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Experimental determination of the flexoelectric coefficients of some nematic liquid crystals

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We report measurements of the temperature variation of the flexoelectric coefficient (e_1-e_3) of a number of nematic liquid crystals like phenylcyclohexanes, cyanobiphenyls, etc. We have also measured (e_1+e_3) of a few systems using appropriate methods of applying an electric field gradient to the sample. In most of the systems, $(e_1-e_3)/k$, where k is a curvature elastic constant, is found to be positive and independent of temperature, as expected. However, in 4-heptyl-1-(4-cyanocyclohexyl)cyclohexane and a few other compounds with relatively flexible parts, $|(e_1-e_3)/k|$ increases with temperature. We discuss the possible molecular origin of the sign and temperature dependence of the flexoelectric coefficients of the systems studied.

1. Introduction

Nematic liquid crystals have an apolar director. However, a macroscopic polarization can be induced in the medium by splay and bend distortions of the director field. As was first shown by Meyer [1], this flexoelectric polarization is given by

$$\mathbf{P}=e_1\mathbf{n}(\nabla\cdot\mathbf{n})+e_3(\nabla\times\mathbf{n})\times\mathbf{n} \tag{1}$$

where e_1 and e_3 are the two flexoelectric coefficients corresponding to splay and bend distortions, respectively. According to the Meyer model, only a sub-class of nematics that are made up of polar molecules with specific shape asymmetries exhibit the flexoelectric effect. It was later pointed out by Prost and Marcerou [2] that the electric quadrupole moments of the molecules also make a significant contribution to the flexoelectric effect. Nematogenic molecules generally have non-zero electric quadrupole moments, and hence nematic liquid crystals usually have non-zero flexoelectric coefficients. The response of a nematic to an electric field is significantly influenced by flexoelectricity in many experiments [3].

A large number of theoretical papers on the flexoelectric effect have been published recently [4–10]. In particular, the relationship between the flexoelectric effect and the orientational order parameter (S) is discussed in several of these. Earlier phenomenological models indicated that the dipolar contribution to e_1 and e_3 (hereafter indicated by the subscript d) varies as S^2 if the molecular structure is rigid [4–6]. On the other hand, the leading contribution from the quadrupole density of the orientationally ordered medium varies as S [2]. Osipov [5] made a detailed molecular calculation including both short range repulsive and attractive interactions between molecules which have shape asymmetries. He concluded that in general the flexoelectric coefficients have terms depending both on S and S^2. (Even the purely quadrupolar effect can give rise to an S^2 dependence due to the tensor nature of the Lorentz factor in the anisotropic medium.) $e^*=(e_1-e_3)$, the difference in the flexoelectric coefficients is mainly determined by the dipolar contributions. Further, Osipov [5] showed that e_d^*

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depends essentially on the transverse dipole moment of banana-shaped molecules, rather than the longitudinal dipole moments. Indeed he has argued that e_d^* should be very small for compounds with zero transverse dipole moments $\mu_\perp$. He has also shown that e_d^* is proportional to the molecular length (L). More recently, Singh and Singh [7] used a density functional formalism to calculate the flexoelectric coefficients. Their conclusions are similar to those of Osipov. There have also been several measurements of flexoelectric coefficients of nematics [11–20]. In particular, many different techniques have been used to measure the flexoelectric coefficients of 4-methoxybenzylidene-4′-butylaniline (MBBA), a room temperature nematic liquid crystal. Marcerou and Prost [16] devised an interdigitated electrode technique to measure the intensity of light scattering produced by the spatially periodic flexoelectric distortion due to an applied AC field. They could measure $|e_1+e_3|$ from this experiment and they demonstrated that a symmetric tolane which does not have a dipolar contribution has a fairly large value of $|e_1+e_3|$ arising from the quadrupole moments. More interestingly, even in cases with permanent dipoles and hence a non-zero value of the dipolar contribution, $|e_1+e_3|$ was found to be nearly proportional to S, thus demonstrating that this combination of the flexoelectric coefficients arises mainly from the quadrupolar effect. The sign of (e_1+e_3) is not determined by this technique. Dozov *et al.* used a simple electrode configuration to generate a field gradient and obtained the negative sign for (e_1+e_3) of MBBA. This sign has been confirmed by the later measurements of (e_1+e_3) by an optical measurement on a hybrid aligned cell with weak anchoring [19, 20]. Beresnev *et al.* [18] have also measured (e_1+e_3) of MBBA using a pyroelectric technique, though it is not clear if the sign has been determined by the authors. More recently, e_1 and e_3 have been measured by a technique based on an acoustic wave induced periodic deformation [21, 22] which yields values which are relatively high, but the sign of e_1 and e_3 appears not to have been determined.

