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The angle of twist between the two phenyl rings in the nematic liquid crystal 4-n-pentyl-4'-cyanobiphenyl

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The angle of twist between the two phenyl rings in the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl

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The NMR spectrum of the protons in the biphenyl group of 4-*n*-pentyl-4′-cyanobiphenyl (5CB), was obtained by Sinton *et al.* (1984, *Molec. Phys.*, **53**, 333) and analysed by them to give an angle of twist, ϕ_{min}, between the normals to the two phenyl rings of 30 ± 2°. Their analysis made the assumption that $V(\phi)$, the potential for rotation about the inter ring bond, is such that only the structures with the minimum energy need be considered when calculating averaged dipolar couplings. Re-analysis of their data by a method which allows for the whole of $V(\phi)$ to be sampled when averaging the dipolar couplings yields a value for ϕ_{min} of 38·4 ± 0·1°.

1. Introduction

Both 4-*n*-alkyl- (NCB) and 4-*n*-alkyloxy- (NOCB) substituted 4′-cyanobiphenyls form liquid crystal phases, which are the focus of many studies which attempt to relate mesophase stability with molecular structure. This is mainly because of their importance as the active components of many electro-optic displays, but also because of their relatively simple structures. It is intriguing too that their aromatic core is a substituted biphenyl, since biphenyl itself is unusual in having a planar structure in the solid state [1], whilst having a minimum in $V(\phi)$, the potential energy as a function of the inter-ring angle ϕ, at about 44° in the gas phase [2]. The values of $V(0°)$ and $V(90°)$, which are maxima in $V(\phi)$, have also been determined from an electron diffraction study of a gaseous sample [2] to be 6·0 and 6·5 kJ mol^{-1}, respectively. These refer to isolated molecules, and it is possible, therefore, that in a condensed fluid phase the barriers may be considerably different, and that $V(\phi)$ may have a minimum at or close to zero. This indeed was the conclusion reached by a study of the NCB series, both as solutes in carbon tetrachloride, and in the solid state, by infrared and Raman spectroscopy [3]. The conclusions reached by Proutiere, Legoff and Chabanel [3] were that the minimum in $V(\phi)$ is close to $\phi = 0°$ for $N = 0$–12 in the carbon tetrachloride solutions, whereas ϕ_{min} appears to change in the solid state from being zero in 4-cyanobiphenyl (i.e. $N = 0$) to about 40° in 3CB and 4CB. The purpose of this present communication is to point out, however, that the value of ϕ_{min} can be obtained with high precision from the dipolar couplings which can be determined from the proton NMR spectrum of a liquid-crystalline sample [4]. One such study, that by Pines and his colleagues [4] has been reported for 5CB and they concluded that $\phi_{\mathrm{min}} = 30 \pm 2°$. The difference between ϕ_{min} determined by the NMR method, and which is for a nematic sample, and that derived from the infrared and Raman data, which are for an isotropic solution, is hard to reconcile, since it implies an unusually large change in $V(\phi)$ with solvent and phase. In order to determine $\phi_{\min}$ from the dipolar couplings Sinton *et al.* [4] made the assumption that only the structures corresponding to the energy minima need be considered, which we shall refer to as the rotational isomeric state (RIS) model. The use of this assumption can be expected to affect the value derived for $V(\phi)$, and we present here a re-analysis of the NMR data which averages the dipolar couplings over the whole potential energy path for rotation about the inter-ring bond.

Our approach is that introduced by Emsley and Luckhurst [5], in which the partially averaged dipolar couplings, D_{ij}, are related to conformationally dependent order parameters, $S_{\alpha\beta}$, the probability distribution $p(\phi)$, and the dipolar tensor elements $D_{ij\alpha\beta}(\phi)$ by [5]

$$D_{ij} = (2/3) \sum \int p(\phi) S_{\alpha\beta}(\phi) D_{ij\alpha\beta}(\phi). \tag{1}$$

The ϕ dependence of the dipolar coupling tensor is determined by the geometry, so that the major unknown factors are $p(\phi)$ and $S_{\alpha\beta}(\phi)$.

