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## Liquid Crystals

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## The conformations adopted by alkyl chains in $\alpha,\omega$ -bis(aryl)alkanes in liquid-crystalline phases

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The conformations adopted by the alkyloxy chains in the  $\alpha,\omega$ -bis(4-phenyloxy)alkanes (PONOP) with 2, 3 and 4 methylene groups in the alkyl chain have been investigated for an isotropic solution in acetone for the compound with  $N=2$ , and for samples dissolved in three nematic solvents for all three compounds. The energy difference,  $E_{tg}^{CC}$ , between *gauche* and *trans* conformers produced by rotation about the C-C bond in PO2OP dissolved in acetone was derived from the scalar coupling constants obtained by analysing the proton spectrum from molecules containing a  $^{13}\text{C}$  atom at one  $\text{C}_\alpha$  position. This gave  $E_{tg}^{CC}$  in the range  $-0.58$  to  $0.49$   $\text{kJ mol}^{-1}$ . The deuterium NMR spectra of fully deuteriated samples of the PONOP dissolved in the nematic solvents were used to obtain local order parameters from the quadrupolar splittings. These were compared with values calculated by the mean field method of Emsley, Luckhurst and Stockley (ELS) to give values of  $E_{tg}^{CC}$  in the liquid-crystalline phases. The values obtained for  $E_{tg}^{CC}$  change from being negative for PO2OP, through zero for PO3OP to  $2.5$   $\text{kJ mol}^{-1}$  for PO4OP. The deuterium NMR data obtained previously for the mesogenic molecules  $\alpha,\omega$ -bis(4-cyanobiphenyloxy)alkanes in their nematic phases have been re-interpreted and it is shown that  $E_{tg}^{CC}$  in these compounds is also strongly dependent on chain length.

### 1. Introduction

The deuterium spectra of  $\alpha,\omega$ -bis(4-cyanobiphenyloxy)alkanes (CBONOBC) show that the alkyl chains are flexible [1]. The precise nature of the conformational distribution can in principle be obtained by comparing the observed quadrupolar splittings,  $\Delta\nu_i$ , with values calculated by a molecular, mean field model, such as that introduced initially by Marcelja [2], and modified subsequently by Emsley, Luckhurst and Stockley (ELS) [3]. This model describes the conformational distribution in alkyl chains by the rotational isomeric state approximation (RIS), which assumes that only the three minimum energy structures, *trans* (*t*) and *gauche*  $\pm$  (*g*  $\pm$ ), as shown in figure 1, are populated. In the RIS model the conformational distribution in the isotropic phase of a mesogen is determined by the energy differences  $E_{tg}(\text{CC})$  and  $E_{tg}(\text{OC})$ , and these are often assumed to be independent of the location in the molecule of the bonds involved. The mean field model also invokes the idea that the average interaction between a molecule in the *n*th conformation is a sum of the interactions between the molecular, mean field and individual rigid fragments of the molecule, such as the aromatic part, and the individual C-C and O-C segments of the chain, and that these will be the same for each member of the series. These assumptions have been found to be consistent with the data for mesogens with terminal end chains [4,5], but they do not both seem to be

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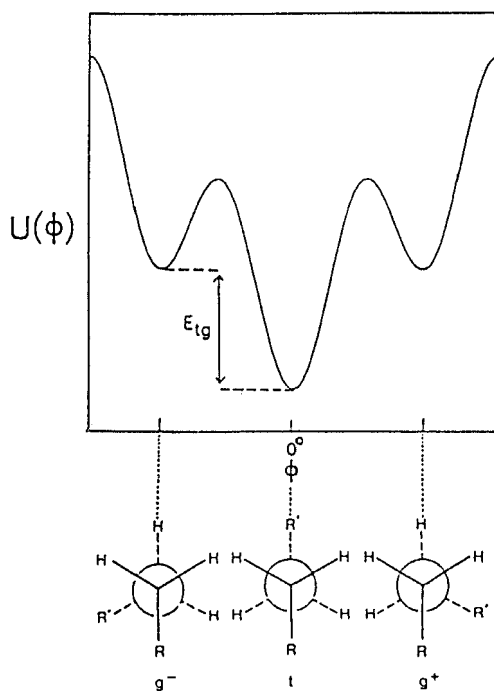


Figure 1. The dependence of the potential energy  $U(\phi)$  on the angle of rotation,  $\phi$ , about a C-C bond in an alkyl chain.

valid for the CBONOBC molecules with  $N=2, 3$  and  $4$ . To shed more light on the reasons for these discrepancies between theory and experiment we have investigated the similar series of non-mesogenic molecules,  $\alpha,\omega$ -bis-(phenyloxy)alkanes (PONOP) dissolved in nematic solvents. There are advantages in studying solutes rather than pure mesogens in that more data can be produced simply by changing the solvent. These particular solutes also have the advantage of having a para-deuteron, which enables a more accurate measurement of the orientational order parameters for the aromatic moiety than was obtained in the case of the CBONOBC mesogens. Finally, it has proved possible in the case of PO2OP to obtain a value for  $E_{tg}(CC)$  by measuring the scalar coupling constants,  ${}^3J_{HH}$ , for samples dissolved in isotropic solvents. This provides crucial evidence to support the interpretation of the nematic phase NMR spectra.

## 2. Experimental

The general method of synthesis of the PONOP molecules involves the reaction between phenol and an  $\alpha,\omega$ -dibromoalkane.

### 2.1. 1,2-Bis(phenyloxy)ethane- $d_{14}$

12.5 g of phenol- $d_6$  (0.125 mol) were dissolved in ethanol (25 ml), and 7 g of potassium hydroxide (0.125 mol) dissolved in water (10 ml) added dropwise over a 30 min period. Then 10 g of 1,2-dibromoethane- $d_4$  (0.05 mol) were added dropwise followed by stirring and boiling for 2 h. After cooling, the mixture was shaken with dichloromethane, and after washing with water ( $3 \times 50$  ml), the organic layer was evaporated to dryness. Recrystallization from propanol gave the desired product (60 per cent yield, mp  $95^\circ\text{C}$ ).

2.2. *1,3-Bis(phenyloxy)propane-d<sub>16</sub>* and *1,4-bis(phenyloxy)butane-d<sub>18</sub>*

0.6 g of phenol-*d*<sub>6</sub> (0.06 mol) were dissolved in dimethylformamide (25 ml) and 3 g of anhydrous potassium carbonate added, followed by the  $\alpha,\omega$ -dibromoalkane (0.003 mol), and the mixture stirred and heated under reflux for 18 h. After cooling, the mixture was shaken with water (2  $\times$  50 ml), and the white solid filtered off and dried. The white solid was recrystallized from methanol, giving white crystals of the desired product (85–90 per cent yields, mp 60°C for *N* = 3, and 99°C for *N* = 4).

The liquid-crystalline solvents used were Merck phase 5 (Merck, Darmstadt, mp –5°C, *T*<sub>NI</sub> 75°C), ZLI 1132 (Merck, Darmstadt, mp –10°C, *T*<sub>NI</sub> 70°C) and EBBA (Eastman-Kodak, mp 37°C, *T*<sub>NI</sub> 80°C). Samples containing 2 wt% of the PONOP compounds were prepared and their deuterium spectra obtained at 30.7 MHz with a Bruker CXP spectrometer. The proton spectrum of PO2OP dissolved in acetone was recorded on a Bruker AM 360 spectrometer.

