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The conformation of the aromatic rings relative to the alkyl chain in 4-*n*-pentyl-4′-cyanobiphenyl

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A partially-deuteriated sample of the nematogen 4-*n*-pentyl-4′-cyanobiphenyl has been synthesized which contains six protons, four in an aromatic ring and two on the attached methylene group. The proton–deuterium NMR spectrum of a pure sample, and of a mixture with the nematogen I35 have been recorded and analysed to yield a set of inter-proton dipolar couplings. These have been used to derive the potential governing rotation about the ring–C bond, which is found to have a minimum when the bond is in the plane perpendicular to the ring plane. The barrier to rotation is found to be larger ($>22\,\mathrm{kJ\,mol^{-1}}$) than in ethylbenzene ($\approx 3\,\mathrm{kJ\,mol^{-1}}$).

1. Introduction

The compounds which form stable liquid crystalline phases have shapes which fluctuate by virtue of rotations about bonds in the molecules. The molecular flexibility is an important factor in determining the phase transition temperatures, and also in determining their physical properties. There are often several bond rotational motions in mesogens, and characterizing these in terms of the shapes of their rotational potentials, $V(\phi_i)$, is a formidable task. The magnitudes of nuclear spin dipolar couplings, D_{ij}, and deuterium quadrupolar splittings, $\Delta\nu_i$, are observed by NMR spectroscopy as averages over the internal motions, as well as over motion of the whole molecule in the mesophase, and provide a means of investigating the rotational potentials. In the case of the 4-*n*-alkyl-4′-cyanobiphenyl (*n*CB) mesogens there are rotations about the inter-ring bond, through an angle ϕ_R, the ring–chain bond, through ϕ_{RC}, and each of the C–C bonds in the chain through angles ϕ_{CC}. The rotational potential $V(\phi_R)$ has been investigated by proton NMR [1, 2], and the flexibility of the chain explored by deuterium resonance [3]. These previous NMR investigations, however did not produce data which could be used to determine $V(\phi_{RC})$, and we report here the results of proton NMR experiments which enable the form of this rotational potential to be established. This involved the synthesis of a specifically deuteriated sample of 5CB, whose structure is shown in figure 1, and the analysis of a deuterium-decoupled proton spectrum in order to obtain the dipolar couplings between the six protons.

Experiments were done on the pure sample (mp 24°C, T_{NI} 35°C), and also on a mixture with an equal volume of the nematogen I35 (mp 32°C, T_{NI} 107°C), a single component, commercial liquid crystal obtained from Merck Ltd., U.K.

2. Experimental

2.1. *The synthesis of 5CB-d_{13}*

The synthesis involved the preparation of the following compounds.

Valeryl chloride-d_9 (**I**). The first stage in the synthesis of the deuteriated valeryl chloride (**I**) was to obtain deuteriated valeric acid. Valeric acid (20 g, 200 mmol), sodium hydroxide pellets (9 g), D_2O (99·9%, 100 ml)

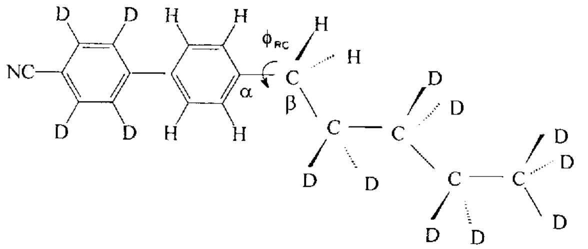

Figure 1. Partially-deuteriated 4-*n*-pentyl-4′-cyanobiphenyl.

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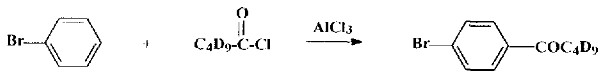
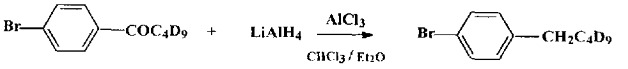
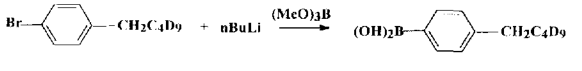
and platinum on carbon catalyst (10%, 6 g) were heated and stirred in a stainless steel high pressure vessel at 180°C for 7 days. The acid was isolated by acidification, extracted into ether and distilled giving randomly 90% deuteriated valeric acid. After a second exchange reaction under identical conditions the valeric acid was 98% deuteriated. The deuteriated valeric acid was chlorinated with thionyl chloride, following the procedure described in Vogel and Furniss [4] to give valeryl chloride-d_9 (D = 98%; yield 90%; bp = 124–127°C).



