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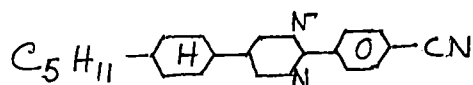
CHAPTER IV

THE CRYSTAL STRUCTURE

4.1. Introduction

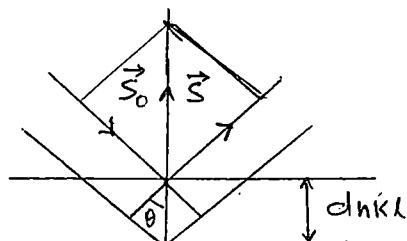
In this section, the complete crystal structure & determination of 5-(4"-n-pentyl-cyclohexyl)-2-(4'-Cyanophenyl)-Pyrimidine (PCGPP) by means of X-ray crystallography is described. Attempts have been made to investigate the relationship between the molecular organization in the crystalline and liquid crystalline state. Study of the meso-phase of this compound utilizing X-ray diffraction has been described in Chapter III. Optical birefringence study in the liquid crystalline phase is also given in the same chapter.

The molecular structure of this compound is given below



4.2. The geometry of diffraction

The phenomenon of diffraction by crystals results from a scattering process in which X-ray are scattered by the electrons of the atoms without change in wavelength. A diffraction beam is produced by such scattering only when certain geometrical conditions are satisfied, which may be in either of the two forms, the Bragg's Law or Laue's equations.



(Laue's equations)

$$\vec{a} \cdot \vec{S} = h, \vec{b} \cdot \vec{S} = k, \vec{c} \cdot \vec{S} = l$$

$$2 d_{hkl} \sin \theta_{hkl} = n \lambda$$

(Bragg's equations)

h, k, l are integers θ is the angle of reflection, d_{hkl} is interplanar spacing λ the wavelength, n is an integer determining the order of reflection

$$|\vec{S}| = \left| \frac{s - s_0}{\lambda} \right| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d}$$

...(4.1)

The resulting diffraction pattern of a crystal comprising both the positions and intensities of the diffraction effects, is a fundamental physical property of the substance which is used for the complete elucidation of the structure. Analysis of the positions of the diffraction effects leads immediately to a knowledge of the size, shape and orientation of the unit cell. To locate the positions of individual atoms in the cell, the intensities must be measured and analysed. Most important in relating the positions of the atoms to the diffraction intensities is the structure factor equation

$$\vec{F}_{hkl} = \sum_{j=1}^N f_j \exp 2\pi i (hx_j + ky_j + lz_j) \quad \dots(4.2)$$

The quantity \vec{F}_{hkl} a function of $h k l$ is called the structure factor which expresses the resultant scattering effect from the atom contents of the unit cell as compared to that of a single electron at the origin. $|\vec{F}_{hkl}|$ called the structure amplitude is thus a pure number-

number of electrons. f_j is the atomic scattering factor or form factor of the j th atom. If the unit cell contents, X_j , Y_j and Z_j are the fractional coordinates of the j th atom.

Now the atoms in the unit cell are the positions of the high electron density $\rho(xyz)$ so \vec{F}_{hkl} can be expressed as

$$\vec{F}_{hkl} = \int_V \rho(xyz) \exp 2\pi i(hx + ky + lz) dV \quad \dots(4.3)$$

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

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l \vec{F}_{hkl} \exp 2\pi i(hx + ky + lz) \quad \dots(4.4)$$

If we could obtain a larger number of \vec{F}_{hkl} by diffraction experiment, we could have directly derive the crystal structure by making a Fourier summation.

The complex form of the expression for the structure factor merely means that the phase of the scattered wave is not simply related to that of the incident wave. The phase however is not an observable quantity the only observable quantity being the intensity which is proportional to $|F|^2$

Without a knowledge of the phase a straightforward Fourier summation to evaluate $\rho(xyz)$ is not possible. This is the well known phase problem of X-ray crystallography.

From the intensity data I_{hkl} we determine $|F_{hkl}|$ and direct mathematical relationships are being used to give phase information.

4.3. Crystal Data Collection:

Transparent plate like crystals were obtained from a solution of acetone by slow evaporation. Lattice parameters and space group were determined by taking oscillation and Weissenberg photographs along different axes. The crystal belong to the monoclinic system. The space group $P2/a$ was uniquely determined from the observed systematic absence of $h0l$ reflections with $h = 2n + 1$. By floatation technique the density of the crystal was found to be 1.18 gm.cm^{-3} . Taking four molecules per unit cell (i.e. $Z = 4$) the calculated density became 1.15 gm.cm^{-3} which is very close to the observed value.

A crystal of dimension $0.075 \times 0.3 \times 0.4 \text{ mm}^3$ was used in the collection of intensity data. It was mounted on the tip of a glass fibre and the fibre was in turn fastened to a goniometer head. Accurate cell parameters were determined by a least square fit of $\sin \theta$ values of 25 reflections within $20^\circ < \theta < 25^\circ$ measured on an 'Enraf Nonius' Gad-4 computer controlled diffractometer, ~~using~~ $\text{Cu K}\alpha$ radiation monochromated by a graphite monochromator was used throughout. The name of the 4-circle diffractometer arises from its possession of four arcs which may be used to adjust the orientation of the crystal as to bring any desired $(h k l)$ plane into reflecting position and the detector to the corresponding diffraction position. A schematic diagram of GAD4 single crystal orienter¹ is given in Fig. 4.1. The intensity data were collected by $\omega - 2\theta$ scan mode. A total of 3277 reflec-

tions were collected in the interval 4° (2θ of which 2246 reflections were taken as observed and had intensities greater than $2\sigma(I)$. The important crystallographic data are given in table 1. The measured value of the intensity is given by

$$I_{raw} = \frac{A}{n} (c - R.B) \quad \dots(4.5)$$

where A = attenuation factor (26.55 for $Cu K\alpha$)

n = an integer varying from 8 to 24 to suit the particular case.

C = total count.

R = Ratio of scan time to background

B = Total background count.

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

$$\sigma(I_{raw}) = \frac{20.166}{n} \cdot A (c + R^2 B)^{1/2} \quad \dots(4.6)$$

Applying appropriate Lorentz polarization factor correction L_p (described below) we get I_{corr} and $\sigma(I_{corr})$

$$I_{corr} = \frac{I_{raw}}{L_p} \quad \text{and} \quad \sigma(I_{corr}) = \frac{\sigma(I_{raw})}{L_p} \quad \dots(4.7)$$

This intensity value is then converted to F_o , the observed structure factor with

$$|F_o| = K (I_{corr})^{1/2} \quad \dots(4.8)$$

K being scaling constant and the corresponding standard deviation is

$$\sigma |\vec{F}_0| = \frac{\sigma(I_{corr})}{2 |\vec{F}_0|} \dots(4.9)$$

4.4. Intensity data reduction

The intensities collected are subjected to corrections for certain geometrical and physical factors before being used in the structure determination. These are described below:

Lorentz factor

For each reciprocal lattice point to pass through the surface of the sphere of reflection the required length of time varies as a function of its position in reciprocal space and the direction of its approach to the sphere. Because the intensity of a reflection is proportional to this time a correction is needed. Such correction is called the Lorentz factor L^2 and it varies with diffraction geometry. For single crystal of normal beam equation geometry, it is given by

$$L_{hkl} = \frac{1}{\sin 2\theta_{hkl}} \dots(4.10)$$

Polarisation factor

In the usual experimental arrangements, the X-ray beam is unpolarized which means that the azimuth of the electric vector assumes all directions with time. The effective amplitude of the radiation after it is reflected by the crystal at the angle 2° consists of only

the components of these azimuthals after reflection. This feature has the effect of reducing the intensity of the X-ray beam by a factor p , known as the polarisation factor.

$$P = \frac{1}{2} (1 + \cos^2 2\theta) \quad \dots(4.11)$$

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

$$P_{hkl} = P_{\text{ref}} \frac{\cos^2 2\theta_m + \cos^2 2\theta_{hkl}}{1 + \cos^2 2\theta_m} + (1 - P_{\text{ref}}) \frac{\cos^2 2\theta_m + \cos^2 2\theta_{hkl}}{1 + \cos^2 2\theta_m} \quad \dots(4.12)$$

where P_{ref} = a constant depending on the crystal used in the monochromator (0.5 in our expt.)

θ_m = Bragg angle of reflection from the monochromator crystal.

These two correction factors L and P are combinedly termed as Lorentz Polarization factor L_p because of the dependence of both on the scattering angle θ .

Extinction correction:

Attenuation of diffracted beams may also be caused when the crystal is set at the Bragg angle. Darwin⁴ first treated the effect mathematically and termed this as primary and secondary extinction effect. Primary extinction involves the loss of intensity of the incident beam

by an interference process following multiple reflections as the beam penetrates deeper and deeper into the crystal. Secondary extinction may, however, be considered in case of strong reflections. In this case as the incident beam itself travels inside the crystal, it goes on losing considerable fractions of its energy by reflection in the planes it encounters. Thus the plane lying deeper receive less and less incident intensity. Consequently the diffracted intensity is attenuated. This effect is predominantly observed in low angle region. Correction for this effect has been derived⁵⁻⁶. Kato⁷ derived a method based on dynamical theory for correction to both the effects.

24 Temperature factor

While introducing the idea of atomic scattering factor, 'f' we have not taken into consideration the finite size of the atom i.e. of the electron cloud about the atomic nucleus and also the thermal vibration of the atom which increases the effective volume of the electron cloud. Because of the first effect, the scattered intensity falls off with increasing $\sin \theta$ and the second factor acts for more rapid fall. The first effect is corrected by taking 'f' values from standard f Vs. $\sin \theta$ curve^{5,8,9} and the effect of thermal vibration, assuming it isotropic, can be taken care by multiplying f_0 , the form factor for an

atom at rest, by a temperature factor¹⁰

$$f = f_0 \exp(-B \sin^2 \theta / \lambda^2) \dots(4.13)$$

where the parameter B, called isotropic temperature factor is equal to $8\pi^2 \bar{u}^2$, \bar{u}^2 being the mean square displacement of the atoms from their mean positions.

A method introduced by A.J.C. Wilson¹¹ enables us to obtain an overall value of B, and at the same time, places all the observed intensities on an approximately absolute basis.

He 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

$$\langle | \vec{F} |^2 \rangle = \sum_{j=1}^N f_j^2 \dots(4.14)$$

Dividing the entire reciprocal space observed into annular zones of equal s^2 ($s = \sin \theta / \lambda$)

$\langle | \vec{F}_{obs} |^2 \rangle$ is determined for each of them and then $\sum_{j=1}^N f_{0j}^2$ (Smid) is calculated using the mean value of s^2 for each zone. Since $| \vec{F}_{obs} |^2$ is usually known on an arbitrary scale, we may write

$$\langle | \vec{F}_{obs} | \rangle = K \langle | \vec{F} |^2 \rangle \dots(4.15)$$

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

$$\langle |\vec{F}|^2 \rangle = \sum_{j=1}^N f_j^2 = \sum_{j=1}^N f_{0j}^2 \exp(-2B_j s^2) \quad \dots(4.16)$$

Assuming B same for all atoms

$$\langle |\vec{F}|^2 \rangle = \exp(-2Bs^2) \sum_{j=1}^N f_{0j}^2 \quad \dots(4.17)$$

Substituting this in equation (19) we get

$$\begin{aligned} \langle |\vec{F}_{obs}|^2 \rangle &= K \exp(-2Bs^2) \sum_{j=1}^N f_{0j}^2 \\ &= \ln K - 2 \frac{B \sin^2 \theta}{\lambda^2} \end{aligned} \quad \dots(4.18)$$

The plot of $\ln \langle |\vec{F}_{obs}|^2 \rangle / \sum_{j=1}^N f_{0j}^2$ against $\sin^2 \theta / \lambda^2$ called the Wilson plot is therefore a straight line except for the scatter 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 known 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 Debye¹²

$$\langle |F_s|^2 \rangle = \sum_{k=1}^G \sum_{i=1}^{M_k} \sum_{j=1}^M f_i f_j \frac{\sin 2\pi r_{ij} S}{2\pi r_{ij} S} + \sum_{j=1}^N f_j^2 \quad \dots(4.19)$$

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

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

$$K(S_{\text{mid}}) = \frac{\sum_{\ell=1}^N \sum_{j=1}^M f_{oj}(s)}{\sum |F_{o1}|^2(s)} \quad \dots(4.20)$$

where ℓ is a small integer depending on the space group¹³ A least squares procedure is used to fit a best smooth analytical functions, usually $\ln K = A + BS^C$ to experimental points. When $C = 2.0$, the curve is the same as Wilson's plot.

After scaling the data and without estimating the temperature factors we try to postulate, a trial structure by direct methods.

4.5. Determination of the trial structure

The trial structure was determined by direct method. Direct methods of crystal structure determination are usually associated with techniques in which phases for a set of structure factors are determined from the corresponding experimental amplitude by probabilistic calculations.

A large number of operating procedures for direct phase determination have been proposed. Most of these are based on the same fundamental principles, but differs in the manner of handling the data and extracting the phases. We shall consider only the fundamentals of the method and the technique which has been used in the present case.

Unitary and Normalised Structure Factors

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

$$U(\vec{h}) = F(\vec{h}) / \sum_{j=1}^N f_j$$

So that $|U(\vec{h})| \leq 1$

writing the unitary scattering factor as

$$m_j = f_j / \sum_{j=1}^N f_j$$

We may write

$$U(\vec{h}) = \sum_{j=1}^N m_j \exp 2\pi i \vec{h} \cdot \vec{r}_j \quad \dots(4.21)$$

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

$$|E_{\vec{h}}|^2 = \frac{|F_{\vec{h}}|^2}{\epsilon_{\vec{h}} \sum_{j=1}^N f_j^2}$$

where $\epsilon_{\vec{h}}$ takes into account

the effect of space group symmetry. Now if \hat{f} be the common shape for all atoms then $f_j = z_j \hat{f}$

$$\begin{aligned} E_{\vec{h}} &= \epsilon_{\vec{h}}^{-\frac{1}{2}} \frac{F_{\vec{h}}}{\left(\sum_{j=1}^N z_j^2 \hat{f}^2 \right)^{1/2}} \\ &= \epsilon_{\vec{h}}^{-\frac{1}{2}} \sum_{j=1}^N \left(z_j / \sigma_2^{1/2} \right) \exp 2\pi i (\vec{h} \cdot \vec{r}_j) \end{aligned}$$

...(4.22)

where $G_m = \sum_{j=1}^N z_j^m$

$\vec{E}_{\vec{h}}$ is called the normalised structure factors because of its property. This relationship shows that the averaging of E^2 can be carried out regardless of θ . The same is not true, however, of either and this simplification is one of the main reasons why 'E's are preferred for use in direct methods.

