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ON THE APPLICATIONS OF MIXED LIQUID CRYSTALS OF OPPOSITE DIAMAGNETIC ANISOTROPIES TO ORGANOMETALLIC SYSTEMS; NMR SPECTRA OF ORIENTED PHENYLSELENYL BROMIDE

N. SURYA PRAKASH

Indian Institute of Science, Bangalore 560012 (India)

A.C. KUNWAR and C.L. KHETRAPAL

Raman Research Institute, Bangalore 560080 (India)

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Summary

NMR spectra of molecules oriented in mixed liquid crystals of opposite diamagnetic anisotropies, which permit the unique evaluation of the heteronuclear direct and indirect spin–spin couplings separately, have been used to determine the $^{1}H-^{77}Se$ coupling constants in phenylselenyl bromide. The derived direct dipolar couplings have been used to determine molecular geometry.

Introduction

NMR spectra of molecules oriented in mixed liquid crystals of opposite diamagnetic anisotropies provide unique novel applications [1,2]. Of these, the most important for organometallic compounds containing a spin 1/2 metal atom, is the one which permits the determination of the spectral parameters which cannot otherwise be obtained from the spectra of oriented molecules.

The natural abundance of the spin 1/2 ^{77}Se nucleus is nearly 7.6%. The proton spectra of organoselenium compounds including $^{1}H-^{77}Se$ satellites oriented in liquid crystal(s) of either positive or negative diamagnetic anisotropies, provide the sum $(J(HSe) + 2D(HSe))$ where $J(HSe)$ and $D(HSe)$ are the indirect spin–spin and the direct dipolar coupling constants, respectively. However, when the spectra are obtained in mixed liquid crystals of opposite diamagnetic anisotropies, at a critical temperature and concentration, the spectra due to both of the two orientations, in which the liquid crystal molecules align preferentially with the optic axes along and perpendicular to the applied magnetic field, appear [1,2]. The dipolar couplings in the two orientations differ by a factor of two and have opposite signs, whereas the indirect couplings remain unchanged. The experiment at the critical point where

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both the orientations coexist thus provides $J(\mathrm{HSe}) + 2D(\mathrm{HSe})$ and $J(\mathrm{HSe}) - D(\mathrm{HSe})$ where $D(\mathrm{HSe})$ is the $^1\mathrm{H}-^{77}\mathrm{Se}$ direct dipolar coupling corresponding to the orientation of the liquid crystal molecules with their optic axis aligned along the magnetic field direction. The two quantities, namely $J(\mathrm{HSe}) + 2D(\mathrm{HSe})$ and $J(\mathrm{HSe}) - D(\mathrm{HSe})$ then yield $J(\mathrm{HSe})$ and $D(\mathrm{HSe})$ separately, information which cannot be derived in any other way from the spectra of oriented molecules. Such studies on phenyl selenyl bromide have been undertaken and the results are presented. The derived dipolar couplings have been used to determine the molecular shape.

Experimental

About 7 and 5 wt.% solutions (referred to as A and B hereafter) of commercially available phenylselenyl bromide were prepared in Merck Phase IV and Merck ZLI-1167, respectively. The solutions A and B were mixed in the weight ratio of 0.3/1. The proton NMR spectra were recorded on a Bruker WH-270 spectrometer at 312, 313 and 315 K as shown in Fig. 1. 224 free induction decays were accumulated and Fourier transformed with the help of a BNC-12 computer with a core memory of 20 K.

Figure 1 shows that at 313 K the spectra due to both the orientations are observed. The spectra above and below this temperature correspond to those due to the orientations corresponding to the solvent with positive (Phase IV-like) and negative (ZLI-1167 like) diamagnetic anisotropies respectively.