Dozov *et al.* [13, 23] devised a remarkably simple experimental technique of measuring $e^*=(e_1-e_3)$ which arises mainly from the dipolar contribution to flexoelectricity. One of the interesting results is that 4-octyl-4′-cyanobiphenyl (8CB) which has a very strong terminal dipole moment (–C≡N) has a value of e^* which is comparable to that of MBBA which has a significant lateral dipole. Both 8CB and MBBA have a temperature independent value of (e^*/k), where k is the elastic constant, i.e. $e^*\propto S^2$, as expected of the dipolar contribution [13]. In 8OCB, which has an octyloxy chain giving rise to a transverse component of the dipole moment in each molecule, the sign of e^*/k is negative. Further, e^*/k increases with temperature. e^* appears to be proportional to S in this case. Even though (e_1+e_3) of 8OCB also is $\propto S$, that result arises from the fact that the main contribution to (e_1+e_3) comes from the quadrupolar effects. e^* on the other hand has a significant contribution from the dipolar effect and the observed S-dependence was attributed to the flexibility of the octyloxy chain by Dozov *et al.* [13]. Osipov [6] has more recently confirmed that inclusion of the flexibility of molecules can, in principle, give rise to an additional S^{-1}-dependence of e^*. If this is the dominating factor, e^* becomes proportional to S. Nemtsov and Osipov [8] have developed a general correlation function approach to calculate e_1 and e_3. In particular they argue that the additional transverse dipole moment of 8OCB can give rise to the reversal of the sign of e^* compared to that of 8CB.

We are interested in measuring flexoelectric coefficients of nematics in connection with our work on electrohydrodynamic instabilities [3, 27, 28]. In the present paper we report our data on e^* for a large number of compounds which are structurally related. We have also estimated (e_1+e_3) for some of these compounds.

2. Experimental techniques

2.1. *Measurement of* $(e_1 - e_3)$

We have used the method of Dozov *et al.* [23] for the measurement of e^*/k. The sample geometry used is illustrated in figure 1. The nematic liquid crystal is taken in a hybrid aligned cell, with one glass plate coated with polyimide and rubbed to get homogeneous alignment and the other plate coated with ODSE (octadecyl triethoxy silane) to get homeotropic alignment. The anchoring at the two surfaces is assumed to be strong. The director field in such a cell has a permanent splay–bend distortion, which gives rise to a flexoelectric polarization **P**. If a vertical field is applied between the plates, the flexoelectric energy $(-\mathbf{P}\cdot\mathbf{E})$, which is linear in the curvature $(d\theta/dz)$ depends only on one distortion angle θ [24], and the corresponding contribution to the bulk torque density is zero. On the other hand, when an electric field **E** is applied along Y, a twist distortion is produced in the medium due to the action of **E** on **P**, and in such a case, the flexoelectric effect contributes to the bulk torque density. Since the dielectric free energy is proportional to E^2, the influence of the dielectric anisotropy can be neglected as long as E is small. The maximum value of twist (ϕ) occurs close to the plate with homeotropic alignment and is given by [23]

$$\phi = -\left[\frac{e_1 - e_3}{k}\right]\frac{Ed}{\pi} \tag{2}$$

where d is the sample thickness and k the isotropic elastic constant. ϕ is measured by passing a polarized light beam through the sample such that it enters the cell through the homogeneously aligned plate. Then the state of polarization follows the twisted director pattern, since the optical phase difference is greater than the angle of twist produced in the sample.

The transverse electric field was applied to the HAN cell by using stainless steel or phosphor-bronze wires which also served as spacers. The diameter of the wires used was 35 to 50 μm. The cell is placed between the crossed polarizers of a polarizing

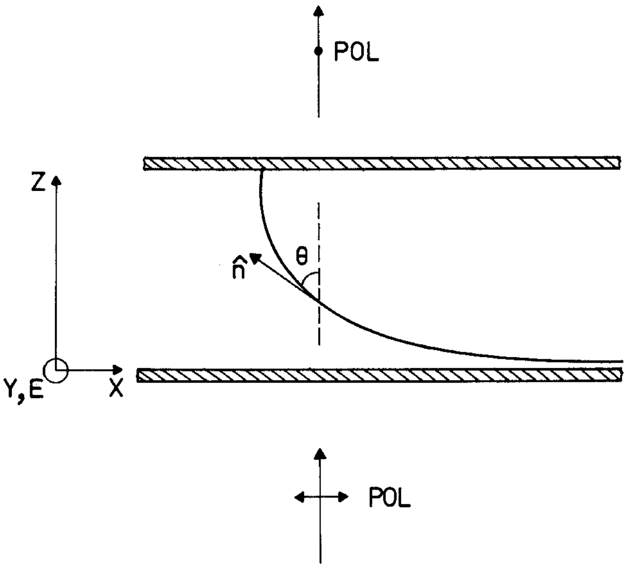

Figure 1. The geometry of the HAN cell used to measure (e^*/k). An electric field E_y applied perpendicular to the plane of the paper produces a twist distortion.