Structure invariant and semi-invariant

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

It can be shown that the intensities of reflection i.e. , are structure invariants.

However, the structure factor itself is not structure invariant. Otherwise the phase problem would not exist in crystallography. The structure factor $F_{\vec{h}}$ is given by

$$F_{\vec{h}} = |F_{\vec{h}}| \exp i \left(\Phi_{\vec{h}} \right) = \sum_{j=1}^N f_j \exp(2\pi i \vec{h} \cdot \vec{r}_j) \quad \dots(4.23)$$

whith shift $\Delta \vec{r}$ of the origin, the equation changes to

$$\begin{aligned} F'_{\vec{h}} &= \sum_{j=1}^N f_j \exp[2\pi i \vec{h} \cdot (\vec{r}_j + \Delta \vec{r})] \\ &= |F_{\vec{h}}| \exp(-2\pi i \vec{h} \cdot \Delta \vec{r}) \quad \dots(4.24) \end{aligned}$$

Thus we see that the phase changes by $-2\pi \vec{h} \cdot \Delta \vec{r}$ while the amplitude is π invariant.

In a similar way it can be shown that $|F_{\vec{h}}|^2$ is structure invariant

$$\begin{aligned} |F_{\vec{h}}|^2 &= F_{\vec{h}} F'_{-\vec{h}} = \exp(-2\pi i \vec{h} \cdot \Delta \vec{r}) F_{\vec{h}} \exp(2\pi i \vec{h} \cdot \Delta \vec{r}) F_{-\vec{h}} \\ &= F_{\vec{h}} F_{-\vec{h}} \quad \dots(4.25) \end{aligned}$$

It can be shown that although the values of the individual phases depend on the structure and choice of origin, some combinations of them is a structure invariant. For example if $\vec{h}_1 + \vec{h}_2 + \vec{h}_3 = 0$ then $\Phi_{\vec{h}_1} + \Phi_{\vec{h}_2} + \Phi_{\vec{h}_3}$ is a structure invariant for every space group. It follows directly from the fact that $F_{\vec{h}_1} F_{\vec{h}_2} F_{-\vec{h}_3} = F_{-\vec{h}_3}$

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is an invariant.

$$F_{\vec{h}}' F_{\vec{k}}' F_{-\vec{h}-\vec{k}}' = F_{\vec{h}} \exp(-2\pi i \vec{h} \cdot \Delta \vec{r}) F_{\vec{k}} \exp(-2\pi i \vec{k} \cdot \Delta \vec{r}) \\ F_{-\vec{h}-\vec{k}} \exp(2\pi i \vec{h} \cdot \Delta \vec{r} + 2\pi i \vec{k} \cdot \Delta \vec{r}) = F_{\vec{h}} F_{\vec{k}} F_{-\vec{h}-\vec{k}}$$

...(4.26)

Since the moduli of the structure factors are invariant themselves, the angular part of $F_{\vec{h}} F_{\vec{k}} F_{-\vec{h}-\vec{k}}$ is also invariant i.e. $\Phi_{\vec{h}} + \Phi_{\vec{k}} + \Phi_{-\vec{h}-\vec{k}}$ is an invariant, however, this does not imply that its value is known.

The structure seminvariants¹⁴ are those linear combinations of the phases whose values are uniquely determined by the crystal structure alone, when the choice of origin is restricted within permissible values. Semi-invariants originate from space group symmetry. For each space group they have to be derived separately. The structure invariants and semi-invariants have been tabulated for all space groups in reference¹⁵.

In any space group any structure invariant is also a structure seminvariant, but in general the converse is not true. A complete theory concerning this subject is given in a series of papers by Hamphman and Karle^{16,17} and recently by Schenk^{18,19}.

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some relations involving the magnitudes and the phases
Harker-Kasper Inequalities:-

In 1948 Harker and Kasper²⁰ using Cauchy inequality relation derived the following inequality relation between magnitudes and phases of unitary structure factors,

$$U(\vec{h})^2 \leq \frac{1}{2} \{ 1 + U_{2\vec{h}} \} \quad \dots(4.27)$$

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

$$S(\vec{h}) S(\vec{h}') S(\vec{h} + \vec{h}') = 1$$

A development made by Karle and Hauptman²¹ in the form of an inequality does depend on the non-negativity of electron density. For a centro symmetric structure where

$$\frac{U(\vec{h})}{U(\vec{h}')} = U(\vec{h}) \quad \text{This gives } 1 - U(\vec{h})^2 - U(\vec{h}')^2 \\ U(\vec{h} - \vec{h}') + 2 U(\vec{h}) U(\vec{h}') U(\vec{h} - \vec{h}') \geq 0$$

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

$$S(\vec{h}) S(\vec{h}') S(\vec{h} - \vec{h}') = 1$$

A significant step in the development of direct methods was the one by Sayre²². This is the most funda-

mental and developed, what we refer to as Sayre's equation. The electron density is given by the summation

$$P(\vec{r}) = \frac{1}{V} \sum_{\vec{H}} F(\vec{H}) \exp(-2\pi i \vec{h} \cdot \vec{r})$$

and we may also write

$$P(\vec{r})^2 = \frac{1}{V} \sum G(\vec{h}) \exp(-2\pi i \vec{h} \cdot \vec{r})$$

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

If the structure consists of equal resolved atoms, then both $P(\vec{r})$ and $P(\vec{r})^2$ 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

$$F(\vec{h}) = \frac{f}{gV} \sum_{\vec{h}'} F(\vec{h}') F(\vec{h} - \vec{h}') \dots(4.28)$$

This is Sayre's equation and is an exact relationship between structure factors for equal and resolved atoms.

For a centrosymmetric structure it might be assumed that a large product on the right hand side of (28) was likely to have the same sign as $F(\vec{h})$

This leads to the relationship that for large structure factors

$$S(\vec{h}) S(\vec{h}') S(\vec{h} - \vec{h}') \approx +1 \dots(4.29)$$

where \approx means probably equals. This was the sign relationship given in the papers by Cochran²⁵ and Zachariason²⁴. Expressions for the probability of (4.29) have been found by a number of authors, one which is sufficiently accurate for most purposes and is of convenient form, was given by Cochran and Woolfson²⁵. This is for an equal atom structure

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh \left\{ N^{\frac{1}{2}} / E(\vec{h}), E(\vec{h}') E(\vec{h}-\vec{h}') \right\} \quad \dots(4.30)$$

where P_+ is the probability that the product of signs in (4.29) is positive.

This expression also gives the probability that $s(\vec{h})$ equals the signs $s(\vec{h}) s(\vec{h}-\vec{h}')$. If there are several pairs of known signs all contributing to the indication of new one then the probability for the new sign being +ve will be

$$P_+(\vec{h}) = \frac{1}{2} + \frac{1}{2} \tanh \left[N^{\frac{1}{2}} |E_h| \sum_{\vec{h}'} E(\vec{h}) E(\vec{h}-\vec{h}') \right] \quad \dots(4.31)$$

In (4.30) and (4.31) if the atoms are not equal then

$$N^{\frac{1}{2}} \text{ is replaced by } \sigma_3 \sigma_2^{-\frac{3}{2}} \quad \text{where}$$

$$\sigma_n = \sum_{j=1}^N z_j^n$$

where z_j is the atomic number of the j th. atom.

The approximate phases thus obtained have to be refined

and that this may be convenient-by done by using following tangent formula of Karle and Hauptman

$$\tan \Phi_{\vec{h}} = \frac{\sum_{\vec{k}} K(\vec{h}\vec{k}) \sin(\Phi_{\vec{h}-\vec{k}} + \Phi_{\vec{k}})}{\sum_{\vec{k}} K(\vec{h}\vec{k}) \cos(\Phi_{\vec{h}-\vec{k}} + \Phi_{\vec{k}})} \quad \dots(4.32)$$

A quantity $L_n^{\vec{h}}$ which gives a measure of the reliability with which $\Phi_{\vec{h}}$ may be determined was defined by Karle and Karle

$$L_n^{\vec{h}^2} = \left[\sum_{\vec{k}} K(\vec{h}\vec{k}) \sin(\Phi_{\vec{h}-\vec{k}} + \Phi_{\vec{k}}) \right]^2 + \left[\sum_{\vec{k}} K(\vec{h}\vec{k}) \cos(\Phi_{\vec{h}-\vec{k}} + \Phi_{\vec{k}}) \right]^2 \quad \dots(4.33)$$

All the theory given above is the launching pad from which modern direct methods have grown to the present form.

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In our trial structure determination we have used the complete direct method program SIMPEL⁽²⁶⁾. There are other direct method program 'viz.' SHELX⁽²⁷⁾, MULTAN⁽²⁸⁾, XTAL⁽²⁹⁾ SAPI⁽³⁰⁾, X-RAY⁽³¹⁾.

The program system Simpel is a complete direct methods system, which may be entered with $/F/$ -values and may produce an E-map of the structure. 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 ϕ for the symbols and finally executing a numerical phase extension and refinement.

The program system SIMPEL is completely devoted to the symbolic addition method.

In a symbolic addition the following expressions play important roles.

The triplet relation

$$\Phi_{\vec{H}} \approx \Phi_{\vec{K}} + \Phi_{\vec{H}-\vec{K}}$$

for large

$$E_3 = 1/N^{1/2} |E_{\vec{H}} E_{\vec{K}} E_{\vec{H}-\vec{K}}|$$

and its centrosymmetric analogue.

$$S_{\vec{H}} \approx S_{\vec{K}} S_{\vec{H}-\vec{K}}$$

in which S is the sign of a reflection.

These formulae have their counter parts when more than one relation is available.

$$\Phi_{\vec{H}} = \frac{\sum_{\vec{K}} E_3 (\Phi_{\vec{K}} + \Phi_{\vec{H}-\vec{K}})}{\sum_{\vec{K}} E_3}$$

and

$$S_{\vec{H}} = A \sum_{\vec{k}} E_{\vec{k}} S_{\vec{k}} S_{\vec{H}-\vec{k}}$$

In general, in the final stage of a symbolic addition also numerical phases have to be refined. This is carried out by means of the tangent formula or rather, because phases must be known on the interval $0 \leq \Phi \leq 2\pi$ by its exponential analogue,

$$\exp i \Phi_{\vec{H}} = \frac{\sum_{\vec{k}} E_{\vec{k}} \exp i (\Phi_{\vec{k}} + \Phi_{\vec{H}-\vec{k}})}{|\sum_{\vec{k}} E_{\vec{k}} \exp i (\Phi_{\vec{k}} + \Phi_{\vec{H}-\vec{k}})|}$$

Elements of a symbolic addition:-

Calculation of the normalised structure factors

In the first step the experimental structure factor data are corrected for thermal motion (Wilson plot, Debye curve, K curve), brought to absolute scale and finally converted into normalised structure factors /E/.

generation of the phase relationships

The phase relationships are collected. In the program system SIMPEL not only triplet relations are generated, but also positive and negative quartets, relationship. Harker Koupor relations and quintets are generated.

Σ_1 relation³²

$$S E_{2h,0,2L} \approx S \sum_{\vec{k}} (L)^{k+l} \left(\sum_{hkl}^2 - 1 \right)$$

The positive quartet relation is formulated as

$$\Phi_{\vec{H}} + \Phi_{\vec{K}} + \Phi_{\vec{L}} + \Phi_{\vec{H}-\vec{K}-\vec{L}} \approx 0$$

for large value of $E_4 = N^{-1} |E_{\vec{H}} E_{\vec{K}} E_{\vec{L}} E_{-\vec{H}-\vec{K}-\vec{L}}|$
 and large $|E_{\vec{H}+\vec{K}}|$, $|E_{\vec{H}+\vec{L}}|$ and $|E_{\vec{K}+\vec{L}}|$

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Negative quartet relation

For reasonably large values of E_4 and small

$$|E_{\vec{H}+\vec{K}}|, |E_{\vec{H}+\vec{L}}| \text{ and } |E_{\vec{K}+\vec{L}}| \quad 34$$

Marker Kasper relations³⁵

Using the probability that the product $s(\vec{H}+\vec{K}) \times s(\vec{H}-\vec{K})$ is negative, the large $|E_{\vec{H}}|$, $|E_{\vec{H}+\vec{K}}|$ and $|E_{\vec{H}-\vec{K}}|$ and the smaller $|E_{\vec{K}}|$ and $|E_{2\vec{H}}|$. Of course this is the result of a special negative quartet, the main terms being $E_{\vec{H}}$, $E_{\vec{K}}$, $E_{\vec{H}+\vec{K}}$ and $E_{\vec{H}-\vec{K}}$.

Quintets

From the general Hughes formula derived by Simerka³⁶ the quintet phase relation can be written as

$$\Phi_{\vec{H}} + \Phi_{\vec{K}} + \Phi_{\vec{L}} + \Phi_{\vec{M}} + \Phi_{-\vec{H}-\vec{K}-\vec{L}-\vec{M}} \approx \varphi$$

In a first approximation φ is expected to be zero for

(23)
131
large values of

$$E_5 = N^{-\frac{3}{2}} | E_{\vec{H}} E_{\vec{K}} E_{\vec{L}} E_{\vec{M}} E_{-\vec{H}-\vec{K}-\vec{L}-\vec{M}} |$$

Starting set determination

The determination of the starting set begins with a convergence procedure similar to that devised by Germain, Main and Woolfson (1970)³⁷. 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 a 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 step is a few cycles of symbolic addition using quartets and triplets, employing very strict acceptance criteria not allowing relations among the symbolic phases. This leads to a much larger starting set.

