The Crystal and Molecular Structure of 1,2,3,5-Tetramethylbenzo[*b*]-thiophenium Tetrafluoroborate and Some Theoretical Calculations on the Hypothetical 1*H*-Thiophenium Cation

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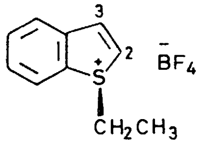
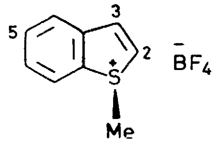
The *X*-ray crystal structure of 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate, refined to *R* 0.043, shows the bonding about sulphur to be pyramidal and not planar. This structure and the ^{13}C n.m.r. spectral data suggest that benzo[*b*]thiophenium salts should be considered as cyclic styrene derivatives. Theoretical calculations also showed an energy maximum for the planar configuration of the 1*H*-thiophenium cation.

THIOPHENE, benzo [*b*]thiophen, and dibenzo[*b*,*d*]thiophen have been converted into their *S*-alkyl derivatives by reaction with alkyl halides in the presence of silver tetrafluoroborate, though the yields of thiophenium salts are low.[1] If the sulphur atom in the parent heterocycle is considered to have a formal sp^2 hybridisation, then the salts might be expected to have a planar geometry about sulphur, so that maximum overlap in an aromatic type $(4n + 2)$ π electron system could be retained. However the ^1H n.m.r. spectra of 2-substituted 1-ethylbenzo[*b*]-thiophenium salts [*e.g.* (1)] and the 3-bromo salt (2) show magnetic non-equivalence of the methylene protons of the ethyl group. This could be explained by the sulphur atom being pyramidal so the methylene hydrogen atoms would be diastereotopic. Diastereotopic hydrogen atoms could also be observed for a planar sulphur atom if there was restricted rotation about the S–CH_2 bond. This explanation would be unlikely for the 3-bromo compound (2) and furthermore 1-ethyl-2-methylquinolinium iodide which is more sterically hindered than (1) does not show the phenomenon. To remove any doubt concerning the stereochemistry, the crystal structure of 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate (5) was therefore examined.



(1) 2-Me
(2) 3-Br



(3)
(4) 2,3-Me_2
(5) 2,3,5-Me_3

RESULTS AND DISCUSSION

Our *X*-ray crystal structure determination has shown that the bonds about the sulphur atom in the benzo[*b*]-thiophenium salt (5) are arranged pyramidally (Figures 1 and 2). The angles about sulphur are 104.0, 105.5, and 92.2°, the last one being in the five-membered ring and is similar to those [2] of the corresponding angles for the benzothiophen (6) (91.7°) [2] and the thiophenium ylid [3] (8) (92.2°). The other two angles are typical of a sulphonium salt [*e.g.* 100.8, 102.5, and 102.3° in (9)].[4] The $^+S–CH_3$ bond length (1.806 Å) is also normal [*cf.* (10),[5] 1.794 and 1.817 Å and (11),[6] 1.800 Å]. The ring S–C bond lengths (1.768 and 1.779 Å) are shorter than in benzo[*b*]thiophen 1,1-dioxide (12) [7] (1.80 and 1.82 Å) and the *S*-phenylsulphonium salt (10) [5] (1.82 Å). The five-membered ring is slightly puckered with the sulphur deviating from the best plane through the benzene ring in the opposite sense to the C(2) and C(3) atoms and the 1-, 2-, and 3-methyl carbon atoms (Table 1).

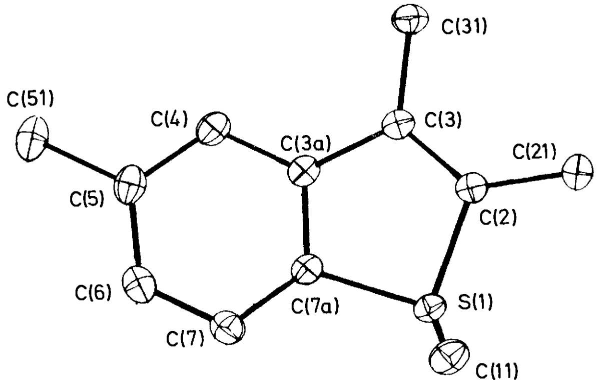


FIGURE 1 1,2,3,5-Tetramethylbenzo[*b*]thiophenium tetrafluoroborate thermal ellipsoid plot. View perpendicular to the plane of the carbocyclic ring

