Journal of Organometallic Chemistry, 277 (1984) 359–363
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SOLVENT EFFECTS ON THE STRUCTURE OF BENZO[*b*]SELENOPHENE ORIENTED IN LIQUID CRYSTALS

N. SURYAPRAKASH, S. RAGHOTHAMA, C.L. KHETRAPAL *
Indian Institute of Science, Bangalore 560012 (India)

A.C. KUNWAR
Raman Research Institute, Bangalore 560080 (India)

M. BAIWIR and G. LLABRES
Institute De Physique, Universite de Liege (Belgium)

(Received June 29th, 1984)

Summary

Proton magnetic resonance spectra of benzo[*b*]selenophene including ^{77}Se satellites have been investigated in thermotropic liquid crystal solvents. Relative proton–proton and proton–selenium distances have been derived from the dipolar couplings. A comparison of the results on benzo[b]-furan, -thiophene and -selenophene and the application of bond polarisation hypothesis indicate significant solvent effects in the liquid crystal formed by an eutectic ternary mixture of propyl-pentyl- and heptyl-bicyclohexylcarbonitrile.

Introduction

There has recently been much interest in the study of solvent effects on the molecular structure derived from studies in nematic solvents [1–6]. The observed solvent effects on the molecular structure of diazines such as pyridazine [7] and phthalazine [8] have been interpreted in terms of hydrogen bonding involving the nitrogens of the solute and water of the lyotropic mesophase. The solvent ZLI-1167 (an eutectic ternary mixture of propylpentyl- and heptyl-bicyclohexylcarbonitrile) has been shown to exhibit smaller effects [2] than thermotropic solvents containing aromatic rings, and also to show larger distortions [3]. The use of mixed liquid crystals of opposite diamagnetic anisotropies around the critical point where macroscopic diamagnetic anisotropy nearly vanishes has in general been found to lead to minimal solvent effects [1,9]. We describe below a proton magnetic resonance study of benzo[*b*]selenophene including ^{77}Se satellites in: (a) a mixture of 65 mol%

0022-328X/84/$03.00

p-n-butyl-*p*′-methoxyazoxybenzene and 35 mol% *p*-ethyl-*p*′-methoxyazoxybenzene (Merck phase V) and (b) ZLI-1167. A comparison of the results with those obtained from studies without ^{77}Se–H satellites in a lyotropic phase [10], the data on benzo[*b*]-furan [11] and -thiophene [12] and the bond polarisation hypothesis [13] are in accord with larger distortions in this system when the solvent is ZLI-1167.

Experimental

The proton magnetic resonance spectra of nearly 4.5 weight% solutions of benzo[*b*]selenophene were investigated in Merck phase V and ZLI-1167 on a Bruker WH-270 FT-NMR spectrometer. 940 Free-Induction-Decays (FID's) for the solution in ZLI-1167 and 240 FID's in the Merck phase V solvent were accumulated, and Fourier transformed with the help of a BNC-12 computer using 16k data points. The spectra were recorded at 21°C. A typical spectrum in ZLI-1167 is shown in Fig. 1. The average line width was 4 Hz.

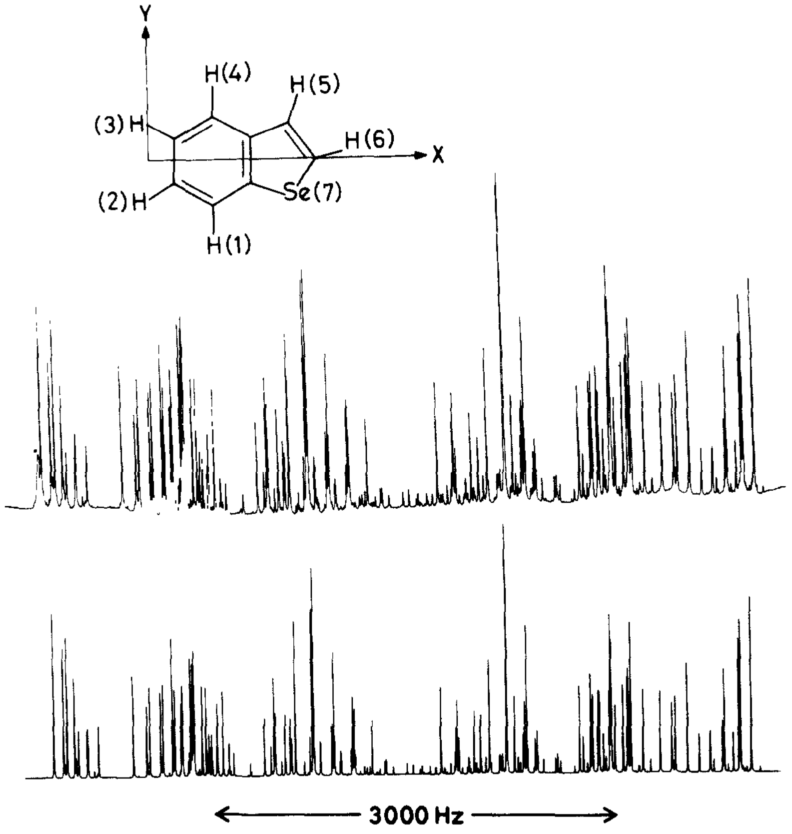

Fig. 1. Proton magnetic resonance spectra of benzo[*b*]selenophene oriented in ZLI-1167. Observed spectrum (upper trace), calculated spectrum (lower trace). Concentration: 4.5 weight%. Temperature: 21°C. Number of Scans: 940. Spectrometer: WH-270.