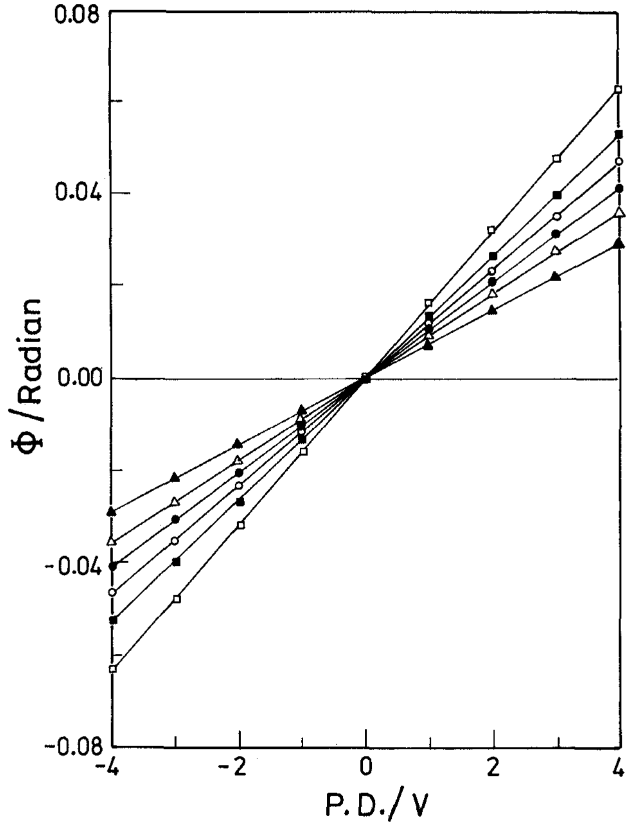

Figure 2. Variation of the angle of rotation (ϕ) of the plane of polarization with the applied voltage in CCH-7 at different temperatures; (▲) 323 K, (△) 328 K, (●) 333 K, (○) 338 K, (■) 343 K and (□) 348 K.

microscope (Leitz Orthoplan). A Mettler hot stage (Model FP 82) is used to regulate the sample temperature. The HAN cell is placed such that linearly polarized light with its plane of polarization parallel to the nematic director enters the cell through its wall treated for homogeneous alignment. The transmitted beam emerges from the plate treated for homeotropic alignment. ϕ is measured by rotating the anlayser to get the minimum intensity. In order to locate the minimum accurately, we use a Mettler photomonitor (Model ME-17517). At lower values of the electric field, the twist angle ϕ is small ($\sim 0{\cdot}5^\circ$) and the error in ϕ measurement is relatively large. However at higher fields, the twist angles ϕ being of the order of 2° to 3°, the relative error is reduced considerably. We estimate that the error, which is mainly due to the measurement of ϕ is $\simeq 10$ per cent. e^*/k is obtained from the slope of the plot of ϕ versus E (see figure 2) and the sign of e^* is deduced from the sign of ϕ for a given sign of E. We measured e^* mainly for two homologous series, namely, cyanobiphenyls and cyanophenylcyclohexanes and for some other compounds with different structures. We have also studied the temperature dependence of e^* for most of the compounds.

2.2. *Measurement of* (e_1+e_3)

In most of our experiments we have measured (e_1+e_3) by following the technique of Dozov *et al.* [25] in which a quadrupolar field is generated by an appropriate arrangement of the electrodes (see figure 3). Aluminium electrodes are vacuum coated with a gap of $\simeq 1$ mm on an ITO plate with high resistivity. Two such plates are used in the construction of the cell of thickness $\simeq 50\,\mu$m. The nematic is aligned homeotropically with strong anchoring and the field gradient gives rise to a bend distortion described by the angle θ. Optically, for small θ, the nematic behaves as a cell of uniform tilt [25]

$$\bar{\theta}=\frac{1}{d}\int_0^d \theta(z)\,dz=\frac{2}{3}\theta_0 \tag{3}$$

where

$$\theta_0=\frac{Vd}{2L}\frac{(e_1+e_3)}{k_3}, \tag{4}$$

V is the DC voltage applied to the electrodes, d the sample thickness, L the lateral separation between the electrodes and k_3 the bend elastic constant. The conoscopic pattern which is observed between crossed polarizers in a Leitz polarizing microscope, is tilted by an angle $n_0\bar{\theta}$, n_0 being the ordinary refractive index of the medium. Hence, by measuring the tilt of the conoscopic pattern, $(e_1+e_3)/k_3$ can be calculated. The sign of (e_1+e_3) is obtained from the direction of tilt of the conoscopic pattern for a given sign of the field gradient.

The conoscopic pattern in the form of a uniaxial cross is observed using monochromatic radiation from a sodium vapour lamp. By applying a DC electric field as in figure 3, a shift in the conoscopic pattern is seen. Using the numerical aperture (NA = 0·40) of the objective used, the shift of the conoscopic pattern is converted to the tilt angle (θ_0). These measurements of (e_1+e_3) have relatively large errors for the following reason. At low fields, the field is screened due to double layer formation [29]. We cannot however use very large fields as this will result in charge injection (at voltages above the redox potential of the liquid crystal), which can give rise to undesirable field gradients. Thus we apply a relatively small voltage, and the errors involved in the measurements could be $\simeq 40$ per cent. Because of this large uncertainty, we did not measure the temperature dependence of (e_1+e_3).

