

CHAPTER 8

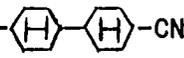
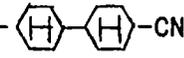
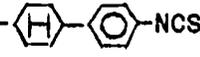
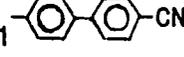
Determination of molecular properties of some polar mesogenic compounds.

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 phases¹. 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 ($^{\circ}\text{C}$) of the compounds are given in Table 8.1.

TABLE - 8.1

	STRUCTURES	ABBREVIATION	NEMATIC RANGE
(1)	C_3H_5 - 	1d(1)CC	$65.0^{\circ}\text{C} - 100^{\circ}\text{C}$
(2)	C_5H_9 - 	1d(3)CC	$79.5^{\circ}\text{C} - 100^{\circ}\text{C}$
(3)	C_3H_7 - 	3CPS	$39.0^{\circ}\text{C} - 42.0^{\circ}\text{C}$
(4)	C_5H_{11} - 	5CB	$22.5^{\circ}\text{C} - 35.3^{\circ}\text{C}$
(5)	C_7H_{15} - 	CPFB	$44.2^{\circ}\text{C} - 56.5^{\circ}\text{C}$

8.2 EXPERIMENTAL DETAILS

The liquid crystalline compounds under investigation were extensively studied by small angle x-ray diffraction and by optical methods²⁻⁵.

Molecular dipole moments were determined⁶ 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 Guggenheim⁷ equation,

$$\mu^2 = \frac{27KT}{4\pi N (\epsilon_0 + 2) (n_0^2 + 2)} \frac{(\epsilon - n^2) - (\epsilon_0 - n_0^2)}{c}$$

where N = Avogadro's number

K = Boltzman's constant

ϵ_0 = Dielectric constant of the solvent (p-xylene)

ϵ = Dielectric constant of the solution.

n_0 = 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 moment 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 theory¹⁰ with the help of package program SYBYL¹¹.

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

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

The term H_{ij} are called Coulomb integrals.

The terms H_{ij} for $i \neq j$ are called the resonance or bond integrals.

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 integral and have finite values. The overlap integral S_{ij} is zero for $i \neq j$ and is equal to one for $i=j$.

The total 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

$$Q_i = Q_i^0 + \sum_{j=\text{bonded}} q_{ij}$$

Where Q_i^0 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 al¹⁴, the only literature value available for the compounds under investigation. Values for various molecular

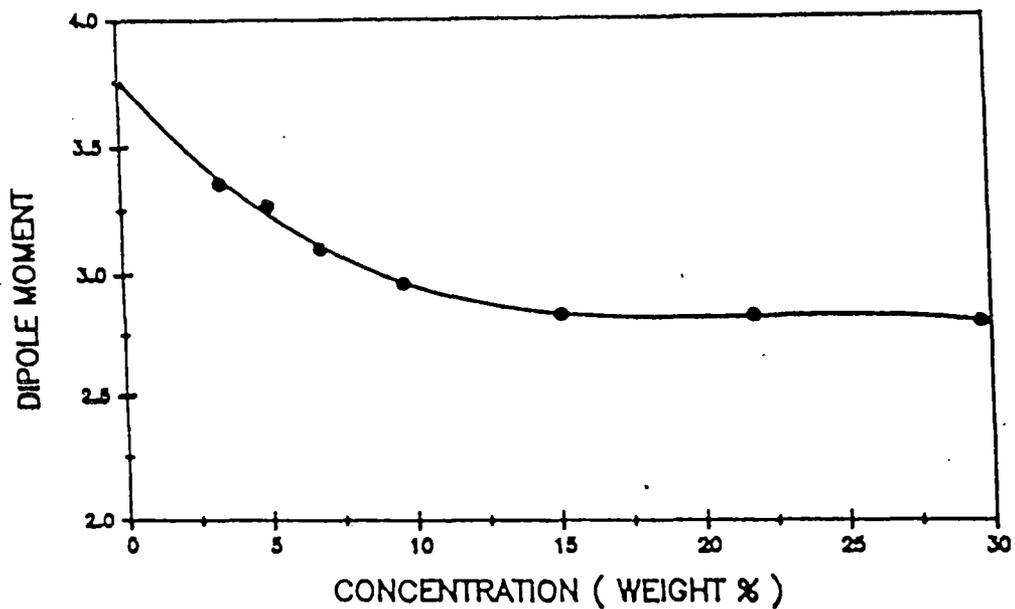


Figure 8.1 : The dipole moment of 1d(1)CC in p-xylene solution as a function of concentration.

