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A comparison of the structure, flexibility and mesogenic properties of 4-methoxy-4′-cyanobiphenyl and the α,α,α-trifluorinated derivative

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The compound 4-cyano-4′-(α,α,α-trifluoromethoxy)biphenyl ($1OCBF_3$) has been synthesized. Unlike the fully protonated analogue, 4-cyano-4′-methoxybiphenyl (1OCB), it does not show a liquid crystalline phase on cooling from the melting point (51°C) to room temperature. The transition temperature to a monotropic nematic phase was obtained as approximately 0°C by determining the transition temperatures of mixtures with 1OCB. The structures, conformational properties and orientational ordering of both 1OCB and $1OCBF_3$ as solutes in a nematic solvent ZLI 1132 have been investigated via the 17 dipolar couplings obtained by analysing the proton and fluorine NMR spectra of these solutions. It is concluded that the major difference between the two molecules lies in the potential, $V(\phi_2)$, governing rotation about the ring–oxygen bonds. In 1OCB the potential has the same form as in anisole, with a minimum when the C–O bond is in the plane of the attached ring ($\phi_2 = 0°$), and a maximum of about 15 kJ mol^{-1} when ϕ_2 is 90°. In $1OCBF_3$ the barrier to rotation about the ring–O bond decreases substantially to being near zero.

1. Introduction

The simplest molecule to form a nematic phase, which can be studied at ambient pressure is 4-methoxy-4′-cyanobiphenyl (1OCB), whose structure is shown in figure 1. The present study was motivated by the question as to what effect would be produced on the transition temperatures by replacing the CH_3 by a CF_3 group? As we shall see, the effects are large, which implies that large changes in the intermolecular forces are produced by substituting the CH_3 by the CF_3 group. Whatever the origin of the intermolecular forces, they will depend on the shape of the molecules, which in the case of flexible molecules such as 1OCB and $1OCBF_3$ is affected by the nature of the rotations about bonds, and in the present molecules there are three bond rotational motions as shown in figure 1. In principle it is possible to determine the form of the rotation potentials $V(\phi_i)$, from the dipolar couplings, D_{ij}, which are obtained by analysing the proton spectra of samples in the liquid crystalline phase. These spectra are, however, very complex and previous attempts to analyse the proton spectrum given by 1OCB failed. The spectra can be simplified by replacing some of the protons by deuterium atoms, followed by deuterium decoupling, and such an approach was used to study the structure and orientational ordering of pure 1OCB [1]. Reducing the

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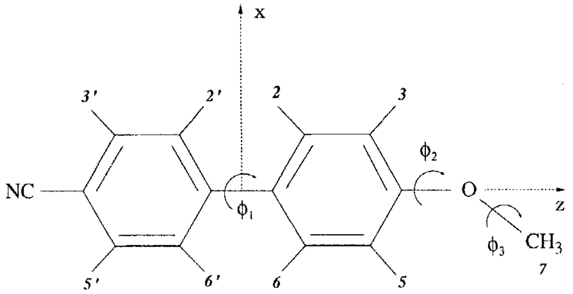


Figure 1. Structure of 4-methoxy-4′-cyanobiphenyl.

complexity of the spectrum, however, also means a reduction in the number of dipolar couplings that are obtained, and for 1OCB this required that a number of simplifying assumptions had to be made concerning the nature of the internal motion, and the symmetry of the biphenyl moiety. We shall present here an analysis of the full proton spectrum of a sample of 1OCB dissolved in the nematic solvent ZLI 1132. The spectrum of 1OCB as a solute was studied, rather than that of the pure compound, because we wished to compare the structure with that of the α,α,α-trifluorinated derivative ($1OCBF_3$). This could not be cooled into a nematic phase, and so both compounds were studied as solutes in the same solvent. In fact, the proton spectra from the solutes have sharper lines than that from pure 1OCB, and hence are better resolved.

2. Experimental

The 200 MHz proton spectrum of a sample of 1OCB dissolved in ZLI 1132 is very complex. The analysis of this spectrum was achieved by first analysing the simpler proton–{deuterium} spectrum of the deuteriated methyl derivative, 1OCB-d_3, dissolved in the same solvent. The next step was to analyse the proton spectrum given by the same sample, and this provided good estimates of the dipolar couplings in 1OCB. The parameters obtained from the analysis of 1OCB are shown in table 1.

A similar strategy was adopted for the spectrum of the sample of $1OCBF_3$ dissolved in ZLI 1132. The starting point was to analyse the ^1H–{^2H} spectrum of 2′,3′,5′,6′-tetradeuterio-4-(α,α,α-trifluoromethoxy)-4′-cyanobiphenyl ($1OCBF_3$-d_4). It then proved possible to analyse the proton and fluorine spectra from a sample of $1OCBF_3$ dissolved in ZLI 1132 with the results given in table 2.

The sample of 1OCB was obtained form Merck Ltd, U.K., and the deuteriated sample was synthesized from CD_3I and 4-hydroxy-4′-cyanobiphenyl by the method described by Gray and Mosley [2].

2.1. *Synthesis of* $1OCBF_3$

The procedure followed was that described by Whitesides *et al.* [3].

