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The conformation of phenyl benzoate when dissolved in a nematic liquid crystalline solvent

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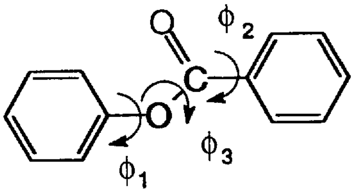
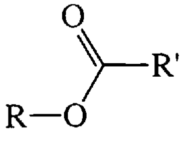
The proton NMR spectrum of a sample of phenyl benzoate dissolved in the nematic liquid crystalline solvent ZLI 1132 has been analysed to yield a set of dipolar couplings. These have been used to obtain the probability distribution for the conformations generated by rotations through the angles ϕ_1, ϕ_2 and ϕ_3



1. Introduction

Phenyl benzoate, whose structure is shown in figure 1, is the simplest example of a structural unit which occurs frequently in both low molar mass and polymeric liquid crystals. The structure of a solid sample has been established by X-ray diffraction, and this has ring 2 rotated about z_2 by $\phi_2 = 9{\cdot}8^\circ$, and ring 1 rotated about z_1 by $\phi_1 = 65{\cdot}1^\circ$, both relative to the OCO plane, so that the normals to the two rings are at 55·3° to one another [1]. A molecular orbital theory calculation [2] on a single, isolated molecule determined the minimum energy structure to have $\phi_1 = 46{\cdot}4^\circ$, $\phi_2 = 0{\cdot}2^\circ$ and $\phi_3 = 0^\circ$. Phenyl benzoate in either gaseous or liquid samples is expected to have rotational motions about z_1 and z_2 which are subject to potentials $V(\phi_1)$ and $V(\phi_2)$ which are sufficiently low that all angles ϕ_1 and ϕ_2 are populated at temperatures >300 K, that is in the temperature ranges of liquid crystalline phases. The evidence concerning rotation about z_3 through ϕ_3 is less certain. Rotation about z_3 will generate conformations in which there is severe steric hindrance, but this could be avoided by co-operatively rotations about ϕ_1 and ϕ_2. A survey of crystal structures of esters [3] found no structures of type 2 ($\phi_3 = 180^\circ$), and most approximate to structure 1 with $\phi_3 = 0^\circ$. However, this does not rule out the possibility of rotational freedom about z_3 in fluid phases. We present here a study of the rotational potentials in phenyl benzoate when dissolved in a nematic liquid crystalline solvent. The proton NMR spectra of such a sample can be analysed to yield dipolar



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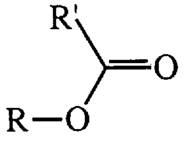

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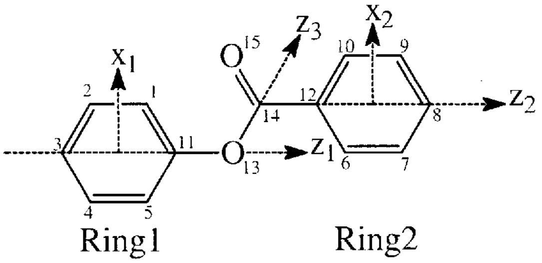

Figure 1. Phenyl benzoate molecule showing axes and atomic labelling.

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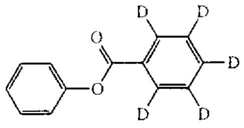
couplings, D_{ij}, which are averages over the motion of the molecule in the phase, and over the bond rotations.

2. Experimental

The 200 MHz proton spectrum of phenyl benzoate as a 10 wt % solution in the nematic mixture ZLI 1132 (Merck Ltd.) is shown in figure 2. The analysis of this complex spectrum proceeded in stages by first analysing the deuterium decoupled proton spectra of samples of the four isotopomers **3**, **4**, **5** and **6** dissolved at approximately the same concentration in ZLI 1132, and whose spectra are shown in figure 3.



