

The Conformation of Thioanisoles studied using Nuclear Magnetic Resonance Spectra of Liquid Crystalline Solutions

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The n.m.r. spectra of [^{13}C] CH_3 thioanisole, 4-chloro[^{13}C] CH_3 thioanisole and 4-nitro[^{13}C] CH_3 thioanisole as solutes in liquid crystal solvents have been analysed. The results are used to test models of the potential function $V(\phi)$ describing the reorientation of the SCH_3 group about the phenyl-S bond. It is concluded that the molecules cannot be entirely in the forms with all the heavy atoms coplanar. The data are shown to be consistent with two models for $V(\phi)$, one with a single minimum between ϕ 0 and 90° and the other having minima of different values at ϕ 0 and 90° . The latter model, a mixture of planar and orthogonal forms, is considered to be the more probable and gives the percentage in the planar form to be between 84 and 50% for thioanisole and between 87 and 78% for 4-nitrothioanisole.

THE structure (meaning the magnitudes of bond lengths and angles) and conformations (meaning the lowest energy forms when internal motion is present) are difficult to determine for molecules in solution. There are a number of methods which are based on empirically derived relationships between structure, conformation, and spectroscopic parameters, but such methods are of doubtful precision and questionable reliability. The method which uses partially averaged dipolar coupling constants, D_{ij} , derived from the n.m.r. spectrum of samples dissolved in liquid crystalline solvents (l.c.n.m.r.) can be of high precision and if a sufficient number of D_{ij} are available, it can be highly discriminatory between different conformational models.¹ The dipolar couplings are related to structure by equation (1). The $l_{ij\alpha}$ are

$$D_{ij} = \frac{-\gamma_i\gamma_j\hbar}{8\pi^2r_{ij}^3} [S_{zz}(3l_{ijz}^2 - 1) + (S_{xx} - S_{yy})(l_{ijx}^2 - l_{ijy}^2) + 4S_{xy}l_{ijx}l_{ijy} + 4S_{xz}l_{ijx}l_{ijz} + 4S_{yz}l_{ijy}l_{ijz}] \quad (1)$$

direction cosines of the vector r_{ij} with the α axes and the $S_{\alpha\beta}$ are elements of the Saupe ordering matrix.¹ The l.c.n.m.r. method does, however, have disadvantages and it is still not certain that structure and conformational studies can be made on molecules with several modes of large amplitude, internal motion. We report here a study of thioanisoles which have two large amplitude internal modes and for which there is evidence for the coexistence of more than one conformation.

Anisole has been shown to exist predominantly in the form in which the carbon and oxygen atoms are coplanar.² There is hindered rotation of the methyl protons about the O-C bond direction and 180° flips of the phenyl group about the C(1)-C(4) axis. This implies a potential function $V(\phi)$ of the form shown in Figure 1(a), with $V(90) \gg V(0)$ (we will refer to this as structure A). The angle ϕ refers to rotation about the C(1)-C(4) axis. Thioanisole most probably has $V(\phi)$ different in form from anisole, although the evidence from physical measurements is not clear. An assignment of the vibrational spectrum of thioanisole³ and of the 4-chloro- and 4-nitro-derivatives⁴ concluded that the lowest energy form has

C_2 symmetry and is planar. A study of the molar Kerr constant and dipole moments of thioanisoles and some 4-substituted compounds⁵ concluded that $V(\phi)$ is of the form shown in Figure 1(b) (structure B) with the mini-

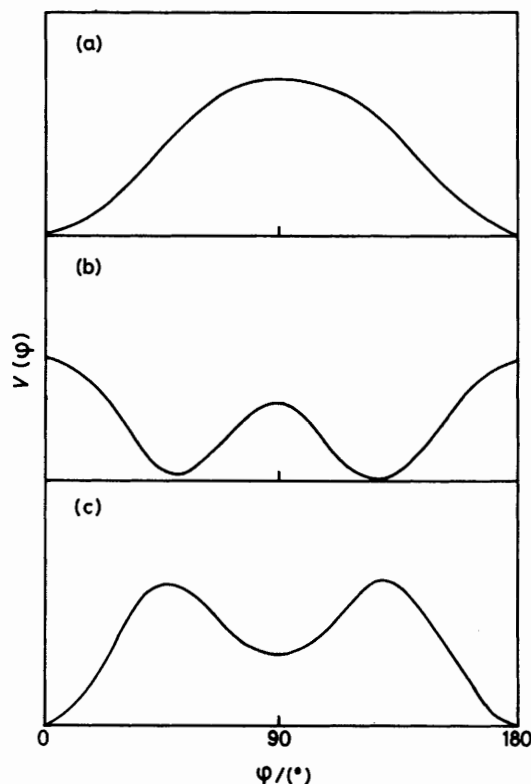


FIGURE 1 Three possible forms for the variation of the potential energy $V(\phi)$ with ϕ , the angle of rotation of the SCH_3 group about the phenyl-S bond in thioanisoles; $\phi = 0$ refers to form with all carbon and sulphur atoms coplanar

mum of $V(\phi)$ at ϕ 23° for thioanisole, $<20^\circ$ for 4-chloro- and 4-bromo-, and *ca.* 0° for 4-nitro-thioanisole. An e.s.r. study of the radical anion and a nitroxide derivative of 4-nitrothioanisole⁶ found from the magnitude and temperature dependence of hyperfine couplings to C-13 at the methyl position that structure A will explain the data,

but only if the minimum at $\phi 0^\circ$ is flat over a wide range of degrees. It was calculated that at room temperature the population of low frequency, large amplitude torsional modes gives rise to an average value for $\sin^2\phi$ about $\phi 0^\circ$ of 0.34 for (4-methylthiophenyl)triethylsilyloxy nitroxide.

