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Dipole–dipole association of mesogenic molecules in solution

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The dielectric polarization has been used to study dipolar association of 4-*n*-pentyl-4′-cyanobiphenyl in benzene solution. The results have been interpreted with the assumption of a monomer–dimer equilibrium. To explain the relatively high effective dipole moment of the dimers, a new structure has been proposed for them.

1. Introduction

Dipolar interactions occurring in all systems containing molecules with a permanent electric dipole moment, play an especially significant role for mesogenic molecules. Although these interactions are not decisive in the process of mesophase creation they strongly affect most physical properties of liquid crystals [1].

The dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) of a nematic composed of molecules with the dipole moment vector parallel to the long molecular axis is approximately proportional to the apparent dipole moment squared (μ^2_{app}) [2]. For strongly polar compounds, like the cyanobiphenyls, the apparent dipole moment of molecules in the nematic state is considerably lower than the value for a single molecule ($\mu_1 \approx 5\,\mathrm{D}$); the Kirkwood correlation factor

$$g = \mu^2_{\mathrm{app}}/\mu^2_1$$

for these compounds amounts to about 0·5 [3–5]. This means, that the dielectric anisotropy of cyanobiphenyls, expected on the basis of the value of μ_1, should be twice as large as that measured. This effect is undoubtedly related to the antiparallel dipolar association of mesogens [6, 7] leading to a considerable reduction of the parallel component of the permittivity. Antiparallel dipolar association is also observed in the isotropic phase as an anomalous decrease in the value of ε in the vicinity of the nematic–isotropic transition [8, 9]. Other physical properties of nematics are also modified by dipolar aggregation [1].

Numerous studies concerning dipolar aggregation of mesogens have been performed both in the pure state and in organic solutions [10–16]. The simplest model used to describe dipolar self-association consists in approximating the bimolecular interaction, i.e. it assumes a thermodynamic monomer–dimer equilibrium.

Here, we present the results of static dielectric polarization studies of dipolar association for 4-*n*-pentyl-4′-cyanobiphenyl (5CB) in benzene solution.

2. Experimental

2.1. *Materials*

4-*n*-Pentyl-4-cyanobiphenyl obtained from BDH (Poole, England) was used without further purification ($T_{\mathrm{CN}} = 22{\cdot}5^{\circ}\mathrm{C}$, $T_{\mathrm{NI}} = 36{\cdot}0^{\circ}\mathrm{C}$).

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2.2. *Apparatus*

The static electric permittivity was measured with a Wayne-Kerr B330 bridge at a frequency of 1·5 kHz with an accuracy of ±0·1 per cent. The temperature was stabilized with an accuracy of ±0·01°C. The density was measured with a Anton Paar DMO6 density meter with an accuracy of ±0·01 per cent.

3. Results and discussion

The dependence of the electric permittivity, ε, on the concentration of 5CB in benzene is shown in figure 1. The measurements were performed over the whole concentration range (at temperatures $T > T_{\mathrm{NI}}$) or up to the appearance of the two-phase nematic–isotropic region (at temperatures $T < T_{\mathrm{NI}}$). The dependence $\varepsilon(c)$ shown in the insert of figure 1 illustrates a pretransitional anomaly (decreasing of the permittivity), analogous to that observed in the temperature dependence of ε for pure cyanobiphenyls in the vicinity of the nematic–isotropic transition [8, 9].

