Conformations of 3,5-Dichloroanisole and 3,5-Dibromoacetophenone determined from ¹H Nuclear Magnetic Resonance Spectra of Nematic Solutions

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The ¹H n.m.r. spectra of samples of 3,5-dichloroanisole and 3,5-dibromoacetophenone dissolved in the liquid crystal Merck Phase V have been analysed to yield sets of dipolar coupling constants. For both molecules the dipolar couplings are consistent only with structures having the side chain groups, COC and CCC, and phenyl rings coplanar, and with one CH bond of the methyl group in this plane and pointing away from the ring. It is also shown that the molecules reorient rapidly in the liquid crystals during each rotation about the C–X bonds.

THE ¹H n.m.r. spectra of molecules dissolved in liquid crystal solvents may be analysed to yield dipolar coupling constants, which are directly related to the relative positions of the protons and a set of ordering matrix elements, $S_{\alpha\beta}$.[1] Thus, neglecting vibrational averaging, the dipolar coupling between two nuclei i and j is given by equation (1). The axes (x, y, z) are fixed in the

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

molecule, and equation (1) is for an arbitrary set. Consider the molecules of the general kind (A) where there is

(A)
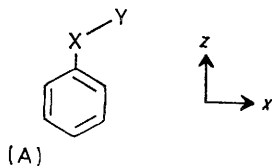
internal rotation about the C–X, and possibly X–Y bonds which is rapid enough to average the dipolar couplings.

The number of order parameters necessary to describe the dipolar couplings in these molecules depends on the extent of correlation between internal rotation and

molecular reorientation. In the absence of correlation, and assuming that there is no distortion on reorientation, then the internal rotation about the C–X bond creates an effective mirror plane, and all the dipolar couplings require at most two independent elements, S_{zz} and $(S_{xx} - S_{yy})$ to describe their relationship with geometry. This situation is probable when the barrier to rotation is low, as in tetrafluoroanisole,[2] so that the rate of internal rotation, ν_{int}, is much greater than the rate of molecular reorientation, ν_{mol}. At the other extreme, a high barrier to rotation about C–X may lead to $\nu_{int} \ll \nu_{mol}$ and hence the molecule is able to reorientate during each internal rotation. In this situation the dipolar couplings between ring protons will still require only S_{zz} and $(S_{xx} - S_{yy})$ but the other dipolar couplings require in addition the three off-diagonal elements, and these will be time-dependent. The problem is tractable only if the barrier to rotation is high enough so that it can be assumed that only the lowest energy conformations are appreciably populated. A further simplification occurs if the equilibrium conformations have a plane of symmetry, in which case only one off-diagonal element $S_{\alpha\beta}$ is required. For benzaldehyde[3] only planar forms were consistent with the dipolar couplings, which means that S_{xz} may be non-zero. It was found, however, that S_{xz} is zero to within experimental error for this molecule.

[1] J. W. Emsley and J. C. Lindon, 'N.M.R. Spectroscopy using Liquid Crystal Solvents,' Pergamon, Oxford, 1975.

[2] J. W. Emsley, J. C. Lindon, and D. S. Stephenson, *J.C.S. Perkin II*, 1975, 1794.

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

The dipolar couplings for 2,3,5,6-tetrafluoroanisole [2] were also consistent with all $S_{\alpha\beta}$ ($\alpha \neq \beta$) zero, presumably because rotation is rapid, and free. We now extend these studies to anisole and acetophenone derivatives in order to examine the possibility of determining conformation and deciding on the extent of correlation between internal rotation and reorientation. The spectra of anisole and acetophenone themselves are very complex, and are greatly simplified by replacing some of the ring protons by chlorine or bromine. The remaining protons do not yield enough dipolar couplings to give a complete description of structure and conformation, but we will show that much information is revealed by making reasonable assumptions about ring and methyl group geometries.

EXPERIMENTAL

The acetophenone derivative was prepared from 1,3,5-tribromobenzene. A Grignard reaction was used to prepare a 1-(3,5-dibromophenyl)ethyl alcohol which was then oxidised with chromic oxide to give the acetophenone. The anisole derivative was prepared from 3,5-dichlorophenol by reaction with sodium in methanol, followed by methyl iodide.