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The next step is the extension of the starting set. This is done in SIMPEL using triplet relations only. It is very essential 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 same symbolic phase, high acceptance limits are applied. In general these precautions make sure that the resulting set of symbolic phases contain the correct solution, that is to say that when the correct values for the symbols are substituted the phases of the reflections are good enough to image the structure.

Numerical values for the symbols:

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).

In general figures of merit can be based on any quantity which can be expected to be extreme for the set of correct signs. In 'SIMPEL' several FOM'S may be used.

- 1) The \sum_2 - consistency FOM Q (Schenk, 1971)³⁸.
- 2) The positive quartet criterion (PQC), Schenk and Kiers (1984)³⁹.
- 3) The Negative Quartet Criterion (NQC), (1974).

- 4) The ~~negative~~ Σ_1 - criterion (Overback and Schenk, 1976)⁴⁰
- 5) The Harker-Kasper criterion (HKC, Schenk, De Jong)⁴¹.

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 reflections can get a numerical phase. These phases are then used as starting point for a numerical phase extension, because in general the number of phased reflections is yet sufficient to calculate a good E-map. In the centrosymmetric case this is achieved by means of a fast Σ_2 refinement and extension, in the non symmetric case by means of a usual tangent refinement.

In the SIMPRL produces a set of h, k, l, E values with phases, which can be fed into an E map calculating program with subsequent interpretation.

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

4.6. Structure determination and refinement.

The structure was determined by the direct methods program SIMPRL-83²⁶ (C.F.Kiers and H.Schenk) using all reflections in order to employ all positive and negative quartet relationships, all signal relations and all special two dimensional quartets apart from triplets. The 300 strongest reflections were phased using 4 symbols. The E map with the highest & combined figure of merit revealed the structure

completely. Eventually the atomic positions were tested. The trial structure showed a R value of 22.9. The structure was refined by four cycles of fast diagonal least squares program having an over all temperature factor and scale factor, the then individual 17.6

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_c|}$$

For the space group $P2/a$

$$F_{hkl} = \sum f_r A_r$$

$$A_r = 2 \cos 2\pi \left(\frac{h}{4} x_r + ky_r + lz_r \right) \cos 2\pi \left(ky_r - \frac{h}{4} \right)$$

x_r, y_r, z_r are the co-ordinates of the rth. atom in the molecule. Summation is over the number of atoms in the asymmetric unit

$$f = \frac{4}{V_c} \sum_0^{\infty} \sum_0^{\infty} \sum_0^{\infty} \left[\sum_{h=2n} F_{hkl} \cos 2\pi (hx + lz) + F(hkl) \cos 2\pi (hx - lz) \right] \cos 2\pi ky - \sum_0^{\infty} \sum_0^{\infty} \sum_0^{\infty} \left[\sum_{h=2n+1} F(hkl) \sin 2\pi (hx + lz) + F(hkl) \sin 2\pi (hx - lz) \right] \sin 2\pi ky$$

isotropic temperature factors. The R value came down to three cycles of block diagonal least squares calculation with anisotropic temperature factors reduced the R value to . At this stage a difference Fourier was computed to locate the positions of the hydrogen atoms. All the hydrogen atoms could be located. For further refinement. For further refinement all reflections with $I \leq 2.5 \sigma(I)$ were removed. The structure was now refined through several cycles of block diagonal least squares allowing the non-hydrogen atoms, to vibrate anisotropically and hydrogen atoms having an overall fixed temperature factor.

A weighting scheme with

$$W = (5.96 + F_{\text{obs}} + 0.0031 F_{\text{obs}})^2 - 1 \text{ was applied.}$$

Extinction was taken into account with $\text{exp. } R = 0.85$. The R value converged to $R = 0.049$. $R_w = \left\{ \frac{\sum (W \Delta^2)}{\sum F_o^2} \right\}^{\frac{1}{2}} = 0.048$

The calculations were carried out with X-Ray-76 (Stewart et al)⁴³. The scattering factors were taken from Cromer and Mann⁴⁴.

4.7. Newman Projection

Newman projections along different C-C bonds are shown in the fig. 4.2. We can get an estimate of the dihedral ring angle from it.

4.8. Results and Discussions:

Molecular geometry and conformation.

In table - 1, important crystallographic data of the sample are given, in Fig. 4.3 shows the perspective drawing of the molecule viewed normal to the least squares plane. Final positions and thermal parameters of all the atoms are listed in Tables 4.2, 4.3 and 4.4 using the numbering scheme shown in Fig. 4.3.

Bond length and angles are given in Table 4.5. The average C-C bond length in the phenyl ring (C₁ - C₆) is 1.385 (2) Å the expected value⁴⁵ being 1.395 Å. The C-C bond lengths in the pyrimidine ring (C₇-N₂) are 1.374(2) Å and 1.381 (2) Å whereas the C-N bonds have the average value 1.336(2) Å which are comparable to those found in other pyrimidine compounds⁴⁶⁻⁴⁸. The cyclohexyl group (C₁₁ - C₁₆) has the average C-C bond length 1.530(3) Å which is reasonable. The average C-C, single bond length in the alkyl chain (C₁₄-C₂₂) is 1.516(3) Å which is lower by about 8 than the expected⁴⁵ value 1.541 Å. The cyano-group bond length (C₁₇-N₃) is 1.142 (3) Å which is close to the values found in other mesogenic compounds⁴⁹⁻⁵². The average internal (C-C-C) bond angles in the phenyl ring is 120.0(2)°. In the pyrimidine ring the internal angles (N₁-C₇-N₂), C₈-C₉-N₂ and C₁-C₈-C₉) have average value 124.5(2)° and the remaining three angles have average value 115.4(2)°. The internal (C-C-C) angles in the cyclohexane ring vary from 108.9° to 112.2° with an

average of $110.9(2)$ which is close to the reported values. The external non-hydrogen angles in the phenyl ring have an average value of $120.4(2)^\circ$ as expected. But the angles C4-C7-N1 and C4-C7-N2 have values $113.4(2)^\circ$ and $111.6(2)^\circ$ respectively indicating some strain between the pyrimidine and cyclohexane rings. The tetrahedral C-C-C bond angles in the alkyl chain range from 113.1° to 115.9° with a mean value $114.2(2)^\circ$ which exceeds the expected value by about 5° . The bond angle C1-C7-N3 is $178.2(2)^\circ$. Deviation from the linearity of the cyanobond was found in other cyanocompounds⁴⁹⁻⁵². The C-H distances ranges from 0.96 \AA to 1.14 \AA with a mean value of $1.03(2) \text{ \AA}$.

The length of the fully extended molecule estimated from a stereo model is found to 21.2 \AA whereas the length of the molecule (in the crystalline state) is 20.7 \AA . This indicates that in the crystalline state the molecule is in nearly most extended form.

The least squares planes for different parts of the molecule have been calculated. The equation of the constituent atoms have been listed in table 4.6. As expected, the phenyl ring and the pyrimidine ring show a high degree of planarity. The dihedral angle between the phenyl ring and the pyrimidine ring is 2° . The cyano-group atoms C7 and N 3 are displaced slightly upward from the plane of the phenyl ring. The equation of the plane of the cyclohexane ring is given in table 4.6. The cyclohexane ring is in chair form. Three atoms are displaced

upward from the plane and three are displaced downward. The displacements for C11 and C14 are approximately $\pm 0.2 \text{ \AA}$, for C12 and C15 $\pm 0.4 \text{ \AA}$ and for C13 and C16 $\pm 0.5 \text{ \AA}$. The dihedral angle between the cyclohexane ring and the pyrimidine ring is 78.4° .

Molecular Packing

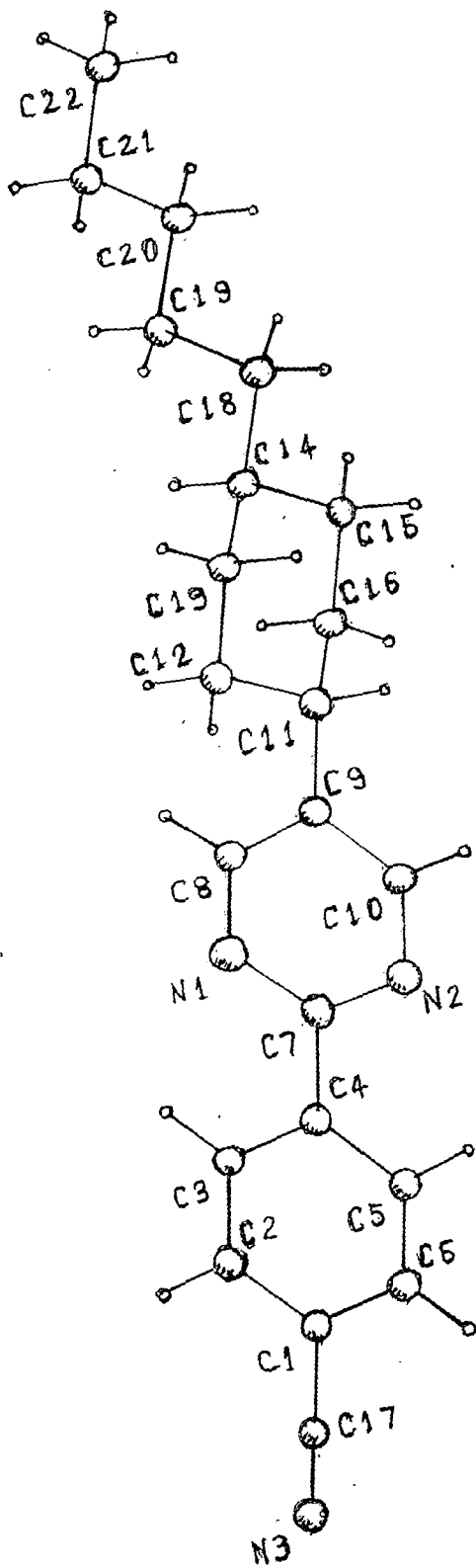
Packing of PCGP molecules in *ab* and *ac* plane are shown in Figure 4.4 and Figure 4.5 respectively. From these figures it is clear that the phenyl and pyrimidines are almost in the *ac* plane whereas the cyclohexane ring is almost at right angles to this plane. Pairs of molecules related by a centre of symmetry give rise to a sheet of parallel molecules in *ac* plane and these sheets of paired parallel molecules are stacked in an imbricated mode along the *b*-axis. The crystalline modification of PCGP therefore corresponds to the commonly found molecular packing in a nematogenic precursor. With the increase in thermal energy, a transformation in the liquid crystalline state is presumably accomplished by the breakdown of the molecular stacking along *b*-axis. This gives rise to three translational degrees of freedom of the pair of parallel molecules accompanied by rotation about the long molecular axis. The transition is thus displacive type.

All interatomic contact distances less than 4 Å involving non-hydrogen atoms only have been listed in table 4.7. We note that the only distance between C6 of molecule at x, y, z and N3 of molecule at

$$1 + \frac{1}{2} - x, y, z \text{ is close to the sum of the}$$

Vander Waal's radii of the atoms. The length of these pair of molecules which are in head to head configuration is 39.8 Å. On the otherhand the apparent length of the molecule in nematic state is found to be 26.2 Å, which is 1-2 times the most extended molecular length. This is often found in cyanocompounds and to explain this a bimolecular association of the molecules, because of cyanogroup interaction, is involved^{49,52-55}. We therefore infer that interaction between dipoles of cyanogroups exists both in crystalline and nematic phase. In crystalline state the overlap is small (in cyanoregion only) due to steric hindrance and in nematic state this is surpassed by increased thermal energy giving rise to large overlap (extending cyano to pyrimidine).

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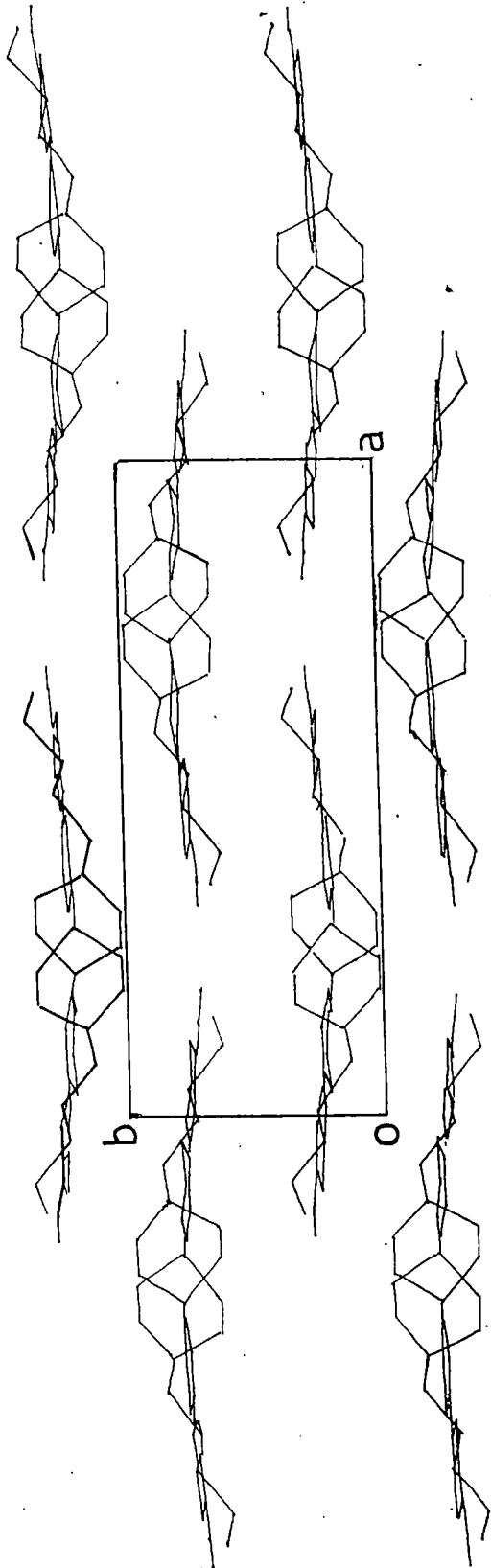


