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HIGH-RESOLUTION PROTON MAGNETIC RESONANCE SPECTRA OF POLYNUCLEAR HETEROCYCLES—II*

BENZO [*b*] THIOPHEN AND DIBENZOTHIOPHEN

K. D. Bartle†, D. W. Jones and R. S. Matthews‡

School of Chemistry, University of Bradford, Bradford, BD7 1DP

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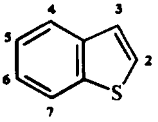
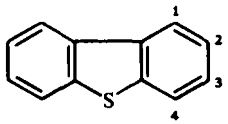
Abstract—Full iterative analyses have been carried out of 60 MHz spectra of benzo [*b*] thiophen (I) and of 60 and 100 MHz spectra of dibenzothiophen (II) in acetone and carbon tetrachloride solutions at several concentrations. From the 33 peaks in the spectrum of I, analysed as a six-spin system with appreciable inter-ring coupling between H(3) and H(7) and between H(2) and H(6), 15 parameters were determined and 190 transitions assigned. For II, inter-ring coupling is absent but H(2) and H(3) of the ABCD system have closely similar shifts. Deshielding of protons of I and II in acetone solution relative to carbon tetrachloride is attributed to reaction-field effects; some ordering of the polar solute molecules is suggested. For the thiophen rings in I and II, currents calculated from chemical shifts remote from the C-S bonds are comparable with those in benzene. In terms of partial bond fixation, the $J_{4,5}$, $J_{5,6}$ coupling constants observed in I lead to an aromaticity comparable with that in naphthalene, and $J_{2,3}$ of II implies a π-bond equivalence approaching that in fluorene.

INTRODUCTION

Reactivity and aromaticity of heteroaromatic compounds can be studied by high-resolution proton magnetic resonance (PMR) spectroscopy in two main ways: (1) identification of the products of substitution and other reactions;[1-4] and (2) measurements of aromatic character based on chemical shifts,[5,6] coupling constants,[7] or study of the inversion of derivatives containing prochiral groupings.[8] Furthermore, polynuclear sulphur heterocyclic constituents of petroleum[4] and coal tar[4] may be identified[9] by PMR spectroscopy. As part of a study of the PMR spectroscopy and carcinogenic activity of polycyclics and their heterocyclic analogues, we report an investigation of the spectra of benzo[*b*]thiophen (I), and dibenzothiophen (II), aimed at an understanding of the structure and PMR spectra[10,11] of sulphur isosteres of polycyclic hydrocarbons which may have carcinogenic[12] and antitumour[11] properties.



I



II

RESULTS AND DISCUSSION

Spectra. Although the influence of substitution on the PMR spectrum of I has been

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* Reference 1 is regarded as Part I of this series.

† Present address: School of Chemistry, University of Leeds, Leeds, LS2 9JT.

‡ Present address: Department of Chemistry, University of Durham.

investigated extensively,[4, 13] we are not aware of any fuller analysis than the approximate ones by Angeloni and Tramontini[14] and Takahashi *et al.*[15] *via* the spectra of deuterated derivatives, and by Chapman *et al.*[13] who applied the nomograms of Batterham *et al.*[16]

While superposed AB [H(2) and H(3)] and ABCD [H(4) – H(7)] systems might be expected in the spectrum of I, inter-ring coupling, well-documented in derivatives,[4, 13–15, 17] demands simultaneous consideration of all six spins. For I in CCl_4 and acetone, the analyses referred to above, together with new spectra* recorded at 220 MHz, gave approximate chemical shifts which enabled the ABMX and AB components in the spectra recorded at 60 Hz in these solvents to be recognised. To reduce the labour involved in preliminary line assignments for the six-spin system in CCl_4 (10·8% w/w), separate analyses were first carried out for the four-spin (iteratively) and two-spin (directly) sub-spectra. With these as starting parameters, three cycles of a six-spin iteration, which admitted inter-ring coupling between H(3) and H(7) only, converged with 0·063 MHz root-mean-square (RMS) deviation of transition frequencies. In further iterations, $J_{2,6}$ was introduced; its value was fixed, since it corresponded only to line broadening rather than separations. With