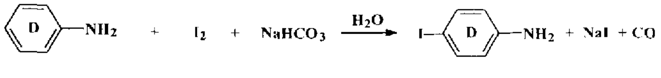
1-Bromo-4-pentanoylbenzene-d_9 (**II**). Aluminium chloride (12·4 g, 93 mmol) was placed in a three neck RB flask fitted with a reflux condenser, stirrer and funnel, and bromobenzene (44·73 g, 284 mmol) was added. The temperature was allowed to rise to 0°C and valeryl chloride-d_9 (10 g, 83 mmol) was added dropwise. The mixture was stirred at 0°C for 1 h, heated at 80°C for 2 h, cooled and poured into 18% hydrochloric acid. The organic layer was shaken with chloroform (3 × 50 ml) and the combined organic extracts were washed with water and finally distilled to remove the excess of bromobenzene. The product was dissolved in chloroform, and the solution washed with water and dried ($MgSO_4$). After removal of the solvent, the residue was distilled to yield 1-bromo-4-pentanoylbenzene-d_9 (14·43 g, 34% yield).



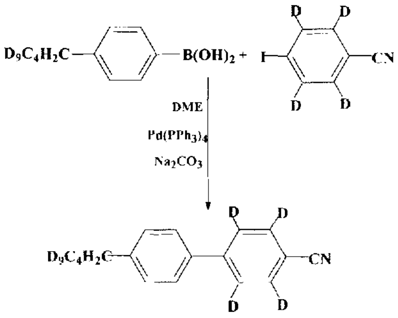
1-Bromo-4-pentylbenzene-d_9 (**III**), $LiAlH_4$ (0·49 g, 0·013 mol) in dry Et_2O (9 ml) was added, under N_2, to a stirred mixture of $AlCl_3$ (3·5 g, 22·61 mmol) in dry Et_2O (9 ml). The mixture was stirred for 20 min after which 1-bromo-4-pentanoylbenzene-d_9 (1 g, 3·8 mmol) in chloroform (18 ml) was added slowly; then the mixture was heated at reflux for 21 h. The excess of reducing agent was destroyed by careful addition of water (7·6 ml) followed by concentrated hydrochloric acid (12·5 ml). The product was extracted into Et_2O (3 × 20 ml) and dried (Na_2SO_4). Removal of the solvent left the crude product which was distilled to yield 1-bromo-4-pentylbenzene-d_9 (0·8 g, 3·0 mmol).



4-Pentylphenylboronic acid-d_9 (**IV**). 1-Bromo-4-pentylbenzene-d_9 (1·5 g, 6·3 mmol) in THF/hexane (12 ml/4 ml) was cooled to −100°C in a liquid nitrogen/ethanol/ether bath. *n*-Butyl lithium (1·6 M, 10 ml) was added slowly, dropwise, keeping the temperature below −95°C. The mixture was stirred at −100°C for 4 h after which trimethyl borate (2 ml, 17·5 mmol) was added cautiously. The cooling bath was removed and the mixture left overnight to reach room temperature. HCl (20 ml, 10%) was added and the mixture stirred for one hour before shaking with ether (2 × 50 ml) and drying the extract ($MgSO_4$). Removal of the solvent left the crude product (1·4 g, 7·0 mmol) which was used in the next stage without purification.



4-iodo-aniline-d_4 (**V**) *and 4-iodo benzonitrile-d_4* (**VI**). The 4-iodo aniline-d_4 (**V**) was synthesized from aniline-d_7 and used to prepare 4-iodo benzonitrile-d_4 (**VI**) as described by Emsley *et al.* [5].



4-n-Pentyl-d_9-4′-cyanobiphenyl-d_4. 4-Pentylboronic acid-d_9 (1 g, 4·76 mmol) in ethanol (3 ml) was added to 4-iodocyanobenzene-d_4 (0·8 g, 3·61 mmol) in DME (10 ml). To this mixture was added sodium carbonate (2 M, 7·78 ml) and palladium tetrakis(triphenylphosphine) (153 mg, 0·0133 mmol). The mixture was heated under reflux under N_2 overnight, left to cool and shaken with 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/acetone 20/3) yielded 5CB-d_{13} (0·5 g, 41% yield).