The conformationally dependent order parameters $S_{\alpha\beta}(\phi)$ are determined by the nature of a ϕ dependent potential of mean torque $U_{\text{ext}}(\phi, \beta, \gamma)$,

$$U_{\text{ext}}(\phi, \beta, \gamma) = -\varepsilon_{2,0}(\phi) C_{2,0}(\beta, \gamma) - 2\varepsilon_{2,2}(\phi) C_{2,2}(\beta, \gamma), \tag{2}$$

where the $C_{2,m}(\beta, \gamma)$ are reduced spherical harmonics. The angles β and γ are the polar angles made by the director of the uniaxial mesophase in a molecule fixed set of axes. The $\varepsilon_{2,m}(\phi)$ depend on the anisotropic intermolecular potential and their ϕ dependence is obtained by expressing them as a tensorial sum of ϕ dependent contributions $\varepsilon^{j}_{2,p}$ from individual rigid fragments of the molecule [6]. Thus,

$$\varepsilon_{2,m}(\phi) = \sum \varepsilon^{j}_{2,p} D^{2}_{p,m}(\alpha(\phi), \beta(\phi), \gamma(\phi)), \tag{3}$$

so that the ϕ-dependence has been transferred to the arguments of the Wigner rotation matrix elements $D^{2}_{p,m}(\alpha(\phi), \beta(\phi), \gamma(\phi))$ which relates the orientation of the jth fragment to the reference frame in which the $\varepsilon_{2,m}(\phi)$ are expressed.

For 5CB we locate the reference frame xyz as shown in figure 1 since in this frame only diagonal terms $S_{\alpha\alpha}(\phi)$ appear in equation (1) for the dipolar couplings between the protons in the biphenyl group. This means that we need consider only interaction tensor elements $\varepsilon_{2,0}(\phi)$ and $\varepsilon_{2,2}(\phi)$, which are obtained from $\varepsilon^{\mathrm{R}}_{2,0}$ and $\varepsilon^{\mathrm{R}}_{2,2}$, the average of the interaction tensor elements for each of the phenyl rings. Note that all of these tensor elements have magnitudes determined in part by the alkyl chain contributions to the intermolecular potential, but it is not necessary to know the individual contributions to these composite interaction tensors.

The value of $p(\phi)$ is related to $V(\phi)$ and $U_{\text{ext}}(\phi, \beta, \gamma)$ by,

$$p(\phi) = ZQ^{-1} \exp\{-V(\phi)/kT\}, \tag{4}$$

where

$$Z = \int \exp\{-U_{\text{ext}}(\phi, \beta, \gamma)/kT\} \sin\beta \, d\beta \, d\gamma, \tag{5}$$

and

$$Q = \int \exp\{-V(\phi)/kT\} \exp\{-U_{\text{ext}}(\phi, \beta, \gamma)/kT\} \sin\beta \, d\beta \, d\gamma \, d\phi. \tag{6}$$

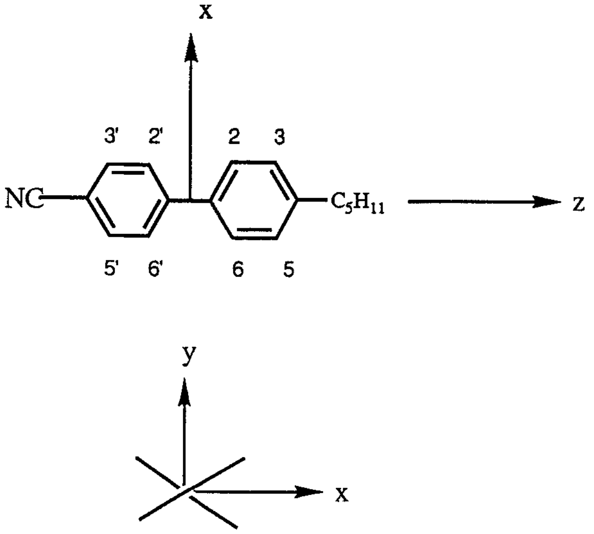

Figure 1. Atomic labelling and axes used for 5CB.

2. Analysis of the data

Sinton *et al.* [4] give the results of two analyses of their multiple quantum spectra, which differ in the permutation symmetry assumed for the proton spins. When the two phenyl rings are considered to be different (D_2 symmetry) the dipolar couplings obtained imply distortions from regular hexagonal structures which are unbelievably large. The analysis which assumes the two rings to be identical (D_4 symmetry) gives a more reasonable set of dipolar couplings and these are used in our analyses. We should note, however, that adopting the D_2 set leads to distorted rings, but to virtually the same conclusions about the inter-ring angle.