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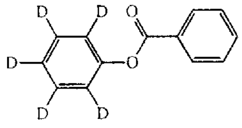

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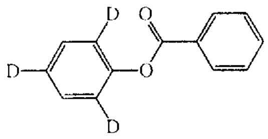

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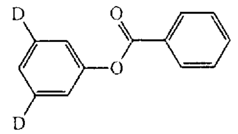

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The analyses gave good estimates for the dipolar couplings, and with these as starting values it was possible to analyse the spectrum shown in figure 2, to give the parameters in table 1

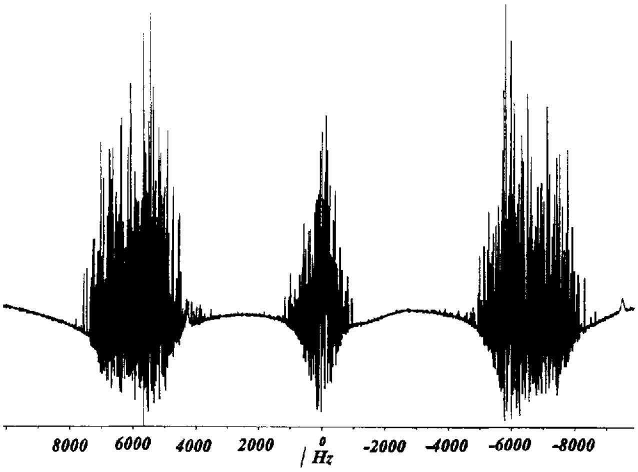
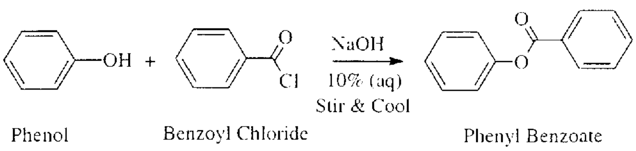


Figure 2. 200 MHz proton NMR spectrum of a sample of phenyl benzoate dissolved (approx 10 wt %) in the nematic solvent ZLI 1132 at 300 K.

2.1. *Synthesis of phenyl benzoates*

The four isotopomers were synthesised from the appropriate deuteriated materials by the following procedure by Vogel [4].



Phenol (0·95 g, 0·0101 mol) and 10 wt % NaOH solutions (15 ml) were stirred together in a round bottom flask fitted with a condenser. Benzoyl chloride (1·42 g, 0·0101 mol) was added and the mixture was stirred and allowed to cool for 30 min. After this time the solid product formed was filtered off under suction and washed with water. The solid was recrystallised using rectified spirit, and refiltered; the colourless crystals produced were dried and weighed.

The isotopomers **3**–**6** were synthesized by the same procedure, but using deuteriated starting materials.

2.2. *Synthesis of fully deuteriated benzoyl chloride*

Thionyl chloride (2·5 g, 0·0210 mol) was added dropwise to deuteriated benzoic acid (1 g, 0·0079 mol) (Aldrich) in a flask, in a water bath at 70°C, fitted with a separating funnel and a condenser. The water bath was removed and the mixture stirred for 2 h under reflux. The excess of thionyl chloride was then distilled off, followed by the deuteriated benzoyl chloride, both under reduced pressure, to yield the product.

2.3. *Synthesis of 2,4,6-d_3-phenol*

A solution of 20 wt % DCl/D_2O (8 ml) was added to phenol (2·01 g, 0·0214 mol) in a round bottom flask and heated under reflux for 48 h at 150°C, whilst stirring. The deuteriated phenol was extracted into diethyl ether. The product was dried overnight with $CaCO_3$, and filtered. The solvent was removed using a rotary evaporator to leave an oily product, which was used without further purification in the synthesis of compound **5**.

2.4. *Synthesis of 2,4,d_2-phenol*

The preparation was similar to the synthesis of 2,4,6-d_3-phenol. However, the reaction was carried out over 72 h, using 20 wt % HCl/H_2O (8 ml) and fully deuteriated phenol (2 g, 0·0202 mol), which was used without further purification to yield compound **6**.

