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PRELIMINARY COMMUNICATIONS

On the relative propensities of ether and methylene linkages for liquid crystal formation in calamitics

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The nematic–isotropic transition temperatures for aromatic calamitic compounds with terminal alkyl chains attached via a methylene group are usually found to be lower than those with an ether link. This difference is generally attributed to the higher anisotropy of the molecular polarizability expected for an ether linkage in comparison with a methylene group. However these two modes of attachment for the chain also differ in their geometry and here we show, using a molecular field theory for flexible molecules, that this also results in higher transition temperatures for nematogens, both monomers and dimers, with the alkyl chains attached through ether rather than methylene linkages.

The classic molecular structure of a calamitic nematogen is a semi-rigid, anisometric central group attached to which is one or two alkyl chains [1]. The anisometry of the central group enhances the liquid crystal transition temperature while the flexibility of the terminal alkyl chains lowers the melting point. The chains also influence, although to a lesser extent, the nematic–isotropic transition temperature and produce the familiar odd–even alternation. The alkyl chains can be attached through a variety of linkages although methylene and ether links are especially common. It is generally observed that the nematic–isotropic transition temperatures are higher for compounds with an alkyloxy chain than for an alkyl chain with the same total number of atoms [1]. An example of such behaviour is shown for the 4-*n*-alkyl-4′-cyanobiphenyls and the 4-*n*-alkyloxy-4′-cyanobiphenyls in figure 1. Here N is the total number of atoms in the chain, that is including the oxygen for the alkyloxy chain, and the transition temperatures T_{NI} have been scaled with that for 4-methyl-4′-cyanobiphenyl to facilitate comparison with theory. The clear difference in behaviour of nematogens with terminal alkyloxy and alkyl chains has been attributed to the higher anisotropy in the molecular polarizability expected when the $2p_\pi$ orbitals on the oxygen conjugate with those on the phenyl ring to which it is attached [2]. Implicit in such an explanation is the notion that anisotropic dispersion forces make a significant contribution to nematic stability; a view which is not universally accepted [3]. There is, however, another difference resulting from the two modes of attachment, namely in the geometry in the vicinity of the atom attached to the linking group. For example, the $C_{ar}\hat{O}C_{al}$ bond angle would be expected to be of the order of 120° whereas the corresponding $C_{ar}\hat{C}_{al}C_{al}$ angle should be

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close to 109°. If the chain is in its all-trans conformation then this difference in the angle means that it will be more parallel to the central semi-rigid group for the ether than for the methylene linkage, as illustrated schematically in figure 2. This enhancement of the molecular anisotropy should then result in a higher transition temperature for nematogens with alkyloxy rather than alkyl chains. Of course, the chains do not exist exclusively in the all-trans conformation and so, to investigate the influence of the different geometry quantitatively, we need to allow the chain to exist in other conformations. Here we present the results of such an investigation for the 4-*n*-alkyloxy- and 4-*n*-alkyl-4′-cyanobiphenyls using the Marcelja molecular field theory [4], as corrected and extended by Luckhurst [5]. This approach is not as advanced as that developed by Samulski and his colleagues in which the potential of mean torque contains a new contribution from chord as well as bond or group interactions [6]. However, we do not believe that the qualitative nature of our predictions would be altered significantly by this novel parameterisation.

The Marcelja–Luckhurst theory is described in detail elsewhere [5] and so we shall just sketch those features which are necessary to appreciate the significance of the parameters entering the calculations. A molecule is assumed to exist in a discrete number of conformations given by the rotameric state model. The potential of mean torque, responsible for the alignment of the *n*th conformer, is approximated by

$$U_n(\omega) = -\sum_m X^{n*}_{2,m} C_{2,m}(\omega), \qquad (1)$$

where $C_{2,m}(\omega)$ is a modified spherical harmonic and ω denotes the orientation of the director in a molecular frame. The strength of the potential is governed by the interaction tensor $X^n_{2,m}$ which is assumed to be a sum of segmental interaction tensors.

