	37	43	1024
8	19	16	1663
	3, 6, 1		
0	243	217	474
1	23	32	1271
2	29	24	1035
6	24	21	1506
7	30	34	1257
	3, 7, 1		
0	338	330	473
1	300	280	493
2	31	42	1074
3	90	83	644
5	15	19	2299

STRUCTURE FACTORS OF PENTENYL CYANO BICYCLOHEXANE
Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	3, 7, 1			7	34	39	1133		3, 22, 1				4, 0, 1			6	35	40	1042		4, 17, 1		
6	20	20	1781	8	40	47	828	0	17	17	2105	6	21	21	1510	7	23	26	1310	0	48	47	922
7	18	27	1850		3, 15, 1			1	29	32	1400		4, 1, 1			8	13	21	1464	2	26	25	1338
9	10	7	2094	0	26	30	1389	4	12	7	2365	0	17	15	1851		4, 10, 1			3	15	6	2335
	3, 8, 1			2	108	107	688	5	13	15	2290	1	17	28	1966	0	23	7	1544	4	38	42	1024
0	155	147	516	3	49	51	932	7	15	19	1529	2	26	25	1400	1	65	65	764	5	43	46	928
1	168	150	523	4	63	67	842		3, 23, 1			3	72	78	768	2	37	33	1152	6	11	19	2228
2	20	17	1404	5	90	101	737	0	48	42	932	4	50	54	894	4	24	22	1466	7	13	14	1384
3	23	12	1518	6	19	20	1926	2	52	53	942	5	28	31	1392	5	52	59	872		4, 18, 1		
4	34	39	1170	7	47	45	874	3	39	39	980		4, 2, 1			6	21	22	1716	2	26	28	1338
6	17	10	2111	8	23	26	1130	4	37	40	968	0	19	23	1717	7	39	50	861	3	42	40	990
	3, 9, 1				3, 16, 1			5	23	24	1332	2	81	84	741		4, 11, 1			4	36	38	1043
0	46	45	784	0	81	84	688		3, 24, 1			3	18	18	1893	0	59	50	826	5	14	5	2049
1	259	239	508	1	144	144	638	1	55	55	892	4	39	44	1017	1	14	13	2609	6	15	22	1557
2	65	67	693	2	86	82	756	2	57	63	833	5	23	29	1519	2	36	35	1098		4, 19, 1		
4	71	78	737	3	47	48	1012	3	59	61	831		4, 3, 1			3	30	23	1200	2	22	20	1550
6	37	47	1074	4	20	19	1799		3, 25, 1			0	62	64	752	5	24	19	1515	4	47	54	831
	3, 10, 1			7	15	13	1906	0	37	41	1075	1	14	16	2374	6	36	37	1047	5	17	18	1581
0	39	36	874		3, 17, 1			1	45	50	973	2	21	17	1733	7	48	53	778		4, 20, 1		
1	127	134	572	0	49	53	936	3	16	22	1982	3	18	13	1948		4, 12, 1			3	32	30	1092
2	105	96	600	1	153	159	651	5	12	16	2190	5	13	10	2444	0	77	67	759	5	26	32	1125
3	66	78	775	2	76	76	768		3, 26, 1				4, 4, 1			1	131	131	653		4, 21, 1		
5	67	69	791	3	118	122	705	0	25	18	1351	0	159	160	592	2	47	45	941	3	31	33	1187
	3, 11, 1			4	64	65	834	1	57	59	813	1	98	97	657	4	17	14	2058	4	18	22	1549
0	181	173	529	5	20	17	1756	2	25	30	1426	2	55	64	878	5	30	35	1186	5	12	6	2087
1	82	76	618	6	33	33	1163	4	13	12	2195	3	55	55	856	7	25	35	1028		4, 22, 1		
2	14	15	2265		3, 18, 1				3, 27, 1				4, 5, 1				4, 13, 1			0	19	18	1785
3	40	45	940	0	63	65	822	0	28	31	1331	0	194	179	586	0	86	81	740	1	21	20	1524
4	36	39	1140	1	117	112	668	2	37	38	1020	1	119	118	645	1	41	41	1153	3	18	14	1706
5	21	18	1651	2	25	29	1710	5	19	21	1310	2	38	36	1081	2	58	62	920	6	12	15	1433
6	44	49	988	3	155	156	684		3, 28, 1			4	28	28	1266	3	66	69	813		4, 23, 1		
7	53	50	882	4	66	61	806	0	38	41	1024		4, 6, 1			4	16	17	2181	1	16	11	1884
	3, 12, 1				3, 19, 1			1	24	27	1427	0	89	79	710		4, 14, 1			3	15	13	1955
0	77	68	644	0	72	74	809	4	26	26	1100	1	42	39	916	0	40	38	1089	4	23	23	1173
1	64	60	667	1	24	25	1564	5	15	14	1516	2	15	22	2247	1	34	32	1164		4, 24, 1		
2	24	31	1469	2	171	169	661		3, 29, 1			3	44	46	977	2	108	105	701	0	17	12	1771
3	47	44	900	3	57	56	938	0	13	12	2299	5	34	35	1145	3	49	49	990	2	30	27	1119
4	110	111	693	4	25	18	1588	2	14	9	1886	6	15	13	1990	5	41	45	1020	3	27	28	1977
6	140	145	684	5	21	19	1579	4	15	15	1463		4, 7, 1			7	24	31	1019	4	17	18	1417
7	20	31	1687	7	12	10	1989		3, 30, 1			2	24	30	1397		4, 15, 1				4, 25, 1		
8	18	20	1590	8	22	21	900	0	16	13	1675	3	25	26	1383	0	24	22	1614	0	31	27	1027
	3, 13, 1				3, 20, 1				3, 31, 1			5	40	42	1070	1	76	79	760	1	15	16	1793
0	25	20	1309	0	99	97	688	2	12	11	2095	6	36	38	1048	2	106	101	715	2	30	35	1047
1	33	29	1019	2	54	59	981		3, 32, 1			7	37	37	939	4	37	37	1128	3	24	24	1127
2	29	31	1268	4	44	46	999	0	12	13	2252		4, 8, 1			5	50	52	864	4	13	15	1752
3	25	17	1448	5	37	37	1089		3, 33, 1			0	31	32	1251	7	17	18	1300		4, 26, 1		
4	66	58	847	6	17	19	1729	0	15	12	1653	2	47	49	990		4, 16, 1			0	29	34	1140
5	15	20	2439	8	19	26	950	1	23	22	1106	5	25	19	1518	0	36	47	1108	1	24	23	1176
	3, 14, 1				3, 21, 1				3, 34, 1			6	40	42	1015	1	26	32	1531	2	25	31	1123
0	19	16	1582	1	113	114	704	1	27	25	884		4, 9, 1			2	16	28	2452	3	21	24	1111
1	64	58	716	2	46	46	974		3, 35, 1			0	55	45	859	3	76	74	805	4	11	12	1833
4	167	166	653	3	53	54	922	1	16	19	1162	3	14	7	2479	4	14	14	2320		4, 27, 1		
5	109	112	694	5	17	19	1745		4, 0, 1			4	25	26	1407	5	58	62	778	0	18	20	1510
6	122	130	691	6	18	19	1568	4	58	63	839	5	49	53	954	6	25	29	1156	1	25	26	1158

