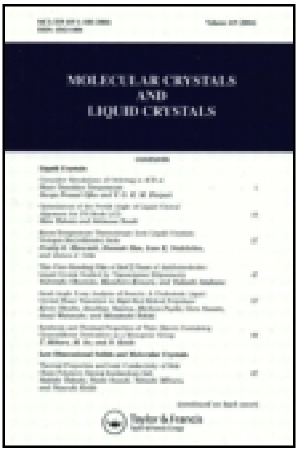

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DIELECTRIC METHOD OF DETERMINATION OF THE ASSOCIATION ENERGY BETWEEN POLAR MOLECULES IN NEMATIC LIQUID CRYSTAL

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Abstract Effective values of the parallel and perpendicular components of the molecular dipole moment per one molecule have been calculated for the 5CB compound, from the values of the parallel and perpendicular components of the dielectric permittivity tensor, using Maier and Meier equations. Necessary molecular parameters, such as transverse and longitudinal polarizabilities, as well as temperature dependence of nematic order parameter for 5CB, have been calculated from ordinary and extraordinary refractive indices and density. In this case Neugebauer equations, combined with Haller extrapolation procedure, have been used. The calculated values of effective dipole moment are much lower than for an isolated molecule. This effect decreases with increasing temperature. This has been regarded as an evidence of the antiparallel association occurrence in 5CB. Obtained results and discussion, on the basis of van't Hoff equation, allow determination of equilibrium constant K(T) and association energy ΔE.

INTRODUCTION

In 1975, Lydon and Coakley[1] found, on the basis of the X-ray investigations, layer thickness of the smectic phases of 4-n-octyl-4'-cyanobiphenyl (8CB) and 4-n-octyloxy-4'-cyabobiphenyl (8OCB) to be about 1.4 times greater than the length of constituent molecules. In the same time, Leadbetter et al.[2] found the same effects in the nematic phases of 5CB and 7CB. Structural investigations of both these compounds reveal a tendency for layer-type ordering of molecules in small regions (100 to 150 molecules) even in the nematic phase. Furthermore, the thickness of such layers is also about 1.4 times greater than the molecule length. This ordering does not disappear during transition to the isotropic phase. It was therefore suggested that these effects might be a result of strong association of molecules. Various arrangements of molecules have been suggested, in order to explain the difference between layer thickness and molecule length. An explanation finally accepted is the one assuming local molecular structure in the nematic phase similar to that schematically presented in Fig. 1 for 5CB[2] . This model is based on the principle of antiparallel orientation of molecules, with only rigid (in most cases aromatic) molecule cores overlapping and alkyl chains protruding out and thus increasing layer thickness over molecule length.

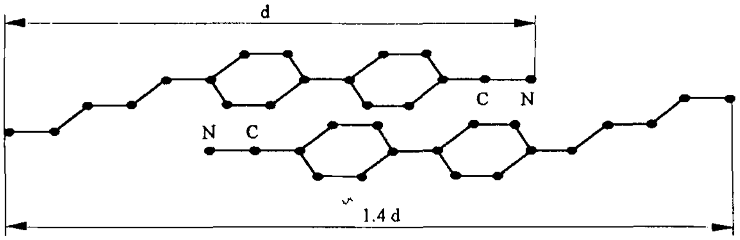
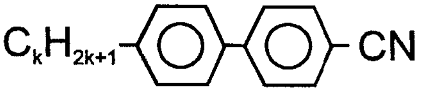


FIGURE 1 Sketch of the local structure of 5CB nematic phase[2].

EXPERIMENT

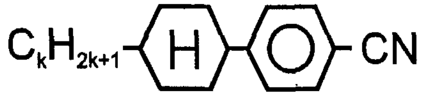
Temperature dependence of density, refractive indices and dielectric constants have been investigated for three homologous series of:

- 4-n-alkyl-4'-cyanobiphenyls (ACB)



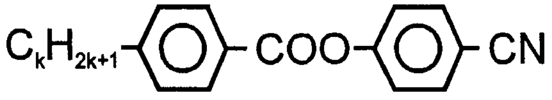
k=5,6,7,8

- 4-(trans-4'-n-alkylcyclohexyl)cyanobenzens (ACHCP)



k = 5,7,10

- 4'-cyanophenyl-4-n-alkylbenzoate (ABCP)



k = 6,7,8,9.