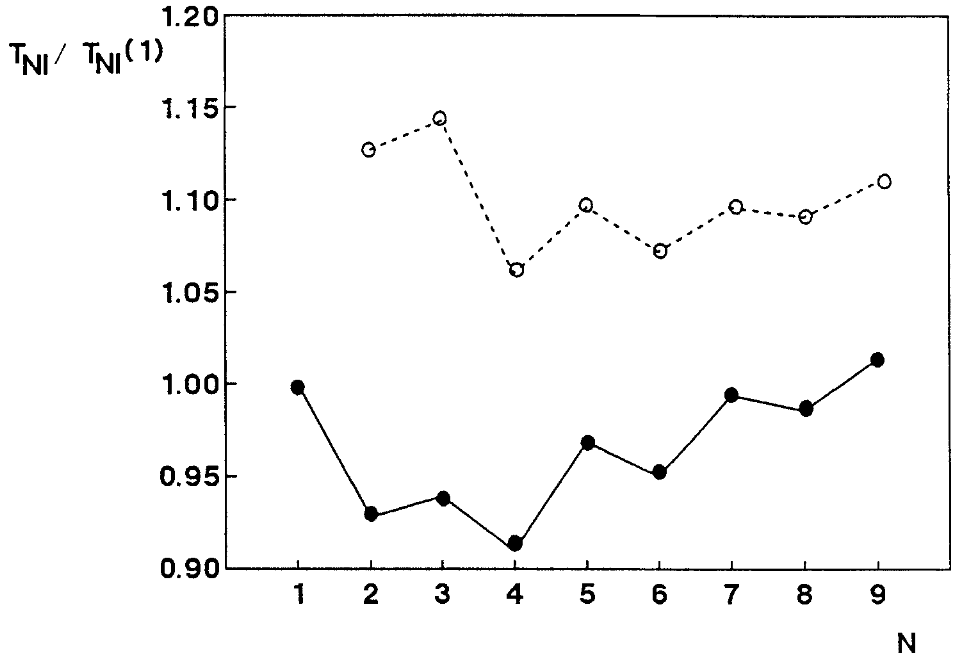

Figure 1. The nematic–isotropic transition temperatures for the 4-*n*-alkyl-(●) and 4-*n*-alkyloxy-4′-cyanobiphenyls (○) as a function of the number of atoms N in the chain. The results are scaled with T_{NI} for 4-methyl-4′-cyanobiphenyl.

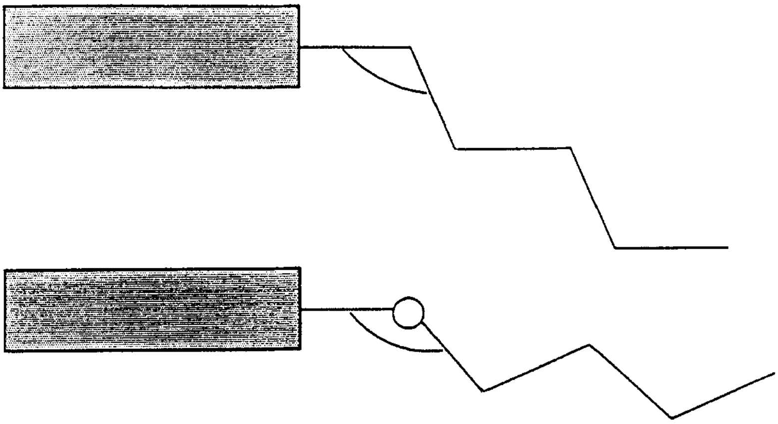

Figure 2. A sketch showing the difference in the molecular anisotropy which results when the alkyl chain, in the all-trans conformation, is linked to a mesogenic group via an ether or a methylene group.

It is this sum which introduces the molecular geometry into the theory. If the basic segments are taken to have cylindrically symmetric interaction tensors X_j then

$$X^n_{2,m}=\sum_j X_j C_{2,m}(\omega_{n,j}), \tag{2}$$

where $\omega_{n,j}$ defines the orientation of the jth segment in the molecular frame of the nth conformer. For the 4-*n*-alkyl- and 4-*n*-alkyloxy-4′-cyanobiphenyls the basic units are taken to be the cyanobiphenyl group and the carbon–carbon bonds with interaction tensor components X_a and X_c, respectively; contributions from the carbon–hydrogen bonds are ignored. In our calculations the interaction tensors for the carbon–oxygen bonds are set equal to X_c so that any difference in behaviour between the cyanobiphenyls with alkyloxy and alkyl chains can be attributed entirely to that of the geometry.