Spectral analysis

The spectra were analysed using the LAOCOONOR program [14] on a DEC-1090 computer. The analysis was first carried out for the 6-spin sub-spectra of the type ABCDEF corresponding to the species without the ^{77}Se–H satellites.

The number of lines fitted was 248 in the ZLI-1167 solution and 229 in Merck phase V; the root-mean-square (rms) error between the calculated and the observed line positions was 0.42 Hz in both cases. In each case, the direct dipolar couplings (D_{ij}'s) and the chemical shifts ($\nu_i - \nu_j$) between the interacting nuclei i and j were iterated. The indirect spin–spin couplings (J_{ij}'s) used were determined separately from the spectrum in an isotropic medium and they are included in Table 1 along with other parameters. In the spectra with ^{77}Se–^{1}H satellites, 93 lines were assigned for the ZLI-1167 solution and 73 for that in phase V; the spectra were analysed as ABCDEFX types where X is selenium-77 (with spin $(I) = 1/2$ and a natural abundance of 7.6%). In these cases J_{ij}'s were not iterated but the values reported in Table 1 were used. The HH dipolar couplings and the chemical shifts with rms errors of 0.43 and 0.35 Hz between the observed and calculated line positions for the ZLI-1167 and Merck phase V solutions derived from the 7-spin spectra were similar (within experimental error) to the corresponding values obtained from the spectra without the ^{77}Se–^{1}H satellites. They are shown in Table 1.

Results and discussion

The structure of the 7-spin system in benzo[*b*]selenophene with 6 protons and a selenium atom lying in a plane can be specified by 10 relative internuclear distances, and the planar molecule needs 3 parameters to define its orientation. The system

TABLE 1

SPECTRAL PARAMETERS[a] (at 270 MHz) IN BENZO[*b*]SELENOPHENE ORIENTED IN MERCK PHASE V AND ZLI-1167 (The numbering of nuclei corresponds to that given in Fig. 1)

Parameter	Value (Hz)		Parameter	Value (Hz)	
	Merck V	ZLI-1167		Merck V	ZLI-1167
D_{12}	−1098.22 ± 0.05	1050.49 ± 0.34	D_{36}	−67.48 ± 0.11	63.41 ± 0.08
D_{13}	−67.34 ± 0.23	88.65 ± 0.28	D_{37}	−17.37 ± 0.14	17.70 ± 0.14
D_{14}	16.69 ± 0.24	13.16 ± 0.39	D_{45}	−1030.68 ± 0.16	969.77 ± 0.17
D_{15}	−8.79 ± 0.24	28.07 ± 0.26	D_{46}	−150.72 ± 0.39	143.38 ± 0.22
D_{16}	−69.05 ± 0.20	76.61 ± 0.27	D_{47}	−13.85 ± 0.23	14.45 ± 0.17
D_{17}	−100.09 ± 0.33	103.88 ± 0.54	D_{56}	−695.03 ± 0.55	700.98 ± 0.24
D_{23}	137.63 ± 0.26	94.29 ± 0.25	D_{57}	5.23 ± 0.26	6.04 ± 0.18
D_{24}	−20.11 ± 0.28	61.63 ± 0.34	D_{67}	−58.83 ± 0.15	86.12 ± 0.14
D_{25}	−48.07 ± 0.22	55.48 ± 0.25	$\nu_1 - \nu_2$	−47.43 ± 0.49	−292.23 ± 2.8
D_{26}	−52.61 ± 0.19	52.89 ± 0.25	$\nu_1 - \nu_3$	−11.26 ± 0.39	−285.34 ± 1.95
D_{27}	−28.26 ± 0.34	29.76 ± 0.51	$\nu_1 - \nu_4$	21.88 ± 0.44	−88.75 ± 1.96
D_{34}	−847.41 ± 0.62	902.87 ± 0.37	$\nu_1 - \nu_5$	52.75 ± 0.46	−236.96 ± 1.96
D_{35}	−151.82 ± 0.49	146.92 ± 0.25	$\nu_1 - \nu_6$	189.12 ± 0.40	−117.41 ± 1.95