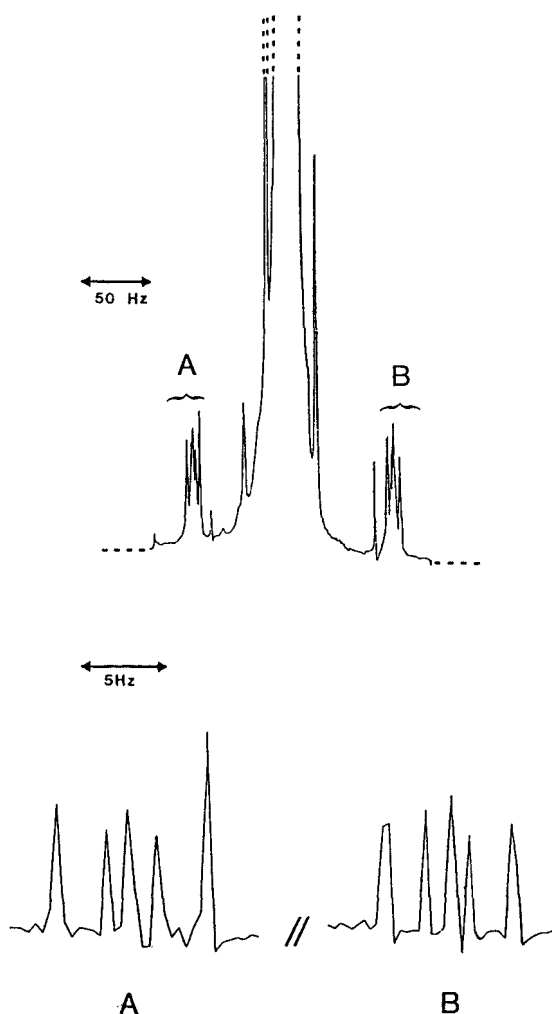


Figure 2. 360 MHz proton spectrum of a sample of PO2OP dissolved in acetone containing one <sup>13</sup>C in the alkyl chain. The top trace shows the aliphatic proton resonances, and the bottom trace shows the <sup>13</sup>C satellite lines on an expanded scale.

### 3. Analysis of the spectra

#### 3.1. The isotropic solutions

The aliphatic protons in PO2OP form an equivalent group and give rise to a single intense peak in the proton spectrum. However, the same group of protons in those molecules containing a single  $^{13}\text{C}$  nucleus at either of the methylene sites are the AA'BB' part of an AA'BB'X spin system. Only the outer parts of this spin system can be observed as weak satellite lines on either side of the peak from  $^{12}\text{C}$  containing molecules, as shown in figure 2. Labelling the nuclei as shown in table 1, the analysis of this spectrum yields  $|J_{13} + J_{14}|$ ,  $|J_{13} - J_{14}|$ ,  $|J_{15}|$ , and the chemical shift difference  $\delta_{13}$ .

#### 3.2. The nematic solutions

The assignment of peaks in the deuterium spectra to sites in the molecule is based on relative intensities, except for the  $\alpha$  and  $\beta$  sites in PO4OP, which give peaks of equal

Table 1. The NMR parameters obtained from the analysis of the 360 MHz  $^{13}\text{C}$  satellite lines of the methylene protons of a sample of PO2OP dissolved in acetone.

2 H		H4
5 $\text{C}^{13}\text{-C}$		
1 H		H 3
$ J_{13} + J_{14} /\text{Hz}$		$9.6 \pm 0.2$
$ J_{13} - J_{14} /\text{Hz}$		$1.6 \pm 0.2$
$ J_{15} /\text{Hz}$		$143.6 \pm 0.1$
$(\nu_1 - \nu_3)/\text{Hz}$		$1.0 \pm 0.1$

Table 2. The local order parameters for the phenyl rings,  $S_{zz}^R$  and  $S_{xx}^R - S_{yy}^R$ , and for the aliphatic C-D bonds,  $S_{CD}^\alpha$  and  $S_{CD}^\beta$ , for the PONOP molecules dissolved in Merck phase 5, EBBA, and ZLI 1132, at  $T_{\text{NI}}$  and at the lowest temperature for which spectra were recorded.

Molecule	Solvent	$T/\text{K}$	$S_{zz}^R$	$S_{xx}^R - S_{yy}^R$	$S_{CD}^\alpha$	$S_{CD}^\beta$
PO2OP	Phase 5	342	0.159	0.041	-0.066	
		300	0.415	0.070	-0.170	
	EBBA	347	0.161	0.042	-0.068	
		305	0.474	0.073	-0.193	
		ZLI 1132	337	0.184	0.120	-0.082
305	0.399		0.191	-0.176		
PO3OP	Phase 5	342	0.097	0.048	-0.038	-0.051
		300	0.264	0.107	-0.106	-0.144
	EBBA	344	0.106	0.055	-0.041	-0.054
		307	0.267	0.112	-0.106	-0.142
		ZLI 1132	340	0.136	0.146	-0.058
300	0.307		0.280	-0.139	-0.152	
PO4OP	Phase 5	342	0.149	0.038	-0.062	-0.062
		301	0.418	0.067	-0.175	-0.175
	EBBA	345	0.162	0.044	-0.067	-0.067
		306	0.455	0.074	-0.188	-0.188
		ZLI 1132	339	0.186	0.127	-0.086
300	0.433		0.207	-0.197	-0.170	

intensity. In this case the assignment is based on the chemical shift difference in the isotropic phase being  $\delta_a > \delta_b$ , an order which is expected to persist in the nematic phase.

Assignment of the signs of the quadrupolar couplings is more difficult. The deuterons at the *para*-positions give large quadrupolar splittings, and the local order parameters,  $S_{zz}^R$ , obtained from

$$\Delta\nu_i = (3/2)q_{CD}^i S_{CD}^i \quad (1)$$

are shown in table 2. The value of the quadrupolar coupling constant,  $q_{CD}$ , used was 185 kHz. Note that  $|S_{zz}^R|$  is always less than 0.5, so that the sign cannot be assigned unambiguously. However, values close to 0.5 are achieved, and molecules of this shape in thermotropic, calamitic nematic solvents with positive values of the diamagnetic anisotropies are expected to have positive order parameters for vectors such as the *para* C–D bond which are close to being parallel to the axis of minimum moment of inertia. It is safe to conclude, therefore, that  $\Delta\nu_{para}$  and  $S_{zz}^R$  are positive.

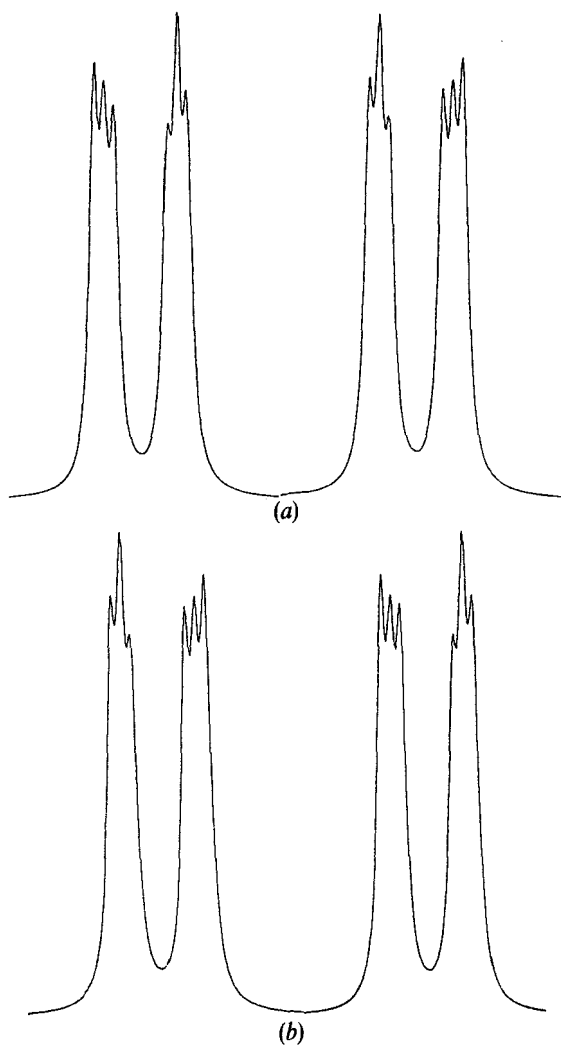


Figure 3. Calculated spectra for two deuterons for which the quadrupolar and dipolar couplings have (a) at the same, (b) opposite signs.