The potential of mean torque can now be used to evaluate the orientational partition function for the conformer.

$$Q_n=\int \exp\{-U_n(\omega)/kT\}\,\mathrm{d}\omega \tag{3}$$

and with this the ordering tensor can be calculated. These tensors are averaged over all conformations using the distribution function

$$p_n=Z^{-1}\exp(-U_{int}(n)/kT)Q_n. \tag{4}$$

Here $U_{int}(n)$ is the internal energy of the nth conformer and is given by

$$U_{int}(n)=N_g E_{tg}+N_{g\pm g\mp}E_{g\pm g\mp}, \tag{5}$$

where N_g is the number of gauche links, $N_{g\pm g\mp}$ is the number of g ± g ∓ sequences, E_{tg} is the energy difference between a trans and a gauche link and $E_{g\pm g\mp}$ is the additional energy of a g ± g ∓ sequence. The conformational–orientational partition function Z is

$$Z=\sum_n \exp(-U_{int}(n)/kT)Q_n. \tag{6}$$

We now have sufficient information to obtain the Helmholtz free energy per particle which is

$$A=(X_a\langle \bar{P}^a_2\rangle+X_c\langle \bar{P}^c_2\rangle)/2-kT\ln Z. \tag{7}$$

In this expression $\langle \bar{P}_2^a \rangle$ is the conformationally averaged order parameter for the *para* axis of the cyanobiphenyl group and $\langle \bar{P}_2^c \rangle$ is the corresponding average for the sum of the order parameters for the carbon–carbon bonds in the terminal chain. The free energies of the nematic and isotropic phases are equal at the transition which allows us to determine T_{NI}.

The additional approximation introduced into the Marcelja theory [4] by Luckhurst [5] means that the ratio X_c/X_a is independent of temperature which simplifies the calculations considerably. However the individual strength parameters do depend on the orientational order parameters, and hence the temperature, via equations such as

$$X_a = (\varepsilon_{aa}\langle \bar{P}_2^a \rangle + \varepsilon_{ac}\langle \bar{P}_2^c \rangle)/v_m, \tag{8}$$

where v_m is the molecular volume. The ratio of the interaction parameters $\varepsilon_{ac}/\varepsilon_{aa}$ is just X_c/X_a and ε_{aa} is used to scale the transition temperatures predicted by the theory.

The variables entering the theory are then the conformational energies E_{tg} and $E_{\mathrm{g}\pm\mathrm{g}\mp}$, the ratio X_c/X_a, the molecular volume and the geometry. We shall set E_{tg}/kT equal to 1 and $E_{\mathrm{g}\pm\mathrm{g}\mp}/E_{\mathrm{tg}}$ to 4, which are reasonable values for an alkyl chain near room temperature [7]. We shall also use the same values for the chain with an ether link since we wish to confine our attention to those differences resulting solely from variations in the molecular geometry. The molecular volumes for the 4-*n*-alkyl-4′-cyanobiphenyls were calculated from the atomic and group values tabulated by Bondi [8]; in keeping with our previous comment we shall use the same volumes for the 4-*n*-alkyloxy-4′-cyanobiphenyls. The ratio of group interaction parameters X_c/X_a is taken to be 0·3 which is typical of values found by fitting the theory to the variation of the C–D order parameters along the terminal chains of the 4-*n*-alkyl-4′-cyanobiphenyls [7].

This now leaves the molecular geometry. The $\mathrm{C_{al}\hat{C}_{al}C_{al}}$ bond angle for the chain in the 4-*n*-alkyl-4′-cyanobiphenyls has been optimized by fitting the methylene group D...D order parameter profile along the chains of the pentyl and octyl homologues [9]. The optimum value for the $\mathrm{C_{ar}\hat{C}_{al}C_{al}}$ and $\mathrm{C_{al}\hat{C}_{al}C_{al}}$ bond angles for all carbon atoms in the chain is 113·5°. The torsional angle for the gauche conformations is equal to ±68°. In addition the symmetry axis for the cyanobiphenyl group is assumed to be parallel to the *para* axis. For the alkyloxy chain the $\mathrm{C_{al}\hat{C}_{al}C_{al}}$ and torsional angles are taken to have the same values as for the alkyl chain. The configuration about the oxygen atom is somewhat more complicated but the net result is that the O–C bond in the chain makes an angle of 126·4° with the *para* axis of the cyanobiphenyl group. This value was obtained by fitting the C–D bond order parameter profile for several 4-*n*-alkyloxy-4′-cyanobiphenyls [10]; it is in reasonable agreement with the value obtained by electron diffraction for anisole [11].

