The Conformation of α,α,α,-Trifluoroanisoles Investigated *via* the N.M.R. Spectra of Liquid Crystalline Solutions

Mark Barnes, James W. Emsley, Timothy J. Horne, and Gavin M. Warnes
Department of Chemistry, The University of Southampton, Southampton SO9 5NH
Giorgio Celebre and Marcello Longeri
Dipartimento di Chimica, Universita della Calabria, 87030 Arcavacata di Rende(Cs), Italy

The proton and fluorine n.m.r. spectra of samples of 4-fluoro- and 4-iodo-α,α,α- trifluoromethoxybenzene dissolved in the nematic liquid crystal solvent I35 have been obtained. Analysis of these spectra yields a set of dipolar coupling constants whose values are used to investigate the form of $V(\varphi)$, the potential governing rotation about the phenyl O-bond. $V(\varphi)$ is found to be very different from the form found for the corresponding potential in methoxybenzene in that the minimum occurs when the $O-CF_3$ bond is in the plane orthogonal to the phenyl ring ($\varphi = 90°$). The data cannot, however, distinguish between a potential of the form $V_0 + V_2 \cos 2\varphi$, and one containing a substantial V_4 term, that is $V(\varphi) = V_0 + V_2 \cos 2\varphi + V_4 \cos 4\varphi$.

The structure of methoxybenzene (anisole), whose molecular structure is shown in Figure 1, has been investigated by many experimental methods,[1-3] and also by *ab initio* molecular orbital calculations.[4-6] There is agreement that the structure with the lowest energy has the $O-CH_3$ bond in the plane of the benzene ring, so that the potential energy $V(\varphi)$, where φ is the angle of rotation of the $O-CH_3$ bond out of the phenyl plane, has the approximate shape shown in Figure 2. The α,α,α-trifluoro derivative has been known for some time,[7,8] but there are no reported determinations of the structure or conformational preference of this trifluorinated anisole, or of any of its derivatives. We present here such an investigation on the 4-fluoro and 4-iodo derivatives by a method developed recently[9] which utilizes the relationship between the structure and conformation of a molecule and the dipolar couplings, D_{ij}, which can be obtained by analysing the n.m.r. spectra of a sample dissolved in a liquid crystalline solvent. We have chosen to study these two *para* substituted derivatives rather than the unsubstituted trifluoroanisole because of the simplification produced in their proton spectra by eliminating a proton. The method used to investigate the form of $V(\varphi)$ has been described in detail by Celebre, Longeri and Emsley,[9] and its reliability tested on several molecules. The present study is, however, the first example of applying this method to a molecule whose conformational preference was previously completely unknown.

Experimental

The samples of 4-iodo- and 4-fluoro-α,α,α-trifluoroanisole were obtained from the Maybridge Chemical Co., Ltd, and approximately 20% w/w solutions were prepared in the liquid crystal solvent 1-(4-*trans*-propylcyclohexyl)2-(2'-fluoro-4'-pentyl-4-biphenyl)ethane (I35), which was obtained from B.D.H. Chemicals Ltd. The 360 MHz proton and 338 MHz fluorine spectra were obtained at 300 K with a $^1H/^{19}F$ double tuned probe, so that the spectra of both nuclei could be obtained without removing the sample from the magnet. The spectrometer used was a Bruker AM 360, and the spectra obtained are shown in Figures 3 and 4; their analysis yielded the parameters given in Tables 1 and 2.

Results and Discussion

The dipolar couplings between nuclei in the phenyl ring were used to obtain the positions of these nuclei and the order
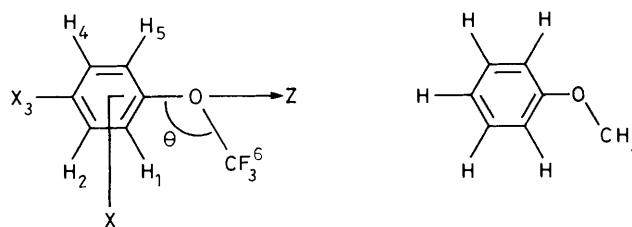