The evidence from the above three techniques therefore favours planarity or near planarity for thioanisoles, but there are studies by photoelectron and microwave spectroscopy which argue convincingly for structure C [Figure 1(c) for $V(\phi)$]. The photoelectron study⁷ concluded that anisoles are planar but that for thioanisole the shape of $V(\phi)$ is that shown in Figure 1(c) (structure C) with 90% planar and 10% orthogonal forms. Similarly, a broad band microwave study of 4-fluorothioanisole⁸ concluded that structure C is correct, again with *ca.* 10% of the orthogonal form.

Finally, although the photoelectron spectrum of thiophenol⁷ was interpreted as indicating a planar molecule there has been an l.c.n.m.r. study⁹ which showed that the molecule certainly is not planar, or rather that $V(\phi)$ cannot be as in Figure 1(a) with a steep minimum at 0° . If thiophenol is non-planar it is reasonable to suppose that thioanisole will be the same.

The proton spectra of compounds like thioanisole are very complex and difficult to analyse. Replacing the *para*-proton by a non-interacting atom or group makes a major simplification of the spectra and has only a small effect on the structure. We analysed first therefore the spectra of 4-chlorothioanisole and the same compound with a CD₃ group replacing the methyl. Previous experience of similar spin systems¹⁰ suggested that such spectra could be analysed and would probably provide a basis for the analysis of the more complex spectrum of thioanisole. We also anticipated that a thioanisole molecule enriched with ¹³C at the methyl site would yield more data with which to test the form of $V(\phi)$. To simplify the spectral analysis we chose to examine spectra from 4-nitro[¹³CH₃]thioanisole, which was available from a previous e.s.r. study.⁶

EXPERIMENTAL

Thioanisole was available commercially and the synthesis of the ¹³C-labelled 4-nitrothioanisole has been described previously.⁶ The samples of 4-chlorothioanisole were synthesized by the reaction of either methyl iodide or [²H₃]methyl iodide with 4-chlorothiophenol by standard procedures.¹¹ The ¹H and ¹³C spectra were recorded on Varian XL 100 spectrometers at *ca.* 300 K. A fluorine external lock was used and 8 K of computer store for the free induction decays. The ¹H-²H experiments were carried out as described previously.¹⁰ The liquid crystal solvents used were E5, a nematic from B.D.H. Chemicals Limited, Phase IV and ZLI 1167 mixtures supplied by E. Merck (Darmstadt). The solvents chosen were those giving the best resolved spectra.

Analysis of Spectra.—The ¹H spectra of the [²H₃]-4-chlorothioanisole samples were the easiest to analyse, particularly by first analysing the proton-(deuterium) spectra. Figure 2 shows ¹H-²H, ¹H, and ²H spectra of a

sample in solution in E5. Having analysed the spectra of the deuterium-labelled compounds it was relatively easy to analyse the spectra of the 4-chlorothioanisole itself. The results for both of these compounds are shown in Tables 1 and 2. Spectra of thioanisole were recorded in several

TABLE 1

N.m.r. parameters obtained from the analyses of spectra of 4-chloro[²H₃]thioanisole in liquid crystal solvents

<i>ij</i> †	Dipolar couplings D_{ij} /Hz		Scalar couplings J_{ij} /Hz *
	E5 Solution	ZLI 1167 Solution	
9,10	-2 602.3 ± 0.1	1 591.6 ± 0.1	8.6
9,12	-19.8 ± 0.1	22.2 ± 0.1	0.4
9,13	121.9 ± 1.1	-53.6 ± 1.1	2.9
9,14	-121.7 ± 0.4	74.5 ± 0.4	0.0
10,12	123.5 ± 1.1	56.2 ± 1.1	2.4
10,14	30.1 ± 0.4	17.9 ± 0.4	0.0
Chemical shift $\delta_{9,10}$			
	E5	ZLI 1167	
	0.406 ± 0.020	-0.040 ± 0.020	
Quadrupolar splitting (Hz)			
	E5	ZLI 1167	
	-304 ± 10	±2 360 ± 10	

* Taken from T. Schaefer and W. J. E. Parr, *Can. J. Chem.*, 1977, **55**, 552, and kept fixed in the analysis. † The atomic labelling is shown in Figure 4.

TABLE 2

N.m.r. parameters obtained from the analyses of ¹H spectra of 4-chlorothioanisole in liquid crystal solvents

<i>ij</i> †	Dipolar couplings (Hz)		Scalar couplings (Hz) *
	Phase IV Solution	ZLI 1167 Solution	
9,10	-2 201.2 ± 0.1	1 591.7 ± 0.1	8.6
9,12	7.8 ± 0.1	22.0 ± 0.1	0.4
9,13	153.3 ± 0.2	-55.3 ± 0.2	2.9
9,14	-648.1 ± 0.1	481.5 ± 0.1	0.0
10,12	154.0 ± 0.2	-55.2 ± 0.2	2.4
10,14	-156.5 ± 0.1	119.0 ± 0.1	0.0
14,15	-253.9 ± 0.1	-246.7 ± 0.1	
Chemical shifts			
	Phase IV Solution	ZLI 1167 Solution	
ν_9	0.0	0.0	
ν_{10}	0.415 ± 0.004	-0.009 ± 0.002	
ν_{14}	-3.740 ± 0.003	-5.466 ± 0.003	

*, † As Table 1.

liquid crystals at different concentrations, but a successful analysis has been achieved only of the spectrum of a Phase IV solution, with the results shown in Table 3. Table 4 gives the results obtained by analysing the proton spectrum of 4-nitro[¹³CH₃]thioanisole as a solution in ZLI 1167. In this case the ¹³C spectrum was also recorded and analysed and both ¹H and ¹³C spectra are shown in Figure 3.