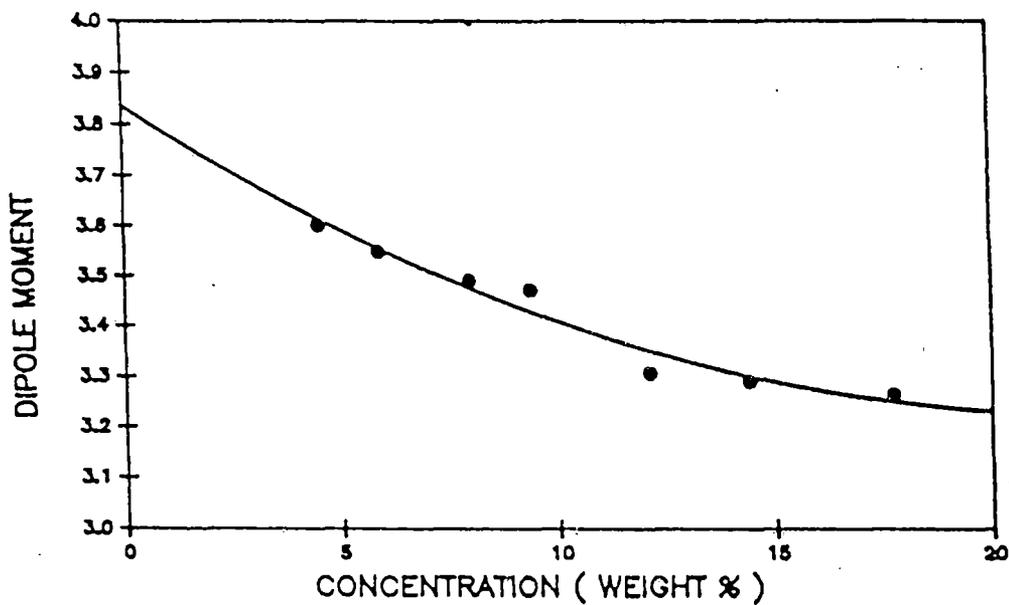


Figure 8.2 : The dipole moment of 1d(3)CC in p-xylene solution as a function of concentration.

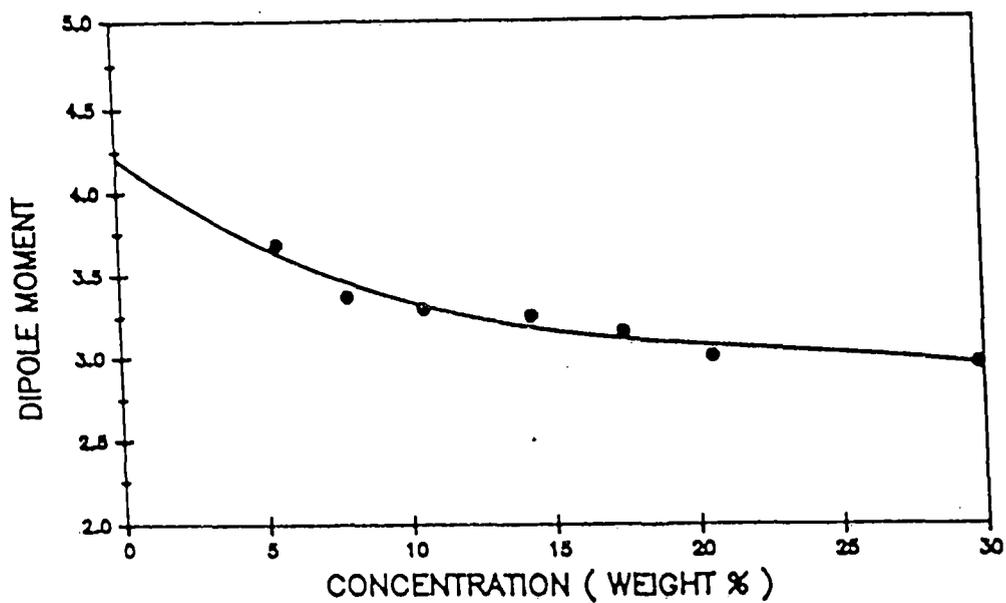


Figure 8.3 : The dipole moment of 3CPS in p-xylene solution as a function of concentration.

