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An NMR study of the conformational flexibility of phenyl acetate dissolved in a nematic liquid crystalline solvent

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The ^{1}H, ^{2}H and ^{13}C NMR spectra of phenyl acetate, phenyl acetate–[^{13}CO] and phenyl acetate–[$C^{2}H_3$] dissolved in a nematic liquid crystalline solvent have been analysed to yield dipolar coupling, D_{ij}. These have been interpreted using the additive potential model to provide information on the molecular conformation, resulting in three possible shapes for $V(\phi)$, the potential energy for rotation about the ring-oxygen bond. A comparison with the results of molecular orbital calculations leads to the conclusion that a potential with a minimum at 54·4° ± 0·1° is the most probable.

1. Introduction

Many thermotropic liquid crystal materials contain an ester linkage between an aromatic ring and an alkyl chain and in order to relate the phase properties of the mesophases to molecular structure, it is necessary to determine the conformations adopted by the chain and the conformation of the chain relative to the ring. The possibility of investigating this latter conformational flexibility has been studied using NMR spectroscopy of the model compound phenyl acetate, dissolved in a nematic mesophase. An earlier study of 4-nitrophenyl acetate by Emsley and Lindon [1] using NMR spectroscopy of a sample dissolved in a nematic solvent concluded that the derived dipolar couplings were consistent with the acetoxy group being coplanar with the ring. However, in the solid state the acetoxy group is found to be perpendicular to the phenyl ring in a wide range of similar compounds [2]. In addition, semi-empirical molecular orbital (MO) calculations for a single isolated molecule of phenyl acetate using the AM1 parameterization [3] results in a minimum where the ester group is midway between the planar and perpendicular conformations. Re-examination of the data on 4-nitrophenyl acetate revealed that the set of ^{1}H–^{1}H dipolar coupling constants (D_{ij}) is consistent with both planar and orthogonal structures, and also with an intermediate conformation. In order to resolve the conformational ambiguity found for 4-nitrophenyl acetate, the NMR spectrum of phenyl acetate (I) has been examined. Although the additional hydrogen spin provides more dipolar couplings, a further

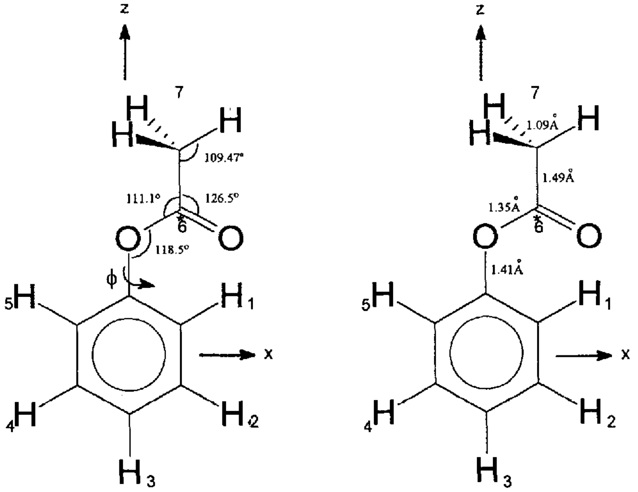

Figure 1. Structure, atomic labelling, axes and geometry assumed for phenyl acetate. (* denotes the ^{13}C position).

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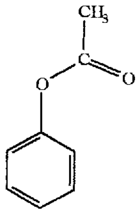
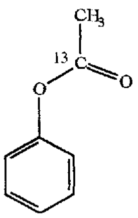
magnetically susceptible nucleus was inserted into the molecule by the synthesis of phenyl acetate with the acetyl carbonyl carbon labelled with ^{13}C (**II**). In addition, to simplify the spectral analysis, phenyl acetate was also synthesized with the acetyl methyl hydrogens replaced by deuterium (**III**). The structure of the molecule, the labelling of the nuclei and the geometrical assumptions are described in figure 1.

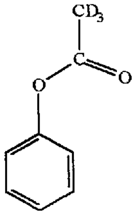
In this study the NMR spectra of **I–III** have been recorded and analysed to yield a set of dipolar couplings which has been interpreted in terms of theoretical models for the conformational distribution.