RESULTS AND DISCUSSION

The data in Tables 1–4 enable models for the conformation of thioanisole to be tested but it is important to note that there are insufficient data to determine uniquely the structure and conformation. It is necessary to make some assumptions about the molecular structure in order to test the less certain features of the conformation. The

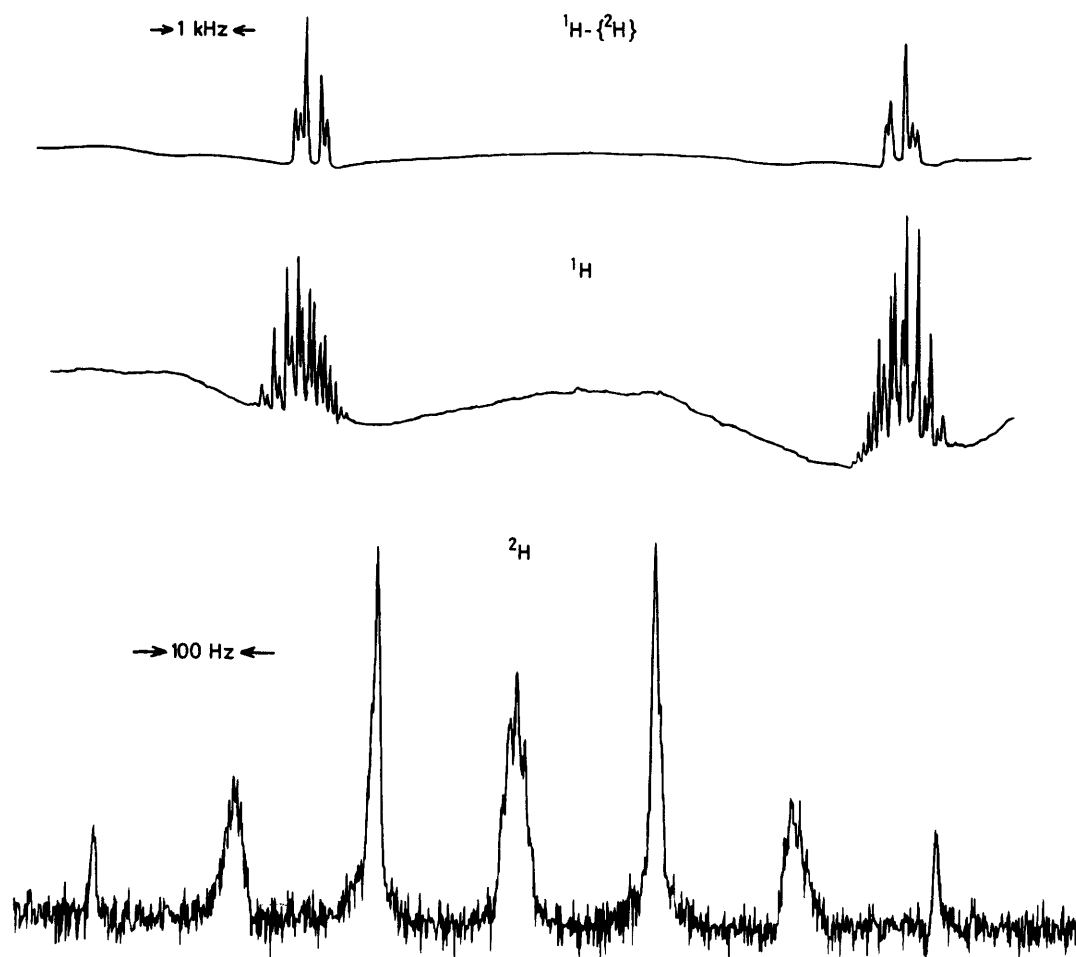


FIGURE 2 Proton-{deuterium}, proton, and deuterium spectra of 4-chloro[$^2\text{H}_3$]thioanisole dissolved in the nematic mixture E5

TABLE 3

N.m.r. parameters obtained from the analysis of the ^1H 100 MHz spectrum of thioanisole in the nematic liquid crystal Phase IV

$ij \dagger$	Dipolar coupling (Hz)	Scalar coupling (Hz) *
9,10	$-1\ 431.1 \pm 0.1$	7.8
9,11	-188.1 ± 0.2	1.2
9,12	-15.7 ± 0.1	0.6
9,13	56.9 ± 0.3	2.0
9,14	-451.9 ± 0.1	0.0
10,11	-134.9 ± 0.2	7.5
10,12	56.1 ± 0.3	1.6
10,14	-106.6 ± 0.1	0.0
11,14	-77.4 ± 0.1	0.0
14,15	96.2 ± 0.1	0.0

Chemical shifts	
ν_9	0.0
ν_{10}	0.205 ± 0.006
ν_{11}	0.338 ± 0.006
ν_{14}	-4.146 ± 0.005

* Taken from W. J. E. Parr and T. Schaefer, *J. Magn. Reson.*, 1977, **25**, 171, and kept constant in the analysis. † As Table 1.

most important assumption is that the methyl protons are related by a threefold symmetry axis.

The data in Tables 1–4 imply that the molecules can-

not be entirely in either the planar or orthogonal forms but it is not possible to distinguish between models B and C for $V(\phi)$ shown in Figure 1. To show why we reach this conclusion and also to demonstrate the strengths and limitations of the l.c.n.m.r. method we will discuss each set of data in turn.