Fig. 4.4

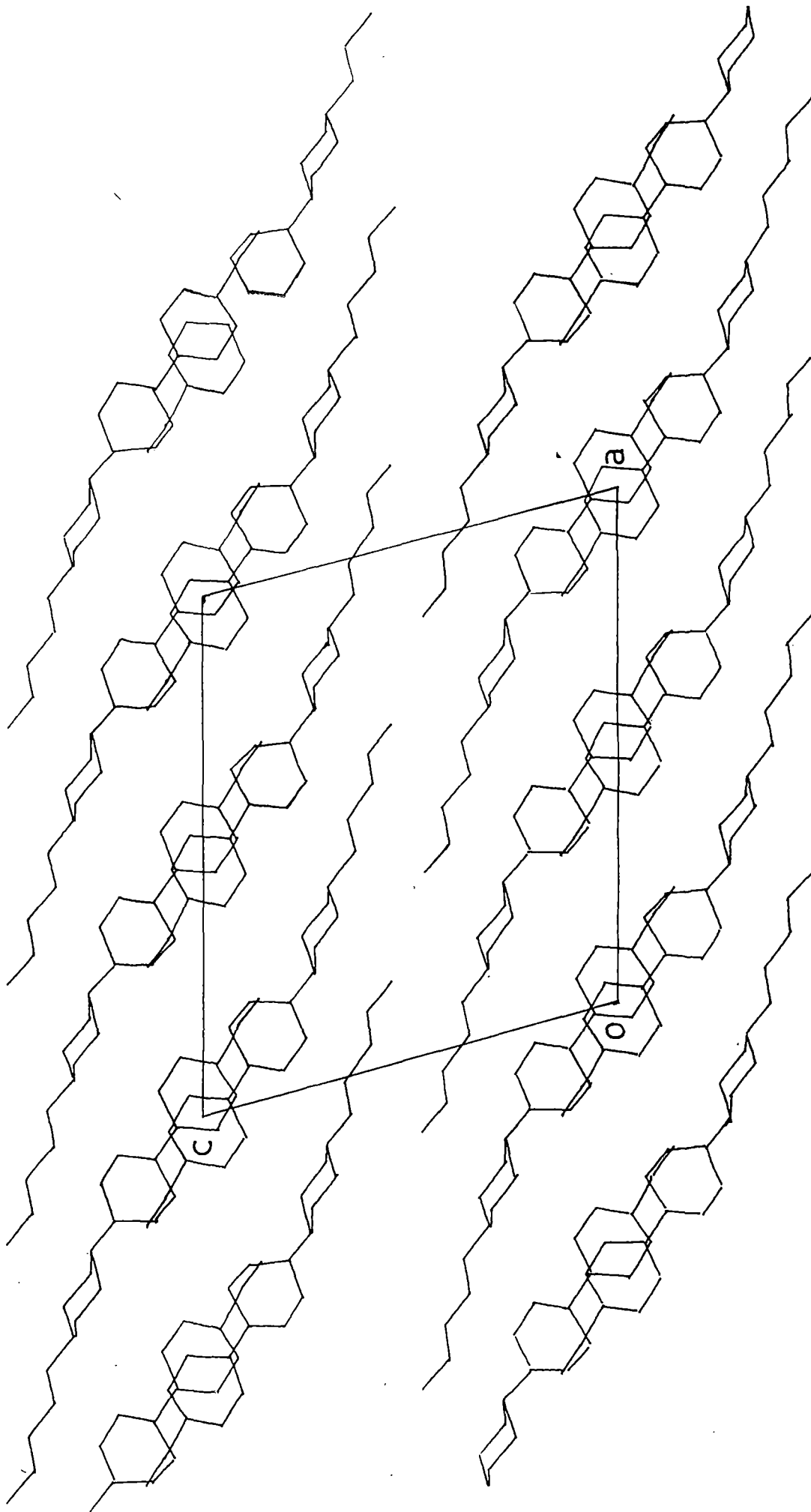
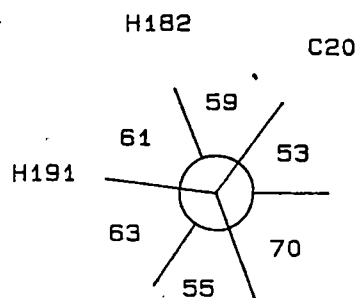
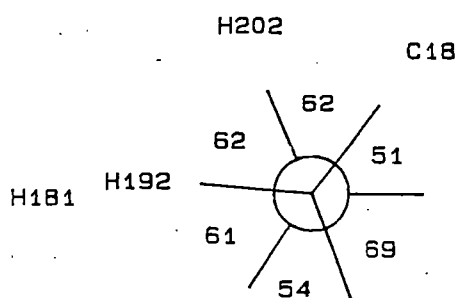


Fig. 4.5

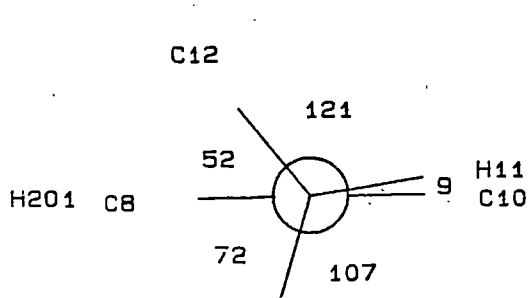
Newman projections of Page No. 1



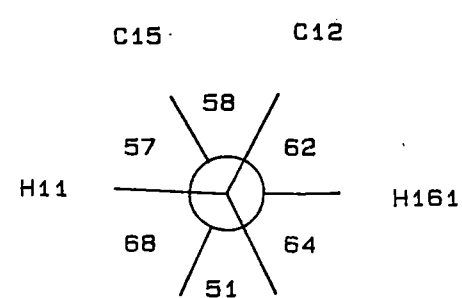
C14
(C19 - C18)



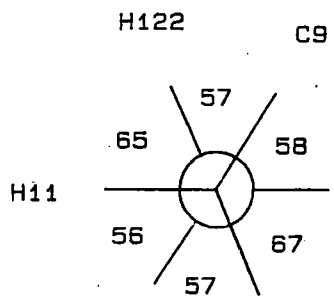
C21
(C19 - C20)



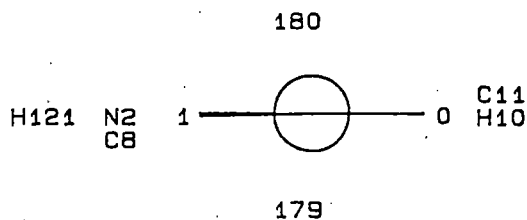
C16
(C11 - C9)



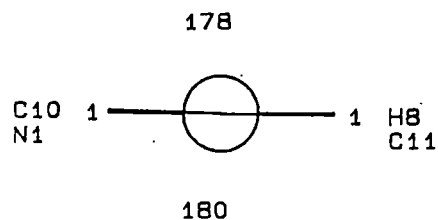
H162
(C11 - C16)



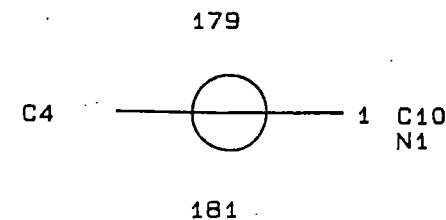
C13
(C11 - C12)



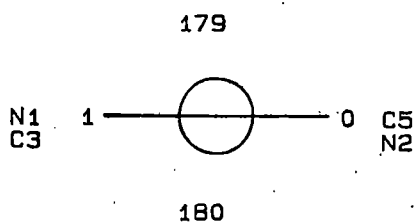
(C9 - C10)



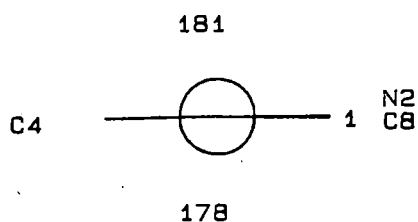
(C9 - C8)



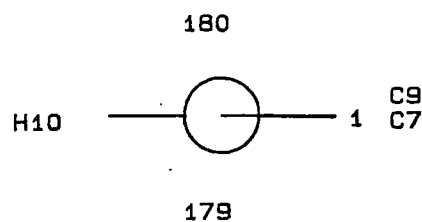
(C7 - N2)



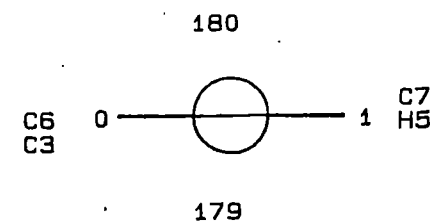
(C7 - C4)



(C7 - N1)



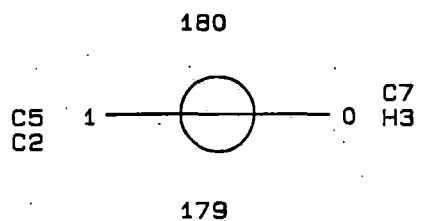
(N2 - C10)



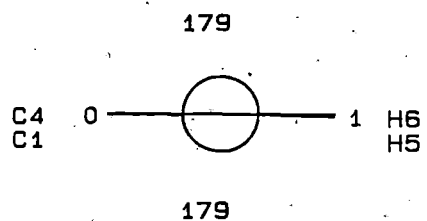
(C4 - C5)

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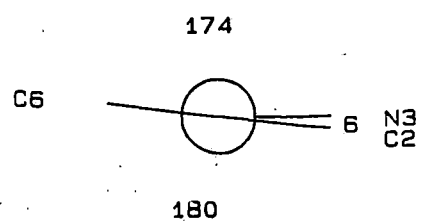
Newman projections of Page No. 2



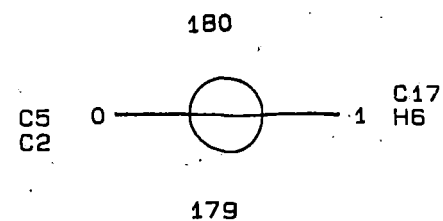
(C4 - C3)



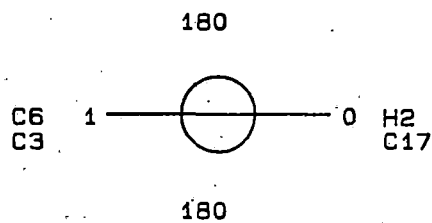
(C5 - C6)



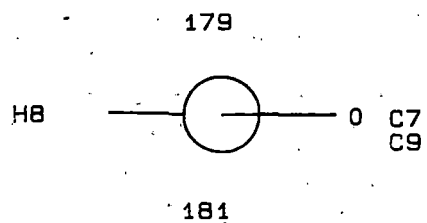
(C1 - C17)



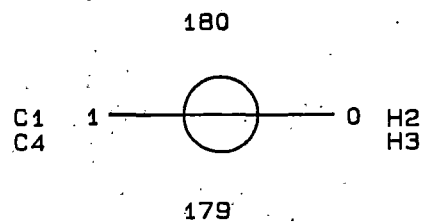
(C1 - C6)



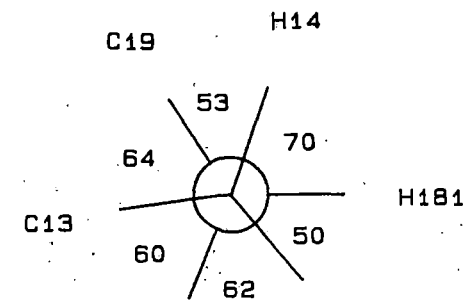
(C1 - C2)



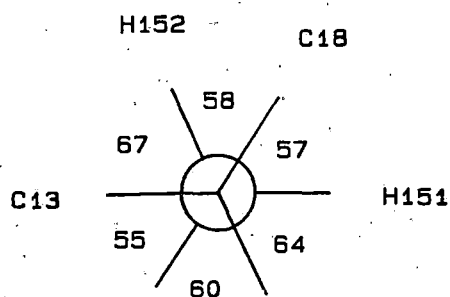
(N1 - C8)



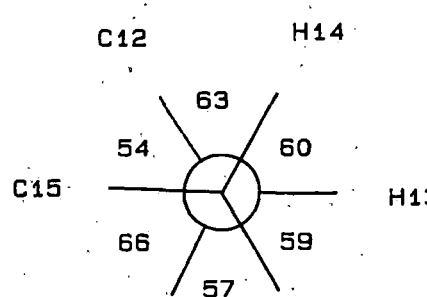
(C3 - C2)



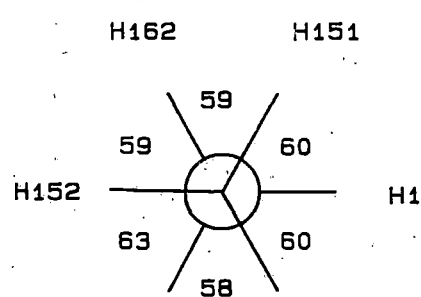
(C14 - C18)



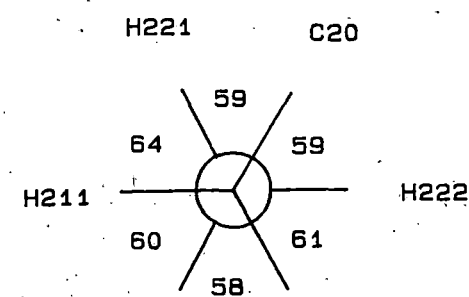
(C14 - C15)



(C14 - C13)

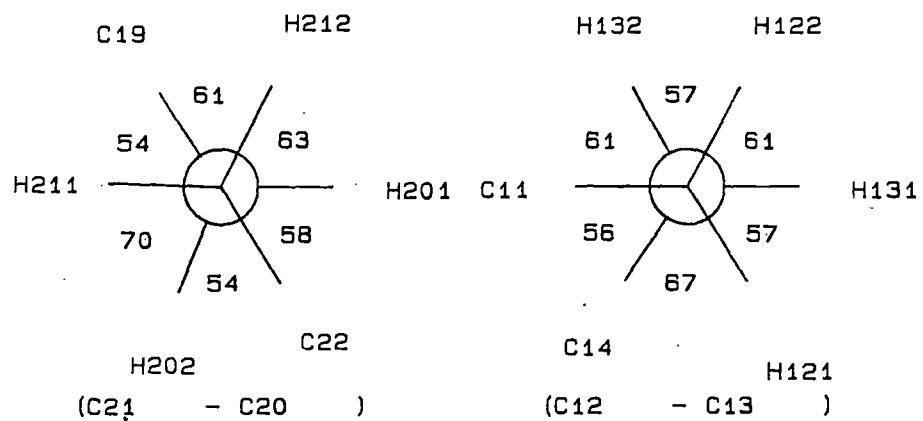


(C15 - C16)



(C21 - C22)

Newman projections of Page No. 3



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Table 4.1

Important Crystallographic Data

Mol. Formula	$C_{22}H_{27}N_3$
Mol. Weight	333.48 g/mol.
Crystal system	Monoclinic
Space group	$P2_1/a$
$a = 18.437(1) \text{ \AA}$	
$b = 7.1027(5) \text{ \AA}$	
$c = 15.342(1) \text{ \AA}$	
$\beta = 106.35(5)^\circ$	
$V = 1927.83 \text{ \AA}^3$	
$D_C = 1.15 \text{ g.cm}^{-3}$	
$D_m = 1.17 \text{ g.cm}^{-3}$	
$Z = 4$	

$$\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$$

Number of independent reflections 3277

Number of observed reflections 2246

(33)

Table 4.2

Fractional coordinates of the non-hydrogen atoms with e.s.d. in the parenthesis and equivalent isotropic thermal parameters.