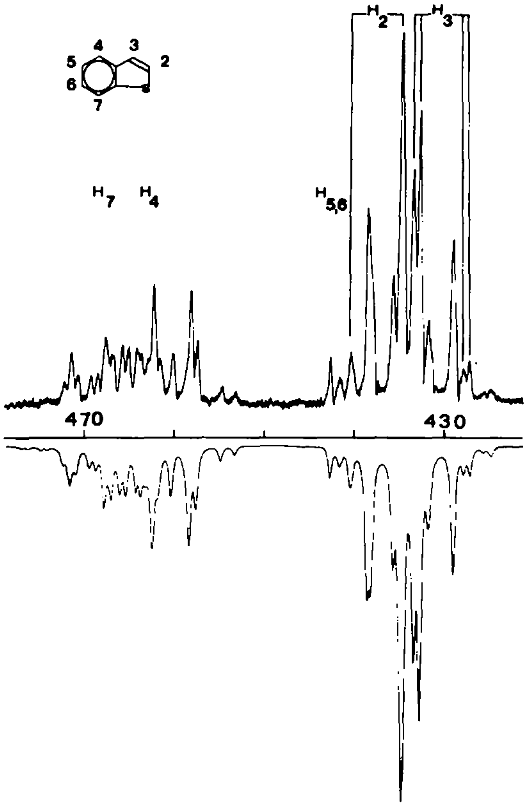

Fig 1. Experimental (upper) and computed (lower) 60 MHz spectra for a 10·8% w/w solution of benzo [*b*] thiophen (I) in CCl_4 (Frequencies are in Hz downfield from T.M.S.).

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* We should like to thank Dr. J. K. Becconsall, Mr. M. McIvor, Mr. D. Loraine and Mr. I. Struthers, I.C.I. Ltd., Petrochemical and Polymer Laboratories, for recording these spectra.

$J_{2,6} = 0{\cdot}300$ Hz, convergence with RMS deviation 0·088 Hz after three cycles gave agreement with the experimental spectrum illustrated in Fig. 1. From the 33 distinct peaks in the observed spectrum, 15 parameters were determined and 190 transitions were assigned; final parameters are listed in Table 1.

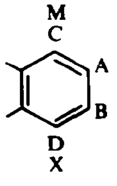
TABLE 1. CHEMICAL SHIFTS (ν, P.P.M. DOWNFIELD FROM TMS) AND SPIN-SPIN COUPLING CONSTANTS (J, Hz) IN BENZO [*b*] THIOPHEN (I)

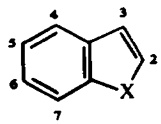
Solvent Concentration	CCl_4 10·8% w/w	Standard deviation (Hz)	CCl_4 Infinite* dilution	Acetone 7·4% w/w	Standard deviation (Hz)
ν_2	$7{\cdot}27_0$	0·02	$7{\cdot}36_5$	$7{\cdot}61_5$	0·02
ν_3	$7{\cdot}19_5$	0·02	$7{\cdot}27_7$	$7{\cdot}41_0$	0·02
ν_4	$7{\cdot}70_0$	0·01	$7{\cdot}74_2$	$7{\cdot}87_5$	0·02
ν_5	$7{\cdot}25_0$	0·02	$7{\cdot}28_5$	$7{\cdot}37_5$	0·03
ν_6	$7{\cdot}22_5$	0·02	$7{\cdot}25_8$	$7{\cdot}35_0$	0·03
ν_7	$7{\cdot}77_5$	0·01	$7{\cdot}81_5$	$7{\cdot}95_5$	0·02
$J_{2,3}$	5·57	0·02		5·52	0·02
$J_{2,6}$	0·30	—		0·30	—
$J_{3,7}$	0·86	0·02		0·91	0·02
$J_{4,5}$	8·09	0·05		8·15	0·07
$J_{4,6}$	1·16	0·06		1·21	0·08
$J_{4,7}$	0·73	0·02		0·76	0·02
$J_{5,6}$	7·22	0·02		7·10	0·03
$J_{5,7}$	1·17	0·05		1·47	0·07
$J_{6,7}$	8·06	0·05		8·07	0·07
Root-mean-square deviation of transition frequencies (Hz)	0·088‡			0·089	

* by extrapolation

‡ 0·063 Hz for iteration with $J_{2,6} = 0$

While computed standard deviations for all the chemical shifts and for a number of the coupling constants are less than 0·02 Hz, those for the *ortho* and *meta* couplings $J_{4,5}$, $J_{4,6}$, $J_{5,7}$, and $J_{6,7}$ are much larger; the correlation matrix of parameters shows (Table 2) numerically large values between these couplings. A study[18] of four-spin





III

TABLE 2. CORRELATION MATRIX FOR $J_{4,5}$, $J_{4,6}$, $J_{5,7}$ AND $J_{6,7}$ FOR ITERATIVE ANALYSIS OF THE SPECTRUM OF I (CCl_4 SOLUTION)