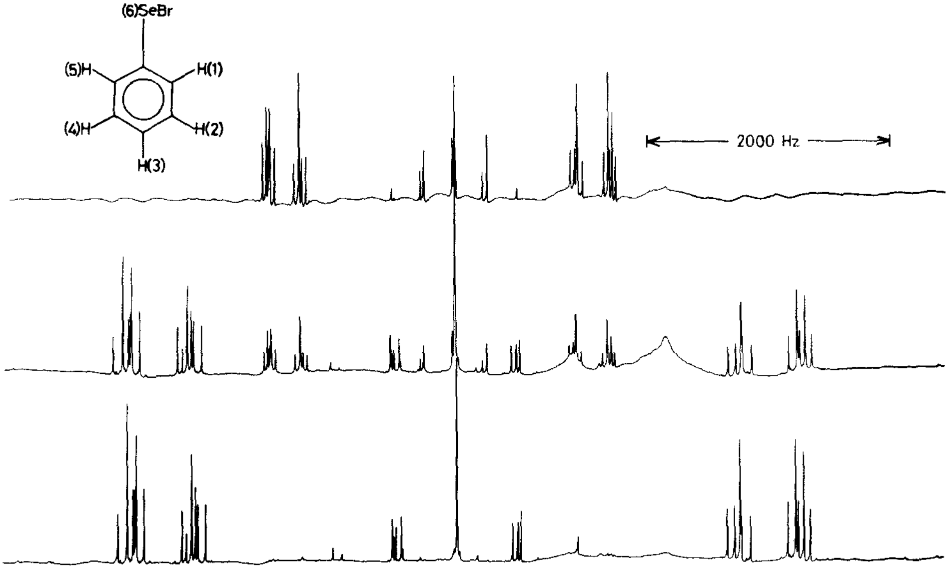

Fig. 1. Proton NMR spectra of phenylselenyl bromide oriented in a mixture of phase IV and ZLI-1167. Experimental details are given in the text. Top, central and bottom traces are at 312, 313 and 315 K respectively.

Spectral analysis

The analysis of the spectra was carried out iteratively using the LAOCOONOR programme [3] on a DEC-10 computer. The spectra including the ^1H–^{77}Se-satellites were analysed separately for the two types of coexisting molecular orientations. The indirect HH couplings (i.e., the homonuclear indirect couplings) were not varied during the analysis, and were given the same values as those for phenylselenyl chloride [4]. The chemical shifts (ν_i–ν_j) and the direct dipolar couplings (D_{ij}'s) were iterated upon. 41 lines were assigned to a root-mean-square (r.m.s.) error of 0.7 Hz for the orientation of the Phase IV type and 31 to an r.m.s. error of 0.8 Hz for the ZLI-1167 type of orientation. It was found that the precision of individual determination of D_{13}, D_{23}, D_{15}, D_{24}, D_{16} and D_{26} was low, but the sums ($D_{13} + D_{23}$), ($D_{15} + D_{24}$) and ($D_{16} + D_{26}$) could be determined precisely and, so these were used as the parameters for the iterative analyses rather than the individual coupling constants.

As is usual, each spectrum was sensitive to the sum ($J_{ij} + 2D_{ij}$) when *i* and *j* were heteronuclei, i.e., ^1H and ^{77}Se. Consequently, from each spectrum D_{12}, $D_{13} + D_{23}$, D_{14}, $D_{15} + D_{24}$, $J_{16} + J_{26} + 2(D_{16} + D_{26})$, $(J_{36} + 2D_{36})$, ν_1–ν_2, and ν_1–ν_3 were derived. The values are listed in Table 1.

Results and discussion

Table 1 shows that when both types of orientation are present, the observed dipolar couplings, namely, d_{12}, $D_{13} + D_{23}$, D_{14} and $D_{15} + D_{24}$, in the Phase IV orientation are within experimental error twice as large as those in the ZLI-1167 type of orientation and of opposite sign. Similar observations have also been made earlier [1,2], and have been interpreted theoretically [5,6]. This result has been used to separately evaluate ($J_{16} = J_{26}$) and ($D_{16} + D_{26}$), since the experiments at each orientation provide $[J_{16} + J_{26} + 2(D_{16} + D_{26})]$ and $[J_{16} + J_{26} - (D_{16} + D_{26})]$ where D_{16} and D_{26} are the ^1H–^{77}Se direct dipolar couplings for the Phase IV type of orientation. In the like manner, J_{36} is estimated to be negligible.

