A Study of the Structure of 4-Chlorophenyl Methyl Selenide by Nuclear Magnetic Resonance of Liquid Crystalline Solutions

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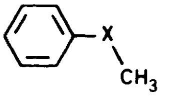
Proton and deuteron spectra of samples of 4-chlorophenyl [$^2H_3$]methyl selenide dissolved in the liquid crystal solvent E9 have been recorded. Their analysis was a first step towards analysing the proton spectrum of the non-deuteriated compound, including the satellite spectra from molecules containing 7.6% of ^{77}Se. The dipolar couplings were used to determine the two C–Se bond lengths and to test models for the rotational potential describing the relative conformation of the phenyl ring and the C–Se–C plane.

Aryl methyl ethers which are not sterically hindered, such as anisole, have structures in which the heavy atoms are coplanar.[1,2] There is, however, hindered internal rotation about the O–CH_3 and Ph–O bonds in the fluid phases, and it is the latter motion which is of most interest since it has the greater effect on the space occupied by the molecule and on the electronic structure. It is useful to describe the structure of compounds of the general type (**1**) by giving $V(\varphi)$, the variation



(**1**)

of the potential energy of the molecule with respect to φ, the angle of rotation about the ring–X bond. The four simplest forms taken by $V(\varphi)$ in such molecules are represented diagrammatically in Figure 1, and it is the principal aim of structure investigations to determine whether one of these simple forms describes the molecules in liquid or gaseous states. In a crystalline solid the molecule will usually adopt the form with the lower value of $V(\varphi)$, which would be the same structure as that in the fluid phases if $V(\varphi)$ has the form (a), (b), or (c) in Figure 1. However, if $V(\varphi)$ has at least two minima, as in (d) in Figure 1, then the structure in the solid state will correspond to the lowest value of $V(\varphi)$, whereas the molecule in a fluid phase will have a probability $P(\varphi)$ of existing with any value of φ {proportional to $\exp[-V(\varphi)/kT]$}. For barriers to rotation between minima of a few kJ mol^{-1}, the molecules essentially divide their time amongst positions where $V(\varphi)$ has minima. For barrier heights of the order of kT, the function $P(\varphi)$ has appreciable magnitude at all values of φ.

Most methods of characterizing $V(\varphi)$ in fluid phases are of an indirect nature in that the relationship between the quantity measured and molecular structure is of uncertain precision. This is particularly true of methods which seek to determine molecular structure *via* its effect on electronic wavefunctions. Photoelectron spectroscopy is such a method which is used to probe the structure, and although there are problems in relating the observed spectra to $V(\varphi)$,[3] this method does appear to be able to differentiate between the forms of $V(\varphi)$ shown in Figure 1. The best method of obtaining $V(\varphi)$ in principle is rotational spectroscopy on gaseous samples, since rotational constants are directly related to structure. However, this method is limited by the difficulty of obtaining and analysing spectra of reasonably complex molecules. The only other direct method is to analyse the n.m.r. spectrum of a sample dissolved in a liquid crystal solvent. This method yields structural information on a molecule in a liquid phase, although it is possible that the presence of long-range orientational order in liquid crystal phases, which is essential for the observation of the structure-sensitive parameters, will also contribute to changing $P(\varphi)$ from the value at the same temperature in an isotropic phase.[4,5] Such changes are yet to be fully understood and will not concern us