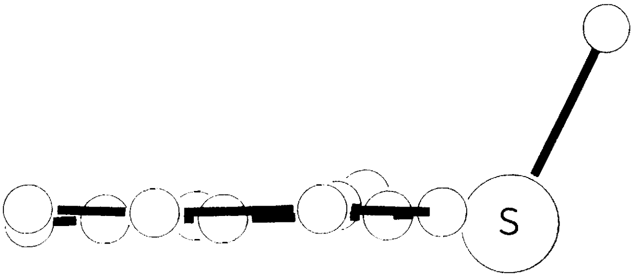


FIGURE 2 View through plane of the carbocyclic ring of 1,2,3,5-tetramethylbenzo[*b*]thiophenium tetrafluoroborate

When compared with the molecular structure of the

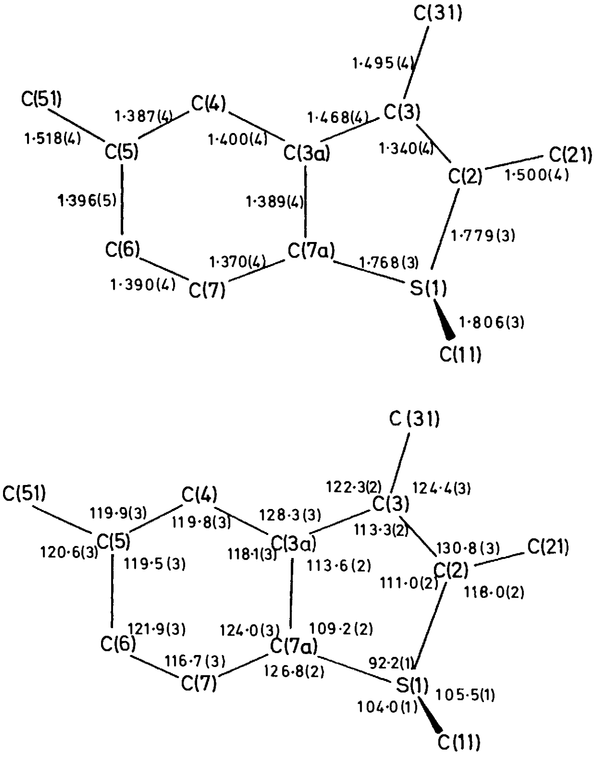
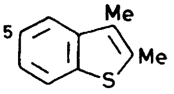
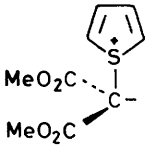


Figure 3 Bond lengths and angles for (5). E.s.d.s. in parentheses



(6)
(7) 5-Br



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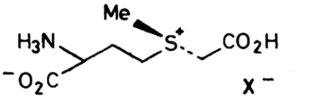
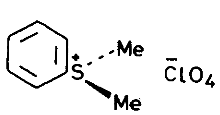
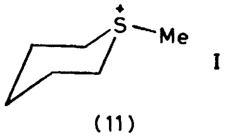


(9) $X^- = 2,4,6\text{-}(NO_2)_3C_6H_2SO_3^-$



(10)



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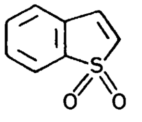