I



II



III

2. Experimental

Phenyl acetate with a deuteriated methyl group (**III**) was synthesized from phenol and acetyl chloride-d_3 (CD_3COCl), and phenyl acetate with a ^{13}C in the carbonyl group (**II**) was synthesized from phenol and acetyl chloride-^{13}C ($CH_3{}^{13}COCl$) [4].

Solutions of **I–III** were made up to 10 wt % in the liquid crystal ZLI 1167 (Merck Ltd, UK). This solvent does not have any aromatic or carbonyl groups, and so the ^{13}C spectrum of the solute can be obtained without a background signal from the solvent. The 200 MHz ^{1}H NMR spectra of **I** (see figure 2) and **II** (see figure 3 (*a*)), the 200 MHz ^{1}H–{^{2}H} NMR spectrum (see figure 4 (*a*)) and the 30·7 MHz ^{2}H NMR spectrum (see figure 4 (*b*)) of **III**, and the 50·3 MHz ^{13}C NMR spectrum of **II** (see figure 3 (*b*)) were recorded at 300 K using a Bruker MSL 200 spectrometer with samples approximately 10 mm long in 4 mm i.d. and 5 mm o.d. tubes in a double tuned solenoid coil. Details of the acquisition parameters are given in the relevant figure caption. Resolution enhancement of the spectra was achieved using the lorenzian–gaussian method [5].

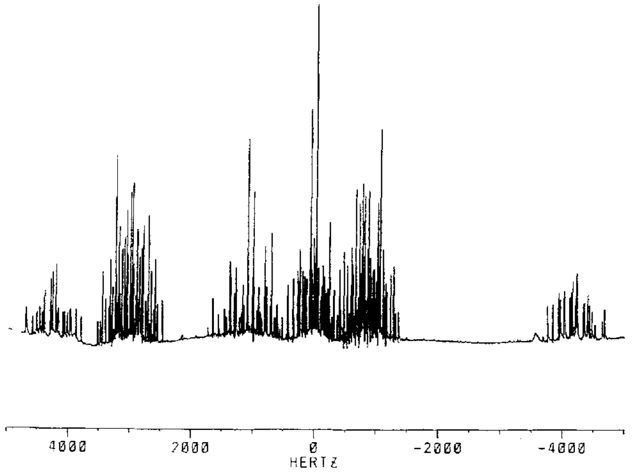


Figure 2. 200 MHz ^{1}H NMR spectrum of **I** dissolved in the nematic solvent ZLI 1167. The spectrum was acquired using 400 scans, with a recycle time of 3 s and a spectral width of 10 640 Hz.