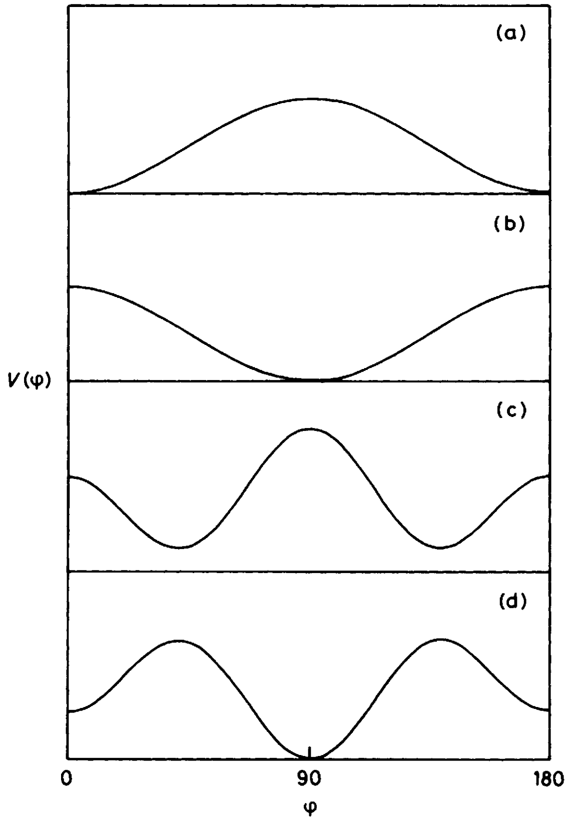


Figure 1 Variation of $V(\varphi)$, the potential energy with respect to φ, the angle between the normals to the phenyl ring and the C–Se–C plane

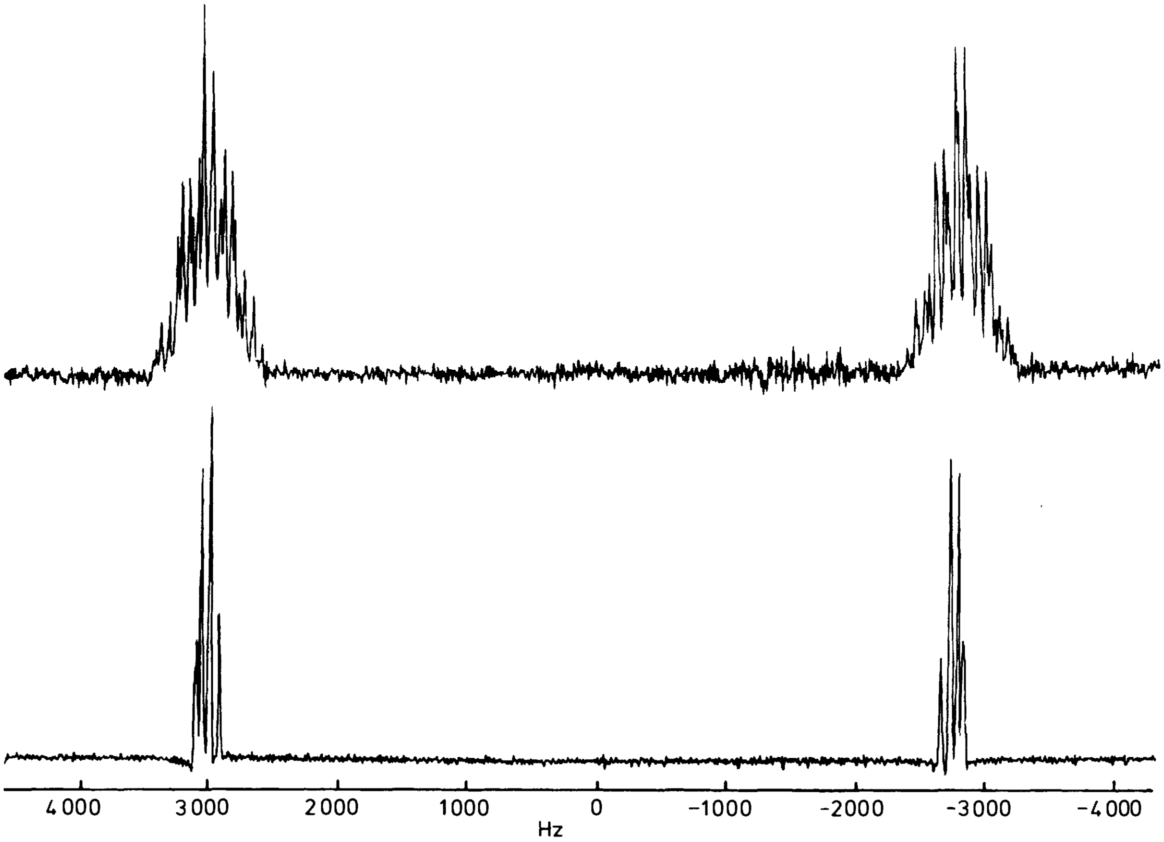


Figure 2 30.7 MHz Deuteron (upper) and deuteron-{proton} (lower) spectra of 4-chlorophenyl [$^2H_3$]methyl selenide dissolved in E9

