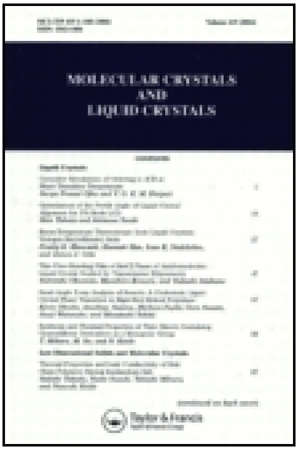

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Determination of Molecular Properties of Some Polar Mesogenic Compounds

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Determination of Molecular Properties of Some Polar Mesogenic Compounds

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

Keywords: Dipole moment, polarizability, mesogenic compounds.

INTRODUCTION

For a molecule to exhibit a liquid crystalline phase, it must satisfy certain structural requirements. But it is often very difficult to predict the effect of changes in the molecular structure on the stability and properties of liquid crystals. In reality the situation is very complicated, because, in addition to molecular structure, intermolecular interactions must be considered. Dipole–dipole interactions and steric factors play a major role in stabilizing liquid crystal phases.[1] Knowledge of dipole moments of mesogenic molecules is, therefore, very useful. In this paper we have reported our results on dipole moment determination of some polar compounds. We 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.

EXPERIMENTAL DETAILS

The liquid crystalline compounds under investigation were extensively studied by small angle x-ray diffraction and by optical methods.[2–5] The molecular formula and transition temperatures (°C) of the compounds are given in Table 1.

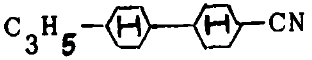
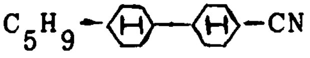
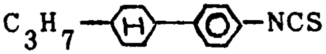
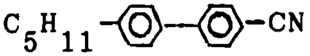
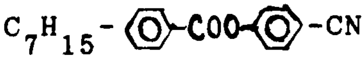
Molecular dipole moments were determined[6] by measuring the dielectric constants and refractive indices of solutions of the compounds in a non-polar solvent *p*-xylene at different concentrations of the solute. Dielectric constants were measured using a digital LCR bridge at 1 KHz. A cell was constructed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

The dipole moment (μ) is calculated using the Guggenheim[8] equation,

$$\mu^2 = \frac{27KT}{4\pi N_A(\varepsilon_1 + 2)(n_1^2 + 2)} \frac{(\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^2)}{C}$$

where N_A = Avogadro's number
K = Boltzmann's constant
ε_1 = Dielectric constant of the solvent (*p*-xylene)
ε_{12} = Dielectric constant of the solution.
n_1 = Refractive index of the solvent (*p*-xylene).
n_{12} = Refractive index of the solution.
C = Molar concentration.

TABLE 1

	Structures	Abbreviation	Nematic Range
(1)		ld(1)CC	65.0°C–100°C
(2)		ld(3)CC	79.5°C–100°C
(3)		3CPS	39.0°C–42.0°C
(4)		5CB	22.5°C–35.3°C
(5)		CPHB	44.2°C–56.5°C

(Abbreviation of the first three compounds is given according to Schadt *et al*[7]).

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.

RESULTS AND DISCUSSIONS

The variation of dipole moments with concentration for the five compounds are shown in Figures 1–5. 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 agrees well with that obtained by Dunmur *et al*[9], the only literature value available for the compounds under investigation. Values for various molecular parameters obtained for the mesogens studied are listed in Table 2.