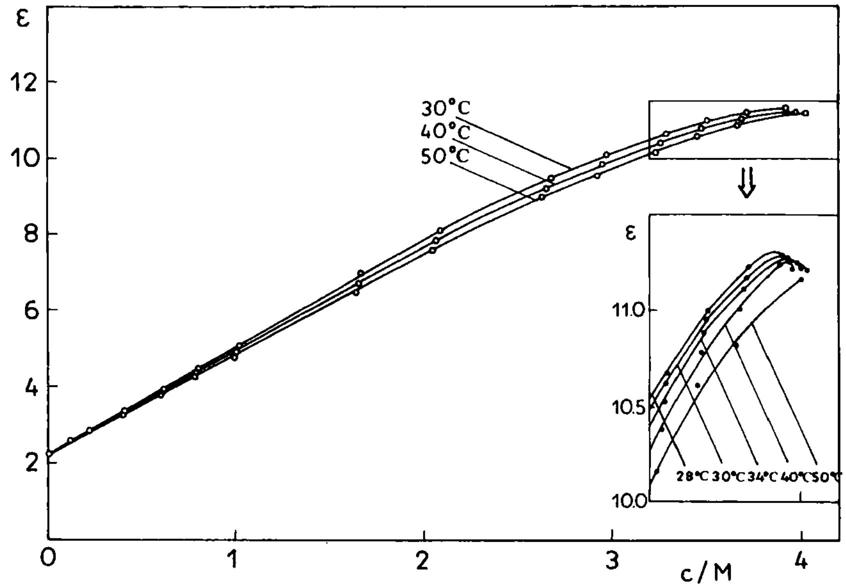

Figure 1. Static electric permittivity versus the molar concentration of 4-*n*-pentyl-4′-cyanobiphenyl in benzene.

The experimental results for the static dielectric measurements can be conveniently expressed in terms of an apparent molecular dipole moment squared, μ^2_{app}, which for a non-polar solvent is related to the measured macroscopic quantities by [17, 18]

$$\begin{aligned}\mu^2_{\mathrm{app}} &= g\mu_1^2 \\ &= \frac{9\varepsilon_0 kT}{cN_{\mathrm{A}}}\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} \qquad (1)\end{aligned}$$

where ε denotes the static electric permittivity, ε_∞ (often replaced by the square of the refractive index n^2) is the permittivity measured at a frequency high enough to prevent orientational polarization and c is the nominal molar concentration of the dipolar compound. In the ideal case of non-interacting molecules, μ_{app} is the dipole moment of

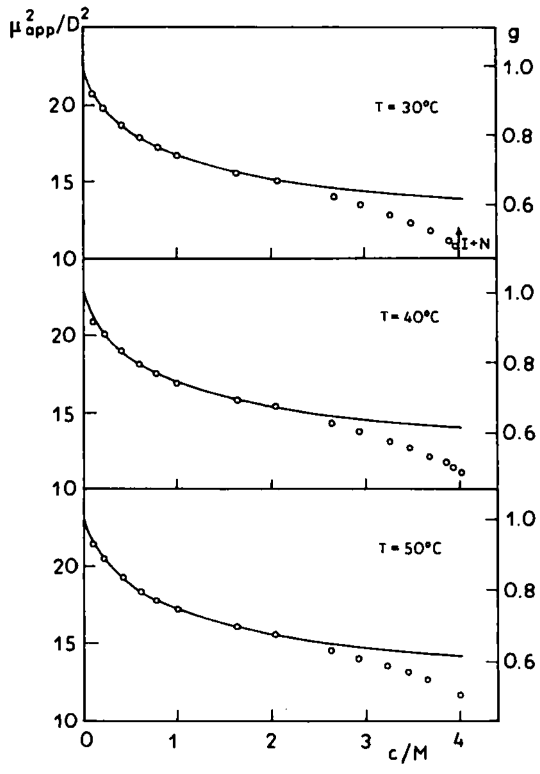

Figure 2. Experimental dependence of the apparent dipole moment squared of 4-*n*-pentyl-4′-canobiphenyl on concentration in benzene (points). $g = \mu^2_{app}/\mu^2_1$ is the Kirkwood correlation factor. The solid lines represent the best fit of the experimental values (for concentrations up to ~2 M) to the monomer–dimer model predictions (equations (3) and (4)).

an individual molecule (μ_1), i.e. the Kirkwood factor g is 1, and does not depend on concentration. The points in figure 2 show the experimental dependence of μ^2_{app} on the concentration obtained for benzene solutions of 5CB.

