Structure of 2,3,5,6-Tetrafluoroanisole determined from the Analysis of a Nuclear Magnetic Resonance Spectrum of a Nematic Solution

By **James W. Emsley,*** **John C. Lindon,** and **David S. Stephenson,** Chemistry Department, University of Southampton, Southampton SO9 5NH

Analysis of the ^1H and ^{19}F n.m.r. spectra of a sample of 2,3,5,6-tetrafluoroanisole dissolved in the nematogen Merck Phase IV yields a set of dipolar coupling constants which have been used to determine the relative positions of the protons and fluorines in the phenyl ring, and to test various models of internal motion. It is concluded that the rotation about the phenyl–oxygen bond has either a very low barrier (essentially free rotation), or that there are *n* symmetrically placed equilibrium positions where *n* is 4 or 8 or 16, *etc*. The height of the barrier to methyl group rotation about the methyl–oxygen bond cannot be determined. Vibrational averaging of dipolar couplings has been allowed for when determining the phenyl ring structure.

THE analysis of the spectrum of a molecule, partially oriented as a result of using a nematic solvent, gives dipolar coupling constants, D_{ij}, between magnetically interacting nuclei, which are a sensitive indication of molecular shape. The D_{ij} values are averages over all internal motions with frequencies greater than D_{ij}, and hence their magnitudes can be used to test models of internal motion. The method has been applied to many examples where there is one internal rotation, and a few such studies are benzaldehyde,[1] toluene,[2] phenol,[3] biphenyls,[4,5] bithienyls,[6,7] 4,4′-bipyridyl,[8] and acetaldehyde,[9] and to some examples with two identical rotors such as *o*-xylene,[10] *p*-xylene,[11] and *cis*-but-2-ene.[12] In this study we describe the application of the method to a molecule which has two internal rotation axes, 2,3,5,6-tetrafluoroanisole. The particular compound was chosen because of a lack of structural data on such molecules, and because it was anticipated that the spectrum would be easier to analyse than that of anisole itself. Less sterically hindered anisoles have been studied and their structures will be reported in forthcoming publications.

EXPERIMENTAL

The sample was purchased from Bristol Organics Ltd., and used without further purification. The spectra were recorded on a JEOL PS 100 spectrometer operating in the continuous wave mode, and using an external field-frequency lock. The ^{19}F and ^1H spectra were recorded without removing the sample from the probe, and within a short time interval. Their analysis showed that couplings common to both spectra were equal to within experimental error (±1 Hz). The Figure shows observed and calculated ^1H and ^{19}F spectra. The nematogen used was Merck Phase IV, and spectra were recorded at probe ambient temperature, *ca.* 25°.

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[1] P. Diehl, P. M. Henrichs, and W. Niederberger, *Org. Magnetic Resonance*, 1971, **3**, 243.

[2] P. Diehl, H. P. Kellerhals, and W. Niederberger, *J. Magnetic Resonance*, 1971, **4**, 352.

[3] P. Diehl and P. M. Henrichs, *Org. Magnetic Resonance*, 1971, **3**, 791.

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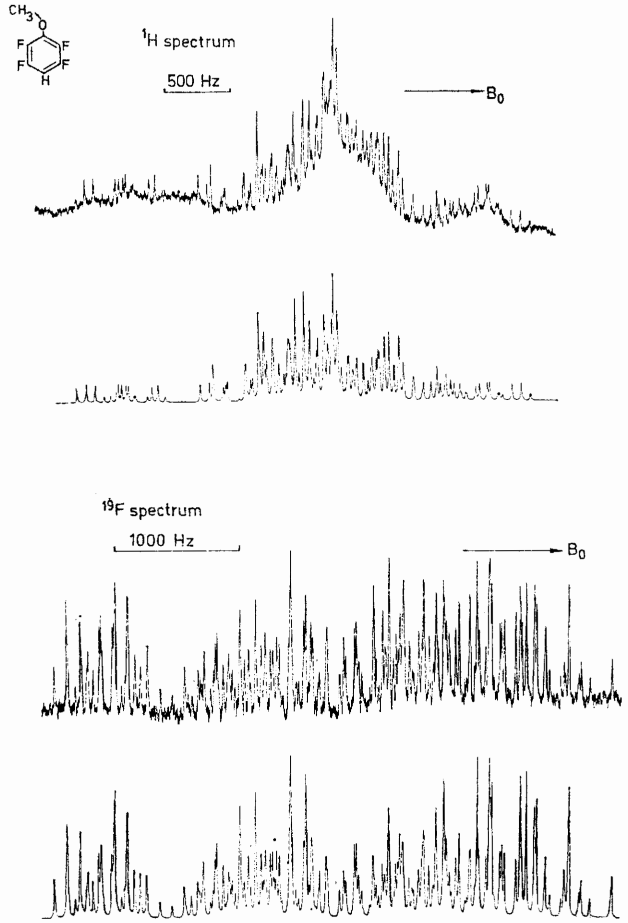
[10] E. E. Burnell and P. Diehl, *Mol. Phys.*, 1972, **24**, 489.