Refractive indices have been measured by means of an appropriately prepared Abbe refractometer, with λ= 589 nm. Density ρ of ACB, ACHCP and ABCP has been obtained by means of a pycnometer.

The isotropic ε_i, perpendicular $\varepsilon_\perp$ and parallel $\varepsilon_\parallel$ components of the dielectric permittivity tensor as well as the proper conductivity ones have been measured with a Tesla BM 484 bridge at 1592 Hz, measuring voltage being 3 V. Measurements have been performed on samples placed in a double plane capacitor with silver electrodes. Liquid crystal layers of 2 mm thickness have been used, with magnetic field of 1 T applied to induce orientation. Temperature during measurement has been kept constant to within ±0.2 K.

RESULTS AND DISCUSSION

Results of dielectric ($\varepsilon_i(T)$, $\varepsilon_\perp(T)$, $\varepsilon_\parallel(T)$) and refractometric ($n_o(T)$, $n_e(T)$, $n_i(T)$) measurements, as well as density $\rho(T)$ values for ACB, ACHCP and ABCP series have been described in details in[3-6]. On the basis of these results and employing well-known Maier-Meier formulae[7,8] mean effective values of dipole moment p_e and its components $p_{e\perp}$ and $p_{e\parallel}$ have been calculated for a single nematogen molecule of the given nematic liquid crystal.

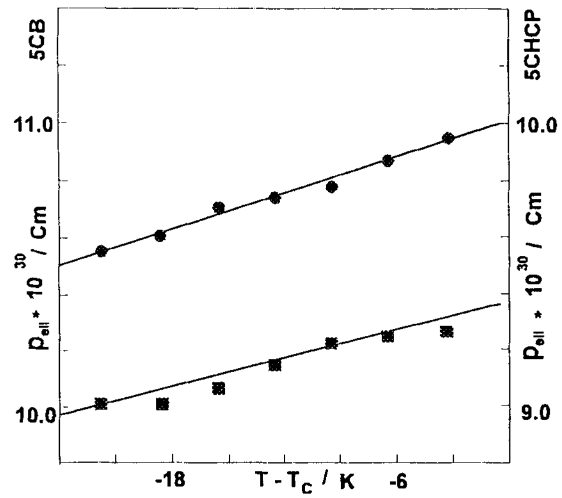


FIGURE 2 Correlation of $p_{e\parallel}(T)$ results for 5CB (•) and 5CHCP (■)

Full results of calculations for 5CB and 5CHCP are given in Table 1 and Fig.2 shows correlation of $p_{e\parallel}$ for these liquid crystals.

Table 1 gives averaged (over the whole nematic temperature range) parallel $p_{e\parallel}$ and perpendicular $p_{e\perp}$ with respect to the long molecular axis, components of effective dipole moments, resultant moments p_e and angles γ between resultant moments and long axes of individual molecules.

TABLE 1 Values of effective dipole moment p_e and its components $p_{e\parallel}$ and $p_{e\perp}$ of 5CB and 5CHCB molecules, calculated from Maier--Meier formulae[7]; values of $p_{e\parallel}$, $p_{e\perp}$ and p_e in (10^{-30} Cm), values of γ in ( ).

series	k	$p_{\parallel}$	$p_{\perp}$	p	γ
ACB	5	10.7	0.3	10.7	1.6
	6	10.8	0.4	10.8	2.1
	7	10.5	0.4	10.5	2.2
	8	10.3	0.2	10.3	1.0
	average	10.6±0.3	0.3±0.1	10.6±0.3	1.7±0.4
	addition*	15.2	0.0	15.2	0.0
ABCP	6	14.9	4.3	15.5	16
	7	14.8	5.2	15.6	19
	8	14.8	6.2	16.1	23
	9	14.4	3.6	14.8	14
	10	13.2	4.5	13.9	19
	average	14.4±0.7	4.8±1.0	15.2±0.9	18±3
	addition*	16.9	5.6	17.8	18
ACHCP	5	9.2	3.4	10.3	20
	7	8.7	3.6	9.4	23
	10	9.0	3.5	9.7	21
	average	9.0±0.2	3.5±0.1	9.8±0.3	21±1
	addition*	13.0	4.9	15.1	21