Figure 1. Structures of methoxybenzene (right) and the trifluoromethoxy derivatives studied (left), showing the atomic labelling and location of axes referred to in the text.
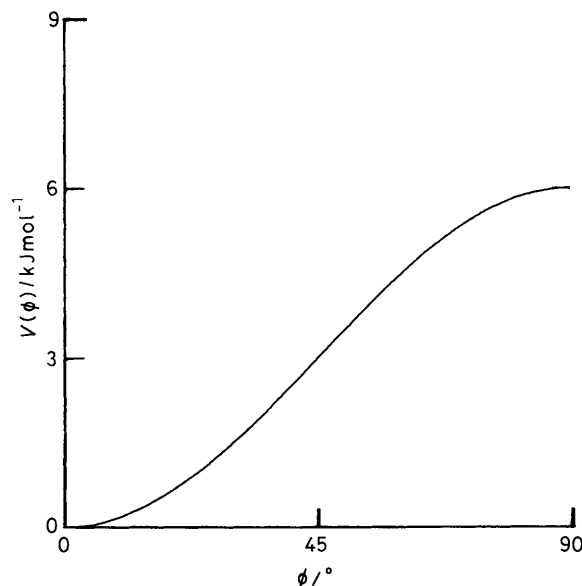

Figure 2. Shape of the potential $V(\varphi)$ governing rotation about the phenyl O-bond in methoxybenzene; φ is the angle of rotation out of the plane of the benzene ring.

parameters S^R_{zz} and $S^R_{xx} - S^R_{yy}$, shown in Table 3, which are averages over both internal and external modes of motion. The positions of the ring protons and the fluorine remain fixed at these optimized values in all subsequent calculations. The CF_3
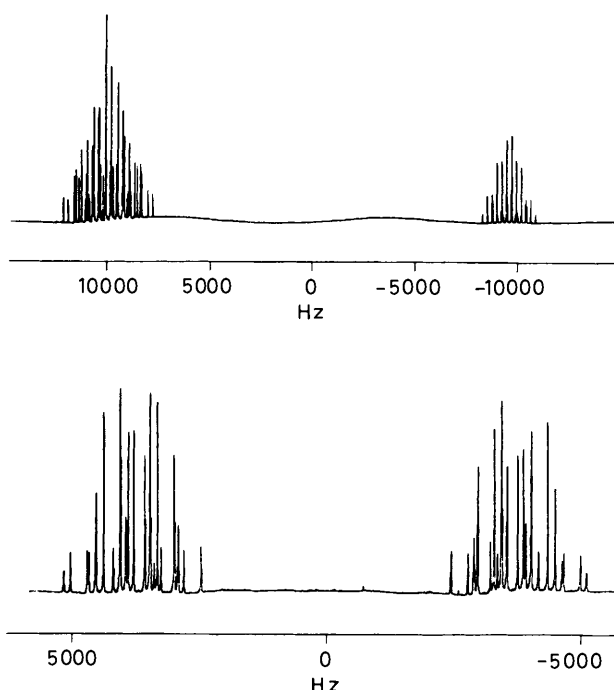
Figure 3. 360 MHz proton and 338 MHz fluorine spectra of a sample of 4-fluoro-α,α,α-trifluoromethoxybenzene dissolved in the nematogen I35.

Table 1. Spectral parameters obtained from the analysis of the proton and fluorine spectra of a sample of 4-fluoro-α,α,α-trifluoromethoxybenzene dissolved in the nematic solvent I35. The values of D_{ij}(calc.) are those calculated with the potential $V(\varphi) = V_2(1 + \cos 2\varphi)$.

i,j	D_{ij}/Hz	J_{ij}/Hz[a]	D_{ij}(calc.)/Hz
1,2	$-2\,488.20 \pm 0.05$	9.10 ± 0.03	$-2\,488.1$
1,3	-284.9 ± 0.1	4.40 ± 0.04	-286.6
1,4	-5.4 ± 0.05	0.20 ± 0.03	-5.7
1,5	160.5 ± 0.2	2.97 ± 0.05	161.1
1,6	-414.6 ± 0.1	1.02 ± 0.03	-414.4
2,3	-194.1 ± 0.1	7.93 ± 0.04	-193.9
2,4	159.7 ± 0.2	3.14 ± 0.04	160.1
2,6	-167.9 ± 0.1	0.0	-168.4
3,6	-118.92 ± 0.03	0.0	-117.5
6,6	294.00 ± 0.02	0.0	294.1

chemical shifts/Hz

$v_2 - v_1$	35.2 ± 0.4
$v_6 - v_3$	$19\,516.8 \pm 0.2$

[a] Obtained by analysing the proton spectrum of the neat liquid and kept fixed in the iteration.

group is assumed to have C_{3v} symmetry about the $O-CF_3$ bond and to rotate between three equivalent conformations, that is, the barrier to this rotation is assumed to be large.