We have also used a simpler method to measure (e_1+e_3) of a nematic having negligible dielectric anisotropy. The field gradient is produced by using a wedge shaped cell (see figure 4). The nematic is aligned homeotropically with strong anchoring at the two plates. Since the field gradient that can be produced in this geometry is relatively

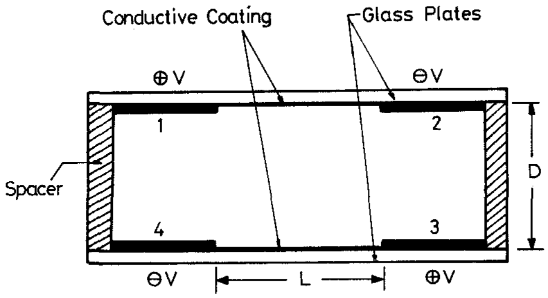

Figure 3. Electrode configuration used to produce a quadrupolar field. 1, 2, 3 and 4 are coated aluminium electrodes. Voltages with signs as shown produce the required field distribution in the centre of the sample.

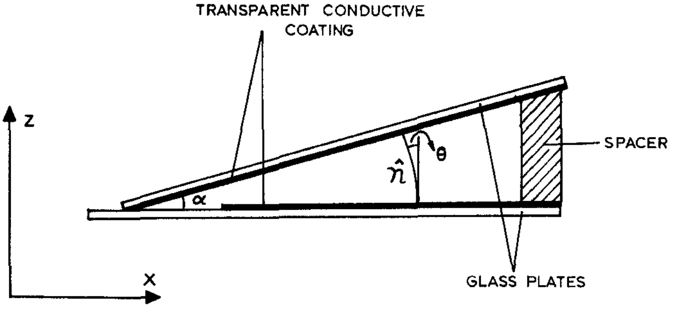

Figure 4. Schematic diagram of the wedge shaped cell used in measuring (e_1+e_3) of materials with low values of dielectric anisotropy.

small, the dielectric anisotropy of the material under study has to be negligible so as to reduce the dielectric coupling to the applied field. Neglecting the dielectric anisotropy, the distortion of the director field can be calculated by equating the flexoelectric and elastic torques.

The initial bend distortion of the director is negligible, since the wedge angle is very small. On applying an electric field, we assume a small distortion of the director so that $n=(\theta,0,1)$. The resulting components of flexoelectric polarization along x and z are

$$P_x=(e_1+e_3)\theta\frac{\partial\theta}{\partial x}+e_3\frac{\partial\theta}{\partial z}, \tag{5}$$

$$P_z=-(e_1+e_3)\theta\frac{\partial\theta}{\partial z}+e_1\frac{\partial\theta}{\partial x}. \tag{6}$$

Minimizing the flexoelectric free energy density, $f=-\mathbf{P}\cdot\mathbf{E}$, and neglecting the higher order terms, the flexoelectric torque is found to be

$$\Gamma^{\mathrm{fl}}=(e_1+e_3)\frac{\partial E_z}{\partial x}. \tag{7}$$

Equating this to the elastic torque, we get

$$k_3\frac{\partial^2\theta}{\partial z^2}-(e_1+e_3)\frac{\partial E_z}{\partial x}=0 \tag{8}$$

The boundary conditions are: $\theta(z=0)=0$ and $\theta(z=d)=\alpha$, where α is the wedge angle. The solution of equation (8) satisfying the above boundary conditions is

$$\theta(z)=[(e_1+e_3)V\alpha/(2k_3)]\left[\frac{z}{d}-\left(\frac{z}{d}\right)^2\right]+\frac{\alpha z}{d}, \tag{9}$$

where V is the applied voltage. As in the previous method, (e_1+e_3) can be obtained from the tilt of the conoscopic pattern, which is given by

$$n_0\bar{\theta}=\frac{n_0}{d}\int_0^d\theta(z)\,dz=\frac{\alpha}{2}[1+(e_1+e_3)V/(6k_3)] \tag{10}$$

The first term on the right-hand side of this equation gives the tilt of the conoscopic pattern due to the initial bend distortion of the director field, and the second term gives the tilt due to the flexoelectric distortion. Since the latter depends on the sign of the

Table. List of compounds studied.