$[^2\text{H}_3]$ -4-Chlorothioanisole and 4-Chlorothioanisole.—If the molecule exists as the planar structure A in Figure 1 then the order parameters S_{xy} and S_{yz} are zero in equation (1). Assuming the structure of the methyl group to have $r_{\text{CH}} 1.09 \text{ \AA}$ and $\widehat{\text{HCH}} 109.5^\circ$ and for there to be a threefold axis of rotation for the methyl protons leads to large discrepancies between observed and calculated dipolar couplings for *all* planar structures. The same conclusion is reached for the orthogonal form structure B with $V(\phi)$ a minimum at 90° ,⁶ for which S_{xy} and S_{xz} are zero. The data on the deuteriated sample confirm this conclusion if a value is assumed either for the quadrupolar coupling constant *or* the ratio $\Delta\nu/D_{14,15}$ as discussed by Emsley *et al.*¹⁰

The discrepancies between observed and calculated dipolar couplings for 4-chlorothioanisole are an order of magnitude larger than the effects on dipolar couplings of vibrational averaging for similar molecules, such as

anisoles;¹² however, to be sure that this is the case here we carried out the necessary averaging. There has been an assignment of the vibrational spectrum of 4-chlorothioanisole⁴ and in Table 5 we give force constants derived to give a reasonable, although not an exact, fit to the experimental frequencies shown in Table 6, using the method of Beattie *et al.*¹³ As expected vibrational averaging has a small effect on the dipolar couplings between protons and does not alter our conclusion from these data that 4-chlorothioanisole in the liquid state cannot exist exclusively in the planar or orthogonal forms. Structures B or C cannot be tested for this compound because of insufficient data.

TABLE 4

N.m.r. parameters obtained from the analysis of the ¹H spectrum of 4-nitro[¹³CH₃]thioanisole dissolved in the liquid crystal solvent ZLI 1167

<i>ij</i> †	Dipolar couplings (Hz)	Scalar couplings (Hz) *
9,10	1 569.4 ± 0.1	8.6
9,12	26.5 ± 0.1	0.4
9,13	-44.8 ± 0.3	2.9
9,14	534.0 ± 0.1	0.0
8,9	140.5 ± 0.2	0.0
10,12	-45.2 ± 0.3	2.4
10,14	120.3 ± 0.1	0.0
8,10	32.8 ± 0.3	0.0
8,14	-300.1 ± 0.1	140.1
14,15	-384.1 ± 0.1	

Chemical shifts	
<i>v</i> ₉	0.0
<i>v</i> ₁₀	-0.576
<i>v</i> ₁₄	-5.599

* Obtained from data (T. Schaefer and W. J. E. Parr, *Can. J. Chem.*, 1977, **55**, 552; J. Martin and B. P. Dailey, *J. Chem. Phys.*, 1962, **37**, 2554) for similar compounds and from the analysis of the ¹³C spectrum of 4-nitro[¹³CH₃]thioanisole in CDCl₃ solutions. † As Table 1.

Thioanisole.—Again, the data in Table 3 are inconsistent with the planar or orthogonal structures. There are now four dipolar couplings, $D_{9,14}$, $D_{10,14}$, $D_{11,14}$, and $D_{14,15}$ which are sensitive to the form of $V(\phi)$ and hence it is possible to test the two models B and C of Figure 1. To do this it is necessary, however, to place further constraints on the structure of the molecule, notably on the values of the bond lengths r_{17} and r_{78} and the α_{217} and α_{178} angles. Following the discussion of Lister *et al.*⁸ we have used r_{17} 1.78, r_{78} 1.80 Å, α_{217} 125° for planar and 120° for orthogonal or non-planar structures; α_{178} was 103°.

Both models fit the data. There are sufficient dipolar couplings to determine S_{zz} , $S_{xx} - S_{yy}$, x_9 , z_9 , x_{10} , z_{10} from the dipolar couplings within the phenyl ring. This is true for both models if it is assumed that the ring protons do not change their relative positions in the different conformational states. The non-planar model B requires that S_{xy} , S_{xz} and S_{yz} are also non-zero in equation (1) and since there are only four dipolar couplings dependent on the nature of $V(\phi)$ then there are just sufficient data to determine the $S_{\alpha\beta}$ and ϕ values which fit the data. The result is shown in Table 7 and it is seen that exact agreement is obtained with permissible values of $S_{\alpha\beta}$ and with

ϕ 41°. This model, therefore, is consistent with the n.m.r. data and hence cannot be rejected on the basis of l.c.n.m.r. alone. It is, however, not consistent with the microwave data of Lister *et al.*³ nor does it agree with their potential surface calculated by an *ab initio* molecular orbital method.

To test model C we write the dipolar couplings in the form (2) where the superscripts p and o refer to planar

$$D_{ij} = wD_{ij}^p + (1 - w)D_{ij}^o \quad (2)$$

and orthogonal forms. The values of D_{ij}^p are obtained from equation (1) with S_{zz}^p , $S_{xx}^p - S_{yy}^p$, and S_{xz}^p as the only non-zero ordering matrix elements; similarly D_{ij}^o is calculated with S_{zz}^o , $S_{xx}^o - S_{yy}^o$, and S_{yz}^o . The planar and orthogonal forms have different values of the α_{217} bond angle as noted earlier; however, the main conclusions are not affected appreciably by this structural feature.