[a] J values used: $J_{12} = 7.96$, $J_{13} = 1.04$, $J_{14} = 0.53$, $J_{15} = 0.70$, $J_{16} = 0.09$, $J_{17} = 0.00$, $J_{23} = 7.01$, $J_{24} = 0.96$, $J_{25} = 0.01$, $J_{26} = -0.01$, $J_{27} = 0.00$, $J_{34} = 8.31$, $J_{35} = 0.04$, $J_{36} = 0.11$, $J_{37} = 0.00$, $J_{45} = 0.12$, $J_{46} = 0.11$, $J_{47} = 0.00$, $J_{56} = 5.83$, $J_{57} = 9.60$, $J_{67} = 47.62$ Hz.

provides 21 D_{ij}'s in each solvent. These are more than sufficient for the determination of a total of 13 structural and order parameters (S_{ij}'s). The least square-fit program SHAPE [15] was used to determine the best-fit relative internuclear distances and the order parameters, with rms errors between the observed and calculated D_{ij}'s of 0.35 and 0.26 Hz, respectively, for the ZLI-1167 and Merck phase V solutions. They are shown in Table 2. The results on the same system (without the ^{77}Se–^{1}H satellites) obtained from a study in a lyotropic phase are included in the table for comparison. The corresponding distance ratios for benzo[*b*]-furan and -thiophene are also reproduced in the table.

Table 2 shows that the relative interproton distances in the lyotropic and Merck V phases are in better agreement with each other than those derived from lyotropic phase and ZLI-1167 solutions. This means that either the solvent effects influence the relative internuclear distances in the lyotropic and Merck phase V solutions similarly or that the effects are less pronounced in these solvents than in ZLI-1167. In order to establish which of the two possibilities is more likely, a comparison of the geometrical data for the various benzo[*b*] heterocycles was made with selenium, sulphur and oxygen as the heteroatoms. Of the three heteroatoms, the first is least and the last the most electronegative. Therefore, on the basis of bond polarisation hypothesis, r_{56}/r_{23} should be smallest for benzo[*b*]selenophene and largest for the oxygen analogue. Table 2 shows that this is true only for the values in the lyotropic and Merck V phases. The results thus indicate that the solvent ZLI-1167 produces larger distortions in the relative internuclear distances in benzo[*b*]selenophene than Merck phase V. Similar observations were made in the case of thiophene.

Vibrational corrections were not applied to the observed dipolar couplings since such effects were not taken into consideration for the other benzo[*b*] heterocycles with which comparison is being made. Furthermore, the force fields required for

TABLE 2

GEOMETRICAL AND ORDER PARAMETERS IN BENZO[*b*]SELENOPHENE (The values for the oxygen and the sulphur analogues are reproduced for comparison)

Parameter	Benzo[*b*]selenophene	Benzo[*b*]-	Benzo[*b*]-

application of the harmonic corrections to derive the r_α structure are not available to our knowledge.

The results (Table 2) also indicate that the phenyl ring is not significantly distorted from the regular hexagonal arrangement of the protons in benzo[*b*]selenophene.

Conclusion

It has been shown that application of the bond polarisation hypothesis can lead to an unambiguous prediction of solvent effects which produce distortions in the molecular structure.

Acknowledgement

We are grateful to Dr. L. Christiaens, Universite De Liege, Belgium for providing the sample of benzo[*b*]selenophene.

References

1 N. Suryaprakash, A.C. Kunwar and C.L. Khetrapal, Chem. Phys. Lett., 107(3) (1984) 333.
2 P. Diehl, H. Bosiger and H. Zimmermann, J. Magn. Res., 31 (1979) 113.
3 P. Diehl, J. Jokisaari, S. Muller and T. Vaananen, Org. Magn. Res., 21 (1983) 143.
4 J. Lounila and P. Diehl, Chem. Phys. Lett., 104 (1984) 13.
5 J. Lounila and P. Diehl, Mol. Phys., 827 (1984) 52.
6 J. Lounila and P. Diehl, J. Magn. Res., 254 (1984) 56.
7 C.L. Khetrapal, A.C. Kunwar and A.V. Patankar, Pramana Suppl., 1 (1975) 471.
8 C.L. Khetrapal, A.C. Kunwar and A.V. Patankar, Mol. Cryst. Liq. Cryst., 51 (1979) 247.
9 C.L. Khetrapal, Bull. Magn. Res., 5 (1983) 140.
10 W.E. Bechtold and J.H. Goldstein, Org. Magn. Res., 16 (1981) 14.
11 S. Arumugam, A.C. Kunwar and C.L. Khetrapal, Org. Magn. Res., 18 (1982) 157.
12 C.L. Khetrapal, A.C. Kunwar and A. Saupe, Pramana Suppl., 1 (1975) 495.
13 C.L. Khetrapal and E.D. Becker, J. Magn. Res., 43 (1981) 8.
14 P. Diehl, C.L. Khetrapal and H.P. Kellerhals, Mol. Phys., 15 (1968) 333.
15 P. Diehl, P.M. Henrichs and W. Niederberger, Mol. Phys., 20 (1971) 139.