It is possible that there is a contribution to the total anisotropic spin-spin coupling from J^{aniso}_{FF}, the anisotropic part of the spin-spin coupling which is transmitted through the electrons. The magnitudes of J^{aniso}_{FF} have been obtained for a small number of molecules[10] and on this evidence it is probable that J^{aniso}_{36} is neglible, but J^{aniso}_{66} could be as large as 30% of D_{66}. This is the largest estimate for the magnitude of J^{aniso}_{66} in a CF_3 group, and more probably it is no more than a few percent of D_{66}, and in the absence of any experimental or theoretical estimates of its magnitude in OCF_3 compounds, we shall assume that is also of negligible magnitude.

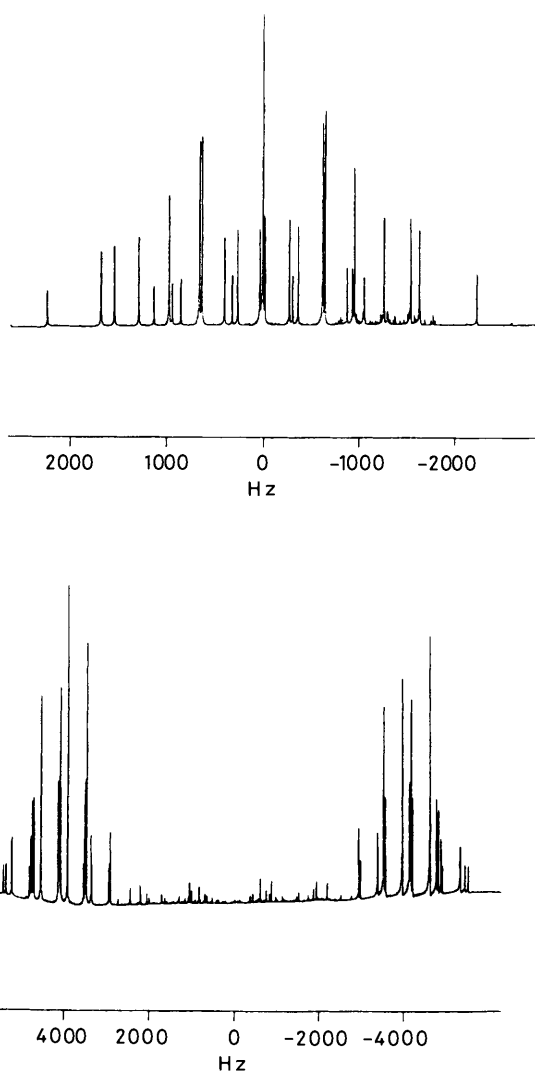If $V(\varphi)$ is such that only the planar forms are populated

Figure 4. 360 MHz proton and 338 MHz fluorine spectra of 4-iodo-α,α,α-trifluoromethoxybenzene dissolved in the nematogen I35.

Table 2. Spectral parameters obtained from the analysis of proton and fluorine spectra of a sample of 4-iodo-α,α,α-trifluoromethoxybenzene dissolved in the nematic solvent I35. The dipolar couplings D_{ij}(calc.) were calculated with the potential $V(\varphi) = V_2(1 + \cos 2\varphi)$.

i,j	D_{ij}/Hz	J_{ij}/Hz[a]	D_{ij}(calc.)/Hz
1,2	$-2\,760.6 \pm 0.1$	8.8 ± 0.1	$-2\,760.6$
1,4	12.2 ± 0.1	0.15 ± 0.2	12.1
1,5	204.6 ± 0.5	2.5 ± 0.1	204.4
1,6	-462.2 ± 0.2	1.00 ± 0.04	-462.5
2,4	201.5 ± 0.5	2.4 ± 0.2	201.2
2,6	-176.1 ± 0.3	0.0	-175.4

chemical shifts/Hz

$v_2 - v_1$	124.3 ± 1.0

[a] Obtained from the analysis of the proton spectrum of a sample of the neat liquid and kept fixed in the iteration.

appreciably, then the dipolar couplings between the CF_3 fluorines and the protons and fluorine in the aromatic fragment depend on S^R_{zz}, $S^R_{xx} - S^R_{yy}$, and on S^R_{xz}, as does the coupling within the CF_3 group. There is also a dependence on geometry, and we assume the following lengths and angles:

Table 3. Co-ordinates of the protons and the ring fluorine, and the order parameters of the phenyl ring, S^R_{zz} and $S^R_{xx} - S^R_{yy}$, for 4-iodo and 4-fluoro-α,α,α-trifluoromethoxybenzenes dissolved in the nematic solvent I35.

| | Co-ordinates/Å | | | |
| | 4-iodo | | 4-fluoro | |
Position	x	z	x	z
1	2.140	2.640	2.112	2.640
2	2.152	0.160	2.117	0.160
3	—	—	0.0	−1.261

| order parameters | | |
	4-iodo	4-fluoro
S^R_{zz}	0.351	0.316
$S^R_{xx} - S^R_{yy}$	0.083	0.114

$$r_{CO} = 1.36 \text{ Å } [1]$$

$$r_{OC} = 1.42 \text{ Å } [1]$$

$$r_{CF} = 1.40 \text{ Å } [11]$$

$$C\hat{O}C = 120° [1]$$

$$O\hat{C}F = F\hat{C}F = 109.471°$$

When anisole was also considered as a single, planar structure, the ring-O bond was[1] determined to be bent away from z by $\alpha = 4°$, and a similar distortion is taken into account in our calculations. Testing this model for the trifluoro anisole gives unacceptable values for the error function,

$$R = \sum_{i<j} \sum \{[D_{ij}(\text{observed}) - D_{ij}(\text{calculated})]^2/F\}^{\frac{1}{2}} \quad (1)$$

with F the number of degrees of freedom. Varying the geometrical parameters over reasonable ranges does not reduce R to an acceptable value and hence this model for $V(\varphi)$ can be rejected, and we can conclude that the trifluoroanisole has a different conformational preference to the parent compound. Similarly, if $V(\varphi)$ has a minimum at 90° and a barrier high enough that only the orthogonal structure need be considered, then again R is unacceptably large and this structure can also be rejected.

To investigate more realistic forms for $V(\varphi)$ we use the theoretical model of Emsley and Luckhurst,[12] which expresses the D_{ij} as,

$$D_{ij} = (2/3) \sum_n p_n \sum_{\alpha,\beta} D^n_{ij\alpha\beta} S^n_{\alpha\beta} \quad (2)$$

which is based on the assumption that the molecule exists in n discrete conformations with statistical weights p_n. This is equivalent to sampling $V(\varphi)$ at n angles. The dipolar coupling in the nth conformation is

$$D^n_{ij\alpha\beta} = -\gamma_i\gamma_j h(3l_{ij\alpha n}l_{ij\beta n} - \delta_{\alpha\beta})/8\pi^2 r^3_{ijn} \quad (3)$$

where $l_{ij\alpha n}$ is the direction cosine of the internuclear vector r_{ijn} with respect to axis α ($\equiv x,y,z$), and $\delta_{\alpha\beta}$ is the Kronecker delta function. The components $S^n_{\alpha\beta}$ of the conformationally dependent ordering matrix depend on a potential of mean torque, $U(n,\omega)$, which depends on n and on the orientation ω of the director in a molecular reference frame:

$$S^n_{\alpha\beta} = Q_n^{-1} \int [(3l_\alpha l_\beta - \delta_{\alpha\beta})/2] \exp\{-U_{ext}(n,\omega)/RT\}d\omega \quad (4)$$

Here Q_n is the orientational partition function,

$$Q_n = \int \exp\{-U_{ext}(n,\omega)/RT\}d\omega \quad (5)$$

and l_α and l_β are direction cosines of the director with respect to the reference axes.

The potential of mean torque is assumed to have the form

$$U_{ext}(n,\omega) = -\varepsilon^n_{2,0}C_{2,0}(\omega) - 2\varepsilon^n_{2,2}C_{2,2}(\omega) \quad (6)$$

where the $C_{2,m}(\omega)$ are modified spherical harmonics and the conformationally dependent interaction tensor elements $\varepsilon^n_{2,m}$ are obtained as sums of terms, $\varepsilon^j_{2,p}$, which represent the contribution to the solute–solvent interaction from each rigid sub-unit in the molecule, thus

$$\varepsilon^n_{2,m} = \sum_j \sum_p \varepsilon^j_{2,p} D^2_{p,m}(\Omega^n_j) \quad (7)$$

$D^2_{p,m}(\Omega^n_j)$ is a second rank, Wigner rotation matrix which relates the reference frame to axes fixed in the jth sub-unit in the nth conformation.