There are six unknown quantities determining the D_{ij} , each of which is a product of the statistical weight of the isomer, w or $1 - w$, and an ordering matrix element for the individual form. The terms involving the diagonal elements of S^p and S^o are related to the diagonal elements of the average order matrix S by equations (3) and (4) and the values of S_{zz} and $S_{xx} - S_{yy}$ are those in

$$wS_{zz}^p + (1 - w)S_{zz}^o = S_{zz} \quad (3)$$

$$w(S_{xx}^p - S_{yy}^p) + (1 - w)(S_{xx}^o - S_{yy}^o) = S_{xx} - S_{yy} \quad (4)$$

Table 7. Four other equations are obtained by using equation (2) to express $D_{9,14}$, $D_{10,14}$, $D_{11,14}$, and $D_{14,15}$ in terms of the unknowns and solving the six simultaneous equations yielded the values in Table 8. The first point to note is that the values are all within the permissible range for weighted order parameters, hence the model is an acceptable one. For each value of w we can calculate the elements of S^p and S^o in their respective principal frames (*abc*). In each case *a* and *b* lie in the molecular mirror plane with *a* the closest axis to *z*. Thus *c* coincides with *y* for the planar and with *x* for the orthogonal form. Values of these principal elements are plotted against w for thioanisole in Figure 5(a) and it can be seen that w must lie between 0.27 and 0.94 corresponding to the maximum and minimum values permissible for ordering matrix elements. A comparison with the ordering matrices for anisoles^{2,12} suggests that S_{aa}^p should be greater than S_{aa}^o and hence w should be less than 0.84. It is also improbable that S_{aa}^p will be greater than about 0.3 hence more realistic limits on w are between 0.5 and 0.84. These limits are in good agreement with the value of 0.74 found by microwave spectroscopy for 4-fluorothioanisole by Lister *et al.*⁸ and the estimate of 0.90 found by photoelectron studies for thioanisole.⁷

4-Nitro[¹³CH₃]thioanisole.—The spectrum now yields sufficient dipolar couplings to test the two models B and C more critically and it is also possible to determine the ratio $r_{\text{HH}}/r_{\text{CH}}$ for the methyl group, or equivalently the HCH angle if r_{CH} is fixed. The ratio $R = D_{\text{CH}}/D_{\text{HH}}$ for

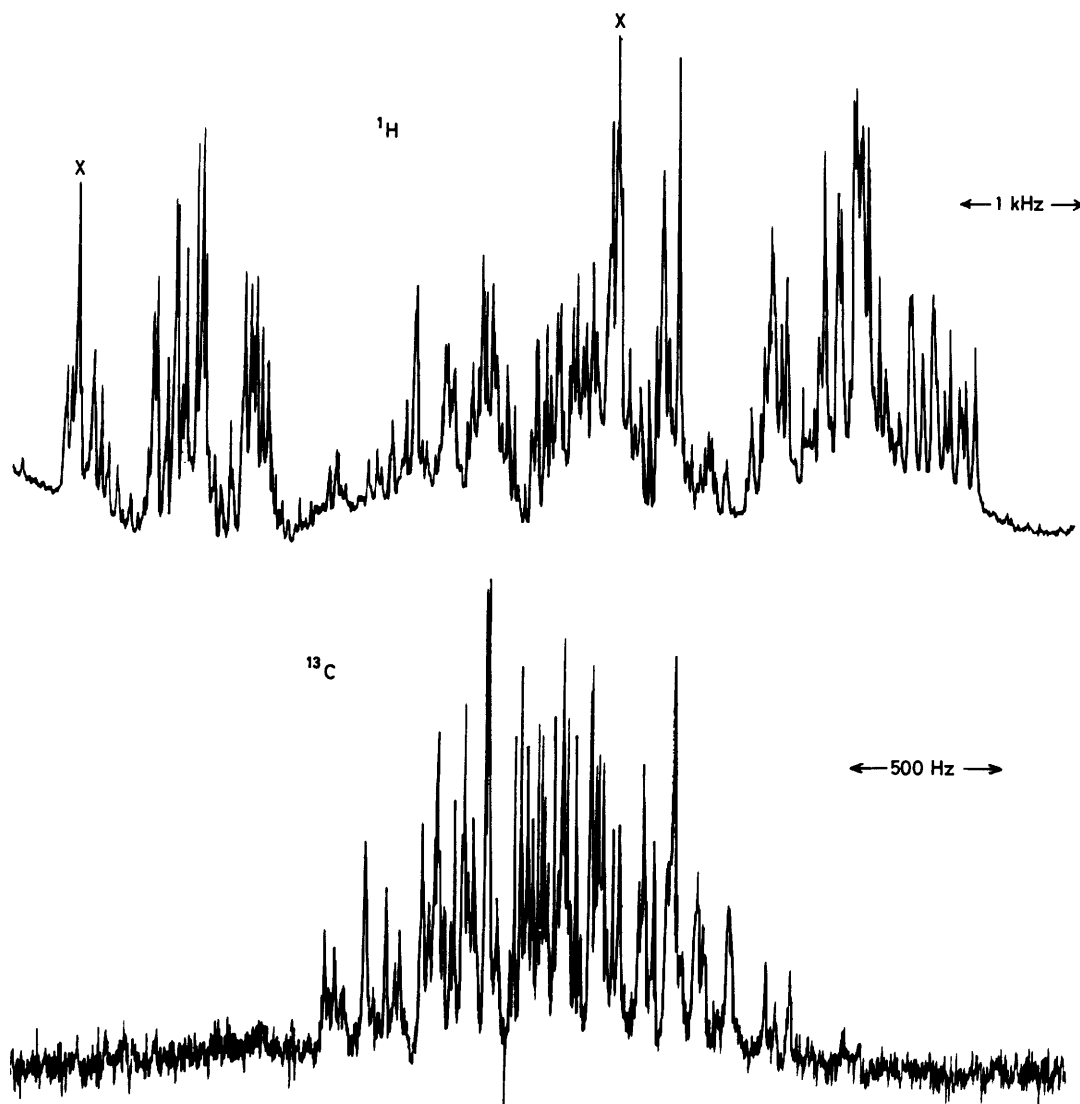


FIGURE 3 ^1H and ^{13}C spectra of 4-nitro $^{13}\text{CH}_3$ thioanisole dissolved in the liquid crystal mixture ZLI 1167

the methyl group is independent of ordering if the protons are related by a three-fold rotation axis and it is interesting to compare the value found here of 0.7815 ± 0.0005 with that obtained for other methyl compounds. For 3,5-dichloroanisole $R = 0.7187 \pm 0.0007$ and for 2,6-dichloroanisole $R = 0.7406 \pm 0.0006$.¹² These values of R are much closer to that for thioanisole than the values

