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# An enhanced odd–even effect of liquid crystal dimers

## Orientational order in the α,ω-bis(4′-cyanobiphenyl-4-yl)alkanes

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The odd–even behaviour observed for liquid crystal dimers has been predicted to be a sensitive function of the geometry of the link joining the mesogenic groups to the flexible spacer. Here we report the synthesis of two cyanobiphenyl dimers with methylene links, together with a determination of their transitional properties. In particular we have probed their orientational order via the major and biaxial orientational order parameters of a solute molecule, anthracene-$d_{10}$, using NMR spectroscopy. For comparison we have also determined the corresponding quantities for the cyanobiphenyl dimers with ether links. The enhanced odd–even effect observed for the methylene linked dimers relative to those with ether links is in good accord with theory.

Liquid crystal dimers in which two anisometric or mesogenic groups are linked by a flexible spacer exhibit pronounced odd–even effects [1]. For example, the members of the series with an even number of atoms in the spacer have significantly higher nematic–isotropic transition temperatures than the odd members, although this difference is attenuated as the length of the spacer increases. In contrast, the entropy of transition is essentially unattenuated as the spacer length increases, with the even members having considerably higher values than the odd. The magnitude of the odd–even effect is, however, a sensitive function of the geometry of the link between the alkyl chain and the mesogenic groups. As the angle between the long axis of the mesogenic group and the bond between the first two atoms in the chain decreases so the alternation grows, largely as a result of a reduction in the liquid crystallinity of the odd dimers. This behaviour can be understood at a simple level in terms of the increase in the molecular biaxiality of the odd dimers as the link angle is reduced. Such a change in the molecular shape is illustrated in figure 1 for the all-*trans* conformer, but similar increases occur for other conformations of the spacer. The methylene group provides a smaller link angle than an ether, and so the odd–even effect is predicted [2], and observed [3], to be greater for methylene linked dimers than for those with an ether link. As a consequence of this, the transitional entropy for the odd members is predicted to be sufficiently small, especially for short spacers, that the transition might even be second order, with the associated, exciting possibility that a biaxial nematic phase could be formed [2].

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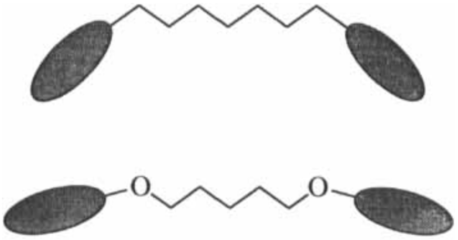


Figure 1. The change in the molecular shape of the all-*trans* conformer for a dimer with an odd number of atoms in the spacer when an ether link is replaced by a methylene group.

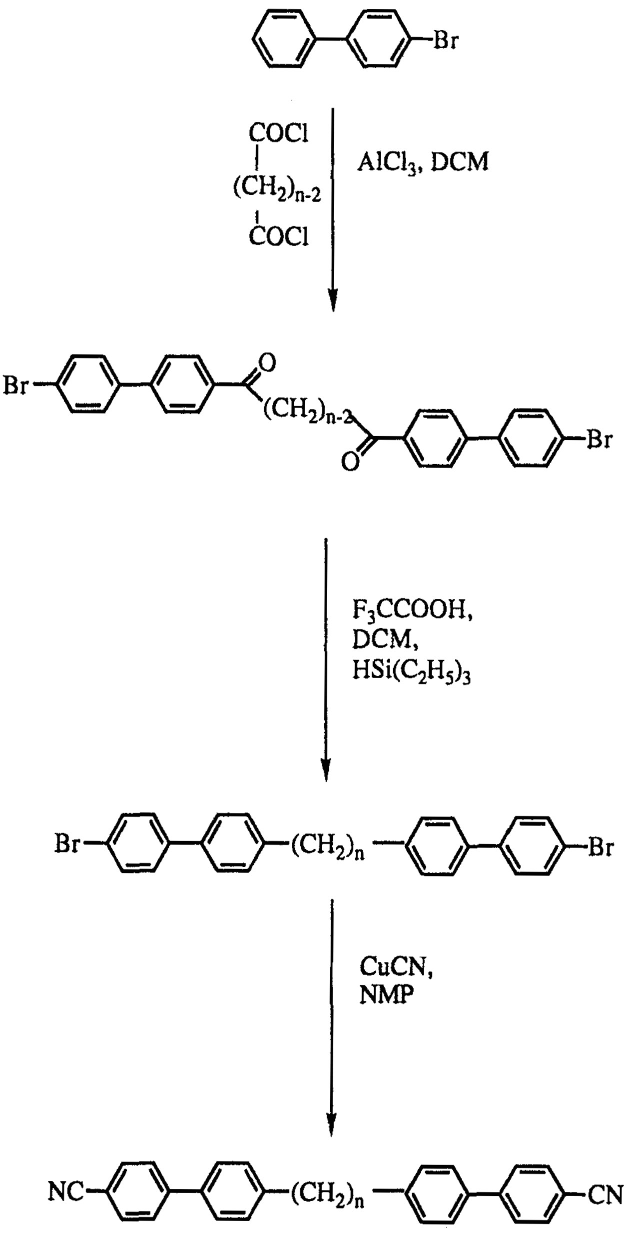
In order to explore the properties of methylene linked dimers further we have synthesized two members of the homologous series of α,ω-bis(4′-cyanobiphenyl-4-yl)alkanes with $-(CH_2)_6-$ and $-(CH_2)_7-$ spacers and determined their transitional properties. In addition the orientational order in the liquid crystalline phases of these compounds was probed by determining the major and biaxial order parameters for anthracene-$d_{10}$ dissolved in them, using deuterium NMR spectroscopy. For comparison we have repeated the measurements using the analogous ether linked dimers, the α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes [1].