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

Atom	X(6)	Y(6)	Z(6)	Ueq
C1	0.5925 (1)	0.2702 (3)	-0.0344 (2)	0.066 (1)
C2	0.5153 (1)	0.2615 (4)	-0.0779 (2)	0.070 (1)
C3	0.4647 (1)	0.2477 (3)	-0.0269 (2)	0.064 (1)
C4	0.4889 (1)	0.2442 (3)	0.0664 (1)	0.055 (1)
C5	0.5667 (1)	0.2534 (4)	0.1096 (2)	0.068 (1)
C6	0.6177 (1)	0.2668 (4)	0.0590 (2)	0.069 (1)
C7	0.4341 (1)	0.2310 (3)	0.1210 (1)	0.056 (1)
C8	0.3122 (1)	0.2178 (4)	0.1262 (2)	0.070 (1)
C9	0.3338 (1)	0.2169 (3)	0.2195 (1)	0.060 (1)
C10	0.4111 (1)	0.2204 (4)	0.2581 (2)	0.071 (1)
C11	0.2803 (1)	0.2084 (3)	0.2776 (2)	0.064 (1)
C12	0.2178 (1)	0.3576 (3)	0.2528 (2)	0.071 (1)
C13	0.1664 (1)	0.3466 (4)	0.3155 (2)	0.075 (2)
C14	0.1311 (1)	0.1515 (4)	0.3155 (2)	0.066 (1)
C15	0.1935 (1)	0.0040 (4)	0.3380 (2)	0.079 (2)
C16	0.2440 (1)	0.0143 (4)	0.2740 (2)	0.075 (2)
C17	0.6449 (1)	0.2834 (3)	-0.0883 (2)	0.069 (1)
C18	0.0824 (1)	0.1378 (4)	0.3813 (2)	0.077 (2)
C19	0.0130 (1)	0.2619 (4)	0.3598 (2)	0.077 (2)
C20	-0.0347 (1)	0.2347 (4)	0.4256 (2)	0.073 (2)
C21	-0.1003 (1)	0.3684 (4)	0.4102 (2)	0.081 (2)
C22	-0.1487 (2)	0.3382 (5)	0.4736 (2)	0.095 (2)
N1	0.36050(10)	0.2251(3)	0.0753 (1)	0.066 (1)
N2	0.46167(10)	0.2282 (3)	0.2106 (1)	0.071 (1)
N3	0.6849 (1)	0.2933 (4)	-0.1530 (2)	0.092 (2)



Table 4.3

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

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hkab^{*2} + 2U_{23}klbc^{*2})]$$

Atom	U11	U22	U33	U12	U13	U23
C1	0.056 (1)	0.054 (1)	0.080 (1)	0.0026(10)	0.033 (1)	-0.001(1)
C2	0.059 (1)	0.087 (2)	0.069 (1)	-0.005 (1)	0.026 (1)	-0.006(1)
C3	0.050 (1)	0.077 (2)	0.071 (1)	-0.002 (1)	0.023 (1)	-0.003(1)
C4	0.049 (1)	0.048 (1)	0.072 (1)	0.0042(9)	0.0247(10)	0.000(1)
C5	0.051 (1)	0.084 (2)	0.073 (1)	0.007 (1)	0.022 (1)	0.003(1)
C6	0.049 (1)	0.079 (2)	0.085 (2)	0.005 (1)	0.027 (1)	0.003(1)
C7	0.050 (1)	0.054 (1)	0.069 (1)	0.0047(9)	0.0220(10)	-0.002(1)
C8	0.051 (1)	0.090 (2)	0.074 (1)	-0.001 (1)	0.027 (1)	-0.003(1)
C9	0.056 (1)	0.062 (1)	0.070 (1)	0.003 (1)	0.027 (1)	-0.003(1)
C10	0.056 (1)	0.097 (2)	0.067 (1)	0.009 (1)	0.025 (1)	0.000(1)
C11	0.053 (1)	0.079 (2)	0.068 (1)	0.003 (1)	0.026 (1)	-0.002(1)
C12	0.065 (1)	0.066 (1)	0.094 (2)	0.003 (1)	0.041 (1)	0.002(1)
C13	0.066 (1)	0.073 (2)	0.100 (2)	0.005 (1)	0.047 (1)	-0.001(1)
C14	0.055 (1)	0.077 (2)	0.072 (1)	0.001 (1)	0.026 (1)	0.006(1)
C15	0.076 (1)	0.087 (2)	0.099 (2)	0.010 (1)	0.048 (1)	0.014 (1)
C16	0.076 (1)	0.070 (2)	0.093 (2)	0.009 (1)	0.046 (1)	0.008 (1)
C17	0.063 (1)	0.068 (1)	0.088 (2)	0.002 (1)	0.038 (1)	-0.003 (1)
C18	0.063 (1)	0.093 (2)	0.085 (2)	0.007 (1)	0.038 (1)	0.013 (1)
C19	0.059 (1)	0.093 (2)	0.088 (2)	0.005 (1)	0.036 (1)	0.011 (1)
C20	0.062 (1)	0.082 (2)	0.085 (2)	0.002 (1)	0.035 (1)	0.003 (1)
C21	0.066 (1)	0.087 (2)	0.102 (2)	0.004 (1)	0.040 (1)	0.003 (2)
C22	0.082 (2)	0.109 (2)	0.111 (2)	0.010 (2)	0.054 (2)	0.001 (2)
N1	0.0492 (9)	0.083(1)	0.070(1)	-0.0015(9)	0.0242(9)	-0.003(1)
N2	0.0523(10)	0.096(2)	0.070(1)	0.008 (1)	0.0245(9)	0.001(1)
N3	0.079 (1)	0.102(2)	0.113(2)	0.001 (1)	0.058 (1)	0.000(1)

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Table 4.4

Fractional coordinates of the hydrogen atoms and isotropic thermal parameters with e.s.d. in parenthesis. Atoms are numbered according to the heavy atoms to which they are attached.

Atom	x (σ)	y (σ)	z (σ)	U
H2	0.498 (1)	0.265 (3)	-0.148 (1)	0.078 (7)
H3	0.407 (1)	0.241 (3)	-0.057 (2)	0.090 (7)
H5	0.583 (1)	0.248 (3)	0.179 (1)	0.074 (6)
H6	0.673 (1)	0.274 (3)	0.092 (1)	0.083 (7)
H8	0.257 (1)	0.211 (3)	0.090 (2)	0.089 (7)
H10	0.433 (1)	0.217 (3)	0.326 (1)	0.076 (7)
H11	0.310 (1)	0.227 (3)	0.346 (1)	0.068 (6)
H14	0.098 (1)	0.130 (3)	0.249 (1)	0.062 (6)
H121	0.187 (1)	0.344 (3)	0.184 (2)	0.084 (7)
H122	0.244 (1)	0.483 (3)	0.258 (1)	0.083 (7)
H131	0.127 (1)	0.444 (4)	0.299 (2)	0.095 (8)
H132	0.198 (1)	0.371 (3)	0.385 (2)	0.092 (7)
H151	0.169 (1)	-0.118 (4)	0.336 (2)	0.104 (8)
H152	0.230 (1)	0.025 (4)	0.411 (2)	0.094 (8)
H161	0.211 (1)	-0.009 (3)	0.208 (1)	0.074 (6)
H162	0.284 (1)	-0.078 (4)	0.286 (2)	0.111 (9)
H181	0.065 (1)	-0.001 (4)	0.386 (2)	0.101 (8)
H182	0.117 (1)	0.166 (3)	0.447 (2)	0.085 (7)
H191	0.029 (1)	0.397 (4)	0.363 (2)	0.096 (8)
H192	-0.019 (1)	0.239 (3)	0.297 (1)	0.082 (7)
H201	0.001 (1)	0.247 (3)	0.496 (2)	0.088 (7)
H202	-0.055 (1)	0.099 (4)	0.422 (2)	0.097 (8)
H211	-0.133 (1)	0.356 (4)	0.340 (2)	0.099 (8)
H212	-0.078 (2)	0.502 (4)	0.419 (2)	0.125 (10)
H221	-0.169 (1)	0.204 (4)	0.466 (2)	0.119 (9)
H222	-0.117 (1)	0.352 (4)	0.541 (2)	0.114 (9)
H223	-0.191 (2)	0.431 (4)	0.465 (2)	0.128 (10)

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Table 4.5

Bond distances of the non hydrogen atoms in angstrom with standard deviations in parenthesis.

C1 - C2	1.393 (2)	C10 - N2	1.536 (2)
C1 - C6	1.377 (2)	C11 - C12	1.533 (2)
C1 - C17	1.441 (2)	C11 - C16	1.527 (2)
C2 - C3	1.380 (2)	C12 - C13	1.531 (3)
C3 - C4	1.374 (2)	C13 - C14	1.531 (3)
C4 - C5	1.402 (2)	C14 - C15	1.522 (3)
C4 - C7	1.486 (2)	C14 - C18	1.531 (2)
C5 - C6	1.381 (2)	C15 - C16	1.533 (3)
C7 - N1	1.341 (2)	C17 - N3	1.142 (3)
C7 - N2	1.325 (2)	C18 - C19	1.512 (3)
C8 - C9	1.374 (2)	C19 - C20	1.526 (3)
C8 - N1	1.341 (2)	C20 - C21	1.503 (3)
C9 - C10	1.381 (2)	C21 - C22	1.509 (3)
C9 - C11	1.505 (2)		

Bond distances of the hydrogen atoms in angstrom, with standard deviations in parenthesis.

C2 - H2	1.03 (1)	C16 - H161	1.04 (1)
C3 - H3	1.03 (2)	C16 - H162	0.96 (2)
C5 - H5	1.02 (1)	C18 - H181	1.05 (2)
C6 - H6	1.00 (2)	C18 - H182	1.05 (2)
C8 - H8	1.01 (2)	C19 - H191	1.00 (2)
C10 - H10	1.01 (1)	C19 - H192	0.99 (2)
C11 - H11	1.05 (1)	C20 - H201	1.10 (2)
C12 - H121	1.05 (2)	C20 - H202	1.03 (2)
C12 - H122	1.01 (2)	C21 - H211	1.08 (2)
C13 - H131	0.98 (2)	C21 - H212	1.03 (2)
C13 - H132	1.08 (2)	C22 - H221	1.02 (2)
C14 - H14	1.04 (1)	C22 - H222	1.04 (2)
C15 - H151	0.97 (2)	C22 - H223	1.00 (2)
C15 - H152	1.14 (2)		

Contd.....

(Table V contd...)

Bond angles of the non hydrogen atoms with standard deviations in parenthesis.

C2 - C1 - C6	119.9 (2)	C9 - C11 - C12	113.4 (2)
C2 - C1 - C17	119.2 (2)	C9 - C11 - C16	111.6 (2)
C6 - C1 - C17	120.9 (2)	C12 - C11 - C16	108.9 (2)
C1 - C2 - C3	119.6 (2)	C11 - C12 - C13	111.3 (2)
C2 - C3 - C4	121.3 (2)	C12 - C13 - C14	112.6 (2)
C3 - C4 - C5	118.7 (2)	C13 - C14 - C15	109.2 (2)
C3 - C4 - C7	121.0 (2)	C13 - C14 - C18	112.7 (2)
C5 - C4 - C7	120.3 (2)	C15 - C14 - C18	110.7 (2)
C4 - C5 - C6	120.4 (2)	C14 - C15 - C16	112.2 (2)
C1 - C6 - C5	120.2 (2)	C11 - C16 - C15	111.0 (2)
C4 - C7 - N1	117.1 (2)	C1 - C17 - N3	178.2 (2)
C4 - C7 - N2	117.6 (2)	C14 - C18 - C19	115.9 (2)
N1 - C7 - N2	125.3 (2)	C18 - C19 - C20	113.1 (2)
C9 - C8 - N1	124.2 (2)	C19 - C20 - C21	113.8 (2)
C8 - C9 - C10	114.1 (2)	C20 - C21 - C22	113.9 (2)
C8 - C9 - C11	124.8 (2)	C7 - N1 - C3	115.9 (2)
C10 - C9 - C11	121.1 (2)	C7 - N2 - C10	116.3 (2)
C9 - C10 - N2	124.1 (2)		

Bond angles of the hydrogen atoms with standard deviations in parenthesis.