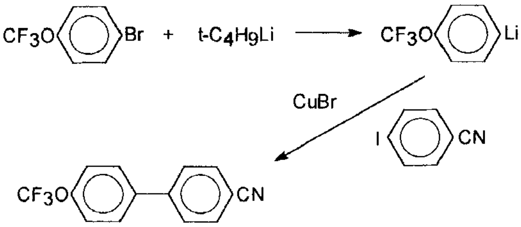


Table 1. Parameters obtained from the analysis of the 200 MHz spectrum of the protons in a sample of 4-methoxy-4′-cyanobiphenyl dissolved in the nematic solvent at 300 K.

i,j	D_{ij}/Hz	J_{ij}/Hz	*i,j*	D_{ij}/Hz	J_{ij}/Hz
2,3	−5260·6±0·1	8·0	2′,2	−2008·4±0·1	0·0
2,5	53·6±0·1	0·0	2′,3	−440·5±0·1	0·0
2,6	425·8±0·3	2·0	3′,2	−438·9±0·2	0·0
2,7	−385·9±0·1	0·0	3′,3	−163·4±0·1	0·0
3,5	426·2±0·3	2·0	7,7	1169·2±0·1	0·0
3,7	−1633·4±0·1	0·0			
2′,3′	−5199·3±0·1	8·0	*i,j*	Chemical shifts/Hz	
2′,5′	55·6±0·1	0·0			
2′,6′	431·6±0·3	2·0	2,7	427·0±0·3	
2′,7	−180·6±0·1	0·0	3,7	390·3±0·2	
3′,5′	432·8±0·3	2·0	2′,7	427·1±0·2	
3′,7	−82·1±0·1	0·0	3′,7	591·9±0·2	

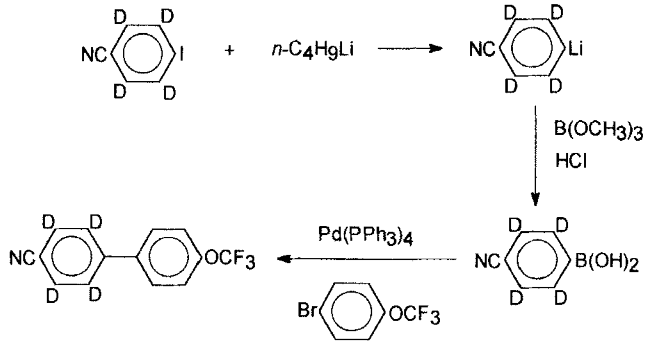
Table 2. Parameters obtained from the analysis of the 360 MHz spectrum of the protons, and the 338 MHz spectrum of the fluorines, in a sample of 4-(α,α,α-trifluoromethoxy)-4′-cyanobiphenyl dissolved in the nematic solvent at 300 K.

i,j	D_{ij}/Hz	J_{ij}/Hz	*i,j*	D_{ij}/Hz	J_{ij}/Hz
2,3	−4891·3±0·1	8·0	2′,2	−1671·3±0·1	0·0
2,5	49·0±0·1	0·0	2′,3	−409·1±0·1	0·0
2,6	45·8±0·2	2·0	3′,2	−411·4±0·1	0·0
2,7	−297·8±0·1	0·0	3′,3	−154·3±0·1	0·0
3,5	408·9±0·2	2·0	7,7	444·9±0·1	0·0
3,7	−786·6±0·1	0·0			
2′,3′	−4958·7±0·1	8·0	*i,j*	Chemical shifts/Hz	
2′,5′	46·8±0·1	0·0			
2′,6′	401·9±0·2	2·0	2,3	5·2±0·1	
2′,7	−154·3±0·1	0·0	2′,3	−0·5±0·1	
3′,5′	401·2±0·2	2·0	3′,3	239·9±0·2	
3′,7	−72·7±0·1	0·0			

t-Butyl lithium in pentane (9·7 ml, 1·8 M) was added at −75°C to a stirred solution of 4-bromotrifluoromethoxybenzene (Maybridge Chemicals) (2·06 g, 8·55 mmol) in dry THF (20 ml). The clear, brownish-yellow solution was stirred for 90 min at −75°C, the temperature allowed to rise to −15°C and copper(I) bromide (0·644 g, 4·49 mmol) added. After stirring at −15°C for 15 min, 4-iodobenzonitrile (0·9 g, 3·95 mmol) in THF (5 ml) was added. The temperature was allowed to rise to 0°C, and the mixture stirred at this temperature for 48 h. Dry oxygen gas was then blown on to the surface of the vigorously stirred mixture for 15 min, and then a saturated solution of ammonium chloride (10 ml) was added. The organic layer was separated, and the aqueous layer shaken with ether (4 × 50 ml); the organic phases were combined and dried (Na_2SO_4). The solvent was removed at reduced pressure, and the residue purified by flash chromatography (eluent: petroleum ether 40/60: acetone ratio 100: 2). Both the desired product (0·435 g, 42 per cent yield) and unreacted 4-iodobenzonitrile (0·338 g, 37·5 per cent) were obtained. The $1OCBF_3$ was sublimed (180°C/0·5 torr) and recrystallized from *n*-hexane.

2.2. *Synthesis of 1OCBF$_3$-d$_4$*

A different synthetic route was tried for the preparation of the deuteriated derivative, which gave a better yield. This used a boronic acid in the ring coupling step [4].