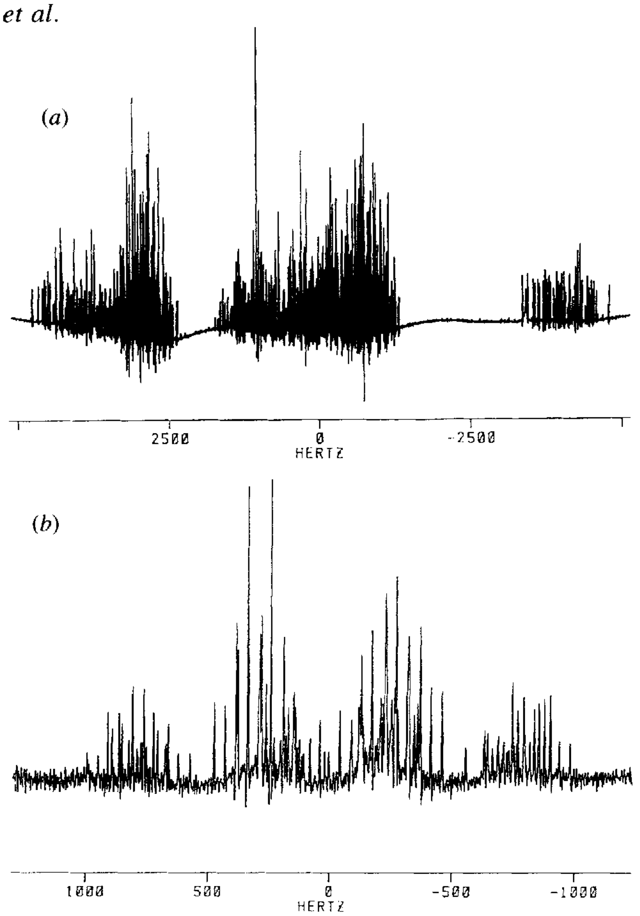


Figure 3. (*a*) 200 MHz ^{1}H NMR spectrum, acquired using 400 scans with a 3 s recycle time and a spectral width of 11 630 Hz, and (*b*) the 50·3 MHz ^{13}C NMR spectrum, acquired using 46 600 scans with a recycle time of 0·6 s and a spectral width of 3520 Hz, of **II** dissolved in the nematic solvent ZLI-1167.

3. Analysis of the NMR spectra

The ^{1}H NMR spectrum of the nine spin system of **II** is too complex to analyse without good prior estimates of the magnitudes of the dipolar couplings. All the dipolar couplings, with the exception of those involving the ^{13}C, can be found by analysis of the NMR spectra of **I** and **III**. In the analysis of all the spectra it has been assumed that the indirect couplings (J_{ij}) are unchanged from their values in the isotropic phase.

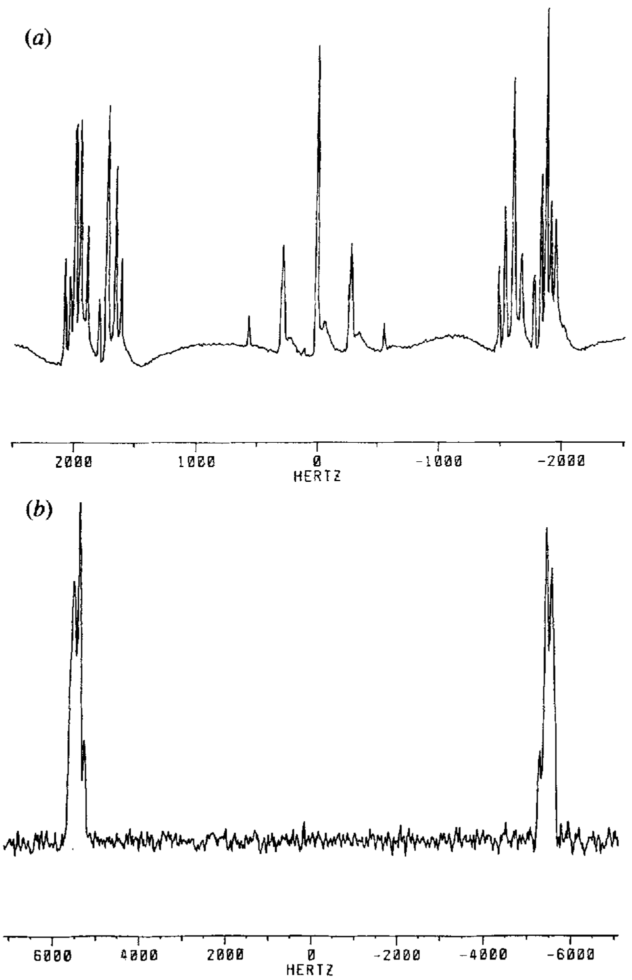


Figure 4. (a) 200 MHz $^{1}H-\{^{2}H\}$ NMR spectrum, acquired using 16 scans with a recycle time of 3 s and a spectral width of 38 460 Hz, and (b) the 30·7 MHz ^{2}H NMR spectrum, acquired using 100 scans, with a recycle time of 1 s and a spectral width of 18 520 Hz, of **III** dissolved in the nematic solvent ZLI 1167.

Analysis of the $^{1}H-\{^{2}H\}$ NMR spectrum of **III** yields the dipolar couplings between the ring protons, and the analysis of the deuterium spectrum yields $\Delta\nu$, the quadrupolar splitting, for the methyl deuterons. The value of $\Delta\nu$ can be directly related to D_{77}, the $^{1}H-^{1}H$ dipolar coupling within the CH_3 group. With these data it is possible to analyse the ^{1}H NMR spectrum of **I** to give a set of couplings which can then be used, along with estimated values for the $^{1}H-^{13}C$ dipolar couplings, as starting parameters in the analysis of the ^{1}H and ^{13}C NMR spectra of **II**. The final derived dipolar couplings are given in table 1. Analysis of the spectra was achieved using the iterative simulation program PANIC (Parameter Adjustment in NMR by Iterative Calculation) on a Bruker Aspect 1000 computer (Bruker, Rheinstetten, Germany).