We precede by first using the dipolar couplings between protons within each ring to determine the proton coordinates relative to axes fixed in each ring; this is achieved without any assumptions being necessary about the inter-ring potential or the separation between the protons in different rings. The relative proton coordinates in each ring were kept fixed in all subsequent calculations at the values shown in table 1. The inter-proton distances obtained have the same ratios to r_{35} as those obtained by Sinton *et al.* [4].

We have also repeated the kind of analyses carried out by Sinton *et al.* to determine ϕ_{min}, that is by adopting the RIS approximation. The dipolar couplings depend on two local order parameters, S_{zz} and $S_{xx} - S_{yy}$, and varying these together

Table 1. Inter-proton distances r_{ij} between nuclei in the same phenyl ring of 5CB from analysis of the inter-proton dipolar couplings assuming that the two rings are structurally equivalent.

$r_{23} = r_{56} = r_{2'3'} = r_{5'6'} = 2{\cdot}473\,\text{Å}\ (2{\cdot}47)^{\dagger}$

$r_{35} = r_{3'5'} = 4{\cdot}299\,\text{Å}\ (4{\cdot}299)^{\ddagger}$

$r_{26} = r_{2'6'} = 4{\cdot}262\,\text{Å}\ (4{\cdot}27)$

† Values in parentheses are those obtained by Sinton *et al.* [4].
‡ Fixed.

Table 2. Observed and calculated dipolar couplings, the inter-ring angle ϕ_{min}, the inter-ring separation $(z_2 - z_{2'})$, and the order parameters S_{zz} and $S_{xx} - S_{yy}$ obtained by analysing the data of Sinton *et al.* [4] for 5CB, assuming D_4 symmetry, and a single set of minimum energy, symmetry related structures.

	D_{ij}/Hz		
i, j	Observed	Calculated	ΔD_{ij}/Hz
2, 3	−4478	−4478·1	−0·1
3, 6	47	47·0	0·0
3, 5	380	380·1	0·1
3, 3′	−147	−133·7	13·3
3, 2′	−365	−367·0	−2·0
2, 6	390	390·0	0·0
2, 2′	−1741	−1740·9	0·1

$(z_2 - z_{2'})/\text{Å} = 1{\cdot}988\ (1{\cdot}98)$†

$\phi_{\text{min}}/\text{deg} = 30{\cdot}2 \pm 0{\cdot}2\ (30{\cdot}4 \pm 0{\cdot}2)$

$S_{zz} = 0{\cdot}564\ (0{\cdot}565)$

$S_{xx} - S_{yy} = 0{\cdot}077\ (0{\cdot}071)$

† Values in parentheses were obtained by Sinton *et al.* [4].

with ϕ_{min} and $r_{22'}$ to minimize the difference between observed and calculated D_{ij} gave the results shown in table 2. Again, as expected, our results are essentially identical with those of Sinton *et al.*, and we present them here to facilitate comparison with our analysis of the data by the method introduced by Emsley, Luckhurst and Stockley [6], which we shall refer to as the ELS method. In particular, we show in table 2 the individual calculated dipolar couplings and the differences

$$\Delta D_{ij} = D_{ij}(\text{experimental}) - D_{ij}(\text{calculated}). \tag{7}$$

This reveals that almost all the error is contained in $\Delta D_{3,3'}$. To analyse the data by the ELS method it is necessary to adopt a model for $V(\phi)$, and we use a cosine expansion with the minimum number of terms dictated by symmetry,