Figure 3 200 MHz Proton spectrum of 4-chlorophenyl [$^2H_3$]methyl selenide dissolved in the liquid crystal solvent E9 shown with a spectral width of 14.7 kHz

here since our primary aim will be to show how structural information which is independent of the nature of $V(\varphi)$ can be obtained from the compound 4-chlorophenyl methyl selenide, as well as demonstrating how some of the possible forms of $V(\varphi)$ are incompatible with the spectral parameters.

The structure of phenyl methyl selenide is unknown, although a photoelectron study suggests the presence of more than one minimum in $V(\varphi)$.[6] Its study by liquid crystal n.m.r. is facilitated by the presence of 7.6% of ^{77}Se, an isotope with a nuclear spin quantum number of $\frac{1}{2}$. The satellite peaks from molecules containing the ^{77}Se nucleus are partially obscured in the proton spectrum by peaks from the more abundant molecules containing nuclei with zero spin. As we shall see, the detection of dipolar couplings between ^{77}Se and ^{1}H nuclei gives interesting structural information, and to aid in the detection of the satellite lines we chose to simplify the proton spectrum by studying the molecule with a *para*-chlorine substituent. However, even with this simplification the spectrum is still difficult to analyse, and to facilitate these processes we first recorded and analysed the proton and deuteron spectra of 4-chlorophenyl [$^2H_3$]methyl selenide.

Experimental

4-Chlorophenyl Methyl Selenide.—To Mg turnings (7.50 g, g, 0.308 g-atom) covered with dry diethyl ether was added

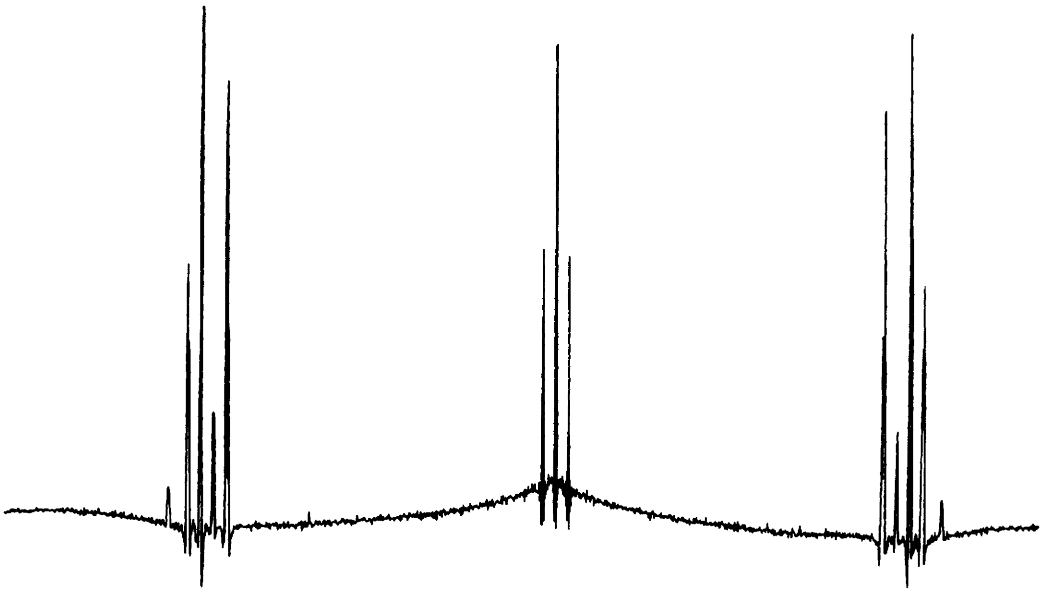


Figure 4 200 MHz Proton spin-echo spectrum of 4-chlorophenyl [$^2H_3$]methyl selenide dissolved in the liquid crystal solvent E9 shown on a spectral width of 14.7 kHz