3. Results and discussion

3.1. *Structure of each phenyl ring*

The dipolar couplings between protons within a rigid group, such as each of the phenyl rings, is given by

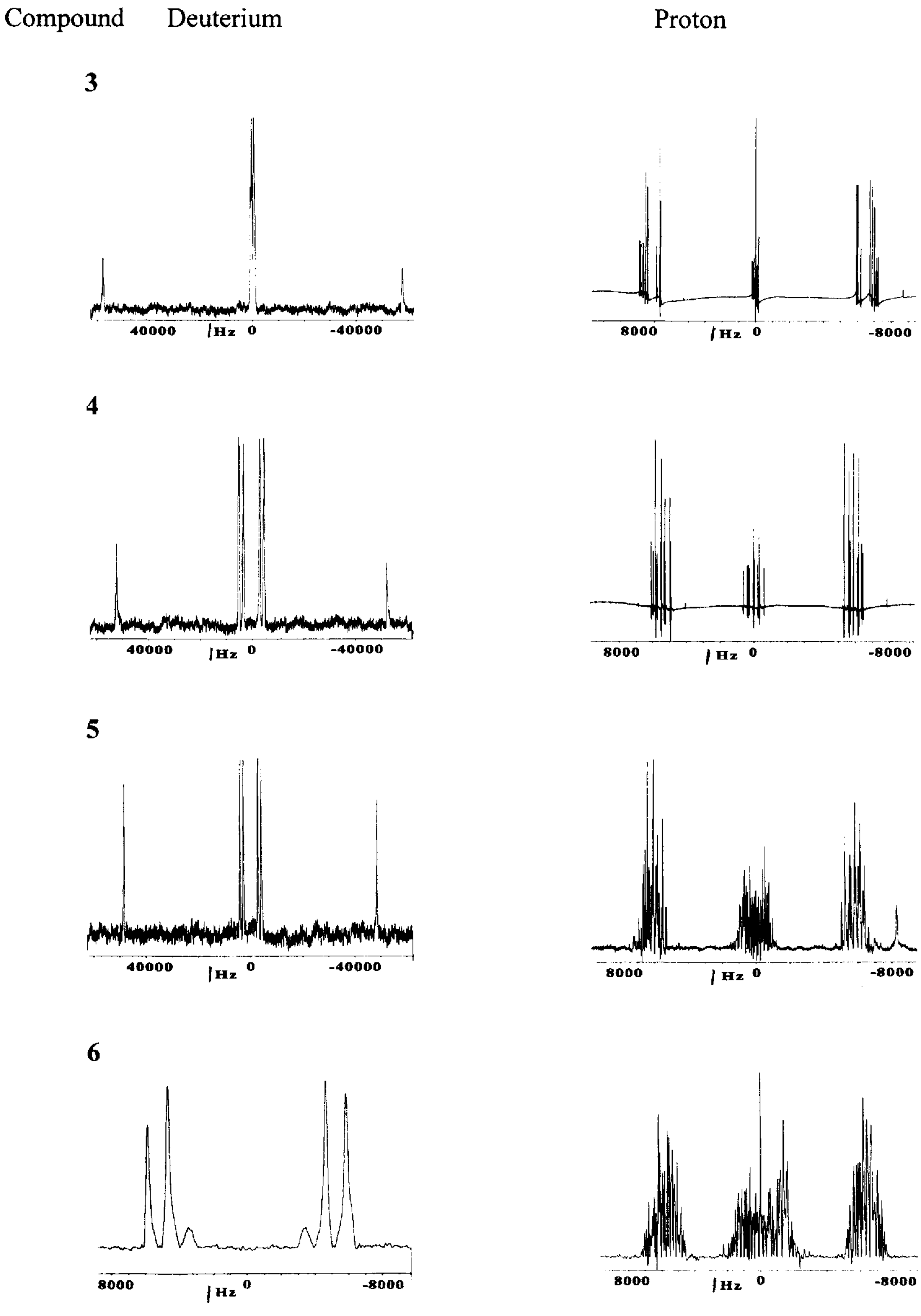


Figure 3. 30·7 MHz deuterium and 200 MHz proton-{deuterium} spectra of the partially deuteriated samples of phenyl benzoate dissolved (approx 10 wt %) in the nematic solvent ZLI 1132 at 300 K.

