

Use of Subspectra of ^{77}Se in the ^1H Nuclear Magnetic Resonance Spectroscopy of Molecules partially oriented in a Nematic Mesophase. Analysis of Selenophen-2-carbaldehyde

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The 100 MHz ^1H n.m.r. spectrum of selenophen-2-carbaldehyde dissolved in a nematic mesophase was recorded and analysed. The ^{77}Se subspectrum was also used to obtain a set of ^{77}Se - ^1H anisotropic coupling constants. A theoretical force field was derived in order to take the vibrational averaging effects in the D_{ij} direct coupling calculations into account. The contribution of ^{77}Se - ^1H anisotropic indirect couplings appears to be negligible. The existence of a single Se-O *cis*-conformer was confirmed and some evidence was found for the presence of a small percentage of Se-O *trans*-conformer.

SUBSPECTRA of heteronuclei have recently been employed when carrying out ^1H n.m.r. spectroscopy on molecules partially orientated in nematic or lyotropic solvents.¹ The number of independent direct coupling constants available for geometrical determination can thus be increased without a corresponding increase in difficulty of spectral analysis.

Apart from some preliminary indications for selenophen^{2a} and 1,2,5-selenadiazole,^{2b} there are no data available for ^{77}Se even though it does not, in fact, present any particular experimental problems since its natural abundance is 7% and since there is generally only one atom present in organic molecules. However, difficulties arise when the correlation between the ^{77}Se - ^1H total anisotropic coupling constants T_{ij} and the molecular structure is concerned because the T_{ij} parameters which appear in the spin Hamiltonian (1) depend

$$H = -\sum_i \nu_i (1 - \sigma_{izz}) I_{zi} + \sum_{i < j} (J_{ij} + 2I_{ij}) I_{zi} I_{zj} + \frac{1}{2} \sum_{i < j} (J_{ij} - T_{ij}) (I_{+i} I_{-j} + I_{-i} I_{+j}) \quad (1)$$

on the dipolar direct couplings and on the anisotropic part J_{ij}^{anis} of the spin-spin indirect coupling as in equation (2). But only the dipolar direct coupling

$$T_{ij} = D_{ij} + 1/2 J_{ij}^{\text{anis}} \quad (2)$$

can be directly related to geometrical parameters as shown by equation (3) where the $\langle \dots \rangle$ denotes averaged

$$D_{ij} = -\frac{\gamma_i \gamma_j h}{8\pi^2} \langle (3 \cos^2 \theta_{ij} - 1) V_{ij}^{-3} \rangle \quad (3)$$

quantities over the molecular motions, r_{ij} is the distance between nuclei i and j , and θ_{ij} is the angle between r_{ij} and the external magnetic field.

This paper is concerned with an analysis of the ^1H spectrum of selenophen-2-carbaldehyde and its ^{77}Se subspectrum in an attempt to prove the validity of the assumption $T_{ij} = D_{ij}$ for ^{77}Se - ^1H couplings. This molecule was chosen since (i) it possesses many independent T_{ij} parameters, (ii) its ring geometry can be assumed to be like that described for selenophen,³ and (iii) its force field, which is required for vibrational averaging, can be easily derived. Moreover, previous

authors have shown that, within experimental error, the molecule exists in the Se-O *cis*-conformation.⁴

EXPERIMENTAL

Selenophen-2-carbaldehyde was synthesized as described.⁵ Solutions in Merck Phase IV nematic phase containing 10 mole % solute were used. Spectra were recorded at room temperature with a Varian XL-100-12 spectrometer in the Fourier transform mode with a ^{19}F external lock. Some thousands of transients were needed before the ^{77}Se subspectrum became clear. In order to eliminate lines due to impurities, a second spectrum was recorded using a sample that had been still further purified. All lines whose relative intensity decreased were then discarded. The spectra were analysed using our version of the LEQUOR programme modified to fit the two spectra simultaneously. The analysis was conducted in terms of four chemical shifts and ten total anisotropic couplings on the basis of 41 lines for the ^1H spectrum and 20 for the ^{77}Se subspectrum. The results are reported in the Table. It was assumed that indirect J_{ij} coupling constants were similar to those found in isotropic spectra.^{3a} The spectra are reported in Figure 2.

Vibrational Averaging.—When calculating direct dipolar coupling constants, the effect of vibrational averaging was taken into account using relationship (4).^{1a} The force

$$D_{ij} = D_{ij}^0 - \frac{h\gamma_i\gamma_j}{8\pi^2} \{ S_{zz}(2f_{ijzz} - f_{ijxx} - f_{ijyy} + (S_{xx} - S_{yy})(f_{ijxx} - f_{ijyy}) + 4S_{xy}f_{ijxy} \} \quad (4)$$

field was calculated, without further refinement, using the formyl group constants for furan-2-carbaldehyde⁶ together with force constants fitting the selenophen experimental frequencies.⁷ This procedure was preferred to that used by Aleksanyan *et al.*⁸ since it is easier to transfer valence force constants than symmetry force constants.