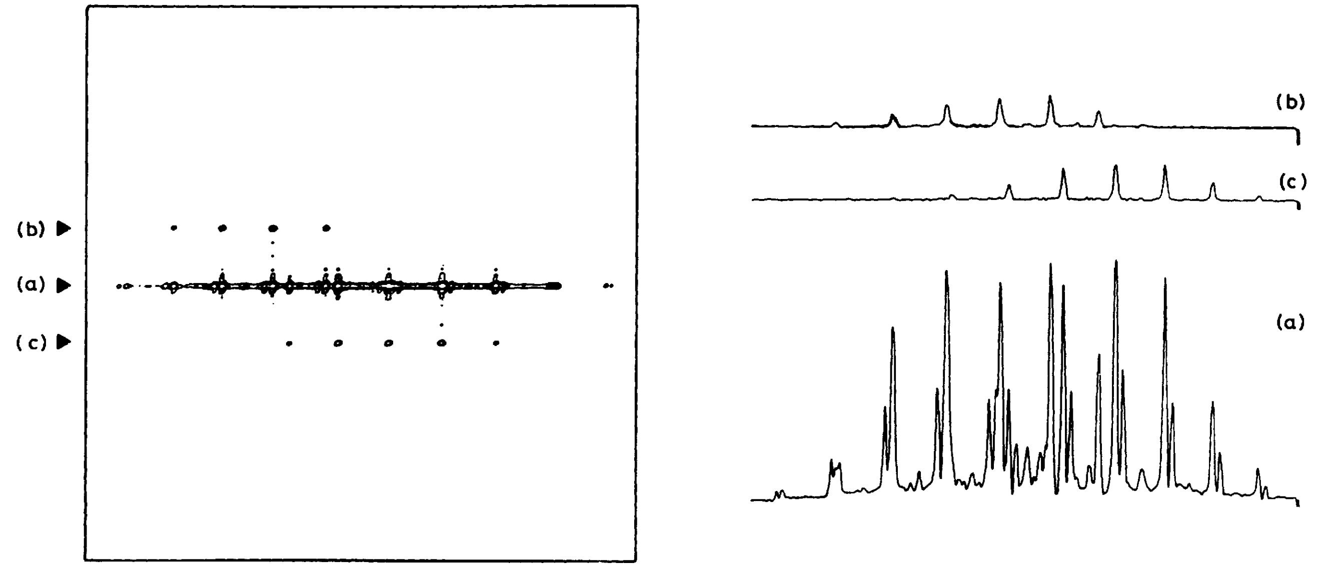
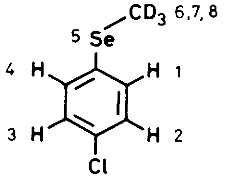


Figure 5 200 MHz Proton autocorrelation spectrum of 4-chlorophenyl [$^2H_3$]methyl selenide in the liquid crystal solvent E9. The spectral width was 2 kHz and the radio frequency pulse was centred on the middle of the group of lines at lower field in Figure 3

1-bromo-4-chlorobenzene (38.4 g, 0.2 mol) in Et_2O (300 ml) at a rate such as to maintain rapid reflux. The resultant solution was refluxed for a further 15 min. The solution of the Grignard compound was decanted from the excess of Mg and cooled to 0 °C, and Se powder (15.0 g, 1.95 g-atom) was carefully added over 20 min with vigorous stirring. The resultant solution was refluxed for 2 h, cooled to 0 °C, and hydrolysed with dilute HCl (*ca.* 200 ml). The solution was filtered and the ether layer separated; to it was added hydrogen peroxide solution (100 ml; 6% w/v) with stirring. The ether layer was again separated, and evaporated to dryness. The resulting bis-(4-chlorophenyl) diselenide was recrystallized from EtOH (300 ml), giving an orange-yellow solid (9.6 g, 21%).