STRUCTURE FACTORS OF PENTENYL CYANO BICLOHEXANE

Columns are 10Fo 10Fc 10000Sig

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	4, 27, 1			0	33	27	1212		5, 25, 1				6, 16, 1				6, 19, 1			0	12	17	1434
2	30	31	923	1	23	22	1549	0	42	48	702	0	13	15	1626								
4	14	17	1315	6	32	41	870	1	19	24	1179												
	4, 28, 1				5, 8, 1			2	10	14	1827												
1	23	27	1230	0	17	11	2047		5, 26, 1														
2	28	34	935	1	37	30	1073	0	15	13	1481												
	4, 29, 1			2	28	27	1386		5, 27, 1														
1	43	49	718	3	24	21	1466	0	18	16	1052												
2	23	27	1041	4	20	16	1588		6, 0, 1														
3	15	22	1247	6	27	30	920	0	50	63	841												
	4, 30, 1				5, 9, 1			2	27	33	1062												
0	54	56	646	0	38	35	1043	4	24	26	940												
	4, 31, 1			1	25	21	1569		6, 1, 1														
0	38	38	713	2	41	41	1027	0	41	43	942												
1	18	19	1136	4	15	15	1844	1	46	51	849												
	5, 0, 1			6	12	16	1630	2	20	23	1415												
1	28	28	1409		5, 10, 1				6, 2, 1														
3	41	52	1028	1	33	29	1200	0	56	60	810												
	5, 1, 1			2	53	56	871	1	31	37	1054												
0	162	169	689	3	14	17	2396		6, 4, 1														
1	39	40	1132	6	18	17	1149	0	31	29	1094												
2	15	12	2375		5, 11, 1				6, 5, 1														
4	36	42	1066	1	40	41	961	0	22	22	1369												
6	12	16	1915	2	30	31	1210	2	21	20	1278												
	5, 2, 1			3	30	33	1132	3	18	17	1217												
0	104	104	731	4	20	21	1419	4	11	11	1761												
1	88	89	757		5, 12, 1				6, 6, 1														
2	36	37	1094	0	14	13	2102	3	16	20	1329												
3	20	20	1691	1	29	30	1294	4	21	26	978												
4	31	36	1081	2	22	21	1437		6, 7, 1														
5	12	13	2344	3	41	41	963	1	13	16	2011												
	5, 3, 1				5, 13, 1			4	23	31	848												
0	20	10	1822	3	16	26	1956		6, 8, 1														
1	43	45	1035		5, 14, 1			1	15	13	1696												
4	14	16	2110	1	18	11	1820	2	46	45	763												
5	13	17	2115		5, 15, 1			4	29	36	685												
6	13	13	1883	1	13	10	2139		6, 9, 1														
	5, 4, 1				5, 16, 1			2	16	15	1497												
2	52	49	923	0	15	17	2055	3	18	24	1236												
3	47	47	971		5, 17, 1				6, 10, 1														
4	27	28	1253	0	17	16	1842	1	12	14	2053												
5	60	66	717	3	12	8	2063	2	13	17	1743												
6	23	28	1118		5, 18, 1			3	15	21	1414												
	5, 5, 1			3	12	3	1919		6, 11, 1														
0	23	20	1569	4	11	11	1897	2	21	20	1168												
1	28	21	1456		5, 19, 1				6, 12, 1														
3	87	92	712	4	16	20	1358	2	16	15	1382												
	5, 6, 1				5, 20, 1				6, 13, 1														
0	28	25	1296	4	19	22	1061	0	15	15	1710												
1	38	38	1057		5, 21, 1				6, 14, 1														
3	14	16	2335	2	13	11	1760	1	12	12	1803												
4	27	32	1218		5, 24, 1				6, 15, 1														
6	24	26	1024	0	12	13	2066	0	13	15	1742												
	5, 7, 1			2	13	15	1469		6, 16, 1														

STRUCTURE FACTORS OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig
h, 0, 0			
4	259	275	800
h, 1, 0			
1	24	39	855
2	40	33	990
5	18	8	2541
h, 2, 0			
0	60	78	278
2	19	19	1798
3	627	621	3226
5	18	23	2679
h, 3, 0			
1	39	57	606
2	14	27	2169
3	31	40	1598
5	16	12	2975
h, 4, 0			
1	189	189	394
2	513	444	2600
3	18	19	2575
4	52	43	1353
h, 5, 0			
2	43	56	911
h, 6, 0			
0	336	365	2050
1	126	132	490
2	146	125	608
5	42	32	1286
h, 7, 0			
1	16	12	1855
2	13	24	2497
5	27	19	1850
h, 8, 0			
0	26	37	1244
1	206	203	536
2	29	24	1406
3	48	46	1323
4	46	41	1392
h, 9, 0			
1	28	12	1311
4	26	20	2440
h, 10, 0			
0	104	136	652
1	97	95	697
2	44	41	1246
5	21	11	1753
h, 11, 0			
3	24	14	2430
5	21	10	1648
h, 12, 0			
0	156	145	710
1	21	11	2229
2	53	64	1221
3	24	20	2462

h	kFo	Fc	Sig
h, 13, 0			
2	26	28	2402
4	26	13	1920
h, 14, 0			
0	38	9	1536
1	39	39	1550
2	38	25	1570
h, 15, 0			
1	18	33	3229
3	40	36	1501
h, 16, 0			
1	21	8	2873
2	20	9	2768
4	18	7	1838
h, 17, 0			
2	31	31	1826
h, 18, 0			
1	40	31	1464
h, 19, 0			
2	23	26	2076
3	18	22	1721
h, 20, 0			
0	115	126	983
1	18	14	2613
2	90	90	716
h, 21, 0			
1	30	31	1360
h, 0, 1			
2	16	8	2160
3	346	328	635
4	24	16	2399
h, 1, 1			
0	100	96	194
1	478	425	1610
2	55	36	724
3	141	123	701
4	24	20	2355
h, 2, 1			
1	79	84	410
2	398	295	2453
4	100	73	930
5	16	9	3120
h, 3, 1			
0	525	559	1402
1	300	296	1831
2	200	175	518
3	64	65	904
4	46	47	1393
h, 4, 1			
0	50	46	457
1	352	346	1959
2	88	84	615
3	58	67	964
4	33	40	1778

h	kFo	Fc	Sig
h, 5, 1			
0	313	335	1847
1	133	141	454
2	140	116	581
3	38	39	1295
4	26	20	2320
5	23	21	2148
h, 6, 1			
0	782	818	2026
1	154	149	470
2	289	262	563
3	85	94	886
4	47	50	1391
5	28	34	1817
h, 7, 1			
0	57	63	620
1	81	73	608
2	38	44	1057
3	30	20	1851
4	30	35	2144
h, 8, 1			
1	353	340	521
2	112	114	702
3	86	81	913
4	48	60	1351
5	19	8	2391
h, 9, 1			
0	27	63	1230
1	125	123	623
2	22	28	1842
3	17	22	3260
5	26	21	1560
h, 10, 1			
0	115	100	645
1	79	92	772
2	37	50	1357
3	69	82	1085
4	30	15	2018
5	17	25	2233
h, 11, 1			
0	221	226	627
1	68	73	892
2	100	97	900
3	40	36	1639
h, 12, 1			
0	26	22	1808
1	52	39	1152
2	90	102	965
3	57	43	1261
4	43	59	1289
h, 13, 1			
0	163	182	766
1	154	150	796
2	91	80	1008

h	kFo	Fc	Sig
h, 13, 1			
3	46	61	1402
4	37	28	1428
h, 14, 1			
0	44	55	1318
1	58	67	1234
2	44	34	1496
3	62	73	1160
4	34	19	1434
h, 15, 1			
0	67	71	1116
1	106	104	937
2	32	48	1823
3	52	46	1249
h, 16, 1			
0	21	2	2870
2	34	33	1842
3	29	25	1803
h, 17, 1			
0	17	6	3150
1	40	33	1579
3	25	17	1919
h, 18, 1			
1	32	22	1838
2	32	42	1649
3	29	30	1446
h, 19, 1			
0	68	64	1080
1	90	96	922
2	62	50	988
3	43	46	860
h, 20, 1			
0	36	39	1567
1	55	54	1069
2	56	54	909
h, 21, 1			
0	48	115	1783
1	54	52	904
h, 0, 2			
0	31	45	361
1	116	104	355
3	93	95	770
4	23	17	2506
h, 1, 2			
0	130	127	229
1	314	298	1686
2	66	59	654
3	43	38	1116
4	50	44	1279
5	28	15	1910
h, 2, 2			
0	51	73	341
1	50	66	474
2	120	108	548