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.[10,11] We observe from the Table 2 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 an intermediate value of

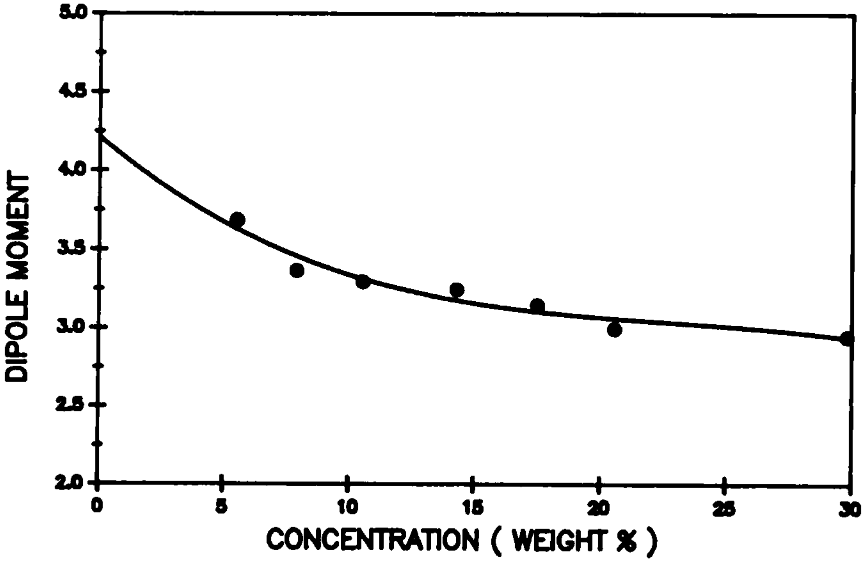


FIGURE 1 The dipole moment of 3CPS in *p*-xylene solution as a function of concentration.

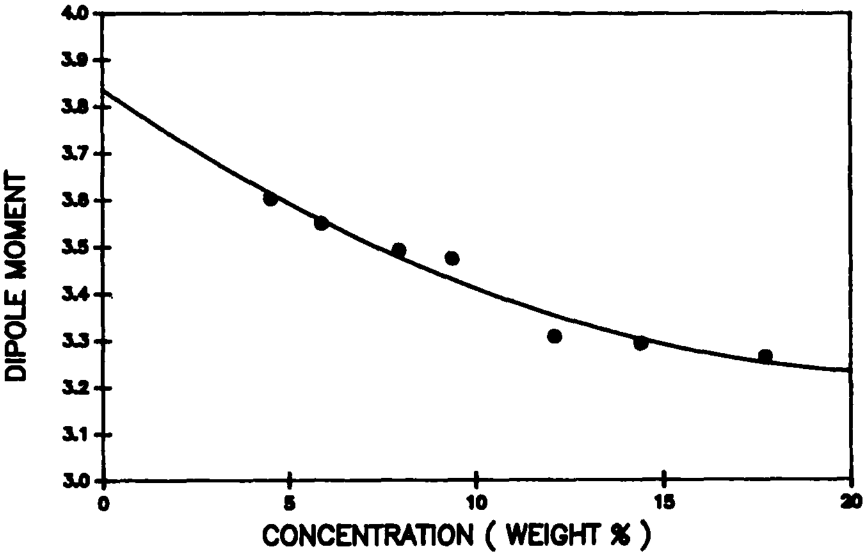


FIGURE 2 The dipole moment of 1d(3)CC in *p*-xylene solution as a function of concentration.