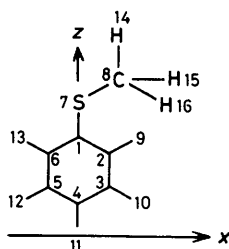


FIGURE 4 Atomic labelling and axes used to describe thioanisole

of $R = 0.6863 \pm 0.0006$ for acetaldehyde¹⁴ and 0.8833 for methyl iodide.¹⁵ Clearly, methyl groups differ structurally in these compounds but it is not possible to determine whether this arises because of changes in symmetry or changes in r_{CH} and $\widehat{\text{HCH}}$. Assuming for thioanisole that r_{CH} is 1.10 \AA , compared with $1.11 \pm 0.03 \text{ \AA}$ and 1.10 \AA determined for the dichloroanisoles,¹² gives $\widehat{\text{HCH}}$ as $111.83 \pm 0.01^\circ$ when vibrational averaging is included and $110.50 \pm 0.01^\circ$ when it is not.

Testing models B and C with the data on 4-nitrothioanisole gives the results in Tables 9 and 10. In both cases there is one extra dipolar coupling to the minimum number required to determine all the parameters of each model. In both cases, however, the models give a satisfactory fit to the data. For model B we performed a least squares fit to all the data and the small r.m.s. error allows us to conclude that the model is acceptable. For model C we used the couplings $D_{8,14}$,

TABLE 5

Internal co-ordinates and force constants used to calculate the normal co-ordinates of 4-chlororothioanisole