Table 1. Chemical shifts, δ_i, scalar couplings J_{ij}, and dipolar couplings, D_{ij}, obtained from the analysis of the 200 MHz proton NMR Spectrum, of 10 wt-% phenyl benzoate dissolved in the nematic solvent ZLI 1132.

Couplings

ij	J_{ij}/Hz[a]	D_{ij}/Hz
12	8·0	−3918·3 ± 0·1
13	2·0	−499·6 ± 0·2
14	0·5	13·9 ± 0·1
15	2·0	285·1 ± 0·1
16	0·0	−373·9 ± 0·1
17	0·0	−155·1 ± 0·1
18	0·0	−126·0 ± 0·1
23	6·0	138·9 ± 0·2
24	2·0	285·1 ± 0·1
26	0·0	−156·4 ± 0·1
27	0·0	−73·2 ± 0·1
28	0·0	−60·1 ± 0·1
36	0·0	−126·5 ± 0·1
37	0·0	−59·5 ± 0·1
38	0·0	−48·2 ± 0·1
67	8·0	−4167·3 ± 0·1
68	2·0	−518·3 ± 0·2
69	0·5	42·7 ± 0·1
610	2·0	364·3 ± 0·1
78	6·0	363·3 ± 0·2
79	2·0	364·3 ± 0·1

Chemical shifts

i	δ_i/Hz
1	0·0 ± 0·2
2	−155·0 ± 0·2
3	330·6 ± 0·1
6	−167·3 ± 0·1
7	−176·6 ± 0·2
8	−162·0 ± 0·1

[a] Fixed at values assumed by comparison with similar compounds.

$$\begin{aligned} D_{ij} = {} & -(K_{ij}/r_{ij}^3)[S_{zz}(n)(3\cos^2\theta_{ijz}-1) \\ & + (S_{xx}(n)-S_{yy}(n))(\cos^2\theta_{ijx}-\cos^2\theta_{ijy}) \\ & + 4S_{xy}(n)\cos\theta_{ijx}\cos\theta_{ijy} + 4S_{xz}(n)\cos\theta_{ijx}\cos\theta_{ijz} \\ & + 4S_{yz}(n)\cos\theta_{ijy}\cos\theta_{ijz}] \end{aligned} \qquad (1)$$

where $\theta_{ij\alpha}$ is the angle that the internuclear vector $\mathbf{r}_{ij}$ makes with the αth axis fixed in the rings ($\alpha \equiv x_1, y_1, z_1$ or x_2, y_2, z_2). The $S_{\alpha\beta}(n)$ are local order parameters for axes fixed in the nth rigid group, and

$$K_{ij} = (\mu_0/4\pi)h\gamma_i\gamma_j/8\pi^2 \qquad (2)$$

The proton and deuterium spectra both established that there is 2-fold permutation symmetry of the nuclear spin Hamiltonian. This is a consequence of rapid rotational motion about the z_i molecular axes, and with the assumption that the rings rotate as rigid entities, this implies that the molecular symmetry is also effectively C_{2v} for each phenyl fragment, so that the terms in equation (1) with $S_{\alpha\beta}$, $\alpha \neq \beta$, vanish.

Table 2. Local order parameters $S_{\alpha\beta}(1)$ and $S_{\alpha\beta}(2)$ for the phenyl rings of phenyl benzoate dissolved in the nematic solvent ZLI 1132, together with the relative coordinates (Å) of the protons.

	Ring 1		Ring 2
$S_{xx}(1)$–$S_{yy}(2)$	0·0597	$S_{xx}(2)$–$S_{yy}(2)$	0·1300
$S_{zz}(1)$	0·5490	$S_{zz}(2)$	0·5142
$x_1 = x_5$	2·1636	$x_6 = x_{10}$	2·1689
$y_1 = y_5$	0·0000	$y_6 = y_{10}$	0·0000
$z_1 = z_5$	1·2450	$z_1 = z_{10}$	1·2450
$x_2 = x_4$	2·1564	$x_7 = x_9$	2·1564
$y_2 = y_4$	0·0000	$y_7 = y_9$	0·0000
$z_2 = z_4$	−1·2652	$z_7 = z_9$	−1·2620
x_3	0·0000	x_8	0·0000
y_3	0·0000	y_8	0·0000
z_3	−2·5084	z_8	−2·4966