2.2. *NMR spectra*

The proton–deuterium spectra of pure 5CB at T = 291 K, and of a mixture with the nematogen I35 to 330 K are shown in figures 2 and 3. These were obtained at 200·14 MHz on a Bruker MSL 200 spectrometer. The sample was approximately 10 mm in length in a 4 mm i.d. 5 mm o.d. tube and was held horizontally in a double-tuned, solenoid probe. The decoupler frequency was at the centre of the deuterium spectrum, and was applied as a single pulse for the duration (50 ms) of the acquisition of the proton spectrum. A delay between

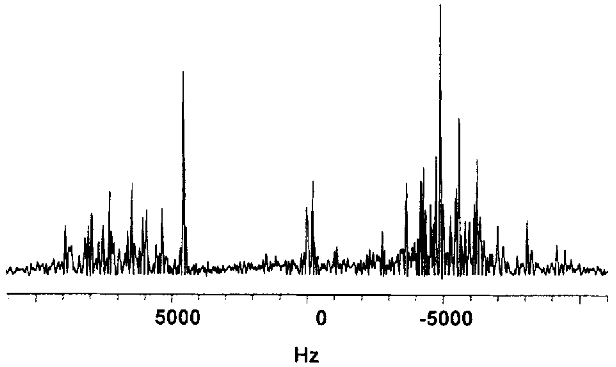


Figure 2. 200 MHz proton–deuterium spectrum of 5CB-d_{13} recorded at 291 K.

pulses of 3 s was used in order to allow the sample to remain at a constant temperature. Analysis of these spectra gave the parameters shown in table 1.

3. Determination of the conformation

For a flexible molecule in the conformation defined by a set of bond rotational angles Φ, and at an orientation in the mesophase specified by the polar angles (β, γ) made by the mesophase director in a frame fixed in the molecule, the observed dipolar couplings are

$$D_{ij} = \int D_{ij}(\Phi) P_{\mathrm{LC}}(\Phi)\,\mathrm{d}\Phi \tag{1}$$

$D_{ij}(\Phi)$ is the dipolar coupling for a rigid conformation with probability density $P_{\mathrm{LC}}(\Phi)$, and is given by

$$D_{ij}(\Phi) = -\gamma_i\gamma_j h[S_{zz}(\Phi)(3\cos^2\theta_{ijz} - 1) + (S_{xx}(\Phi) - S_{yy}(\Phi))(\cos^2\theta_{ijx} - \cos^2\theta_{ijy})]/8\pi^2 r_{ij}^3 \tag{2}$$

The angles $\theta_{ij\alpha}$ are between the αth axis and the inter-proton vector $\mathbf{r}_{ij}$. The conformationally-dependent order parameters, such as $S_{zz}(\Phi)$, are related to a potential of mean torque, $U_{\mathrm{ext}}(\beta, \gamma, \Phi)$ by

$$S_{zz}(\Phi) = Z^{-1} \int \tfrac{1}{2}(3\cos\beta - 1) \times \exp\{-U_{\mathrm{ext}}(\beta, \gamma, \Phi)/RT\} \sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma \tag{3}$$

with

$$Z = \int \exp\{-U_{\mathrm{ext}}(\beta, \gamma, \Phi)/RT\} \sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma \tag{4}$$

The probability distribution $P_{\mathrm{LC}}(\Phi)$ is obtained as

$$P_{\mathrm{LC}}(\Phi) = \frac{\int \exp\{-U(\beta, \gamma, \Phi)/RT\} \sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma}{\int \exp\{-U(\beta, \gamma, \Phi) \sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma\,\mathrm{d}\Phi} \tag{5}$$

which is different from $P_{\mathrm{iso}}(\Phi)$, which is

$$P_{\mathrm{iso}}(\Phi) = \frac{\exp\{-U_{\mathrm{int}}(\Phi)/RT\}}{\int \exp\{-U_{\mathrm{int}}(\Phi)/RT\}\mathrm{d}\Phi} \tag{6}$$

The potential of mean torque has been constructed by the Additive Potential method [6], in which the mean potential of the molecule, $U(\beta, \gamma, \Phi)$ is written as the sum

$$U(\beta, \gamma, \Phi) = U_{\mathrm{ext}}(\beta, \gamma, \Phi) + U_{\mathrm{int}}(\Phi) \tag{7}$$