	$J_{4,5}$	$J_{4,6}$	$J_{5,7}$	$J_{6,7}$
$J_{4,5}$	1·000			
$J_{4,6}$	−0·853	1·000		
$J_{5,7}$	+0·839	−0·823	1·000	
$J_{6,7}$	−0·792	0·808	−0·875	1·000

systems with parameters typical of those found for polynuclears shows that J_{AC}, J_{BC}, J_{AD}, and J_{BD} are under-determined; in the ABMX limit[19] no separation of transition frequencies corresponds even approximately to these couplings, whose sensitivity to line position increases as $|\nu_A - \nu_B|$ decreases. On the other hand, J_{AB} and J_{CD} are directly measurable in ABMX treatments,[16, 19] and their standard deviations are correspondingly smaller for I. This effect, even more marked in analyses of spectra of II (*vide infra*), was noted by Black and Heffernan[20] for benzofuran (III:X=O): when $|\nu_A - \nu_B|$ changed in different solvents, only the sums of couplings ($J_{AM} + J_{BM}$) and ($J_{AX} + J_{BX}$) in ABMX terminology,[16, 19] which correspond to separations between "unmixed" lines, remained constant. No such separations correspond to the differences ($J_{AM} - J_{BM}$) or ($J_{AX} - J_{BX}$), however. Haigh and Williams[21] have made similar observations for a more complex spin system which could be approximated first as ABMRX.

Comparison with the spectrum of I in CCl_4 allowed assignment of lines for that of a 7·4% w/w solution in acetone at 60 MHz. Iteration, again with $J_{2,6}$ constant, gave the parameters listed in Table 1 after four iterations to a final RMS deviation of 0·089 Hz. Coupling constants determined in acetone are similar to those in CCl_4, but again the standard deviations of $J_{4,5}$, $J_{4,6}$, $J_{5,7}$ and $J_{6,7}$ are high.

Chemical shifts at infinite dilution in CCl_4 were determined for I by fitting spectra calculated with coupling constants for the 10·8% w/w solution to those recorded at

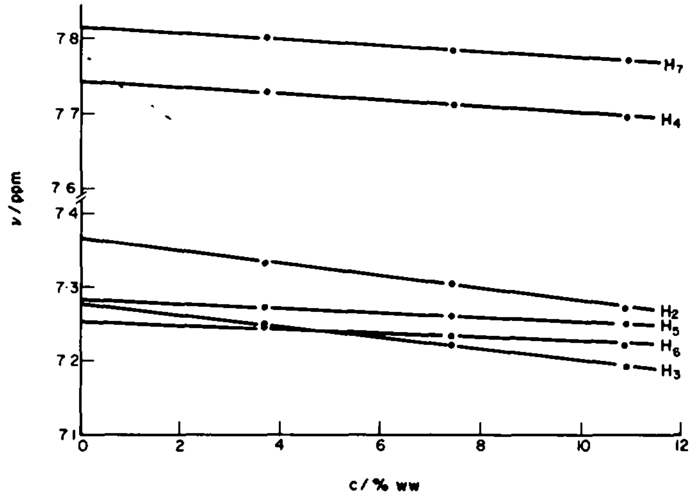


FIG 2. Graphs of chemical shift, ν, against concentration, c, for I in CCl_4

two other concentrations and extrapolating graphs of chemical shift against concentration (Fig. 2).

The spectrum of II at both 60 and 100 MHz has been assigned by several authors.[2, 9, 22, 23] Faller applied[10] an approximate ABMX treatment and, when the present work was substantially complete, Clin and Lemanceau reported[24] an iterative analysis of the 100 MHz spectrum in acetone solution.

As with the analogous dibenzofuran[20] and fluorene,[25] line widths and lack of extra splittings confirm the absence of significant inter-ring coupling in II. While analysis of the ABCD spectrum should therefore be straightforward, near co-incidence of the H(2) and H(3) shifts renders the spectrum insensitive to variations in $J_{1,2}$, $J_{1,3}$, $J_{2,4}$ and $J_{3,4}$ but not to the other couplings or to the four chemical shifts. Table 3 shows values of ν and J obtained by iterative analysis for solutions in CCl_4 at 60 and 100 MHz,* and for an acetone solution at 60 MHz; the iterations converged after two cycles, starting from ABMX parameters. Despite transition frequency RMS deviations below 0·1 Hz for each analysis, and plotted spectra (*e.g.* Fig. 3) in excellent agreement with experiment, the standard deviations for the above couplings are as large as 0·25 Hz, with correlation coefficients (Table 4) greater than |0·94|. In view of these inaccuracies, there is fair overall agreement with the coupling constants reported by Clin and Lemanceau.[24]