The nematic–isotropic transition temperatures predicted for the alkyl and the alkyloxy homologous series from these calculations are shown as a function of the number of atoms N in the chain in figure 3. To facilitate comparison with the experimental results the transition temperatures have been scaled with that predicted for 4-methyl-4′-cyanobiphenyl. As we had anticipated the T_{NI} for the homologous series with an ether linkage are higher than the corresponding members of the series with the chain attached through a methylene group. In addition we also see that the odd–even effect is predicted to be more pronounced for the alkyl- than the alkyloxycyanobiphenyls which is also in agreement with experiment (see figure 1). On average the magnitude of the difference in T_{NI} for methylene and ether linkages is predicted to be of the order of 15 per cent, which is close to the observed value. This difference clearly

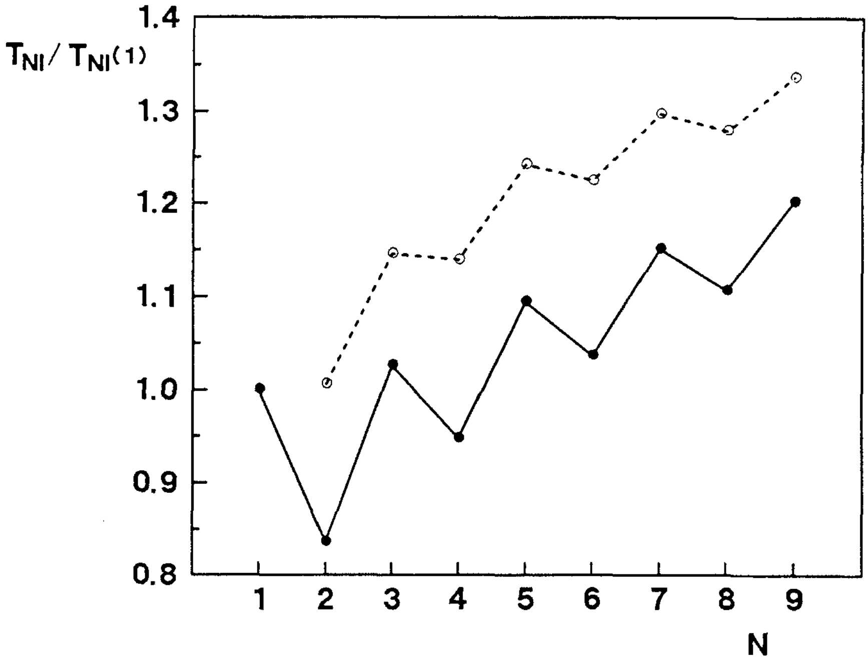

Figure 3. The predicted dependence of the nematic–isotropic transition temperatures for the 4-*n*-alkyl-(●) and 4-*n*-alkyloxy-4′-cyanobiphenyls (○) on the number of atoms in the chains. The results have been scaled with the transition temperature predicted for 4-methyl-4′-cyanobiphenyl.

depends on the parameters employed in the calculation but it was not our aim to obtain an exact correspondence between theory and experiment. Indeed the predicted variation of T_{NI} with the length of the terminal chain is seen to be in rather poor overall agreement with experiment because the parameters were not so optimized. Rather we wished simply to see if by using reasonable values of the parameters the difference in the geometry at the linkage for the alkyl and alkyloxy chains could account for the difference in the transition temperatures. This clearly is the case although our calculations do not exclude completely the possibility that a difference in the anisotropic molecular polarisability also makes a contribution to the increase in T_{NI} when a methylene group is replaced by an ether link.

We anticipate that the geometrical effects on T_{NI} predicted and observed for the monomers will be even greater for dimers where the alkyl chain links two mesogenic groups, because the relative orientation of these groups is controlled by the molecular geometry. Indeed this would appear to be the case although the data available for methylene linked dimers is somewhat limited in contrast to the situation for those with ether linkages. For example the first twelve members of the α,ω-bis(4′-cyanobiphenyl-4-oxy)alkane series have been prepared and characterised [12] whereas only four members ($N = 7$–10) of the analogous methylene linked dimers have been studied [13]. The transitional behaviour for these and their ether linked counterparts in which the two oxygens are counted as methylene groups is given in the table. The nematic–isotropic transition temperatures are reduced on replacing the oxygen links by methylene groups, although the reduction is far greater for an odd member then for an even member of the series. The entropy change at the nematic–isotropic transition also

Comparison of the transitional properties of dimers with ether and methylene linkages; the α,ω-bis(4′-cyanobiphenyl-4-oxy)alkanes and α,ω-bis(4′-cyanobiphenyl-4-)alkanes.