Both positive and negative quadrupolar splittings are observed for the *meta*- and *ortho*-deuterons. The determination of their signs depends on noting that the shape of the peaks depends on the relative signs of  $\Delta\nu_i$  and  $D_{om}$ , the dipolar coupling between the two deuterons on adjacent ring *ortho*- and *meta*-positions relative to the oxygen. The sign of  $D_{om}$  is negative if  $S_{zz}$  is positive. To illustrate this method of deducing the relative signs, the simulated spectra are shown in figure 3 for a pair of deuterons with the signs for  $D_{om}$  and the two quadrupolar splittings,  $\Delta\nu_o$  and  $\Delta\nu_m$ , (A) equal and (B) opposite. The spectra of PO2OP dissolved in Merck phase 5 and ZLI 1132, both at the same shifted temperature of  $(T_{NI} - T) = 21$  K, are shown in figures 4 and 5, demonstrating a sign reversal of the ratio  $D_{om}/\Delta\nu_{o,m}$ .

The relative signs of  $\Delta\nu_i$  and  $D_i$ , the dipolar coupling between *geminal* deuterons, for the deuterons in the alkyl chains can also be determined from the line shapes, but the evidence for the sign of either of these couplings is less unequivocal. Application of the theoretical model, which is discussed later, supports  $\Delta\nu_\alpha$  and  $\Delta\nu_\beta$  both being negative.

#### 4. Results and discussions

##### 4.1. The isotropic solution spectrum

The values of the two combinations of coupling constants,  $N = J_{13} + J_{14}$ , and  $L = J_{13} - J_{14}$  are related to  $J_i$  and  $J_g$ , which are the 3-bond couplings between pairs of

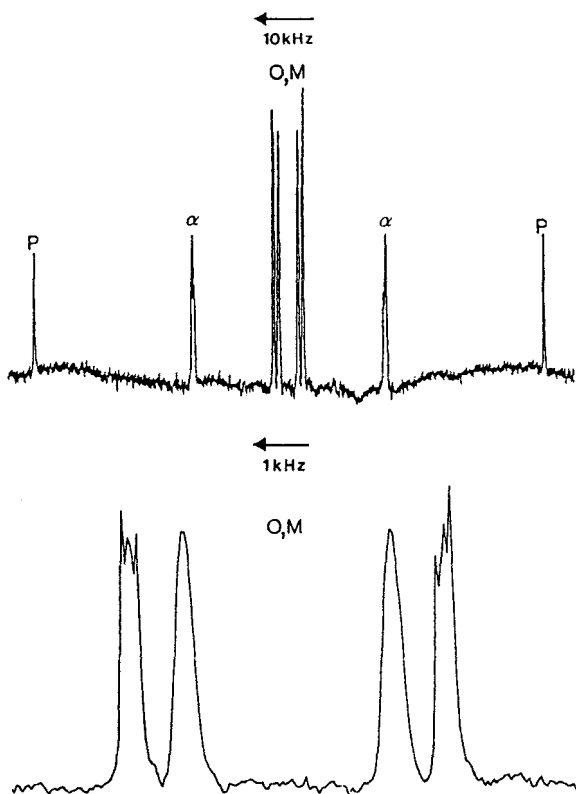


Figure 4. 30.7 MHz spectra (top) of the deuterons in PO2OP- $d_{14}$  dissolved in Merck Phase 5 at 322 K. The bottom trace is an expansion of the peaks which are assigned to the *ortho*- and *meta*- positions in the phenyl rings.

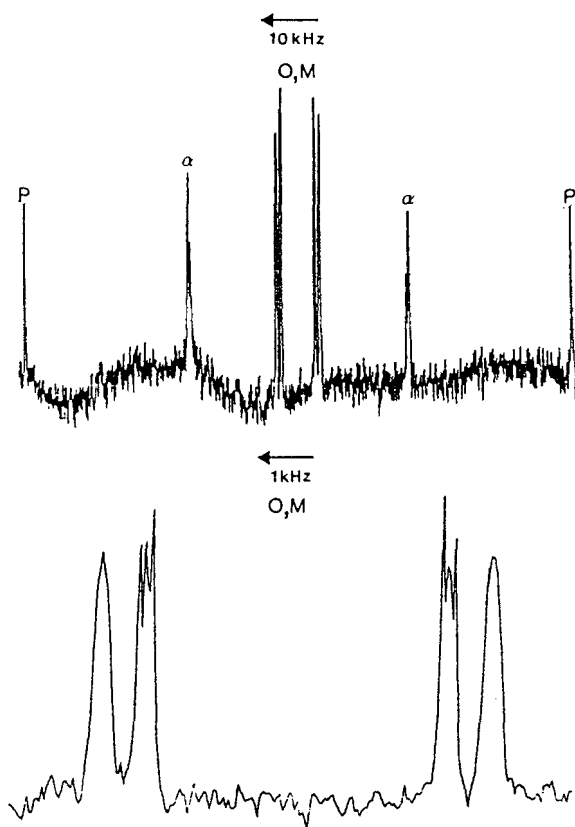


Figure 5. 30.7 MHz spectra (top) of the deuterons in PO2OP- $d_{14}$  dissolved in ZLI1132 at 316 K. The bottom trace is an expansion of the peaks which are assigned to the *ortho*- and *meta*-positions in the phenyl rings.

protons which are *trans* or *gauche* to each other, by

$$N = \frac{1}{2}[J_t + 3J_g + n_t(J_t - J_g)] \quad (2)$$

and

$$L = (\frac{1}{2} - (3/2)n_t)(J_t - J_g), \quad (3)$$

where  $n_t$  and  $n_g$  are the populations of the *trans* and *gauche* forms. Studies on similar compounds [6–8] have established that  $J_t - J_g$  is about 10 Hz, so that from equation (3), taking both possible signs for  $L$ ,

$n_t = 0.12$ ,  $J_t = 11.7$  Hz,  $J_g = 1.7$  Hz, and  $E_{tg} = -0.58$  kJ mol $^{-1}$  when  $L$  is positive;

$n_t = 0.54$ ,  $J_t = 11.2$  Hz,  $J_g = 1.2$  Hz, and  $E_{tg} = 0.49$  kJ mol $^{-1}$ , when  $L$  is negative.

The values of  $J_t$  and  $J_g$  are in excellent agreement with those found for 1,2-dimethoxy-1,4-dioxane [7] (11.6 and 1.7 Hz). It is safe to conclude therefore for the acetone solution of PO2OP that  $E_{tg}$  lies in the range  $0 \pm 0.5$  kJ mol $^{-1}$ .

#### 4.2. Nematic phase spectra

The quadrupolar splittings can be used to obtain the local parameters  $S_{zz}^R$  and  $S_{xx}^R$   $-S_{yy}^R$  for axes  $xyz$  fixed in the phenyl rings, and  $S_{CD}^{\alpha}$  and  $S_{CD}^{\beta}$  for the chain positions.



Thus, for the *ortho*-, *meta*- and *para*-positions in the phenyl rings,

$$\Delta v_i = 3q_{CD}^{Ar} [S_{zz}^R (3 \cos^2 \theta_{zi} - 1) + (S_{xx}^R - S_{yy}^R) \cos^2 \theta_{xi}] / 4, \quad (4)$$

where it has been assumed that the asymmetry parameter,  $\eta$ , for the deuteron quadrupolar tensors is zero. The angles  $\theta_{xi}$ , etc., are those for a regular hexagon structure for the phenyl rings with all CCH angles being  $120^\circ$ . The quadrupolar coupling constant  $q_{CD}^{Ar}$  is assigned a value of 185 kHz. The splitting for the *para*-deuteron gives  $S_{zz}^R$  directly with a precision, determined by the uncertainty in  $\Delta v^{Ar}$ , of  $\pm 2$  per cent. The splittings for the *ortho*- and *meta*-deuterons differ, most probably because CCH angles at these positions differ. Fixing both these angles to be  $120^\circ$ , and using a mean of the two quadrupolar splittings gives  $S_{xx}^R - S_{yy}^R$  with an error of about  $\pm 10$  per cent.