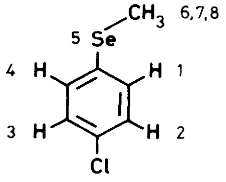
To the diselenide (4.7 g, 12.3 mmol) in ether (150 ml) was added $NaBH_4$ (1.0 g, 26.3 mmol) in EtOH (100 ml) at a rate such as to maintain gentle reflux (*ca.* 15 min). The solution was then refluxed for a further 30 min and cooled to room temperature, and iodomethane (2.4 g, 25.3 mmol) in ether (100 ml) was added at such a rate as to maintain gentle reflux (*ca.* 15 min). The solution was then refluxed for 1 h and cooled to room

Table 1. Dipolar couplings obtained from the 200 MHz proton spectrum of 4-chlorophenyl [$^2H_3$]methyl selenide dissolved in the liquid crystal solvent E9



δ_i/Hz	δ_1	0.0
	δ_2	85 ± 2
Indirect couplings J_{ij}/Hz (assumed)	12	8.0
	13	0.0
	14	2.0
	23	2.0
	16	0.0
	26	0.0
Dipolar couplings D_{ij}/Hz	12	−3 053.0 ± 0.2
	13	−7.6 ± 0.2
	14	179.5 ± 1.1
	16	−125.5 ± 0.6
	23	172.8 ± 1.1
	26	−31.9 ± 0.6

Table 2. Dipolar couplings obtained from the analysis of the 300 MHz proton spectrum of 4-chlorophenyl methyl selenide dissolved in the liquid crystal solvent E9



δ/Hz	1	0.0
	2	122.8 ± 0.3
	6	−984.0 ± 0.2
Indirect coupling constants J/Hz (from ref. 7)	12	8.6
	13	0.4
	14	2.9
	15	0.0
	16	0.0
	23	2.4
	25	0.0
	26	0.0
	56	11.26
Dipolar couplings D_{ij}/Hz	12	−3 021.66 ± 0.06
	13	−30.71 ± 0.06
	14	128.2 ± 0.1
	15	−122.1 ± 0.2
	16	−786.68 ± 0.05
	23	128.1 ± 0.1
	25	−53.1 ± 0.1
	26	−204.63 ± 0.05
	56	54.82 ± 0.07
	67	−474.95 ± 0.04

temperature, and water (100 ml) was added. The organic layer was separated and the aqueous layer extracted with ether (2 × 100 ml). The combined organic solution was evaporated, leaving an oil, which was distilled *in vacuo*; b.p. 65 °C at 0.015 mmHg. On cooling, the pure compound solidified as a yellow solid (2.6 g, 51%).

The trideuterio derivative was prepared similarly by using CD_3I at the appropriate stage.

N.m.r. Spectra.—Spectra were recorded in Southampton with a Bruker CXP 200 and in Calabria with a Bruker WM 300 instrument. Two samples were used, one containing fully protonated and the other partially deuteriated solute, dissolved (*ca.* 5% w/w) in the liquid crystal solvent E9 (B.D.H.). The ^{77}Se spectrum obtained at 38.135 MHz on the isotropic phase of the E9 solution is a 1:3:3:1 quartet, interpreted as arising from spin–spin coupling of the ^{77}Se to the methyl protons with $|J_{\text{Se–CH}_3}|$ 11.7 ± 0.5 Hz, in good agreement with a value for the same coupling found by Kalabin *et al.*[7] Spin–spin coupling to the aromatic protons was not resolved and is therefore assumed to be zero. Figure 2 shows the ^{2}H spectrum of the $^2H_3$-substituted sample and a proton-decoupled spectrum. The analysis of the ^{2}H–{^{1}H} spectrum yields a value for the quadrupolar splitting of ±5 775 ± 15 Hz, and for the dipolar coupling between the deuterons of ±16.5 ± 0.5 Hz. Figure 3 shows the proton spectrum of the $^2H_3$ sample; it consists of a superposition of seven subspectra of the type AA′BB′ and its analysis is made simple by identifying the subspectra. To do this we recorded first the 200 MHz proton spin-echo spectrum,[8] as shown in Figure 4, analysis of which yields the dipolar couplings between the ring protons. The subspectra are revealed by a two-dimensional autocorrelation spectrum which for this spin system has a particularly simple form.[9] Only two peaks in one of the two well resolved multiplets share energy levels, so that only one connection is identified for each subspectrum. This is shown in Figure 5, where we give a 200 MHz proton autocorrelation spectrum in which the spectral width was reduced so that only one of the two multiplets was observed. The cross peaks form a 1:3:6:7:6:3:1 septet with separation $2(D_{16} + D_{26})$, and this information together with the location of one peak in each of the seven subspectra greatly simplified the analysis of the spectrum and led to the data in Table 1.