The relative positions of the protons and the $S_{\alpha\beta}(n)$ were obtained by comparing observed and calculated values of D_{ij} and minimising the error function

$$R = \sum_{i<j} \Delta D_{ij}^2$$

with respect to

$$\Delta D_{ij} = [D_{ij}\ (observed) - D_{ij}\ (calculated)]$$

To do this the protons were initially located by assuming the X-ray structure for the fragment C(11)–O(13)–C(14)–C(12). The rings in the solid state are distorted from regular hexagonal symmetry by small amounts, but in solution these distortions may not be the same. In addition, the averaging of the D_{ij} by rotations about z_1 and z_2 means that the structure is in effect more symmetric. The two phenyl rings were therefore assumed to have hexagonal symmetry with $r_{CC} = 1{\cdot}4$ Å and $r_{CH} = 1{\cdot}09$ Å. For ring 1, for example, the proton coordinates $x_1(= -x_5)$, $z_2(= z_4)$, and z_3 were varied together with $S_{zz}(1)$ and $S_{xx}(1) - S_{yy}(1)$ to minimise R. A similar procedure was adopted for ring 2. The results are shown in table 2.

3.2. *Conformational analysis*

The intra-ring dipolar couplings cannot be calculated with equation (1) since in principle the order parameters for the whole molecule vary with the angles ϕ_1, ϕ_2 and ϕ_3. This dependence will be modelled using the Additive Potential (AP) method [5]. This gives the angular dependent order parameters as, for example:

$$S_{zz}(\{\phi_k\}) = [Q(\{\phi_k\})]^{-1}\int((3\cos^2\beta - 1)/2) \times \exp[-U_{\mathrm{ext}}(\beta,\gamma,\{\phi_k\})/RT]\sin\beta\, d\beta\, d\gamma \qquad (3)$$

with

$$Q(\{\phi_k\}) = \int \exp[-U_{\mathrm{ext}}(\beta,\gamma,\{\phi_k\})/RT]\sin\beta\, d\beta\, d\gamma \qquad (4)$$

The β and γ are the polar angles made by the mesophase director in a molecule-fixed reference frame. The conformationally-dependent potential of mean torque, $U_{\mathrm{ext}}(\beta,\gamma,\{\phi_k\})$ is given by:

$$U_{\mathrm{ext}}(\beta,\gamma,\{\phi_k\}) = -\varepsilon_{2,0}(\{\phi_k\})C_{2,0}(\beta,\gamma) - 2\varepsilon_{2,2}(\{\phi_k\})C_{2,2}(\beta,\gamma) \qquad (5)$$

where the $C_{2,m}(\beta,\gamma)$ are modified spherical harmonics, and the conformation dependence of the coefficients $\varepsilon_{2,m}(\{\phi_k\})$ is constructed by the tensorial addition of contributions, $\varepsilon_{2,p}(j)$, from the j rigid sub-units in the molecule:

$$\varepsilon_{2,m}(\{\phi\}) = \sum_p \varepsilon_{2,p}(j)D^2_{p,m}(\Omega(j)), \qquad (6)$$

where $D^2_{p,m}(\Omega(j))$ is the Wigner matrix relating the orientation of the jth fragment to the reference frame when the molecule is in the conformation $\{\phi_k\}$.

The D_{ij} are obtained as

$$D_{ij} = \int D_{ij}(\{\phi_k\})P_{\mathrm{LC}}(\{\phi_k\})d\{\phi_k\} \qquad (7)$$

The $D_{ij}(\{\phi_k\})$ are calculated from equation (1), whilst $P_{\mathrm{LC}}(\{\phi_k\})$, the probability that the molecule is in a conformation specified by $\{\phi_k\}$, is

$$P_{\mathrm{LC}}(\{\phi_k\}) = Z^{-1}\int \exp[-U(\beta,\gamma,\{\phi_k\})/RT]\sin\beta\, d\beta\, d\gamma \qquad (8)$$

with

$$Z = \int \exp[-U(\beta,\gamma,\{\phi_k\}]/RT]\sin\beta\, d\beta\, d\gamma\, d\{\phi_k\}. \qquad (9)$$