Table 1. Dipolar couplings and relative chemical shifts obtained from the analysis of the spectra of **I–III** dissolved in the nematic solvent ZLI 1167 and derived by iterative analysis.

ij	D_{ij}/Hz	J_{ij}/Hz
1,2	1209·0 ± 0·2	8·0
1,3	164·7 ± 0·8	2·0
1,4	15·9 ± 0·2	0·0
1,5	− 48·3 ± 0·8	2·0
1,6	68·9 ± 0·3	0·0
1,7	137·4 ± 0·8	0·0
2,3	119·3 ± 0·6	8·0
2,4	− 47·4 ± 0·8	2·0
2,6	26·2 ± 0·3	0·0
2,7	50·2 ± 0·8	0·0
3,6	21·0 ± 0·1	0·0
3,7	39·0 ± 0·2	0·0
6,7	252·5 ± 0·2	7·0
7,7	− 1346·3 ± 0·1	–
i	Chemical shifts/Hz	
1	69·6 ± 0·8	
2	121·4 ± 0·8	
3	40·6 ± 0·2	
7	− 978·0 ± 0·2	
	RMS error = 2·13	

4. Semi-empirical molecular orbital calculations

Calculations were carried out using the MOPAC software [6] on a Silicon Graphics Iris computer. The AM1 Parameterization [3] was used and geometry optimization was carried out on all bonds and angles to achieve the lowest energy structure. In order to search as much of the conformational space as possible, the geometry optimization used a variety of starting points achieved by incrementing the dihedral angle around the Ph–O bond.

5. Results and discussion

5.1. *Structure of the rigid sub-units within phenyl acetate*

It is assumed in the analysis of the conformational distribution that the molecule can be divided into rigid sub-units whose geometry is fixed. To ensure that the errors in the fit depend on the conformation and not on errors in the rigid sub-unit geometry, the positions of the protons in each rigid sub-unit were adjusted to give agreement with the dipolar couplings within each sub-unit. The initial geometry used in the calculations was that obtained from diffraction studies [2]. The geometry of the ring sub-unit, figure 5 (a), was obtained by fixing the distance between H_2 and H_4 at 4·300 Å, this being the value appropriate for a ring with r_{C-C} = 1·4 Å, r_{C-H} = 1·09 Å and all angles fixed at 120°, and allowing the order parameters

S_{xx} and S_{yy} and the coordinates x_1, z_1, z_2 and z_3 to vary to minimize the error function E,

$$E = \{\Sigma_{ij}[D_{ij}(\text{calculated}) - D_{ij}(\text{observed})]^2/M - N\}^{1/2}, \quad (1)$$

While preserving the symmetry of the sub-unit. M is the number of couplings and N is the number of variables involved in the minimization. The order parameters and geometry of a rigid fragment (R), such as a phenyl ring, are related to the dipolar couplings between interacting spins i and j by

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

The ring geometry obtained is slightly distorted from a regular hexagon as might be expected for a mono-substituted benzene ring.