The methylene linked dimers were synthesized according to the procedure outlined in the scheme. The first step is the synthesis of the α,ω-bis(4′-bromobiphenyl-4-carbonyl)alkane followed by the reduction of the carbonyl groups to give the α,ω-bis(4′-bromobiphenyl-4-yl)alkane and then the cyanation of this to produce the desired product, namely the α,ω-bis(4′-cyanobiphenyl-4-yl)alkane. The details for each of these synthetic steps are exemplified for the $C_6$ spacer; similar procedures were used for the $C_7$ spacer.

*α,ω-Bis(4′-bromobiphenyl-4-carbonyl)butane.* A solution of freshly distilled adipoyl chloride (5·49 g, 0·03 mol) and 4-bromobiphenyl (15 g, 0·065 mol) in dichloromethane (30 ml) was added dropwise to a stirred suspension of aluminium trichloride (7·72 g, 0·062 mol) in dichloromethane (25 ml) at 0°C. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into water (200 ml) and shaken with dichloromethane (3 × 40 ml). The remaining aqueous suspension was filtered; the solid was washed thoroughly with water and recrystallized from toluene. Yield 7·95 g (46 per cent), mp 244–247°C.

*α,ω-Bis(4′-bromobiphenyl-4-yl)hexane.* Triethylsilane (7·54 g, 0·065 mol) was added dropwise to a stirred solution of α,ω-bis(4′-bromobiphenyl-4-carbonyl)butane (7·49 g, 0·013 mol) in trifluoroacetic acid (23·26 g, 0·20 mol) and dichloromethane (20 ml) at 0°C [4]. The reaction mixture was allowed to reach room temperature and stirred for 48 h. The white solid was then filtered off, washed thoroughly with water and recrystallized from toluene. Yield 3·0 g (42 per cent), mp 217–219°C.

*α,ω-Bis(4′-cyanobiphenyl-4-yl)hexane.* The cyanation was carried out using the method employed by Coates and Gray [5]. A mixture of α,ω-bis(4′-bromobiphenyl-4-yl)hexane (2·10 g, 0·0038 mol), cuprous cyanide (1·02 g, 0·011 mol) and dry *N*-methylpyrrolidone (30 ml) were stirred at 200°C for 4 h. This was then cooled to 80°C and a solution of ferric chloride (5 g) in water (10 ml) and hydrochloric acid (4 ml) was added. After stirring for a further 30 min, the mixture was allowed to cool overnight, poured into water (100 ml) and shaken with dichloromethane (3 × 100 ml). The organic layer was washed with water (3 × 50 ml), dried over $CaCl_2$ and the solvent removed.



The product was purified by column chromatography (dichloromethane/silica 60) and recrystallized from toluene. Yield 0·85 g (51 per cent).