h	kFo	Fc	Sig
3	47	36	1130
4	39	42	1638
h, 3, 2			
0	492	525	1476
1	137	113	392
2	174	165	525
3	59	55	990
5	26	22	2006
h, 4, 2			
0	109	125	357
1	156	156	415
2	51	59	771
3	55	61	1028
4	31	37	1907
h, 5, 2			
0	378	361	1891
1	135	139	450
2	123	98	602
4	26	31	2281
5	30	25	1775
h, 6, 2			
0	407	395	2093
1	34	40	914
2	156	156	600
3	33	37	1743
4	24	37	2515
5	26	30	1869
h, 7, 2			
0	77	92	579
1	226	201	497
2	53	53	910
3	83	92	906
4	48	47	1471
5	29	43	1691
h, 8, 2			
0	229	208	506
1	278	262	536
2	136	143	668
3	88	88	958
4	62	62	1234
5	30	38	1513
h, 9, 2			
0	25	3	1348
1	56	61	797
2	91	104	779
3	57	52	1257
4	67	85	1096
5	21	19	1999
h, 10, 2			
0	134	134	638
1	329	311	606
2	93	87	842
3	131	135	884
4	48	57	1357

h	kFo	Fc	Sig
5	39	32	1068
h, 11, 2			
0	117	107	680
1	173	174	690
2	49	59	1334
3	95	97	992
5	30	39	1233
h, 12, 2			
0	446	442	658
1	67	50	969
2	236	239	782
3	51	51	1403
4	66	67	1036
h, 13, 2			
0	297	325	719
1	216	218	761
2	176	170	818
3	79	94	1033
4	64	49	1002
h, 14, 2			
0	120	97	888
1	324	330	774
2	76	71	1085
3	125	138	880
4	23	28	2026
h, 15, 2			
0	254	266	791
1	201	213	816
2	141	159	880
3	103	93	919
4	26	39	1562
h, 16, 2			
0	234	247	813
1	43	29	1533
2	135	149	876
3	24	20	2008
4	24	30	1410
h, 17, 2			
0	89	108	988
1	93	106	991
2	67	67	1076
3	29	44	1598
h, 18, 2			
0	55	65	1197
1	65	78	1128
2	41	45	1397
3	46	44	1005
h, 19, 2			
0	24	23	2210
1	30	36	1791
2	32	26	1449
3	50	62	793
h, 20, 2			
1	81	85	851

STRUCTURE FACTORS OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig
	h, 20, 2			4	186	192	856	0	228	210	834		h, 5, 4			4	39	40	1374	1	139	118	454
2	52	55	952	5	16	14	3005	1	126	134	894	2	176	146	592		h, 14, 4			2	95	78	628
	h, 21, 2				h, 8, 3			2	134	118	878	3	95	72	842	0	92	85	950	3	99	92	818
1	56	63	894	0	367	384	2564	3	59	59	1074	4	119	109	946	1	67	66	1106	4	70	74	1105
	h, 0, 3			1	201	202	551	4	24	18	1308	5	74	72	957	2	56	55	1271	5	73	68	960
1	342	354	1744	2	209	195	648		h, 17, 3				h, 6, 4			3	31	29	1929		h, 4, 5		
2	54	29	737	3	163	167	821	1	158	155	831	0	326	325	2266		h, 15, 4			0	227	244	398
3	93	81	786	4	101	99	981	2	18	8	3046	1	350	321	2493	0	39	49	1658	1	114	103	493
4	23	30	2512	5	100	117	780	3	53	65	1054	2	178	180	618	1	127	120	887	2	117	113	615
	h, 1, 3				h, 9, 3				h, 18, 3			3	241	236	738	2	31	21	2091	3	61	65	1065
0	123	114	279	0	495	488	2755	0	26	36	2095	4	84	90	1063	3	82	79	936	4	20	14	2914
1	42	34	540	1	243	256	590	1	68	49	1070	5	120	116	787	4	18	16	2121	5	44	39	1259
2	31	32	1063	2	227	224	678		h, 19, 3				h, 7, 4				h, 16, 4				h, 5, 5		
3	45	49	1083	3	207	205	811	0	38	31	1508	0	290	302	481	0	89	86	1000	0	237	250	433
4	30	20	1931	4	43	48	1573	1	25	30	1993	1	255	217	520	1	66	56	1158	1	313	293	470
5	21	12	2287	5	123	127	674	2	23	35	1939	2	157	134	650	2	53	51	1252	2	276	243	583
	h, 2, 3				h, 10, 3				h, 20, 3			3	161	162	805	3	25	31	1967	3	171	164	739
0	279	296	1450	0	105	115	677	1	55	45	1036	4	111	107	950		h, 17, 4			4	190	190	844
1	95	95	396	1	100	103	745		h, 21, 3			5	102	104	782	0	94	80	988	5	81	91	896
2	140	128	537	2	126	109	780	1	23	28	1660		h, 8, 4			1	48	38	1420		h, 6, 5		
3	30	25	1538	3	88	84	993		h, 0, 4			0	141	140	558	2	78	69	1022	0	121	117	516
4	22	23	2432	4	99	111	920	0	108	105	320	1	301	287	551	3	26	19	1685	1	194	201	516
	h, 3, 3			5	50	48	946	1	39	33	605	2	308	301	649		h, 18, 4			2	72	88	778
0	113	119	344		h, 11, 3			2	20	23	1619	3	126	124	865	1	41	34	1508	3	64	63	1106
1	338	312	1947	0	220	196	652	3	76	84	821	4	216	211	827	2	15	11	3020	4	49	50	1448
2	35	9	1016	1	172	161	684		h, 1, 4			5	35	44	1412	3	22	17	1733	5	19	19	2579
3	50	47	1021	2	151	142	810	0	228	251	1543		h, 9, 4				h, 19, 4				h, 7, 5		
4	47	35	1386	3	53	62	1350	1	259	243	371	0	82	60	706	0	40	35	1386	0	354	327	2543
	h, 4, 3			4	101	99	888	2	135	101	551	1	118	113	661	2	27	19	1604	1	313	297	529
0	97	130	392	5	26	24	1313	3	86	85	782	2	109	107	805		h, 20, 4			2	192	182	651
1	68	87	527		h, 12, 3			4	41	51	1563	3	74	71	1147	1	48	56	1081	3	216	218	784
2	75	53	694	0	220	218	698		h, 2, 4			4	98	97	969	2	17	18	2302	4	95	107	987
3	34	35	1439	1	130	124	794	1	150	135	395	5	59	66	911		h, 21, 4			5	138	140	705
4	41	35	1576	2	130	122	847	2	49	70	783		h, 10, 4			0	23	52	2042		h, 8, 5		
5	31	38	1756	3	46	44	1423	3	47	58	1183	0	218	196	608	1	28	21	1378	0	85	80	652
	h, 5, 3			4	59	55	1071	4	18	15	2915	1	167	156	665		h, 0, 5			1	79	73	715
0	730	738	1933		h, 13, 3			5	17	11	2738	2	113	110	844	1	179	182	405	2	49	60	1089
1	234	220	441	0	21	2	2545		h, 3, 4			3	179	173	819	2	87	80	631	3	51	61	1310
2	280	260	556	1	259	247	741	0	18	22	966	4	30	29	1905	3	74	81	872	4	23	24	2680
3	119	99	774	3	97	107	953	1	122	110	428	5	94	85	661	4	28	26	2065	5	29	36	1604
4	39	45	1695	4	17	14	2735	2	22	30	1567		h, 11, 4			5	38	30	1461		h, 9, 5		
5	85	78	908		h, 14, 3			3	34	33	1405	1	19	16	2294		h, 1, 5			1	94	77	714
	h, 6, 3			0	192	202	788	4	28	30	2114	2	21	27	2735	0	207	225	337	2	124	115	768
0	33	59	879	1	276	259	772	5	32	30	1724	3	32	20	2044	1	182	182	405	3	22	27	2582
1	332	327	2422	2	118	119	908		h, 4, 4			4	27	32	2014	2	51	40	823	4	107	106	922
2	146	131	614	3	113	107	911	0	336	345	1881	5	22	20	1486	3	25	34	1700		h, 10, 5		
3	128	126	794	4	37	29	1236	1	143	152	445		h, 12, 4				h, 2, 5			0	38	20	1148
4	113	125	949		h, 15, 3			2	201	179	552	0	38	38	1309	0	158	169	358	1	42	35	1128
5	60	54	1006	0	307	305	790	3	52	54	1127	1	21	16	2543	1	109	106	446	2	41	47	1426
	h, 7, 3			1	36	42	1807	4	97	94	982	2	62	60	1170	2	92	76	620	4	41	48	1502
0	31	3	1039	2	177	181	863	5	33	44	1590	4	47	30	1208	3	52	36	1106		h, 11, 5		
1	556	532	2522	3	29	17	1870		h, 5, 4				h, 13, 4			4	65	61	1173	0	68	64	856
2	256	229	605	4	38	48	1093	0	372	356	2057	0	76	74	985		h, 3, 5			1	80	72	836
3	162	159	785		h, 16, 3			1	242	221	455	2	78	74	1040	0	99	78	412	2	80	73	988