N, atoms in flexible spacer	T_{NI}/K		$\Delta S/R$	
	Ether link	Methylene link	Ether link	Methylene link
7	459	387·3	0·66	0·22
8	494	469·0	1·98	2·71
9	454	408·8	0·78	0·97
10	474	447·7	2·01	3·05

varies, with that for the even members ($N = 8, 10$) increasing on replacing the oxygens by methylene groups whereas for one odd member ($N = 7$) the entropy of transition decreases and for the other ($N = 9$) $\Delta S/R$ is slightly larger.

In order to see if these changes in T_{NI} and $\Delta S/R$ can also be accounted for purely in terms of the difference in geometry for ether and methylene links we have calculated the nematic–isotropic transition temperatures for the two types of dimer using the same theory as for monomers and indeed with the same parameters. The calculations were performed for N, the number of atoms in the spacer, ranging from 1 to 8. The early members of the series were studied in order to explore how the differences might vary with the length of the flexible spacer and the later members were excluded because of the high computational cost of these calculations. The results for the nematic–isotropic temperatures, scaled with that for bis(4′-cyanobiphenyl-4)methane are shown in figure 4. We note first that the transition temperatures for $N = 7$ and 8 both decrease on replacing the ether link by a methylene group and that the decrease is much larger for the odd than for the even member. The magnitude of these predicted changes are comparable to those observed which supports the view that the difference in behaviour may be attributed largely to variations in the molecular geometry at the link to the mesogenic groups. We now turn to the general behaviour predicted for the two homologous series. The strong alternation in T_{NI} with its associated attenuation as the length of the alkyloxy spacer increases is in qualitative agreement with the behaviour of the α,ω-bis(4′-cyanobiphenyl-4-oxy)alkanes [12]. The predictions for the analogues with methylene groups show a considerably greater alternation in the scaled nematic–isotropic transition temperature with a smaller attenuation as the number of atoms in the spacer increases. This major difference in behaviour results largely from a reduction in the nematic–isotropic transition for the odd members; indeed the scaled T_{NI} for even members are mainly unchanged. Such variations in the transitional behaviour can be understood in simple terms as an increase in the molecular biaxiality of the odd members, at least in the all-trans form, when the linkage is changed from methylene to ether. In contrast, the relative increase in the biaxiality for even members is far smaller because the mesogenic groups are essentially parallel in the all-trans conformer. Inclusion of the other conformations into the model changes this explanation quantitatively but not qualitatively.

To see if the changes in the entropy of transition on replacing oxygen atoms by methylene groups can also be explained simply in geometrical terms we have used the Marcelja–Luckhurst theory [5] to predict the entropies of transition from

$$\Delta S/R = (X_a^{NI}\langle \bar{P}_2^a \rangle_{NI} + X_c^{NI}\langle \bar{P}_2^c \rangle_{NI})/2kT_{NI} + (\langle U_{int}\rangle_I^{NI} - \langle U_{int}\rangle_N^{NI})/kT_{NI}, \tag{9}$$

where the first term is the contribution from the orientational order and the second comes from the change in the conformational distribution at the transition. The results

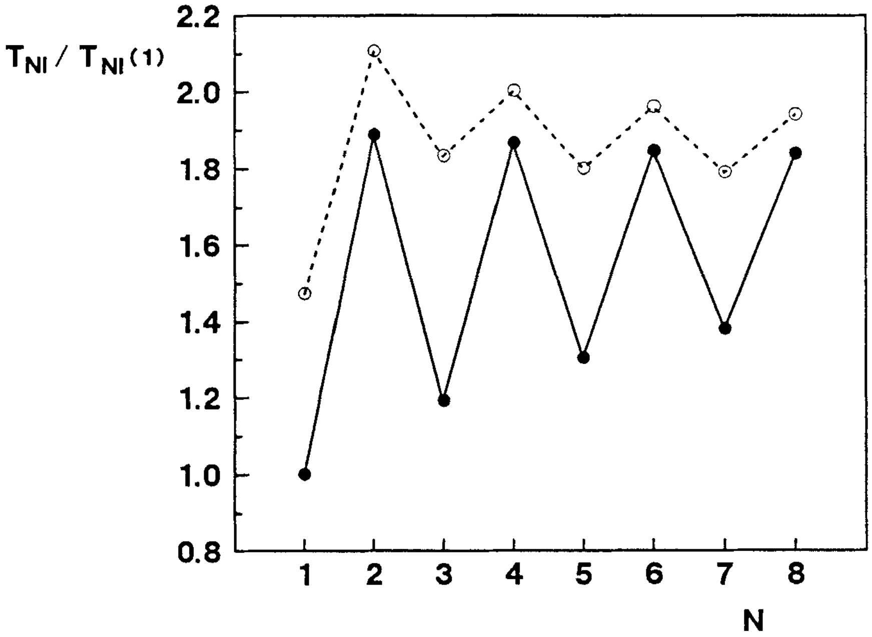

Figure 4. The variation of the nematic–isotropic transition temperatures with the number of atoms *N* in the flexible spacer predicted for the cyanobiphenyl dimers with methylene (●) and ether (○) linkages. The transition temperatures have been scaled with T_{NI} for bis(4′-cyanobiphenyl-4)methane.