TABLE 3. CHEMICAL SHIFTS (ν, P.P.M. DOWNFIELD FROM TMS) AND SPIN-SPIN COUPLING CONSTANTS (J, Hz) IN DIBENZOTHIOPHEN (II)

Solvent	CCl_4		CCl_4	Acetone		CCl_4
Concentration	5·3% w/w		8·8% w/w	6·5% w/w		Infinite dilution*
Frequency (MHz)	100	Standard deviation (Hz)	60	60	Standard deviation (Hz)	
ν_1	8·04$_5$	0·02	7·99$_5$	8·30$_0$	0·04	8·15$_0$
ν_2	7·34$_5$	0·04	7·30$_5$	7·49$_5$	0·07	7·40$_5$
ν_3	7·35$_5$	0·05	7·32$_0$	7·50$_5$	0·09	7·41$_8$
ν_4	7·76$_0$	0·03	7·73$_5$	7·95$_5$	0·05	7·84$_2$
$J_{1,2}$	7·99	0·19	8·33	7·47	0·20	
$J_{1,3}$	1·21	0·20	1·03	1·89	0·21	
$J_{1,4}$	0·67	0·03	0·69	0·64	0·06	
$J_{2,3}$	7·21	0·03	7·26	7·37	0·06	
$J_{2,4}$	1·09	0·21	1·30	0·43	0·25	
$J_{3,4}$	8·05	0·19	7·96	8·74	0·23	
Root-mean-square deviation of transition frequencies (Hz)	0·061		0·031	0·097		

* by extrapolation of least squares plot

Spin-tickling experiments (100 MHz), restricted by overlapping to two lines in

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* 100 MHz spectra were recorded by Physico-Chemical Measurements Unit, A.E.R.E., Harwell.

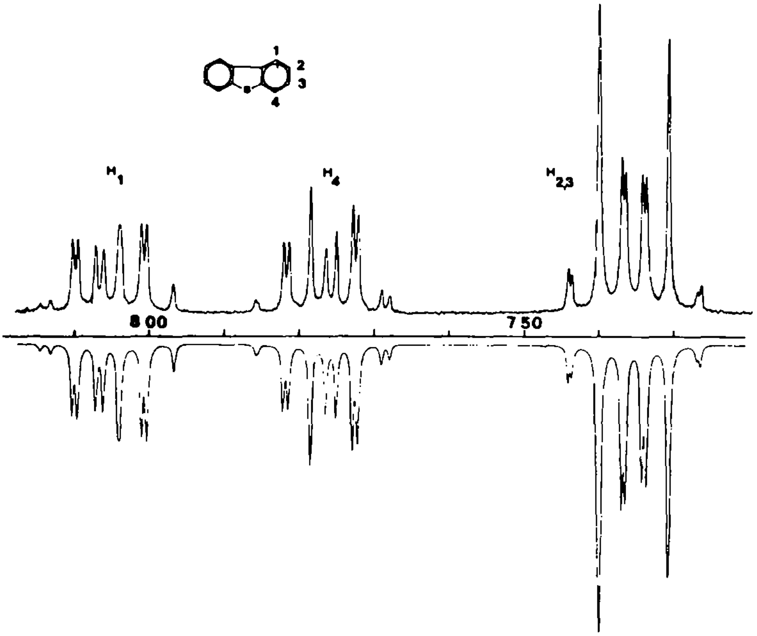


FIG 3. Experimental (upper) and computed (lower) 100 MHz spectra for a 5·3% w/w solution of dibenzothiophen (II) in CCl_4 (Frequencies are in Hz downfield from T.M.S.).

TABLE 4. CORRELATION MATRIX FOR $J_{1,2}$, $J_{1,3}$, $J_{2,4}$ AND $J_{3,4}$ FOR ITERATIVE ANALYSIS OF THE SPECTRUM OF II (CCl_4 SOLUTION AT 100 MHz)

	$J_{1,2}$	$J_{1,3}$	$J_{2,4}$	$J_{3,4}$
$J_{1,2}$	1·000			
$J_{1,3}$	−0·960	1·000		
$J_{2,4}$	−0·950	−0·944	1·000	
$J_{3,4}$	−0·940	−0·946	−0·961	1·000

each of the H(1) and H(4) multiplets, confirmed that the transitions labelled (a) in Fig. 4 have a common energy level, as had those labelled (b). These results are in accord with the ABCD energy-level diagram for all couplings with the same sign.[16, 19]

The spectra II for 12·1 (saturated), 6·1 and 3·2% w/w solutions in CCl_4 were also analysed; graphs of chemical shift against concentration (Fig. 5) were extrapolated to infinite dilution.