(12)

benzo[*b*]thiophen (7) (Figure 4) the salt (5) has longer (by 0.03 Å) ring C–S bonds, a shorter (by 0.02 Å) C(2)–C(3) bond and a longer C(3)–C(3a) bond, supporting the involvement of a sulphur lone pair in the π bonding of benzo[*b*]thiophens. However the large e.s.d.s for the bond lengths of (7) (0.012 Å) weaken the value of this comparison. A similar relationship holds between the thiophenium ylid (8) and thiophen [8] with the ylid having longer C–S bonds (by 0.02 Å), shorter formal double bonds (by 0.05 Å), and a longer formal single bond (0.06 Å). 1-Methylbenzo[*b*]thiophenium tetrafluoroborate (3) adds bromine *trans* to the 2,3-double bond [1] while benzo[*b*]thiophen is substituted [9] mainly at position 3. This is strong evidence for the relative lack of aromaticity in the fused thiophenium ring. Even if benzo[*b*]thiophen is substituted by an initial addition of bromine to the 2,3-bond, the corresponding bromine addition product (13) of the benzo[*b*]thiophenium salt would be expected to lose hydrogen bromide more readily due to the greater acidity of a hydrogen α to a positively charged sulphur. Although the loss of hydrogen bromide from (13) would involve increasing the steric interaction between the 1- and 2-substituents this is unlikely to be critical.

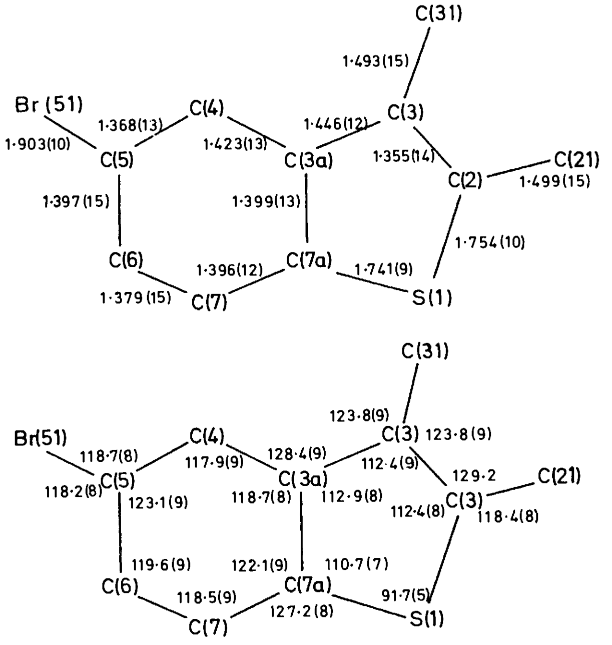
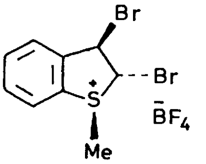


Figure 4 Bond lengths and angles for (7). E.s.d.s. in parentheses



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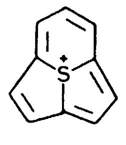

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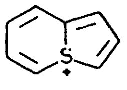


(15)

Doubts are therefore cast on calculations which suggest that cations (14) and (15) should be stable.[10] Furthermore *ab initio* calculations, performed with a minimal basis set using STO-3G,[11] on the hypothetical thiophenium cation (16) for varying values of θ gave an energy maximum for the planar conformation (θ 180°).

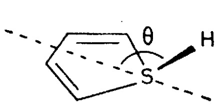
The ^{13}C n.m.r. spectrum (Table 2) of the benzo[*b*]thiophenium salt (4) shows the $^{+}$S–CH$_3$ resonance at δ 30.0 p.p.m. in good agreement with δ 27.5 p.p.m. for a trimethylsulphonium salt.[12] The doublet resonances of the benzene ring are deshielded compared with the corresponding benzo[*b*]thiophen (6) [13] and are similar to the doublet resonances of methyl phenyl sulphoxide [14] (Table 2). However C(2) and C(3) show smaller shifts when the sulphur is alkylated, the former being, surprisingly, upfield. This does not seem too unreasonable by comparison with styrene (Table 2) [15] in which the terminal olefinic carbon resonates at δ 112.3 p.p.m. The 2- and 3-methyl groups would be expected to deshield C(2) by *ca.* 3 p.p.m. and the sulphonium group should effect a further deshielding of C(2) by *ca.* 18 p.p.m., judging from the effect of a sulphoxide substituent on a benzene ring carbon in methyl phenyl sulphoxide.