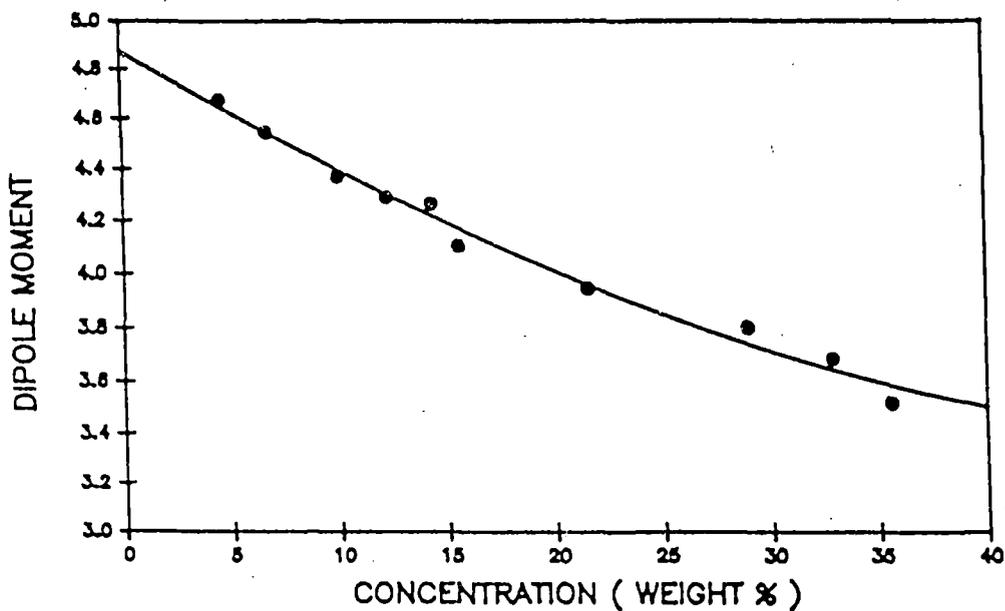


Figure 8.4 : The dipole moment of 5CB in p-xylene solution as a function of concentration.

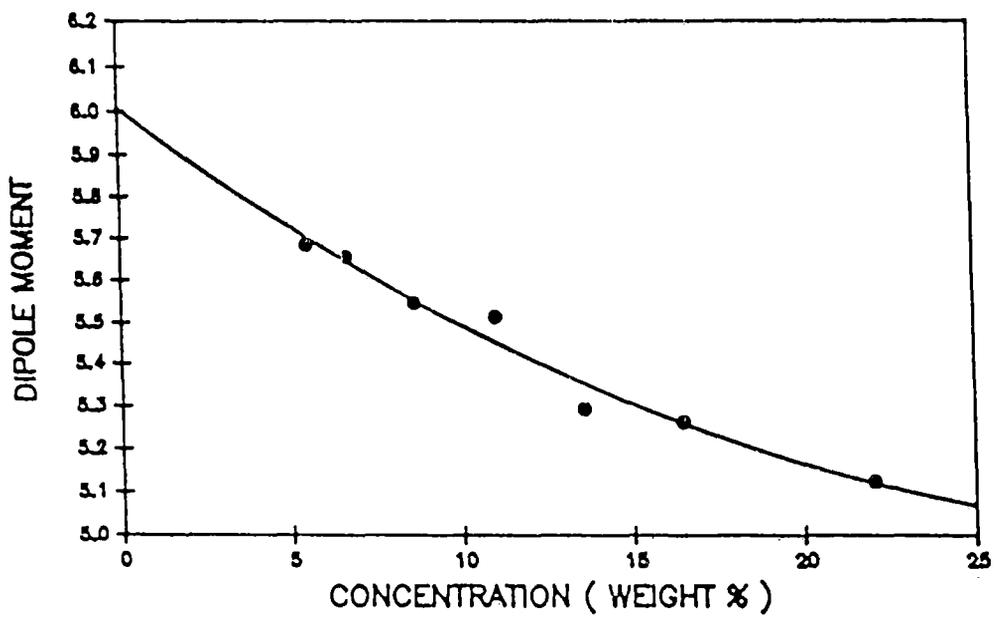


Figure 8.5 : The dipole moment of CPHB in p-xylene solution as a function of concentration.

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 anisotropy¹⁷. 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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