The structures of all intermediates and final products were confirmed using a combination of IR (Perkin–Elmer 1600 series FT-IR), $^1H$ and $^{13}C$ NMR (Jeol FX90 and Bruker AM360) and mass spectrometry (VG 70–250). All results were consistent with the required structures and no unaccounted peaks were present. For the hexane linked dimer we find: NMR ($CDCl_3$, $\delta$). $^1H$; 1·4 (m, 4 H), 1·7 (m, 4 H), 2·7 (t, 4 H), 7·3 (d, 4 H, $J = 8$ Hz), 7·5 (d, 4 H, $J = 8$ Hz), 7·7 p.p.m. (m, 8 H). $^{13}C$; 29·25, 31·38, 35·71, 110·72, 119·72, 127·21, 127·59, 129·29, 132·67, 136·65, 143·73, 145·71 p.p.m. IR (NaCl): $\nu$

(CN) 2224 cm$^{-1}$. MS (EI, 70 eV) 440 (M$^+$, 46 per cent', 192 (100 per cent) and essentially the same proton and carbon-13 chemical shifts for the heptane spacer for which mass spectrometry gave 454 (M$^+$, 27 per cent), 192 (100 per cent). The purity of the two final products was estimated to be better than 99 per cent from both the $^1$H and $^{13}$C NMR spectra. This is in keeping with the observation of a single spot when examined by thin layer chromatography (polygram sil g/UV$_{254}$, dichloromethane).

The transitional properties of the two liquid crystal dimers were investigated using a Perkin–Elmer DSC 7 differential scanning calorimeter as well as a Nikon polarizing microscope fitted with a Linkam hot stage. This was also used to observe the optical textures of the liquid crystalline phases. Both materials exhibit enantiotropic nematic phases; these were identified by their schlieren textures combined with high mobility of the phase which flashed when subjected to mechanical stress. In addition the α,ω-bis(4′-cyanobiphenyl-4-yl)heptane forms a smectic phase which was judged to be smectic by its focal conic-like texture and the weak transition from the nematic phase. We have not, however, been able to identify the nature of the smectic phase; this must await an X-ray investigation. The transitional properties of the two dimers are listed in the table; the nematic–isotropic transitions were found to be sharp ($< 2$°C for the $C_6$ spacer and $< 1$°C for the $C_7$ spacer), again indicating the purity of these products. The results obtained for $T_{NI}$ and $\Delta S_{NI}/R$ with the $C_7$ spacer are in good agreement with those found previously [3], although the smectic phase does not seem to have been recognized in that study.

The larger difference in both $T_{NI}$ and $\Delta S_{NI}/R$ for the methylene linked pair of dimers in comparison with that for the pair with the ether links is clearly apparent. This is also in agreement with predictions based on the Marcelja–Luckhurst theory for nematics composed of flexible molecules [2]. In addition, the predicted larger differences in $T_{NI}$ and $\Delta S_{NI}/R$ between methylene linked dimers and ether linked dimers when the spacer contains an odd number of atoms in the spacer rather than an even number is clearly confirmed by these results. The enhanced difference in the entropy change at the nematic–isotropic transition should also be reflected by the orientational order of the various dimers. To test this prediction, we have determined the Saupe ordering matrix of anthracene-$d_{10}$ dissolved in the four dimers using deuterium NMR spectroscopy. The spectra of solutions containing about 2 per cent by weight of anthracene-$d_{10}$ were measured using a Bruker MSL 200 spectrometer over the entire liquid crystal range. The spectra obtained at the nematic–isotropic transition for the two methylene linked dimers are shown in figure 2; they are both composed of two sets of quadrupolar doublets from anthracene-$d_{10}$ in the nematic, together with a single peak coming from the isotropic phase coexisting with the nematic. The larger of the quadrupolar doublets is assigned to the β-deuterons and the other to the α- and γ-deuterons; strictly the latter two are not completely equivalent [6], but the small difference in quadrupolar splittings is not resolved in our experiments. What is clearly apparent from the spectra, however, is the very large difference in the quadrupolar splittings, with those for the even spacer being far larger than for the odd spacer. This indicates a significant difference in the orientational order for the two liquid crystal dimers, as we had anticipated. We can quantify this difference by determining the principal components of the Saupe ordering matrix for anthracene-$d_{10}$ via the relationship [6]

$$\Delta\tilde{\nu}_i = \tfrac{3}{2} q^i_{aa} [S_{zz}\{(3 l^{i2}_{za} - 1)/2 + \eta^i l^{i2}_{zb}/2\} + (S_{xx} - S_{yy})\{l^{i2}_{xb} + (\tfrac{1}{3})\eta^i (l^{i2}_{xb} + 1)\}/2].$$

Here $xyz$ denote the principal axes of the ordering matrix **S** for anthracene; they are determined by the molecular symmetry. In addition the axes are labelled such that the