$$V(\phi) = V_0 + V_2 \cos 2\phi + V_4 \cos 4\phi, \tag{8}$$

where the term independent of ϕ is included so that the minimum value of $V(\phi)$ is zero. The averaging of the D_{ij} over the bond rotation is done by taking 91 points equidistant in ϕ, and finding the values of V_q, $\varepsilon^{\text{R}}_{2,0}$, $\varepsilon^{\text{R}}_{2,2}$ and $z_2 - z_{2'}$ which minimize the difference between experimental and dipolar couplings; note that there are five independent parameters to fit to seven dipolar couplings. The results, which are given in table 3, show that the potential now has a minimum at 38·4 ± 0·1°. The ELS model does give a smaller rms error, but not appreciably so, and again the error is concentrated in $D_{3,3'}$, which has $\Delta D_{3,3'}$ about five times larger than the experimental error. The residual may be a consequence of choosing the truncated Fourier form for $V(\phi)$, although including a V_8 term did not lead to any improvement, and we have not explored larger departures of $V(\phi)$ from the form given by equation (8) since it is also possible that the failure of any of the models considered for $V(\phi)$ to fit $D_{3,3'}$ more closely could be a combination of the use of an over simplified model for $U_{\text{ext}}(\phi, \beta, \gamma)$ and the neglect of small amplitude vibrational motion [7].

Table 3. The difference between observed and calculated dipolar couplings, the Fourier coefficients V_q, the inter-ring angle $\phi_{\min}$, the inter-ring separation $z_2 - z_{2'}$, and the interaction parameters $\varepsilon^{R}_{2,0}$ and $\varepsilon^{R}_{2,2}$ obtained by analysing the data of Sinton *et al.* [4] by the ELS method.

i, j	$\Delta D_{ij}/\text{Hz}$
2, 3	0
3, 6	−1
3, 5	−1
3, 3′	10
3, 2′	0
2, 6	−3
2, 2′	0

$(z_2 - z_{2'})/\text{Å} = 1{\cdot}82 \pm 0{\cdot}01$

$V_0/\text{kJ mol}^{-1} = 1{\cdot}83$†
$V_2/\text{kJ mol}^{-1} = -1{\cdot}51 \pm 0{\cdot}19$
$V_4/\text{kJ mol}^{-1} = 1{\cdot}66 \pm 0{\cdot}23$

$\varepsilon^{R}_{2,0}/\text{kJ mol}^{-1} = 6{\cdot}98 \pm 0{\cdot}01$
$\varepsilon^{R}_{2,2}/\text{kJ mol}^{-1} = 1{\cdot}75 \pm 0{\cdot}08$

$\phi_{\min} = 38{\cdot}4 \pm 0{\cdot}1°$.

† A finite V_0 is included so that $V(\phi)$ is zero at the minima.

Table 4. Angles of twist $\phi_{\min}$ found for the rings in some NCB and NOCB compounds.

Compound	Phase	$\phi_{\min}$/deg.	Reference
1OCB	Nematic†	36	[9]
1OCB	Solid	40	[13]
3CB	Solid	43	[14]
4CB	Solid	40	[15]
5CB	Nematic	38	This work

† Over a temperature range of 20°C in the nematic phase.

The value obtained for $\phi_{\min}$ when using the ELS model is now closer to those obtained for biphenyls in the gas phase by experiment [2], or by calculation [8]. There is no report of a determination of the structure of 5CB in the solid phase, but there have been investigations of the crystal structures of a number of NOCB molecules, and the twist angles found are compared with that determined here for 5CB in table 4. We also include in table 4 the value obtained for 1OCB in the nematic phase by an analysis of the dipolar couplings by the ELS method [9]. For this compound the form derived for $V(\phi)$ is independent of temperature over the whole of the nematic range.

The ϕ dependence of $U_{\text{ext}}(\phi, \beta, \gamma)$ is such that the small biaxial order parameter $S_{xx} - S_{yy}$ changes with ϕ, as shown in figure 2, but S_{zz} is invariant to the bond rotation. Note too that the relatively weak ϕ dependence of $U_{\text{ext}}(\phi, \beta, \gamma)$ means that the probability distribution $p(\phi)$ given by equation (4) changes by only a small amount on going isothermally from nematic to isotropic phases, so that the value derived for $\phi_{\min}$ is appropriate for both liquid-crystalline and isotropic phases.