2.3. *4-Iodobenzonitrile-d$_4$*

Aniline-d_7 was iodinated by the method described by Brewster [5]. To a solution of sodium hydrogen carbonate (10 g, 0·119 mol) in water (75 ml), aniline-d_7 (5·38 g, 0·548 mol) was added and the mixture treated with solid iodine (17·48 g, 0·689 mol) in 2 g portions with magnetic stirring at 10°C for 10 min. The mixture was then stirred at room temperature until the colour of the iodine disappeared (25 min). The insoluble 4-iodoaniline-d_6 was filtered off, air dried, and recrystallized from petroleum ether (b.p. 60–80°C). The yield was 5·3 g (43 per cent) and the m.p. 62–63°C.

The 4-iodoaniline-d_6 (4·9 g, 0·022 mol) was dissolved in water (15 ml) and concentrated HCl (5 ml) and diazotized with sodium nitrite (2·58 g, 0·037 mol) in water (10 ml). The diazonium salt solution was neutralized with solid sodium carbonate and poured into a solution of sodium dicyanocuprate prepared by dissolving copper(I) chloride (2·8 g, 0·0283 mol) and sodium cyanide (3·61 g, 0·0736 mol) in water (20 ml). Benzene (50 ml) was added to the semi-solid mixture which was then left for 30 min at room temperature, and finally heated at reflux for 2 h. The benzene layer was separated, washed several times with 10 per cent sodium hydroxide, then with water, and dried with sodium sulphate. Removal of the solvent left a dark residue which was sublimed at 100°C and 0·05 Torr, and then purified by flash chromatography (silica gel, eluent petroleum ether 60/80 : ethyl acetate 100 : 4) to give 4-iodobenzonitrile-2,35,6-d_4 (1·36 g, 26 per cent yield), m.p. 127–128°C.

2.3. *4-Cyanophenyl boronic acid-d$_4$*

4-Iodobenzonitrile-d_4 (1·9 g, 8·15 mmol) in THF/hexane (12 ml/4 ml) was cooled to −100°C in a liquid nitrogen/ethanol/ether bath. n-Butyl lithium (1·4 M, 9·6 ml) was added slowly, dropwise, keeping the temperature below −95°C. The mixture was stirred at −100°C for 2 h, after which trimethyl borate (1·86 ml, 16·3 mmol) was added cautiously. The cooling bath was removed and the mixture left overnight to reach room temperature. HCl (25 ml, 10 per cent) was added and the mixture stirred for 1 h, shaken with ether (50 ml) and the organic layer dried (MgSO$_4$). Removal of the solvent left the crude product (0·98 g, 78 per cent yield), which was used in the next stage without purification.

2.4. *1OCBF*$_3$-d_4

The 4-cyanophenyl boronic acid -d_4 (0·5 g, 3·31 mmol) in methanol (2 ml) was added to 4-bromotrifluoromethoxybenzene (0·67 g, 2·78 mmol) in toluene (7 ml). To this mixture was added sodium carbonate (2 M, 2 ml) and palladium tetrakis(triphenylphosphine) (40 mg) and the mixture heated at reflux under N_2 for 27 h, left to cool, and the organic material extracted into ether (50 ml). The organic layer was washed with brine and dried ($MgSO_4$). Removal of the solvent, and purification by flash chromatography (eluent : petrol 60/80 : acetone 5 : 1) yielded 1OCBF$_3$-d_4 (0·6 g, 81 per cent yield).

3. Results and discussion

3.1. *Phase transitions for 1OCBF*$_3$

On heating 1OCBF$_3$ melts at 51°C to the isotropic phase. On cooling rapidly, the isotropic phase persists under the polarizing microscope until room temperature (about 24°C). Mixing 1OCBF$_3$ with 1OCB gave an almost linear depression of both the melting, T_{CI}, and nematic–isotropic transition temperature, T_{NI}, as shown in figure 2. Extrapolation of the T_{NI} curve to pure 1OCBF$_3$ gave a virtual T_{NI} value of approximately 0°C. Thus, the changes on replacing the methyl by the trifluoromethyl group are $\Delta T_{CI} = 56°C$, and $\Delta T_{NI} = 85°C$.

3.2. *Structure and orientational order*

The 17 dipolar couplings obtained for each molecule can be used to determine the relative positions of the protons within each ring, and the local order parameters for each rigid sub-unit. To proceed further, so as to determine the relative dispositions of the three fragments within each molecule, requires either that simplifying assumptions be made about the bond rotational motions, or that a model is chosen for the dependence of orientational order on the angles ϕ_1, ϕ_2, and ϕ_3.