The total mean potential $U(\beta,\gamma,\{\phi_k\})$ is

$$U(\beta,\gamma,\{\phi_k\}) = U_{\mathrm{ext}}(\beta,\gamma,\{\phi_k\}) + U_{\mathrm{int}}(\{\phi_k\}) \qquad (10)$$

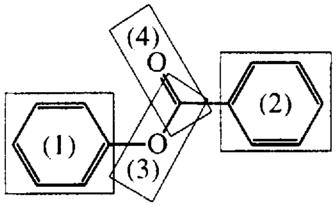
with $U_{\mathrm{int}}(\{\phi_k\})$ being an effective conformational energy. In the case where rotation about each bond is governed by a rotational potential $V(\phi_k)$, that is the motions are not co-operative, then

$$U_{\mathrm{int}}(\{\phi_k\}) = \sum_{k,n} V_{k,n}\cos(n\phi_k) \qquad (11)$$

Note that $P_{\mathrm{LC}}(\{\phi_k\})$ depends on the orientational energy $U_{\mathrm{ext}}(\beta,\gamma,\{\phi_k\})$ as well as on $U_{\mathrm{ext}}(\{\phi_k\})$, and in general will differ from $P_{\mathrm{ISO}}(\{\phi_k\})$, which is defined as

$$P_{\mathrm{ISO}}(\{\phi_k\}) = Q(\{\phi_k\})\exp[-U_{\mathrm{int}}(\{\phi_k\})/kT]/Z \qquad (12)$$

The molecular fragments used to construct $\varepsilon_{2,m}(\{\phi_k\})$ are



Symmetry requires $\varepsilon_{2,0}(1)$ and $\varepsilon_{2,2}(1)$ to be non-zero, but the only non-zero elements for fragments 3 and 4 are $\varepsilon_{2,0}(3)$ and $\varepsilon_{2,0}(4)$. Ring 2 also requires $\varepsilon_{2,0}(2)$ and $\varepsilon_{2,2}(2)$, but in practice it was found that the data cannot distinguish $\varepsilon_{2,0}(1)$ from $\varepsilon_{2,0}(2)$ and $\varepsilon_{2,2}(1)$ from $\varepsilon_{2,2}(2)$, and so these pairs of interaction coefficients were kept equal.

3.3. *The two rotor model*

An attempt was made to fit the D_{ij} to the case with no motion about ϕ_3. The rotation about ϕ_1 and ϕ_2 were subject to potentials of the form

$$V_k = V_{2k}\cos 2\phi_k + V_{4k}\cos 4\phi_k \qquad (13)$$

Varying the V_{2k}, V_{4k} and the $\varepsilon_{2,m}(j)$ values gave the differences ΔD_{ij} shown in table 3. The agreement between calculated and observed couplings is unacceptable, and in particular, ΔD_{38} is large, but D_{38} is virtually independent of the motion about z_1 and z_2. D_{38} could be reduced by bringing the two rings closer together, but reasonable changes in the bond lengths and angles fails to improve the value of R. This indicates that there is an additional motion required to average D_{38}, and the most reasonable candidate is motion about z_3.

3.4. *Evidence for average non-parallel alignment of* z_1 *and* z_2 *from quadrupolar splittings*

A deuterium spectrum of a mixture of **3** and **4** in ZLI 1132 in a ratio of 2:1 was recorded and is shown in figure 4 and the quadrupolar splittings, $\Delta\nu_i$, are given in table 4. The quadrupolar splittings are related to $S_{\mathrm{CD}}(i)$, the orientational order of the C–D(i) bond by

$$\Delta\nu_i = (3/2)S_{\mathrm{CD}}(i)q_{\mathrm{CD}}(i) \qquad (14)$$

The values of the quadrupolar coupling constants, $q_{\mathrm{CD}}(i)$

Table 3. The values of ΔD_{ij} obtained by the AP method with a 2- or 3-rotor model for the internal rotations.