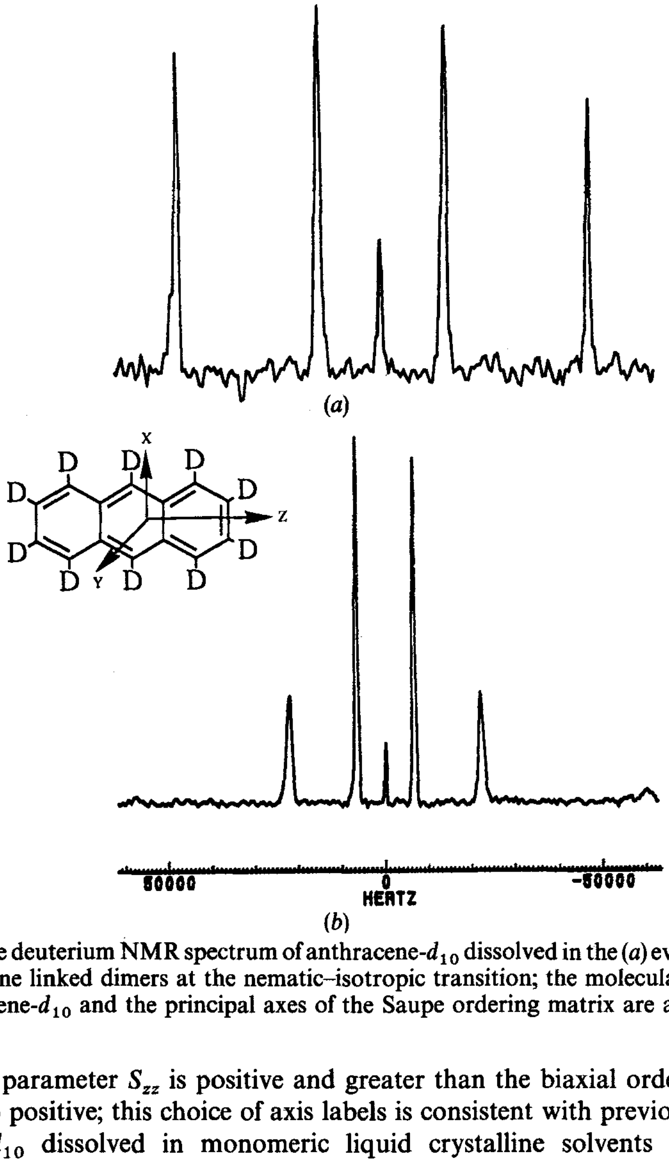


Figure 2. The deuterium NMR spectrum of anthracene-$d_{10}$ dissolved in the (*a*) even and (*b*) odd methylene linked dimers at the nematic–isotropic transition; the molecular structure of anthracene-$d_{10}$ and the principal axes of the Saupe ordering matrix are also shown.

major order parameter $S_{zz}$ is positive and greater than the biaxial order parameter which is also positive; this choice of axis labels is consistent with previous studies of anthracene-$d_{10}$ dissolved in monomeric liquid crystalline solvents [6]. This is equivalent to taking $\Delta\tilde{\nu}_{\alpha,\gamma}$ to be negative and $\Delta\tilde{\nu}_{\beta}$ to be positive. The other quantities occurring in the equation are the quadrupolar tensors $\mathbf{q}_i$ and the direction cosines $l^i$ relating the principal axes ($xyz$) of $\mathbf{S}$ with those ($abc$) of $\mathbf{q}$. Thus $a$ lies along the C–D bond, $c$ is normal to the molecular plane and $b$ is orthogonal to $a$ and $c$. The asymmetry parameter $\eta$ for $\mathbf{q}$ is defined as $(q_{bb}-q_{cc})/q_{aa}$. In the analysis $q_{aa}$ and $\eta$ are taken to be identical for all of the deuterons in the molecule; $q_{aa}$ was set equal to 181 kHz and $\eta$ to 0·064 [7]. The direction cosines were calculated using the bond angles obtained from an X-ray diffraction study [8].

As we have seen from the NMR spectra at the nematic–isotropic transition there is a small biphasic region caused by the presence of anthracene dissolved in the liquid crystal. As long as the two phases coexist, the quadrupolar splittings and hence the orientational order of the solute are essentially independent of temperature. It is, therefore, relatively straightforward to obtain accurate values for the order parameters

The transitional properties of the two α,ω-bis(4′-cyanobiphenyl-4-yl)alkanes; the corresponding results for the ether linked dimers are included for comparison.