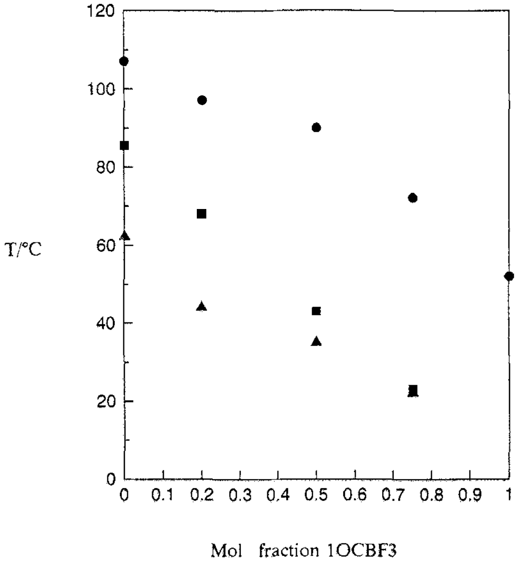


Figure 2. Transition temperatures for mixtures of 1OCBF$_3$ in 1OCB; crystal–isotropic (●), isotropic–nematic (■), and nematic–crystal (▲).

Rotation of the primed relative to the unprimed ring is probably virtually independent of the conformation of the methoxy or trifluoromethoxy group, and so the rotation through ϕ_1 can be considered in isolation. This means that the dipolar couplings within the biphenyl fragment can be used to determine the structure and conformation of this unit independently of the rest of the molecule.

Rotation of the CH_3 or CF_3 groups about the O–C_7 bond is strongly hindered when ϕ_2 is zero or 180°, but much easier when ϕ_2 is 90 or 270°. As a consequence, the bond rotational motions about C_4–O and O–C_7 have to be considered together.

In analysing the dipolar couplings our strategy is to consider first the approximate jump models for motion, that is that only symmetry-related, minimum energy structures are populated. The advantage of this simple, rotational isomeric state model (RIS), if it fits the data, is that the orientational order parameters of the conformers are identical, except for symmetry-determined changes in sign of the off-diagonal elements, when a common reference frame is used for all the conformers. This is equivalent to the order matrices for the conformers having identical components, but with the orientation of the principal axes changing for each conformer in a manner dictated by the symmetry.

The dipolar couplings will also be used to test models for continuous rotations about the bonds. This is a more realistic description for the motion, but depends on a strongly model-dependent approach to analysing the data.

3.3. *Structures of the biphenyl rings*

The relative positions of the protons in the unprimed ring were determined from the dipolar couplings $D_{23}=D_{56}$, $D_{36}=D_{25}$, D_{26}, D_{35}. These are related to the inter-proton distances r_{ij}, and the local order parameters, S^R_{zz} and $S^R_{xx}-S^R_{yy}$, where the axes xyz are fixed in the unprimed ring plane (see figure 1), by

$$D_{ij}=-\gamma_i\gamma_j h[S^R_{zz}(3\cos^2\theta_{ijz}-1)+(S^R_{xx}-S^R_{yy})\sin^2\theta_{ijz}]/8\pi^2 r^3_{ij}, \qquad (1)$$

where θ_{ijz} is the angle that r_{ij} makes with z. It is necessary to fix one inter-proton distance, and taking this to be $r_{26}=4{\cdot}296$ Å, which is the value appropriate to a regular hexagon of side 1·4 Å for the benzene ring, and a C–H distance of 1·08 Å, gave the values shown in table 3.

Table 3. Proton coordinates, local order parameters, $S^R_{\alpha\beta}$, inter-ring, ϕ_1 (min), and α, the angle between x and x_p, a principal axis of S^R for 1OCB and $1OCBF_3$.

	1OCB	$1OCBF_3$
x_2/Å	2·149 ± 0·003	2·154 ± 0·002
x_3/Å	2·148†	2·148†
z_2/Å	0·946 ± 0·003	0·943 ± 0·003
z_3/Å	3·397†	3·416†
$z_{2'}$/Å	2·151 ± 0·003	2·148 ± 0·002
$x_{3'}$/Å	2·148 ± 0·003	2·148 ± 0·003
$z_{2'}$/Å	−0·946 ± 0·003	−0·943 ± 0·003
$z_{3'}$/Å	−3·407 ± 0·003	−3·404 ± 0·003
S^R_{zz}	0·645 ± 0·002	0·616 ± 0·002
$S^R_{xx}-S^R_{yy}$	0·082 ± 0·002	0·076 ± 0·002
$\|S^R_{xy}\|$	0·019 ± 0·001	0·030 ± 0·001
ϕ_1(min)/°	30·8 ± 0·3	33·0 ± 0·3
α/°	12·4 ± 0·9	19·1 ± 0·9

† Fixed.

All the dipolar couplings between the eight protons in the biphenyl fragment were then used to determine the relative proton coordinates in the primed ring, together with $|S^{R}_{xy}|$, and the inter-ring angle, $\phi_1(\mathrm{min})$. To do this it was assumed that the motion about the inter-ring bond comprises jumps between four equivalent minimum energy structures, referred to as the rotational isomeric state approximation (RIS). The inability to obtain the sign of S^{R}_{xy} stems from the symmetry imparted to the inter-ring couplings by the averaging between the four structures. This analysis yielded the data in table 3. Note that the relative positions of the protons within each ring are determined independently of the model assumed for the bond rotation, but that the inter-ring separation, and the inter-ring angle, $\phi_1(\mathrm{min})$, are model dependent.