RESULTS AND DISCUSSION

In order to discuss the problem, it is essential that a number of geometrical and motional hypotheses be made. Nothing can be found in the literature about the geometrical microwave structure of the molecule in question. Therefore an approximate geometrical starting point was taken using the undistorted microwave structure of selenophen³ for the ring protons together with the microwave data available for the aromatic formyl group for 4-H. The angle θ in Figure 1 was

	Experimental		Calculated with vibrational averaging procedure			
	J_{ij}	T_{ij}	(1)	(2)	(3)	(4)
H(1)H(2)	5.4	256.4 ± 0.1	256.5	256.5	256.5	256.5
H(1)H(3)	1.2	3.3 ± 0.1	3.2	3.3	3.0	3.3
H(1)H(4)	1.1	-58.7 ± 0.1	-57.5		-57.6	-59.4
H(2)H(3)	3.9	-832.8 ± 0.2	-832.8	-832.9	-832.8	-832.8
H(2)H(4)	0.0	-175.5 ± 0.1	-176.2		-176.2	-175.2
H(3)H(4)	-0.2	$1\ 287.4 \pm 0.1$	-1\ 287.4		-1\ 278.4	-1\ 287.4
H(2)Se	45.7	-246.8 ± 0.4		-246.9	-247.0	-246.8
H(3)Se	7.7	-43.1 ± 0.3		-43.2	-43.9	-43.3
H(4)Se	5.2	14.4 ± 0.3		13.7	13.1	13.7
R.m.s.	8.2	-6.8 ± 0.3			-2.4	-6.1
R.m.s.		0.67_3				
XH(4)			5.71_9^a	5.69_9	5.71_5	5.69_8
YH(4)			0.80_7^a	0.80_4	0.80_7	0.84_2
XSe			2.33_2^a		2.30_5	2.30_3
YSe			-1.11_2^a		-1.18_1	-1.17_9
S_{zz}			-0.146_2	-0.146_3	-0.149_1	-0.146_2
S_{zz}			0.122_5	0.122_5	0.123_4	0.122_7
S_{xy}			-0.104_2	-0.104_2	-0.105_3	-0.104_2
R.m.s.			0.46_2	0.11_0	0.74_5	0.29_4

J_{ij} and T_{ij} are the spectral parameters used in the simulation of the 100 MHz spectrum of selenophen-2-carbaldehyde dissolved in Merck Phase IV and its ^{77}Se subspectrum ($\nu_1 - \nu_2 = -59\ 213$, $\nu_1 - \nu_3 = 10.14_5$, $\nu_1 - \nu_4 = 176.15_3$ Hz). Values in (1)–(4) are the calculated parameters (D_{ij} in Hz, optimized co-ordinates in Å): (1) proton spectrum only; (2) rigid part of the molecule; (3) complete spectrum for the 100% *cis* conformer hypothesis; (4) complete spectrum for the conformational equilibrium hypothesis, respectively. ^a Derived from microwave data, see text.

initially taken as a bisecting angle. In all calculations, the ring protons were kept invariable while the Se and 4-H geometrical parameters were varied wherever possible.

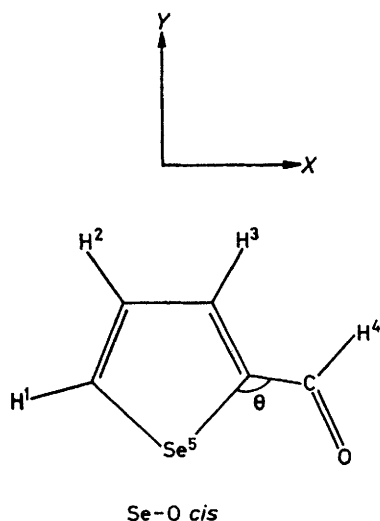


FIGURE 1 Molecular axis and atomic numbering for selenophen-2-carbaldehyde. The origin of a reference frame is on 1-H

For internal motion, a physical model was taken. The hypothesis of free rotation was discarded since it has already proved invalid for similar compounds.^{9,10} Two other possibilities were considered, that of a single planar conformer or a *cis-trans*-equilibrium.

All the calculations were performed with and without vibrational averaging procedure but no appreciable differences were found.

¹H Spectrum.—Since the six proton-proton independent T couplings available are not sufficient for the correct treatment of a possible conformational equilibrium (six independent orientational parameters, three for each conformer, would be required together with the relative percentages) we attempted to find out

whether the experimental data fitted the single conformer hypothesis.