| | | Number of atoms in spacer | |
|---|---|---|---|
| | | 6 | 7 |
| $T_{NI}$/K | Methylene link | 503 | 388 |
| | Ether link [1] | 523 | 459 |
| $\Delta S_{NI}/R$ | Methylene link | 2·61 | 0·34 |
| | Ether link [1] | 1·95 | 0·66 |
| $S_{zz}^{NI}$ | Methylene link | 0·479 | 0·224 |
| | Ether link | 0·398 | 0·268 |
| $S_{xx}^{NI}-S_{yy}^{NI}$ | Methylene link | 0·249 | 0·122 |
| | Ether link | 0·228 | 0·161 |
| $T_{S?N}$/K | Methylene link | — | 375 ($\Delta S/R=0{\cdot}31$) |
| | Ether link | — | — |
| $T_{C-}$/K | Methylene link | 456 | 374 |
| | Ether link [1] | 482 | 410 |
| $\Delta S_{C-}/R$ | Methylene link | 9·50 | 7·67 |
| | Ether link [1] | 10·4 | 8·8 |

$S_{zz}^{NI}$ and $(S_{xx}^{NI}-S_{yy}^{NI})$ at the transition and these are given in the table. We can see immediately that there is a very large difference in the major order parameter $S_{zz}^{NI}$ between the even and odd spacers equal to 0·25 which is significantly greater than that for the corresponding ether linked dimers for which the difference is just 0·13. This variation in behaviour of the odd and even dimers with methylene and ether links is in keeping with the entropies of transition and hence with theory [2]. The data certainly suggest that the orientational order in the methylene linked dimers is significantly different to that in the ether linked mesogens with the same number of atoms in the spacer. Thus $S_{zz}^{NI}$ for the even spacer is greater for the methylene than the ether linked dimer by 0·08 while $S_{zz}^{NI}$ for the odd spacer with the methylene link is less than that for the ether link by 0·04. Such differences are in qualitative agreement with theory, although it should be noted that the changes in $\Delta S/R$ are predicted to be greatest for the odd rather than the even spacer on going from an ether to a methylene link.

The behaviour of the biaxial order parameter $(S_{xx}^{NI}-S_{yy}^{NI})$ is somewhat harder to understand. Thus it is greater for the dimers with even rather than odd spacers, which is surprising, given the greater molecular biaxiality of the dimers with odd spacers. However, similar differences have been observed for another solute molecule dissolved in the α,ω-bis(4′-cyanobiphenyl-4-yloxy)alkanes [9]. We shall return to a consideration of this feature later. For the moment we note that the biaxial order parameter of the solute molecule is also expected to reflect the orientational order of the liquid crystal host. This would certainly appear to be the case, for $(S_{xx}^{NI}-S_{yy}^{NI})$ is greater for the dimers with an even spacer than those with an odd. In addition $(S_{xx}^{NI}-S_{yy}^{NI})$ is greater for an even spacer with a methylene rather than an ether link; in contrast when the spacer contains an odd number of atoms $(S_{xx}^{NI}-S_{yy}^{NI})$ is greater for the ether rather than the methylene link. Such behaviour clearly parallels that for the major order parameter $S_{zz}^{NI}$.

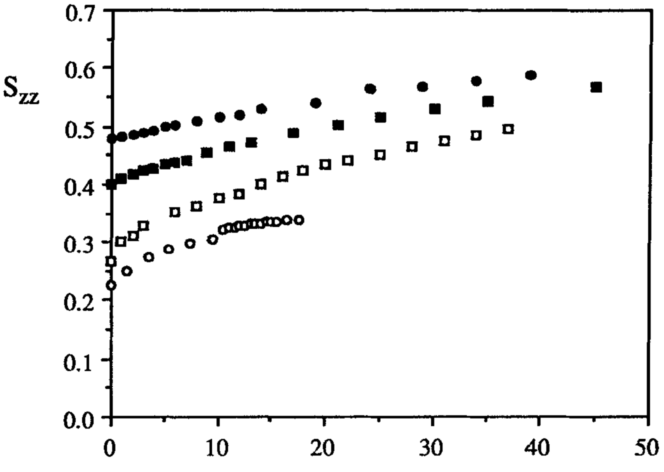


Figure 3. The dependence of the major order parameter $S_{zz}$ for anthracene-$d_{10}$ dissolved in CB6CB (●), CB7CB (○), CBO4OCB (■) and CBO5OCB (□) on the shifted temperature $(T_{NI}-T)$.