$U_{\mathrm{int}}(\Phi)$ is the mean potential which is independent of orientation in the mesophase, and which is the only contribution to $U(\beta, \gamma, \Phi)$ which remains in the isotropic phase. The potential of mean torque is written as

$$U_{\mathrm{ext}}(\beta, \gamma, \Phi) = -\varepsilon_{2,0}(\Phi) C_{2,0}(\beta) - 2\,\mathrm{Re}\,\varepsilon_{2,2}(\Phi) C_{2,2}(\beta, \gamma) \tag{8}$$

where the $C_{2,m}(\beta, \gamma)$ are modified spherical harmonics, and the conformation dependence of the interaction coefficients is allowed for by expressing them as sums of

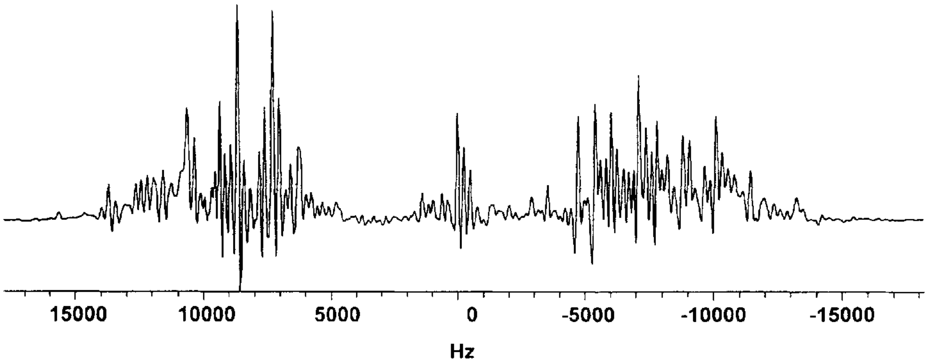
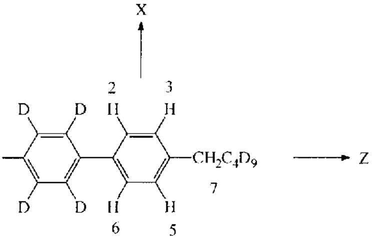


Figure 3. 200 MHz proton–deuterium spectrum of a 50:50 by volume mixture of 5CB-d_{13} in I35 at 330 K.

Table 1. Chemical shifts, ν_i, and dipolar couplings D_{ij}, obtained from the analysis of the ^1H-$\{^2H\}$ 200 MHz spectrum of 5CB-d_{13} pure and as a mixture with I35. The calculated values were obtained by the AP method.



		D_{ij}/Hz			
		Pure		In I35	
ij	J_{ij}/Hz[a]	Observed	Calculated	Observed	Calculated
2, 3	8·0	-3757 ± 4	-3757	-6084 ± 2	-6085
2, 5	0·5	44 ± 4	44	86 ± 2	87
2, 6	2·0	322 ± 4	323	541 ± 4	544
2, 7	0·0	-316 ± 10	-312	-486 ± 6	-480
3, 5	2·0	322 ± 4	323	558 ± 4	561
3, 7	0·0	-861 ± 9	-862	-1371 ± 6	-1372
7, 7	0·0	4849 ± 3	4849	8016 ± 2	8016
$(\nu_7 - \nu_2)$/Hz		432 ± 16		671 ± 8	
$(\nu_7 - \nu_3)$/Hz		491 ± 17		649 ± 8	

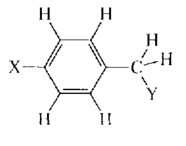
[a] Taken from Brugel, W., 1967, *NMR Spectra and Chemical Structure* (New York: Academic Press), and kept fixed.

contributions $\varepsilon_{2,m}(j)$, from each rigid sub-unit in the molecule:

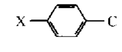
$$\varepsilon_{2,m}(\Phi) = \Sigma_p \Sigma_j \varepsilon_{2,p}(j) D^2_{p,m}(\Omega_j) \tag{9}$$

$D^2_{p,m}(\Omega_j)$ are Wigner functions describing the orientation of the jth sub-unit with respect to a fixed frame of reference.

