

Structure and Conformation of 4-Nitrophenyl Acetate from Proton Nuclear Magnetic Resonance of Nematic Solutions

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

The 100 MHz proton spectrum of 4-nitrophenyl acetate dissolved in a nematic mesophase has been analysed to yield a set of partially averaged dipolar coupling constants, D_{ij} . These parameters are shown to be consistent with interconversion between two conformations with all carbon and oxygen atoms coplanar. It is also shown that the side chain conformation has one methyl C-H bond and the C=O bond in an eclipsed arrangement.

THE determination of conformational preferences by n.m.r. spectroscopy of nematic solutions relies on the sensitivity of partially averaged dipolar coupling constants, D_{ij} , to internal motion.¹ It has been shown recently for some benzaldehydes,²⁻⁴ acetophenones,^{5,6} and anisoles⁵ that molecular reorientation in the nematic phase occurs on each internal rotation; hence each conformation requires a separate ordering matrix, S , and the averaged value of a dipolar coupling $\langle D_{ij} \rangle$ is therefore given by an expression of the form (1),⁵ where

$$\langle D_{ij} \rangle = p_A G_{ij}^A S_{\alpha\beta}^A + p_B G_{ij}^B S_{\alpha\beta}^B + \dots \quad (1)$$

p_A and p_B are the relative populations of different conformational sites; $G_{ij}^A S_{\alpha\beta}^A$ is the value of D_{ij} for conformation A, and G_{ij}^A contains its geometrical dependence. Equation (1) may be used to investigate conformational preferences only in two special cases: (a) symmetry related conformations, such that $p_A = p_B$, and where $S_{\alpha\beta}^A$ and $S_{\alpha\beta}^B$ are related in a known manner; it is also necessary that the molecule does not undergo geometrical distortion on changing conformation; and (b) where $S_{\alpha\beta}^A = S_{\alpha\beta}^B$, because each conformation has a similar shape; again it is necessary to assume the absence of geometrical distortions. Case (a) holds for molecules like acetophenone, for example, in which the different conformations are related by a mirror plane.

We present here the results of a study on a molecule possessing the possibility of internal rotation about three

EXPERIMENTAL

4-Nitrophenyl acetate was obtained commercially. After dissolving in the nematogen Merck Phase V, proton spectra were obtained on an XL100 spectrometer operating in the Fourier transform mode at 31 °C, and individual line positions were measured to within ± 1.4 Hz. The spectrum was analysed with the aid of the computer program LEQUOR,⁷ and in the iterative part 88 transitions were matched to give root mean square error of 2.7 Hz. The isotropic couplings were kept fixed in the analysis at values appropriate for aromatic protons. The parameters obtained are given in Table 1.

TABLE 1

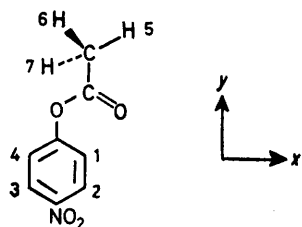
Best fit n.m.r. parameters for 4-nitrophenyl acetate dissolved in Merck Phase V (nuclei numbered as in the text)

i, j	D_{ij}/Hz	J_{ij}/Hz
1,2	$-2\,663.9 \pm 0.3$	8.0
1,3	15.1 ± 0.3	0.5
1,4	213.4 ± 1.9	1.0
1,5	-289.8 ± 0.5	0.0
2,3	209.3 ± 1.9	1.0
2,5	-106.5 ± 0.5	0.0
5,6	$3\,029.0 \pm 0.2$	0.0
$\delta_{1,2}$ * (p.p.m.)	-0.94 ± 0.04	
$\delta_{1,5}$	4.497 ± 0.04	

* δ_{ij} is the chemical shift between nuclei i and j .

RESULTS AND DISCUSSION

We will discuss first a model for the motional possibilities which does fit the observed dipolar couplings. The model has interconversion between the two equally probable forms A and B. The co-ordinates of the protons, and the values



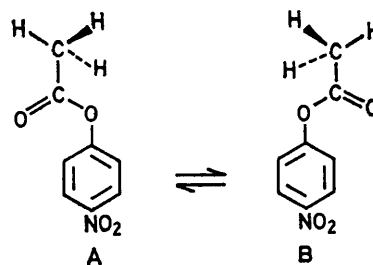
separate axes, the Ph-O bond, the O-C(=O) bond, and the C-CH₃ bond. Our aim is to ascertain whether simplified models of the motional possibilities, but which are structurally probable, are consistent with the observed dipolar coupling constants.

¹ J. W. Emsley and J. C. Lindon, 'NMR Spectroscopy using Liquid Crystal Solvents,' Pergamon, Oxford, 1975.

² T. C. Wong and E. E. Burnell, *J. Magnetic Resonance*, 1976, **22**, 227.

³ K. G. Orrell and V. Sik, *J.C.S. Faraday II*, 1976, 941.