We turn now to the temperature dependence of the major and biaxial order parameters for anthracene-$d_{10}$ dissolved in the various dimers. The dependence of $S_{zz}$ on the shifted temperature $(T_{NI}-T)$ is shown in figure 3; here $T_{NI}$ is taken to be the temperature at which the isotropic peak in the NMR spectrum just vanishes. The difference in behaviour for the odd and even dimers with methylene and ether links observed at the nematic–isotropic transition clearly continues into the nematic phase; indeed the differences in $S_{zz}$ are almost independent of temperature. However, we do see that the temperature dependence of $S_{zz}$ near the transition decreases as $S_{zz}^{NI}$ increases, which is to be expected, since the order parameter has to increase less rapidly to achieve the limiting high values at low shifted temperatures than when it starts with a low value. Finally, we note that the small jump in $S_{zz}$ for the odd membered methylene linked dimer occurs at the point at which a transition to the smectic phase was identified optically. The orientational order in this smectic phase is comparable to that in the preceding nematic phase and so suggests that the phase has a local structure similar to that in a smectic A phase. This conclusion is in keeping with the small entropy change at the smectic–nematic transition (see the table) and is consistent with that observed for smectic A–nematic transitions with similar values of the McMillan ratio$T_{SN}/T_{NI}$ [10]. The temperature dependence of the biaxial order parameter $(S_{xx}-S_{yy})$ shown in figure 4 reveals an apparently greater variation in behaviour. Thus for the even methylene linked dimer, the order parameter decreases with decreasing temperature, while for the corresponding odd spacer, $(S_{xx}-S_{yy})$ first increases and then decreases with decreasing temperature. In addition, the rate of decrease increases at the transition from the nematic to the smectic phase. The odd ether linked dimer shows the same qualitative behaviour; $(S_{xx}-S_{yy})$ first increases with decreasing temperature, passes through a maximum, and then decreases slowly with further decreasing temperature. The rate of decrease is, however, constant because α,ω-bis(4′-cyanobiphenyl-4-yloxy)pentane does not possess a smectic phase unlike its methylene linked counterpart. The biaxial order parameter for the even ether linked dimer shows

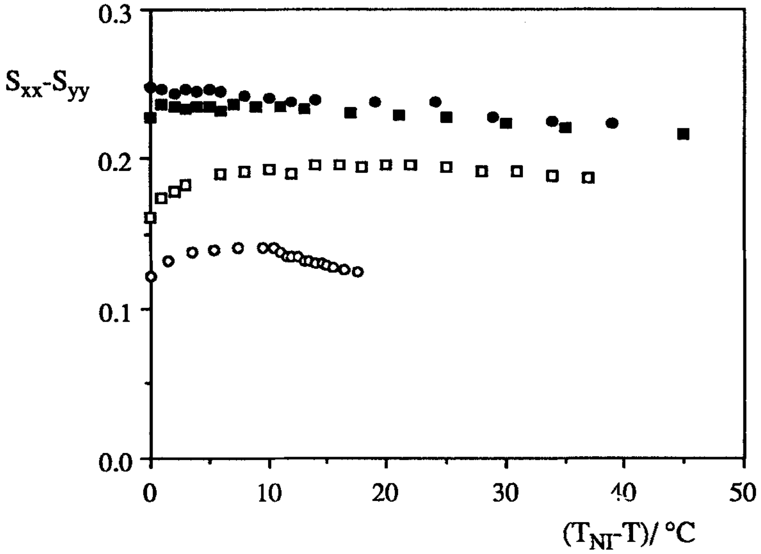


Figure 4. The dependence of the biaxial order parameter $(S_{xx}-S_{yy})$ for anthracene-$d_{10}$ dissolved in CB6CB (●), CB7CB (○), CBO4OCB (■) and CBO5OCB (□) on the shifted temperature $(T_{NI}-T)$.

a jump from its value at the nematic–isotropic transition and then decreases with further decrease in temperature in a manner which approximates closely to that of its methylene linked analogue.