The order parameters of the C–D bonds at  $\alpha$  or  $\beta$  positions in the alkyl chain are given by

$$\Delta v_i = 3q_{CD}^{Al} S_{CD}^i / 2, \quad (5)$$

with  $q_{CD}^{Al}$  as 168 kHz. Table 2 gives the values of the local order parameters which were obtained for each of the PONOP compounds in each of the solvents at both  $T_{NI}$  and at the lowest temperature in each case that spectra were recorded.

Note that for each solution, the values of  $S_{zz}^R$  at  $T_{NI}$  show a marked even–odd alternation in magnitude, which parallels the behaviour found previously for the same order parameter in the CBONOBC mesogens [1]. The biaxial order parameter for the phenyl rings,  $S_{xx}^R - S_{yy}^R$  is similar in magnitude to those for the CBONOBC when the solvent is Merck phase 5 or EBBA, but is much larger for ZLI 1132.

#### 4.2. Comparison of observed with calculated order parameters

The ELS model used to calculate the order parameters represents  $U(\omega, n)$ , the energy of a molecule at orientation  $\omega$  with respect to the nematic director and in the  $n$ th conformation, as a sum

$$U(\omega, n) = U_{\text{ext}}(\omega, n) + U_{\text{int}}(n). \quad (6)$$

Here  $U_{\text{ext}}(\omega, n)$  is a potential of mean torque, which vanishes in the isotropic phase, and  $U_{\text{int}}(n)$  is the contribution to the mean potential which depends only on  $n$  and which does not vanish in the isotropic phase. In the case where the conformations are generated by rotations about the bonds in an alkyloxy chain the form adopted by  $U_{\text{int}}(n)$  in the RIS approximation is

$$U_{\text{int}}(n) = N_g^{\text{OC}} E_{ig}^{\text{OC}} + N_g^{\text{CC}} E_{ig}^{\text{CC}}, \quad (7)$$

where  $N_g^{\text{OC}}$  and  $N_g^{\text{CC}}$  are the number of *gauche* arrangements about O–C and C–C bonds.

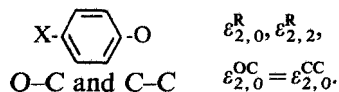
The potential of mean torque is approximated as

$$U_{\text{ext}}(\omega, n) = -\varepsilon_{2,0}(n) C_{2,0}(\omega) - 2\varepsilon_{2,2}(n) \text{Re } C_{2,2}(\omega), \quad (8)$$

where  $C_{2,m}(\omega)$  are reduced spherical harmonics. The conformational dependence of the interaction parameters is written as

$$\varepsilon_{2,m}(n) = \sum_j \sum_p \varepsilon_{2,p}(j) D_{p,m}^2(\Omega_{nj}). \quad (9)$$

The  $\varepsilon_{2,p}(j)$  are interaction parameters for rigid fragments of the molecule, and  $D_{p,m}^2(\Omega_{jn})$  is a Wigner function which depends on the orientation,  $\Omega_{jn}$ , of this fragment in a molecular reference frame fixed in one of the submolecular units. For both CBONOBC and PONOP molecules the molecular fragments and their interaction tensor components are:



X is H for the PONOP and 4-cyanophenyl for the CBONOBC molecules. The  $\varepsilon_{2,m}(j)$  are solvent-solvent parameters for the pure mesogens, and solute-solvent parameters for the PONOP.

The observed order parameters,  $S_{ij}$ , for particular vectors  $\mathbf{r}_{ij}$ , such as C-D bonds or the  $xyz$  axes, are averages over values,  $S_{ij}^n$ , for each conformation,

$$S_{ij} = \sum_n p_n^{\text{LC}} S_{ij}^n \quad (10)$$

The conformation order parameters are calculated from

$$S_{ij}^n = Q_n^{-1} \int (3 \cos^2 \theta_{nij} - 1) / 2 \exp \{ -U_{\text{ext}}(\omega, n) / kT \} d\omega, \quad (11)$$

where  $\theta_{nij}$  is the angle between  $\mathbf{r}_{ij}$  and the director, and

$$Q_n = \int \exp \{ -U_{\text{ext}}(\omega, n) / kT \} d\omega. \quad (12)$$

It is necessary to assume a geometry for each molecule, and the bond angles used here for both PONOP and CBONOBC molecules are identical to those adopted by Emsley *et al.* [1] in their calculations on the CBONOBC, except that for the PONOP the angle between  $z$  and the O-CH<sub>2</sub> bond was changed from 126.4 to 122°; this change was necessary in order to obtain acceptable agreement between observed and calculated values of  $S_{\text{CD}}^z$  and  $S_{\text{CD}}^y$  for PO3OP.

#### 4.3. Calculations with $E_{ig}^{\text{OC}}$ and $E_{ig}^{\text{CC}}$ independent of chain length

The theoretical model contains 5 adjustable parameters:  $E_{ig}^{\text{OC}}$ ,  $E_{ig}^{\text{CC}}$ ,  $\varepsilon_{2,0}^{\text{R}}$ ,  $\varepsilon_{2,2}^{\text{R}}$ ,  $\varepsilon_{2,0}^{\text{OC}} = \varepsilon_{2,0}^{\text{CC}}$ , and the number of observed order parameters is 4 for  $N=3$  and 4, and 3 for  $N=2$ . Clearly it is necessary to fix the values of some of these parameters, and the obvious candidates are the energy parameters,  $E_{ig}^{\text{OC}}$  and  $E_{ig}^{\text{CC}}$ , since the model assumes that these are independent of phase and hence their values could be taken from measurements made for these, or similar molecules in isotropic or liquid-crystalline solutions. Measurements of  $E_{ig}^{\text{OC}}$  have been reported for the isotropic phases of ethers [9], and for nematogens such as the 4- $n$ -alkoxy-4'-cyanobiphenyls [4]. These values lie in the narrow range 4.6–5.0 kJ mol<sup>-1</sup>, and so we have fixed this parameter in all our calculations at 5.0 kJ mol<sup>-1</sup>. Note that with a value this large, the populations of isomers with *gauche* arrangements about these bonds are very small, and so increases in  $E_{ig}^{\text{OC}}$ , which might be expected as the alkyl chain increases in length, have little effect on the calculated order parameters.

The calculations reported by Emsley *et al.* [1] also fixed  $E_{ig}^{\text{CC}}$  at 2.5 kJ mol<sup>-1</sup>, which is of similar magnitude to values determined for alkanes, and used extensively in

calculations of chain conformations. The calculated and observed order parameters obtained with these fixed energy parameters and varying the three  $\varepsilon_{2,m}(j)$  values are in good agreement, but they produce values for the ratio  $\varepsilon_{2,2}^{\text{CC}}/\varepsilon_{2,0}^{\text{R}} = \lambda_{\text{CC}}$  which vary strongly with chain length, which is difficult to reconcile with the expected behaviour of this parameter. Thus, for the CBONOB, the interaction parameters  $\varepsilon_{2,0}^{\text{R}}$  and  $\varepsilon_{2,0}^{\text{CC}}$  must depend on the orientational order of the molecules. The average interaction between an aromatic core in one molecule and all other aromatic cores will depend on  $S_{zz}^{\text{R}}$ , and on the fraction,  $x_a$ , of the molecule which is aromatic. Similarly, the average interaction of a core with the aliphatic, chain region of the molecules will depend on  $x_c$  and  $S_{\text{CC}}$ , an average order parameter for the chain [1]. In this model the values of  $\varepsilon_{2,0}^{\text{R}}$  and  $\varepsilon_{2,0}^{\text{CC}}$  are given by

$$\varepsilon_{2,0}^{\text{R}} = x_a \varepsilon^{\text{aa}} S_{zz}^{\text{R}} + x_c \varepsilon^{\text{ac}} S_{\text{CC}} \quad (13)$$

and

$$\varepsilon_{2,0}^{\text{CC}} = x_a \varepsilon^{\text{ca}} S_{zz}^{\text{R}} + x_c \varepsilon^{\text{cc}} S_{\text{CC}} \quad (14)$$

