

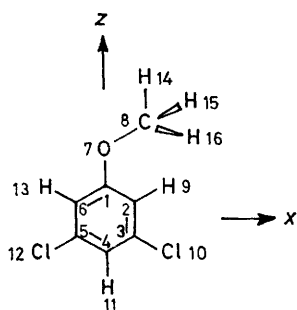
## Conformation of 2,6- and 3,5-Dichloroanisole from $^1\text{H}$ and $^2\text{H}$ Nuclear Magnetic Resonance Studies on Liquid Crystalline Solutions

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The  $^1\text{H}$  n.m.r. spectra of liquid crystalline solutions of the two dichloroanisoles labelled with  $^{13}\text{C}$  in the methyl groups have been analysed to yield sets of dipolar coupling constants,  $D_{ij}$ . It is shown that the  $D_{ij}$  values involving  $^{13}\text{C}$  and ring protons can be used to determine the minimum energy positions for reorientation about the ring-oxygen bonds independently of the nature of reorientation of the methyl protons about the oxygen-methyl bond. It is found that the minimum energy positions for the 3,5-dichloroanisole have all C and O atoms coplanar, whilst for the 2,6-dichloroanisole the COC and phenyl planes are orthogonal. The  $D_{\text{CH}}$  and  $D_{\text{HH}}$  values within the methyl groups are used to derive the HCH angles of 109.5 and 110.0 respectively, whilst using all the  $D_{ij}$  values fixes  $r_{\text{OH}}$  as  $1.11 \pm 0.03$  and  $1.14 \pm 0.04$  Å respectively. The  $^2\text{H}$  and  $^1\text{H}$  n.m.r. spectra of compounds labelled with  $\text{OCD}_3$  groups yield values for the quadrupole coupling constants of the C-D bonds of  $132 \pm 10$  for 3,5- and  $144 \pm 24$  kHz for 2,6-dichloroanisole.

THE shapes of anisole<sup>1</sup> and the 3,5-dichloro derivative<sup>2</sup> have been investigated by analysing  $^1\text{H}$  n.m.r. spectra of liquid crystalline solutions.<sup>3</sup> In both cases it was concluded that the molecules had coplanar carbon and oxygen atoms, and high barriers to reorientation about both C(1)-O(7) and O(7)-C(8) bonds.



These conclusions depend upon making several assumptions about the structures of the molecules, because the number of dipolar coupling constants available from analysing these spectra is insufficient to specify the structure, conformation, and orientation of the molecules in the liquid crystalline solutions. More dipolar couplings become available from molecules containing carbon-13 nuclei, and hence fewer assumptions are necessary in the interpretation of the data, and for this reason we present here the results of a study of the  $^1\text{H}$  n.m.r. spectra of 3,5-dichloroanisole labelled with  $^{13}\text{C}$  in the methyl group. We also have recorded  $^2\text{H}$  spectra of the compound with an  $\text{OCD}_3$  group, with the aim of obtaining an experimental value for the relationship between the quadrupole splitting and the magnitude of the order parameter for the three-fold axis of reorientation of the methyl group. This ratio is useful for studying the conformational preferences of methoxy groups in more complex anisole derivatives, such as the

<sup>1</sup> P. Diehl, H. Huber, A. C. Kunwar, and M. Reinhold, *Org. Magnetic Resonance*, 1977, **9**, 374.

<sup>2</sup> J. W. Emsley, J. C. Lindon, and J. M. Street, *J.C.S. Perkin II*, 1976, 805.

<sup>3</sup> J. W. Emsley and J. C. Lindon, 'N.M.R. Spectroscopy using Liquid Crystal Solvents,' Pergamon, Oxford, 1975.

liquid crystal 4,4'-dimethoxyazoxybenzene, by  $^2\text{H}$  n.m.r.<sup>4</sup>

2,3,5,6-Tetrafluoroanisole has also been studied by the n.m.r. method,<sup>5</sup> and it was concluded that reorientation about the C(1)-O(7) bond was either free, or that there are at least four positions of minima with similar magnitudes. This suggests that for 2,6-dichloroanisole the methoxy reorientation should be either free, or possibly have two-fold symmetry but with minima having the COC plane perpendicular to the aromatic ring. To test this hypothesis we have analysed the  $^1\text{H}$  and  $^2\text{H}$  n.m.r. spectra of 2,6-dichloroanisole with either a  $^{13}\text{CH}_3$  or  $\text{CD}_3$  group in the molecule.