Assignment of chemical shifts. Of the four combinations of chemical shifts for I, that listed in Table 1 is the only one compatible with investigations of deuterated derivatives.[13-15] For II, the resonance of H(1) has previously been taken to be to low field of that of H(4) arbitrarily,[10] or by analogy[22, 24] with dibenzofuran[20] (IV : X=O) and carbazole (IV : X=NH).[20]

For 100 MHz spectra, double irradiation at the H(2, 3) multiplet collapsed both H(1) and H(4) multiplets to broadened singlets (1·0 ± 0·3 Hz wide at half-height,

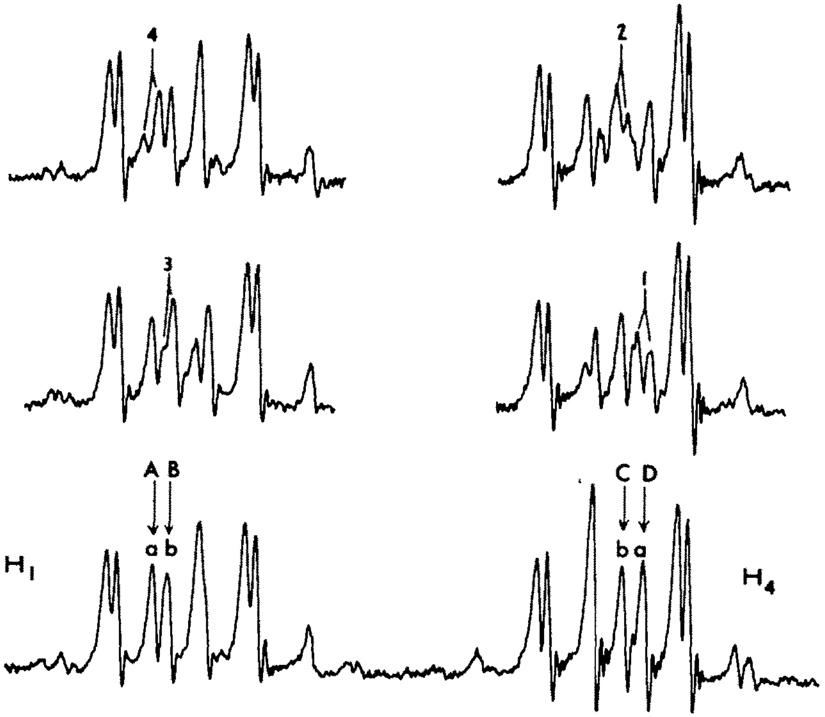
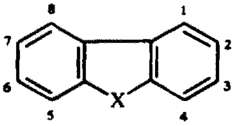


FIG 4. 100 MHz spin-tickling experiments on the H(I) and H(4) multiplets of II; irradiation at A induces splitting 1; irradiation at B induces splitting 2; irradiation at C induces splitting 3; and irradiation at D induces splitting 4.

because of unresolved *para* coupling) rather than affording support[3] for Faller's assignment.[10]

However, when taken with the known shift effects of substituent groups in benzene,[26] polynuclear hydrocarbons[27] and heterocycles,[1, 13] block diagrams[2] of spectra of numerous derivatives of II are compatible only with $\delta_1 > \delta_4$. Recently, Acheson and Harrison[23] have justified this assignment by similar arguments.



IV

Solvent and Dilution shifts. Overall proton de-shielding in acetone relative to CCl_4, especially marked at position 2, has been noted[20] for III : X=O and NH, and is now confirmed for I. Acetone also de-shields all protons of II. In the absence of effects arising from hydrogen bonding and from the anisotropy of magnetic susceptibility of solvent molecules, both expected to be small for acetone and CCl_4 solutions of I and II, solvent shifts may be interpreted in terms of the reaction electric field which arises as a result of the polarisation of the surrounding medium by a polar molecule.[28] This field (E) directed along the X-H direction of an X-H bond draws the electrons away from the proton, and causes a downfield shift. The change in shielding of such a proton is given by

$$\Delta\sigma = -AE_z - BE^2 \qquad (1)$$

where E_z is the component of E along X—H. The reaction field is parallel to the dipole axis but opposite in polarity.* Now for thiophen, following earlier controversy, summarised by Clark,[29] about the direction of the dipole moment, the present consensus is that it is directed (positive to negative) from ring to sulphur atom. If II, for which μ has been measured[30] as $0{\cdot}28 \times 10^{-29}$ C m, is taken to be analogous, its molecules may be considered to be in a uniform electric field aligned along the C_{2v} axis (Fig. 6) so that the following angles