C1 - C2 - H2	118 (1)	H151 - C15 - H152	107 (2)
C3 - C2 - H2	122 (1)	C11 - C16 - H161	108 (1)
C2 - C3 - H3	122 (1)	C11 - C16 - H162	108 (2)
C4 - C3 - H3	117 (1)	C15 - C16 - H161	109 (1)
C4 - C5 - H5	117 (1)	C15 - C16 - H162	114 (1)
C6 - C5 - H5	123 (1)	H161 - C16 - H162	107 (2)
C1 - C6 - H6	121 (1)	C14 - C18 - H181	111 (1)
C5 - C6 - H6	118 (1)	C14 - C18 - H182	108 (1)
C9 - C8 - H8	121 (1)	C19 - C18 - H181	108 (1)

Contd.....

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Table - 4.6

Equations of least squares planes, the individual and r.m.s. displacements (Δ) of the atoms from them.

Equations of the planes	Atoms	Δ in \AA	r.m.s. Δ in \AA
1. $-.0677 X + .9974$ $+ 0.246 = 1.156$	C ₁	-.0044	.0025
	C ₂	.0018	
	C ₃	.006	
	C ₄	-.0024	
	C ₅	.0032	
	C ₆	.0012	
	Other atoms	C ₁₇	
	N ₃		
2. $-.0365 X + .992$ $+ .0131 = 1.384$	C ₇	.0058	
	C ₈	-.0040	
	C ₉	.0077	
	C ₁₀	-.0059	
	N ₁	-.0025	
	N ₂	-.0012	
3. $.0406 X + .1891$ $+ .9819 = 4.5425$	C ₁₁	-.2060	
	C ₁₂	-.3757	
	C ₁₃	.5024	
	C ₁₄	.2352	
	C ₁₅	.3702	
	C ₁₆	-.5259	

Dihedral angle between plane 1 and plane 2 is 2.001° , plane 3 and plane 2 is 78.80°

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Table 4.7

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

C1 - C3 ^b	3.779	C6 - C16 ^e	5.996
C1 - C4 ^a	3.928	C6 - N3 ^d	3.499
C1 - C4 ^b	3.738	C7 - C17 ^a	3.913
C1 - C7 ^a	3.783	C7 - C17 ^b	3.723
C1 - C7 ^b	3.767	C8 - C8 ^c	3.906
C1 - N1 ^a	3.718	C8 - C17 ^a	3.828
C1 - N1 ^b	3.782	C8 - C17 ^b	3.711
C2 - C3 ^a	3.933	C8 - N1 ^c	3.762
C2 - C3 ^b	3.813	C8 - N3 ^a	3.632
C2 - C4 ^a	3.598	C8 - N3 ^b	3.474
C2 - C4 ^b	3.517	C9 - N3 ^a	3.841
C2 - C5 ^a	3.935	C9 - N3 ^b	3.705
C2 - C5 ^b	3.739	C10 - C21 ^f	3.781
C2 - C7 ^a	3.727	C10 - C21 ^g	3.781
C2 - C7 ^b	3.827	C11 - C21 ^f	3.937
C2 - C14 ^c	3.955	C11 - C21 ^g	3.937
C3 - C3 ^a	3.762	C12 - N3 ^b	3.821
C3 - C3 ^b	3.823	C15 - C22 ^e	3.911
C3 - C4 ^a	3.688	C16 - N3 ^a	3.573
C3 - C4 ^b	3.797	C17 - N1 ^a	3.620
C3 - C5 ^a	3.768	C17 - N1 ^b	3.500
C3 - C5 ^b	3.753	C17 - N3 ^d	3.922
C3 - C6 ^a	3.935	C18 - N2 ^e	3.910
C3 - C6 ^b	3.744	N1 - N3 ^a	3.932
		N1 - N3 ^b	3.688

None: x y z a: 1-x, y, z b: 1-x, 1-y, z c: 1/2-x, y, z,
 d: 1 + $\frac{1}{2}$ -x, y, z e: 1/2 + x, y, z f: 1/2+x-1, 1-y, z
 g: 1/2 + x, 1-y, z.

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In the present work I have reported the optical birefringence and X-ray diffraction studies of liquid crystalline substances. The samples studied are PCCPP, PCTP, PBBA, EBBA, PDCPP, 5OCB.

A hat stage was designed to study the textures and the phase transitions of the compounds under a polarizing microscope. A high temperature X-ray camera was designed and fabricated in our laboratory for taking flat plate photographs of liquid crystal samples in presence and absence of magnetic field.

From the observed textures under polarising microscope and diffraction photographs were samples PCTP, PBBA, EBBA and PCCPP were found to have nematic phase only.

X-ray diffraction photographs were analysed to obtain apparent molecular length (l), and average intermolecular distance (D) in the mesophase. In case of PBBA the apparent molecular length (l) in its most extended form determined by Princeton molecular model Kit is slightly higher than the length of the molecule (L). In case of PCCPP and PCTP π the ratio of l to L is 1.25 and 1.28 respectively which are probably due to molecular association as in other cyano compounds. It is a common feature in the liquid crystalline samples. The l and D values of the sample EBBA π were calculated and found to be almost equal to that obtained by Leadbetter et al.². As the results were already reported by them, so these are not repeated. The average intermolecular distances (D) are found to be in the expected range of 4.8 Å to 5.3 Å in all substances. The values are some time found to increase slightly with temperatures.

X-ray diffraction photographs of the samples were circularly scanned with a microdensitometer and the measured optical densities were converted to relative X-ray intensities using standard calibration method. From these intensity data normalised orientational distribution function $f(\beta)$ in a power series of $\cos^2\beta$ and the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were calculated. In principle we could also obtain $\langle P_6 \rangle$, $\langle P_8 \rangle$ etc. from our data but experimental uncertainties and truncation errors involved in series representation would make the values of these higher order parameters unreliable.

The experimentally obtained $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are compared with these obtained theoretical estimation. The $\langle P_2 \rangle$ values of the samples PCTP agree well with the M.S. theoretical values that of PBBA and BBBA also agrees well but slightly, lower near transition, but similar results found $\langle P_4 \rangle$ values of other also³, near the nematic - isotropic transition temperature, where the experimental $\langle P_2 \rangle$ values are significantly lower than the theoretical values. In case of PCOPF the order parameters are slightly less than the theoretical values even at lower temperatures. Such behaviour of the transition temperature, have been found in the determination of $\langle P_2 \rangle$ by magnetic anisotropy measurements⁵ Mitra and Paul, 1987. Low values of $\langle P_2 \rangle$ at near nematic isotropic transition temperatures have been reported⁶ (Chang, 1975; Sen et al, 1983; Madhusudana et al, 1971; Dunsauer et al, 1978). As said earlier this may be due to the fluctuation of the director which is more pronounced.

Crystal and molecular structure of FCCPP in the solid phase have also been determined. This is a part of our program to determine the conformational behaviour of a mesogenic compound in the crystalline phase.

We have undertaken the study of the crystal and molecular structure of a homologous series 5-(4-Alkylcyclohexyl)-2-(4-cyanophenyl) Pyrimidines all of them having nematic phase. In homologous series of thermal mesogens containing alkyl chains, the type of liquid crystalline phases formed, if any, depends on the chain length. The lowest members of the series may not yield liquid crystals those with intermediates chain lengths yield only nematic phases. Smectic phases of * 6 types A or C appears only when some critical chain length is reached. These properties clearly have a structural basis. The structures of ECCPP and HCCPP have also been determined which will be reported elsewhere.

The structures was solved by applying direct method package program 'SINPEL-83' to X-ray diffraction intensity data. The crystal belong to monoclinic system with space group $P2_1/a$. I found $a = 18.437 \text{ \AA}$, $b = 7.1027 \text{ \AA}$, $c = 15.342 \text{ \AA}$ and $\beta = 106.35^\circ$ with 4 molecules per unit cell. Least squares refinement leads to $R = .049$ and $R_w = .048$ for 2246 observed reflections. The molecules are find to be in their most extended conformation. As expected the phenyl ring and the pyrimidine ring show a high degree of planarity.

The dihedral angle between the phenyl ring and the pyrimidine ring is 2° . And the dihedral angle between the cyclohexane ring and the pyrimidine ring is 78.4° . The phenyl and pyrimidines are almost in the ac plane whereas the cyclohexane ring is almost at right angles to this plane. Pairs of molecules related by a centre of symmetry give rise to a sheet of parallel ~~axis~~ molecules in ac plane and these sheets of paired molecules are stacked in an imbricated mode along the c - axis. The crystalline modification of the sample therefore corresponds to the commonly found molecular packing in a nematogenic precursor. With the increase in thermal energy, a transformation in the liquid crystalline state is presumably accomplished by the breakdown of the molecular stacking along b-axis. It could transform from the solid phase to nematic phase by means of a single dispersive transition.

LISTFC FOR ** Q27SLA **

①

	H,0,0		-8	111	-103	4	133	140		H,0,7	
			-4	170	178	6	298	-306			
2	373	387	-2	169	189	8	34	31	12	68	-65
4	222	-227	0	182	-205	10	52	-56	8	236	-241
6	335	328	2	1677	1769	12	124	-121	6	219	-235
8	50	-53	4	914	-946	16	35	-29	4	183	181
10	61	56	6	339	346	18	43	38	2	534	-539
12	74	61	8	519	517				0	222	-214
14	24	24	10	39	-45		H,0,5		-2	23	-19
16	48	-45	12	32	35				-4	60	-61
18	78	-75	14	44	48	18	17	-16	-6	598	-595
20	34	-32	16	154	151	16	29	-25	-8	102	-113
			18	37	33	10	75	71	-10	63	65
	H,0,1					8	32	29	-12	141	141
				H,0,3		6	223	-224	-14	268	-276
20	45	-43				4	287	312	-16	47	-49
18	79	-74	16	43	43	2	830	914	-18	38	40
16	68	63	10	259	243	0	643	-705	-20	64	-62
14	75	86	8	465	466	-2	34	37			
12	51	49	6	193	-200	-4	48	-46		H,0,8	
10	77	-76	4	352	-368	-6	326	-323			
8	211	205	2	465	509	-8	508	-483	-20	39	-41
6	347	352	0	530	601	-10	118	112	-18	40	-41
4	156	160	-2	326	-358	-12	89	-84	-16	42	39
2	675	726	-4	522	548	-14	576	-580	-14	88	92
0	558	645	-6	73	-72	-16	437	-437	-12	24	-26
-2	41	50	-8	161	166	-18	65	63	-10	288	294
-4	179	-200	-10	21	25	-20	29	30	-8	58	52
-6	55	-52	-16	186	-178				-6	442	-439
-8	238	-256	-18	45	-48		H,0,6		-4	130	143
-10	43	44	-20	19	20				-2	82	-90
-12	92	-104				-20	27	-27	0	12	-10
-14	24	-23		H,0,4		-18	38	40	2	168	-163
-16	108	113				-16	194	191	4	123	131
-18	45	51	-18	36	38	-14	183	-199	6	154	-159
-20	29	29	-16	502	-516	-12	69	68	8	415	-423
			-14	206	-211	-10	28	-29	12	102	99
	H,0,2		-12	31	32	-8	468	-456	14	18	17
			-10	253	-247	-6	748	743			
-20	87	82	-8	769	746	-4	237	-235		H,0,9	
-18	166	-178	-6	152	-167	0	633	-682			
-16	148	-152	-4	161	178	2	254	-274	14	47	-45
-14	32	-33	-2	114	115	4	60	59	12	29	-27
-12	124	-131	0	312	-353	8	39	-38			
-10	107	111	2	706	-782	12	50	-52			

LISTFC FOR ** Q27SLA **

	H,1,1		6	219	-217	2	864	-831	2	491	-482
			5	368	-375	1	271	265	4	123	127
-13	35	-35	4	259	254	0	1329	-1266	5	113	119
-12	53	49	3	183	181	-1	305	294	7	28	-25
-11	50	-52	2	150	-149	-2	507	505	8	481	-463
-10	64	-56	1	641	-627	-3	529	-533	9	43	-41
-9	76	77	0	312	303	-4	80	-75	11	19	-18
-8	20	-22				-5	380	386	12	24	-25
-6	51	-54		H,2,0		-6	366	371	14	46	-47
-5	55	-60				-7	161	160	15	19	25
-4	69	-72	0	2622	-2381	-8	126	131	16	133	-129
-3	19	13	1	621	-595	-10	48	-47	19	43	-42
-2	207	217	2	1069	-1011	-11	35	35			
-1	39	-38	3	647	-626	-12	23	28		H,2,3	
0	50	-56	4	215	205	-13	39	41			
1	98	104	5	196	189	-15	109	-112	18	29	-26
2	96	-104	6	472	-449	-16	73	-79	17	18	-19
3	79	78	7	242	232	-17	19	20	16	33	-32
4	161	-165	8	31	26	-18	15	16	11	24	-22
5	286	-289	9	22	15	-19	53	57	10	113	-108
6	188	181	14	51	-51	-20	55	-55	8	477	-447
7	648	-624	16	60	62				7	405	391
8	137	131	17	54	-52		H,2,2		6	105	104
9	445	-416	18	20	18				5	200	-195
11	49	-48	19	43	44	-20	39	-35	4	182	184
12	25	-26	20	40	40	-19	52	-55	3	161	-161
13	50	48				-18	118	127	2	390	-388
14	28	25		H,2,1		-17	40	-40	1	161	167
15	27	30				-16	45	47	0	173	179
16	51	-48	19	24	21	-15	135	145	-1	96	-96
17	62	58	18	56	51	-14	105	114	-2	235	-229
19	64	62	16	69	-65	-12	68	65	-3	55	53
20	39	37	15	42	-43	-11	26	-25	-4	208	-218
			14	60	-63	-10	25	24	-5	49	53
	H,1,0		13	19	18	-9	61	-61	-6	40	42
			12	43	-40	-8	35	-34	-7	67	-64
19	20	-20	11	30	28	-7	47	-49	-8	109	-108
18	61	-55	10	27	-20	-6	57	-57	-10	75	-75
16	66	63	9	63	-66	-5	152	-156	-11	122	127
15	95	-89	8	33	-17	-4	217	-221	-12	44	48
13	30	31	7	316	-299	-3	64	-67	-13	110	-113
10	40	-37	6	423	-395	-2	177	171	-14	57	-58
9	88	-82	5	343	327	-1	425	428	-15	78	75
8	55	-50	4	388	375	0	488	-483	-16	255	256
7	317	-306	3	214	-200	1	48	-47			