[11] D. Canet, *Compt. rend.*, 1973, **276C**, 807.

[12] E. E. Burnell and P. Diehl, *Org. Magnetic Resonance*, 1973, **5**, 137.

Analysis of Spectra.—The analyses were carried out with the aid of the program LAOCN 3, modified to include dipolar coupling. The coupling constants, J_{ij}, were kept fixed at their isotropic values. Bruce [13] has determined J_{12}, J_{14}, J_{15}, and J_{24}, but only the modulus of the latter two values was obtained. By comparison with the signs in similar molecules [14-16] it was decided to assign both as negative; their magnitude is small (see Table 1) and reversing the signs changes T_{15} and T_{24} by *ca.* 3 Hz. The J_{HF} values were measured from the spectrum of a sample dissolved in carbon tetrachloride (10% v/v), and their signs fixed by comparison with those found for 2,3,5,6-tetrafluoroaniline [15] and pentafluorobenzene [16] where appropriate. The small coupling from the methyl protons to the *o*-fluorines was given a positive sign, and again it cannot be determined accurately from the spectrum of the oriented sample. Table 1 gives the results of the analysis. A total of 282 lines were used in the iterative part of the analysis and a final root mean square of 2.1 Hz obtained.

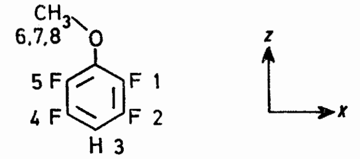


Observed and calculated ^{1}H and ^{19}F n.m.r. spectra of a sample of 2,3,5,6-tetrafluoroanisole dissolved in the nematogen Merck Phase IV. The spectra were recorded in the continuous wave mode on a JEOL PS 100 spectrometer at *ca.* 25°

Vibrational Analysis.—Dipolar coupling constants are averages over vibrational modes, and in order to calculate the magnitude of the couplings it is necessary to evaluate the matrix $L_{ik\alpha}$ connecting normal co-ordinates of the k vibrational modes with the α^{th} displacement co-ordinate of the i^{th} atom.[17] Our approach here has been theoretical as there has not been an analysis of the vibrational spectrum of this molecule, moreover, vibrational corrections are small for dipolar couplings involving protons and fluorines alone, hence it is not necessary for the $L_{ik\alpha}$ matrix to be very precise. The force field used is given in Table 2, and is taken from one giving a good fit to the observed vibrational spectrum of hexafluorobenzene [18,19] together with force constants appropriate to the vibrations involving the OCH_3 group of anisole.[20,21] Fewster [22] has assigned a frequency of 30 cm^{-1} to the torsional motion of the OCH_3 group in pentafluoroanisole, and this was assumed as a value for tetrafluoroanisole also, and used to determine the torsional force constant.

TABLE 1

Parameters determined from the analysis of the 94.1 MHz ^{19}F and 100 MHz ^{1}H n.m.r. spectra of 2,3,5,6-tetrafluoroanisole dissolved in the nematogen Merck Phase IV



Chemical shifts $\delta_2 - \delta_1 = 14.14$ p.p.m.
$\delta_3 - \delta_6 = 2.19$ p.p.m.

Interaction	Isotropic coupling * J_{ij}/Hz	Anisotropic coupling T_{ij}/Hz
1,2	−20.4	−910.7 ± 0.2
1,3	7.0	−232.3 ± 0.6
1,4	9.6	−161.5 ± 0.3
1,5	−1.75	−247.7 ± 0.3
1,6	1.4	−370.8 ± 0.4
2,3	10.0	−1 462.0 ± 0.4
2,4	−1.75	−251.1 ± 0.3
2,6	0.0	−101.5 ± 0.3
3,6	0.0	−70.7 ± 0.6
6,7	0.0	−341.9 ± 0.4

* Assumed.