The dipolar couplings obtained for 5CB-d_{13} are for the fragment



and they depend on local order parameters $S^L_{\alpha\beta}(\phi_{RC})$ [7]. The local order parameters are calculated by constructing local tensor elements $\varepsilon^L_{2,m}(\phi_{RC})$ from contributions from the two sub-units:



which requires $\varepsilon^L_{2,0}$(ring) and $\varepsilon^L_{2,2}$(ring), and C–Y, which is assumed axially-symmetric, and hence requires just $\varepsilon^L_{2,0}$(CY). In principle the C–Y fragment has lower symmetry, and should therefore require extra interaction tensor elements, but in practice their inclusion was found to be unnecessary in order to fit the dipolar couplings.

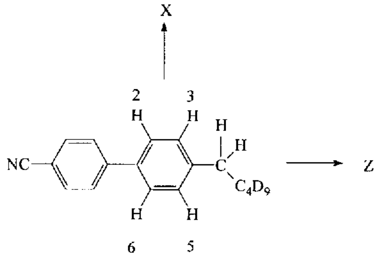
The dipolar couplings within the ring are related to order parameters S^R_{zz} and $S^R_{xx} - S^R_{yy}$, which are averages over all conformations. The four intra-ring couplings were used to obtain these two order parameters and the x and z coordinates of protons 1–4, whilst keeping r_{12} fixed at 2·48 Å, which is a value appropriate for a benzene ring. The values are given in table 2. The geometry of the rest of the fragment was assumed to be the same as in ethylbenzene [8], and the bond lengths and angles are also shown in table 2.

The internal potential, $U_{int}(\phi_{RC})$, is expressed as a cosine series,

$$U_{int}(\phi_{RC}) = V(\phi_{RC}) = \tfrac{1}{2} V_2(1 + \cos 2\phi_{RC}) + V_4 \cos 4\phi_{RC} \tag{10}$$

All seven couplings were then used to explore the form of the rotational potential. Dipolar couplings were calculated from equations (1) to (8) and brought into agreement with those observed by variation of $\varepsilon^R_{2,0}$, $e^R_{2,2}$, $\varepsilon^{CC}_{2,0}$ and V_2 and V_4. It was found, however, that the best agreement was obtained with V_4 as zero. With only a V_2 term in the potential, the number of variable parameters is reduced to four, and this compared with

Table 2. Coordinates of the ring protons which fit the observed dipolar couplings obtained for samples of pure 5CB-d_{13} and the mixture with I35, together with the local order parameters, S^{R}_{zz} and $S^{R}_{xx}-S^{R}_{yy}$. The bond lengths, r_{CH} and r_{CC}, and angles, α, β and HCH, are for the C–CH_2 fragment.



	Pure		In I35	
	x/Å	z/Å	x/Å	z/Å
2 position	2·1626	−1·2400	2·128	−1·2400
3 position	2·1626	1·2400	2·128	1·2400
S^{R}_{zz}	0·477		0·746	
$S^{R}_{xx}-S^{R}_{yy}$	0·044		0·030	

r_{CH}/Å = 1·085; r_{CC}/Å = 1·53; HCH/° = 109·47; α/° = 120; β/° = 120.

the seven dipolar couplings, gives three degrees of freedom in the fitting procedure. The results are shown in table 3.

The value obtained for V_2 depends on the geometry adopted for the CH_2 fragment. Thus, the CH bond length in the CH_2 group was initially fixed at 1·085 Å together with a HCH angle of 109·471°, which are those used in calculations on ethylbenzene [8] and 4-chloroethylbenzene [9]. With this geometry (geometry 1), the potential is found to have a minimum at 90°, and a barrier at 0° of 55 kJ mol^{-1} for the pure sample, and 35 kJ mol^{-1} for the mixture in I35 (which is shown in figure 4). The shape of the potential is the same as that found [8, 9] for ethylbenzene, but the barrier height is much larger. The barrier height is reduced when the HCH angle is increased to 112°, (geometry 2), and it is also reduced if the CH bond length is increased to 1·1 Å (geometry 3). Changing the bond length and angle together did not reduce the potential barrier further by a significant amount.

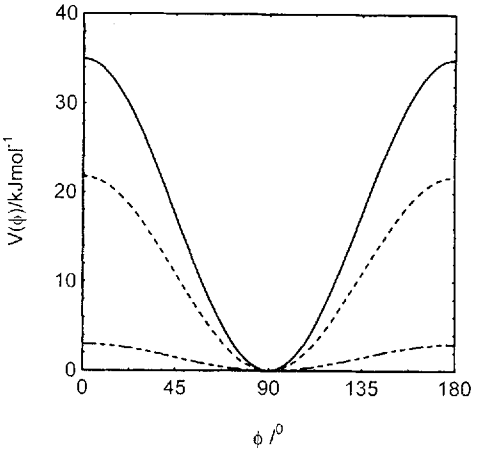


Figure 4. Potential $V(\phi_{RC})$ for rotation about the ring–C bond in 5CB-d_{13}; the upper, full line is for geometry 1, the middle, dashed line is for geometry 2, and the lower, dashed line is for 4-chloroethylbenzene.