The geometry of the ^{13}C–CH$_3$ sub-unit, figure 5 (b), can be adjusted using the two dipolar couplings D_{67} and D_{77}. There are insufficient experimental data to determine the geometry of this fragment completely, and it is therefore necessary to fix some of the geometrical parameters. The first approach was to choose a local axis system, as shown in figure 5 (b), with a along the assumed threefold symmetry axis ^{13}C–C, in which case the dipolar couplings depend only upon S_{aa} and the geometry. The two dipolar couplings D_{67} and D_{77} can then be used to obtain S_{aa} and one geometrical parameter. Choosing a tetrahedral geometry for the methyl and $r_{\mathrm{CH}} = 1{\cdot}09$ Å, the parameters a_7 and S_{aa} are varied to fit the two couplings (geometry (1)). This increases the length of $r_{\mathrm{C\text{-}C}}$ from 1·490 Å to 1·525 Å, whilst an average bond length for an sp^3–sp^3 C–C bond is 1·50 Å [7]. This bond length is at the upper limit of acceptability as sp^3–sp^3 bonds have lengths of about 1·54 Å. As will be seen, some of the models tested for the potential governing rotation about the Ph–O bond suggest that S_{aa} obtained in this way is too large by about 3 per cent. Reducing S_{aa} by 3 per cent to a fixed value of $-0{\cdot}134$, the two D_{ij} were fitted by varying both a_7 and b_7 because the data are sensitive to the distance between the ^{13}C and H$_7$. It has then to be ascertained what combination of bond lengths and angles would allow the ^{13}C and H$_7$ to have these positions. Assuming, therefore, that $r_{\mathrm{C\text{-}C}}$ retained its original length found by diffraction [2] then the fitting of the couplings resulted in a combination of bond length, $r_{\mathrm{C\text{-}H}}$, of 1·13 Å and an angle H$_7$C$_{10}$H$_8$ of 106° (geometry (2)). Evidence for the planarity of the acetoxy group itself and its internal geometry was obtained from the diffraction studies carried out on similar compounds [2] and studies carried out on the internal geometry of ester groups [8].

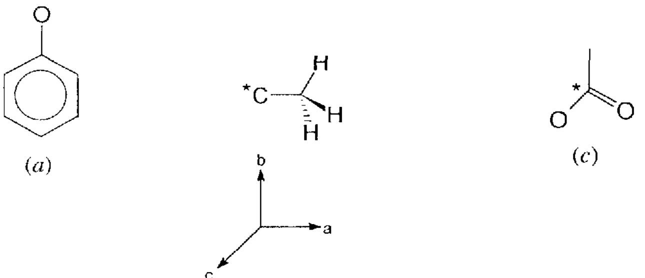


Figure 5. Sub-units of phenyl acetate. (a) the ring–O, (b) the ^{13}C–CH$_3$ and local axes and (c) the acetoxy sub-unit showing the assumed C$_3$ axis.

5.2. *Conformational analysis*

Phenyl acetate is a flexible molecule and it is expected that NMR spectroscopy will observe an average of rapid exchange over all of the populated conformations. The simplest conformational model is that in which the molecule spends virtually all of the time in a discrete set of low energy forms, and initially attempts were made to fit the NMR data to such sets. The O–acetyl group is assumed to be rigid so that only rotations about the ring–O and C–CH$_3$ bonds are considered, the latter being between three equivalent positions. In addition, if the conformations generated by rotation about the ring–O bond are related by symmetry, then the dipolar couplings are given by equation (2) with the addition of terms involving off-diagonal elements $S_{\alpha\beta}$ of the order matrix. There are three such symmetry related sets: (i) interconversion between the two planar conformations, (ii) interconversion between the two positions in which the acetoxy group is perpendicular to the ring and (iii) interconversion between the four conformations in which the acetoxy group has some intermediate fixed angle.

(i) *The planar conformation*: Using the geometries obtained from fitting the individual fragments, the first conformational model to be tested is one in which the acetoxy group jumps between the two conformations in which it is planar with the ring. The parameters varied in the calculation were the order parameters S_{xx}, S_{yy} and S_{xz}. The standard error function, E, for the calculations using both geometries is large, at 5·06 Hz for geometry (1) and 8·80 Hz for geometry (2). Particularly large residuals are found on the couplings D_{16} and D_{56} for both geometries (18·80 Hz and 33·37 Hz respectively). An acceptable fit could not be obtained by reasonable variation of the geometry and it was therefore concluded that phenyl acetate does not exist solely in the planar conformation in the liquid phase.

(ii) *The orthogonal conformation*: S_{xx}, S_{yy} and S_{yz} are varied in this case and again the standard error, E, for the calculations using both geometries is large, at 3·05 Hz and 18·46 Hz, respectively. Large errors are found in couplings D_{17} and D_{57} for both geometries at 6·1 Hz and 68·6 Hz, respectively. Reasonable changes in the geometry fail to give an acceptable fit and it is therefore concluded that phenyl acetate does not exist solely in the orthogonal conformation either.