The  $\varepsilon^{\text{aa}}$ , etc., are average interaction strengths between the different molecular subunits. Invoking the approximation that,

$$\varepsilon^{\text{ac}} = \varepsilon^{\text{ca}} = (\varepsilon^{\text{aa}} \varepsilon^{\text{cc}})^{1/2} \quad (15)$$

and introducing

$$\lambda = (\varepsilon^{\text{cc}}/\varepsilon^{\text{aa}})^{1/2}, \quad (16)$$

gives

$$\varepsilon_{2,0}^{\text{R}} = \varepsilon^{\text{aa}} [x_a S_{zz}^{\text{R}} + \lambda x_c S_{\text{CC}}] \quad (17)$$

and

$$\varepsilon_{2,0}^{\text{CC}} = \varepsilon^{\text{aa}} [x_a S_{zz}^{\text{R}} + x_c \lambda S_{\text{CC}}] \quad (18)$$

so that  $\lambda \equiv \lambda_{\text{CC}}$  and is predicted to be independent of both temperature and chain length. A doubling of  $\lambda_{\text{CC}}$  for the CBONOB molecules on changing from  $N=3$  to 4, which is obtained when  $E_{\text{ig}}^{\text{CC}}$  is set equal for both molecules, is therefore unexpected. Similar calculations on the PONOP data also gives values of  $\lambda_{\text{CC}}$  which change by a large amount on going from PO3OP to PO4OP.

The variations in  $\lambda_{\text{CC}}$  obtained by maintaining  $E_{\text{ig}}^{\text{CC}}$  to be independent of  $N$  suggest that this assumption is incorrect. The value obtained for  $E_{\text{ig}}^{\text{CC}}$  for PO2OP when dissolved in acetone ( $0.0 \pm 0.5 \text{ kJ mol}^{-1}$ ) is certainly much smaller than the value of  $2.5 \text{ kJ mol}^{-1}$  used previously for the CBONOB series [1]. This larger value is probably appropriate for compounds with alkyloxy chains with  $N \geq 4$ , as suggested by calculations on compounds of the type  $\text{CH}_3(\text{CH}_2)_{N-1}\text{O}(\text{CH}_2)_N\text{O}(\text{CH}_2)_{N-1}\text{CH}_3$  by Miyasaka *et al.* [10].

#### 4.4. Calculations with $\lambda_{\text{CC}}$ fixed and $E_{\text{ig}}^{\text{CC}}$ allowed to vary with $N$

In view of the probable dependence of  $E_{\text{ig}}^{\text{CC}}$  on  $N$  we have explored the effect of fixing  $\lambda_{\text{CC}}$  and bringing observed and calculated order parameters into agreement by varying this energy parameter together with  $\varepsilon_{2,0}^{\text{R}}$  and  $\varepsilon_{2,2}^{\text{R}}$ . The data for the PONOP are considered first, and  $E_{\text{ig}}^{\text{CC}}$  for  $N=4$  is fixed as  $2.5 \text{ kJ mol}^{-1}$ . The observed and calculated order parameters for the PO4OP were brought into agreement by varying  $\varepsilon_{2,0}^{\text{R}}$ ,  $\lambda_{\text{R}} = \varepsilon_{2,2}^{\text{R}}/\varepsilon_{2,0}^{\text{R}}$  and  $\lambda_{\text{CC}}$  to give the results in table 3. Note that  $\lambda_{\text{CC}}$  is found to have only a

weak dependence on temperature, as expected, whilst the increase in  $\lambda_R$  with decreasing temperature is similar in magnitude and direction to that obtained for other aromatic solutes in liquid-crystalline phases [11–17]. For PO2OP and PO3OP, the data at  $T_{NI}$  were used with  $\lambda_{CC}$  fixed at the value found for PO4OP at  $T_{NI}$  to obtain  $\epsilon_{2,0}^R$ ,  $\lambda_R$  and  $E_{tg}^{CC}$ . The value obtained for  $E_{tg}^{CC}$  was then used with the data obtained for each solution at the lowest temperatures to obtain  $\epsilon_{2,0}^R$ ,  $\lambda_{CC}$  and  $\lambda_R$ . The results are shown in table 3. The error on the values of  $E_{tg}^{CC}$  obtained in this way is estimated to be  $\pm 0.5 \text{ kJ mol}^{-1}$ . Changing the fixed value of  $E_{tg}^{CC}$  for PO4OP leads to changes in the absolute values obtained for PO2OP and PO3OP, but has little effect on their relative magnitudes.

The most striking result obtained by this analysis of the data is that a value close to zero is obtained for  $E_{tg}^{CC}$  for the PO3OP in all three solvents, and a negative value is obtained for PO2OP. The variation in the magnitude of  $E_{tg}^{CC}$  with solvent obtained for PO2OP mirrors the behaviour found for isotropic solutions of  $\text{ROCH}_2\text{CH}_2\text{OR}$  compounds [8], where  $E_{tg}^{CC}$  has been found to vary in the range  $0$ – $-4 \text{ kJ mol}^{-1}$  on changing from solvents of low to high dielectric constant,  $\epsilon$ . The liquid crystal solvents used here do contain strongly polar groups, and this may be a factor in stabilizing individual conformations, but their complex structures make it unlikely that there should be a simple correlation between  $E_{tg}^{CC}$  and their mean dielectric coefficients.

#### 4.5. Calculations with $\lambda_{CC}$ fixed for CBONOBC molecules

Applying the same model to CBONOBC data gave the results in table 4. Note that for these molecules the values obtained for  $S_{xx}^R - S_{yy}^R$  are small, and have a large uncertainty [1]. This leads to a large uncertainty in  $\lambda_R$  if this is included as a variable when fitting the observed and calculated order parameters. In practice, the important results of the calculations are virtually unchanged if  $\lambda_R$  is fixed at 0.1, which is the approximate average obtained when it was allowed to vary, and this therefore was the

Table 3. The values of  $E_{tg}^{CC}$ ,  $\epsilon_{2,0}^R$ ,  $\lambda_R$  and  $\lambda_{CC}$  obtained for the PONOP molecules.

Molecule	Solvent	$T/\text{K}$	$E_{tg}^{CC}/\text{kJ mol}^{-1}$	$\epsilon_{2,0}^R$	$\lambda_R$	$\lambda_{CC}$
PO4OP	EBBA	344	2.5†	1.60	0.06	0.34
		306	2.5†	3.59	0.10	0.32
	Phase 5	342	2.5†	1.49	0.04	0.34
		301	2.5†	3.20	0.07	0.33
	ZLI 1132	339	2.5†	1.97	0.41	0.22
		300	2.5†	3.99	0.54	0.19
PO3OP	EBBA	344	0.00	1.37	0.17	0.34†
		307	0.00†	3.14	0.18	0.29
	Phase 5	342	0.145	1.25	0.15	0.34†
		300	0.145†	3.02	0.17	0.28
	ZLI 1132	340	0.00	1.89	0.48	0.22†
		300	0.00†	4.16	0.56	0.18
PO2OP	EBBA	347	-1.71	1.64	0.15	0.34†
		305	-1.71†	3.83	0.22	0.29
	Phase 5	342	-2.46	1.62	0.16	0.34†
		300	-2.46†	3.24	0.22	0.34
	ZLI 1132	337	-0.87	1.91	0.46	0.22†
		305	-0.87†	3.58	0.57	0.22

† Fixed.

procedure used to obtain the data in table 4. The uncertainties in the values obtained for  $E_{ig}^{CC}$  are estimated at  $\pm 0.5$  kJ mol<sup>-1</sup>. For CBO3OBC the value of  $E_{ig}^{CC}$  is again found to be close to zero, and  $\lambda_{CC}$  is again found to be essentially temperature independent.