$$\theta(H(1)), 22°; \theta(H(2)), 38°; \theta(H(3)), 98°; \theta(H(4)), 158°$$

between C—H and the direction of E are measured. In the model (as for I, *vide infra*, and in the ring-current calculation), regular hexagons with benzene dimensions were taken for the six-membered rings, and thiophen[31] bond lengths and angles for the five-membered ring.† The Onsager model,[28] which assumes a spherical solute molecule, predicts that the reaction field is proportional to $(\varepsilon + 1)(2\varepsilon + n^2)^{-1}$ (=R), where ε is the permittivity of the continuum and n is the refractive index of the pure solvent. Since R is greater for acetone solution than for CCl_4,[32] $\Delta\sigma$ for H(1) and H(2) will always be negative; but, depending on the magnitude of E, $\Delta\sigma$ may be positive or

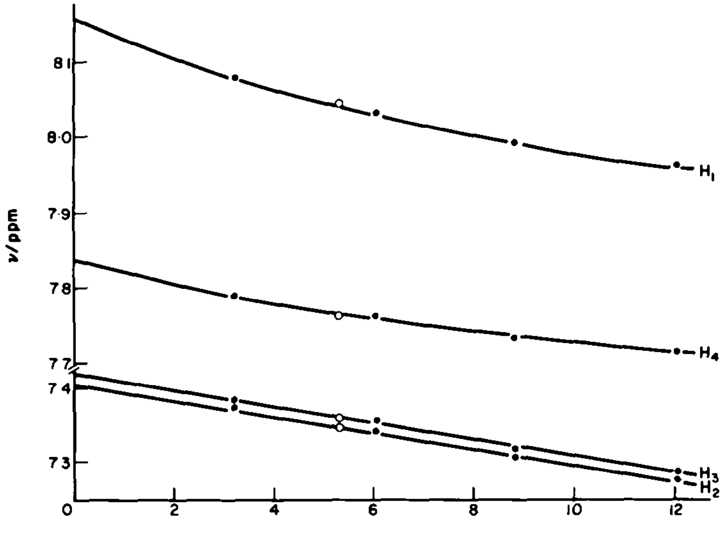


FIG 5. Graphs of chemical shift, ν, against concentration, c, for II in CCl_4. Closed circles refer to analysis at 60 MHz; open circles apply to 100 MHz.

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* Our treatment of reaction-field effects in I and II follows that for pyridine by V. I. P. Jones and J. A. Ladd, *Mol. Phys.* **19**, 233 (1970) and J. A. Ladd, private communication (1970)

† Only small differences are introduced if dimensions recently determined [R. H. Schiaffrin and J. Trotter, *J. Chem. Soc.* (A), 1561 (1970)] for the crystal of II are used.

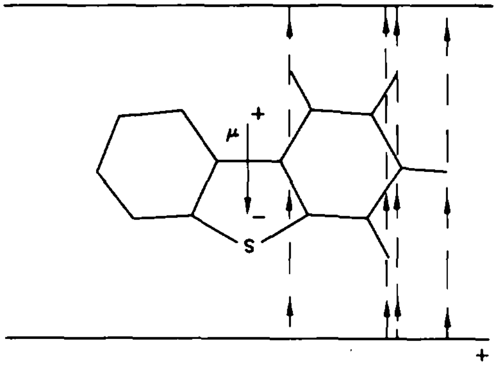


FIG 6. Reaction electric field (dotted arrows) in II. The molecule is considered to be immersed in a uniform electric field (represented by a condenser) with the molecular dipole (full arrow) antiparallel to the field.

negative for H(3) and H(4). The sequence of reaction field de-shieldings for II in going CCl_4 to acetone should be, therefore, H(1) > H(2) > H(3) > H(4).

Agreement with experiment (Table 5 – H(1) > H(4) > H(2) ~ H(3)) is only partial; the reaction field may not be homogeneous, particularly for protons near the periphery of the solute molecule whose shape deviates markedly from the sphere assumed in the Onsager treatment.