### EXPERIMENTAL

The samples of the two dichloroanisoles labelled with  $^{13}\text{C}$  (90%) or  $\text{CD}_3$  (99%) were prepared from the reaction of the corresponding phenols with the appropriately labelled methyl iodide and potassium carbonate. The liquid crystal solvent was 4,4'-di-n-hexylazoxybenzene, and the solute concentrations were ca. 3% by weight. Such mixtures have a nematic-isotropic transition temperature of ca. 55 °C, and a nematic-smectic A transition temperature of ca. 40 °C. The samples were maintained in a nematic phase for several hours in the n.m.r. probe, slowly cooled into the smectic A phase, and left overnight before recording spectra. This procedure gives very good spectral resolution, as shown in the Figure, which compares the spectra of [ $^{13}\text{C}$ ]-2,6-dichloroanisole in nematic and smectic A phases. The partially deuteriated samples were mixed with the unlabelled anisole before dissolving in the liquid crystal, and both  $^1\text{H}$  and  $^2\text{H}$  spectra were recorded on the same sample.

All spectra were recorded by the pulse Fourier transform method using a Varian XL100 spectrometer with an external fluorine lock signal.

*Analysis of Spectra.*—The proton spectra were analysed using the iterative computer program LEQUOR.<sup>6</sup> The isotropic coupling constants,  $J_{ij}$ , were kept fixed during

<sup>4</sup> J. W. Emsley, S. K. Khoo, and G. R. Luckhurst, unpublished work.

<sup>5</sup> J. W. Emsley, J. C. Lindon, and D. S. Stephenson, *J.C.S. Perkin II*, 1975, 1794.

<sup>6</sup> P. Diehl, H. P. Kellerhals, and W. Niederberger, *J. Magnetic Resonance*, 1971, **4**, 352.

the iterations at the values given in Table 1. The  $^1J_{\text{CH}}$  values were measured from  $^{13}\text{C}$  spectra of the samples in the isotropic phase. In Table 2 we give the results of analysing the  $^1\text{H}$  spectra of mixed samples of  $\text{OCD}_3$  labelled and unlabelled compounds. The sign of the quadrupole splitting was measured relative to  $D_{\text{HD}}$  couplings by  $^1\text{H}$ - $\{^2\text{H}\}$  double resonance experiments.<sup>7</sup>

*Vibrational Averaging.*—It is now well established<sup>3</sup> that vibrational corrections to dipolar couplings may be large for  $^{13}\text{C}$ -H coupling, and for H-H coupling between groups capable of large-amplitude torsional motions.<sup>8-10</sup> We have,

dipolar couplings can be averaged only between the minimum energy forms. These conclusions are dependent on the following assumptions: (a) a value for the HH distance in the methyl group; (b) the methyl group has a three-fold symmetry axis of reorientation; (c) a value for the angle between the three-fold axis and the two-fold reorientation axis of the  $\text{OCH}_3$  group,

By introducing  $^{13}\text{C}$  into the methyl group it is possible to study the nature of the  $\text{OCH}_3$  reorientation about  $z$  separately from that of the methyl protons about their

TABLE 1

N.m.r. parameters determined from the analysis of samples of 3,5- and 2,6-dichloroanisole labelled with  $^{13}\text{C}$  in the methyl group and dissolved in a smectic A solvent