STRUCTURE FACTORS OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig
h, 11, 5				0	24	30	848	1	146	141	660	h, 19, 6				1	170	152	596	4	45	54	879
3	19	3	3148	1	58	53	603	2	177	171	740	0	52	54	1163	2	159	157	711	h, 16, 7			
4	56	46	1198	2	56	54	759	3	77	66	1057	1	24	17	1981	3	51	59	1302	0	105	110	953
h, 12, 5				3	23	30	1954	4	106	101	914	2	46	48	1041	4	111	119	922	1	76	79	1063
0	103	110	809	4	24	21	2511	5	39	38	1100	h, 20, 6				5	17	24	2736	2	139	136	851
1	31	25	1737	5	19	15	2614	h, 10, 6				0	21	15	2117	h, 8, 7				3	105	101	788
2	63	56	1165	h, 2, 6				0	178	166	645	2	20	10	1737	0	243	223	577	h, 17, 7			
3	42	42	1524	0	143	165	402	1	90	82	788	h, 21, 6				1	238	228	608	0	73	87	1056
h, 13, 5				1	148	138	457	2	96	90	897	1	33	36	1154	2	149	148	727	1	122	127	872
0	98	111	890	2	64	67	719	3	111	115	905	h, 0, 7				3	195	194	822	2	140	142	798
1	92	91	941	3	80	72	918	4	35	34	1722	1	27	27	1143	4	67	67	1138	3	56	71	954
2	43	30	1495	5	42	47	1327	5	68	73	720	2	73	48	707	5	95	105	709	h, 18, 7			
3	83	77	1021	h, 3, 6				h, 11, 6				3	33	36	1563	h, 9, 7				0	25	40	2215
4	22	27	2222	0	219	232	402	1	52	47	1153	4	38	50	1717	0	219	199	624	1	109	105	855
h, 14, 5				1	218	196	458	2	35	40	1705	5	25	39	2013	1	121	122	718	2	26	39	1990
0	22	9	2516	2	101	91	631	3	55	48	1302	h, 1, 7				2	101	99	868	3	84	86	642
1	72	60	1042	3	154	141	728	4	17	13	3268	0	70	76	503	3	96	98	975	h, 19, 7			
2	30	27	1952	4	58	54	1238	h, 12, 6				1	64	58	622	4	26	28	2236	0	21	20	2352
3	38	40	1533	5	70	63	966	0	32	24	1648	2	69	59	711	5	57	65	838	1	89	97	817
4	22	25	1965	h, 4, 6				1	33	27	1704	3	48	47	1171	h, 10, 7				2	25	30	1703
h, 15, 5				0	32	5	874	2	35	33	1775	4	28	27	2122	0	105	100	734	h, 20, 7			
0	43	37	1513	1	322	315	464	3	35	25	1849	5	19	17	2489	1	146	129	715	0	50	61	1098
1	50	44	1429	2	197	169	581	4	27	18	1797	h, 2, 7				2	98	91	911	2	44	49	870
2	53	54	1309	3	79	82	911	h, 13, 6				1	33	44	932	3	93	97	1027	h, 21, 7			
4	28	29	1405	4	140	146	890	0	88	84	898	2	22	27	1686	4	62	59	1085	0	18	49	2485
h, 16, 5				h, 5, 6				1	61	68	1171	3	38	38	1523	5	30	33	1122	1	39	39	958
1	33	22	1789	0	247	257	453	2	54	43	1323	4	35	44	1699	h, 11, 7				h, 0, 8			
2	31	24	1911	1	319	309	495	4	32	21	1553	h, 3, 7				0	21	23	2192	0	92	95	509
3	17	23	2826	2	323	289	590	h, 14, 6				0	17	5	1514	1	108	99	803	1	63	94	672
h, 17, 5				3	152	145	789	0	46	31	1477	1	89	93	568	2	31	33	1767	2	24	26	1620
0	50	47	1384	4	190	186	841	1	82	79	991	3	25	32	2129	3	67	71	1147	4	32	22	2056
1	22	20	2576	5	75	74	924	2	37	34	1758	h, 4, 7				4	30	37	1779	5	19	17	2550
2	40	29	1449	h, 6, 6				3	104	93	931	0	114	124	494	h, 12, 7				h, 1, 8			
3	24	26	1869	0	551	576	2405	4	22	23	1928	1	114	110	559	0	65	62	996	0	51	56	664
h, 18, 5				1	267	272	522	h, 15, 6				2	51	57	941	1	72	66	1021	1	37	34	973
0	26	15	2027	2	244	230	631	0	98	106	967	3	87	82	925	2	117	110	891	2	111	116	653
1	20	18	2499	3	228	232	754	1	91	86	983	4	35	26	1713	3	74	72	1081	3	23	20	2155
3	27	25	1505	4	43	45	1626	2	68	77	1103	5	44	51	1219	4	79	79	879	4	32	35	2020
h, 19, 5				5	136	145	740	3	61	47	1106	h, 5, 7				h, 13, 7				5	55	62	1073
0	22	21	2232	h, 7, 6				4	59	60	789	0	87	89	562	0	44	44	1343	h, 2, 8			
1	43	26	1284	0	350	361	512	h, 16, 6				1	149	157	540	1	117	123	868	0	15	27	1891
2	30	27	1512	1	360	347	548	1	19	28	3119	2	54	61	942	2	122	116	876	1	81	88	607
h, 20, 5				2	201	177	652	2	99	89	914	3	81	79	963	3	67	79	1134	2	61	73	833
0	19	22	2504	3	239	240	772	3	20	24	2441	4	30	34	1981	4	105	108	747	3	65	67	1075
2	31	22	1248	4	121	119	908	h, 17, 6				5	54	60	1076	h, 14, 7				5	47	49	1165
h, 21, 5				5	105	102	748	0	64	60	1143	h, 6, 7				1	113	109	939	h, 3, 8			
0	22	16	1939	h, 8, 6				1	82	81	1005	0	177	172	522	2	140	129	882	0	78	89	565
1	26	26	1501	0	38	44	1005	2	64	48	1103	1	186	177	567	3	138	133	822	1	195	201	515
h, 0, 6				1	351	331	584	3	74	78	813	2	223	215	643	4	120	120	652	2	69	69	812
0	141	171	385	2	238	237	690	h, 18, 6				3	90	88	957	h, 15, 7				3	137	135	816
1	18	38	1405	3	113	115	895	0	51	53	1315	4	142	148	899	0	188	201	820	4	73	82	1126
2	85	94	660	4	188	201	836	1	44	39	1317	5	37	39	1354	1	110	115	916	5	44	48	1193
3	33	24	1479	h, 9, 6				2	28	29	1823	h, 7, 7				2	125	139	901	h, 4, 8			
h, 1, 6				0	154	155	613	3	54	46	835	0	143	141	573	3	151	154	769	0	14	21	2113