LISTFC FOR ** Q27SLA **

	H, 2, 3		11	20	-19	0	459	443		H, 2, 8	
			10	62	-59	1	21	28			
-17	31	32	9	156	158	2	154	152	-20	25	28
-19	22	-24	8	58	-62	3	205	207	-18	48	47
-20	17	-13	7	28	-25	4	152	-156	-17	23	23
			6	97	98	5	66	-67	-16	88	-84
	H, 2, 4		5	121	-124	6	142	140	-15	41	-40
			4	321	-318	7	49	46	-14	28	28
-20	13	-13	3	142	-140	8	25	-25	-13	78	77
-17	43	-46	2	180	-185	10	47	52	-12	82	-79
-16	416	414	1	160	164	11	51	-51	-11	49	-49
-15	37	-37	0	331	348	13	24	25	-10	166	-169
-14	155	156	-1	22	-10	14	18	19	-9	26	-29
-13	102	103	-2	66	57				-8	42	38
-12	53	53	-4	30	34		H, 2, 7		-7	25	-25
-10	57	-57	-6	18	19				-6	118	115
-9	118	118	-7	94	-97	12	37	37	-5	52	-51
-8	231	-230	-8	153	155	9	28	-26	-4	76	77
-7	27	23	-9	36	-35	8	256	254	-3	53	58
-5	56	54	-10	220	217	7	43	45	-2	18	-21
-4	28	-24	-11	138	-138	6	136	136	-1	17	-21
-3	32	31	-12	33	-34	5	54	-47	0	32	34
-1	168	-163	-13	271	270	4	25	-24	1	59	-61
0	230	242	-14	582	578	3	106	99	2	180	175
1	144	152	-16	233	231	2	293	277	3	25	-23
2	39	-46	-17	169	-169	1	29	-30	4	58	-55
3	30	27	-19	23	-26	0	244	250	5	45	-45
4	216	220				-1	33	-32	6	86	90
5	116	112		H, 2, 6		-2	32	28	7	113	-109
6	151	150				-3	25	-28	8	337	328
7	53	-47	-21	15	-14	-4	33	27	9	133	131
8	125	123	-19	20	20	-5	32	31	11	59	59
9	127	-127	-18	95	-92	-6	203	200	12	30	-27
10	42	-42	-17	31	35	-7	20	-19	13	42	-44
11	26	23	-15	21	-21	-8	363	361	14	23	-25
12	74	76	-14	166	172	-9	301	-296			
13	27	25	-13	222	-216	-10	222	-217		H, 2, 9	
16	26	25	-12	107	-108	-11	154	156			
17	15	14	-9	118	120	-12	117	113	14	34	32
18	29	-27	-8	114	105	-13	106	104	11	16	-15
			-7	147	152	-14	70	68	10	215	211
	H, 2, 5		-6	20	8	-15	88	-91	8	244	239
			-4	21	0	-16	44	44	7	55	-53
16	18	16	-2	57	48	-20	57	56	6	62	63
12	57	50	-1	103	-100						

LISTFC FOR ** Q27SLA **

H,2,9			7	28	-30	H,2,13			-14	17	-15
			8	61	66				H,2,16		
5	60	58	9	46	-46	8	25	-22			
4	43	41	10	129	126	3	29	-29			
2	31	-34	11	36	38	2	56	64	-13	21	-18
0	65	-64	12	21	-18	-2	33	31	-10	22	-20
-2	35	30	H,2,11			-5	59	-59	-9	20	-17
-3	67	-68				-6	255	-249	-5	23	19
-4	137	-140				-8	208	-200	-3	20	18
-5	27	29	0	52	55	-9	82	76	-2	38	34
-6	68	-62	-2	31	-34	-10	49	47	0	15	-16
-7	43	43	-3	43	-45	-12	30	-32	2	24	-28
-8	141	-137	-4	72	-68	H,2,14			H,2,17		
-9	87	81	-5	41	40						
-10	74	-74	-6	61	-61	-14	24	20	-2	18	17
-11	44	-40	-7	66	63	-10	24	22	-4	19	16
-12	39	-37	-8	162	-158	-9	28	-24	-8	27	20
-13	67	-65	-9	38	-35	-8	39	-35	-9	14	-8
-14	23	24	-10	84	-80	-7	92	87	-10	17	-18
-16	108	-108	-11	75	-76	-6	269	-255	H,3,16		
-17	22	21	-13	48	-48	-5	27	27			
-18	28	26	-14	186	-196	-4	66	-65			
-19	24	-24	-15	38	39	-3	35	-35	-6	22	23
-20	17	-14	-16	39	-46	-2	51	-48	-8	26	-25
H,2,10			-18	16	-14	0	47	-47	-11	32	31
			-19	20	18	1	42	-42	H,3,15		
-18	16	13	H,2,12			3	40	42			
-17	25	24				4	31	-31			
-16	94	-95	-15	42	37	6	21	-18	-13	19	20
-14	116	-115	-14	100	-99	H,2,15			-11	36	33
-13	69	-73	-12	41	-41				-9	21	23
-12	215	208	-11	18	-17				-5	22	-24
-11	194	194	-10	57	54	4	17	25	-2	17	-14
-10	40	-36	-9	130	129	2	32	-36	1	59	65
-9	48	-45	-8	335	-327	0	16	-18	2	17	-18
-8	50	45	-7	89	-86	-1	44	42	3	41	46
-7	144	-141	-6	76	-77	-2	52	51	H,3,14		
-6	74	75	-5	81	-83	-5	43	-38			
-5	24	21	-3	44	48	-6	33	-31			
-4	26	-25	-1	43	-42	-7	39	41	2	37	37
-2	66	65	0	62	62	-8	37	37	1	78	84
-1	51	53	1	38	41	-10	31	28	0	20	-22
5	29	-30	3	16	-10	-12	36	-28			
6	53	-48	4	27	26	-13	25	20			

LISTFC FOR ** Q27SLA **

	H, 3, 14		-12	28	-28	-11	79	-77	-13	121	-114
			-13	59	-58	-12	66	62	-14	60	60
-1	27	28	-15	36	-40	-15	20	21	-15	26	-24
-5	22	23	-17	39	-39				-16	40	39
-6	66	-64					H, 3, 9		-17	20	-20
-8	61	61		H, 3, 11					-19	33	-35
-9	26	28				-17	25	25			
-11	15	11	-18	13	-13	-15	33	33		H, 3, 7	
-12	23	20	-17	23	-24	-14	31	34			
-15	41	-38	-15	25	-25	-13	84	-84	-20	15	16
			-14	16	13	-11	39	37	-19	24	-25
	H, 3, 13		-12	22	-18	-10	155	154	-17	23	-23
			-11	37	-39	-9	39	41	-16	30	-30
-16	38	-33	-10	114	-105	-8	182	-180	-15	28	-29
-13	20	-25	-9	130	125	-7	70	68	-14	78	-77
-12	21	18	-8	105	103	-6	23	21	-13	130	125
-11	24	-24	-7	117	114	-3	27	-27	-12	198	195
-10	57	-57	-6	48	46	-2	27	-25	-11	52	61
-9	41	-36	-5	31	-29	-1	36	38	-10	178	-178
-8	67	-66	-4	33	37	0	25	-24	-9	134	136
-7	47	43	-3	27	-24	1	102	95	-8	48	47
-6	72	66	-2	49	-53	3	44	41	-7	104	-95
-5	47	47	-1	19	-18	7	68	63	-6	21	-23
-1	53	55	1	28	-24				-5	118	-116
0	21	-22	2	48	47		H, 3, 8		-3	25	25
1	29	37	3	40	-37				-2	58	-55
2	31	38	5	35	-35	10	70	-68	-1	201	198
4	23	21	9	50	45	9	88	-89	1	166	154
						8	60	56	3	20	16
	H, 3, 12			H, 3, 10		6	30	32	5	59	-53
						4	55	51	7	253	-243
9	18	-14	10	52	50	3	89	87	8	21	-19
5	17	-19	9	44	44	2	25	25	9	122	-121
3	28	25	8	34	-32	1	149	141	11	32	32
2	40	-38	6	30	-30	-1	101	100	14	20	-23
1	48	48	5	20	-19	-2	86	-86			
0	46	50	1	39	32	-3	48	-45		H, 3, 6	
-1	85	88	0	49	-49	-4	36	40			
-4	23	25	-2	49	49	-5	29	-22	13	20	23
-5	66	62	-4	43	-47	-7	39	-42	12	22	24
-7	276	268	-5	23	-25	-8	126	125	11	45	40
-8	122	-116	-6	49	46	-9	191	-192	10	34	-35
-9	112	108	-8	120	119	-10	53	53	9	63	63
-10	72	69	-9	145	131	-11	84	-81	8	195	-186
-11	20	19	-10	146	-143	-12	251	-251			

LISTFC FOR ** Q27SLA **

(1)

	H,3,6		-2	88	80	-19	34	35	13	39	-38
			-1	65	-60	-20	17	14	12	18	20
7	61	-57	0	100	-91				11	40	37
6	112	105	2	22	-20		H,3,3		9	158	149
5	50	48	3	173	170				8	90	87
4	44	39	4	24	-19	-18	79	82	7	42	-44
3	41	31	5	73	-74	-17	120	-118	6	179	175
1	21	17	6	90	-90	-16	40	40	5	99	-90
0	64	63	7	29	-23	-15	210	-217	4	449	-435
-1	101	86	8	95	93	-14	215	-225	3	352	-335
-2	30	35	9	22	-22	-12	76	74	2	68	68
-3	74	74	15	23	-25	-11	94	-95	1	381	-358
-4	137	-148	16	21	20	-10	40	43	0	114	110
-5	173	-173				-9	69	-65	-1	105	-102
-6	46	55		H,3,4		-8	18	21	-2	309	301
-7	340	-329				-7	92	-84	-3	22	-22
-8	39	40	17	58	-61	-6	50	-47	-4	65	-63
-9	122	-117	15	44	-44	-5	197	182	-5	27	-23
-10	82	82	11	29	33	-4	244	223	-6	222	-220
-11	41	-41	9	31	-31	-3	170	170	-7	34	-32
-12	72	70	8	85	80	-2	286	-270	-10	25	28
-13	97	95	7	80	76	-1	203	193	-11	60	64
-14	109	-106	6	126	-120	0	71	64	-12	53	-53
-15	77	72	5	56	55	1	16	20	-13	63	61
-17	14	-14	4	132	127	2	184	172	-15	54	-53
-18	18	-16	3	179	181	3	24	-18	-16	23	-18
-19	26	-26	2	106	-104	4	20	20	-17	116	-117
			1	88	87	5	261	243	-18	20	16
	H,3,5		0	19	-21	6	88	83			
			-1	66	-60	7	82	76		H,3,1	
-20	17	-17	-2	47	43	8	193	-183			
-19	40	-39	-3	42	41	9	65	57	-19	26	29
-18	22	20	-4	118	-106	12	26	23	-17	20	-20
-17	16	-15	-5	62	-53	14	24	26	-16	41	-44
-15	21	23	-6	117	-125	15	90	-87	-14	52	55
-14	66	64	-7	211	-209	16	16	-16	-12	29	-30
-13	103	-106	-8	23	-18	17	59	-62	-11	56	58
-12	172	-173	-9	132	-118	18	23	-22	-10	41	43
-10	238	239	-10	129	-139				-9	99	-96
-9	336	-328	-11	105	107		H,3,2		-8	26	-28
-7	294	-288	-12	30	34				-6	282	282
-6	108	-109	-14	97	101	17	21	-15	-5	35	-28
-5	70	-72	-15	123	-124	16	41	-40	-4	254	-244
-4	38	-27	-17	22	-19	15	80	-75	-3	326	320
-3	42	38	-18	19	-20	14	33	29			

LISTFC FOR ** Q27SLA **

(10)

	H,3,1		3	245	230				-2	66	63
			4	265	266	-16	63	-64	-4	115	107
-2	272	258	5	135	-127	-15	49	-51	-5	29	-34
-1	343	-315	6	115	109	-13	20	16	-6	17	-13
0	79	-79	8	20	-17	-12	130	-138	-7	39	36
1	441	-415	10	22	-17	-9	16	18	-8	23	14
2	67	-62	13	17	-16	-8	17	15	-9	17	17
3	185	183	14	24	-22	-6	27	32	-10	90	94
4	210	207	15	20	24	-5	47	44	-11	78	-79
5	241	236	16	42	37	-4	62	62	-12	26	-26
6	431	-403	17	22	19	-3	76	71	-13	31	34
7	467	440	18	39	-38	-2	69	65	-14	41	-36
8	48	39				-1	195	-181	-15	100	-104
9	175	169		H,4,1		0	162	147	-16	115	-115
10	39	40				1	155	-147	-18	63	-68
11	20	23	17	33	28	2	280	251			
13	69	-68	16	27	27	3	106	101		H,4,4	
14	39	-30	15	30	28	4	130	-133			
16	34	33	14	76	72	5	85	-82	-18	30	-33
19	26	-28	9	48	46	6	131	122	-17	100	104
			8	116	112	7	72	-73	-16	194	-196
	H,3,0		7	143	139	8	137	127	-15	39	-38
			6	66	65	9	89	86	-14	203	-205
18	20	18	5	183	-173	10	50	45	-13	86	-86
15	28	33	4	243	-243	11	19	-15	-12	96	100
14	34	-34	3	247	217	14	49	51	-11	20	-15
13	16	16	2	496	458	15	16	-15	-10	22	-18
12	49	49	1	42	-37	16	40	42	-9	78	-78
11	17	20	0	660	617	17	26	28	-8	102	100
10	54	49	-1	383	-360				-7	54	55
9	68	64	-2	102	-94		H,4,3		-5	57	-52
8	25	27	-3	159	130				-3	30	-28
7	221	201	-4	195	-195	16	38	36	-2	89	-73
6	131	129	-5	156	-150	15	38	-35	0	68	-65
5	93	91	-6	83	-88	13	34	-28	1	86	-83
4	74	69	-8	38	-38	11	41	35	2	109	105
2	381	-355	-9	38	38	10	68	64	3	33	34
1	35	33	-11	41	-38	8	192	182	4	80	-79
0	238	220	-12	57	67	7	220	-214	6	248	-237
			-13	63	-60	5	42	41	8	35	35
	H,4,0		-15	32	38	4	110	100	14	16	-20
			-16	16	-14	3	72	70	15	29	21
0	858	799	-17	17	-21	2	21	-24			
1	388	369				1	106	-98			
2	326	306		H,4,2		-1	52	52			