The results obtained for CBO2OBC are not in complete agreement with the model. Thus, fixing  $\lambda_{CC}$  at the value of 0.205, the value found for CBO4OBC at  $T_{NI}$ , gives  $E_{ig}^{CC}$  as 1.76 kJ mol<sup>-1</sup>, which although quite different from the values obtained for the solutions of PO2OP, is acceptable in view of the large variations possible for these derivatives of ethylene glycol. However, fixing  $E_{ig}^{CC}$  as 1.76 kJ mol<sup>-1</sup> and fitting the data for  $T = 455$  K by varying  $\lambda_{CC}$ ,  $e_{2,0}^R$  and  $\lambda_R$  gives  $\lambda_{CC}$  as 0.250, compared with 0.205 at  $T_{NI}$ , which is a much larger temperature dependence of this parameter than is observed for any of the other systems. Repeating this calculation with  $E_{ig}^{CC}$  fixed at  $-1.76$  kJ mol<sup>-1</sup> gives  $\lambda_{CC}$  as 0.33 at 538 K and 0.34 at 455 K; thus the temperature variation of this parameter can be eliminated, but at the expense of a large change in  $\lambda_{CC}$  on going from  $N = 4$  to  $N = 2$ .

#### 4.6. Conformational distributions

The ELS model predicts a change in the relative populations of the conformations on changing isothermally from an isotropic to a liquid-crystalline phase. The two probabilities,  $p^{iso}$  and  $p^{LC}$  are given by

$$p^{iso} = \exp\{-U_{int}(n)/kT\} / \sum_n \exp\{-U_{int}(n)/kT\} \quad (19)$$

and

$$p^{LC} = QZ^{-1} \exp\{-U_{int}(n)/kT\}, \quad (20)$$

where

$$Z = \sum_n \int \exp\{-U(n, \omega)/kT\} d\omega. \quad (21)$$

#### 4.7. Conformations of the PONOP molecules

In table 5 we list the populations of all the conformations of PO2OP when dissolved in ZLI 1132; data for the other solutions are very similar. The number of conformations increases rapidly with  $N$ ; it is impracticable therefore to list all the conformations for PO3OP and PO4OP, and so we give in tables 6 and 7 the populations of the four most populated conformations.

Table 4. The values of  $E_{ig}^{CC}$ ,  $e_{2,0}^R$ , and  $\lambda_{CC}$  obtained by applying the ELS model to the CBO3OBC data and constraining  $\lambda_{CC}$  to be independent of  $N$  at  $T_{NI}$ .

Molecule	$T/K$	$E_{ig}^{CC}/\text{kJ mol}^{-1}$	$e_{2,0}^R/\text{kJ mol}^{-1}$	$\lambda_R \dagger$	$\lambda_{CC}$
CBO4OBC	524	2.5†	8.76	0.1	0.205†
	470	2.5†	13.06	0.1	0.192
CBO3OBC	443	0.00	5.75	0.1	0.205†
	419	0.00	8.78	0.1	0.183
CBO2OBC	538	1.76	8.41	0.1	0.205†
	455	1.76†	9.80	0.1	0.250

† Fixed.

Table 5. The populations  $p^{\text{iso}}$  and  $p^{\text{LC}}$  of the conformations adopted by PO2OP when dissolved in ZLI1132 at  $T_{\text{NI}}$  together with the values of the local order parameters,  $S_{zz}^{\text{R}}(n)$  and  $S_{xx}^{\text{R}}(n) - S_{yy}^{\text{R}}(n)$ , and the order parameters for the conformations,  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  referred to the principal axes.

Conformer	$G^\dagger$	$p^{\text{iso}}$	$p^{\text{LC}}$	$S_{zz}^{\text{R}}(n)$	$S_{xx}^{\text{R}}(n) - S_{yy}^{\text{R}}(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
(1) <i>ttt</i>	1	0.19	0.22	0.30	0.21	0.30	0.20
(2) <i>ttg</i> $\pm$	4	0.13	0.12	0.04	0.16	0.16	0.16
(3) <i>tg</i> $\pm t$	2	0.26	0.27	0.30	0.03	0.31	0.09
(4) <i>tg</i> $\pm g$ $\pm$	4	0.17	0.15	0.02	0.06	0.07	0.12
(5) <i>tg</i> $\pm g$ $\mp$	4	0.17	0.16	0.09	0.15	0.16	0.20
(6) <i>g</i> $\pm tg$ $\pm$	2	0.01	0.01	0.06	0.24	0.13	0.25
(7) <i>g</i> $\pm tg$ $\mp$	2	0.01	0.01	0.25	0.22	0.26	0.21
(8) <i>g</i> $\pm g$ $\pm g$ $\pm$	2	0.02	0.02	0.27	0.04	0.27	0.08
(9) <i>g</i> $\pm g$ $\pm g$ $\mp$	4	0.02	0.01	0.11	0.18	0.18	0.18
(10) <i>g</i> $\pm g$ $\mp g$ $\pm$	2	0.02	0.02	0.22	0.23	0.25	0.21

$\dagger G$  is the degeneracy of the conformer.

Table 6. The populations  $p^{\text{iso}}$  and  $p^{\text{LC}}$  of the four most populated conformations adopted by PO3OP when dissolved in ZLI 1132 at  $T_{\text{NI}}$ , together with the values of the local order parameters,  $S_{zz}^{\text{R}}(n)$  and  $S_{xx}^{\text{R}}(n) - S_{yy}^{\text{R}}(n)$ , and the order parameters for the conformations,  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  referred to the principal axes.

Conformer	$G^\dagger$	$p^{\text{iso}}$	$p^{\text{LC}}$	$S_{zz}^{\text{R}}(n)$	$S_{xx}^{\text{R}}(n) - S_{yy}^{\text{R}}(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
<i>ttg</i> $\pm t$	4	0.25	0.25	0.15	0.13	0.25	0.13
<i>tg</i> $\pm g$ $\mp t$	2	0.12	0.12	0.05	0.15	0.09	0.26
<i>tg</i> $\pm g$ $\pm t$	2	0.12	0.11	0.03	0.04	0.11	0.06
<i>tttt</i>	1	0.06	0.07	0.23	0.29	0.29	0.24

$\dagger G$  is the degeneracy of the conformer.

Table 7. The populations  $p^{\text{iso}}$  and  $p^{\text{LC}}$  of the four most populated conformations adopted by PO4OP when dissolved in ZLI 1132 at  $T_{\text{NI}}$ , together with the values of the local order parameters,  $S_{zz}^{\text{R}}(n)$  and  $S_{xx}^{\text{R}}(n) - S_{yy}^{\text{R}}(n)$ , and the order parameters for the conformations,  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  referred to the principal axes.

Conformer	$G^\dagger$	$p^{\text{iso}}$	$p^{\text{LC}}$	$S_{zz}^{\text{R}}(n)$	$S_{xx}^{\text{R}}(n) - S_{yy}^{\text{R}}(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
<i>tttg</i> $\pm t$	4	0.15	0.17	0.34	0.03	0.35	0.08
<i>tttt</i>	1	0.09	0.11	0.34	0.20	0.35	0.19
<i>ttg</i> $\pm tt$	2	0.08	0.07	0.05	0.17	0.18	0.17
<i>ttg</i> $\pm g$ $\mp t$	4	0.06	0.06	0.10	0.16	0.18	0.21

$\dagger G$  is the degeneracy of the conformer.

In rationalizing the behaviour of flexible molecules in liquid-crystalline phases it is tempting to assume that it is a reasonable approximation to discuss the results only in terms of the most extended, all-*trans* structure. This approximation assumes that this conformer will be the most abundant. This is not the case for the three PONOP molecules. Even for PO4OP, where  $E_{tg}^{\text{CC}}$  is positive and large, the *tttt* conformer can achieve only second place behind the 4-fold degenerate conformers *tg*  $\pm ttt$  and *tttg*  $\pm t$ . For PO3OP *tttt* drops even lower in the ranking to fourth place, the most populated being the 4-fold degenerate *ttg*  $\pm t$  and *tg*  $\pm tt$ .

## 4.8. Conformations of the CBONOBC molecules

The data for the CBONOBC are contained in tables 8, 9 and 10. The pure mesogens are more strongly ordered than the PONOP solutes; that is the anisotropic potential is larger. This has the consequence of favouring more strongly those conformations which have a larger ordering potential and thus giving larger values to  $\Delta p = (p^{LC} - p^{iso})/p^{iso}$ . Thus  $\Delta p = 0.22$  for *tttt* in PO4OP dissolved in ZLI 1132 at  $T_{NI}$ , and 2.0 for the same conformer in CBO4OBC at  $T_{NI}$ .

