Liquid Crystal Proton Magnetic Resonance Spectrum of Thieno[2,3-*b*]thiophen

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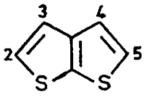
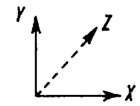
The 100 MHz ^{1}H n.m.r. spectra of the title compound in the nematic phase of two liquid crystals have been obtained and interpreted in terms of chemical shifts, indirect coupling constants, and direct dipolar couplings. The sign of the J values, the ratio of the interprotonic distances, and the orientation of the molecule with respect to the magnetic field have been determined.

THE first successful experiment of Saupe and Englert[1] in obtaining high resolution n.m.r. spectra of partially oriented molecules led to a great deal of investigation in this field. The interpretation of the spectral patterns of molecules dissolved in liquid crystals is now almost as easy as for those in isotropic solvents. The applications to structural, spectroscopic, and chemical problems have been reviewed in detail.[2]

Among the information which can be obtained from liquid crystal ^{1}H n.m.r. spectra are the sign of the indirect coupling constants, J, the geometrical arrangement of the protons within the molecule, and the way in which the molecule is oriented with respect to the magnetic field. The accuracy of the results has been checked in many cases against microwave and electronic diffraction determinations.[3] The limit of the method lies however in the impossibility of giving absolute distances; only internal ratios can be obtained.



(I)



Because of our interest in molecules containing thiophen rings[4] we have undertaken a liquid crystal ^{1}H n.m.r. investigation of thieno[2,3-*b*]thiophen (I). The spectrum in the isotropic phase (acetone) has been reported;[5] however, changing the solvent to carbon tetrachloride reduces differences in chemical shifts, thus yielding a more strongly coupled spectrum where two additional lines can be detected. This allows an independent check of the results of ref. 5 and satisfactory agreement between the two sets of parameters is observed (Table 1). The spectral analysis however only gives the relative signs of the J_{HH} couplings and one cannot decide which of the two greater or the two smaller couplings are those with positive sign. The spectra of compound (I), partially oriented in the nematic phase, were obtained either at the probe temperature (30°) in Merck's Phase IV [compound (II)], or at 78° in *pp*′-dihexyloxyazoxybenzene (III). The Figure shows the experimental (100 MHz) and computed spectra for the first case.

TABLE 1

Spectral parameters (Hz) of thieno[2,3-*b*]thiophen (I) obtained from the 60 MHz spectrum in carbon tetrachloride. Chemical shifts are downfield from Me_4Si (internal reference) and the root mean square error is 0·03 Hz. The values in parentheses are from ref. 5

$\nu_2 = \nu_5$ 436·3$_6$ ± 0·01	$J_{2.3} = J_{4.5}$ ±5·25 ± 0·01 (±5·23)
$\nu_3 = \nu_4$ 424·9$_5$ ± 0·01	$J_{2.4} = J_{3.5}$ ∓0·03 ± 0·01 (∓0·02)
	$J_{2.5}$ ±1·17 ± 0·02 (±1·20)
	$J_{3.4}$ ∓0·18 ± 0·02 (∓0·18)

TABLE 2

Spectral parameters (Hz) obtained from the 100 MHz spectrum of thieno[2,3-*b*]thiophen (I) partially oriented in the nematic phase of compounds (II) and (III) at 30° and 78°, respectively. The values of $J_{2.4}$, $J_{2,5}$, and $J_{3,4}$ were those for the isotropic phase

	(II)	(III)
$\Delta\nu$	11·9 ± 0·4	0
$D_{2,3} = D_{4.5}$	−480·9 ± 0·3	−686·1 ± 0·4
$D_{2.4} = D_{3.5}$	−77·9 ± 0·4	−103·6 ± 0·4
$D_{2.5}$	−40·6 ± 0·7	−55·5 ± 0·6
$D_{3,4}$	−392·3 ± 0·7	−513·4 ± 0·8
$J_{2.3}$	+4·1 ± 0·5	+3·6 ± 0·6
R.m.s. error	1·3	1·1

The values of the parameters obtained from the analysis are given in Table 2. The results show that $J_{2,3}$ is opposite in sign to the direct dipolar couplings, D_{ij}, whose values are known to be negative since molecules are found to orient preferentially with their aromatic planes along the direction of the magnetic

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[1] A. Saupe and G. Englert, *Phys. Rev. Letters*, 1963, **11**, 462.

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[3] (*a*) G. Englert and A. Saupe, *Mol. Crystals*, 1966, **1**, 503; (*b*) A. D. Buckingham, E. E. Burnell, and C. A. De Lange, *Mol. Phys.*, 1968, **15**, 285; (*c*) P. Diehl and C. L. Khetrapal, *ibid.*, p. 327, 333; (*d*) A. D. Buckingham, E. E. Burnell, C. A. De Lange, and A. J. Rest, *ibid.*, p. 105; (*e*) S. Meiboom and C. L. Snyder, *J. Amer. Chem. Soc.*, 1967, **89**, 1038.