3,5-Dichloroanisole				2,6-Dichloroanisole			
$i, j$	$J_{ij}/\text{Hz}^*$	$D_{ij}/\text{Hz}$	$\delta_{ij}$	$ij$	$J_{ij}/\text{Hz}^*$	$D_{ij}/\text{Hz}$	$\delta_{ij}$
9, 11	2.0	$-265.4 \pm 0.9$	$0.63 \pm 0.30$	10, 11	8.0	$-938.5 \pm 0.3$	$0.24 \pm 0.01$
9, 13	2.0	$-21.8 \pm 1.0$		10, 12	2.0	$-198.5 \pm 0.7$	
8, 9	0.0	$-150.8 \pm 1.2$	$2.39 \pm 0.02$	8, 10	0.0	$-19.3 \pm 0.4$	
9, 14	0.0	$-566.4 \pm 0.4$		10, 14	0.0	$-65.3 \pm 0.2$	$2.69 \pm 0.01$
8, 11	0.0	$-33.5 \pm 2.0$		8, 11	0.0	$-12.7 \pm 0.7$	
11, 14	0.0	$-116.6 \pm 0.8$		11, 14	0.0	$-43.6 \pm 0.3$	
8, 14	$144.6 \pm 0.2$	$1173.7 \pm 1.0$		8, 14	$145.3 \pm 0.3$	$-668.0 \pm 0.4$	
14, 15	0.0	$1633.1 \pm 0.5$		14, 15	0.0	$-902.0 \pm 0.2$	

\* Fixed.

TABLE 2

N.m.r. parameters obtained from solutions in a smectic A solution of mixtures of  $\text{OCD}_3$  labelled, and unlabelled 3,5- and 2,6-dichloroanisoles

$^1\text{H}$ Spectrum				$^1\text{H}$ Spectrum			
2,6-Dichloroanisole				3,5-Dichloroanisole			
$i, j$	$J_{ij}/\text{Hz}^*$	$D_{ij}/\text{Hz}$	$\delta_{ij}$	$i, j$	$J_{ij}/\text{Hz}^*$	$D_{ij}$	$\delta_{ij}$
10, 11	8.0	$-943.6 \pm 0.2$	$0.24 \pm 0.01$	9, 11	2.0	$-260.2 \pm 0.9$	$0.66 \pm 0.03$
10, 12	2.0	$-203.2 \pm 0.5$		9, 13	2.0	$-28.2 \pm 1.0$	
10, 14	0.0	$-61.2 \pm 0.2$	$2.70 \pm 0.01$	9, 14	0.0	$-555.2 \pm 0.5$	$2.37 \pm 0.03$
11, 14	0.0	$-39.7 \pm 0.3$		11, 14	0.0	$-112.5 \pm 0.8$	
14, 15	0.0	$-901.1 \pm 0.2$		14, 15	0.0	$1611.6 \pm 0.5$	

$^2\text{H}$  Spectrum

$\Delta\nu/\text{Hz}$	$\Delta\nu/\text{Hz}$
$+7400 \pm 50$	$-11550 \pm 50$

\* Fixed.

therefore, included vibrational averaging into our analysis of the relationship between dipolar couplings and structure. There has not been an analysis published of the vibrational spectra of either 3,5- or 2,6-dichloroanisole, consequently we have adopted a purely theoretical approach, and have used force constants derived for anisole<sup>11</sup> and 1,3,5-trichlorobenzene<sup>12</sup> in order to calculate normal co-ordinates for the dichloroanisoles. The vibrational averaging was carried out by the method proposed by Lucas.<sup>13</sup>

## RESULTS AND DISCUSSION

*3,5-Dichloroanisole.*—In our previous study of this molecule<sup>2</sup> it was concluded that the lowest energy conformation has carbon and oxygen atoms coplanar, and that the barriers to reorientation about the C(1)-O(7) and O(7)-C(8) bonds are both large enough that

<sup>7</sup> J. W. Emsley, J. C. Lindon, J. M. Street, and G. E. Hawkes, *J.C.S. Faraday II*, 1976, 1365.

<sup>8</sup> J. W. Emsley, J. C. Lindon, and J. Tabony, *J.C.S. Faraday II*, 1975, 586.