TABLE 1

Deviations from the best plane through the benzene ring of (5)

Atom	Deviation (Å)	Atom	Deviation (Å)
S(1)	0.044	C(11)	−1.557
C(2)	−0.151	C(21)	−0.279
C(3)	−0.071	C(31)	−0.041

Equation of plane: $7.40x - 7.05y - 3.10z = -5.36$



(16)

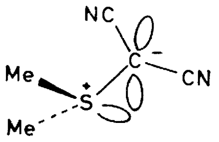
TABLE 2

^{13}C n.m.r. spectra measured at 22.63 MHz in deuteriochloroform [δ (p.p.m.) from internal Me$_4$Si]. ^{13}C–^{1}H Attachments were confirmed by off-resonance decoupling

	Compound	
	(4)	(6) [13]
Assignment	Resonance positions	
1-*C*H$_3$	30.0	
2-*C*H$_3$	11.3	11.2
3-*C*H$_3$	12.4	13.7
2-*C*	130.5 *	133.6
3-*C*	129.2 *	127.9
3a-*C*	143.0 ‡	140.9
4-, 5-*C*,	127.2,† 133.5,	121.0, 123.7,
6-, 7-*C*	129.9,† 124.4	123.3, 121.9
7a-*C*	144.5 ‡	138.1
	PhSOMe [14]	Styrene [15]
1-*C*	146.3	138.2
2-, 6-*C*	123.6	126.7
3-, 5-*C*	129.4	128.9
4-*C*	131.0	128.2
1′-*C*		135.8
2′-*C*		112.3
S-*C*H$_3$	44.0	

*,†,‡ Indicate interchangeable assignments.

It is difficult to estimate the contribution sulphur 3*d* orbitals make to the bonding in benzo[*b*]thiophenium salts. On the one hand the benzene ring is deshielded compared with styrene or a benzo[*b*]thiophen, which could be accounted for by back-donation of π electrons from the benzene ring into sulphur 3*d* orbitals. On the other hand, the S(1)–C(7a) bond (1.768 Å) is comparable with the S–C (phenyl) bond (1.763 Å) in 2,3,5,6-tetrachloro-4-cyanophenyl methyl sulphide.[16] Shortening of the C–S bond in the latter compound by conjugation of the sulphur 3*p* orbitals with the aromatic π system is precluded by the conformation of the molecule. The S–C (phenyl) bond length in the sulphonium salt (10) (1.82 Å) is surprisingly long but must be regarded cautiously due to the large e.s.d.s (0.02 Å). The S–C bond lengths in the ylids (8) [3] and (17),[17] 1.72 and 1.71 Å, respectively, are considerably shorter than the comparable length in (5). The possibility that 3*d* orbitals are involved to a greater extent in the first two compounds than in the last cannot be established as coulombic interactions would be expected to shorten this bond in any event. The conformations of the substituents about the S–C bonds of these ylids, and in the salt (10), in the crystalline state are very similar with the lone pair of the sulphur atom almost at 90° to the *p*-orbital on the adjacent carbanion, or aromatic carbon atom [for (10)].



(17)

It may be concluded that the crystal structure for (5), the easy addition of bromine to (3), and the spectral data suggest that these benzothiophenium salts are best considered as cyclic derivatives of styrene rather than as highly stabilised 10π aromatic systems.

EXPERIMENTAL

Crystal Structure Determination for Compound (5).—Crystals of (5), $C_{12}H_{15}BF_4S$, prepared as described,[1] were grown by diffusion of ether into a dichloromethane solution. Oscillation and Weissenberg photographs suggested that the crystal was triclinic. It was transferred to an Enraf Nonius CAD4 four-circle diffractometer, and the crystal system, actually monoclinic ($Z = 8$, $\mu = 2.73$ cm^{-1}), and accurate cell dimensions [$a = 16.37(1)$, $b = 7.91(1)$, $c = 22.01(2)$ Å, $\beta = 111.37(4)°$] were determined. Diffraction data were collected using Mo-K_α radiation by a ω–2θ scan and standard reflections were checked every hour. The space group ($C2/c$) was assumed from systematic absences and the number of formula units (8) per unit cell. The crystal density, 1.40 g cm^{-3} (theoretical value 1.40 g cm^{-3}), was determined using a Westphal balance. Lorentz and polarisation corrections were applied to the 2 599 reflections, equivalent reflections merged, and structure amplitudes derived for 1 528 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods using MULTAN 77,[18] and refined by full-matrix least squares to an R value of 0.178 using isotropic temperature factors. Further refinement using anisotropic temperature factors lowered the R value to 0.075, after which a differential Fourier synthesis located all