(iii) *The set of symmetry related conformations with O-acetyl at some intermediate fixed angle*: In this case the dihedral angle ϕ (see figure 1) was also allowed to vary along with the order parameters S_{xx}, S_{yy}, S_{xy}, S_{xz} and S_{yz}. The standard error on the calculation is reasonable for both ^{13}C–CH_3 geometries with a minimum error of 0·45 Hz at a $\phi = 68°$ for geometry (1), and a minimum error of 0·93 Hz at $\phi = 44°$ for geometry (2). Much of the error is concentrated in the couplings D_{26}, D_{36} and D_{46}. It is therefore possible that phenyl acetate exists solely in a set of symmetry related conformations with ϕ in the range 44–68°.

5.3. *Attempt to fit the NMR data to a conformational distribution*

It is possible that the potential for rotation about the ring–O bond is sufficiently low that the conformational probability is distributed smoothly over the entire range of ϕ.

The dipolar couplings for a system of conformers existing at discrete angles ϕ on a potential surface, which have probabilities p_ϕ, are given by

$$D_{ij} = -\gamma_i\gamma_j h \Sigma_\phi \mathrm{p}_\phi \Sigma_{\alpha,\beta} S^{\phi}_{\alpha\beta} \cos\theta^{\phi}_{ij\alpha} \cos\theta^{\phi}_{ij\beta}/4\pi^2 r^3_{ij\phi}, \quad (3)$$

where $S^{\phi}_{\alpha\beta}$ is an element of an ordering matrix for the ϕth conformation. To use equation (3) in order to test models of the conformational distribution, it is necessary to formulate a model for how the order parameters $S^{\phi}_{\alpha\beta}$ depend on ϕ. The model used here is known as the additive potential (AP) method [9] in which the order parameters are given by

$$S^{\phi}_{zz} = Q_\phi^{-1} \int C_{2,0}(\omega) \exp\{-U_{\mathrm{ext}}(\omega,\phi)/RT\}\, d\omega \quad (4)$$

and

$$S^{\phi}_{xx} - S^{\phi}_{yy} = Q_\phi^{-1} \sqrt{6} \int C_{2,2}(\omega) \exp\{-U_{\mathrm{ext}}(\omega,\phi)/RT\}\, d\omega. \quad (5)$$

Here, ω is the set of angles which defines the orientation of the mesophase director in the molecular frame, and $C_{2,m}(\omega)$ is a modified spherical harmonies. Q_ϕ is

$$Q_\phi = \int \exp\{-U_{\mathrm{ext}}(\phi,\omega)/RT)\}\, d\omega. \quad (6)$$

The conformationally dependent potential of mean torque, $U_{\mathrm{ext}}(\omega,\phi)$ is

$$U_{\mathrm{ext}}(\omega,\phi) = -\varepsilon^{\phi}_{2,0} C_{2,0}(\omega) - 2\varepsilon^{\phi}_{2,2} C_{2,2}(\omega), \quad (7)$$

in which the interaction parameters are

$$\varepsilon^{\phi}_{2,m} = \Sigma_j \Sigma_p \varepsilon^{j}_{2,p} D^2_{p,m}(\Omega_{j\phi}). \quad (8)$$

The $\varepsilon^{j}_{2,p}$ are interaction parameters for the jth rigid molecular sub-unit, and $D^2_{p,m}(\Omega_{j\phi})$ is the second rank Wigner rotation matrix describing the orientation of the jth sub-unit in a molecular reference frame. The probabilities, p_ϕ, depend upon $U_{\mathrm{ext}}(\phi,\omega)$ and upon the potential $V(\phi)$ for rotation about the ring–O bond

$$p_\phi = Z^{-1} \exp[-V(\phi)/RT] \int \exp[-U_{\mathrm{ext}}(\omega,\phi)/RT]\, d\omega, \quad (9)$$

where

$$V(\phi) = V_0 + V_2 \cos 2\phi + V_4(1 + \cos 4\phi), \quad (10)$$

$$Z = \Sigma_\phi \exp[-V(\phi)/RT] \int \exp[-U_{\mathrm{ext}}(\phi,\omega)/RT]\, d\omega. \quad (11)$$

Equation (10) contains the minimum number of terms needed to represent a potential which has the correct symmetry, and which can have either a minimum only at 0° (V_4 zero, V_2 negative), at 90° (V_4 zero, V_2 positive) or at $0° < \phi < 90°$ (V_4 non-zero). The V_0 term ensures that the minimum value of $V(\phi)$ is zero and is not used as an adjustable parameter in the fitting procedure.