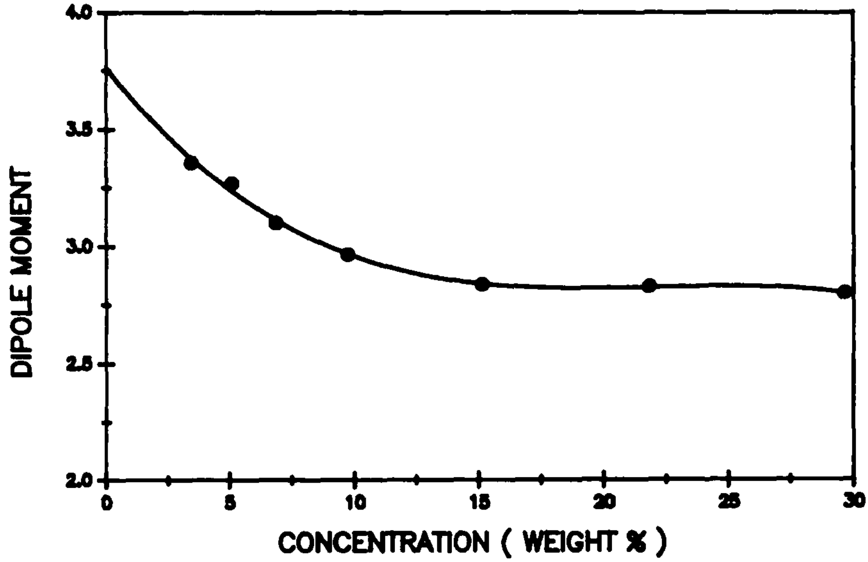


FIGURE 3 The dipole moment of 1d(1)CC in *p*-xylene solution as a function of concentration.

dipole moment which have phenyl and cyclohexane as core. The large value of dipole moment of *CPHB* may be due to different core structure. The anisotropy $\Delta\alpha$ mainly comes from the central core, the alkyl chain on the other hand contributes more to the mean polarizability than to the anisotropy.[12] As can be seen, for the two homologous

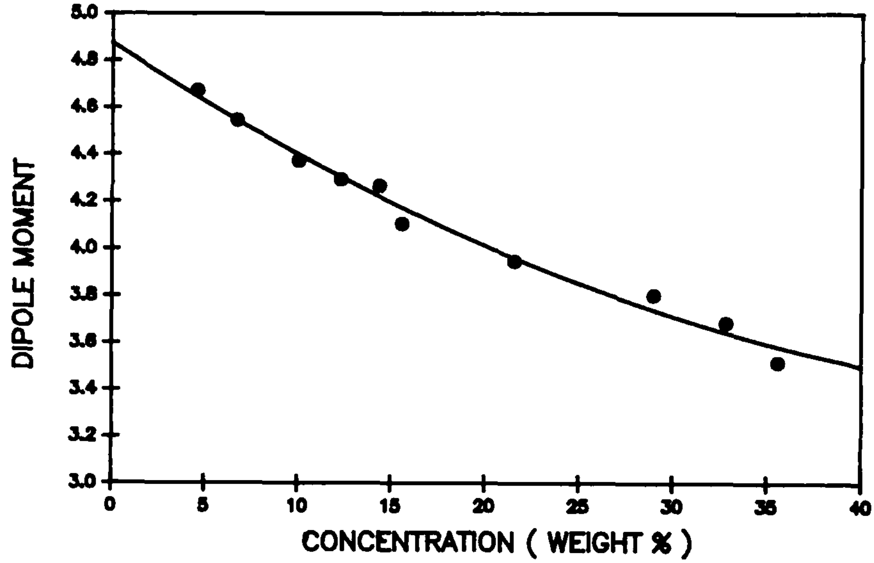


FIGURE 4 The dipole moment of 5CB in *p*-xylene solution as a function of concentration