TABLE 5. SOLVENT AND DILUTION SHIFTS IN BENZO [*b*] THIOPHEN (I) AND DIBENZOTHIOPHEN (II)

		$\Delta = \delta_{Acetone} - \delta_{CCl_4}$ ppm*	Dilution shift 10^3 ppm/% w/w
Benzo [*b*] thiophen (I)	H-2	$0{\cdot}27_3$	8·2
	H-3	$0{\cdot}15_3$	7·7
	H-4	$0{\cdot}14_5$	4·0
	H-5	$0{\cdot}10_0$	3·3
	H-6	$0{\cdot}10_2$	3·2
	H-7	$0{\cdot}15_2$	3·8
Dibenzothiophen (II)	H-1	$0{\cdot}20_7$	12·7‡
	H-2	$0{\cdot}11_3$	10·8
	H-3	$0{\cdot}11_5$	10·9
	H-4	$0{\cdot}15_2$	7·9‡

* at same mole fraction
‡ linearity assumed

While lack of symmetry in I precludes quantitative discussion of reaction fields, a somewhat similar orientation of the dipole seems likely: the smaller magnitude of μ ($0{\cdot}21 \times 10^{-29}$ C m)[30] as compared with II then leads to slightly less acetone-induced de-shielding (Table 5) for the benzenoid protons. The CCl_4-to-acetone shifts for I and II parallel those of the isosteres III and IV : X=O[20] (Fig. 7): dipole moments for the latter are expected to be similar in magnitude and direction to those of their sulphur analogues in view of similarities for the parent monocycles.[33]

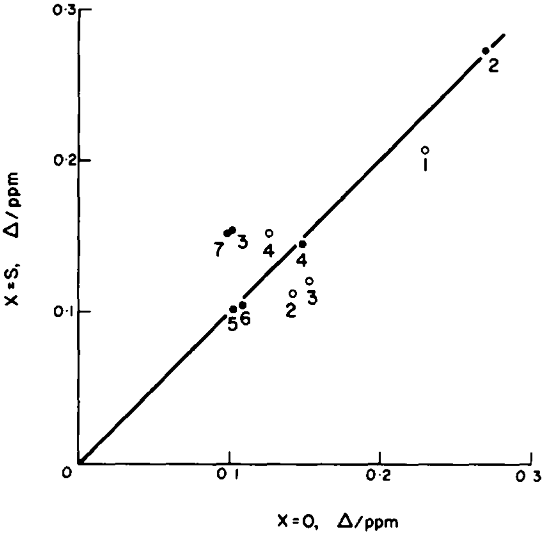


FIG 7. Graphs of $\Delta = (\delta_{Acetone} - \delta_{CCl_4})$ for III and IV: X = S (*i.e.*, I and II, this work) against Δ for III and IV: X = 0 (data of ref. 20). Closed circles represent isosteres of III and open circles isosteres of IV; straight lines is drawn through the origin with gradient unity.

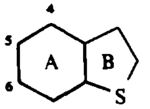
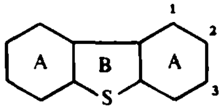
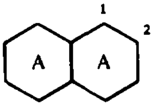
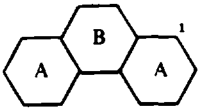
Interactions between solute molecules appear to be responsible for the different dilution shifts of the protons of I and II (Table 5). Alignment of solute molecules with long axes parallel[34, 35] is consistent with the generally larger values found for the three-ring II, compared with I, and with the larger values for the "bay" H(1) of II compared with H(2) and H(3). Larger dilution shifts have been observed for the "bay" protons of a number of polynuclear hydrocarbons[34, 35] which, in the aligned association of molecules assumed, are nearest to most ring centres. Association effects arising from the dipole of the sulphur-containing ring may be responsible for the dilution shifts of H(2) and H(3) of I. Alternatively, one may postulate an arrangement with the sulphur-containing ring held above the (larger) benzenoid ring of the associated molecule, so that H(2) and H(3) are more strongly shielded by the ring current.

PMR estimates of aromaticity in I and II. Elvidge and Jackman[5] suggested that an aromatic compound be defined as one that will sustain an induced ring current. Davies[6] has summarised attempts to test this theory for thiophen from both MO calculations and considerations of PMR shifts, while Sutter and Flygare[36] have shown conclusively by measurements of anisotropies of magnetic susceptibility ($\Delta\chi$) that the ring current in thiophen is less than that in benzene.

We have tried to estimate ring currents in I and II from observed chemical shifts with respect to benzene (7·27 ppm) of protons remote from the highly anisotropic C—S bonds[37] (H(4), H(5) and H(6) of I, and H(1), H(2) and H(3) of II). These were corrected for unequal charge densities on attached carbon atoms[38] as suggested by Schaefer and Schneider,[39] and equated with shifts calculated from Johnson and Bovey[40] tables with amendments for ring areas and for the MO-calculated $\Delta\chi$ of benzene[41] (-30×10^{-12} m^3 mol^{-1}), with ring currents as unknowns.