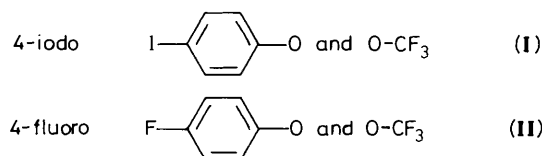The statistical weights p_n are given by

$$p_n = Q_n Z^{-1} \exp\{-U_{int}(n)/RT\} \quad (8)$$

with Z, the total partition function as

$$Z = \sum_n \int \exp\{-(U_{int}(n) + U_{ext}(n,\omega))/RT\}d\omega \quad (9)$$

$U_{int}(n)$ in the present case is a discrete representation of $V(\varphi)$.

For the two molecules studied here there are two rigid sub-units in each case, structures (I) and (II). The aromatic fragments

4-iodo   I—⟨benzene ring⟩—O and O-CF$_3$ (I)

4-fluoro   F—⟨benzene ring⟩—O and O-CF$_3$ (II)

have C_{2v} symmetry and the non-zero solute–solvent interaction parameters are $\varepsilon^R_{2,0}$ and $\varepsilon^R_{2,2}$. With the assumption that the CF$_3$ group rotates between three equivalent positions about the O–CF$_3$ bond, the contribution to the $\varepsilon^n_{2,m}$ of the O–CF$_3$ group is a single term, $\varepsilon^{OCF}_{2,0}$, which is the sum of $\varepsilon^{OC}_{2,0}$ and $\varepsilon^{CF}_{2,0}$. The calculations proceed by expressing $V(\varphi)$ by a cosine series,

$$V(\varphi) = \sum_q V_q \cos(q\varphi) \quad (10)$$

and finding the values of V_q, $\varepsilon^R_{2,0}$, $\varepsilon^R_{2,2}$, and $\varepsilon^{OCF}_{2,0}$, which minimize the error function R of equation (1).

We have assumed that the bond angles and bond lengths do not depend on φ, thus to simplify the problem we have set α to zero, and the angle $C\hat{O}C$, θ, has been optimized to fit the data. Thus, D_{26} depends strongly on θ and only weakly on the form of $V(\varphi)$, so that this angle can be obtained independently of the shape of the potential.

There is a range of shapes for $V(\varphi)$ which fit the data for each compound. The best agreement between observed and calculated dipolar couplings for two-fold barriers is obtained with the
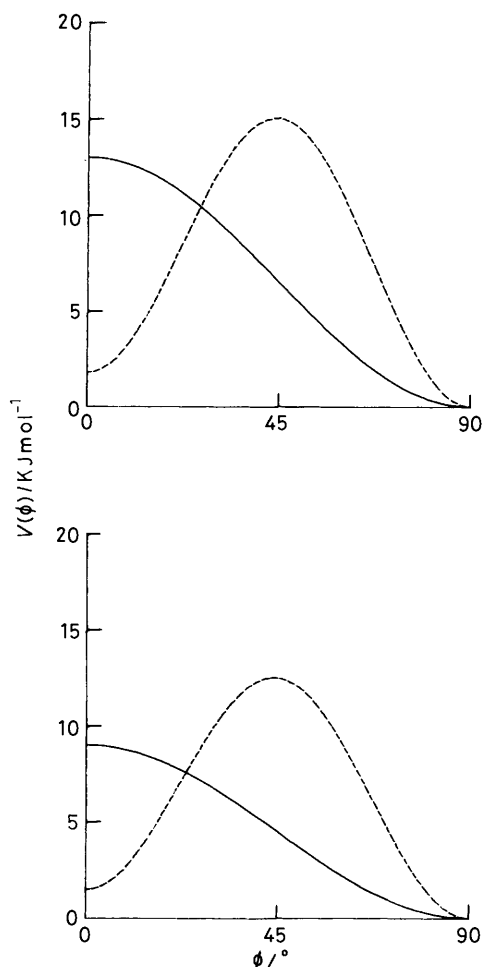
Figure 5. The potential functions $V(\varphi)$ for rotation about the phenyl O-bond in 4-iodo- (bottom) and 4-fluoro-α,α,α-trifluoromethoxybenzene (top) when dissolved in I35. The continuous curves are for the two-fold and the dashed curves for the four-fold representations of the potentials.