RESULTS AND DISCUSSION

The spectrum analyses yield T_{ij}, the total anisotropic value of spin–spin coupling, and in general this is the sum of a dipolar coupling, D_{ij}, and the anisotropic part of electron-coupled spin interactions, J_{ij}^{aniso} [equation (1)].

$$T_{ij} = 2D_{ij} + J_{ij}^{\text{aniso}} \qquad (1)$$

The magnitude of J_{ij}^{aniso} may be appreciable for F–F coupling, but we will initially assume all J_{ij}^{aniso} values to be zero. In this case T_{ij} is equated to $2D_{ij}$, which is

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[13] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459.

[14] I. J. Lawrence and R. G. Jones, *J. Chem. Soc.* (*B*), 1967, 797.

[15] W. MacFarlane, *Mol. Phys.*, 1970, **18**, 817.

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[20] C. V. Stephenson, W. C. Coburn, and W. S. Wilcox, *Spectrochimica Acta*, 1961, **17**, 933.

[21] J. H. S. Green, *Spectrochimica Acta*, 1962, **18**, 39.

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related to molecular structure the equations (2) and (3).

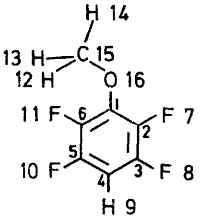
$$D_{ij} = D_{ij}^{0} - \frac{\gamma_i\gamma_j h}{8\pi^2}\left[S_{zz}(2f_{ijzz} - f_{ijxx} - f_{ijyy}) + (S_{xx} - S_{yy})(f_{ijxx} - f_{ijyy})\right] \quad (2)$$

$$D_{ij}^{0} = -\frac{\gamma_i\gamma_j h}{8\pi^2 r_{ij}^{3}}\left[S_{zz}(3\cos^2\theta_{ijz} - 1) + (S_{xx} - S_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy})\right] \quad (3)$$

Equations (2) and (3) refer to a molecule possessing C_{2v} symmetry, and will hold for tetrafluoroanisole provided it is a rigid internal rotor, and that the rate of internal rotation is much greater than whole molecule reorientation. The terms $f_{ij\alpha\alpha}$ depend on the $L_{ik\alpha}$ and are corrections for harmonic vibrational motion.[17] Internal rotation averages the couplings between the methyl group and the ring, and within the methyl group itself.

TABLE 2

Force field for 2,3,5,6-tetrafluoroanisole



Co-ordinate	Force constant	
R_{CC}	7.015 [a]	
R_{CF}	6.949 [a]	
R_{CH} (ring)	5.125 [a]	
R_{CH} (methyl)	4.685 [a]	
R_{CO} (methyl C)	6.000 [a]	
R_{CO} (phenyl C)	4.500 [a]	
α_{CCC}	1.239 [b]	
α_{CCF}	0.632 [b]	
α_{CCH}	0.274 [b]	
α_{COC}	1.200 [b]	
α_{OCH}	0.628 [b]	
α_{HCH}	0.530 [b]	
α_{CCO}	0.500 [b]	
γ_{CF} (wag)	0.500 [b]	
γ_{CH} (ring, wag)	0.484 [b]	
γ_{CO} (wag)	0.480 [b]	
δ_{CCCC} (ring)	0.051 [b]	
$\phi_{FCCF} = \phi_{FCCH} = \phi_{FCCO}$	0.103 [b]	
δ_{COCC}	0.005 [b]	
δ_{HCOC}	0.030 [b]	
$R_{CC}\,R_{CC}$ *ortho*	0.531 [a]	
meta	−0.531 [a]	
para	0.531 [a]	
$R_{CF}\,R_{CF} = R_{CH}\,R_{CF}$ *ortho*	0.002 [a]	
meta	−0.010 [a]	
$R_{CH}\,R_{CH}$ *methyl*	0.050 [a]	
$R_{CF}\,\alpha_{CCC} = R_{CH}\,\alpha_{CCC}$	−0.177 [b]	*e.g.* $R_{2,7}\,\alpha_{123}$
$R_{CC}\,\alpha_{CCF} = R_{CC}\,\alpha_{CCH}$	−0.100 [b]	*e.g.* $R_{23}\,\alpha_{723}$
$R_{CC}\,\alpha_{CCC}$	0.463 [b]	*e.g.* $R_{23}\,\alpha_{123}$
$R_{CO}\,\alpha_{OCH}$	0.180 [b]	*e.g.* $R_{15,16}$ $\alpha_{12,15,16}$
$\alpha_{CCF}\,\alpha_{CCF}$ (and with F replaced by H or O)	0.007 [c]	*e.g.* $\alpha_{723}\,\alpha_{238}$
	0.003 [c]	*e.g.* $\alpha_{723}\,\alpha_{459}$
	−0.013 [c]	*e.g.* $\alpha_{723}\,\alpha_{4510}$
	−0.235 [c]	*e.g.* $\alpha_{238}\,\alpha_{438}$
$\alpha_{CCC}\,\alpha_{CCF} = \alpha_{CCC}\,\alpha_{CCH} = \alpha_{CCC}\,\alpha_{CCO}$	−0.046 [c]	*e.g.* $\alpha_{123}\,\alpha_{834}$
$\alpha_{OCH}\,\alpha_{OCH}$	−0.039 [c]	*e.g.* $\alpha_{12,15,16}$ $\alpha_{13,15,16}$
$\gamma_{CF}\,\gamma_{CF}$ *ortho* (and with F replaced by H or O)	−0.094 [c]	
$\delta_{CCCC}\,\phi_{FCCF}$ (and with F replaced by H or O)	0.193 [c]	