The data obtained from the $^2H_3$ sample was used to predict good initial values for the dipolar couplings, which characterize the spectrum of the fully protonated sample dissolved in E9; the 300 MHz spectrum is shown in Figure 6. This spectrum has strong lines from the molecules containing Se with zero spin and weak lines from the 7.6% of molecules containing ^{77}Se. In order to detect without ambiguity the ^{77}Se satellite lines it is essential to narrow the lines from the molecules not containing this nucleus. To do this with good precision required recording the spectrum in 64 K of memory, with zero filling to 128 K, followed by a Lorentzian to Gaussian transformation. The presence of the ^{77}Se satellite lines is shown more clearly in Figure 7, where we show expansions of two selected regions of the full spectrum, together with spectra simulated for the two kinds of molecule with the data of Table 2.

Results and Discussion

In analysing the data we make the assumption that internal rotation is not accompanied by structural deformations. This is a necessary approximation since the data cannot reveal the presence of such deformations. With this approximation, there are three aspects of the structure of this compound which we can obtain from the data and which are independent of the nature of internal motion. These are the relative positions of the protons and the selenium nucleus in the fragment C_6H_5Se, and in the fragment $SeCH_3$, and the structure of the methyl group. Having first discussed these three points we will consider the conformation of the molecule, *i.e.* the evidence provided for our data on the form of $V(\varphi)$.

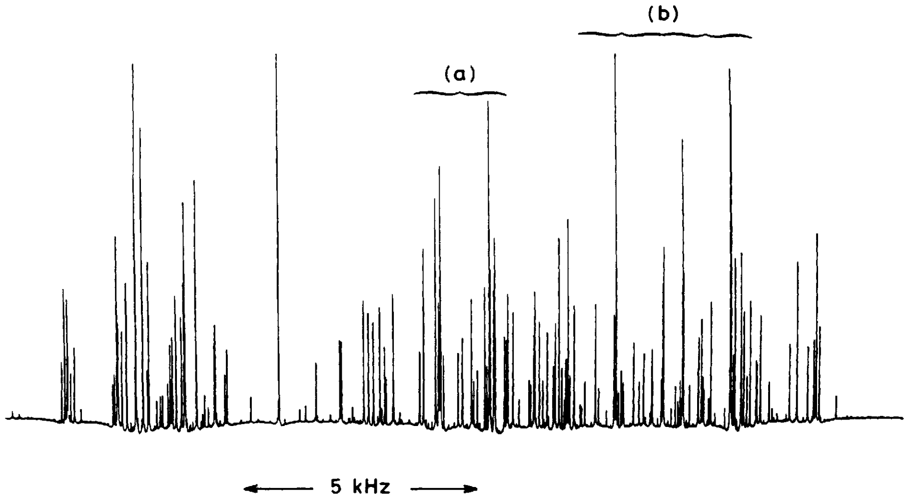


Figure 6 300 MHz Proton spectrum of 4-chlorophenyl methyl selenide dissolved in the liquid crystal solvent E9. The regions (a) and (b) are shown on an expanded scale in Figure 7