Number	Internal co-ordinate	Force constant *
1	r_{13}	$F_{11} = F_{22} = F_{33} = F_{44} = F_{55} = F_{66} = 7.015$
2	r_{23}	$F_{12} = F_{23} = F_{34} = F_{45} = F_{56} = F_{16} = 0.531$
3	r_{34}	$F_{13} = F_{24} = F_{35} = F_{26} = F_{15} = -0.531$
4	r_{45}	$F_{14} = F_{25} = F_{36} = 0.531$
5	r_{56}	$F_{1,24} = -F_{1,23} = F_{1,25} = -F_{1,26} = -F_{2,25} = F_{2,26} = F_{2,27} = -F_{2,28} = -F_{5,31} = F_{5,32} \left. \vphantom{F_{1,24}} \right\} = 0.3$
6	r_{16}	$= F_{3,23} = -F_{5,34} = -F_{6,33} = F_{6,34} = F_{6,23}$
7	r_{17}	$= -F_{6,24} = F_{3,28} = -F_{3,27} = F_{4,31} = F_{4,32}$
8	r_{78}	$F_{3,29} = -F_{3,30} = -F_{4,29} = F_{4,30} = -0.071$
9	$r_{8,14}$	$F_{1,22} = F_{1,17} = F_{2,17} = F_{2,18} = F_{3,18} = F_{3,19} \left. \vphantom{F_{1,22}} \right\} = 0.463$
10	$r_{8,15}$	$= F_{4,19} = F_{4,20} = F_{5,20} = F_{5,21} = F_{6,21} = F_{6,22}$
11	$r_{8,16}$	$F_{77} = 3.8$
12	$r_{2,9}$	$F_{88} = 5.0$
13	$r_{3,10}$	$F_{7,12} = F_{7,16} = 0.002$
14	$r_{4,11}$	$F_{7,15} = F_{7,13} = -0.01$
15	$r_{5,12}$	$F_{7,22} = -0.177$
16	$r_{6,13}$	$F_{8,39} = F_{8,40} = F_{8,41} = -0.4$
17	α_{123}	$F_{99} = F_{10,10} = F_{11,11} = 4.6$
18	α_{234}	$F_{9,10} = F_{9,11} = F_{10,11} = 0.05$
19	α_{345}	$F_{12,12} = F_{13,13} = F_{15,15} = F_{16,16} = 5.125$
20	α_{456}	$F_{14,14} = 3.3$
21	α_{561}	$F_{12,13} = F_{13,14} = F_{14,15} = F_{15,16} = 0.002$
22	α_{612}	$F_{12,14} = F_{13,15} = F_{14,16} = F_{15,16} = -0.01$
23	α_{617}	$F_{12,17} = F_{13,18} = F_{14,19} = F_{15,20} = F_{16,21} = -0.177$
24	α_{217}	$F_{17,17} = F_{18,18} = F_{19,19} = F_{20,20} = F_{21,21} = F_{22,22} = 1.4$
25	α_{129}	$F_{17,23} = -F_{17,27} = F_{17,23} = -F_{17,24} \left. \vphantom{F_{17,23}} \right\} = 0.04$
26	α_{259}	$= F_{18,25} = -F_{18,26} = -F_{18,29} = F_{18,30} = F_{19,27}$
27	$\alpha_{2,3,10}$	$= -F_{19,28} = -F_{19,31} = F_{19,32} = F_{20,29} = -F_{20,30}$
28	$\alpha_{4,3,10}$	$= -F_{20,33} = F_{20,34} = F_{21,31} = -F_{21,32} = -F_{21,23}$
29	$\alpha_{3,4,11}$	$= F_{21,24} = F_{22,23} = -F_{22,34} = -F_{22,25} = F_{22,26}$
30	$\alpha_{5,4,11}$	$F_{23,23} = F_{24,24} = 1.2$
31	$\alpha_{4,5,12}$	$F_{23,24} = -0.2$
32	$\alpha_{6,5,12}$	$F_{23,34} = -F_{23,25} = F_{23,26} = -F_{23,23} \left. \vphantom{F_{23,34}} \right\} = 0.007$
33	$\alpha_{6,6,13}$	$= F_{24,33} = -F_{24,34} = F_{24,35} = -F_{24,36}$
34	$\alpha_{1,6,13}$	$= F_{25,27} = -F_{25,28} = -F_{26,27} = F_{26,28}$
35	α_{178}	$= F_{31,33} = -F_{31,34} = -F_{32,33} = F_{32,34} \left. \vphantom{F_{31,33}} \right\} = -0.003$
36	$\alpha_{7,8,14}$	$F_{23,31} = -F_{23,32} = F_{23,27} = -F_{23,28} \left. \vphantom{F_{23,31}} \right\} = 0.013$
37	$\alpha_{7,8,15}$	$= F_{24,28} = -F_{24,27} = -F_{24,31} = F_{24,32}$
38	$\alpha_{7,8,16}$	$F_{24,29} = -F_{24,30} = -F_{25,29} = F_{25,30} = 0.18$
39	$\alpha_{14,8,15}$	$F_{25,25} = F_{26,26} = F_{27,27} = F_{28,28} = F_{31,31} \left. \vphantom{F_{25,25}} \right\} = 0.18$
40	$\alpha_{14,8,16}$	$= F_{32,32} = F_{33,33} = F_{34,34}$
41	$\alpha_{15,8,16}$	$F_{25,29} = -F_{25,30} = -F_{26,29} = F_{26,30} \left. \vphantom{F_{25,29}} \right\} = -0.003$
42	$\gamma_9 123$	$= F_{27,31} = -F_{27,32} = -F_{28,31} = F_{28,32} = F_{29,33}$
43	$\gamma_{10} 234$	$= -F_{29,34} = -F_{30,33} = F_{30,34} = F_{25,33} = -F_{25,34} \left. \vphantom{\gamma_{10} 234}} \right\} = -0.02$
44	$\gamma_{11} 345$	$= -F_{29,33} = -F_{30,31} = F_{30,33}$
45	$\gamma_{12} 456$	$F_{33,34} = F_{25,26} = F_{27,28} = F_{29,30} \left. \vphantom{\gamma_{12} 456}} \right\} = -0.2$
46	$\gamma_9 561$	$= F_{31,32}$
47	$\gamma_7 612$	$= F_{35,35} = 1.4$
48	$\delta_2 234$	$F_{36,36} = F_{27,27} = F_{38,38} = 0.6$
49	$\delta_3 345$	$F_{36,37} = F_{36,38} = F_{37,38} = -0.039$
50	$\delta_4 456$	$F_{39,39} = F_{40,40} = F_{41,41} = 0.4$
51	$\delta_5 561$	$F_{42,42} = F_{43,43} = F_{45,45} = F_{46,46} = 0.5$
52	$\delta_6 612$	$F_{42,43} = F_{43,44} = F_{43,45} = F_{45,46} = 0.094$
53	$\delta_8 123$	$F_{44,44} = 0.4$
54	$\delta_8 712$	$F_{47,47} = 0.4$
55	$\delta_8 716$	$F_{48,48} = F_{49,49} = F_{50,50} = F_{51,51} = F_{52,52} \left. \vphantom{\delta_8 716}} \right\} = 0.2$
56	$\delta_{14,871}$	$= F_{53,53}$
57	$\delta_{15,871}$	$F_{48,59} = F_{49,60} = F_{50,61} = F_{51,62} = 0.1$
58	$\delta_{16,871}$	$F_{52,63} = F_{53,64} = 0.01$
59	$\delta_{239,10}$	$F_{54,54} = F_{55,55} = 0.2$
60	$\delta_{10,34,11}$	$F_{56,56} = F_{57,57} = F_{58,58} = 0.3$
61	$\delta_{11,45,12}$	$F_{59,59} = F_{60,60} = F_{61,61} = F_{62,62} = 0.12$
62	$\delta_{12,56,13}$	$F_{63,63} = F_{64,64} = 0.1$
63	$\delta_{12,617}$	
64	$\delta_7 129$	

* Force constants have the units

F_{mm}	r_{ij} bond stretch	} $N m^{-1} \times 10^3$	
	α_{ijk} angle bend		
	γ_i out of plane bend		
	δ_{ijkl} torsion		
F_{mm}	$r_{ij}^{\nu} k_i$	} $N m^{-1} \times 10^3$	
	$r_{ij} \alpha_{pqr}$		} $N rad^{-1} \times 10^{-6}$
	$\alpha_{ijk} \alpha_{pqr}$		
	$\gamma_i \gamma_j$		
	$\gamma_i \delta_{jker}$		
		} $N m rad^{-2} \times 10^{-10}$	

TABLE 6

Observed and calculated frequencies for 4-chlorothioanisole

Description	Frequencies (cm ⁻¹)	
	Observed	Calculated
Methyl stretch	3 018	2 928
In plane	3 078	3 071
In plane	3 078	3 068
In plane	3 060	3 056
Methyl stretch	2 986	2 929
Methyl stretch	2 918	2 858
In plane	1 578	1 658
In plane	1 563	1 581
In plane	1 427	1 442
In plane	1 476	1 431
In plane	1 389	1 351
In plane	1 220	1 241
In plane	1 320	1 198
In plane	1 180	1 172
In plane	1 295	1 144
In plane	1 180	1 095
In plane	1 096	1 072
In plane	1 112	1 019
In plane	1 064	933
In plane	719	921
In plane	1 011	885
In plane	747	834
In plane	538	665
In plane	323	529
In plane	380	467
In plane	380	347
In plane	269	287
In plane	179	171
Out of plane	1 437	1 441
Out of plane	969	1 019
Out of plane	950	999
Out of plane	950	975
Out of plane	930	894
Out of plane	818	741
Out of plane	811	713
Out of plane	695	612
Out of plane	486	496
Out of plane	305	258
Out of plane	170	166
Out of plane	73	83

$D_{9,14}$, $D_{8,9}$, $D_{8,10}$ and the values of S_{zz} and $S_{xx} - S_{yy}$, determined from the dipolar couplings between ring protons, to derive the six parameters given in Table 10. We then used these parameters to calculate $D_{10,14}$ and obtained 122.8 Hz, compared with the experimental value of 120.3 Hz; such close agreement supports model C as an acceptable form for $V(\phi)$.