[4] (*a*) L. Lunazzi, G. Placucci, M. Tiecco, and G. Martelli, *J. Chem. Soc.* (*B*), 1971, 1820; (*b*) L. Lunazzi, A. Mangini, G. Placucci, P. Spagnolo, and M. Tiecco, *J.C.S. Perkins II*, 1972, 192; (*c*) L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10; (*d*) L. Lunazzi, M. Tiecco, A. C. Boicelli, and F. Taddei *J. Mol. Spectroscopy*, 1970, **35**, 190; (*e*) L. Lunazzi and C. A. Veracini, to be published.

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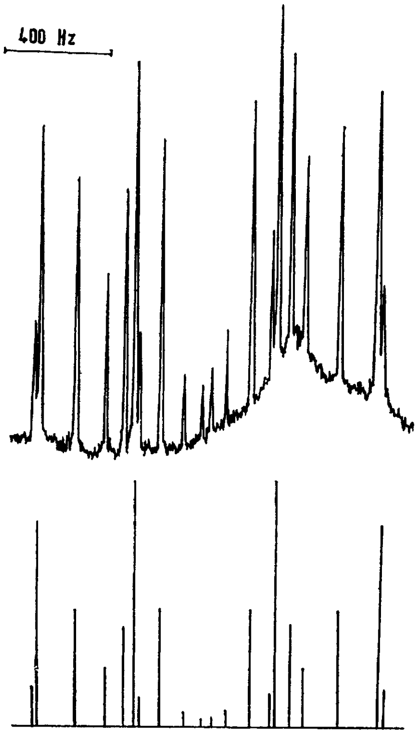
field.[6] It turns out that a positive value can be assigned to both $J_{2,3}$ and $J_{2,5}$, while the values of $J_{2,4}$ and $J_{3,4}$ are negative. Indeed if a negative value is given to $J_{2,3}$, the root mean square error of the oriented spectrum is much greater [4·3 and 5·3 Hz for the mesophase of compounds (II) and (III) respectively] and when the iterative process is performed the initial sign is reversed to positive.



Proton resonance spectrum (100 MHz) of thieno[2,3-*b*]thiophen (I) dissolved in the nematic phase of compound (II) at 30°

From the D values it is possible to obtain [2c] the ratios of the interprotonic distances (Table 3). The differences observed between the two mesophases depend either on experimental error or on the effect of the molecular vibrations upon the equilibrium distances at the two temperatures; they are however reasonably small and never exceed 0·04. Such results can be used to check the accuracy of theoretical calculations as well as the practice of building up models of condensed rings from simpler fragments. In column A of Table 3 the ratios calculated from the computed bond lengths of Trinajstic and Hinchliffe [7] are reported; the angles were those determined by X-ray diffraction [8] measurements for the isomer, and the C–H bonds (1·08 Å) were assumed to bisect these angles. Column B gives the interprotonic ratios of a molecular model formed by two thiophen rings [9] which share a carbon–carbon double bond. In both cases the discrepancies with experimental data are reasonably small, and only slightly exceed the uncertainty of the measurements.

TABLE 3

Ratios of the interprotonic distances and elements (S) of the ordering matrix at 30° (II) and 78° (III). Column A refers to the computed values taken from ref. 7 (see text) and column B to those obtained from the model of two thiophen rings [9] (see text)

	(II)	(III)	A	B
$r_{2,3}/r_{3,4}$	$0{\cdot}79_8$	$0{\cdot}83_7$	0·82	0·85
$r_{2,4}/r_{3,4}$	$1{\cdot}66_3$	$1{\cdot}67_3$	1·70	1·70
$r_{2,5}/r_{3,4}$	$2{\cdot}12_9$	$2{\cdot}10_0$	2·15	2·16
S_{xx}	$0{\cdot}11_0 \pm 0{\cdot}005$	$0{\cdot}13_6 \pm 0{\cdot}015$		
S_{yy}	$0{\cdot}02_9 \pm 0{\cdot}003$	$0{\cdot}08_4 \pm 0{\cdot}010$		

Spectra in the nematic phase can also indicate the way the molecule is oriented with respect to the magnetic field. Because of the C_{2v} symmetry and the choice of the axes, only two elements of the ordering matrix have to be determined. The computation requires, however, knowledge of at least one of the interprotonic distances. In this case $r_{3,4}$ has to be determined.[2c] We made the reasonable assumption that the 2-H · · · 3-H distance is the same as that in thiophen [9] and from the experimental ratios the $r_{3,4}$ value was determined. The matrix elements are given in Table 3 and the errors have been estimated assuming an uncertainty of ±0·1 Å in the value of $r_{2,3}$. The fact that S_{xx} is larger than S_{yy} indicates the preferential orientation of the x-axis in the direction of the magnetic field, while in thiophen the y-axis is that with the greater degree of alignment.[10]

EXPERIMENTAL

Thieno[2,3-*b*]thiophen was synthesised as described.[11] The spectrum in the isotropic phase carbon tetrachloride was recorded on a JEOL JNM C-60 HL spectrometer, and those in liquid crystals were obtained on a JEOL PS-100. The spectra were interpreted by means of the program LAOCOON III, modified for anisotropic calculations, supplied by P. Black of Proctor and Gamble and run on a CDC 6600 computer.

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