The probability distribution, $P_{iso}(\phi_{RC})$, appropriate for the isotropic phase is obtained from equation (6) with the rotational potential $V(\phi_{RC})$, and these are shown in figure 5 for pure 5CB and figure 6 for the mixture with I35, in both cases for the geometries 1 and 2. The probability distributions, $P_{LC}(\phi_{RC})$, are obtained from equation (5) and are also shown in figures 5 and 6. The difference between $P_{iso}(\phi_{RC})$ and $P_{LC}(\phi_{RC})$ depends on the orientational order and is negligible for the less ordered pure 5CB, but significant for the more ordered mixture with I35.

4. Conclusion

The NMR data clearly establish that the potential for rotation about the ring–C bond in 5CB has a minimum at 90°, and a relatively high barrier to rotation past

Table 3. Interaction coefficients, $\varepsilon^{J}_{2,m}$, and rotational potential coefficients, V_2, obtained by fitting observed dipolar couplings for samples of pure 5CB-d_{13}, and a mixture in I35, with those calculated by the AP method.

	Pure			In I35		
	1	2	3	1	2	3
V_2/kJ mol^{-1}	54	30	28	35	25	22
$e^{R}_{2,0}$/kJ mol^{-1}	2·664	2·790	2·724	6·428	8·141	7·222
$\varepsilon^{R}_{2,2}$/kJ mol^{-1}	0·961	1·099	0·993	3·206	4·874	3·723
$\varepsilon^{CC}_{2,0}$/kJ mol^{-1}	1·262	1·555	1·388	3·531	5·492	4·410

1 = geometry 1 given in table 2; 2 = HCH increased to 112° (geometry 2); 3 = r_{CH} increased to 1·1 Å (geometry 3).

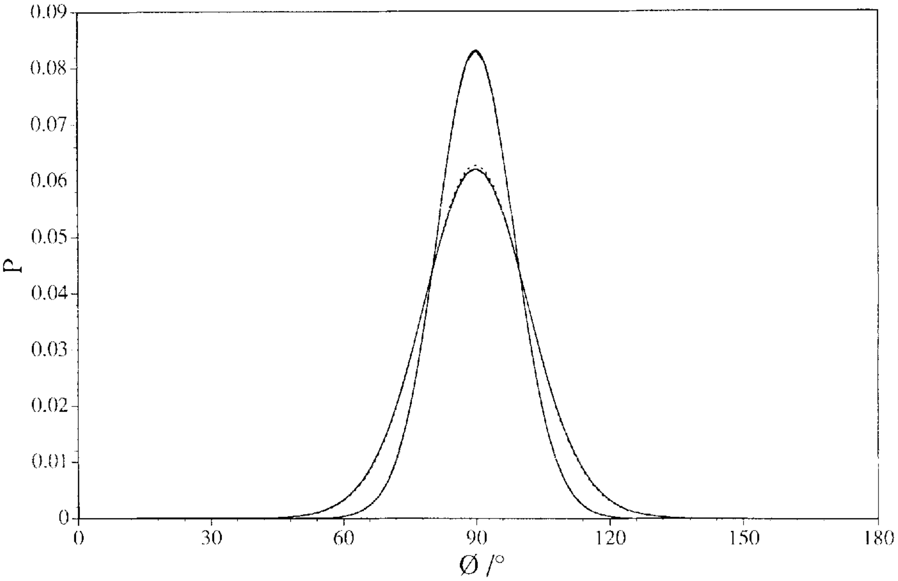


Figure 5. Probability distributions $P_{iso}(\phi_{RC})$ (——) and $P_{LC}(\phi_{RC})$ (------) for rotation about the ring–C bond in pure 5CB. The narrower, more intense curves are for geometry 1 (see table 2), and the broader, less intense lines are for geometry 2 (see table 3).

