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NMR spectra of bicyclic compounds oriented in the nematic phase Part III : The spectrum of benzo(b)thiophene

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Abstract. From the PMR spectrum of benzo(b)thiophene dissolved in a nematic solvent, the shape of the proton skeleton of the molecule is determined. The results are consistent with the molecule being planar. No significant distortions in the geometry of the benzene and the thiophene rings are observed. Information on the molecular orientation is derived. It is found that the molecule orients in the nematic phase such that the largest positive S-value is along the longest molecular dimension.

1. Introduction

The compounds possessing the benzo(b)thiophene nucleus (figure 1) have found applications in the dye industry and are known to possess insecticidal properties[1]. In spite of these applications, the structure of benzo-(b)thiophene molecule does not seem to have been reported. An easy and convenient procedure to obtain information on the molecular geometry is provided by NMR spectroscopy in nematic solvents as discussed earlier for some other bicyclic compounds[2–5]. The benzo(b)thiophene molecule has a lower symmetry than the bicyclic compounds studied earlier, which possess two perpendicular planes of symmetry. There are fifteen different inter-proton dipolar coupling constants in benzo(b)thiophene compared to nine in the other bicyclic compounds. They provide directly information on the relative arrangement of protons and indirectly on the planarity of the carbon skeleton, in addition to the molecular order. A study of the spectra due to ^{13}C in addition, may provide direct information on the geometry of the carbon skeleton. In the present paper, the results obtained from the PMR spectrum of benzo(b)thiophene without the ^{13}C–H satellites are reported. The ^{13}C–H satellites are not observed in the natural abundance of ^{13}C without sufficient spectral accumulations. It may also be mentioned that the results reported in the present paper do not take into account the 'vibrational effects' on the observed dipolar couplings.

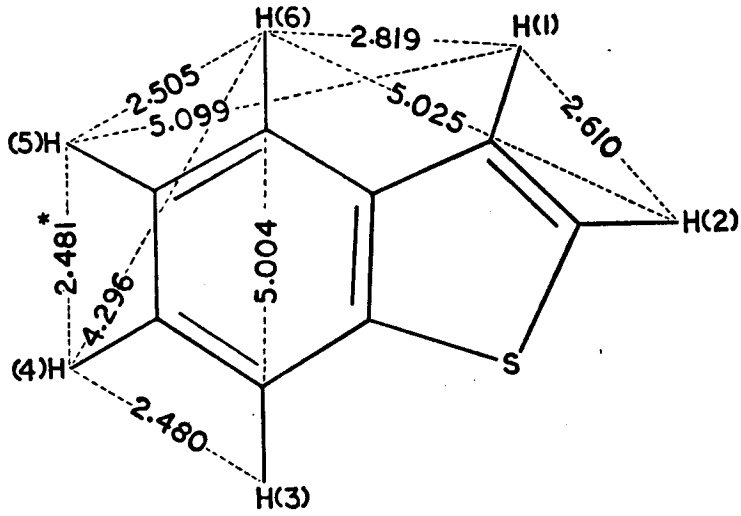

Figure 1 The structure of benzo(b)thiophene. Interporton distances given in the figure are in units of 10^{-10} m.
* The scaling distance $r_{45} = 2.481 \times 10^{-m}$ (assumed).

2. Experimental

A 12 mole per cent solution of locally available benzo(b)thiophene was prepared in 4–ethoxy–benzylidene–4–*n*–butylaniline(a). The solution (in a 5 mm NMR sample tube) was stored horizontally for a few days before recording the final spectrum (figure 2) at 30°C on a Varian XL–100 spectrometer. The spectrum was recorded in two parts with sweep widths of 2500 Hz and sweep times of 2500 s. The strongest line in one part served as the ' lock-signal ' while the other part was being recorded. The total spread was 3830 Hz and the average line width was 6 Hz. The mean statistical error in the measurement of line positions determined by repeated recordings was 1.2 Hz. The maximum deviation of any line position from the mean value was less than 3 Hz.