<sup>9</sup> J. W. Emsley and J. Tabony, *J. Magnetic Resonance*, 1975, 17, 233.

three-fold axis. This arises because the averaged couplings  $D_{8,9} = D_{13,9}$  and  $D_{8,11}$  depend only on the nature of the two-fold reorientation if we assume the position of the ring protons and that methyl group reorientation does not lead to changes in these values. Assuming the phenyl ring to have all CCC and CCH angles equal to  $120^\circ$ ,  $r_{\text{OC}} 1.4$  and  $r_{\text{CH}} 1.09 \text{ \AA}$ , then the couplings  $D_{9,11} = D_{11,13}$  and  $D_{9,13}$  may be used to obtain the values of  $S_{zz}$  and  $S_{xx} - S_{yy}$ , the Saupe ordering matrix elements.<sup>3</sup> The values of  $D_{8,9}$  and  $D_{8,11}$  are then determined by the values of the bond lengths  $r_{1,7}$  and  $r_{1,8}$ , the angles C(2)C(1)O and C(1)OC(8), the nature of reorientational motion, and extra elements of the S matrix, again depending on the nature of reorientational

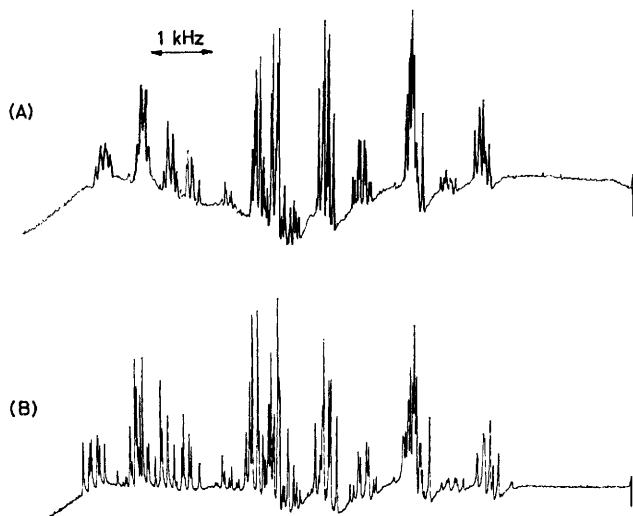
<sup>10</sup> J. W. Emsley, J. C. Lindon, D. S. Stephenson, S. Pulga, and L. Lunazzi, *J.C.S. Perkin II*, 1975, 1541.

<sup>11</sup> D. S. Stephenson, Ph.D. Thesis, University of Southampton, 1975.

<sup>12</sup> J. W. Emsley and J. C. Lindon, *J.C.S. Faraday II*, 1976, 1436.

<sup>13</sup> N. J. D. Lucas, *Mol. Phys.*, 1971, 22, 233.

motion. Clearly there are insufficient dipolar couplings to determine all these parameters and we are reduced to testing models for the structure and reorientation process. If we adopt the values  $r_{1,7}$  1.36,  $r_{7,8}$  1.42 Å, C(2)C(1)O 124.2, C(1)OC(8) 120.2°, as found by an electron diffraction study of anisole,<sup>14</sup> then the values of  $D_{8,9}$  and  $D_{8,11}$  may be used to test simple models of reorientation. Only three reorientation models may be rigorously tested: (i) interconversion between two planar forms, implying a barrier to reorientation in excess of *ca.* 12 kJ mol<sup>-1</sup>, (ii) the same as (i) but between structures with the COC plane perpendicular to the phenyl ring, and (iii) interconversion between planar and perpendicular structures of equal probability, or free rotation. The three reorientational models differ in the  $S$  elements required to relate observed to calculated values of



<sup>1</sup>H N.m.r. spectra of [*Me*-<sup>13</sup>C]2,6-dichloroanisole dissolved in (A) the nematic and (B) the smectic A phase of the mesogen 4,4'-di-n-hexylazoxybenzene