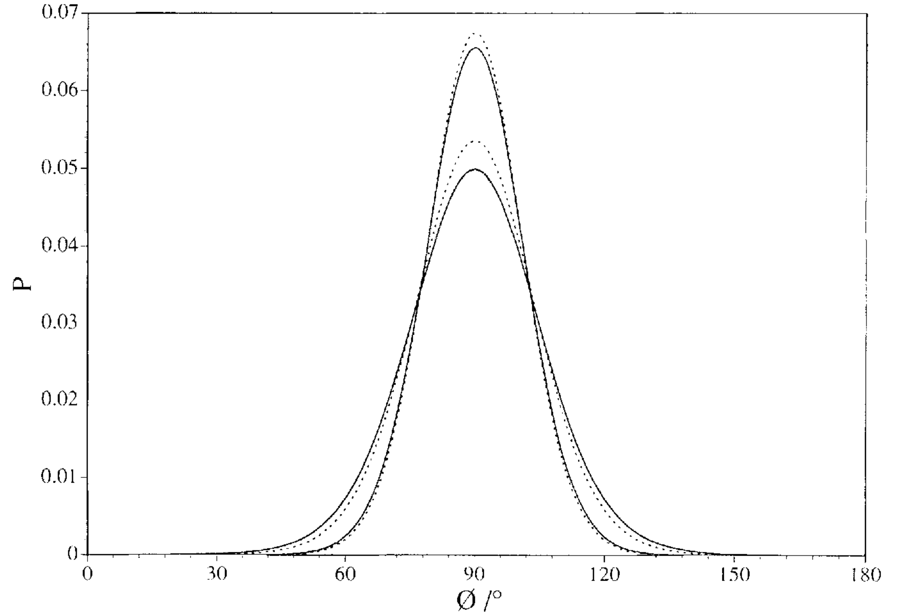


Figure 6. Probability distributions $P_{iso}(\phi_{RC})$ (——) and $P_{LC}(\phi_{RC})$ (------) for rotation about the ring–C bond in a mixture of 5CB with I35. The narrower, more intense curves are for geometry 1 (see table 2), and the broader, less intense lines are for geometry 2 (see table 3).

the planar structure. The barrier height depends on the geometrical assumptions made in the analysis of the data, but it is certainly larger than about 28 kJ mol^{-1} for the pure sample, and 22 kJ mol^{-1} for the mixture in I35. The difference obtained between the barrier height for the pure sample and that for the mixture in I35 could be a consequence of the anti-parallel pairing which seems to occur in pure 5CB, and which would be expected to be diminished in the mixture.

Molecular dynamics simulations on 5CB have been performed by Picken *et al.* [10], and by Komolkin *et al.* [11]. In both cases the potential for rotation about the ring–C bond was expressed as

$$V(\phi_{RC}) = V_6(1 - \cos 6\phi_{RC}) + \Sigma_{i<j}[(A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6}) + q_i q_j/4\pi^2 \varepsilon_0 r_{ij}] \quad (11)$$

Komolkin *et al.* discuss the shape of their potential, and for the values they assume for the Lennard–Jones parameters, A_{ij} and B_{ij}, the partial charges q_i, and the interatomic distances, r_{ij}, together with a value for $V_6 < 0{\cdot}04\,\mathrm{kJ\,mol^{-1}}$, they find that the probability distributions are peaked at $\phi_{RC} = 90°$. Their distributions depend on whether hydrogens are included specifically in the interaction potential, or whether united atoms are used, but in both cases their distributions are flatter than that found here, which reflects their choice of the parameters in equation (11) as being appropriate for a molecule like toluene, for which V_6 is of the order of $0{\cdot}01\,\mathrm{kJ\,mol^{-1}}$. It remains to be established whether replacing the term $V_6(1 - \cos 6\phi_{RC})$ with $V_2(1 + \cos 2\phi_{RC})$ in which V_2 is such as to give a distribution similar to that determined here, would have an appreciable effect on the properties predicted by a molecular dynamics simulation. Note that the use of a $\cos 6\phi_{RC}$ term, which is appropriate for a molecule with the symmetry of toluene, rather than a $\cos 2\phi_{RC}$, which is appropriate for the symmetry of rotation in 5CB, is probably not too important, since the presence of the Lennard–Jones terms produces the correct overall symmetry for $V(\phi_{RC})$. The value of V_2 determined here should not be used in equation (11), since it was derived for the potential, equation (10), which does not include the Lennard–Jones and electrostatic terms of equation (11).

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