While this procedure gave ring currents for the *hydrocarbon* analogues of I and II in fair agreement with those calculated[42] (Table 6), there are difficulties in applying it

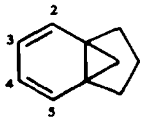
TABLE 6. RING CURRENTS, R, (BENZENE = 1) CALCULATED FROM PROTON CHEMICAL SHIFTS AFTER CORRECTION FOR CHARGE DENSITIES AT ATTACHED CARBON ATOMS

	 I		 II			
R_A	1·06	0·85	1·07*	0·85‡	1·08 (lit.[42] 1·09)	1·08 (lit.[42] 1·13)
R_B	1·11	1·60	1·28*	1·89‡		1·17 (lit.[42] 0·98)
Using shifts of protons	H(4), H(5)	H(4), H(6)	H(1), H(2)	H(1), H(3)	H(1), H(2)	H(1), H(2)

* 1·11 and 1·02 if steric contribution to shift of H(1) is admitted
‡ 0·88 and 1·65 if steric contribution to shift of H(1) is admitted

to the *heterocycles* because combination of the shifts H(4) and H(5) in I gave values for ring currents which differed from those found if H(4) and H(6) are used (Table 6). Similar results are found for II where differences are also observed if a correction to the shift of H(1) is introduced to allow[43] for the steric compression by the opposed H(8). Evidently, these results are, at best, semi-quantitative, but it is noteworthy that in no case is the current in the thiophen ring significantly less than that in benzene, in contrast to the situation in the monocycle.[6, 36]

Since the *ortho* coupling constant in six-membered aromatic ring compounds depends on π-bond order, the aromaticity of heterocyclic compounds may be discussed[7] in terms of partial bond fixation deduced from values of J^{ortho}. The sum of $J_{4,5}$* and $J_{5,6}$ in I in CCl_4 (15·31 Hz) and acetone (15·25 Hz) is close to (a) the sum of the corresponding $J_{1,2}$ and $J_{2,3}$ in (deuterated) naphthalene[44,45] (15·15 Hz and 15·13 Hz); (b) twice J^{ortho} in benzene[46] (7·54 Hz); and (c) the sum (15·19 Hz) of $J_{2,3}$ and $J_{3,4}$ of tricyclo[4.3.1.0]deca-2,4-diene (V).[47]



V

The difference between $J_{4,5}$ and $J_{5,6}$ of I (0·87 Hz. in CCl_4, 1·05 Hz in acetone) is slightly less than the difference in naphthalene (1·44 Hz)[44, 45] and much less than in V (3·31 Hz)[47] or in cyclohexadiene (4·28 Hz),[48] so that I and naphthalene appear to have similar aromaticity. For III :X=O the difference is 0·62 Hz, and for III :X=NH, 0·77 Hz.[20] Günther[49] has suggested that the ratio $J_{5,6} : J_{4,5}$ is a measure of the degree of π-bond localisation ; thus complete localisation gives a value of 0·5, and equivalence a value of unity. For I, the values are 0·89 (CCl_4) and 0·87 (acetone) *c.f.* III :X=O, 0·92; III :X=NH, 0·90.[20]

Arguments based on J^{ortho} are more uncertain in II because of inaccuracies in the determination of $J_{1,2}$ and $J_{3,4}$ discussed earlier ; however, the more precisely extracted $J_{2,3}$ of 7·28 Hz suggests π-bond near equivalence only slightly less than in fluorene

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* $J_{6,7}$ is likely to be more subject to substitution effects.

($J_{2,3}$ = 7·58 Hz)[25, 45] and comparable with that in IV:X=O (7·33 Hz)[20] and IV:X=NH (7·17 Hz).[20]

EXPERIMENTAL

Solutions of commercial samples of I and II, which showed no PMR lines attributable to impurities, were made up by weight in analytical grade CCl_4 and acetone containing a little tetramethylsilane (TMS). The CCl_4 solutions were shaken with a 10% solution of sodium dithionite to remove oxygen.[50] Spectra were recorded on Varian A-60, HA-100 and HR-220 spectrometers. The A-60 operated with the V-6058A spin-decoupler phase lock, and its sweep widths were calibrated against the separation between 2% benzene, 2% TMS in CCl_4 checked against an Advance TC2 timer/counter using sidebands generated by an Advance J2 audio-oscillator. HA-100 and HR-220 spectra were calibrated using sidebands of TMS, which was also the lock signal.

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