The magnitude of the angle, α, between x and x', a principal axis for the local order matrix for the biphenyl fragment, is given by

$$\tan|2\alpha| = \frac{|2S_{xy}|}{S_{xx}-S_{yy}} \tag{2}$$

and the values obtained for 1OCB and $1OCBF_3$ are given in table 3. A symmetrically substituted 4,4′-biphenyl has x' in the plane which bisects the ring planes, so that $\alpha=\phi_1(\mathrm{min})/2$. The difference $|\frac{1}{2}\phi_1(\mathrm{min})-\alpha|$ found for 1OCB and $1OCBF_3$ by assuming a single set of four symmetry related structures is $3{\cdot}0\pm0{\cdot}9^\circ$ for 1OCB and $-2{\cdot}6\pm0{\cdot}9^\circ$ for $1OCBF_3$.

3.4. *The potential function for rotation about the inter-ring bond*

The RIS approximation neglects all torsional states with $\phi\neq\phi_1(\mathrm{min})$, so that the values of $\phi_1(\mathrm{min})$ obtained with this approximation should be regarded as being only approximate. A more realistic, classical approximation assumes that there is a continuous distribution, $p_{\mathrm{LC}}(\phi_1)$, for this angle in the liquid crystalline state, which will be similar to, but not equal to $p_{\mathrm{iso}}(\phi_1)$, the distribution appropriate for an isothermal isotropic phase. The observed dipolar couplings are now given by

$$D_{\mathrm{ij}} = \int D_{\mathrm{ij}}(\phi_1)p_{\mathrm{LC}}(\phi_1)\,d\phi_1, \tag{3}$$

where the $D_{\mathrm{ij}}(\phi_1)$ are

$$D_{\mathrm{ij}}(\phi_1) = -\gamma_{\mathrm{i}}\gamma_{\mathrm{j}}h/(12\pi^2 r^3_{\mathrm{ij}}(\phi_1))\Sigma_{\alpha\beta}S^{\mathrm{R}}_{\alpha\beta}(\phi_1)\cos\theta_{\mathrm{ij}\alpha}\cos\theta_{\mathrm{ij}\beta}. \tag{4}$$

The order parameters $S_{\alpha\beta}(\phi_1)$ are calculated by adopting a potential of mean torque, $U_{\mathrm{ext}}(\beta,\gamma,\phi_1)$

$$U_{\mathrm{ext}}(\beta,\gamma,\phi_1) = -\epsilon_{2,0}(\phi_1)C_{2,0}(\beta,\gamma)-2\epsilon_{2,2}(\phi_1)C_{2,2}(\beta,\gamma), \tag{5}$$

where the $C_{2,\mathrm{m}}(\beta,\gamma)$ are modified spherical harmonics and β and γ are the polar angles made by the director in the principal frame of the interaction tensor $\epsilon(\phi_1)$. Two methods have been proposed for obtaining the coefficients $\epsilon_{2,\mathrm{m}}(\phi_1)$. These are the maximum entropy and additive potential (AP) methods, which have been compared recently [6, 7]. Here we use the AP method, which expresses the $\epsilon_{2,\mathrm{m}}(\phi_1)$ as a sum of contributions from rigid, molecular sub-units, j. Thus, in general

$$\epsilon_{2,\mathrm{m}}(\phi_{\mathrm{k}}) = \Sigma_{\mathrm{j}}\Sigma_{\mathrm{p}}\epsilon_{2,\mathrm{p}}(j)D^2_{\mathrm{p,m}}(\Omega_{\mathrm{j}}(\phi_{\mathrm{k}})), \tag{6}$$

where $D^2_{\mathrm{p,m}}(\Omega_{\mathrm{j}}(\phi_{\mathrm{k}}))$ is an element of a Wigner rotation matrix and $\Omega_{\mathrm{j}}(\phi_{\mathrm{k}})$ is the orientation of the jth unit relative to the molecular reference frame.

The values of $p_{LC}(\phi_1)$ in equation (3) are determined by $U_{ext}(\beta, \gamma, \phi_1)$ and also by $V(\phi_1)$, the effective bond rotational potential

$$p_{LC}(\phi_1) = Z^{-1} \int \exp\{-[U_{ext}(\beta, \gamma, \phi_1) + V\phi_1)]/kT\} \sin\beta \, d\beta \, d\gamma, \tag{7}$$

with

$$Z = \int \exp\{-[U_{ext}(\beta, \gamma, \phi_1) + V(\phi_1)]/kT\} \sin\beta \, d\beta \, d\gamma \, d\phi_1. \tag{8}$$

The interaction coefficients required for the biphenyl fragments in 1OCB and 1OCBF$_3$ are $\epsilon^{R}_{2,0} = \epsilon^{R'}_{2,0}$, $\epsilon^{R}_{2,2}$ and $\epsilon^{R'}_{2,2}$. The potential is written as the same form used to analyse the dipolar couplings in biphenyl [7] and 4-cyanobiphenyl [8]

$$V(\phi_1) = V_0 + V_2 \cos 2\phi_1 + V_4 \cos 4\phi_1, \tag{9}$$

where V_0 scales the potential to be zero at ϕ_1(min).

The calculations proceed by minimizing the differences between observed and calculated D_{ij} between all eight ring protons by varying the three interaction parameters, two potential terms, V_1 and V_2, and the inter-ring separation as measured by $z_2 - z_{2'}$, and the results are shown in table 4, whilst the shape of the potentials are shown in figure 3. In table 5 the data obtained for 1OCB and 1OCBF$_3$ are compared with those found by analysing the dipolar couplings for the protons in biphenyl and 4-cyanobiphenyl dissolved in nematic solvents.