This range of behaviour is readily understood, for theory has shown that the biaxial order parameter is intimately connected with the major order parameter [11, 12]. For example when $S_{zz}$ is greater than about 0·4 $(S_{xx}-S_{yy})$ is predicted to decrease with increasing $S_{zz}$ and hence with decreasing temperature, as we have found for α,ω-bis(4′-cyanobiphenyl-4-yl)hexane. In contrast, for $S_{zz}$ less than about 0·4, $(S_{xx}-S_{yy})$ is predicted to increase with $S_{zz}$, to pass through a maximum when $S_{zz}$ is approximately 0·4, and then to decrease. Since $S_{zz}$ increases continuously with decreasing temperature, theory therefore predicts that the biaxial order parameter can also increase, pass through a maximum, and then decrease with decreasing temperature, as we have found for both dimers with an odd number of atoms in the spacer. An alternative presentation of the data which emphasizes the biaxiality in the molecular interactions more clearly is to eliminate temperature by plotting the biaxial order parameter as a function of the major order parameter; our results are presented in this way in figure 5. They clearly show the anticipated behaviour, namely that the biaxial order parameter increases with increasing $S_{zz}$, passes through a maximum, and then decreases; whether all of this variation is seen or not depends on the value of $S_{zz}$. Thus for the even methylene linked dimer, $S_{zz}$ is larger than 0·4 and so $(S_{xx}-S_{yy})$ can only decrease with increasing $S_{zz}$ and decreasing temperature. For the corresponding ether linked dimer, $S_{zz}$ is just less than 0·4 and so the maximum in the plot is discernible before $(S_{xx}-S_{yy})$ starts to decrease with increasing $S_{zz}$. For the odd membered ether linked dimer, $S_{zz}$ is significantly less than 0·4 and so there is a considerable increase in $(S_{xx}-S_{yy})$ before it passes through the maximum and then decreases slightly. The major order parameter for the analogous methylene linked dimer is still less and so we see an increase in $(S_{xx}-S_{yy})$ with increasing $S_{zz}$. However, since $S_{zz}$ is always less than 0·4, we do not expect the biaxial

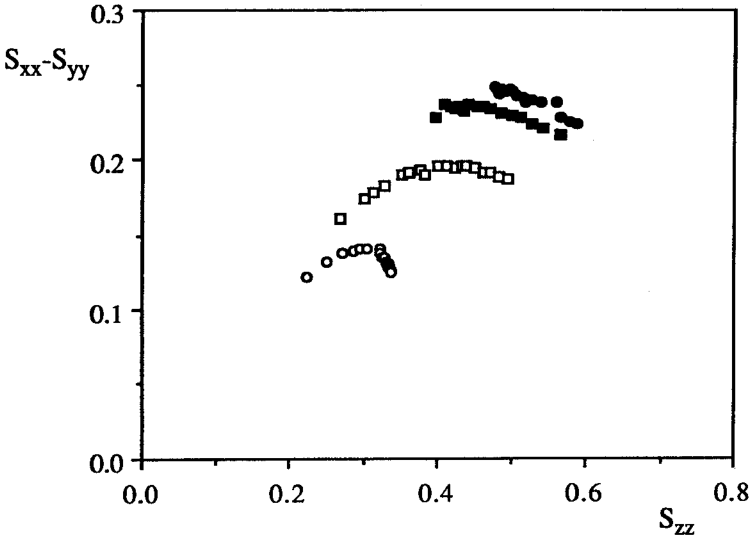
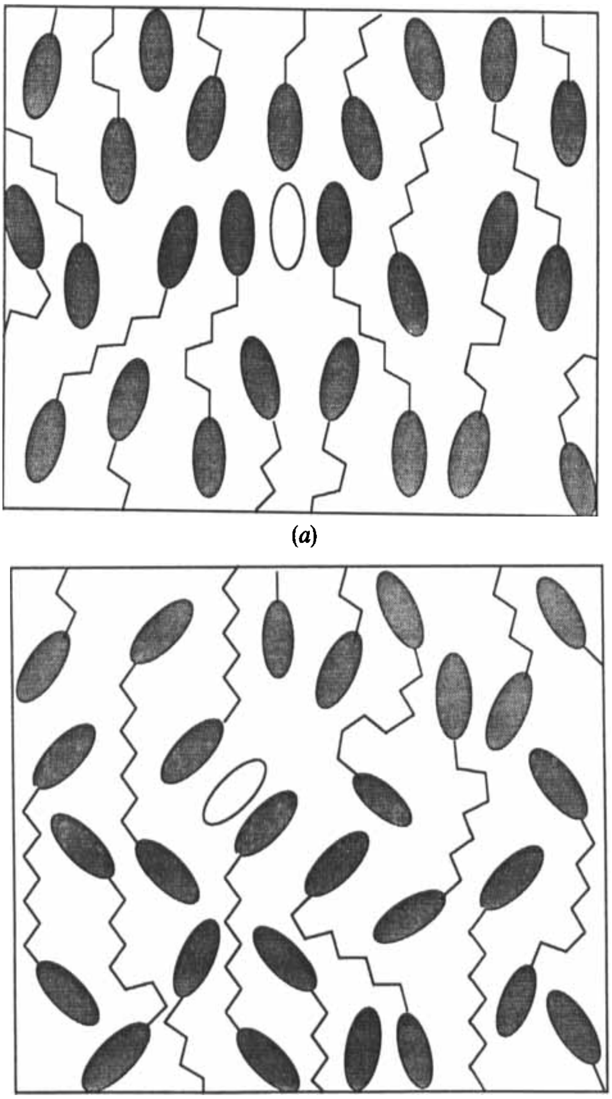