In Figure 5(b) we plot principal components of S^p and S^o against w for 4-nitrothioanisole. In order to compare the data in Figures 5(a) and (b) we have allowed for the different orientations of the magnetic field B and the

TABLE 7

Structure and ordering parameters derived for the non-planar model B for thioanisole

Nucleus	$x/\text{\AA}$	$z/\text{\AA}$
9	2.161	3.749
10	2.157	1.269
11	0.0	0.0
S_{zz}	0.1818	
$S_{xx} - S_{yy}$	0.1054	
S_{xy}	-0.0694	
S_{zz}	0.0120	
S_{yz}	-0.0356	
ϕ	41.2°	

$r_{9,10}$ was fixed as 2.481 Å.

TABLE 8

Weighted ordering matrix elements obtained for thioanisole for model C

wS_{zz}^p	0.1526
$w(S_{xx}^p - S_{yy}^p)$	0.1104
wS_{zz}^o	0.0342
$(1-w)S_{zz}^o$	0.0292
$(1-w)(S_{xx}^o - S_{yy}^o)$	-0.0050
$(1-w)S_{yz}^o$	0.0090

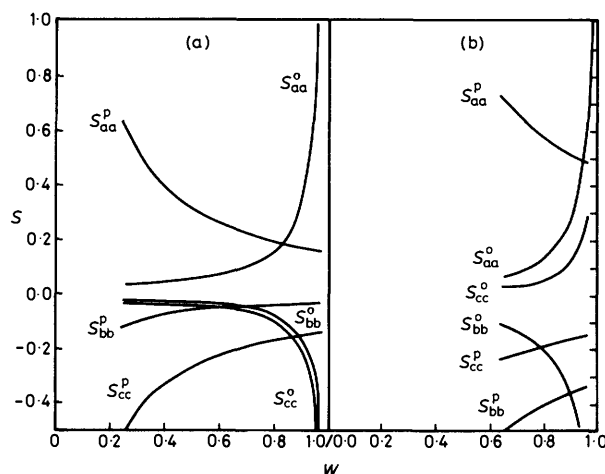


FIGURE 5 Variation of principal components of S^p and S^o with w , the fraction of the planar form, for (a) thioanisole and (b) 4-nitrothioanisole. For each isomer a and b lie in the molecular mirror plan with a closest to z , the 1,4 axis of the benzene ring (see Figure 4)

TABLE 9

Structure and ordering parameters derived for the non-planar model B of 4-nitro[¹³CH₃]thioanisole

Nucleus	$x/\text{\AA}$	$z/\text{\AA}$
9	2.152	3.718
10	2.146	1.240
S_{zz}	-0.1997	
$S_{xx} - S_{yy}$	-0.1404	
S_{xy}	-0.1574	
S_{zz}	0.1761	
S_{yz}	-0.1171	
ϕ	49.8°	

$r_{9,10}$ fixed at 2.481 Å.

TABLE 10

Weighted ordering matrix elements obtained for 4-nitro[¹³CH₃]thioanisole

wS_{zz}^p	-0.1959
$w(S_{xx}^p - S_{yy}^p)$	-0.1252
wS_{zz}^o	-0.1021
$(1-w)S_{zz}^o$	-0.0038
$(1-w)(S_{xx}^o - S_{yy}^o)$	-0.0152
$(1-w)S_{yz}^o$	0.0147

directors n of the mesophases of Phase IV and ZLI 1167. For Phase IV n and B are parallel, hence the order parameters in Table 8 refer equally to both n and B . The phase ZLI 1167 however aligns with n perpendicular to B ; hence the order parameters in Table 10, which refer to B , must be multiplied by -2 in order to refer them to n . The data in Figure 5(b) show that w must lie between 0.93 and 0.64 and that the planar form is

strongly aligned, which is in agreement with data on other 4-nitro-derivatives of benzene. However, S_{aa}^p is unlikely to be >0.6 and S_{bb}^o is unlikely to be <-0.3 , which restricts w to the range 0.78–0.87.

Conclusions.—The n.m.r. data definitely exclude the planar model A for $V(\phi)$ for these thioanisoles, but they cannot differentiate between models B and C. Considering only the n.m.r. data, therefore, gives two possible forms of $V(\phi)$ which are very different from each other. This is particularly marked for the 4-nitro-compound, which is either entirely a non-planar form with an out-of-plane angle of 49.8° or it is a mixture of planar and orthogonal forms with the planar form contributing $>78\%$ of the mixture. Clearly this result from n.m.r. is disappointing, but it is possible to consider ways of improving the ability of l.c.n.m.r. to discriminate between possible forms of $V(\phi)$. The obvious way is to obtain more experimental data, either by analysing the spectrum of the available compounds over wider ranges of temperature and concentration, or by obtaining spectra from other ^{13}C labelled species.

Combining n.m.r. data with the evidence from microwave and photoelectron spectroscopy leads us to conclude that model C is the correct form for $V(\phi)$, with the percentage of the planar form lying between 50 and 84% for thioanisole and between 78 and 87% for the 4-nitro-derivative.

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