Table 4. The interaction coefficients $\varepsilon^{j}_{2,m}$, and the angle θ obtained by optimizing the agreement between observed and calculated dipolar coupling constants for 4-fluoro and 4-iodo-α,α,α-trifluoromethoxybenzenes dissolved in the nematic solvent I35 when the potential for rotation about the phenyl O-bond is $V(\varphi) = V_2(1 + \cos 2\varphi)$.

	4-fluoro	4-iodo
V_2/kJ mol^{-1}	6.5	4.5
$\varepsilon^{R}_{2,0}$/kJ mol^{-1}	0.71	0.99
$\varepsilon^{R}_{2,2}$/kJ mol^{-1}	0.78	0.58
$\varepsilon^{COF}_{2,2}$/kJ mol^{-1}	0.88	0.72
θ/°	122	123

potentials shown in Figure 5 and the Fourier components given in Table 4, where we also give the values of the interaction coefficients. A marginally better agreement between observed and calculated dipolar coupling constants is obtained by including a V_4 term into the potential, such that there is a maximum in $V(\varphi)$ at 45° as shown in Figure 5. The smallest values of R are obtained with the Fourier components, interaction parameters, and values of θ shown in Table 5. We have neglected the effect of small amplitude vibrational motion

Table 5. The interaction coefficients $\varepsilon^{j}_{2,m}$, and the angle θ obtained by optimizing the agreement between observed and calculated dipolar coupling constants for 4-fluoro and 4-iodo-α,α,α-trifluorometoxy-benzenes dissolved in the nematic solvent I35 when the potential for rotation about the phenyl O-bond is $V(\varphi) = V_0 + V_2 \cos 2\varphi + V_4 \cos 4\varphi$.

V_q/kJ mol^{-1}	4-fluoro	4-iodo
V_0	7.95	6.62
V_2	0.90	0.75
V_4	−7.05	−5.88
$\varepsilon^{R}_{2,0}$	0.91	1.12
$\varepsilon^{R}_{2,2}$	0.53	0.41
$\varepsilon^{COF}_{2,0}$	0.65	0.56
θ/°	121	123

on the calculated values of the D_{ij} and we have not considered the effect of small changes in our geometrical assumptions, so that we would not be justified in deciding whether $V(\varphi)$ has only a V_2 term, or whether there is also a large V_4 term.

Conclusion

It is disappointing that our data cannot differentiate between a potential with a maximum at $\varphi = 0°$ and one with the maximum shifted to $\varphi = 45°$. To make this distinction would require more data, which might perhaps be obtained by recording the spectra of molecules labelled with carbon-13. The important conclusion to be drawn from these calculations is that $V(0°)$ is larger than $V(90°)$, in contrast to the potential for anisole (compare Figures 2 and 5).

Acknowledgements

References

1 H. M. Seip and R. Seip, *Acta Chem. Scand.*, 1973, **27**, 4024.
2 P. Diehl, H. Huber, A. C. Kunwar, and M. Reinhold, *Org. Magn. Reson.*, 1977, **9**, 374.
3 M. M. Sax, R. Desiderato, and T. W. Dakin, *Acta Cryst.*, 1969, **B25**, 362.
4 H. Konschin, H. Tylli, and B. Westermark, *J. Mol. Struct.*, 1983, **102**, 279.
5 H. Konschin, *J. Mol. Struct.*, 1983, **105**, 213.
6 T. Schaefer and G. H. Penner, *J. Mol. Struct.*, 1987, **152**, 179.
7 W. A. Sheppard, *J. Org. Chem.*, 1964, **29**, 1.
8 A. E. Feiring, *J. Org. Chem.*, 1979, **44**, 2907.
9 G. Celebre, M. Longeri, and J. W. Emsley, *J. Chem. Soc., Faraday Trans. 2*, 1988, 1041.
10 J. Lounila and J. Jokisaari, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1982, **15**, 249.
11 E. D. Simandiras, R. D. Amos, N. C. Handy, T. J. Lee, J. E. Price, R. D. Remington, and H. F. Schaefer, *J. Am. Chem. Soc.*, 1988, **110**, 1338.
12 J. W. Emsley and G. R. Luckhurst, *Molec. Phys.*, 1980, **41**, 19.