LISTFC FOR ** Q27SLA **

(11)

	H,4,5		2	90	-80	-2	23	-24	-8	74	-75
			3	111	-109	-1	27	29	-7	39	38
12	27	-25	4	82	85	1	69	72	-4	66	65
9	52	-55	5	67	68	2	61	-68	-3	19	24
6	156	142	6	77	-77	4	45	-43	-2	42	-44
5	83	84	7	41	-43	5	29	30	0	45	-44
3	17	17	8	75	-73	6	24	-20	1	17	17
2	48	48	10	34	32	7	88	88	4	15	13
1	152	-141	11	17	16	8	138	-138	7	27	38
0	159	-156	12	29	-29	9	95	-98	9	44	46
-1	50	66				10	55	-57	10	53	-60
-2	32	-29		H,4,7		11	34	-34			
-3	39	34				12	17	15		H,4,11	
-6	17	22	10	36	-37	13	16	19			
-7	19	-19	9	50	-50				9	21	23
-9	24	-21	8	91	-86		H,4,9		6	17	-12
-10	163	-172	6	192	-187				1	25	-26
-11	104	98	5	52	52	11	33	-37	0	19	23
-12	118	-120	4	54	54	10	80	-88	-2	33	-34
-13	176	-174	3	92	-91	8	221	-223	-3	21	22
-14	201	-198	2	126	-124	7	74	71	-4	27	28
-15	60	61	1	34	32	6	18	-22	-6	22	26
-16	179	-181	0	136	-135	0	32	30	-8	160	160
-17	111	113	-1	59	59	-1	39	-41	-10	65	65
-18	32	33	-2	36	-35	-2	41	42	-13	51	55
-19	19	-20	-5	23	-26	-3	29	26	-14	78	81
			-6	87	-89	-4	23	-21	-15	38	-40
	H,4,6		-8	151	-150	-8	66	67	-16	37	42
			-9	192	197	-9	39	-37			
-18	43	44	-10	31	-35	-10	126	131		H,4,12	
-16	52	-54	-11	79	-80	-13	21	20			
-15	69	71	-14	65	-65	-15	40	39	-15	45	-45
-14	143	-135	-15	58	56	-16	40	41	-14	60	64
-13	37	36	-16	38	39	-17	29	-28	-12	17	20
-10	195	207	-18	41	-40				-11	22	24
-8	131	-127					H,4,10		-9	116	-118
-7	79	-80		H,4,8					-8	135	133
-6	60	-60							-7	81	84
-4	23	-16	-15	29	28	-17	43	-44	-6	85	84
-3	34	-35	-13	46	-45	-16	59	61	-5	56	55
-3	34	-35	-12	48	49	-14	67	67	-2	28	33
-2	51	-35	-10	26	29	-13	88	89	-1	23	23
-1	63	65	-7	47	47	-12	44	-43	0	32	-33
0	191	-191	-6	70	-72	-11	104	-105	1	26	-28
1	66	-69	-4	23	-23	-10	44	-47			
						-9	42	42			

LISTFC FOR ** Q27SLA **

H,4,13			-2	40	41	H,5,9			-13	36	-31
			-1	27	-31				-12	45	43
1	16	13	0	29	-30	-14	28	-29	-11	52	-56
0	66	-66	H,5,12			-13	30	29	-10	43	-46
-4	15	17	1	35	-36	-10	36	35	-9	75	-80
-5	73	73	-1	77	-77	-9	57	-54	-7	90	92
-6	135	137	-2	20	24	-8	63	-59	-6	61	-68
-7	28	-24	-3	32	33	-7	55	-52	-5	74	72
-8	115	116	-2	20	24	-6	46	48	-4	60	64
-9	74	-77	-3	32	33	-4	44	-45	-3	49	-58
-10	18	-17	-5	36	-34	-3	22	22	-2	67	68
-12	19	15	-6	41	-43	-2	51	48	-1	69	-70
-13	15	-14	-7	139	-139	-1	46	-48	0	36	33
H,4,14			-8	24	26	0	29	28	1	64	-61
			-9	64	-68	1	39	-44	2	55	-52
-8	68	70	-10	50	46	6	30	25	3	39	-39
-7	80	-82	-13	24	26	7	35	-38	5	21	15
-6	132	138	H,5,11			8	34	-35	6	72	-62
-5	19	20	-13	19	16	H,5,8			7	154	162
-4	52	50	-10	28	33	10	19	23	8	48	53
-2	28	-28	-9	58	-57	9	24	29	9	46	45
-1	15	-8	-8	19	23	6	20	-20	10	39	39
0	60	62	-7	47	-44	5	19	22	H,5,6		
3	20	-19	-6	103	-101	3	38	-41	11	19	-20
H,4,15			-5	24	-27	2	18	-20	8	49	47
			-4	42	42	1	88	-90	5	46	-48
0	22	21	-2	36	-33	-1	25	-25	4	27	-27
-1	28	-30	-1	38	35	-3	40	44	2	19	18
-6	16	20	2	24	-23	-5	32	-33	1	38	-32
-7	37	-42	5	19	16	-6	49	-50	0	65	-62
-8	33	-32	H,5,10			-7	29	29	-1	69	-63
H,5,14			-8	29	29	-8	29	29	-4	26	18
			-9	108	113	-9	108	113	-5	84	90
-4	16	19	8	21	23	-10	31	-31	-6	78	83
H,5,13			-3	39	-42	-11	43	43	-7	109	107
			-5	26	25	-13	30	30	-8	101	-112
-9	16	14	-6	22	-20	-14	25	26	-9	70	70
-8	24	28	-7	30	-30	-16	28	-29	-11	48	53
-6	36	35	-8	60	-59	H,5,7			-12	39	-37
-4	35	-39	-9	65	-61	-15	23	-22	-13	63	-67
-3	25	-24	-11	33	35	-14	34	37	-16	56	62
			-12	20	21						
			-14	37	-38						

LISTEC FOR ** Q27SLA **

	H,5,5					-2	58	57	5	58	-56
			-17	59	68	-3	64	64	4	98	92
-16	16	-20	-15	79	84	-7	23	18	2	86	-83
-13	39	42	-14	38	44	-13	53	-56	1	35	34
-12	43	-40	-13	27	29	-14	52	56	0	194	199
-11	21	19	-12	24	-21	-15	65	72			
-10	51	-51	-11	85	93	-16	24	28		H,6,0	
-9	161	166	-10	25	-17	-17	33	40			
-7	121	123	-9	28	25				0	142	-142
-6	73	79	-8	27	23		H,5,1		1	194	-195
-5	19	18	-7	31	29				2	245	-241
-1	16	19	-6	34	33	-13	18	18	3	19	19
1	31	-30	-5	28	-24	-11	18	-19	4	55	-54
2	81	79	-3	89	-87	-10	33	-35	5	18	15
3	61	-55	-2	57	-56	-9	25	22	7	50	-48
4	81	-78	-1	91	-87	-8	31	-26			
5	80	78	1	82	77	-7	57	54		H,6,1	
6	62	63	2	111	-111	-5	24	17			
9	27	27	3	52	52	-4	46	-48	14	26	-28
			4	70	72	-3	153	-156	9	33	-37
	H,5,4		5	188	-186	-2	66	-65	8	24	-28
			7	23	-22	-1	155	148	6	54	-51
9	30	-28	9	26	-24	0	69	-73	4	83	83
6	26	-21	10	31	29	1	189	183	3	155	-154
4	32	32	12	17	-14	2	115	110	2	158	-158
3	97	-95	14	20	-19	3	121	-131	0	224	-223
2	68	-66	15	46	48	4	97	93	-1	214	208
0	81	76				5	91	-93	-2	42	45
-1	29	20		H,5,2		6	29	30	-3	76	75
-4	53	58				7	180	-174	-6	41	41
-5	28	24	15	30	28	9	73	-76	-9	21	-24
-6	48	50	14	35	-31	10	54	-55	-11	20	23
-7	102	107	13	35	33	13	37	39	-13	30	30
-8	57	63	12	32	-29	14	46	43			
-9	75	70	11	30	-28	15	18	14		H,6,2	
-10	52	-60	9	58	-59						
-11	85	-91	7	54	-51		H,5,0		-14	37	41
-12	64	66	6	64	57				-13	17	-18
-13	20	20	5	125	124	14	20	-19	-12	16	16
-14	21	17	4	33	-32	13	21	-26	-11	23	28
-15	52	52	3	151	149	12	22	-21	-9	19	-22
-16	45	-48	2	90	91	9	64	-64	-2	19	-26
-17	44	48	1	47	40	8	56	-52	-1	25	23
			0	206	-195	7	77	-72	0	154	-153
	H,5,3		-1	92	88	6	37	-40			

LISTFC FOR ** Q27SLA **

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	H,6,2		-1	81	72	3	28	25		H,6,9	
			0	48	46	4	30	-28			
1	149	143	1	24	24	5	28	-31	6	32	36
3	110	-112	2	57	-55	6	56	56	-2	27	-25
4	59	-58	4	83	86	8	18	13	-3	34	36
5	78	79	5	73	-70	9	15	14	-4	16	-20
7	41	40	7	45	51				-5	42	-42
8	56	-60	9	39	35		H,6,7		-6	40	47
9	54	-55	10	18	-20				-8	64	-69
10	22	-27	11	20	-24	9	52	57	-9	33	-39
						8	54	57	-11	42	46
	H,6,3			H,6,5		6	55	53	-12	20	-22
						5	48	-49			
10	21	-25	6	43	-42	4	33	32		H,6,10	
9	19	-16	4	30	-28	3	51	57			
8	66	-68	2	43	45	1	18	-19	-12	22	21
7	49	53	1	73	72	0	59	62	-8	36	36
5	16	13	-1	59	-65	-1	27	-31	-7	18	16
4	51	-48	-2	37	36	-2	28	30	-4	31	-30
3	18	14	-3	17	-23	-3	33	-32	-3	29	-31
2	42	-44	-4	31	37	-5	37	43	-2	53	53
1	32	26	-5	32	-37	-6	21	20	-1	20	-18
0	27	30	-7	38	44	-7	25	-31			
-2	73	-70	-8	19	-16	-8	86	92		H,6,11	
-3	40	-40	-10	71	78	-9	24	-23			
-5	38	41	-12	22	27	-10	20	-23	-1	27	27
-7	30	-34	-13	30	32	-11	27	-25	-3	19	-22
-8	26	-24	-14	114	121	-12	53	55	-4	21	23
-10	34	-32				-13	15	-13	-6	65	-65
-12	27	25		H,6,6					-7	76	-75
-13	39	39					H,6,8		-8	37	-36
-15	59	63	-14	43	50				-9	32	34
			-13	61	64	-13	16	-14	-10	40	-41
			-11	24	23	-12	29	-34			
			-10	31	-33	-11	26	29		H,6,12	
-15	47	51	-9	66	-73	-8	21	21			
-14	71	78	-7	41	48	-7	45	-46	-8	71	-73
-13	51	58	-6	66	72	-5	17	15	-7	30	-30
-10	41	-44	-4	27	-34	-4	56	63	-6	24	-27
-9	50	51	-3	35	42	1	53	-55	-5	32	-32
-8	19	21	-2	27	31	5	21	-22	0	22	22
-7	38	-41	-1	40	-43	6	28	25			
-6	32	-36	0	89	88	7	35	-40			
-5	19	25	1	72	71	8	62	65			
-2	48	43	2	37	35						

LISTEC FOR ** Q27SLA **

115

	H,7,9		-10	24	32	9	25	29	1	57	63
			-9	44	-52	8	39	-42	2	43	51
-7	29	29	-7	45	-50	7	23	23	3	23	26
-2	20	-21	-6	39	-48	3	57	-61	4	23	27
1	20	24	-5	22	-23	1	47	-46			
			3	16	-15	0	49	53		H,8,1	
	H,7,8		7	25	-26	-1	64	-66			
			8	39	-38	-2	38	-34	4	33	38
2	25	25				-9	26	-28	3	48	58
1	37	43		H,7,4					2	17	23
0	13	-17					H,7,1		0	24	34
-3	23	-24	8	18	21				-1	73	-88
-4	19	21	6	23	-22	-7	31	-35	-2	42	50
-6	18	16	2	28	33	-5	20	-16	-3	33	-33
			1	22	-25	-3	23	23	-6	14	15
	H,7,7		0	41	-40	-2	66	69			
			-4	24	-24	-1	26	-30		H,8,2	
-8	35	37	-6	37	-41	0	16	15			
-7	30	-36	-7	40	-42	1	18	-19	-2	32	36
-4	41	-46	-8	20	-21	2	63	-66	-1	24	-24
-3	20	21	-9	26	-25	4	44	-49	0	17	23
-2	26	-32	-10	25	27	5	25	27	1	42	-48
-1	28	28				6	22	-18	2	41	46
0	16	-19		H,7,3		7	35	-39	3	26	32
4	27	27				8	25	24			
			-9	16	-17	9	40	45		H,8,3	
	H,7,6		-5	25	-24						
			-2	18	19		H,7,0		1	16	-24
1	32	30	-1	30	29				0	32	36
0	46	43	0	59	60	10	17	20			
-5	39	-47	1	26	-35	8	45	45		H,8,4	
-6	17	-17	3	15	11	7	50	54			
-7	31	-35	4	36	-40	4	23	-21	-1	26	-27
-8	28	32	6	21	-20	1	22	-24	1	16	-16
-9	34	-41	7	18	18	0	41	-43	2	31	-30
-10	23	27									
				H,7,2			H,8,0				
	H,7,5		10	30	35	0	102	114			

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