One further confirmation that the analysis of the dipolar couplings by the ELS method is giving a more realistic geometry for 5CB is that the inter-ring separation, as measured by $z_2 - z_{2'}$ the distance apart of the protons on sites 2 and 2′, is

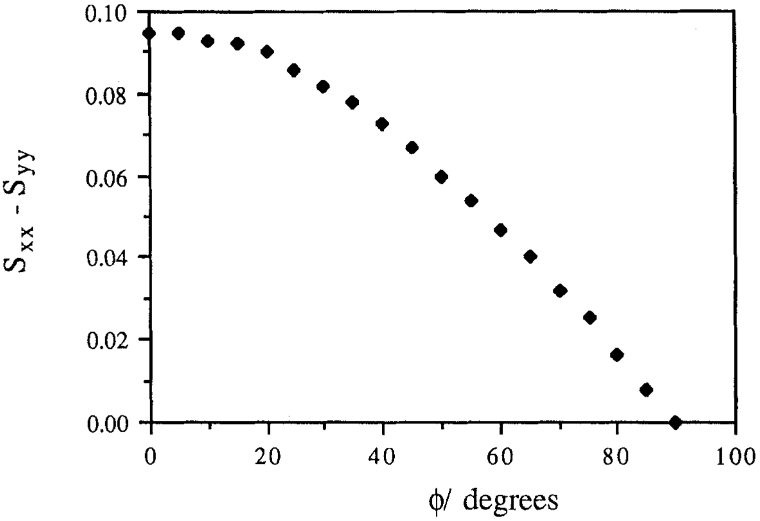

Figure 2. Variation of $S_{xx} - S_{yy}$ with ϕ calculated with the ELS model.

determined to be 1·82 Å, in good agreement with values found for a number of substituted biphenyls [4]. In contrast, the analysis of the data by adopting the RIS approximation gives $z_2 - z_{2'}$ as 1·98 Å [4].

3. Conclusion

The analysis of the dipolar couplings for 5CB shows that $V(\phi)$ has a minimum close to the values determined for other, non-sterically hindered substituted biphenyls in the gas phase [10–12], for 1OCB in the nematic [9] and solid [13] phases, and for solid samples of 3CB [14] and 4CB [15]. It would appear, therefore, that the weight of the available evidence supports the view that the angle of twist of the phenyl rings in liquid crystals containing the biphenyl group does not change appreciably on changing phase. Clearly these results cast doubt on the method used by Proutiere *et al.* [3] to investigate changes in $\phi_{\min}$ produced by changing from a solution in carbon tetrachloride to the solid phase which give changes by up to 40° for some members of the NCB series.

References

[1] Trotter, J., 1961, *Acta crystallogr.*, **14**, 1135.
[2] Almenningen, A., Bastiansen, O., and Fernholt, L., 1985, *J. molec. Struct.*, **128**, 59.
[3] Proutiere, A., Legoff, D., and Chabanel, M., 1989, *Molec. Crystals liq. Crystals*, **167**, 39.
[4] Sinton, S. W., Zax, D. B., Murdoch, J. B., and Pines, A., 1984, *Molec. Phys.*, **53**, 333.
[5] Emsley, J. W., and Luckhurst, G. R., 1980, *Molec. Phys.*, **41**, 19.
[6] Emsley, J. W., Luckhurst, G. R., and Stockley, C. P., 1982, *Proc. R. Soc.* A, **381**, 117.
[7] Diehl, P., 1985, *NMR of Liquid Crystals*, edited by J. W. Emsley (Reidel).
[8] Jaime, C., and Font, J., 1989, *J. molec. Struct.*, **195**, 103.
[9] Emsley, J. W., Horne, T. J., Zimmermann, H., Celebre, G., and Longeri, M., 1990, *Liq. Crystals*, **7**, 1.

[10] Almenningen, A., Bastiansen, O., Fernholt, L., Gundersen, S., and Kloster-Jensen, E., 1985, *J. molec. Struct.*, **128**, 77.
[11] Almenningen, A., Bastiansen, O., Gundersen, S., Samdal, S., and Skancke, A., 1985, *J. molec. Struct.*, **128**, 95.
[12] Bastiansen, O., and Samdal, S., 1985, *J. molec. Struct.*, **128**, 115.
[13] Walz, L., Paulus, H., and Haase, W., 1987, *Z. Kristallogr.*, **180**, 97.
[14] Haase, W., Paulus, H., and Pendzialek, R., 1983, *Molec. Crystals liq. Crystals*, **100**, 211.
[15] Vani, G. V., 1983, *Molec. Crystals liq. Crystals*, **99**, 21.