3.1. *Model of molecular dimerization*

We assume a simple model for the solution of a dipolar substance in a non-polar solvent in which bimolecular interactions are predominant. In thermodynamic equilibrium the system can be considered as a mixture of single molecules (A_1) and dimers (A_2)

$$2A_1 \overset{K_2}{\rightleftharpoons} A_2, \quad K_2 = c_2/c_1^2, \qquad (2)$$

where K_2 is the equilibrium constant and c_1 and c_2 are the molar concentration of monomers and dimers, respectively. According to equation (2) the mass balance of the solute, $c = c_1 + 2c_2$, can be expressed as

$$c_1 + 2K_2c_1^2 - c = 0. \qquad (3)$$

If the value of the equilibrium constant K_2 is known, then the concentration of monomers for a given nominal concentration c can be calculated from this equation.

For dimerization the relation between experimentally determined μ_{app}^2, the concentrations and the dipole moment of the components of the solution is

$$c\mu_{\mathrm{app}}^2 = c_1\mu_1^2 + c_2\mu_2^2. \tag{4}$$

The dipole moment value of a single molecule was determined by extrapolation of μ_{app}^2 to infinite dilution of 5CB. The μ_1 value obtained is equal to $4{\cdot}77 \pm 0{\cdot}03$ D, and does not depend on temperature within the limits of experimental errors. These results agree quite well with the literature data [19, 20]. The values of the dimerization constant K_2 and dipole moment of the dimer, μ_2, needed to complete the description of the dielectric properties of a solution can be obtained by fitting the experimental data (points in figure 2) and the theoretical dependence of $\mu_{\mathrm{app}}^2(c)$ (equations (3) and (4)). Figure 2 shows that the monomer–dimer model (solid lines) works quite well only for concentrations up to about 2 M. The values of K_2 and μ_2 obtained by fitting the data and the enthalpy of interactions calculated with the van't Hoff method ($\ln K_2$ versus T^{-1}) are listed in the table. The most important conclusion resulting from these studies concerns the dimers: lack of a full compensation of dipole moments means that the dimers do not have a strictly antiparallel structure. Interpretation of this fact presents some difficulties, since the values of μ_2 obtained from the best fitting of $\mu_{\mathrm{app}}^2(c)$ refer to an average dimer. The non-zero dipole moments of the dimers can be explained with several equivalent models, each of them agreeing with the experimental dependence of μ_{app}^2 on concentration.

Parameters of dimerization for 4-*n*-pentyl-4′-cyanobiphenyl in benzene.

	5CB: $\mu_1 = 4{\cdot}77$ D	
T/°C	μ_2/D	K_2/M^{-1}
30	4·28	0·685
40	4·29	0·665
50	4·27	0·632
ΔH/kJ mol^{-1} = $-3{\cdot}26 \pm 0{\cdot}54$		

One such model has been proposed by Toriyama and Dunmur [21, 22]. In their approach the solution of polar nematogenic molecules contains two kinds of dimers: antiparallel ($\mu_2 = 0$) and parallel, of the head-tail type, ($\mu_2 = 2\mu_1$). The non-zero dipole moment obtained in experiment, according to this model, results from an equilibrium between these two rigid structures. The physical reality of this model seems to be doubtful. In a dynamic molecular system, such as liquids (and nematics) the dipolar interaction energy only slightly exceeds kT (see the table), which leads to the formation of labile molecular aggregates, and the structure of such aggregates can be discussed in terms of average values. Of course, for higher concentrations of 5CB aggregates larger than dimers can be formed. However, our attempts to explain the observed considerable decrease of $\mu_{\mathrm{app}}^2(c)$ above 2 M by including higher aggregates with different polarity, did not provide any acceptable results.