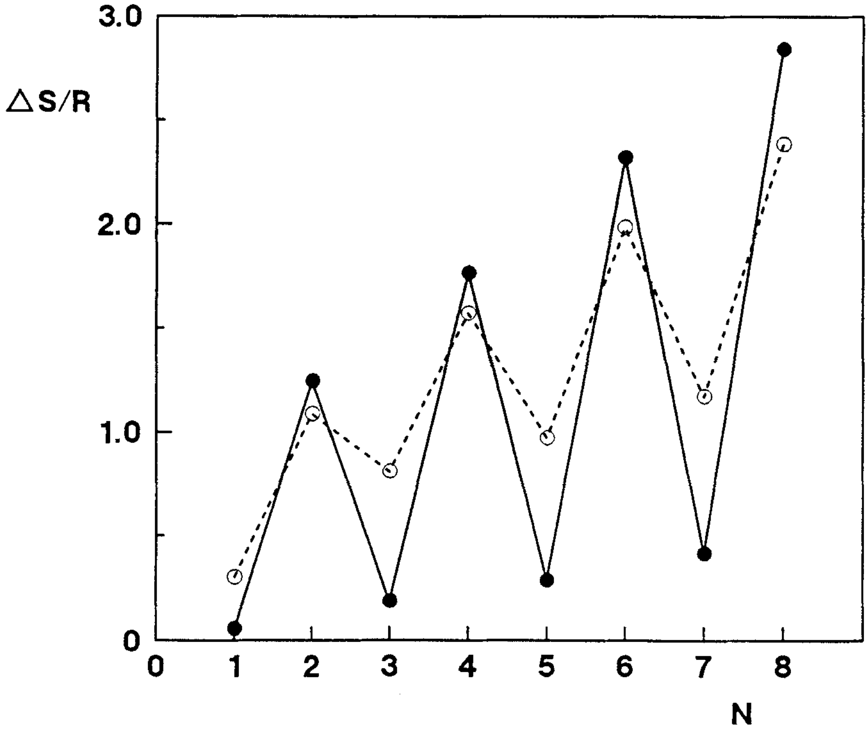

Figure 5. The dependence of the entropy of transition on the number of atoms in the flexible spacer predicted for the cyanobiphenyl dimers with methylene (●) and ether (○) linkages.

of the calculations for the cyanobiphenyl dimers with ether and methylene links are shown in figure 5 as a function of the number of atoms N in the flexible spacer. For the dimers with $N=7$ and 8, for which experimental results are available, the agreement with our predictions is good. Thus, for the odd dimer, replacing the oxygen links by methylene groups is predicted to reduce the entropy of transition, while for the even spacer $\Delta S/R$ increases. The magnitudes of the changes predicted are in reasonable agreement with experiment although such theories based on the molecular field approximation are not expected to be quantitative. Nonetheless the agreement with experiment does provide further strong support for the view that the changes in the transitional behaviour for dimers on replacing ether linkages by methylene groups can be understood in terms of a variation in the geometry. In general the entropies of transition for the dimers with ether linkages show a pronounced alternation with the even members having higher values than the odd, as observed experimentally [12]. However the alternation is predicted to be even larger for the homologous series with methylene links, primarily because the values for the odd members are considerably lower than those with ether linkages. Indeed $\Delta S/R$ is predicted to be so low for the early members of the series that for real compounds the transitions might well be second order. For rigid molecules, theory [14] predicts that as the molecular biaxiality increases so the nematic–isotropic transitional entropy falls. When the molecular biaxiality reaches its maximal value $\Delta S/R$ is predicted to be zero and the isotropic phase undergoes a transition directly into a biaxial as opposed to a uniaxial nematic phase. We speculate, therefore, that early members of the dimers with methylene linkages containing an odd number of atoms may well form biaxial nematic phases. We are attempting to test this fascinating prediction by synthesizing the α,ω-bis(4'-cyanobiphenyl-4) alkanes with $N=1$, 3 and 5.

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