STRUCTURE FACTOR TABLES OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig
	h, 4, 8		
1	188	201	531
2	55	62	935
3	62	60	1098
4	63	65	1205
	h, 5, 8		
0	205	209	512
1	96	94	619
2	186	180	668
3	43	59	1368
4	80	84	1094
5	30	33	1591
	h, 6, 8		
0	231	238	538
1	54	57	806
2	164	159	679
3	41	46	1492
4	42	37	1644
5	17	23	2393
	h, 7, 8		
0	64	57	769
1	201	199	596
2	50	47	1139
3	86	90	991
4	23	26	2455
5	18	21	2176
	h, 8, 8		
0	52	52	853
1	167	161	655
2	96	92	844
3	85	75	1033
4	51	53	1257
	h, 9, 8		
0	159	166	653
1	27	11	1685
2	95	99	905
3	20	21	2952
4	32	34	1715
	h, 10, 8		
0	70	75	854
1	106	105	779
2	65	64	1079
3	52	50	1258
	h, 11, 8		
1	74	83	952
2	29	36	1935
3	47	52	1360
4	32	42	1697
	h, 12, 8		
0	171	186	758
1	21	25	2541
2	106	99	942
3	24	23	2301
4	42	35	1305

h	kFo	Fc	Sig
	h, 13, 8		
0	25	31	2193
1	50	58	1387
2	79	75	1052
3	66	70	1110
4	56	61	961
	h, 14, 8		
0	22	22	2705
1	172	174	864
2	43	45	1497
3	91	81	931
4	57	68	866
	h, 15, 8		
0	63	71	1223
1	61	60	1255
2	70	76	1101
3	65	61	998
	h, 16, 8		
0	134	135	910
1	54	52	1262
2	93	84	906
3	57	67	1000
	h, 17, 8		
1	97	94	899
3	65	70	817
	h, 18, 8		
0	69	63	1032
1	52	50	1194
2	51	47	1075
	h, 19, 8		
0	108	101	791
1	69	75	876
2	79	75	733
	h, 20, 8		
0	40	43	1178
1	68	63	773
	h, 0, 9		
1	493	470	2579
2	520	523	3060
3	122	115	841
4	337	363	805
	h, 1, 9		
0	114	106	542
1	368	366	2620
2	205	207	630
3	111	116	878
4	151	162	899
5	48	51	1157
	h, 2, 9		
0	561	563	2400
1	474	475	2622
2	200	183	642
3	358	357	740
4	60	57	1269

h	kFo	Fc	Sig
5	182	190	691
	h, 3, 9		
0	532	543	2470
1	299	289	534
2	216	216	631
3	202	200	787
4	54	57	1300
5	110	118	755
	h, 4, 9		
0	148	143	539
1	213	207	562
2	231	215	650
3	108	107	897
4	146	141	871
5	42	46	1190
	h, 5, 9		
0	107	92	598
1	239	243	577
2	163	146	687
3	104	102	905
4	109	101	891
5	44	48	1126
	h, 6, 9		
0	85	101	645
1	47	35	944
2	102	99	778
3	32	24	1932
4	62	61	1163
5	18	10	2243
	h, 7, 9		
0	126	138	618
1	51	45	948
2	85	86	877
3	51	44	1357
4	32	33	1819
5	18	18	2132
	h, 8, 9		
1	55	61	954
2	21	25	2409
3	52	48	1375
5	17	19	2098
	h, 9, 9		
0	66	76	878
1	103	105	775
2	42	45	1389
3	41	35	1603
4	26	22	2045
	h, 10, 9		
0	73	81	941
1	32	35	1672
2	34	38	1646
4	22	19	2151
	h, 11, 9		
0	116	124	816

h	kFo	Fc	Sig
	h, 11, 9		
1	54	56	1164
2	80	81	1011
3	42	36	1492
	h, 12, 9		
0	57	65	1238
1	87	95	966
2	40	35	1631
3	24	24	2310
4	25	17	1883
	h, 13, 9		
0	28	34	2067
1	97	103	962
2	51	36	1278
3	41	45	1466
4	38	31	1136
	h, 14, 9		
0	99	102	954
1	50	55	1312
2	49	51	1391
3	31	30	1715
	h, 15, 9		
0	65	65	1175
1	18	19	3227
2	39	48	1476
3	23	14	2108
	h, 16, 9		
0	51	61	1347
1	17	17	3311
2	38	45	1591
	h, 17, 9		
1	27	26	1989
3	37	35	1088
	h, 18, 9		
0	51	53	1143
1	65	68	1023
2	51	45	1048
	h, 19, 9		
1	29	22	1565
2	70	66	729
	h, 20, 9		
0	77	92	833
1	62	60	789
	h, 0, 10		
0	883	938	2509
1	517	511	2729
2	431	430	632
3	430	461	749
4	117	123	944
5	228	259	649
	h, 1, 10		
0	91	102	614
1	169	167	564
2	35	24	1331

h	kFo	Fc	Sig
3	79	87	1022
4	22	19	2961
5	43	46	1166
	h, 2, 10		
0	38	44	957
1	517	484	2770
2	411	392	639
3	198	199	794
4	288	306	800
5	18	20	2585
	h, 3, 10		
0	329	323	522
1	131	134	609
2	173	167	685
3	44	51	1371
4	66	75	1125
	h, 4, 10		
0	101	85	632
1	165	151	608
2	103	91	784
3	153	152	844
4	42	47	1629
5	82	82	768
	h, 5, 10		
0	42	49	960
1	164	149	614
2	55	57	1054
3	60	55	1136
4	38	39	1579
5	21	19	1840
	h, 6, 10		
0	16	14	2057
1	123	124	694
3	52	53	1340
	h, 7, 10		
0	16	11	2331
1	53	40	917
2	50	49	1200
3	37	40	1581
5	15	12	2210
	h, 8, 10		
0	163	175	671
1	35	23	1389
2	83	83	952
3	33	25	1999
4	23	22	2307
5	14	12	2207
	h, 9, 10		
0	51	50	1049
1	65	57	942
2	27	31	2074
3	52	56	1373
	h, 10, 10		
0	61	69	1023

h	kFo	Fc	Sig
1	82	88	935
2	29	36	2212
3	22	18	2661
	h, 11, 10		
0	36	37	1604
1	27	34	2050
2	52	53	1365
3	23	30	2463
4	24	24	1892
	h, 12, 10		
0	60	63	1207
1	75	76	1075
2	27	27	2207
3	30	41	1928
4	26	22	1643
	h, 13, 10		
0	37	40	1753
1	42	45	1550
2	29	32	2012
3	18	23	2905
4	22	30	1741
	h, 14, 10		
0	88	82	1009
1	56	56	1266
2	48	52	1384
	h, 15, 10		
0	58	65	1212
1	54	52	1272
2	41	41	1365
3	42	39	1157
	h, 16, 10		
0	73	75	1056
1	60	55	1138
2	31	39	1715
3	29	29	1400
	h, 17, 10		
0	42	40	1399
1	46	47	1217
2	42	38	1213
3	15	16	2172
	h, 18, 10		
0	35	39	1410
1	16	24	2938
	h, 19, 10		
0	19	12	2314
2	16	7	1944
	h, 20, 10		
0	53	58	934
1	21	31	1614
	h, 0, 11		
1	259	255	573
2	84	87	809
3	97	92	917
4	98	110	924