In our approach, in a solution of polar compound, dimers of various structure are formed in such a way that the axis of dipoles form statistically different angles. In the dielectric experiment we observe an average dimer, the polarity of which results from the fact that an average angle, φ, between the axes of the component dipoles is lower than 180° (strictly the antiparallel structure). For low and medium concentrations of

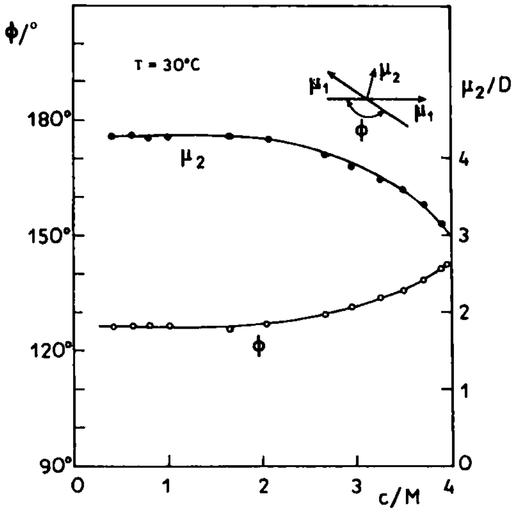

Figure 3. Dependence of φ and μ_2 values on the concentration of 4-*n*-pentyl-4′-cyanobiphenyl in benzene solution.

dipoles, the value of this angle results from a competition between dipole–dipole interactions and thermal excitation. For higher concentrations of dipoles the geometric packing of molecules seems to play a predominant role. It is obvious, that for elongated rod-like molecules of the nematogen the packing should manifest itself in a distinct manner.

A considerable decrease in the experimental value of μ^2_{app} in relation to theoretical expectations, observed for concentrations of 5CB higher than 2 M (see figure 2), is, in our opinion, caused by a specific packing of molecules, i.e. by an increase of the angle φ between the component dipoles of the dimer. Increasing the value of the angle φ means a decrease in μ_2 (see figure 3). With a constant value of K_2, the experimental dependence of $\mu^2_{\mathrm{app}}(c)$ can be reproduced over the whole concentration range after adjusting the value of φ and thereby the dipole moment μ_2, for concentrations of 5CB

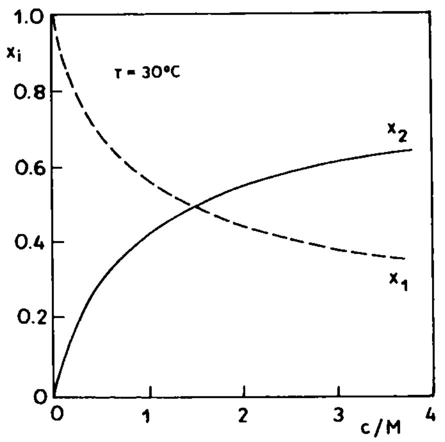

Figure 4. Mole fractions x_i ($=c_i/c$) of monomers and dimers in 4-*n*-pentyl-4-cyanobiphenyl dissolved in benzene at 30°C.

higher than 2 M. The dimer becomes more and more antiparallel. The variations of φ needed to explain this effect are relatively small (see figure 3). According to our model, the value of φ is about 125° for concentrations below 2 M ($\mu_2 \approx 4{\cdot}3$ D), increases up to about 150° ($\mu_2 \approx 3{\cdot}0$ D) just before the transition to the nematic phase. The mole fractions of monomers and dimers are shown in figure 4 as a function of the concentration of 5CB in benzene; just before the transition to the nematic phase occurs about 65 per cent of dimers with polarity $\mu_2 \approx 3$ D ($\varphi \sim 150°$) and 35 per cent of free molecules with the dipole moment, μ_1 of 4·77 D. In terms of the model of rigid dimers [21, 22] our result for the average φ of 150° corresponds to the situation in which the relative fraction of parallel ($\varphi = 0°$) and antiparallel ($\varphi = 180°$) dimers amounts to about 0·15 and 0·85, respectively.

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