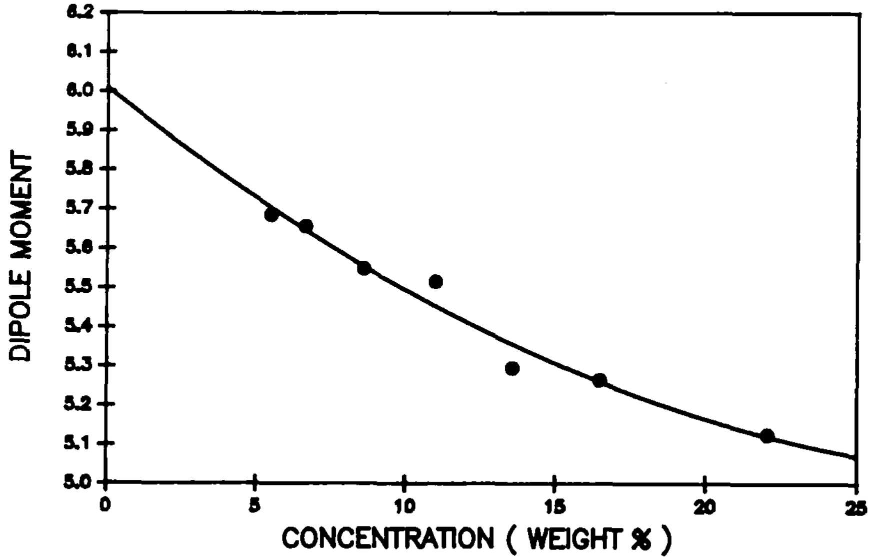


FIGURE 5 The dipole moment of CPHB in *p*-xylene solution as a function of concentration.

compounds 1d(1)CC and 1d(3)CC, increase in chain length does not change the dipole moment significantly.

The molecular dipole moment μ depends on the conformation of the molecules and on the partial charges on the constituent atoms. Electrostatic point charges on the

TABLE 2

Compounds	Mean Polarizability (α) (in 10^{-24}cm^3)	Polarizability Anisotropy ($\Delta\alpha$) (in 10^{-24}cm^3)	Dipole Moment (μ) (in Debye)
ld(1)CC	27.96	8.31	3.76
ld(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.*

TABLE 3

Name of molecular orbital theory	Dipole moment of	
	CPHB	ld(3)CC
Huckel	6.64	1.78
Gust-Huck	7.99	3.54
Pullman	7.37	2.89
Experimental value	6.00	3.83

atoms in a molecule and μ can be calculated by a number of semi-empirical quantum mechanical methods using crystallographic data. Structural analysis have been done by us[13,14] for ld(3)CC and CPHB. For these two compounds atomic charge distribution and dipole moments were calculated by different methods using molecular orbital theory[15] with the help of package program SYBYL.[16] Values of these calculated dipole moments are given in Table 3.

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

For ld(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 Huckel's 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. Both the compounds have contributions from π and σ electrons. Biphenyls have delocalised π electrons, double bonds have π electrons whereas alkyl chain and bicyclohexanes have contributions from σ electrons. The experimental dipole moment was determined for a molecule in solution in which it 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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References

1. D. A. Dunmur and A. E. Tomes, *Mol. Cryst. Liq. Cryst.*, **97**, 241 (1983).
2. A. Nath, B. Chaudhury and S. Paul, *Mol. Cryst. Liq. Cryst.*, **265**, 699 (1994).
3. A. Zeminder, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.*, **61**, 191 (1980).
4. B. Bhattacharjee, S. Paul and R. Paul, *Mol. Phys.*, **44**, 1391 (1981).
5. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976).
6. B. R. Ratna, R. Shashidhar and K. V. Rao, Liquid Crystals, International Conference on Liquid Crystals, Bangalore, India. (1979).
7. M. Schadt, R. Buchecker and K. Muller, *Liq. Cryst.*, **5**, No. 1, 293 (1989).
8. E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).
9. D. A. Dunmur, M. R. Manterfield, W. H. Miller and J. K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978)
10. G. Pelzl and A. Hauser, *Phase Transitions*, **37**, 33 (1991).
11. R. J. W. Le Fevre, *Adv. Phys. Org. Chem.*, **3**, 1 (1965).
12. M. M. M. Abdoh, Srinivasa, N. C. Shivaprakash and J. Shashidhara Prasad, *J. Chem. Phys.* **77**, No. 5, (1982).
13. S. Gupta, A. Nath, S. Paul, H. Schenk and K. Goubitz, *Mol. Cryst. Liq. Cryst.*, (1994) (In Press).
14. P. Mandal, S. Paul, H. Schenk and K. Goubitz, *Mol. Cryst. Liq. Cryst.*, **135**, 35 (1986).
15. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, N. Y., (1961).
16. SYBYL, Molecular modelling software, Ver. 5.2, Tripos Associates Inc., St. Louis, Missouri.