3. Result and discussion

3.1. *Spectral analysis :* Analysis of the spectrum was carried out iteratively with the help of the LAOCOONOR[6] programme on a CDC–3600 computer. In the final analysis, only the chemical shifts ($\nu_i - \nu_j$) and the direct dipolar couplings (D_{ij} as defined in the LAOCOONOR programme) were iterated upon ; the indirect spin–spin couplings (J_{ij}) were given the same values as those obtained from the spectrum in the isotropic media[7]. Values of the derived parameters are given in table 1 along with those of the indirect coupling constants used. The root mean square error between the experimental and the calculated line positions was 1.1 Hz with a maximum deviation of 2.7 Hz for any line. All the

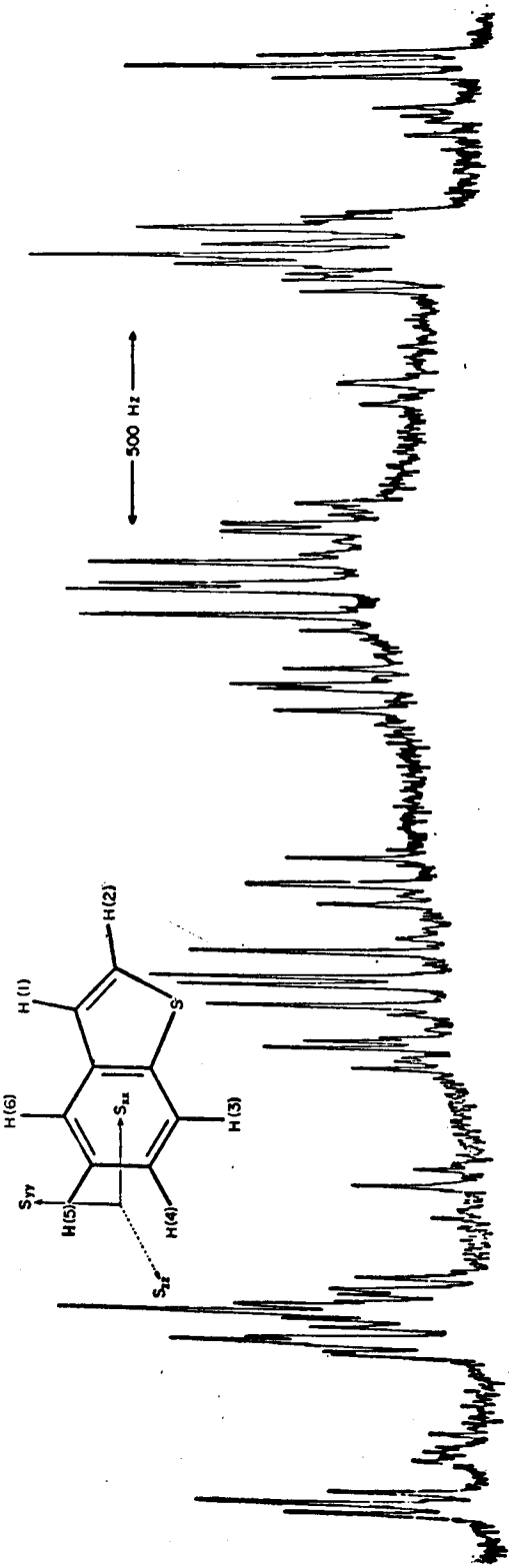

Figure 2 PMR spectrum of benzo(b)thiophene dissolved in the nematic phase of (a). Solute concentration = 12 mole per cent ; Temperature = 30° C ; Spectrometer frequency = 100 MHz.

Table 1 Results of spectral analysis for benzo(b)thiophene oriented in the nematic phase of (a). Numbering of protons refers to figure 1.

ij	Coupling constants			Parameter	Value
	J_{ij} (assumed)	D_{ij} (experimental)	D_{ij} (calculated 'best-fit')		
12	5.45	-544.0 ± 0.9	-544.0	$\nu_1 - \nu_6$	24.2 ± 0.9 Hz (48.96)*
13	0.84	-7.8 ± 0.8	-7.4	$\nu_2 - \nu_6$	16.3 ± 0.7 Hz (40.38)*
14	-0.12	-35.9 ± 0.7	-34.3	$\nu_3 - \nu_6$	3.4 ± 1.4 Hz (-6.95)*
15	0.03	-106.4 ± 0.9	-106.4	$\nu_4 - \nu_6$	27.3 ± 1.4 Hz (47.16)*
16	-0.29	-726.9 ± 0.2	-726.9	$\nu_5 - \nu_6$	20.1 ± 0.7 (45.03)*
23	0.03	-55.9 ± 0.4	-55.8	S_{xx} †	0.1324
24	0.50	-40.5 ± 0.5	-42.4	S_{yy} †	-0.0028
25	0.02	-53.2 ± 0.1	-52.7	S_{xy} †	-0.0257
26	0.17	-120.4 ± 0.8	-120.0	r_{12}/r_{45}	1.052 ± 0.01
34	8.13	-926.4 ± 0.1	-926.4	r_{15}/r_{45}	2.055 ± 0.02
35	1.06	-74.8 ± 0.4	-74.9	r_{16}/r_{45}	1.136 ± 0.01
36	0.74	3.5 ± 0.8	3.5	r_{26}/r_{45}	2.025 ± 0.02
45	7.14	22.3 ± 0.6	22.4	r_{34}/r_{45}	1.000 ± 0.01
46	1.21	-14.4 ± 0.8	-15.0	r_{36}/r_{45}	2.017 ± 0.02
56	8.04	-603.4 ± 1.0	-603.4	r_{46}/r_{45}	1.731 ± 0.02
				r_{56}/r_{45}	1.010 ± 0.01

† $r_{45} = 2.481$ Å (assumed). 1 Å $= 10^{-10}$ m.
* Values in the isotropic phase[7].