[a] In mdyn Å^{-1}. [b] In mdyn rad^{-1}. [c] In mdyn Å^{-2}.

We have first considered the structure of the phenyl ring. There are six intra-ring dipolar couplings, compared with four unknown co-ordinates x_1, x_2, z_1, z_2 (the axis system and numbering of the nuclei is given in Table 1) and two unknown independent $S_{\alpha\alpha}$ elements, assuming C_{2v} symmetry. One inter-nuclear distance must be assumed, and we have chosen this to be r_{24}, which has been fixed at 4.296 Å, a value appropriate for a regular hexagon of side 1.4 Å and a C–F bond length of 1.33 Å. There are therefore five structural unknowns to obtain six D_{ij} values, and we have used a least-squares process to give the best values shown in Table 3. The magnitude of the residual ΔT_{ij} indicates that some of our assumptions must be in error. The large residuals ΔT_{13}, ΔT_{14}, and ΔT_{24} most probably arise from finite values of J_{FF}^{aniso}, which have been found to be of this order of magnitude in other fluorobenzenes.[19,23-25] But there may also be contributions from other effects such as in the case of ΔT_{24}, a wrong sign for J_{24}. However, although significant, the residuals are small and they do not affect the conclusions reached on the gross structural features derived. They do suggest that the co-ordinates and orientation parameters may have an uncertainty of *ca.* 1%.

TABLE 3

Orientation matrix elements, $S_{\alpha\beta}$, and co-ordinates (Å) of ring proton and fluorine nuclei obtained from dipolar couplings

	a	*b*
x_1	2.66 ± 0.04	2.64 ± 0.04
z_1	3.97 ± 0.06	3.97 ± 0.06
x_2	2.63 ± 0.04	2.61 ± 0.04
z_2	1.24 ± 0.02	1.24 ± 0.01
x_3	0.0	0.0
z_3	0.0	0.0
S_{zz}	0.0908 ± 0.0001	0.0871 ± 0.0001
$S_{xx} - S_{yy}$	0.443 ± 0.008	0.431 ± 0.007
ΔT_{12} *	0.3	0.3
ΔT_{13}	−3.3	−3.0
ΔT_{14}	3.9	3.6
ΔT_{15}	−0.6	−0.5
ΔT_{23}	0.6	0.5
ΔT_{24}	−6.5	−6.0

σ $\Delta T_{ij} = 2D_{ij}$(calculated) − T_{ij}(observed) in Hz.

[a] With and [b] without vibrational corrections.

We consider next the internal motions. The rotation of the methyl protons about the methyl–oxygen bond gives an averaged value of intra-methyl dipolar coupling, D_{CH_3}, which depends only on the intramethyl proton–proton distance and the average orientation of the CH_3–O bond, with respect to the axis system used. The couplings from the methyl protons to the ring nuclei depend

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[24] G. J. den Otter and C. MacLean, *Chem. Phys.*, 1974, **3**, 119.