There are two rigid sub-units in phenyl acetate. The phenyl–O group has C_{2v} symmetry and xyz are principal axes for the ε^{R} tensor so that only $\varepsilon^{R}_{2,0}$ and $\varepsilon^{R}_{2,2}$ are necessary for this group. The O–C(O)–CH_3 group has only C_s symmetry; hence only one principal axis of ε^{j}, the plane normal, is known. In principle three components are necessary to characterize the interaction tensor of the acetoxy group, and this can be achieved by using cylindrically symmetric tensor components $\varepsilon^{O\text{–}C}_{2,0}$, $\varepsilon^{C=O}_{2,0}$ and $\varepsilon^{C\text{–}C}_{2,0}$ acting along the three bonds. Also, since ^{13}C–CH_3 is close to being parallel to the rotation axis, z, then the total interaction tensor for each conformation is sensitive to $\varepsilon^{R}_{2,0} + \varepsilon^{C\text{–}C}_{2,0}$ rather that their individual values. In order to test models, the value of E in equation (1) is minimized by varying the ε values, V_2 and V_4, using the D_{ij} given in table 1 as observed data. The resulting parameters from the minimizations are given in table 2.

As mentioned previously, the dipolar couplings between the ring protons and the ^{13}C are not affected by the geometry and orientation of the methyl group or by the internal rotations within the acetoxy group. Minimization of E, excluding all D_{i7} and assuming a threefold rotation symmetry for the acetoxy group as shown in figure 5 (c), making $\varepsilon^{C\text{–}O}_{2,0}$, $\varepsilon^{C=O}_{2,0}$ and $\varepsilon^{C\text{–}C}_{2,0}$ equal, gave a potential with a deep minimum in energy at 90° and a shallower minimum at 0°, see table 2, row (i). If the V_2 term is excluded, E is slightly larger with very deep narrow energy minima at 45° and 135°, see table 2, row (ii), and consequently the probability is shared entirely between these two positions. When V_4 is excluded, the single energy minimum is very shallow and at 90° with an equally small value for E, see table 2, row (iii). These calculations show that this data set cannot discriminate between a potential with minimum at

Table 2. The rms error, E (Hz), potential coefficients V_0, V_2 and V_4 (kJ mol^{-1}) and the interaction parameters $\varepsilon^{j}_{2,m}$ (kJ mol^{-1}) obtained by optimizing the agreement between observed and calculated dipolar couplings.

No.	E	V_0	V_2	V_4	$\varepsilon^{R}_{2,0}+\varepsilon^{C\text{–}C}_{2,0}$	$\varepsilon^{R}_{2,2}$	$\varepsilon^{C\text{–}O}_{2,0}$	$\varepsilon^{C=O}_{2,0}$	$\phi_{\min}$°
i	0·13	78·79	1·59	− 38·60	− 0·50	1·24	2·92	2·92	90, 0
ii	0·52	− 0·13	0·0	580·64	− 2·25	− 0·91	− 0·20	− 0·20	45, 135
iii	0·16	7·90	7·90	0·0	− 0·89	4·71	3·02	3·02	90
iv	0·47	9·38	0·02	− 4·68	− 1·04	− 1·21	4·53	4·53	0, 90
v	0·47	8·60	− 0·42	− 4·09	− 1·39	− 2·11	9·56	− 2·30	0, 90
vi	0·84	1·14	7·16	5·70	− 2·43	− 1·51	− 1·51	0·74	54·4
vii	0·85	3·17	3·17	0·0	− 2·23	− 1·19	− 0·30	− 0·27	90

0° and 90° and a maximum close to 45°, and one with a minimum at 90° and maximum at 0°. In fact, the residuals obtained for the second shape of $V(\phi)$, that with deep minima at 45° and 135°, are also sufficiently small to be acceptable, bearing in mind that geometry relaxation on rotation could further reduce the residuals. It would appear, therefore, that no firm conclusions on the shape of $V(\phi)$ can be drawn from these results. However, during these minimizations it was noted that the D_{ij} that were calculated using the final minimized parameters consistently showed large errors with respect to the observed values. The geometry and orientation of the C–CH$_3$ bond was therefore investigated further to give geometry (2).