In each case there is an appreciable difference in the values obtained for ϕ_1(min) by the AP and RIS methods, but the trends between the compounds are the same for both models; thus ϕ_1(min) is found to be 2° larger for 1OCBF$_3$ than 1OCB by the RIS and 1·4° by the AP method.

The data in table 4 depend on the choice of a 2-term cosine series for $V(\phi_1)$, which is the simplest function having the correct periodicity and which produces a good fit to the data, but it is not a unique choice for the potential and does have some unsatisfactory, restrictive features. Thus, the sign of $\Delta V = V(0°) - V(90°)$ depends entirely on the position of the minimum, ϕ_1(min). If $\phi_1(\text{min}) = 45°$, then $\Delta V = 0$; $\Delta V < 0$ for $\phi_1(\text{min}) < 45°$, and $\Delta V > 0$ for $\phi_1(\text{min}) > 45°$. There is no reason why the real potential function should be restricted in this way.

Using a continuous potential rather than the RIS model for the conformations adopted by the two rings reduces the values obtained for $z_2 - z_{2'}$, which is a measure of

Table 4. Parameters obtained by the analysis of the dipolar couplings for 1OCB and 1OCBF$_3$ by the AP method.

	1OCB	1OCBF$_3$
V_0/kJ mol^{-1}	4·41	4·82
V_2/kJ mol^{-1}	−3·9 ± 0·1	−3·6 ± 0·2
V_4/kJ mol^{-1}	3·9 ± 0·1	4·5 ± 0·2
ϕ_1(min)/°	37·8 ± 0·3	39·2 ± 0·6
$\epsilon^{R}_{2,0}$/kJ mol^{-1}	8·800 ± 0·002	8·155 ± 0·009
$\epsilon^{R}_{2,2}$/kJ mol^{-1}	1·794 ± 0·004	1·375 ± 0·009
$\epsilon^{R'}_{2,2}$/kJ mol^{-1}	1·442 ± 0·005	1·685 ± 0·008
$\alpha(\phi_1$(min))/°	20·1 ± 0·1	20·8 ± 0·1

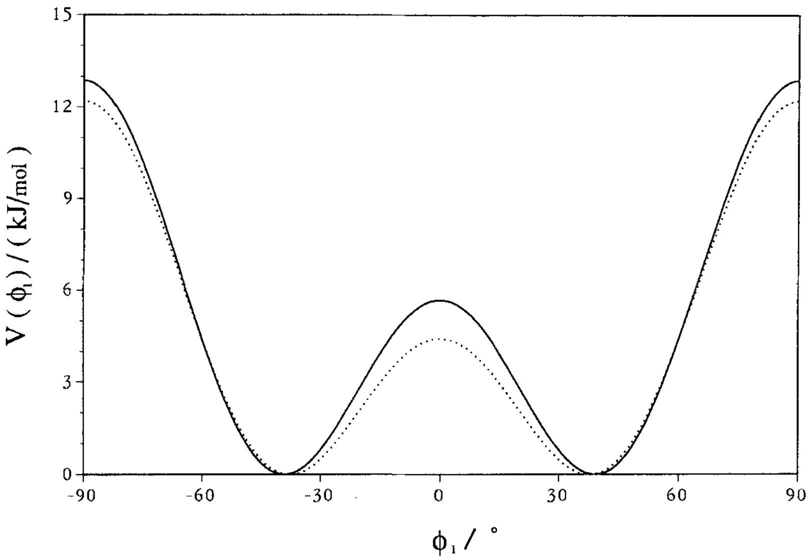


Figure 3. The potential function $V(\phi_1)$ for rotation about the inter-ring bond in 1OCB (·····) and 1OCBF$_3$ (——) obtained by the AP method.

Table 5. Comparison of the rotational potentials, and the ring separations $z_2 - z_{2'}$ obtained by the AP method for biphenyl, 4-cyanobiphenyl, 1OCB and 1OCBF$_3$, and of ϕ_1(min) obtained by both the AP and RIS models.

	$V(0°)$ /kJ mol^{-1}	$V(90°)$ /kJ mol^{-1}	ϕ_1(min)/°		$(z_2 - z_{2'})$/Å		
			AP	RIS	AP	RIS	$\alpha(\phi_1(\mathrm{min}))$
Biphenyl†	7·4	21·7	37·4	31·0	1·79	1·88	18·7
4-cyano-biphenyl†	7·7	23·3	37·0	33·0	1·83	1·88	19·5
1OCB‡	4·4	12·2	37·8	31·0	1·78	1·89	20·1
1OCBF$_3$‡	5·7	12·9	39·2	33·0	1·78	1·88	20·8

† For samples dissolved in the nematic solvent ZLI 1115.
‡ For samples dissolved in the nematic solvent ZLI 1132.

the inter-ring separation, by approximately 0·09 Å to 1·78 Å. This is in excellent agreement with the value of 1·79 Å obtained for biphenyl. In biphenyl the inter-ring separation could be obtained from $D_{44'}$ independently of the model adopted for the ring rotational motion.