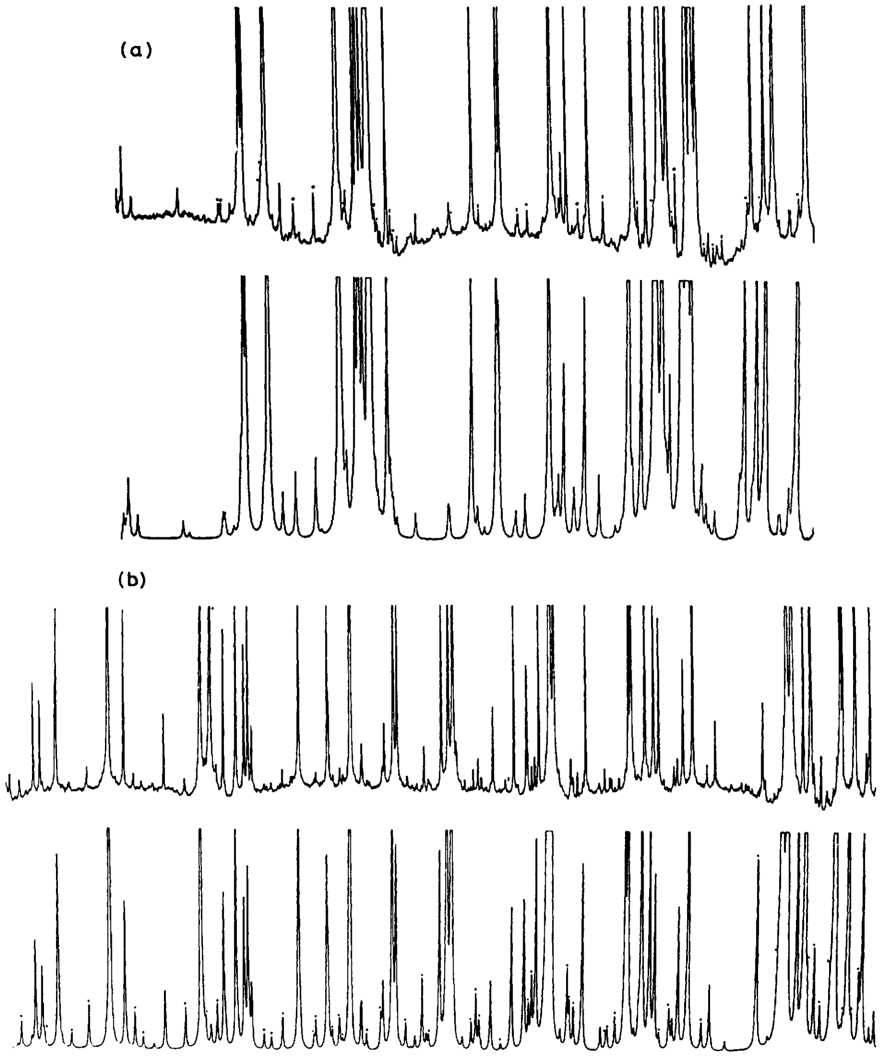
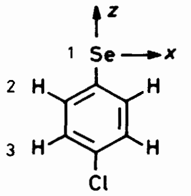
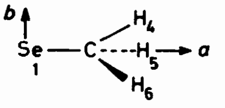


Figure 7 Expansions of the regions (a) and (b) of the proton spectrum shown in Figure 6, with the satellite lines (marked ●) from molecules containing ^{77}Se. A spectrum simulated with the parameters given in Table 2 is shown below that of the experimental spectrum for each section

Table 3. Relative positions of selenium and hydrogen atoms in the PhSe and SeMe fragments



Atom	x	z
1	0.0	0.0
2	2.153	2.113
3	2.161	4.603
S_{xx}–S_{yy}	0.219	
S_{zz}	0.391	



Atom	a	b	c
1	0.0	0.0	0.0
4	2.187	1.037	0.0
5	2.187	−0.519	0.898
6	2.187	−0.519	−0.898
S_{aa}	−0.048		

The analysis of the ^2H–$\{^1H\}$ spectrum gives D_{DD}, the dipolar coupling between deuterons in the methyl group, and the quadrupolar splitting $\Delta\tilde{\nu}$. The methyl group is reorienting rapidly about an axis which we can reasonably assume to be coincident with the Se–CD_3 bond, and which we also assume to be a three-fold symmetry axis for the methyl group. In this case $\Delta\tilde{\nu}$ and D_{DD} are related to a single-order parameter S_{33} ($\equiv S_{Se\text{–}C}$) by equations (1) and (2), so that their ratio is

$$D_{DD} = (\gamma_D^2 h/8\pi^2 r_{DD}^3)S_{33} \qquad (1)$$

$$\Delta\tilde{\nu} = \tfrac{3}{4} q_{CD} S_{33}\,(3\cos^2\alpha - 1) \qquad (2)$$

independent of S_{33} and can vary between methyl groups in different compounds according to the values of r_{DD}, the interdeuteron distance, q_{CD}, the quadrupolar coupling constant of the C–D bonds, and α, the DCD angle. The value obtained for the selenide of −338 ± 15 is to be compared with values obtained for other compounds of −330 ± 10 for a number of liquid crystals[10–12] where the CD_3 is attached to CH_2, and of −305 ± 2 (ref. 13) and −301 ± 33 (ref. 9) for some methoxy groups.