ij	ΔD_{ij}/Hz 2-Rotor model	 3-Rotor model
12	$-1{\cdot}9$	$-0{\cdot}2$
13	$-0{\cdot}3$	$-0{\cdot}0$
14	$-0{\cdot}1$	$-0{\cdot}0$
15	$-0{\cdot}2$	$-0{\cdot}0$
16	$-2{\cdot}2$	$0{\cdot}0$
17	$5{\cdot}7$	$-5{\cdot}7$
18	$15{\cdot}0$	$1{\cdot}7$
23	$-1{\cdot}1$	$-0{\cdot}1$
24	$-0{\cdot}2$	$-0{\cdot}0$
26	$12{\cdot}2$	$4{\cdot}8$
27	$6{\cdot}2$	$-0{\cdot}1$
28	$7{\cdot}9$	$1{\cdot}9$
36	$13{\cdot}2$	$3{\cdot}1$
37	$6{\cdot}3$	$0{\cdot}6$
38	$6{\cdot}3$	$1{\cdot}3$
67	$1{\cdot}1$	$0{\cdot}3$
68	$0{\cdot}0$	$0{\cdot}0$
69	$-0{\cdot}2$	$-0{\cdot}0$
610	$-0{\cdot}5$	$-0{\cdot}0$
78	$-1{\cdot}8$	$-0{\cdot}2$
79	$-0{\cdot}5$	$-0{\cdot}0$

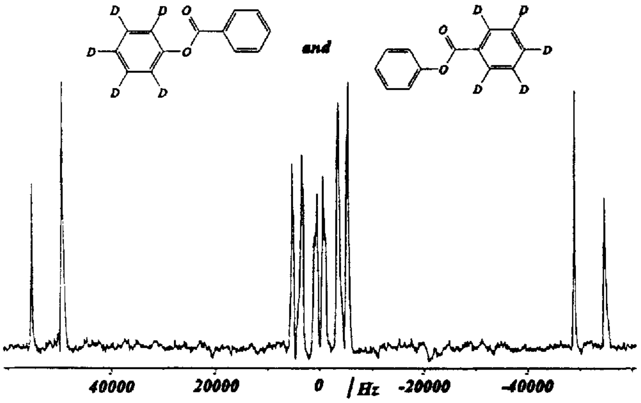


Figure 4. 30·7 MHz deuterium spectrum of a mixture of isotopomers **3** and **4** dissolved in the approximate ratio 2:1 in the nematic solvent ZLI 1132 at 300 K.

Table 4. The magnitude of the quadrupolar splittings, $|\Delta v_i|$, from the mixture of compounds **3** and **4** in ZLI 1132.

i	$\lvert\Delta v_i\rvert$/Hz
1 or 2	6716 ± 150
2 or 1	$10\,218 \pm 36$
3	$109\,889 \pm 56$
6 or 7	1150 ± 21
7 or 6	2108 ± 33
8	$98\,516 \pm 41$

Table 5. Potential Terms, $V_{k,n}$ (kJ mol^{-1}) for rotations about z_1, z_2 and z_3, and values of the fragment interaction parameters, $\varepsilon_{2,0}(j)$ and $\varepsilon_{2,2}(j)$ (kJ mol^{-1}).

Fragment, j	$\varepsilon_{2,0}(j)$	$\varepsilon_{2,2}(j)$
$1=2$	$2{\cdot}98 \pm 0{\cdot}03$	$2{\cdot}77 \pm 0{\cdot}13$
3	$-0{\cdot}85 \pm 0{\cdot}14$	
4	$-0{\cdot}047 \pm 0{\cdot}04$	

Bond, k	V_1	V_2	V_4
1		$1{\cdot}9 \pm 0{\cdot}5$	$2{\cdot}9 \pm 0{\cdot}5$
2		-84	-186
3	$-16{\cdot}3 \pm 1{\cdot}5$		