The difference in the values of $\epsilon^{\mathrm{R}}_{2,2}$ and $\epsilon^{\mathrm{R}'}_{2,2}$ means that the principal axes of the interaction tensor for the biphenyl group do not coincide with the bisector of the ring planes. The angle α now depends on ϕ_1, and for ϕ_1(min) the values of $\phi_1(\mathrm{min}) - \alpha$ are $-1{\cdot}2°$ for both 1OCB and 1OCBF$_3$.

3.5. *The conformations of the methoxy and trifluoromethoxy groups*

We shall again consider two methods of obtaining the conformations from the dipolar coupling constants: either jumps between symmetry related conformations or a continuous potential for cooperative rotations about the two bonds.

Table 6. Bond angles and lengths assumed for the anisole fragments in 1OCB and $1OCBF_3$.

	1OCB	$1OCBF_3$
$r(C_4O)$/Å	1·36†	1·407‡
$r(OC_7)$/Å	1·42†	1·341‡
r(CH)/Å	1·085†	
r(CF)/Å		1·33‡
OC_7H/°	109·47†	109·47
HCH/°	109·47	
C_3C_4O/°	120	120
C_4OC_7/°	122	124

† From reference [13].
‡ From reference [12].

3.6. *Jump models for the conformations*

These models can be tested against the dipolar couplings within the anisole fragments. To do this it is necessary to fix the bond lengths and angles of this group, and the values used are given in table 6.

The protons in the methyl or the fluorines in the trifluoromethyl groups have three positions of minimum energy, which are related by 120° rotations about the O–C_7 bonds. There are two possibilities for jump motion about the C_4–O bonds, with the restriction that only symmetry related structures are considered: the minima are either at 0° or 180° (planar model), or at 90° and 270° (orthogonal model).

The jump models were tested first with the dipolar couplings D_{27}, D_{37} and D_{77}, and with $S_{xx}-S_{yy}$, S_{zz}, and the positions of the protons in the rings given in table 3. The variable parameters were S_{xz} and the angle C_3C_4O, with the rest of the geometry fixed at that given in table 6. Acceptable agreement was obtained for 1OCB only for the planar model, and the optimized values of the variable parameters are given in table 7. The value of 123·5° found for the angle C_3C_4O is very close to those values found for planar methoxylated rings in solid samples. This jump model between planar structures was then used to calculate couplings $D_{2'7}$ and $D_{3'7}$ between the methoxy protons and the protons in the more distant ring, whose inclination to the first ring is set at 31°. The values obtained for $\Delta D_{2'7} = D_{2'7}(\text{observed}) - D_{2'7}(\text{calculated})$ and $\Delta D_{3'7}$ of 2·1 and 0·4 Hz, respectively show that the jump model between planar structures is in good agreement with the data.

The dipolar couplings between the protons and fluorines in the anisole fragment of $1OBCF_3$ were similarly compared with the predictions of the two jump models between symmetry related structures, and neither model fits the data.

It is not possible to test a model in which the methyl group jumps between the four symmetry related positions having ϕ_2 fixed between 0° and 90°. This is because such conformers require all five order parameters in equation (1), which means that there are more unknown parameters than dipolar couplings in the anisole fragment. Including dipolar couplings between the fluorines and protons in the primed ring increases the data set, but raises the problem that conformations with angles ϕ_2, $180° - \phi_2$, $180 + \phi_2$ and $360° - \phi_2$ no longer form an equivalent set, since their relative energies and order matrices depend on the orientation of the primed as well as the unprimed rings. We conclude that for $1OCBF_3$ there is not a single set of symmetry related structures which fits the data.

Table 7. Local order parameters, $S_{\alpha\beta}$, and the angle C_3C_4O optimized to fit the dipolar couplings in the anisole fragment of 1OCB assuming jumps between planar structures.

S_{xz}	0·116
$C_3C_4O/°$	123·5
RMS error	1·7 Hz

3.7. *Continuous potentials for rotation about C_4–O and O–C_7*

Rotation of the methyl of trifluoromethyl group about the O–C_7 bond is expected to be strongly hindered when the O–C bond is confined to the ring plane ($\phi_2 = 0°$ or 180°), and to be virtually free when $\phi_2 = 90°$ or 270°. A potential which describes such a coupling between the rotations about the two bonds has the form

$$V(\phi_2, \phi_3) = \tfrac{1}{2}V_2(1 - \cos 2\phi_2) + \tfrac{1}{2}V_3 \cos^2 \phi_2[1 - \cos(3\phi_3 + 2\phi_2)]. \qquad (11)$$

This potential was used successfully to analyse dipolar couplings for a sample of anisole–C-13 dissolved in nematic solvents [9], and it was used here when applying the AP method to the anisole fragment of 1OCB. The data set was D_{23}, D_{25}, D_{26}, D_{27}, D_{35}, D_{37} and D_{77}, and the positions of the ring protons were fixed at the values in table 3. Molecular orbital calculations [10, 11] on anisole suggest that the angles C_3C_4O and C_4OC_7 vary with rotation about the *z* axis. The data sets for both 1OCB and 1OCBF$_3$ can be fitted with either a varying or fixed geometry for the methoxy fragment, and so for simplicity, a fixed geometry was used. The angle C_3C_4O is taken to be 120°, and C_4OC_7 is set at 122° for 1OCB, which gives the angle between the rotation axis, *z*, and the O–C_7 bond as 58°, in agreement with both experimental and theoretical estimates of this angle. The variable parameters were the three interaction parameters, $\epsilon^{R}_{2,0}$, $\epsilon^{R}_{2,2}$ and $\epsilon^{OC}_{2,0}$, and V_2 and V_3. Very good agreement between the observed and calculated dipolar couplings was obtained for 1OCB, and the optimized parameters are given in table 8. The potential obtained is shown in figure 4 and is virtually identical with that found for anisole [9].