$D_{8,9}$  and  $D_{8,11}$ . In case (iii) only  $S_{zz}$  is required, (ii) requires  $S_{zz}$ ,  $S_{xx}$ — $S_{yy}$ , and  $S_{yz}$ , and (i) needs  $S_{zz}$ ,  $S_{xx}$ — $S_{yy}$ , and  $S_{xz}$ . It was found that cases (ii) and (iii) give large differences  $\Delta D_{ij}$  between observed and calculated values of  $D_{8,9}$  and  $D_{8,11}$ , which are not reduced appreciably by changing the geometrical assumptions by reasonable amounts. For case (i) the value of  $S_{zz}$  can be chosen to fit  $D_{8,11}$  exactly, in which case  $D_{8,9}$  is calculated to be *ca.* 5 Hz larger in magnitude than the observed value. However, case (i) can be made to fit the two dipolar couplings exactly by moving the <sup>13</sup>C nucleus only 0.028 Å away from the ring along the  $z$ -direction, hence we conclude that case (i) from our data, is a reasonable model. The values of the order parameters for this model are  $S_{zz}$  0.235 ± 0.012,  $S_{xx}$ — $S_{yy}$  0.267 ± 0.013,  $S_{xz}$  0.097 ± 0.001, and the angle

between  $z$  and  $z'$  a principal axis for  $S$  is 20.7 ± 0.1°, with  $z'$  rotated towards the CH<sub>3</sub> group.

Next we consider couplings within the methyl group. We assume that the methyl rotates about the O(7)—C(8) bond as a rigid rotor, and that this axis has three-fold symmetry. In this case the ratio  $R = D_{8,14}/D_{14,15}$  depends only on the structure of the methyl group, and is independent of the nature of the reorientation about the  $z$  axis, or the  $S$  values. The value of  $R$  is found to be 0.718 7 ± 0.000 7, compared with 0.883 3 for <sup>13</sup>CH<sub>3</sub>I,<sup>15</sup> and 0.686 3 ± 0.000 6 for <sup>13</sup>CH<sub>3</sub><sup>13</sup>CHO.<sup>16</sup> The ratio  $R$  depends only on the HCH angle,  $\alpha$ , and this is determined to be 109.3° without, and 109.5° with, the inclusion of the effects of vibrational averaging. Changing the vibrational wavefunction, particularly by varying the calculated, low frequency, torsional modes, has practically no effect on the derived value of  $\alpha$ , and the error in our value calculated will be dominated by the assumption of a three-fold symmetry axis. Studies by electron diffraction on anisole,<sup>14</sup> and by microwave spectroscopy on *p*-fluoroanisole<sup>17</sup> find no positive evidence for the local symmetry of the methyl group, but X-ray studies on two heterocyclic compounds<sup>18,19</sup> containing methoxy groups find considerable distortions from three-fold symmetry, hence it is probable that our result of 109.5° for  $\alpha$  is an averaged value and there could be large deviations from this value for the individual HCH angles.

A value for  $r_{CH}$  for the methyl group may be obtained if we know  $S_{33}$ , the order parameter for the three-fold symmetry axis. The value of  $S_{33}$  is related to  $S_{\alpha\beta}$  by equation (1) where  $\theta$  is the angle between the  $z$  and the

$$S_{33} = S_{xx}\sin^2\theta + S_{zz}\cos^2\theta + 2S_{xz}\sin\theta\cos\theta \quad (1)$$

three-fold axis. The value of  $\theta$  determined for anisole by electron diffraction<sup>14</sup> is 55.6°, which gives  $S_{33}$  as 0.176 ± 0.013. It was found that the value derived for  $r_{CH}$  depends strongly on the vibrational wavefunction for the molecule. Without any vibrational averaging the value of  $r_{CH}$  is found to be 1.13 ± 0.03 Å. Carrying out averaging of the dipolar couplings using a vibrational wavefunction derived by transferring force constants found appropriate for anisole and 1,3,5-trichlorobenzene gives  $r_{CH}$  1.04 ± 0.03 Å, which when compared with values determined for other methyl groups<sup>20</sup> is clearly too short by at least 0.03 Å. We next consider the methyl group to be part of a CH<sub>3</sub>X compound, with X a single, heavy atom. For convenience X was taken to be iodine as a force field has been derived for methyl iodide,<sup>21</sup> and vibrational averaging of the dipolar couplings now gave 1.11 ± 0.03 Å. The major difference between the two vibrational wavefunctions lies in the amplitudes predicted for HCH angle bends and the presence of low frequency, large amplitude HCOC

<sup>18</sup> M. Sax, R. Desiderato, and T. W. Dakin, *Acta Cryst.*, 1969, **B25**, 362.