The 220 MHz spectra were recorded on samples dissolved in the liquid crystal Merck Phase V, obtained from E. Merck, Darmstadt. The spectra were analysed using a version of LAOCN 3, modified to include dipolar couplings, and the results are given in Table 1. The only non-zero

TABLE 1

Chemical shifts, δ_{ij} (p.p.m.) and dipolar coupling constants, D_{ij} (Hz) derived from analysis of the 220 MHz spectra of 3,5-dichloroanisole and 3,5-dibromoacetophenone in the nematic liquid crystal, Merck Phase V
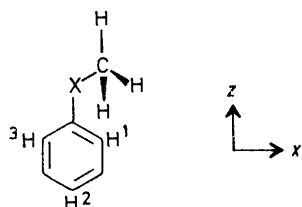
	3,5-Dichloroanisole	3,5-Dibromo-acetophenone
δ_{12}	-0.380 ± 0.001	-0.013 ± 0.004
δ_{1,CH_3}	2.606 ± 0.001	4.354 ± 0.003
D_{12}	-168.3 ± 0.1	-216.2 ± 0.3
D_{13}	-57.5 ± 0.2	-118.9 ± 0.4
D_{1,CH_3}	-351.2 ± 0.1	-442.9 ± 0.2
D_{2,CH_3}	-67.5 ± 0.1	-75.6 ± 0.3
D_{CH_3}	$1\ 024.5 \pm 0.1$	$1\ 381.2 \pm 0.2$
	1.3 Hz on	2.5 Hz on
R.m.s. error	91 transitions	64 transitions

isotropic couplings involved in the analysis of the spectra of each molecule are J_{12} and J_{13}, which were fixed at 1.0 Hz. (See Table 1 for the labelling of the nuclei.)

RESULTS AND DISCUSSION

We will assume first that $\nu_{int} \gg \nu_{mol}$ so that (x, y, z) are principal axes for the order matrix, and the values of S_{zz} and $(S_{xx} - S_{yy})$ may be calculated provided we assume the co-ordinates of the ring protons. We have

taken the phenyl ring to have a regular hexagon structure with $r_{CC} = 1.4$ and $r_{CH} = 1.09$ Å, and all CCH angles 120°. The methyl group is assumed to have a three-fold symmetry axis, $r_{CH} = 1.09$ Å and HCH $= 109.5°$. Rapid reorientation of the methyl group about the three-fold axis makes D_{CH_3}, the dipolar coupling between methyl protons, equal to $10\ 646 \times S_{33}$, where S_{33} is an order parameter for the three-fold axis. The value of S_{33} depends only on the motion about the z-axis in each molecule, and hence the value of D_{CH_3} may be used to test models of this motion independently of the nature of motion about the three-fold axis, with the proviso only that the latter motion is rapid. Our assumption that $\nu_{int} \gg \nu_{mol}$ means that equation (2) applies where

$$S_{33} = (\tfrac{3}{2}\cos^2\theta_{3z} - \tfrac{1}{2})S_{zz} + \tfrac{1}{2}(S_{xx} - S_{yy})(\cos^2\theta_{3x} - \cos^2\theta_{3y})$$
(2)

$\theta_{3\alpha}$ are the angles made by the three-fold and x, y, z axes. Assuming that θ_{3z} is 60° we can calculate values of D_{CH_3} for the following three extreme models for motion about the z-axis: (a) free rotation; (b) hindered rotation, such that only the two forms with the COC or CCO planes and the phenyl ring coplanar are appreciably populated; (c) as in (b) but with the COC or CCO planes perpendicular to the ring. Table 2 gives the calculated

TABLE 2

Calculated values of D_{CH_3} (Hz) for different models of rotation about the two-fold (z) axes in 3,5-dichloroanisole and 3,5-dibromoacetophenone.

| Model	3,5-Dichloroanisole	3,5-Dibromoacetophenone
a	-182	-221
b	$+672$	$1\ 076$
c	$-1\ 036$	$-1\ 518$
D_{CH_3} (observed)	$+1\ 024.5$	$+1\ 381.2$
S_{zz}	0.137	0.166
$S_{xx} - S_{yy}$	0.214	0.325

[a] Free rotation. [b] Interconversion between planar configurations. [c] Interconversion between perpendicular configurations.

values for the anisole and acetophenone molecules, and it is seen that only model (b) gives a value of D_{CH_3} with the correct relative sign. In order to bring model (b) into exact agreement with experiment requires that θ_{3z} be ca. 40° for both molecules. If the three-fold axis of the methyl group is collinear with the bonds O-C and C-C in the two molecules, then a value of 40° seems improbable. For example, an X-ray study on crystalline 1,4-dimethoxybenzene [4] found the COC angle to be 121°, i.e. $\theta_{3z} = 59°$. The small value of θ_{3z} indicates that some of the assumptions implicit to our model are incorrect. One possibility is that rotation about the two-fold axis is such that out-of-plane configurations are appreciably populated as well as in-plane ones. We can reject this modification to our model as an explanation of the small magnitude of θ_{3z} for both molecules by noting that, for a fixed value of θ_{3z}, including non-planar configurations leads to a smaller

[4] T. H. Goodwin, M. Przybylska, and J. M. Robertson, Acta Cryst., 1950, 3, 279.

calculated value of D_{CH_3}. Thus the completely planar model, (b), predicts the largest value of θ_{3z}.