Symbol	Chemical name	Clearing point (in K)	$(e_1-e_3)/k_2$ $\times 10^{-2}\,\mathrm{C\,m^{-1}\,N^{-1}}$ (at temp)	$(e_1+e_3)/k_3$ $\times 10^{-2}\,\mathrm{C\,m^{-1}\,N^{-1}}$ (at temp)
PCH-3	*trans*-4-Propyl-(4-cyanophenyl)cyclohexane	317·5	36 (310 K)	11 (310 K)
PCH-4	*trans*-4-Butyl-(4-cyanophenyl)cyclohexane	312	155 (311 K)	
PCH-5	*trans*-4-Pentyl-(4-cyanophenyl)cyclohexane	324·2	166 (303 K)	12 (303 K)
PCH-7	*trans*-4-Heptyl-(4-cyanophenyl)cyclohexane	327	120 (303 K)	23 (303 K)
5CB	4′-Pentyl-4-cyanobiphenyl	307·8	240 (303 K)	108 (303 K)
6CB	4′-Hexyl-4-cyanobiphenyl	302	251 (301 K)	
7CB	4′-Heptyl-4-cyanobiphenyl	312·6	353 (303 K)	
8CB	4′-Octyl-4-cyanobiphenyl	312	228 (307 K)	
CCH-7	4-Heptyl-(4-cyanocyclohexyl)cyclohexane	355·7	−129 (343 K)	51 (343 K)
ROCP-7037	5-Heptyl-2-(4-cyanophenyl)pyrimidine	323·5	436 (319 K)	5 (319 K)
ROCP-7334	5-(4-Butylphenyl)-2-(4-cyanophenyl)pyrimidine	517·7	252 (373 K)	16 (373 K)
5CT	4′-Pentyl-4″-cyano-*p*-terphenyl	511·5	87 (423 K)	
MPPC	4-Methoxyphenyl *trans*-4-pentylcyclohexylcarboxylate	344	52 (323 K)	
EPPC	4-Ethoxyphenyl *trans*-4-propylcyclohexylcarboxylate	351	28 (323 K)	
PPPC	4-Pentylphenyl *trans*-4-pentylcyclohexylcarboxylate	320	297 (310 K)	
8OCB	4′-Octyloxy-4-cyanobiphenyl	352·6		29 (343 K)
Mixture of				
MBB (46%)	1,4-Di-(4-butylbenzoyloxy)-2-methylbenzene			
PEC (50%)	1-Propyl-4(4-ethoxyphenyl)cyclohexane	342	33 (303 K)	−60 (303 K)
and				
5CB (4%)	4′-Pentyl-4-cyanobiphenyl			

applied field, the pattern should shift in the opposite direction when the field is reversed. By measuring the shift of the conoscopic pattern, $(e_1 + e_3)$ can be estimated. The sign of $(e_1 + e_3)$ is obtained from the direction of tilt of the conoscopic pattern for a given sign of the field.

The names of the compounds used in the present experiments and their transition temperatures are given in the table. The samples were obtained commercially.

3. Results and discussion

We have shown the temperature variation of e^*/k for different compounds in figures 5–7. From these, we note the following points:

(1) Practically all the compounds have a positive value of e^*/k. The only exception is CCH-7, which has a negative value.
(2) e^*/k is constant for most individual compounds as expected theoretically.
(3) However, in CCH-7, MPPC, EPPC and PPPC, the absolute value of $|e^*/k|$ increases with temperature.
(4) When the cyclohexane ring is replaced by a phenyl ring, the magnitude of e^*/k increases. Comparing the seventh homologues of different series, e^*/k, which is negative for CCH-7, becomes positive for PCH-7 and increases further for 7CB.
(5) However, when the number of benzene rings increases from two to three (for example 5CB to 5CT), the magnitude of e^*/k decreases.

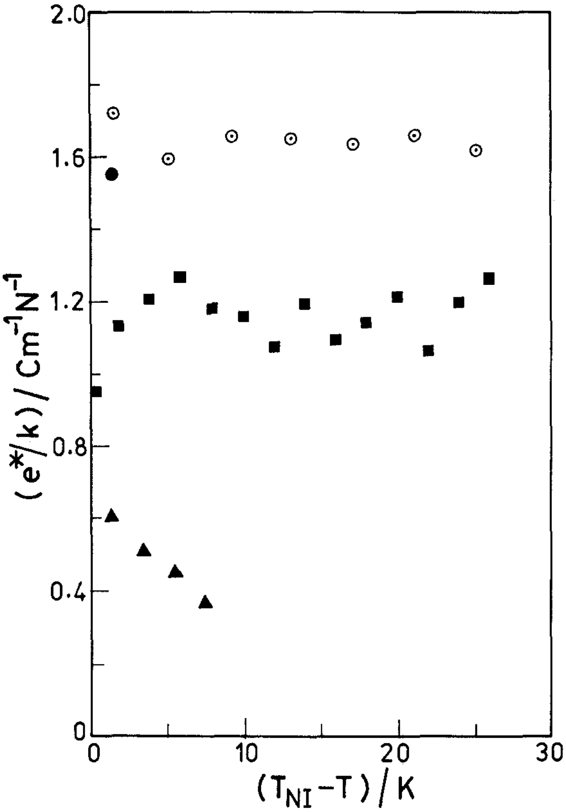

Figure 5. Variation of (e^*/k) with relative temperature $(T_{NI} - T)$ for the phenylcyclohexane series. (■) PCH-7, ⊙ PCH-5, (●) PCH-4 and (▲) PCH-3.