STRUCTURE FACTOR TABLES OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig
h, 1, 11			
0	121	115	597
1	94	91	653
2	62	69	956
3	52	44	1301
4	17	16	3232
h, 2, 11			
0	114	121	600
1	42	39	947
2	86	75	800
3	46	46	1354
4	26	26	2397
5	57	61	874
h, 3, 11			
0	69	60	716
1	129	122	637
2	89	83	798
3	23	27	2435
4	41	31	1494
5	20	20	1977
h, 4, 11			
0	67	81	732
1	137	127	658
2	73	74	939
3	51	57	1367
h, 5, 11			
0	164	159	616
1	60	51	888
2	81	74	887
3	52	53	1346
5	19	14	1872
h, 6, 11			
0	219	217	632
1	115	111	711
2	106	105	846
3	70	67	1090
4	32	29	1765
5	14	17	2486
h, 7, 11			
0	20	22	1810
1	105	92	746
2	53	53	1186
3	36	35	1644
4	29	26	1857
h, 8, 11			
0	50	48	1060
1	72	71	908
2	44	42	1372
3	43	42	1516
h, 9, 11			
0	59	63	1041
1	62	61	1064
2	47	43	1333
3	57	62	1225
4	33	42	1493
h, 10, 11			
0	43	51	1305
1	53	53	1205
2	58	60	1213
3	72	70	1095
4	33	34	1440
h, 11, 11			
0	37	46	1634
1	50	58	1361
2	105	101	959
3	56	64	1248
4	87	86	775
h, 12, 11			
1	53	65	1319
2	101	97	931
3	54	59	1200
4	98	104	673
h, 13, 11			
0	81	94	1095
1	93	90	957
2	56	59	1222
3	116	113	798
4	37	43	1037
h, 14, 11			
0	24	8	2457
1	48	50	1335
2	49	47	1309
3	69	78	932
h, 15, 11			
0	46	47	1354
1	84	83	986
2	89	79	904
3	27	23	1628
h, 16, 11			
1	51	46	1269
3	36	35	1113
h, 17, 11			
0	38	33	1450
1	28	20	1815
2	35	25	1306
h, 18, 11			
1	18	12	2451
2	22	21	1776
h, 19, 11			
1	69	68	751
h, 20, 11			
0	30	49	1436
h, 0, 12			
0	74	78	704
1	83	72	743
2	44	38	1261
3	80	85	1016
4	26	34	2076
5	26	31	1509
h, 1, 12			
0	92	98	680
2	39	45	1313
4	34	34	1606
h, 2, 12			
0	49	45	891
1	79	74	748
2	104	99	813
3	45	44	1417
4	53	59	1205
5	15	21	2290
h, 3, 12			
1	58	71	926
2	25	24	1933
3	39	38	1655
5	26	24	1372
h, 4, 12			
0	66	68	769
1	75	67	801
2	46	42	1281
3	74	74	1041
4	22	30	2395
5	27	30	1336
h, 5, 12			
1	87	77	772
3	34	36	1757
h, 6, 12			
0	74	70	835
1	88	89	804
2	73	64	1018
3	38	40	1567
4	35	39	1491
h, 7, 12			
0	287	303	677
1	31	21	1657
2	142	137	849
3	30	31	1961
4	43	40	1375
h, 8, 12			
0	308	319	693
1	121	117	828
2	168	168	815
3	62	67	1218
4	44	41	1229
h, 9, 12			
0	24	16	2341
1	282	286	756
3	129	132	880
h, 10, 12			
0	123	125	878
1	329	332	767
2	116	108	920
3	140	141	853
h, 10, 12			
4	83	80	798
h, 11, 12			
0	217	218	785
1	73	78	1117
2	176	164	843
3	49	43	1345
4	106	106	687
h, 12, 12			
0	311	326	794
1	97	89	981
2	193	189	838
3	134	126	792
4	59	51	802
h, 13, 12			
0	101	115	997
1	97	85	972
2	92	87	948
3	133	123	760
h, 14, 12			
0	37	37	1591
1	147	145	851
2	116	107	860
3	74	62	875
h, 15, 12			
0	76	87	1009
1	70	81	1059
2	104	96	845
3	63	56	856
h, 16, 12			
0	49	50	1209
1	58	51	1135
2	43	32	1294
3	63	59	737
h, 17, 12			
0	27	36	1910
1	42	40	1228
2	22	24	1872
h, 18, 12			
1	18	13	2263
h, 19, 12			
0	44	55	970
h, 0, 13			
1	74	76	812
3	32	31	1852
h, 1, 13			
0	166	172	650
1	84	85	772
2	89	85	890
3	28	33	2099
4	24	21	2100
5	13	8	2266
h, 2, 13			
0	21	14	1839
1	63	53	921
2	33	37	1548
3	23	25	2564
h, 3, 13			
0	39	40	1109
1	79	77	853
2	40	44	1410
3	33	30	1805
h, 4, 13			
0	32	25	1265
1	72	68	848
2	23	35	2247
3	28	30	1910
h, 5, 13			
0	152	154	703
1	61	69	980
2	72	76	1053
3	53	54	1242
4	20	20	2295
h, 6, 13			
0	225	234	682
1	186	189	727
2	112	113	894
3	67	74	1151
4	38	42	1402
h, 7, 13			
0	61	64	1022
1	311	314	718
2	67	69	1106
3	131	134	887
4	36	30	1495
h, 8, 13			
0	321	329	728
1	244	248	765
2	173	179	847
3	96	103	944
4	32	35	1515
h, 9, 13			
0	413	433	743
1	32	30	1907
2	240	239	817
3	39	31	1524
4	66	66	907
h, 10, 13			
0	266	278	786
1	199	199	816
2	148	156	880
3	70	71	1032
4	28	33	1556
h, 11, 13			
0	53	52	1336
1	215	212	828
2	45	43	1427
3	103	99	870
4	21	20	1787
h, 12, 13			
0	47	47	1509
1	151	155	862
2	58	54	1149
3	61	62	1031
4	54	54	754
h, 13, 13			
0	33	25	1760
1	63	64	1098
2	63	52	1158
3	38	40	1341
h, 14, 13			
0	79	82	1005
1	86	80	946
2	59	56	1105
3	84	82	779
h, 15, 13			
0	31	36	1821
1	72	70	1022
2	23	30	2106
3	60	57	795
h, 16, 13			
0	69	62	992
1	20	20	2398
2	67	62	876
h, 17, 13			
0	48	42	1113
1	22	12	1913
2	34	30	1239
h, 18, 13			
0	26	18	1615
h, 19, 13			
0	34	25	1117
h, 0, 14			
0	202	213	654
2	90	79	886
h, 1, 14			
1	110	107	772
2	24	23	2180
3	31	33	1940
h, 2, 14			
0	135	141	687
1	99	90	783
2	67	68	1046
4	22	27	2288
h, 3, 14			
0	106	111	781
1	167	163	724
2	44	43	1376
3	79	81	1047
h, 4, 14			
0	54	64	991
1	55	55	1046