Dipolar couplings are affected by averaging over the vibrational modes; to assess the magnitude of this effect we have used a valence force field derived for 4-chlorophenyl methyl sulphide.[13] The relative positions of protons and ^{77}Se nuclei in the two rigid fragments are given in Table 3. The effect of vibrational averaging on the co-ordinates given in Table 3 is small, making changes of only 0.5 and 2% in the positions of the ^{77}Se relative to the protons in the Ph–Se and Se–Me fragments, respectively; in both fragments the effect of vibrational averaging is to increase the separation of Se and protons.

If we assume a regular hexagon structure for the phenyl ring, with sides of 1.4 Å and with r_{CH} 1.09 Å, then the C–Se bond length is determined to be 1.96 Å, in good agreement with the range 1.92—1.98 Å found for this bond in various compounds in the solid state.[14–17]. Similarly, if we assume that the methyl group has an HCH angle of 109.5° and r_{CH} 1.1 Å, then the Se–C bond length is 1.92 Å. A search of the Cambridge crystallographic database failed to locate a crystal structure involving an Se–CH_3 group.

The data in Table 2 can be used to test models (a) and (b) for $V(\varphi)$, *i.e.* a planar or orthogonal arrangement of the C–Se–C plane relative to the phenyl ring. Neither structure fits the data when the barrier to rotation is such that intermediate values of φ between 0 and 90° can be neglected, although vibrational motion about each value of φ was taken into account. Model (c) for $V(\varphi)$ can be investigated in the following way. At a fixed value of φ between 0 and 90° there are no elements of symmetry in the structure and the ordering matrix S has five independent non-zero elements for the x,y,z axes shown in Table 3. The diagonal elements can be determined from dipolar couplings within the phenyl group, leaving the three off-diagonal elements to be determined from the three dipolar couplings D_{78}, D_{16}, and D_{26}. To obtain these elements of S it is necessary to assume an angle for C–Se–C bond, and we have chosen this as 100° from comparison with values found in crystalline forms of similar compounds;[12–15] however changing this value by ±5% does not have a large effect on the calculations and does not alter our conclusion. It is found that S_{xy}, S_{xz}, and S_{yz} all lie within their limiting values of ±0.75 only when φ lies between 35 and 45°. We expect $S_{\alpha\beta}$ to be less than their maximum values, and hence we can restrict φ to values close to 40°.

Conclusion

The detection of ^{77}Se satellite lines in selenoanisole enables the Se atom to be located with respect to the protons in the molecule; this leads (with assumptions on the carbon positions) to values of C–Se bond lengths. However, in order to detect these satellite lines it was necessary to reduce the number of interacting nuclei by introducing Cl into the *para*-position. This substitution reduces the number of dipolar couplings to less than the number required to test model (d) for $V(\varphi)$. To test such a model it would be necessary to record and analyse the spectrum of phenyl methyl selenide itself and to use the data obtained from this present work to locate the Se atom. Such a study would parallel that on phenyl methyl sulphide[13] and would provide in addition a more stringent test for model (c) of $V(\varphi)$. Such studies, however, cannot be used to test models for $V(\varphi)$ in which large ranges of φ are of high probability without initial development of reliable theories as to how the elements of the ordering matrix change with φ. At this point the liquid crystal n.m.r. method of investigating structure would cease to be a purely direct method and the results would be as reliable only as the theory for predicting S. Such a method of testing the form of $V(\varphi)$ would, however, considerably improve the usefulness of the liquid crystal n.m.r. method of investigating structure.

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Received 22*nd July* 1985; *Paper* 5/1242