TABLE 1

SPECTRAL PARAMETERS FOR PHENYLSELENYL BROMIDE ORIENTED IN A MIXTURE OF PHASE IV AND ZLI-1167 WHEN THE SPECTRA DUE TO BOTH THE TYPES OF ORIENTATIONS COEXIST

Parameter [a]	Value (Hz)	
	Phase IV type orientation	ZLI-1167 type orientation
D_{12}	-1648.8 ± 0.2	824.3 ± 0.2
$D_{13} + D_{23}$	-526.2 ± 0.2	262.9 ± 0.2
D_{14}	$-39.1 \pm 0..3$	19.5 ± 0.3
$D_{15} + D_{24}$	56.4 ± 0.3	-28.7 ± 0.3
$(J_{16} + J_{26}) + 2(D_{16} + D_{26})$	-209.4 ± 0.2	109.3 ± 0.3
$J_{36} + 2D_{36}$	-49.2 ± 0.4	24.8 ± 0.4
$\nu_1 - \nu_2$ [b]	-42.8 ± 0.4	-155.5 ± 0.4
$\nu_1 - \nu_3$ [b]	67.4 ± 0.4	-204.8 ± 0.5

[a] *J* values used: $J_{12} = 8.1$, $J_{13} = 1.1$, $J_{14} = 0.5$; $J_{24} + J_{15} = 2.6$, $J_{23} = 7.8$ Hz [4]. [b] At 270 MHz.

TABLE 2

GEOMETRICAL PARAMETERS FOR PHENYLSELENYL BROMIDE

Parameter [a]	Value
r_{12}/r_{24}	0.585 ± 0.005 (0.577) [b]
r_{13}/r_{24}	0.997 ± 0.012 (1.000) [b]
r_{15}/r_{24}	1.018 ± 0.012 (1.000) [b]
r_{16}/r_{24}	0.720 ± 0.010

[a] The parameters in Phase IV and ZLI-1167 are similar within experimental error. [b] Regular hexagonal values.

Having determined the indirect spin–spin and the direct dipolar couplings individually, the quantities D_{12}, $D_{13} + D_{23}$, D_{14}, $D_{15} + D_{24}$, $D_{16} + D_{26}$ and D_{36} were used to determine the relative HH and HSe (r_{ij}'s) distances and the molecular order.

The phenylselenyl moiety of the molecule has a C_{2v} symmetry, and hence the 4 HH and HSe distance ratios define the relative proton and the selenium positions. Two independent order parameters specify the molecular orientation. The system can, therefore, be fully defined by evaluation of the relative HH and HSe distances and the order parameters from the experimentally obtained dipolar couplings. The derived values of the geometrical parameters obtained by solving the simultaneous equations relating these dipolar couplings and the necessary geometrical and the order parameters are reported in Table 2.

Table 2 shows that for the phenyl ring, there are deviations outside experimental error from the regular hexagonal arrangement.

Conclusion

The experiments clearly demonstrate the use of mixed liquid crystals of opposite diamagnetic anisotropies in determining the spectral parameters (such as the individual determination of the indirect spin–spin and direct dipolar couplings between heteronuclei) which otherwise cannot be determined. Such studies can be important for organometallic compounds in determining the relative positions of the metal atoms.

References

1 C.L. Khetrapal and A.C. Kunwar, Mol. Cryst. Liq. Cryst., 72 (1981) 13.
2 C.L. Khetrapal and A.C. Kunwar, Chem. Phys. Lett., 80 (1981) 170.
3 P. Diehl, C.L. Khetrapal and H.P. Kellerhals, Mol. Phys., 15 (1968) 333.
4 N. Suryaprakash, A.C. Kunwar and C.L. Khetrapal, J. Mag. Res., submitted.
5 K.P. Sinha, R. Subburam and C.L. Khetrapal, Mol. Cryst. Liq. Cryst., in the press.
6 K.P. Sinha, R. Subburam and C.L. Khetrapal, Chem. Phys. Lett., in the press.