Table 8. The populations  $p^{iso}$  and  $p^{LC}$  of the conformations adopted by CBO2OBC at  $T_{NI}$ , together with the values of the local order parameters,  $S_{zz}^R(n)$  and  $S_{xx}^R(n) - S_{yy}^R(n)$ , and the order parameters for the conformations,  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  referred to the principal axes.

Conformer	$G^\dagger$	$p^{iso}$	$p^{LC}$	$S_{zz}^R(n)$	$S_{xx}^R(n) - S_{yy}^R(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
(1) <i>ttt</i>	1	0.18	0.32	0.69	0.05	0.70	0.05
(2) <i>ttg</i> $\pm$	4	0.19	0.10	0.14	0.11	0.32	0.24
(3) <i>tg</i> $\pm t$	2	0.24	0.34	0.64	0.02	0.67	0.03
(4) <i>tg</i> $\pm g$ $\pm$	4	0.13	0.06	0.12	-0.20	0.21	0.24
(5) <i>tg</i> $\pm g$ $\mp$	4	0.13	0.07	0.19	0.14	0.34	0.25
(6) <i>g</i> $\pm tg$ $\pm$	2	0.03	0.01	0.12	0.28	0.18	0.35
(7) <i>g</i> $\pm tg$ $\mp$	2	0.03	0.03	0.64	0.06	0.65	0.05
(8) <i>g</i> $\pm g$ $\pm g$ $\pm$	2	0.02	0.02	0.62	0.01	0.63	0.02
(9) <i>g</i> $\pm g$ $\pm g$ $\mp$	4	0.02	0.01	0.23	0.18	0.39	0.16
(10) <i>g</i> $\pm g$ $\mp g$ $\pm$	2	0.02	0.02	0.57	0.10	0.64	0.06

$\dagger G$  is the degeneracy of the conformer.

Table 9. The populations  $p^{iso}$  and  $p^{LC}$  of the four most populated conformations adopted by CBO3OBC at  $T_{NI}$ , together with the values of the local order parameters,  $S_{zz}^R(n)$  and  $S_{xx}^R(n) - S_{yy}^R(n)$ , and the order parameters for the conformations,  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  referred to the principal axes.

Conformer	$G^\dagger$	$p^{iso}$	$p^{LC}$	$S_{zz}^R(n)$	$S_{xx}^R(n) - S_{yy}^R(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
<i>ttg</i> $\pm t$	4	0.20	0.21	0.33	0.12	0.51	0.11
<i>tttt</i>	1	0.05	0.08	0.51	0.19	0.62	0.08
<i>tg</i> $\pm g$ $\mp g$ $\pm$	4	0.05	0.08	0.59	0.06	0.62	0.06
<i>tg</i> $\pm g$ $\mp g$ $\mp$	4	0.05	0.07	0.48	0.18	0.59	0.08

$\dagger G$  is the degeneracy of the conformer.

Table 10. The populations  $p^{iso}$  and  $p^{LC}$  of the four most populated conformations adopted by CBO4OBC at  $T_{NI}$ , together with the values of the local order parameters,  $S_{zz}^R(n)$  and  $S_{xx}^R(n) - S_{yy}^R(n)$ , and the order parameters for the conformations,  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  referred to the principal axes.

Conformer	$G^\dagger$	$p^{iso}$	$p^{LC}$	$S_{zz}^R(n)$	$S_{xx}^R(n) - S_{yy}^R(n)$	$S_{z'z'}(n)$	$S_{x'x'}(n) - S_{y'y'}(n)$
<i>tttg</i> $\pm t$	4	0.09	0.19	0.72	0.01	0.76	0.03
<i>tttt</i>	1	0.04	0.12	0.77	0.05	0.78	0.04
<i>tg</i> $\pm tg$ $\mp t$	2	0.03	0.07	0.77	0.03	0.77	0.03
<i>ttg</i> $\pm tg$ $\mp$	4	0.03	0.06	0.72	0.06	0.74	0.04

$\dagger G$  is the degeneracy of the conformer.

The results shown in table 8 for CBO2OBC are those obtained with  $E_{ig}^{CC}$  as  $1.76 \text{ kJ mol}^{-1}$ . Changing  $E_{ig}^{CC}$  to  $-1.76 \text{ kJ mol}^{-1}$  produces relatively small changes in the values of  $p^{LC}$  as shown in figure 6.

The stronger anisotropic potential also produces a much stronger dependence of  $p^{LC}$  on temperature. Thus, decreasing the temperature to 455 K for CBO2OBC produces the changes shown in figure 7, and at this temperature the *ttt* conformation becomes the most probable. Note too the large changes  $p^{LC} - p^{iso}$  at the lower temperature, which are shown in figure 8.

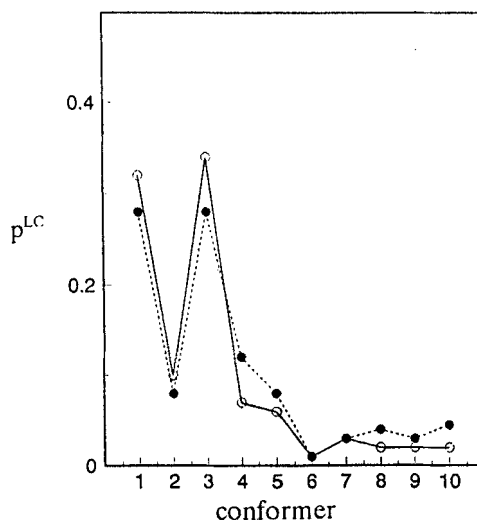


Figure 6. Changes in the populations,  $p^{LC}$ , of the conformers of CBO2OBC at  $T_{NI}$ , when  $E_{ig}^{CC}$  is reduced in value from  $1.76$  (○) to  $-1.76 \text{ kJ mol}^{-1}$  (●). The conformer labels are those in table 8.

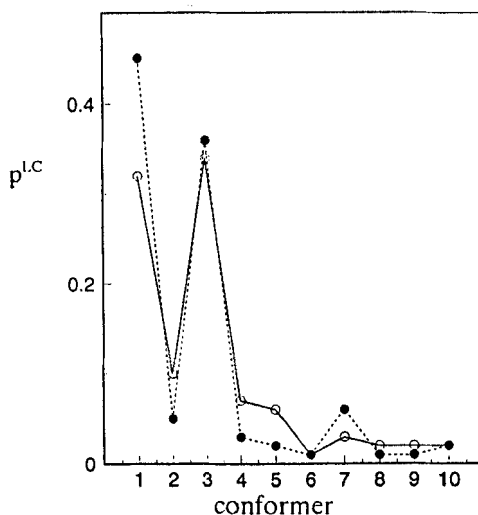


Figure 7. The change in the populations,  $p^{LC}$ , of the conformers of CBO2OBC when the temperature is reduced from  $538 \text{ K}$  ( $T_{NI}$ ) (○) to  $455 \text{ K}$  (●). The conformer labels are those in table 8.



4.9. *Orientational ordering at  $T_{NI}$* 

Tables 5–10 also give the magnitudes of the order parameters  $S_{z'z'}(n)$  and  $S_{x'x'}(n) - S_{y'y'}(n)$  for the individual conformations in their principal coordinate frames, and  $S_{zz}^R(n)$  and  $S_{xx}^R(n) - S_{yy}^R(n)$  for the aromatic cores.