111 observed lines were assigned for the analysis. Errors of the parameters given in table 1 are the standard deviations obtained from the LAOCOONOR programme. Errors of the parameters were also estimated by changing the observed line positions by $\pm$ 1.2 Hz, the accuracy of measurement, in such a way that the position of each line deviated from its calculated value by the maximum possible amount. These values were then used to calculate the spectral parameters iteratively. The errors thus obtained (*i.e.*, the difference between the parameters obtained this way and those obtained using the measured line positions) were found to be smaller than the standard deviations given by the LAOCOONOR programme and hence only the latter are given in table 1. The large errors arise from the fact that relatively large number of parameters are to be determined (15 dipolar couplings and 5 internal chemical shifts) from the experimental line positions. A similar situation has been encountered in the analysis of the spectrum in the isotropic medium[7].

3.2. *Molecular geometry:* If one assumes a plane of symmetry in the benzo(b)thiophene molecule, 3 independent parameters are needed to define its orientation and 9 inter-proton distances suffice to describe the geometry of the proton skeleton. There are 15 different dipolar couplings and if one assumes a scaling distance, such a system is over determined by 4 coupling constants as far as the determination of the geometry of the proton skeleton and the molecular order from the inter-proton dipolar couplings is concerned. If self-consistent results are obtained in the iterative calculations which compute the geometry and the degree of order using a 'weighted least square fit' method, the assumption about the plane of symmetry in the molecule is justified. The programme SHAPE[8] was used for such calculations. All the coupling constants were given equal weights. The direct couplings corresponding to the 'best-fit' parameters are included in table 1. The order parameters and the ratios of the HH distances are also included in the same table.

Table 1 shows that some of the observed, and the 'best-fit' calculated dipolar couplings deviate beyond their experimental errors. A maximum deviation of 1.9 Hz is found for D_{24}. Deviations of similar magnitudes have been observed in some other cases also[9,10] and are attributed to several effects like the neglect of the influence of molecular vibrations and the solvent effects, in addition to experimental errors. The results can be considered as consistent with the assumption of a plane of symmetry in the molecule. In figure 1, various inter-proton distances determined assuming $r_{45} = 2.481 \times 10^{-10}$ m are given in units of 10^{-10} m.

It is seen from table 1 and figure 1 that the geometry of the phenyl part does not deviate, beyond the experimental error, from the benzene ring geometry, unlike in the other rigid bicyclic molecules where significant deviations have been detected in this part of the molecule[2, 3, 11].

The distance r_{12} between the protons of the thiophene ring in this case is found to be 2.61×10^{-10} m under the assumption of $r_{45} = 2.481 \times 10^{-10}$ m. It is very close to the corresponding value (2.64×10^{-10} m) in thiophene[12].

The results, therefore, indicate that there are no significant distortions in the geometry of the benzene and the thiophene rings in benzo (b)thiophene.

3.3. *Molecular orientation :* For the purpose of obtaining the order parameters, the Cartesian coordinate system was chosen such that the axes X and Y lie in the molecular plane with Y-axis being the line joining protons 4 and 5. The values of the order parameters given in the table obtained using the SHAPE programme were derived by assuming $r_{45} = 2.481 \times 10^{-10}$ m. The largest positive S-value (S_{xx}) along the X-axis is in agreement with the fact that the largest S-value corresponds to the largest molecular dimension. Similar results have been obtained for the other rigid bicyclic molecules studied earlier[2, 3, 11].

Acknowledgments

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DISCUSSION

Sharma : How can you derive r_e–values from the observed *D*–values ?

Khetrapal : For the calculation of the relative equilibrium geometry, one needs to apply the anharmonic and the harmonic vibrational corrections to the observed dipolar couplings. However, since the computation of the anharmonic terms in general is not practical, a suggestion has been made by Lucas to derive the 'average structure' from the direct dipolar couplings by taking into account only the 'harmonic corrections' (Molecular Physics 1971 and 1972).