Calculations which include the full set of dipolar couplings were then made with the two geometries. With geometry (1), the best fit to the data gives minima in potential at 0° and 90°, Table 2 row (iv), and this conclusion is not changed by relaxing the assumption that $\varepsilon^{C\text{–}O}_{2,0}=\varepsilon^{C=O}_{2,0}=\varepsilon^{C\text{–}C}_{2,0}$, see table 2 row (v), or by introducing a biaxial term $\varepsilon^{C=O}_{2,2}$ for the C=O group. The best fit potential $V(\phi)$ for geometry (1), corresponding to the parameters in row (iv) of table 2 is shown in figure 6, curve (*a*).

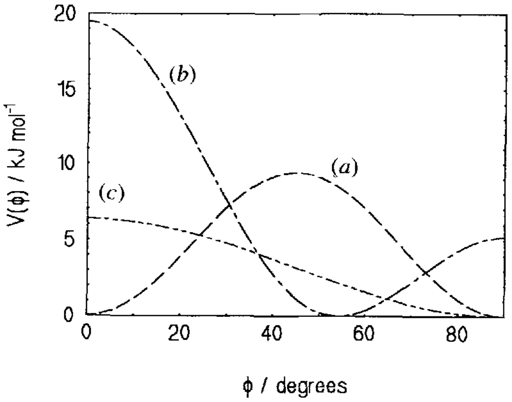


Figure 6. The rotational potential $V(\phi)$ for the best fit for (*a*) geometry (1), row (iv) in table 2, (*b*) geometry (2), row (vi) in table 2 and (*c*) geometry (2) row (vii) in table 2.

The semi-empirical molecular orbital calculations using the AM1 parameterization locate the minimum energy to be at 47·7° and although we already had a good fit, it was therefore decided to explore further. Attempts were made in which V_4 only *or* V_2 similar to V_4 were used to get a minimum in the potential near 45°, but these failed. Using V_2 only gives large residuals with the minimum at 90°.

With the geometry (2) for the ^{13}C–CH$_3$ group, the best fits to the data are quite different. Thus, now the error is reduced by allowing $\varepsilon^{OC}_{2,0}$ and $\varepsilon^{C=O}_{2,0}$ to vary independently, and two potentials give virtually identical fits to the data. In one V_2 and V_4 are similar, see table 2, row (vi), and the minimum in the potential is at 54·4°. In the other, V_4 is zero and V_2 is such that the single minimum in the potential is at 90°, see table 2, row (vii). The potential $V(\phi)$ corresponding to both these results are shown in figure 6, curves (*b*) and (*c*), respectively.

6. Conclusions

The NMR data clearly show that the minimum energy conformation is non-planar. The precise functional form of $V(\phi)$ cannot, however, be established from the NMR data alone. Thus, although a conformational distribution consisting of only four, symmetry-related forms corresponding to ϕ of 68° or 44°, depending on the geometry fixed for the C–CH$_3$ group, give good fits to the NMR data, it is unreasonable to suppose that the potential is a delta function in ϕ, as implied by this solution. When $V(\phi)$ is assumed to be a smooth function, then three forms for $V(\phi)$ fit the data, depending on the geometry chosen for the C–CH$_3$ fragment. That with the minima at 0° and 90° (based on geometry (1) for the C–CH$_3$) we reject primarily because it has a large maximum at 45°. This is unreasonable since the main contributions to $V(\phi)$ will be from π-electron delocalization, with a maximum at 90°, and steric repulsion, whose maximum is at 0°. Of the two remaining solutions, both with geometry (2) for the C–CH$_3$ fragment, the more probable is that with a minimum at 54·4°, since this agrees in form with that determined by the molecular orbital calculations. Such agreement implies that the conformational distribution is essentially unchanged by the environment of the molecule. Note that the probability distribution does depend on the phase (equation (9)), but in the present case this effect is small.

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