STRUCTURE FACTOR TABLES OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig
h, 4, 14			
2	48	56	1277
3	26	29	2257
4	41	36	1283
h, 5, 14			
0	301	290	686
1	54	49	1106
2	163	162	833
3	40	39	1468
4	55	54	1004
h, 6, 14			
0	156	151	756
1	118	124	832
2	84	82	1035
3	75	77	1081
4	20	18	2188
h, 7, 14			
0	169	167	762
1	205	196	790
2	110	110	906
3	94	93	958
4	39	40	1204
h, 8, 14			
0	99	103	926
1	248	242	771
2	65	68	1191
3	97	97	949
4	26	22	1668
h, 9, 14			
0	147	134	847
1	132	133	881
2	86	82	1036
3	70	77	1024
4	33	29	1213
h, 10, 14			
0	220	223	794
2	121	120	917
3	20	14	2651
4	25	17	1457
h, 11, 14			
0	38	36	1716
1	61	53	1161
2	36	43	1728
3	28	24	1836
4	27	33	1188
h, 12, 14			
0	43	41	1524
1	37	38	1751
2	33	32	1762
h, 13, 14			
0	41	37	1536
1	37	33	1660
2	20	18	2633
3	20	17	2048
h, 14, 14			
0	55	46	1163
1	34	33	1664
2	51	43	1164
3	16	17	2291
h, 15, 14			
0	52	48	1217
1	27	27	1865
2	29	22	1595
h, 16, 14			
0	29	22	1750
1	40	28	1341
h, 17, 14			
0	21	22	2132
1	16	7	2418
2	16	14	2007
h, 18, 14			
0	15	20	2301
1	29	23	1292
h, 0, 15			
1	21	12	2332
2	45	44	1369
4	25	29	1890
h, 1, 15			
0	23	23	2031
1	28	21	1742
2	39	30	1438
3	21	19	2471
h, 2, 15			
0	49	57	1044
1	196	204	736
2	31	32	1803
3	89	96	989
h, 3, 15			
0	211	209	728
1	67	68	990
2	117	109	879
3	28	27	2055
4	34	25	1464
h, 4, 15			
0	325	353	713
1	151	138	794
2	182	189	828
3	61	57	1143
4	51	50	1087
h, 5, 15			
0	147	158	799
1	273	269	745
2	83	85	983
3	127	127	895
h, 6, 15			
0	230	220	760
1	195	205	790
2	130	118	907
3	79	83	983
4	37	33	1307
h, 7, 15			
0	241	245	775
1	92	94	988
2	149	148	876
3	35	34	1660
4	50	49	950
h, 8, 15			
0	75	82	985
1	144	134	849
2	48	53	1366
3	54	50	1221
h, 9, 15			
1	29	27	2057
2	33	29	1779
3	33	36	1564
4	19	22	1975
h, 10, 15			
0	74	75	1117
1	18	16	3042
2	40	39	1423
3	25	28	1931
h, 11, 15			
0	129	134	874
1	76	69	995
2	73	73	1027
3	39	37	1282
h, 12, 15			
0	19	24	3004
1	27	30	2047
2	36	33	1494
3	23	27	1851
h, 13, 15			
0	54	50	1212
1	111	113	848
2	35	32	1489
3	43	46	1062
h, 14, 15			
0	31	31	1795
1	35	33	1629
2	23	24	2084
3	31	31	1090
h, 15, 15			
0	33	40	1605
1	21	14	2354
2	48	45	1025
h, 16, 15			
0	50	44	1103
1	33	35	1423
2	38	35	1082
h, 17, 15			
0	41	36	1134
1	40	35	1084
h, 18, 15			
0	20	20	1729
h, 0, 16			
0	20	22	2318
1	17	13	2769
h, 1, 16			
0	142	154	784
1	160	159	795
2	64	65	1101
3	42	46	1496
4	15	15	2858
h, 2, 16			
0	192	207	747
2	107	114	932
4	28	29	1476
h, 3, 16			
0	327	337	732
1	188	189	782
2	174	174	812
3	54	54	1247
4	31	37	1522
h, 4, 16			
1	310	315	769
3	118	129	882
h, 5, 16			
0	312	318	752
1	338	336	771
2	164	164	835
3	118	126	865
4	26	29	1584
h, 6, 16			
0	416	426	757
2	239	244	820
4	54	60	867
h, 7, 16			
0	310	314	780
1	203	201	809
2	169	170	839
3	73	75	948
4	29	32	1375
h, 8, 16			
0	18	24	2866
1	266	269	804
3	107	113	823
h, 9, 16			
0	58	55	1227
1	117	116	917
2	36	37	1708
3	40	42	1386
4	18	20	1748
h, 10, 16			
0	113	115	887
1	32	35	1821
2	71	76	1042
h, 11, 16			
0	28	32	2047
1	50	47	1228
2	25	23	1961
3	32	29	1334
h, 12, 16			
0	63	58	1131
1	58	48	1096
2	31	31	1577
3	35	26	1248
h, 13, 16			
1	32	29	1636
3	27	25	1286
h, 14, 16			
0	146	127	781
1	62	59	960
2	97	80	733
h, 15, 16			
0	75	62	885
1	105	94	748
2	72	65	767
h, 16, 16			
0	41	38	1167
1	105	88	671
2	62	66	668
h, 17, 16			
0	169	157	572
1	73	63	683
h, 0, 17			
1	164	167	792
2	68	68	1142
3	64	71	1086
4	31	39	1375
h, 1, 17			
0	216	227	758
1	150	148	827
2	111	108	913
3	35	37	1542
4	15	4	2360
h, 2, 17			
0	155	159	815
1	52	55	1205
2	90	91	987
3	49	55	1202
4	35	34	1171
h, 3, 17			
0	85	79	915
1	155	148	815
2	40	36	1484
3	25	25	2107
h, 4, 17			
0	35	32	1604
1	69	66	1087
2	41	45	1450
3	27	23	1911
h, 5, 17			
0	94	85	916
2	40	33	1472
4	18	16	2076
h, 6, 17			
0	24	25	2222
1	129	122	870
2	19	16	2758
3	45	48	1251
h, 7, 17			
0	18	8	2926
1	49	43	1348
3	31	27	1556
4	14	3	2234
h, 8, 17			
0	173	167	823
1	25	26	2146
2	103	98	908
3	24	35	1897
h, 9, 17			
0	70	71	1091
1	63	57	1104
2	63	59	1085
3	26	32	1865
h, 10, 17			
1	53	49	1270
h, 11, 17			
0	67	58	1063
1	84	81	943
2	48	49	1212
3	30	34	1380
h, 12, 17			
0	78	74	984
1	41	36	1307
2	63	57	932
3	35	27	1046
h, 13, 17			
0	60	55	1085
1	24	22	1946
2	37	40	1261
h, 14, 17			
0	74	70	875
1	106	98	763
2	78	72	712
h, 15, 17			
0	100	97	735
1	45	44	1072
2	75	63	643
h, 16, 17			
0	32	26	1291
1	67	66	736
h, 17, 17			
0	62	61	677