<sup>19</sup> R. L. Harlow and S. H. Simonsen, *Acta Cryst.*, 1977, **B33**, 2662.

<sup>20</sup> W. Gordy and R. L. Cook, 'Microwave Molecular Spectroscopy,' Wiley-Interscience, New York, 1970.

<sup>21</sup> J. Aldous and I. M. Mills, *Spectrochim. Acta*, 1963, **19**, 1567.

<sup>14</sup> H. M. Seip and R. Seip, *Acta Chem. Scand.*, 1973, **27**, 4024.

<sup>15</sup> P. K. Bhattacharyya and B. P. Dailey, *Mol. Phys.*, 1973, **26**, 1379.

<sup>16</sup> J. W. Emsley, J. C. Lindon, and J. Tabony, *J.C.S. Faraday II*, 1975, 586.

<sup>17</sup> D. G. Lister and N. L. Owen, *J.C.S. Faraday II*, 1973, 1304.

torsional modes predicted by the force field derived from anisole. By increasing the appropriate force constants it is possible to obtain a corrected vibrational wavefunction for 3,5-dichloroanisole which gives the same result for  $r_{\text{CH}}$  as the methyl iodide wavefunction, and which predicts frequencies of acceptable magnitude. This new vibrational wavefunction,  $\psi_{\text{corr}}$ , in contrast to the uncorrected one,  $\psi$ , also gives an acceptable result for the calculated dipolar couplings between ring and methyl protons. Using  $\psi$  the magnitude of the calculated value of  $D_{9,14}$  assuming high barriers to reorientation about C–O and O– $^{13}\text{C}$ , is *ca.* 70 Hz too large, and this disagreement increases either by allowing for lower barriers to reorientation, or by assuming that the minimum energy positions are displaced by a small angle from the  $zx$  plane. In contrast, using  $\psi_{\text{corr}}$  gives a calculated value of  $D_{9,14}$  only 16 Hz smaller in magnitude than that observed, and which could be brought into exact agreement by allowing the methyl protons to spend some time away from the lowest energy forms. However, in view of the approximations made in calculating  $D_{9,14}$ , and the uncertainty in the vibrational wavefunction, it is not possible to attach any significance to the discrepancy between observed and calculated values of  $D_{9,14}$ .

The quadrupole splitting  $\Delta\nu$  is related to the value of  $S_{33}$  via equation (2). The quadrupole coupling constant

$$\Delta\nu = \frac{3}{2}q_{\text{CD}}S_{33}\left[\left(\frac{3}{2}\cos^2\alpha - \frac{1}{2}\right) - \frac{1}{2}\eta\sin^2\alpha\right] \quad (2)$$

$q_{\text{CD}}$  may be determined from the values of  $S_{33}$  and  $\alpha$  found, for 3,5-dichloroanisole, provided that the asymmetry parameter  $\eta$  is known. The value of  $\eta$  is often assumed zero, but may lie between the limits of *ca.*  $3 \pm 0.06$ , giving  $q_{\text{CD}}$   $132 \pm 10$  kHz. The values of  $q_{\text{CD}}$  found for deuterium in some other  $\text{CD}_3$  groups cover a range from 156 to 189 kHz,<sup>3,22</sup> so that the value found for this anisole is significantly lower. The other molecules studied are all of the type  $\text{CH}_{3-n}\text{D}_n\text{X}$ , where X is a single atom, or a similar, sterically small group. The small value found for  $q_{\text{CD}}$  for 3,5-dichloroanisole may be a consequence of the relatively long CH bond, and the sterically crowded environment.