TABLE 2 Dipole moment values for nematogens with terminal cyano group; values of p_{II}, $p_{\perp}$ and p_{I} in (10^{-30}Cm).

	$\|T-T_c\|$	3	6	9	12	15	18	21
5CB	p_{II}	10.91	10.83	10.77	10.73	10.69	10.60	10.55
	$p_{\perp}$	0.15	0.21	0.39	0.40	0.30	0.32	0.21
	p_I	11.04	11.09	11.13	11.18	11.21	11.22	11.26
5CHCP	p_{II}	9.43	9.42	9.22	9.13	9.03	9.00	8.97
	$p_{\perp}$	3.54	3.58	3.41	3.31	3.35	3.30	3.21
	p_I	11.09	11.10	11.11	11.12	11.13	11.14	11.15

Apart from values for individual homologues, average values are given for all series, as well as values obtained by adding group moments, employing the method described by Klingbiel et al.[9] and group moment values given by these authors. Differences between dipole moment values for various homologues, as well as between values of their components, are small as compared to experimental errors. Therefore, average values have been calculated for each series.

Average values of $p_{e||}$ for three considered series are smaller than corresponding values obtained by adding group moments. This effect, as well as marked increase of the $p_{e||}$ component with temperature, found for all liquid crystals listed in Table 2 (see Fig.2), is an evidence of (dimeric) association with antiparallel correlation of dipole moments in nematogens with terminal cyano group.

Above-mentioned measurements and calculations have also shown that dipole moment in ACB are, in practice, parallel to long axes. Total dipole moment value determined from dielectric constants is thus identical with the value of the component parallel to the long molecular axis. One possible explanation for the reduction of the dipole moment is the existence of dimers A_2'

$$A+A \Leftrightarrow A_2 \qquad (1)$$

in which the dipoles compensate each other.

If monomers A produce A_2 units due to weak molecular interactions, these units are, in normal conditions, short-lived, although are continuously reproduced. With A_2 units forming and breaking up, a sort of equilibrium is established in the system.

According to the law of mass action, the association constant K quantity defined as (2)

$$K = \frac{[A_2]}{[A]\cdot[A]} \tag{2}$$

where $[A_2]$ and $[A]$ are molar concentration values of dimers and monomers in equilibrium, has a constant value at constant pressure and temperature

With known N and N_m values, these symbols denoting total number of molecules in the sample and number of monomers in equilibrium state, respectively, we may rewrite Eq.(2) as follows:

$$K = \frac{N^2 - N_m}{N_m^2} \tag{3}$$

N and N_m are in turn related to actual p_0 and effective p_e values of the dipole moment of ACB. Actual dipole moment value means here the value for an isolated molecule. Effective value is the one calculated from dielectric constants of a sample, assuming that it contains only monomers. We may determine mean value of the dielectric constant $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ from Maier-Meier equations[7] and then express it in terms of N and p_e, as:

$$\bar{\varepsilon} = 1 + (NhF/\varepsilon_0)\cdot\bar{\alpha} - (hF^2/3\varepsilon_0 kT)\cdot Np_e^2 \tag{4}$$

or in terms of N, N_m and p_0, as:

$$\bar{\varepsilon} = 1 + (NhF/\varepsilon_0)\cdot\bar{\alpha} - (hF^2/3\varepsilon_0 kT)\cdot N_m p_0^2 \tag{5}$$

Hence

$$Np_e^2 = N_m p_0^2 \tag{6}$$

Substituting (6) in (3) we obtain an expression for K(T):

$$K(T) = \frac{1 - \left[p_e^2(T)/p_0^2\right]^2}{\left[p_e^2(T)/p_0^2\right]^2} \tag{7}$$

Actual dipole moment values for ACB may be derived from calculations based on dielectric constant measurements of dilute solutions of these nematics in neutral dissolvents.