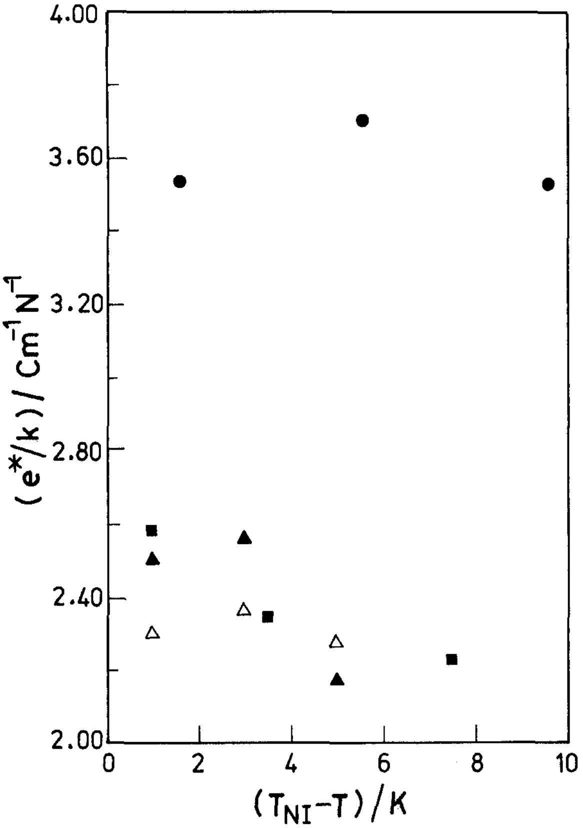

Figure 6. Variation of (e^*/k) with relative temperature $(T_{NI}-T)$ for the cyanobiphenyl series. (△) 8CB, (●) 7CB, (▲) 6CB and (■) 5CB.

(6) e^*/k is not very sensitive to the chain length.

(7) The sign of (e_1+e_3) is positive for all the single component systems we have used. However, it is negative in the case of a mixture of MBB, PEC and 5CB (see table). This mixture, like CCH-7 has opposite signs for (e_1-e_3) and (e_1+e_3).

(8) Beresnev *et al.* [18] measured e_1 of 5CB by a pyroelectric technique and obtained a value of $0{\cdot}5\times10^{-11}\,\mathrm{C\,m^{-1}}$. Our value is comparable to this.

(9) Marcerou and Prost [16] measured (e_1+e_3) of 8OCB by using the interdigital electrode technique and got a value of $(2{\cdot}1\pm0{\cdot}5)\times10^{-11}\,\mathrm{C\,m^{-1}}$ at 73°C. Our value is $+(0{\cdot}6\pm0{\cdot}2)\times10^{-11}\,\mathrm{C\,m}$ which is somewhat lower. The sign and magnitude that we obtain agree with those obtained by Dozov *et al.* [25].

(10) We measure e^*/k experimentally. Here the relevant value of k is the twist elastic constant k_2. In many cases k_2 is known to deviate considerably from the mean field dependence of S^2. Hence, for CCH-7 we obtained e^* using the known values of k_2 [30]. We have also calculated e^*/S and e^*/S^2 using the measured values of S [31, 32]. In order to have a better comparison of the temperature dependence of these quantities, we normalized them with respect to their average values over the given temperature range (see figure 8). It is immediately clear that $e^*\propto S$ in this case. On the other hand, similar plots for PCH and 7CB (see figure 9) clearly show that $e^*\propto S^2$ in these cases.

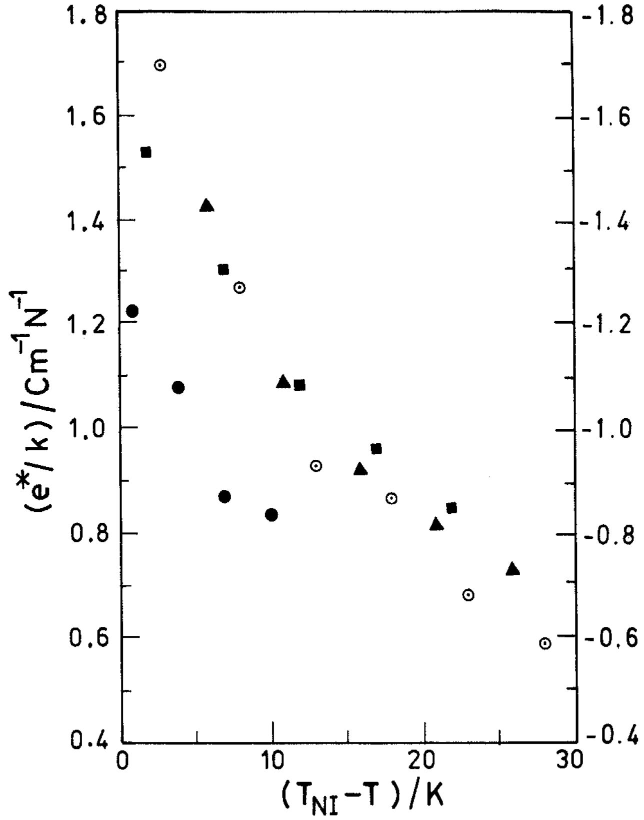

Figure 7. Variation of (e^*/k) with relative temperature $(T_{NI}-T)$ for (▲) MPPC, (⊙) EPPC, (●) PPPC and (■) CCH-7. Note that e^*/k is negative for CCH-7 (scale on right-hand side).