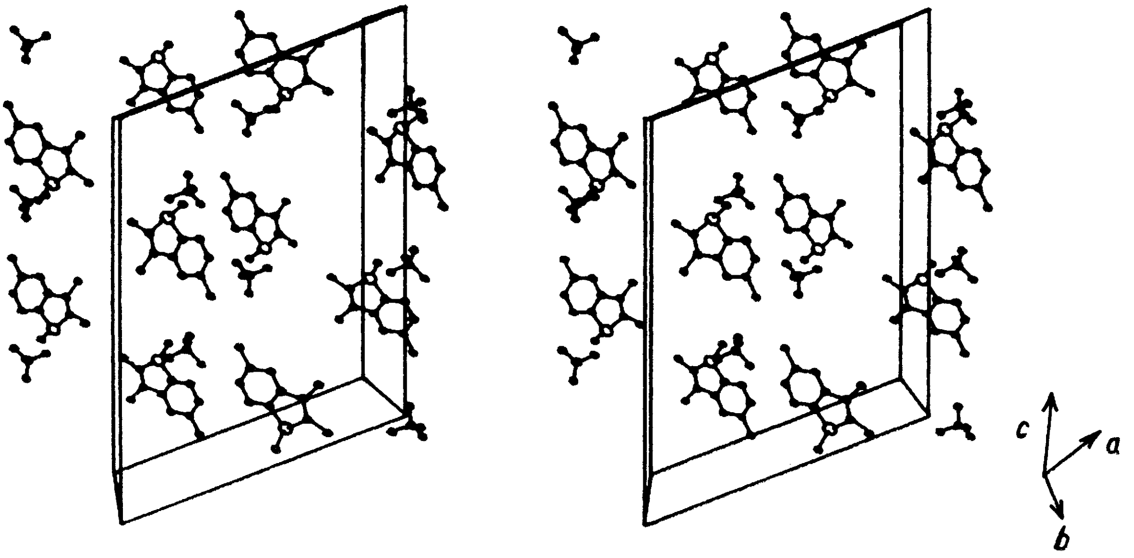


FIGURE 5 Stereoscopic packing diagram for (5)

the hydrogen atoms. The structure was refined to convergence by blocked-matrix least squares, including an isotropic extinction parameter, and with constraints applied to the hydrogen atoms [C–H distance constrained to 1.000 Å with an e.s.d. of 0.01 Å, $C-\hat{C}(sp^2)-H$ constrained to their common mean of 120.18 Å with an e.s.d. of 2.00°]. For each methyl group the $H-\hat{C}-H$ angles were constrained to their common means (Table 3) and $C(S)-\hat{C}-H$ constrained to their common mean, both with an e.s.d. of 2.00°. The components of the temperature factors of hydrogen atoms and of the carbon atoms to which they were bonded were constrained [19] to have the same magnitude in the direction of the bond, with an e.s.d. of 0.004 $Å^2$. Weights were computed from the Chebyshev series $w = [49.13t_0\ (X) + 67.68t_1\ (X) + 19.69t_2\ (X)]^{-1}$ where $(X) = F_o/F_{max.}$[20] Data reduction and structure refinement were done using CRYSTALS [21] and all calculations were made on the Oxford University ICL 1906A computer. Figure 5 shows a structure packing diagram.

TABLE 3

Mean values of $H-\hat{C}-H$ and $C(S)-\hat{C}-H$ for methyl groups in (5)

Methyl carbon	Mean value for $H-\hat{C}-H$ (°)	Mean value for $C(S)-\hat{C}-H$ (°)
C-11	106.737	111.345
C-12	109.774	108.724
C-13	106.392	112.038
C-15	111.821	106.745

Final atomic co-ordinates, anisotropic temperature factors, and structure factors are available in Supplementary Publication No. SUP 22999 (13 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index Issue.