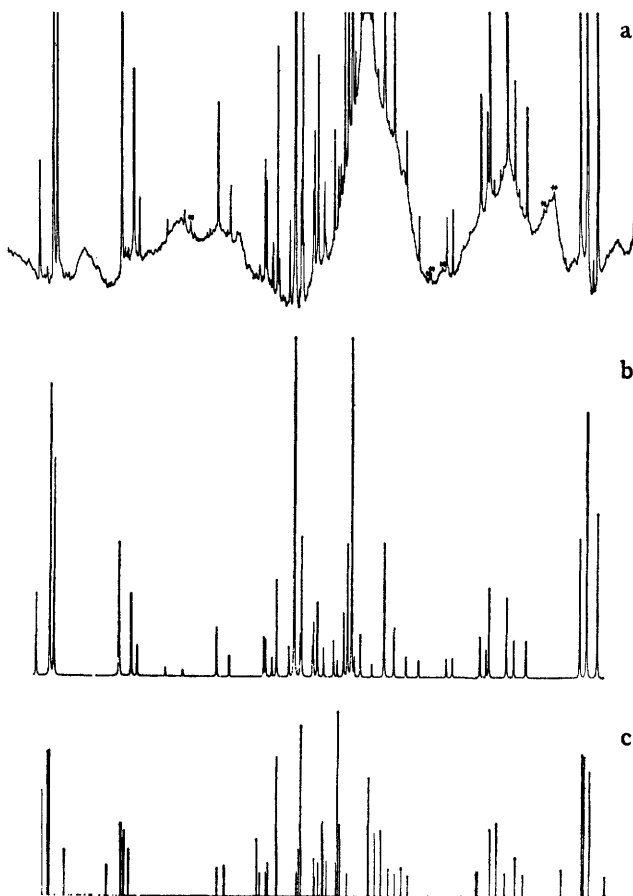


FIGURE 2 Observed, a, and calculated, b, c, 100 MHz ¹H n.m.r. spectra of selenophen-2-carbaldehyde in the nematic Merck Phase IV liquid crystal mixture. b, ¹H and c, the ⁷⁷Se subspectrum. The asterisked peaks are impurities

It was found that by varying the 4-H planar co-ordinates the data did, in fact, fit the hypothesis of an

Se-O *cis*-conformer (Table). However, it was not possible to exclude the existence of a small percentage of *trans*-conformer since the system was not sufficiently overdetermined (five unknowns for six equations) and since the position of the 4-H determined here cannot be verified by comparison with existing data.

Complete Spectrum of Rigid Part.—In order to evaluate the pseudo-dipolar contribution of Se-H couplings and thus their possible application to structural determinations, the six *T* coupling constants of the ring were fitted by varying the Se co-ordinates. The results in the Table indicate that the Se couplings can be used for structural determinations since the pseudo-dipolar contribution appears to be negligible. Moreover, the *S* matrix was like that previously found (Table) within the limits of experimental error.

Complete Spectrum.—The existence of the Se-O *cis*-conformer only appears to be confirmed by the ^1H spectrum. However, in order to gain further information, calculations were made using all ten independent T_{ij} values assuming a single conformer, optimizing both Se and 4-H (x,y) co-ordinates. The results are summarized in the Table. The resultant fit is not completely satisfactory. In fact, considering the smallness of the corresponding isotropic J_{ij} coupling, it is not possible to explain the poor fit of the Se-4-H coupling, certainly not due solely to experimental errors, purely in terms of pseudo-dipolar contribution, since the H-H and ^{77}Se -H couplings are consistent with a reasonable geometry for the rigid part of the molecule. This tends to suggest that the existence of a small percentage of Se-O *trans*-conformer cannot be excluded. In order to verify this possibility, calculations were repeated using a model which assumed an equilibrium between the two planar conformers with the hypothesis either that the two isomers have an identical *S* matrix, or have two sets of three motional parameters (one for each conformer). The single *S* matrix hypothesis is acceptable in this case since the conformers have similar geometry. What is more, it is reasonable to expect that possible errors derived from this assumption would not be determining since the percentage of *trans*-isomer present would necessarily be very small. Calculations made according to the first orientational hypothesis, assuming identical geometries for the two conformers apart from a 180° rotation about the C-C bond for the formyl proton and varying the 4-H and Se (x,y) co-ordinates, give a very good fit for all parameters with *ca.* 4% *trans*-conformer present (Table). Though the root mean square is too low when taking experimental error into account, we

still believe that the result gives an unequivocal indication of the presence of 3–4% of *trans*-conformer.

On the other hand, analysis conducted using two sets of three motional parameters, does not give satisfactory results in that the two sets differ to an unexpected degree gives the fact that the matrix of the rigid part is equal to that obtained for a single conformer and that the two conformers are very similar. This apparent contradiction can probably be explained on the basis that the *trans*-conformer is present in low proportion and therefore, small errors might induce large variations on the optimized *trans*-conformer motional constants. When our results are compared with those obtained for similar aldehydes the ordering matrices of selenophen-, furan-, and thiophen-2-carbaldehydes are very similar. Thus for this type of molecule, the use of a single set of orientational constants seems satisfactory, even when conformational equilibrium occur. We therefore conclude that the ^{77}Se direct couplings can be used for structural determinations (as the pseudo-dipolar contribution to Se-H couplings is negligible) and that they may be extremely useful when there are not enough proton parameters to solve more complex conformational problems.

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