**2,6-Dichloroanisole.**—The results will be discussed in the same manner as for the 3,5-dichloroanisole. The dipolar couplings  $D_{10,11} = D_{11,12}$ ,  $D_{10,12}$ ,  $D_{8,10} = D_{8,12}$ , and  $D_{8,11}$  enable us to choose between the three models (i)—(iii) and in this case model (ii) is the only one which closely fits the data. There have not been any other structural investigations of such a hindered anisole, and

we therefore adopt a model, regular structure with  $r_{1,7}$  1.36,  $r_{7,8}$  1.423 Å,  $\text{C}(2)\text{C}(1)\text{O} = 120^\circ = \text{C}(6)\text{C}(1)\text{O}$ , and the  $\text{C}(1)\text{—O}$  bond in the plane of the phenyl ring. Note that model (ii) cannot be distinguished from a fixed structure with the phenyl ring and the COC planes orthogonal. The order parameters were found to be  $S_{zz}$   $0.0858 \pm 0.0006$ ,  $S_{xx} - S_{yy}$   $0.355 \pm 0.001$ ,  $S_{yz}$   $0.055 \pm 0.005$ . The error in  $S_{yz}$  of  $\pm 10\%$  represents the effect of changing the COC angle  $\pm 1^\circ$ . With these  $S$  values the angle through which the axes  $xyz$  must be rotated to produce principle axes for  $S$  about  $x$  is  $9.0 \pm 0.1^\circ$  towards the methyl group.

For the methyl group the ratio  $D_{8,14}/D_{14,15}$  is  $0.7406 \pm 0.0006$ , which with the inclusion of vibrational averaging corresponds to a HCH angle of  $110.0^\circ$ . The vibrational wavefunction was obtained by using the same corrected force field as for the 3,5-dichloroanisole, and which also has a similar effect for the methyl group as using the wavefunction for methyl iodide. In order to obtain an absolute size for the methyl group it is necessary to know the value of  $S_{33}$ , and in this case it was found to be very sensitive to the choice of the COC angle. For COC  $120 \pm 1^\circ$  the value of  $S_{33}$  is found to be  $-0.10 \pm 0.01$ , and this gives  $r_{\text{CH}}$  as  $1.14 \pm 0.04$  Å. On combining the data from the two molecular fragments and assuming a high value for  $\text{CH}_3$  reorientation it is possible to calculate  $D_{10,14}$  and  $D_{11,14}$ , which are found to be only 2 and 1 Hz smaller than those observed. We conclude that the dipolar couplings for 2,6-dichloroanisole clearly show that the minimum energy configuration has the phenyl and COC planes orthogonal, but that  $r_{\text{CH}}$  cannot be precisely determined in the absence of an experimental value for the  $\text{C}(1)\text{OC}(8)$  angle.

The mixture of 2,6-dichloroanisole containing  $\text{OCH}_3$  and  $\text{OCD}_3$  groups has  $D_{14,15} - 901.1 \pm 0.2$  Hz, which is so close to the value obtained for the  $^{13}\text{C}$  labelled compound that we can state that the  $S_{33}$  values in the two compounds are equal and are  $-0.1 \pm 0.01$ , which gives  $q_{\text{CD}}$  as  $144 \pm 24$  kHz, where the large error limits reflect the uncertainties in both  $\eta$  ( $\pm 0.06$ ) and  $S_{33}$ . An alternative approach is to assume that  $q_{\text{CD}}$  for the C–D bonds in this relatively uncrowded ether should be close to 160 kHz, as found for other methyl compounds (assuming  $\eta = 0$ ).<sup>22</sup> With this value of  $q_{\text{CD}}$  and  $\alpha = 110.0$ ,  $S_{33}$  is calculated to be  $-0.090$ , which gives  $r_{\text{CH}}$  1.10 Å, and  $\text{C}(1)\text{—OC}(8)$   $121^\circ$ .

[7/1956 Received, 7th November, 1977]

<sup>22</sup> J. B. Wooten, J. Jacobus, G. B. Savitsky, and A. L. Beyerlein, *J. Chem. Phys.*, 1977, **66**, 4226.