Figure 5. The variation of the biaxial order parameter $(S_{xx}-S_{yy})$ with the major order parameter $S_{zz}$ for anthracene-$d_{10}$ dissolved in CB6CB (●), CB7CB (○), CBO4OCB (■) and CBO5OCB (□).

order parameter to reach its maximum value. The results in figure 5 certainly indicate a maximum, although with a discontinuous change in slope; we attribute this unexpected behaviour to the transition from the nematic to the smectic phase.

One merit of presenting the order parameters in this way is that it makes it easier to estimate the biaxiality in the molecular interactions. Thus, the larger the value of $(S_{xx}-S_{yy})$ at the maximum, the larger is the biaxiality in the potential of mean torque responsible for the orientational order of the solute molecule [12]. According to the results shown in figure 5, the biaxiality in the interactions is similar for the two even membered dimers, with the methylene linked mesogen having a slightly larger value. There is then a significant reduction in this biaxiality on going to the ether linked dimer with an odd number of atoms in the spacer, and then a further significant reduction on going to the methylene linked, odd membered dimer. These significant reductions in the biaxiality of the molecular interactions on going to the odd membered dimers seem counterintuitive, since the molecular biaxiality of the liquid crystal host increases in the opposite sense. This unusual behaviour can, however, be understood at least qualitatively with the following model [13]. The mesogenic groups in the dimers with an even spacer are parallel for many of the conformations which the molecule can adopt and so, on average, the mesogenic groups will be essentially parallel to the director. In marked contrast, the mesogenic groups in the odd dimers will be inclined to one another and so will be tilted with respect to the global director; such a molecular organization is certainly consistent with the X-ray structure of $\alpha,\omega$-bis(4'-cyanobiphenyl-4-yloxy)heptane in its crystal phase [14]. When a probe such as anthracene is dissolved in a liquid crystal dimer it might be expected to associate itself with the aromatic mesogenic groups according to the caricatures shown in figure 6. For the even membered dimers, the local director associated with the mesogenic groups is essentially parallel to the global director, whereas for the odd membered dimers the local director will be tilted with respect to the global director. The magnitude of the tilt angle $\beta$ will be influenced by the molecular structure and hence the angle made by the



(a)

(b)

Figure 6. A caricature of the molecular organization in a nematic phase composed of dimers with (*a*) even spacers and (*b*) odd spacers showing the probable location of a rigid solute molecule.

mesogenic groups with the spacer, as well as by the extent of the orientational order of the mesophase. The effect of the tilt is to reduce the order parameters measured with respect to the global director (G), as in our experiments, in comparison with their values with respect to the local director (L). The magnitude of this reduction is given by [13]

$$S^{\mathrm{G}}_{zz} = S^{\mathrm{L}}_{zz} P_2(\cos\beta)$$

and

$$S^{\mathrm{G}}_{xx} - S^{\mathrm{G}}_{yy} = (S^{\mathrm{L}}_{xx} - S^{\mathrm{L}}_{yy}) P_2(\cos\beta).$$

If we also assume that the local order at the same shifted temperature is independent of the spacer length and parity, as well as the nature of the link between the spacer and the mesogenic group, then our results for the orientational order parameters for anthracene can be understood at least qualitatively. The similar values of $(S_{xx}-S_{yy})$ found for the two even dimers suggest that the local directors make similar angles with the global director. The large difference between the biaxial order parameters for the odd and even dimers with ether linkages can be understood in terms of an increase in the angle between the local and global directors resulting from the bent shape of the odd dimer. Similarly, the increase in the angle between the mesogenic groups when the ether link is replaced by a methylene group accounts for the further reduction in $(S_{xx}-S_{yy})$ on going from the odd membered ether linked dimer to that with methylene links.

Our studies of liquid crystal dimers containing methylene and ether links have confirmed the predicted strong dependence of their transitional properties on the geometry of the link. In particular the orientational order, as reflected by both the major and biaxial order parameters of a solute molecule dissolved in the liquid crystal dimers, also exhibits a strong dependence on the topology of the link between the spacer and the mesogenic groups. Such variations in order between odd and even dimers can be understood qualitatively in terms of a local director which is tilted with respect to the global director for odd dimers, but essentially parallel to it for even dimers.

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