Molecular orbital calculations on α,α,α-trifluoromethoxybenzene obtained $C_3C_4O = 123·4°$ and $C_4OC_7 = 124·5°$ for the conformation which has the COC and phenyl rings coplanar [12]. These angles both decrease to about 120° when the CF_3 is rotated to the orthogonal position. This suggests that for calculations on 1OCBF$_3$ with a rigid geometry for the trifluoromethoxy group, and with $C_3C_4O = 120°$, the value of C_4OC_7 should be larger than for the same angle in 1OCB, and so a value of 124° was used. The rest of the geometrical parameters used are given in table 6. Calculations with a smaller value for this angle give essentially similar results for the shape of the barrier to rotation. The lowest RMS error (0·2 Hz) was obtained when V_3 is zero and V_2 negative ($-5·5\,\mathrm{kJ\,mol^{-1}}$). This corresponds to the OCF_3 being mainly in the orthogonal position. The zero barrier to rotation about the O–C_7 bond does not seem very probable, and so the effect on the analysis was explored of increasing the value of V_3. The RMS error increases, but reaches only 0·4 Hz when V_3 is 24 kJ mol^{-1}, when V_2 is 2·0 kJ mol^{-1}.

The molecular orbital calculations on trifluoromethoxybenzene [12] obtained a low barrier to rotation about the C_4–O bond, with the position of the minimum in the potential being dependent on the basis set used. Thus, with a STO 3-21G basis set, the minimum is at $\phi_2 = 0°$, that is a planar structure. Extending the basis set to a STO 6-31G shifted the minimum to $\phi_2 = 90°$. Taking the NMR and MO results

Table 8. The interaction parameters, $\epsilon^{R}_{2,m}$ and $\epsilon^{OC}_{2,0}$ (kJ mol^{-1}) and the potential terms V_2 and V_3 (kJ mol^{-1}), obtained by comparing the dipolar couplings observed for the anisole fragments of 1OCB and 1OCBF$_3$ to those calculated by the AP method.

	1OCB	1OCBF$_3$	
V_2	15±2	−5·5±	2·05
V_3	20±5	0†	24†
$\epsilon^{R}_{2,0}$	6·76±0·01	5·98±0·01	6·19±0·01
$\epsilon^{R}_{2,2}$	1·32±0·05	2·41±0·01	2·03±0·01
$\epsilon^{OC}_{2,0}$	2·14±0·01	2·28±0·01	2·01±0·01
RMS/Hz	0·2	0·2	0·4

† Fixed.

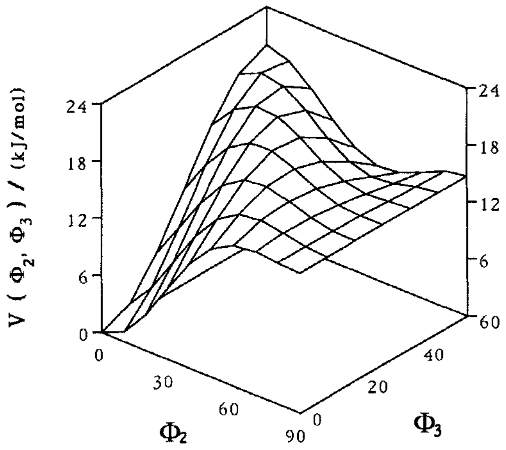


Figure 4. The potential function $V(\phi_2, \phi_3)$ obtained by the AP method for 1OCB.

together we conclude that the barrier to rotation about the C_4–O bond in 1OCBF$_3$ is small, so that V_2 is certainly less than 2 kJ mol^{-1}, corresponding to a minimum energy, planar structure, and is probably close to zero, or negative, corresponding to a minimum energy, orthogonal structure. Our strongest conclusion is that the barriers to rotation in 1OCB and 1OCBF$_3$ are very different.

4. Conclusion

Analysing the dipolar couplings with either the RIS or continuous potentials for the conformational distributions shows that the major difference between the shapes of 1OCB and 1OCBF$_3$ lies in the conformation of the OCH_3 and OCF_3 group with respect to the plane of their neighbouring phenyl ring. The biphenyl fragments in the two molecules are very similar, with the 1OCBF$_3$ having a slightly larger (1·5–2°) angle between the ring normals.

The different shapes of the molecules may be one reason why they have very different transition temperatures. But it is probably not the only reason why their mesogenic phase regions are so different. Certainly, 1OCBF$_3$ is more electrically polarized than 1OCB, so that the contribution of electrostatic interactions to the intermolecular forces will be different in the two molecules, and it is perhaps this factor, in conjunction with the difference in shape, that produced the different transition temperatures.

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