⁴ M. Duchêne, J. W. Emsley, J. C. Lindon, J. Overstall, and D. S. Stephenson, *Mol. Phys.*, 1976, **33**, 281.



of $S_{\alpha\beta}$ for this model are given in Table 2, and since it is an example of case (a), then the two conformations are described by S matrices which differ only in the sign of S_{xy} . The principal axis system ($x'y'z'$) for S has an angle of 24°

⁵ J. W. Emsley, J. C. Lindon, and J. M. Street, *J.C.S. Perkin II*, 1976, 805.

⁶ J. W. Emsley, J. C. Lindon, J. M. Street, and G. E. Hawkes, *J.C.S. Faraday II*, 1976, 1365.

⁷ P. Diehl, H. P. Kellerhals, and W. Niederberger, *J. Magnetic Resonance*, 1971, **4**, 352.

between y and y' , with y' rotated towards the C=O bond in conformation B.

The methyl group has been assumed to occupy only three, equivalent positions and to have $r_{\text{CH}} = 1.09 \text{ \AA}$ and $\widehat{\text{HCH}} = 109.5$; although using a probability distribution appropriate

TABLE 2

Proton co-ordinates (\AA), ordering matrix elements, $S_{\alpha\beta}$, and dipolar coupling constant residuals (Hz), for 4-nitrophenyl acetate

Nucleus	x	y	z	
1	2.156 *	2.523	0.0	
2	2.170	0.0	0.0	
3	-2.170	0.0	0.0	
4	-2.156 *	2.523	0.0	
5	2.058	6.927	0.0	
6	0.523	6.750	0.892	
7	0.523	6.750	-0.892	
S_{xx}	-0.143			
S_{yy}	0.357			
S_{xy}	0.279			
$\Delta D_{1,2} \uparrow$	1.8	$\Delta D_{1,4}$ 0.0	$\Delta D_{2,3}$ 0.0	$\Delta D_{5,6}$ 0.0
$\Delta D_{1,3}$	0.0	$\Delta D_{1,5}$ 1.1	$\Delta D_{2,5}$ -2.4	

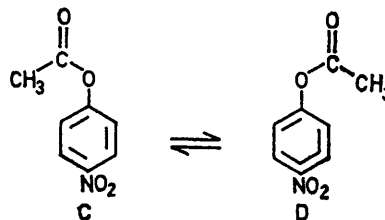
* Fixed values. † $D_{ij}(\text{obs.}) - D_{ij}(\text{calc.})$.

to a more realistic rotational potential has a small effect on the position derived for the group, it does not affect the main conclusion that in the minimum energy configuration the C-H(5) bond eclipses the C=O and not the C-O(Ph) bond. The 3-fold rotation axis of the methyl group, which is probably coincident with the (O')C-CH₃ bond, cannot be parallel to the y -axis, as it would be for a 'model' structure with angles Ph-O-C and O-C-Me each 120°. The derived angle between the y -axis and the 3-fold axis is 6.5°, with the methyl bent away from the C=O group. We cannot definitely exclude a bending of the (O')C-CH₃ bond out of the xy plane by 6.5°, since this requires five $S_{\alpha\beta}$ values, which can always be adjusted to fit the D_{ij} values.

Interconversion between only the two conformations C and D can be definitely excluded on the basis that the

* P. Diehl, S. Sykora, W. Niederberger, and E. E. Burnell, *J. Magnetic Resonance*, 1974, **14**, 260.

difference between the observed and calculated dipolar coupling between the methyl protons and the aromatic *ortho*-protons is very large. The possibility of interconversion amongst A, B, C, and D cannot be rigorously tested, as it is not an example of case (a) and it is unlikely to be case (b) either. Such a model is unlikely, however, because



the diagonal elements $S_{\alpha\alpha}^A$ (equal to $S_{\alpha\alpha}^B$) would probably differ considerably from $S_{\alpha\alpha}^C$ (equal to $S_{\alpha\alpha}^D$), and the proton positions in C and D would probably differ from those in A and B. In these circumstances the averaged dipolar couplings observed amongst the four ring protons would most probably be inconsistent with a single, averaged S matrix and a reasonable, planar arrangement of the four nuclei. Such inconsistencies between experimental and calculated dipolar couplings have been observed, for example, for acetylene⁸ and methyl fluoride,⁹ and the geometrical changes on exchange between sites with different S matrices for these molecules were predicted to be very small. It is possible, although improbable, that case (b) applies, that is, by accident $S_{\alpha\beta}^A = S_{\alpha\beta}^C$. This would then allow us to calculate the terms $G_{ij}^C S_{\alpha\beta}^C$ and $G_{ij}^D S_{\alpha\beta}^D$ in equation (1), and hence to derive $p_A = p_B$, $p_C = p_D$. In conformations C and D the predicted value of the averaged coupling D_{1,CH_3} [= D_{4,CH_3}] is in the region of -12 000 Hz, and hence $p_C = p_D$ cannot be more than about 0.1% for reasonable values of the bond lengths and angles. We conclude, therefore, that 4-nitrophenyl acetate exists almost exclusively in the conformations A and B.

[7/114 Received, 24th January, 1977]

* E. E. Burnell, J. R. Council, and S. E. Ulrich, *Chem. Phys. Letters*, 1975, **31**, 295.