A most striking experimental observation [18] for the CBO2OBC compounds is the odd–even alternation in the magnitudes of  $S_{zz}^R$ . A similar odd–even effect is observed for the PONOP solutes, as shown in figure 9. Changes in a local order parameter such as  $S_{zz}^R$  are difficult to relate to changes that may be occurring in the

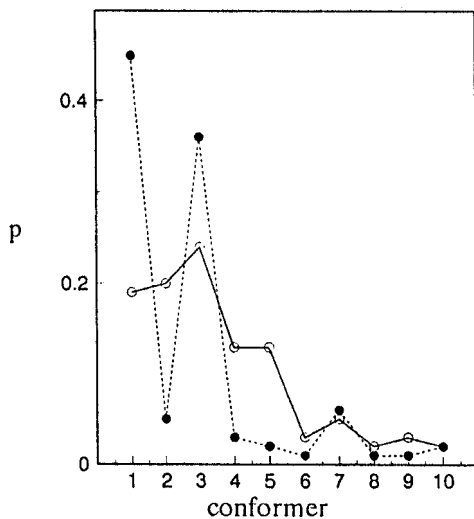


Figure 8. The conformer populations  $p^{iso}$  (○) and  $p^{LC}$  (●) for CBO2OBC at 455 K. The conformer labels are those in table 8.

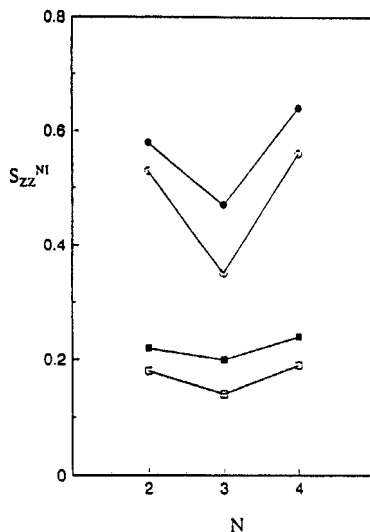


Figure 9. The order parameters  $S_{zz}^R$  for CBO2OBC (○) and PONOP (□) in ZLI 1132 at  $T_{NI}$ , compared with values of  $S_{z'z'}$  (● and ■).

Table 11. The average principal order parameters,  $S_{z'z'}$  and  $S_{x'x'} - S_{y'y'}$ , at  $T_{NI}$  for the CBONOBC and the PONOP dissolved in ZLI 1132.

Molecule	$S_{z'z'}$	$S_{x'x'} - S_{y'y'}$
CBO2OBC	0.58	0.09
CBO3OBC	0.47	0.12
CBO4OBC	0.64	0.09
PO2OP	0.22	0.15
PO3OP	0.20	0.16
PO4OP	0.24	0.16

anisotropic intermolecular potential since they reflect geometrical as well as strength variations with  $N$ . It is possible, therefore, that the orientational order of the whole molecules does not change with  $N$ , and that the changes in  $S_{zz}^R$  are entirely geometrical in origin, and arise because the  $z$  axes change their orientations relative to the principal axes of the interaction tensors  $\epsilon(n)$ . To test this idea we compare in table 11 the values of averaged principal order parameters defined as

$$S_{\alpha'\alpha'} = \sum_n P_n^{LC} S_{\alpha\alpha}(n). \quad (22)$$

The alternation in these values is still present for the CBONOBC series, although considerably reduced, whilst it has virtually disappeared for the PONOP. This suggests that the odd-even effect has a geometrical origin for the PONOP dissolved in a common nematic solvent, but that the orientational ordering of the CBONOBC molecules does alternate with  $N$ .

## 5. Conclusion

The main conclusion reached by applying the ELS model to the data for both the PONOP and CBONOBC compounds is that  $E_{ig}^{CC}$  is strongly dependent on chain length as  $N$  changes from 2 to 4. Here  $E_{ig}^{CC}$  is a mean conformational energy for isotropic solutions of these compounds. This conclusion should be regarded as tentative, as it is unclear how dependent it is on the use of the ELS model rather than some other model for constructing the potential of mean torque, such as the chord model [19]. However, there is considerable support for this conclusion from both experimental and theoretical investigations of alkane diols. Thus, the vicinal scalar coupling constants,  $^3J_{HH}$ , in the fragment  $-\text{CH}_2\text{CH}_2-$  of PO2OP dissolved in acetone are consistent with an  $E_{ig}^{CC}$  value in the range  $\pm 0.5 \text{ kJ mol}^{-1}$ . This compares with values of  $-1.7$  to  $-3.5 \text{ kJ mol}^{-1}$  for  $E_{ig}^{CC}$  obtained by the same method by Viti *et al.* [8] for samples of 1,2-dimethoxyethane in various isotropic solutions. The origin of the forces stabilizing the *gauche* arrangement in  $\text{ROCH}_2\text{CH}_2\text{OR}$  compounds may be in doubt [20], but the effect certainly will decrease with separation of the oxygen atoms [10], so that  $E_{ig}^{CC}$  is expected to become more positive as the number of methylene links increases from 2 to 4.

Finally, it is important to note that although  $E_{ig}^{CC}$  and  $E_{ig}^{OC}$  determine the conformational weights,  $p^{\text{iso}}$ , in the isotropic phase, in liquid-crystalline phases the weights,  $p^{\text{LC}}$ , are also strongly affected by the anisotropic, intermolecular forces.

## References

- [1] EMSLEY, J. W., HEATON, N. J., LUCKHURST, G. R., and SHILSTONE, G. N., 1988, *Molec. Phys.*, **64**, 377.
- [2] MARCELJA, S., 1974, *J. chem. Phys.*, **60**, 3599.
- [3] EMSLEY, J. W., LUCKHURST, G. R., and STOCKLEY, C. P., 1982, *Proc. R. Soc. A*, **381**, 117.
- [4] COUNSELL, C. J. R., EMSLEY, J. W., HEATON, N. J., and LUCKHURST, 1985, *Molec. Phys.*, **54**, 847.
- [5] COUNSELL, C. J. R., EMSLEY, J. W., LUCKHURST, G. R., and SACHDEV, H. S., 1988, *Molec. Phys.*, **63**, 33.
- [6] SHEPPARD, N., and TURNER, J. J., 1959, *Proc. R. Soc. A*, **252**, 506.
- [7] GATTI, G., SEGRE, A. L., and MORANDI, C., 1967, *Tetrahedron*, **33**, 4385.
- [8] VITI, V., INDOVINA, P. L., PODO, F., RADICS, L., and NEMETHY, G., 1974, *Molec. Phys.*, **27**, 541.
- [9] KANESAKA, I., SNYDER, R. G., and STRAUSS, H. L., 1986, *J. chem. Phys.*, **84**, 395.
- [10] MIYASAKA, T., YOSHIDA, T., and IMAMURA, Y., 1986, *Makromolek. Chem.*, **187**, 1515.
- [11] EMSLEY, J. W., HASHIM, R., LUCKHURST, G. R., RUMBLES, G. N., and VILORIA, F. R., 1988, *Molec. Phys.*, **49**, 1321.
- [12] EMSLEY, J. W., HASHIM, R., LUCKHURST, G. R., and SHILSTONE, G. N., 1986, *Liq. Crystals*, **1**, 437.
- [13] CATALANO, D., FORTE, C., VERACINI, C. A., EMSLEY, J. W., and SHILSTONE, G. N., 1987, *Liq. Crystals*, **2**, 357.
- [14] EMSLEY, J. W., LUCKHURST, G. R., and SACHDEV, H. S., 1989, *Liq. Crystals*, **5**, 953.
- [15] EMSLEY, J. W., LUCKHURST, G. R., and SACHDEV, 1989, *Molec. Phys.*, **67**, 151.
- [16] EMSLEY, J. W., LUCKHURST, G. R., and SMITH, S. W., 1990, *Molec. Phys.*, **70**, 967.
- [17] EMSLEY, J. W., HEEKS, S. K., HORNE, T. J., HOWELLS, M. H., MOON, A., PALKE, W. E., PATEL, S. U., SHILSTONE, G. N., and SMITH, A., 1991, *Liq. Crystals*, **9**, 649.
- [18] EMSLEY, J. W., LUCKHURST, G. R., and SHILSTONE, G. N., 1984, *Molec. Phys.*, **53**, 1023.
- [19] PHOTINOS, D. J., SAMULSKI, E. T., and TORIUMI, H., 1992, *J. chem. Soc. Faraday. Trans.*, **88**, 1875.
- [20] ANDERSSON, M., and KARLSTROM, G., 1985, *J. phys. Chem.*, **89**, 4957.