Integrating over temperature the van't Hoff isobar equation, in the form of

$$\left[\frac{\delta}{\delta T}(\ln K)\right]_{P=\mathrm{const}} = \frac{\Delta E}{RT^2} \tag{8}$$

which itself provides a relation between the rate of change of the association constant and pressure, gas constant R and association energy ΔE, we obtain the following equation:

$$\ln[K(T)] = C - (\Delta E / R)\cdot\frac{1}{T} \tag{9}$$

Calculating K(T) from Eq.(7) and then plotting the left-hand side of Eq.(9) vs inverse temperature, one may expect to obtain a straight line, which slope, when multiplied by the gas constant R, should give the value of association energy ΔE for the alkyl-cyanobiphenyl under investigation.

The above-described method has been used to determine dimerization energies of 5CB and 7CB, as reliable results of p_0 measurements in dilute solutions were available for these compounds[10-13]. Fig.3 shows relations ln K = f(1/T), with K calculated from the Eq.(7) for the nematic (straight lines denoted by N) and isotropic (straight lines denoted by I) phases of 5CB and 7CB. This figure shows that experimental data fit the straight lines very well, but ΔE values determined for the isotropic phase differ from those determined for the nematic phase. As a result, mean association energy values are:

- for 5CB: ΔE = (5.6 ± 0.6) kJ/mol, - for 7CB: ΔE = (11.0 ± 1.1) kJ/mol.

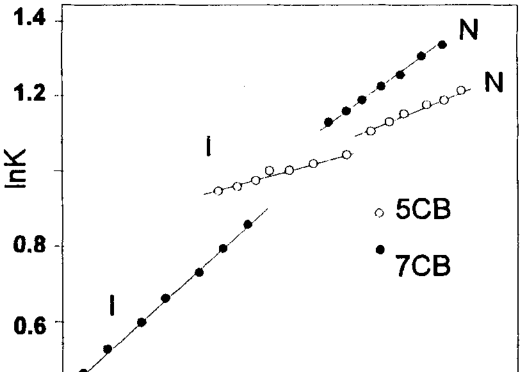


FIGURE 3 Logarithm of the dimerization equilibrium constant K vs inverse temperature: (o) - 5CB; (•) -7CB.

Similar, from the quantitative point of view, results have been obtained for 6CB (4.9 ±1.3) kJ/mol and 8CB (14.9±1.5) kJ/mol, the value of p_0 =15.2 10^{-30} Cm being adopted due to lack of reference data[9]. Some scatter of ΔE values has been caused by low accuracy of $\varepsilon(T)$ measurements for 6CB, 7CB and 8CB, probably disturbed by current effect. Adoption of $\varepsilon(T)$ data for 5CB [10,14] gives even higher values of ΔE = (14 ± 3) kJ/mol, while $\varepsilon(T)$ data for 7CB[10] give value as high as ΔE = (26 ± 5) kJ/mol.

The considerable discrepancies of our ΔE values within ACB homologous series, groundless from the physical point of view, have caused us to calculate an arithmetic average association energy value, which has been found to be:

- for (5 ÷ 8)CB: ΔE = (9.1 ±3.9) kJ/mol.

Calculations of ΔE values for the (6-9 BCP) series, with procedure slightly modified due to non-collinearity between dipole moment p and molecule long axis b, have also revealed considerable scatter of association energy values measured for one series, calculated value being

- for (6 ÷ 9)BCP: ΔE = (8.1 ± 5.5) kJ/mol.

Due to significant scatter of results they should be considered a rough estimation of investigated energy. It may be judged from them, however, that energy of dimers formation from mesogens with terminal cyano group is comparable with the energy of donor-acceptor complexes formation (ΔE ~ 10 kJ/mol) and much greater than the energy of the formation of complexes stabilized by van der Waals forces (ΔE ~ 1 kJ/mol).

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