The predominate contribution to e^* comes from the dipolar effect. As we noted in the introduction, the molecular models [4–6] lead to the result that e^* arises entirely due to the transverse dipole moment of the molecules with shape asymmetry. Thus it is interesting that the cyanophenylcyclohexanes as well as the cyanobiphenyls have a significant value of e^*/k, although in both of them the permanent dipole is due to a terminal cyano group which is oriented outwards along the *para*-axis of the aromatic core. However, we note that the aromatic core has a high polarizability. Further, both cyanobiphenyls and PCHs have relatively low N–I transition points. Consequently, we can assume that their alkyl chains have the all-*trans* conformation [32]. This would give a naturally *bowed* structure (see figures 10 and 11). As the dipole moment induced in the aromatic core by the end cyano group is no longer strictly parallel to the long axis of such a molecule, it produces a reasonable transverse component. In fact, this gives rise to a negative sign of e_3, which in turn gives rise to a positive value of e^* in these compounds. Further, comparing PCHs and cyanobiphenyls, the latter have lower values of the nematic isotropic transition points compared to the former, and have the more polarizable biphenyl cores. Due to both of these reasons, we get higher values of e^*/k for the cyanobiphenyls. On the other hand, in 4-pentyl-4″-cyano-*p*-terphenyl, e^*/k actually decreases compared to 5CB. We must however note that $T_{NI} \simeq 512$ K for 5CT and the alkyl chain can no longer be considered to be in an all-*trans* conformation [32].

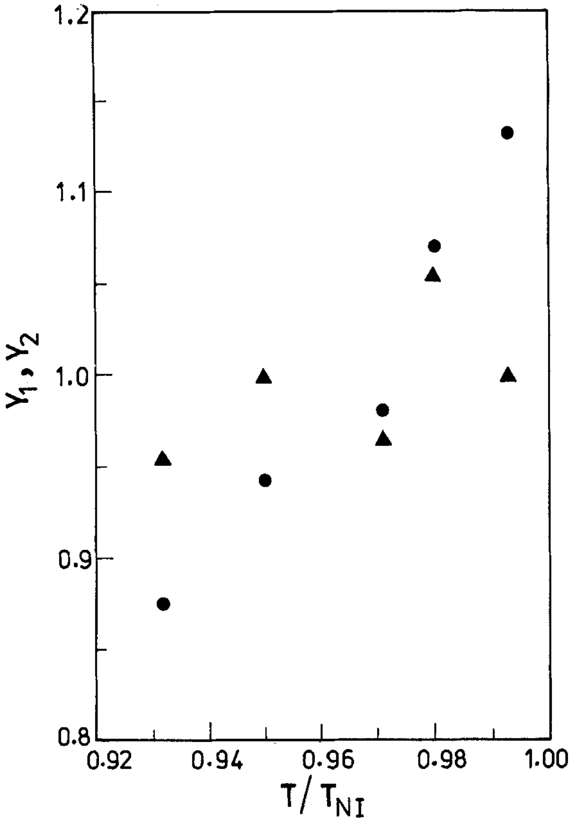

Figure 8. Temperature variations of $Y_1 = (e^*/S)/\langle e^*/S \rangle_{AV}$ (▲) and $Y_2 = (e^*/S^2)/\langle e^*/S^2 \rangle_{AV}$ (●) for CCH-7.

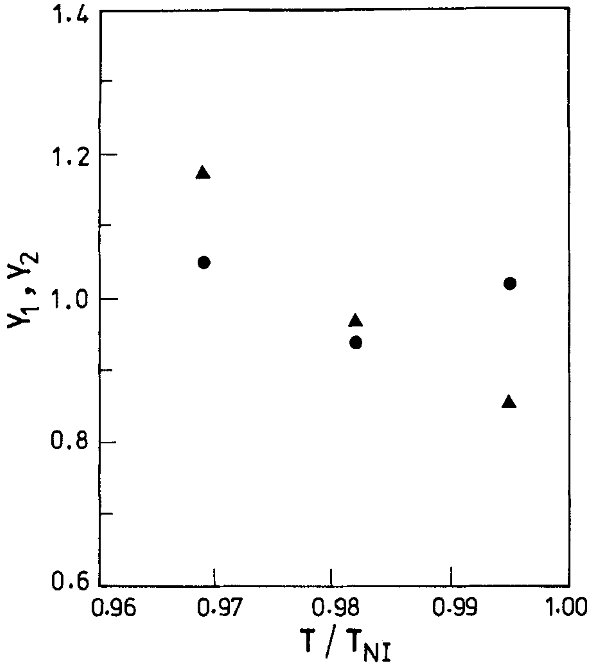

Figure 9. Temperature variations of $Y_1 = (e^*/S)/\langle e^*/S \rangle_{AV}$ (▲) and $Y_2 = (e^*/S^2)/\langle e^*/S^2 \rangle_{AV}$ (●) for 7CB.