[25] J. Bulthuis and C. MacLean, *Chem. Phys. Letters*, 1973, **21**, 611.

on the position of the methyl group relative to the ring, and on the two forms of rotational motion. Clearly there are too many unknown parameters to fix all the details of the structure, and we must resort to testing various models. The intra-methyl coupling D_{CH_3} can be used to rule out some structural models immediately. Structures with the C–O–C atoms coplanar with the ring and having a high barrier to rotation about the phenyl–oxygen bond are incompatible with D_{CH_3} for any reasonable structure; similar results hold for the case of the C–O–C plane perpendicular to the ring.

The value of the intra-methyl coupling D_{CH_3} is compatible with all models for rotation about the phenyl–oxygen bond which have at least four equivalent equilibrium positions. The value of D_{CH_3}, assuming that the oxygen–methyl bond is a three-fold rotation axis, is given by equation (4) where the a direction is the oxygen–methyl bond.

$$D_{CH_3} = \frac{60033.5}{r_{HH}^3} S_{aa} \qquad (4)$$

The value of S_{aa} for a fixed conformation is given by equation (5) where $\theta_{a\alpha}$ is the angle the oxygen–methyl bond makes with the α^{th} axis.

$$S_{aa} = S_{zz}(3\cos^2\theta_{az}/2 - \tfrac{1}{2}) + \tfrac{1}{2}(S_{xx} - S_{yy})(\cos^2\theta_{ax} - \cos^2\theta_{ay}) \qquad (5)$$

Rotation about the phenyl–oxygen bond does not change θ_{az}, but $\theta_{a\alpha}$ and θ_{ay} change such that the average value of S_{aa} is simply as in equation (6) for the following cases: (a) free rotation;

$$\langle S_{aa} \rangle = S_{zz}(3\cos^2\theta_{az}/2 - \tfrac{1}{2}) \qquad (6)$$

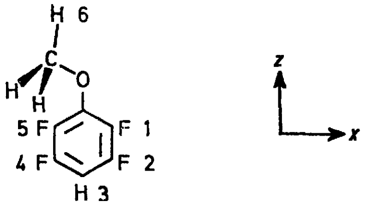
(b) equal population of the structures with ϕ, the rotation angle about z, as 0 (*i.e.* methyl–oxygen in the ring plane), 90, 180, and 270°; (c) equal population of the four structures with $\phi = 45$, 135, 225, and 315°; (d) equal population of eight values of $\pm\phi$, $90 \pm \theta$, $180 \pm \phi$, and $270° \pm \phi$, where ϕ has any value: also 16, 32 *etc.* equivalent structures with the same symmetry properties.

Combining equations (4) and (6) means that models (a)—(d) predict a value for θ_{az}, and with the experimental value for D_{CH_3} this gives a value of 117.5°, assuming that r_{HH} is that appropriate to a methyl group with C–H bond of 1.09 Å and HCH angle of 109° 29′.

The methyl–ring nuclear dipolar couplings depend on the nature of both internal rotations, and on the position of the methyl group relative to the ring. Since the value of D_{CH_3} determines θ_{az} the methyl group can be characterised by the values of x_6 and z_6 if it is assumed that the methyl rotation is either free or has three equivalent equilibrium positions such that one C–H bond eclipses with the C–O bond. Table 4 gives the results of determining x_6 and z_6 with free rotation about phenyl–oxygen and an average of the three equilibrium structures of methyl group relative to the methyl–oxygen bond. We also tested model (c) for the phenyl–oxygen rotation, and the effect of low barriers to methyl rotation. All these models gave essentially the same results. The values of x_6 and z_6 may be combined with a regular hexagon structure for the phenyl ring, of side 1.4 Å, to derive values for the phenyl–oxygen and methyl–oxygen bond lengths of 1.282 ± 0.002 and 1.680 ± 0.003 Å respectively. These values are sufficiently close to those expected to confirm that the model for the structure and rotation is essentially correct.

TABLE 4

Co-ordinates of the methyl proton eclipsing the methyl–oxygen bond in 2,3,5,6-tetrafluoroanisole assuming free rotation about the phenyl–oxygen bond and equal population of three equivalent equilibrium positions for the methyl protons with respect to methyl–oxygen rotation. The COC angle is fixed at 117.461 ± 0.003°



x_6	1.257 ± 0.002
y_6	7.077 ± 0.003
z_6	0.0
ΔT_{16} *	0.0
ΔT_{26}	−0.2
ΔT_{36}	0.6

* $\Delta T_{ij} = 2D_{ij}$(calculated) − T_{ij}(observed).

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