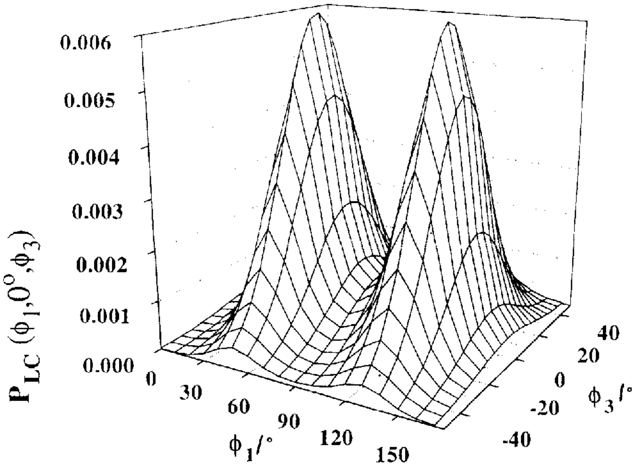


Figure 5. The probability distribution $P_{\mathrm{LC}}(\phi_1, 0°, \phi_3)$ for the bond rotational angles in phenyl benzoate dissolved in the nematic solvent ZLI 1132 at 300 K (fixed ring 2 ($\phi = 0°$)).

can be reasonably assumed to be identical and hence the differences in the splitting arise because $S_{\mathrm{CD}}(3) \neq S_{\mathrm{CD}}(8)$. Combining the evidence from the value of D_{38} with that from the Δv_i suggests that the average separation and orientation of the two rings has to be changed in a way additional to that produced by motion only about z_1 and z_2.

3.5. *The three rotor model*

Rotation about z_3 will be subject to a potential which has a repeat angle of 180°, and so the simplest form for $U_{\mathrm{int}}(\{\phi_k\})$ is:

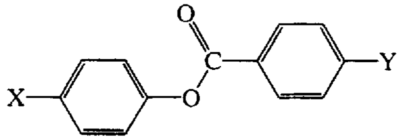
$$U_{\mathrm{int}}(\{\phi_k\}) = V_{12}\cos 2\phi_1 + V_{14}\cos\phi_1 + V_{22}\cos 2\phi_2 + V_{24}\cos 4\phi_2 + V_{31}\cos\phi_3 \qquad (15)$$

Varying all the V_{kn}, and $\varepsilon_{2,0}(1) = \varepsilon_{2,0}(2)$, $\varepsilon_{2,2}(1) = \varepsilon_{2,2}(2)$, $\varepsilon_{2,0}(3)$ and $\varepsilon_{2,0}(4)$ reduced the sum of squares error to 252 Hz with acceptably small ΔD_{ij} values for all the couplings, and gave the parameters shown in table 5.

The very large values for V_{22} and V_{24} are not reliable estimates of the potential function for rotation about z_2 since they give probabilities $P_{LC}(\phi_2)$ everywhere effectively zero except for the positions $\phi_2 = 0°$ or 180°, which correspond to the ring 2 and the C=O bond being coplanar. This is in agreement with the crystal structure of phenyl benzoate, and with the structure of acetophenone [6]. The distribution $P_{LC}(\phi_1, \phi_2, \phi_3)$ can be simplified to $P_{LC}(\phi_1, 0°, \phi_3)$, which is shown in figure 5.

4. Conclusion

The probability distribution obtained for phenyl benzoate in the liquid crystal phase is consistent with the structure determined for a crystalline sample in that the minimum energy form has $\phi_1 = 50°$, $\phi_2 = 0°$, and $\phi_3 = 0°$. However, in the liquid crystalline, and the isotropic phases, of the solution in ZLI 1132 the conformations are distributed over a wide range of values of all three angles. The distribution in ϕ_3 is large, as shown in figure 5, and extends to $\pm 50°$. It is interesting to speculate on whether there will be a wide distribution of conformers with $\phi_3 \neq 0°$ in mesogenic molecules of the type



The presence of bulky substituents X and Y, particularly in polymers in which the ester is part of the backbone, may quench the motion about z_3, but this may not be the case in low molar mass compounds, or when the ester group is part of the side chain in a side chain polymer. To investigate this possibility by the NMR method will be difficult in that the presence of X and Y removes from the data set the valuable coupling D_{38}, whose magnitude was important in revealing the necessity for motion about z_3.

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