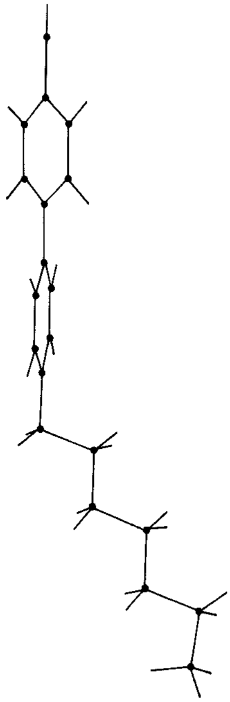

Figure 10. Molecular structure of heptylcyanobiphenyl (7CB). The all *trans*-conformation of the heptyl chain gives rise to a bent structure. The dipole moment induced in the biphenyl part by the end cyano group has a non-zero transverse component in relation to the effective long axis of the bent molecule.

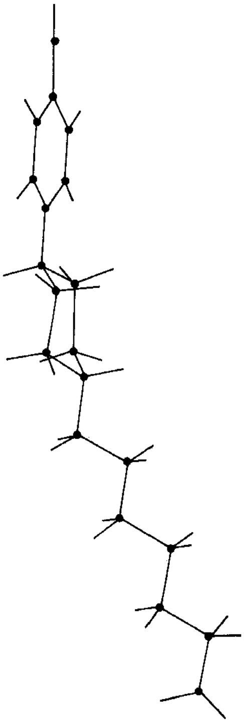

Figure 11. Molecular structure of heptylcyanophenylcyclohexane (PCH-7). As in figure 10, note the bent structure due to the all-*trans* heptyl chain. The induced dipole in the phenyl ring would be smaller than in 7CB.

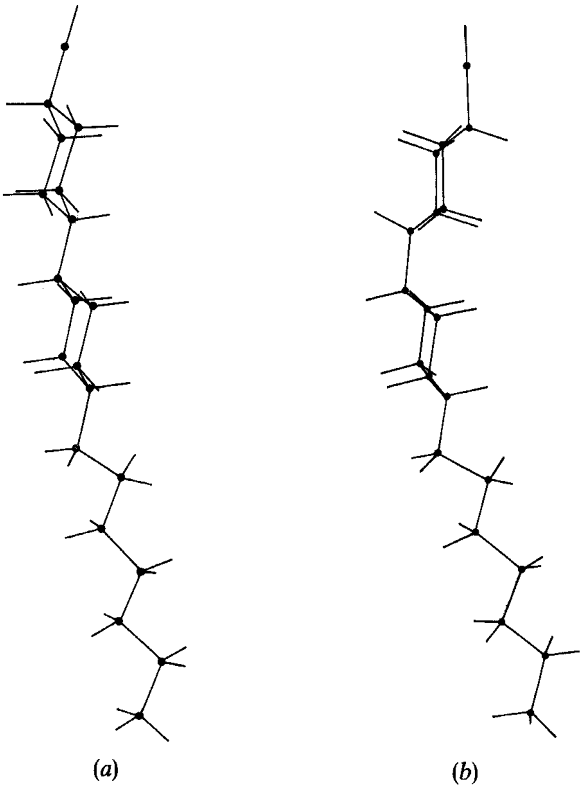

Figure 12. (*a*) Molecular structure of heptylcyanocyclohexylcyclohexane (CCH-7). Note that in the ground state the molecule is nearly straight. (*b*) A rotation about the C–C bond between the two rings produces a bent structure in CCH-7. Note that the dipole of the cyano end group has an opposite transverse component in the bent upper moiety compared to PCH-7.

Thus the shape of the molecule is no longer bowed, and $|e_3|/k$, and, hence, $|e^*/k|$ decrease in magnitude. This trend is also found for pyrimidine compounds: as the aromatic core size is increased, the transition temperature increases and e^*/k decreases.

In CCH-7, on the other hand, the end cyano group makes a non-negligible angle with the long axis of the molecule. Though CCH-7 can be expected to have a fairly straight configuration in the lowest energy state (see figure 12 (*a*)), there is considerable rotational freedom around the single C–C bond between the two cyclohexane rings. Thus, bent conformations, as in figure 12 (*b*), can occur in the molecule. T_{NI} is 355 K in this case, and the temperature is high enough to produce such conformations. Further, as the temperature is increased, the molecule adopts a bent conformation more frequently, thus increasing the effective value of e_3. Further, the transverse dipole moment which is effective in the bent conformation has the opposite direction compared to that in PCH and cyanobiphenyl molecules. Thus the sign of e_3 and, hence, that of $(e_1 - e_3)$ reverse in CCH-7. In MPPC, EPPC and PPPC, there is a –COO– bridging group between a cyclohexane and a phenyl ring. Arguments similar to the above, *viz.*, a relative increase in the number of conformations producing bent structures with changing temperature, can lead to the observed increase of (e^*/k_2) in these cases also.

We recall that Dozov *et al.* [13] found a similar increasing trend of e^*/k with temperature for 8OCB. They attributed this unusual result to the entropic effects arising from the flexibility of the alkyl chains. a point which was later elaborated by Osipov [6]. However, as we have discussed in the case of 5CT, if the flexibility is too high, one cannot expect an additional contribution to the temperature variation of e^*.

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