The value of D_{CH_3} suggests that model (b) is a better description of the conformation of the molecule than (a) or (c) but the need to assume $\delta_{3z} = 40°$ suggests that the assumption made may be in error. A consideration

(I)   (II)
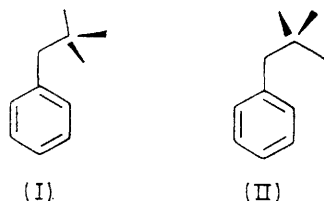
of the values of D_{1,CH_3} and D_{2,CH_3} enables us to test the model further. Two possible minimum energy conformations (I) and (II) of the methyl group relative to the ring were considered. In all cases the angles $C\widehat{X}C$ were fixed at 140° and the position of the methyl group varied to minimise the differences between observed and calculated dipolar couplings D_{1,CH_3} and D_{2,CH_3}. It was found that both structures (I) and (II) for the anisole and the acetophenone lead to positions of the methyl protons which are incompatible with reasonable values of the C–X and X–C bond lengths.

The failure of the models discussed so far to explain the observed couplings most probably arises from the assumption that the molecule does not reorientate on internal rotation about the z-axis. If we now assume that $\nu_{int} \ll \nu_{mol}$ then an extra order parameter is required to describe D_{CH_3}, D_{1,CH_3}, and D_{2,CH_3} in the (x, y, z) axis system. The dipolar couplings between ring protons are still independent of the off-diagonal elements $S_{\alpha\beta}$, and can be used to determine S_{zz} and $(S_{xx} - S_{yy})$. Models were tested in which the angle CXC was fixed at 120°. The condition $\nu_{int} \ll \nu_{mol}$ eliminates free rotation about z as a possibility, and consequently the models tested are interconversion about z between either two planar or perpendicular forms; in each case the methyl group was assumed to reorientate rapidly between three equilibrium positions. It is found that only the planar structures are compatible with the dipolar couplings. The three couplings D_{CH_3}, D_{1,CH_3}, and D_{2,CH_3} were used to derive S_{xz} and the x and z co-ordinates of the methyl protons (whilst maintaining the tetrahedral structure of CH_3 and the angle CXC at 120°). Only structure (I) gives reasonable methyl co-ordinates, as shown in Table 3. The co-ordinates imply $r_{CO} = 1.42$ and $r_{O,CH_3} = 1.28$ Å for 3,5-dichloroanisole, and $r_{C,C=O} = 1.51$ and $r_{C-CH_3} = 1.43$ Å for 3,5-dibromoacetophenone.

The values of S_{xz} found for both molecules are large and clearly significant. In Table 3 we also give the values of the order parameters in the principal axis system (x', y', z') and the angle α made between z and z'. It is interesting to compare the values of α with the angles, β, made between z and the principal inertial

5 W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

axes, which are also given in Table 3. For the acetophenone, factors other than inertia are clearly important in determining the value of α.

Conclusions.—In order to use the dipolar coupling constants to test the conformational preferences of these molecules it has been necessary to make assumptions about the CXC bond angle, the structure of the methyl group, and the relative positions of the ring protons. With these assumptions it is possible to conclude that the molecule reorients more rapidly than rotation about the C–X bond, so that three non-zero independent elements of the order matrix are necessary to describe the dipolar couplings. It is also concluded that only coplanar

TABLE 3

Order parameters and methyl proton co-ordinates for 3,5-dichloroanisole and 3,5-dibromoacetophenone, determined assuming only planar conformation of the CXC and phenyl rings, and that molecular reorientation is more rapid than internal rotation about the C–X bonds

	3,5-Dichloroanisole	3,5-Dibromoacetophenone
x_4 *	0.905 2 Å	1.041 2 Å
z_4 *	7.082 5 Å	7.167 7 Å
S_{zz}	0.076	0.066
$S_{x'x'}$	−0.003	0.044
$S_{y'y'}$	−0.176	−0.246
$S_{z'z'}$	0.179	0.202
α	28.7°	28.3°
β	19°	−1.5°

* The origin is at H-2. PI represents the principal moment of inertia axis system; x',y',z' represents the principal order axis system.

arrangements of the phenyl and CXC atoms are appreciably populated, and that the methyl group reorients between structures having one CH bond in the plane of the phenyl ring and furthest away from it [structure (I)]. The equilibrium structures are in agreement with the theoretical predictions of Hehre *et al.*[5] for anisole and acetophenone. A study of anisole by Aroney *et al.*[6] using the Kerr effect, concluded that the COC plane is perpendicular to the ring. Substituting chlorine atoms at the 3 and 5 positions should destabilise planar forms and hence we conclude that anisole has also a planar configuration, in disagreement with Aroney *et al.*

6 M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc.* (*B*), 1969, 666.