STRUCTURE FACTOR TABLES OF PENTENYL ETHOXY BICYCLOHEXANE

Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig
	h, 0, 18		
0	73	65	1032
1	30	30	1780
2	44	44	1353
3	29	31	1866
	h, 1, 18		
0	155	174	821
1	85	90	963
2	116	121	910
3	103	108	865
4	61	71	814
	h, 2, 18		
0	128	144	863
1	65	61	1087
2	92	98	956
3	61	62	1038
4	35	42	1180
	h, 3, 18		
0	76	67	999
1	189	196	814
2	121	122	916
3	78	87	912
4	101	108	625
	h, 4, 18		
1	156	164	840
2	62	58	1120
3	78	83	942
4	60	66	746
	h, 5, 18		
0	197	197	812
1	104	98	910
2	109	111	883
3	94	96	845
4	16	25	1899
	h, 6, 18		
0	100	104	948
1	28	31	2087
2	74	73	1045
3	23	26	1971
4	33	35	936
	h, 7, 18		
0	44	46	1340
1	109	105	863
2	44	44	1327
3	28	32	1638
	h, 8, 18		
0	63	64	1113
1	24	19	2133
2	29	35	1762
3	28	25	1629
	h, 9, 18		
0	74	72	1003
2	35	40	1642
	h, 10, 18		
1	54	56	1156
2	30	31	1606
3	20	13	1836
	h, 11, 18		
1	51	54	1133
2	15	11	2890
3	17	23	1849
	h, 12, 18		
0	34	31	1510
1	34	38	1548
	h, 13, 18		
0	73	68	901
1	26	20	1761
2	38	43	1132
	h, 14, 18		
1	25	27	1618
2	53	57	806
	h, 15, 18		
0	43	44	1015
1	61	63	788
	h, 16, 18		
0	46	45	864
	h, 0, 19		
1	346	350	791
2	167	161	813
3	98	111	803
4	142	151	532
	h, 1, 19		
0	67	69	1061
1	103	108	925
2	113	106	901
3	62	66	983
4	103	106	571
	h, 2, 19		
0	346	349	772
1	147	143	847
2	190	196	798
3	155	154	751
4	52	57	723
	h, 3, 19		
0	82	95	1017
1	90	86	983
2	71	74	1022
3	125	124	769
4	23	31	1296
	h, 4, 19		
0	167	176	816
1	184	181	832
2	142	139	848
3	87	88	836
	h, 5, 19		
0	75	79	1027
1	41	40	1419
2	86	84	928
3	51	53	1051
	h, 6, 19		
0	83	86	988
1	142	139	847
2	58	60	1054
3	64	60	888
	h, 7, 19		
0	60	62	1157
1	42	46	1464
2	45	47	1179
3	23	28	1659
	h, 8, 19		
0	95	91	879
1	21	22	2306
2	53	53	1031
3	22	15	1694
	h, 9, 19		
1	72	70	991
2	16	13	2954
3	25	22	1408
	h, 10, 19		
1	36	40	1437
2	15	5	2660
	h, 11, 19		
0	59	58	1010
2	33	30	1265
	h, 12, 19		
0	29	40	1659
2	15	23	2531
	h, 13, 19		
0	15	16	2708
1	33	34	1333
	h, 14, 19		
1	22	33	1593
	h, 15, 19		
0	33	37	1072
1	13	10	2277
	h, 0, 20		
0	73	86	966
1	77	71	987
2	50	62	1151
3	125	119	722
	h, 1, 20		
0	94	107	943
1	105	100	884
2	64	66	1071
3	77	75	830
	h, 2, 20		
1	39	44	1486
2	77	69	1010
3	30	36	1459
	h, 3, 20		
0	67	53	1051
1	64	72	1075
2	86	78	890
3	32	31	1463
	h, 4, 20		
0	27	26	1964
2	33	33	1678
3	16	9	2599
	h, 5, 20		
0	41	46	1395
1	35	30	1588
2	33	29	1451
3	38	33	1085
	h, 6, 20		
1	46	45	1289
2	48	49	1143
3	16	23	2385
	h, 7, 20		
0	29	26	1838
1	16	16	2837
2	21	19	2276
3	14	13	2459
	h, 8, 20		
1	47	48	1146
3	40	42	941
	h, 9, 20		
1	61	59	1042
2	42	37	1098
3	29	28	1082
	h, 10, 20		
0	72	74	919
1	58	52	989
2	56	54	884
	h, 11, 20		
0	77	76	868
1	38	38	1237
2	59	56	831
	h, 12, 20		
0	53	44	959
1	72	70	762
2	68	59	673
	h, 13, 20		
0	52	46	910
1	40	41	1049
	h, 14, 20		
0	45	45	908
1	32	32	1028
	h, 0, 21		
1	37	26	1482
2	31	37	1648
	h, 1, 21		
0	22	17	2366
2	15	6	2815
	h, 2, 21		
0	47	38	1192
2	27	23	1701
3	14	19	2625
	h, 3, 21		
1	16	14	3070
3	17	15	1966
	h, 4, 21		
0	18	11	2415
1	47	42	1217
2	31	25	1550
3	21	21	1670
	h, 5, 21		
2	34	32	1356
3	19	14	1827
	h, 6, 21		
0	27	27	1875
1	22	14	1964
2	23	22	1908
3	28	23	1259
	h, 7, 21		
0	26	28	1882
1	35	30	1318
2	27	22	1580
3	35	33	949
	h, 8, 21		
0	30	28	1528
1	20	23	2392
2	47	48	973
	h, 9, 21		
0	85	83	791
1	63	57	925
2	63	61	805
	h, 10, 21		
0	70	61	862
1	80	77	808
2	53	52	844
	h, 11, 21		
0	88	81	743
1	122	116	645
2	69	57	643
	h, 12, 21		
0	50	53	914
1	69	61	710
	h, 13, 21		
0	118	113	562
1	66	56	618
	h, 0, 22		
0	18	16	2324
3	20	20	1625
	h, 1, 22		
2	26	26	1701
3	12	10	2422
	h, 2, 22		
2	24	21	1809
3	19	13	1658
	h, 3, 22		
0	20	13	2266
1	18	20	2388
2	17	1	2245
3	33	33	1001
	h, 4, 22		
1	18	13	2613
2	23	20	1755
3	25	24	1152
	h, 5, 22		
3	18	12	1471
	h, 6, 22		
1	19	20	2185
2	25	21	1514
	h, 7, 22		
0	23	17	1984
1	47	44	1075
2	35	27	1160
	h, 8, 22		
0	36	34	1306
1	64	61	890
2	17	18	2112
	h, 9, 22		
0	84	75	750
1	75	63	753
2	85	79	635
	h, 10, 22		
0	36	38	1179
1	24	25	1551
	h, 11, 22		
0	114	100	614
1	103	89	584
	h, 0, 23		
2	20	21	1937
	h, 1, 23		
0	31	23	1485
2	21	19	1872
	h, 2, 23		
1	19	19	2237
	h, 3, 23		
0	17	12	2363
1	43	35	1141
2	35	36	1217
	h, 4, 23		
0	17	18	2501
1	17	14	2273
2	18	15	1947
	h, 5, 23		
1	14	9	2622
2	26	24	1415
	h, 6, 23		
0	22	22	1939
1	22	18	1898
2	65	62	709

STRUCTURE FACTOR TABLES OF PENTENYL ETHOXY BICYCLOHEXANE
Columns are 10Fo 10Fc 10000Sig

h	kFo	Fc	Sig	h	kFo	Fc	Sig	h	kFo	Fc	Sig
	h, 7, 23				h, 4, 24			0	114	106	614
1	50	47	938	0	21	22	1827	1	73	66	670
2	56	49	747	1	49	48	890		h, 4, 25		
	h, 8, 23			2	43	41	867	0	52	52	812
0	43	42	1012		h, 5, 24			1	77	68	622
1	79	71	707	0	77	71	762		h, 5, 25		
2	62	58	625	1	54	53	864	0	45	39	856
	h, 9, 23			2	58	50	671	1	105	95	546
0	103	91	633		h, 6, 24				h, 6, 25		
1	52	46	813	1	23	21	1473	0	76	65	617
	h, 10, 23				h, 7, 24			1	37	32	860
0	52	47	776	1	68	60	680		h, 7, 25		
1	71	68	636		h, 8, 24			0	64	61	618
	h, 1, 24			0	26	23	1338		h, 0, 26		
0	17	10	2245	1	19	16	1645	0	32	34	1006
1	42	43	1076		h, 9, 24				h, 1, 26		
2	18	13	1732	0	66	56	622	0	16	16	1811
	h, 2, 24				h, 1, 25				h, 2, 26		
0	50	44	986	0	55	49	817	0	50	45	739
1	28	29	1489	1	86	78	644	1	36	36	826
2	36	36	977		h, 2, 25				h, 3, 26		
	h, 3, 24			0	22	24	1574	0	29	28	1050
0	77	76	805	1	59	54	747		h, 4, 26		
1	61	54	859		h, 3, 25			0	16	22	1725
2	73	69	647								

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