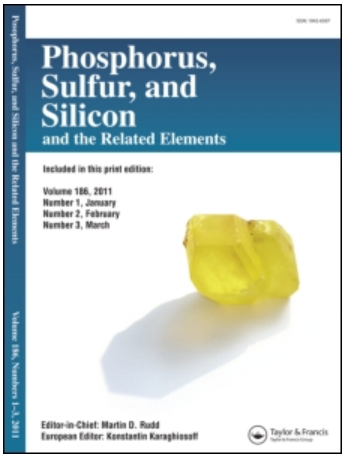

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HETEROCYCLIC CATIONS WITH DELOCALISED PI-SYSTEMS AND SHORT INTRAMOLECULAR SULFUR... SULFUR CONTACTS: THE STRUCTURES OF TWO DERIVATIVES OF THE 2-(1,3-DITHIOL-2-YLIDENEMETHYL)-1,3-DITHIOLIUM CATION

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HETEROCYCLIC CATIONS WITH DELOCALISED PI-SYSTEMS AND SHORT INTRAMOLECULAR SULFUR...SULFUR CONTACTS: THE STRUCTURES OF TWO DERIVATIVES OF THE 2-(1,3-DITHIOL-2-YLIDENEMETHYL)-1,3-DITHIOLIUM CATION

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The effective size of bonded divalent sulfur in S...S contacts is a function of the orientation of the groups, with the shortest contacts occurring when the groups are coplanar. A lower limit for the latter is indicated by the structures of the 2-(1,3-benzodithiol-2-ylidenemethyl)-1,3-benzodithiolium and 2-(1,3-dithiolan-2-ylidenemethyl)-1,3-dithiolanium cations, **2** and **3**. These show almost *mm* symmetry with all four sulfur atoms involved in stabilisation of the positive charge. Short intramolecular sulfur...sulfur contact distances, 0.5–0.7 Å within the sum of traditional van der Waals radii, and maximised by in-plane angular distortions, indicate a lower limit to the effective size of the bonded divalent sulfur atom of ca. 1.45 Å.

Keywords: 2-(1,3-Benzodithiol-2-ylidenemethyl)-1,3-benzodithiolium; 2-(1,3-dithiolan-2-ylidenemethyl)1,3-dithiolanium; atomic size; X-ray; van der Waals radius molecular structure

INTRODUCTION

A knowledge of minimum intermolecular contact distances for particular pairs of bonded atoms is very important for the successful parameterisation of force fields in the modelling of interactions between molecules. This is relevant, on the one hand, to host-guest systems and the binding of a small molecule to a

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biological macromolecular receptor and, on the other hand, to the choice of packing arrangement for molecules in the crystalline state. Such distances are often not reliably predicted by Van der Waals radii which were derived thirty years ago from intermolecular separations in crystals of elements and simple compounds.[1] Depending on the atoms involved, there may be attractive interactions of HOMO/LUMO type[2] or of an electrostatic nature to consider[3], as well as mutual polarisations of functional groups in some cases.[4] Even when the two atoms are identical, the situation is not always straight forward. Thus, whereas carbonyl oxygen behaves more or less as a sphere in C=O...O=C contacts, thiocarbonyl sulfur in C=S...S=C contacts shows its effective size to be larger perpendicular to the C-S axis than parallel to it[5]. Sulfide sulfur, as in a dialkyl sulfide, shows a similar effect. A simple description of this bonded sulfur atom envisages it as using two *p* orbitals to participate in its two covalent bonds so that the two lone pairs of electrons are distributed between an orbital of high *p* character and an orbital of high *s* character. The former has a greater spatial distribution than the latter and lies perpendicular to the plane of the sulfide group while the latter lies in-plane (Fig. 1). However the bonding might be described, two different effective radii can be assigned for this bonded sulfur atom, one directed at right angles to the plane, and one lying in-plane.[6] The former is close to the traditional van der Waals radius (1.8 Å)[1] and the latter radius could be assigned a value of ca. 1.6 Å based on the S...S separation in *meso*-lanthionine dihydrochloride where the sulfide groups are nearly coplanar[7]. However, the large number of structural measurements (> 200) on radical cation salts of *bis*(ethylenedithio)-tetrathiafulvalene ('BEDT-TTF') **1** provides the most evidence for the asymmetric shape of the sulfide sulfur atom; the shortest intermolecular edge to edge S...S contacts (3.3 Å) are less than the shortest S...S contacts within a stack.[8] In general, minimum intramolecular contact distances are likely to be even shorter than the corresponding intermolecular distances by a small amount due to the extra constraints which can be imposed.

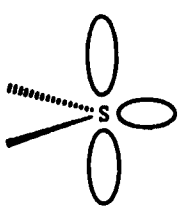
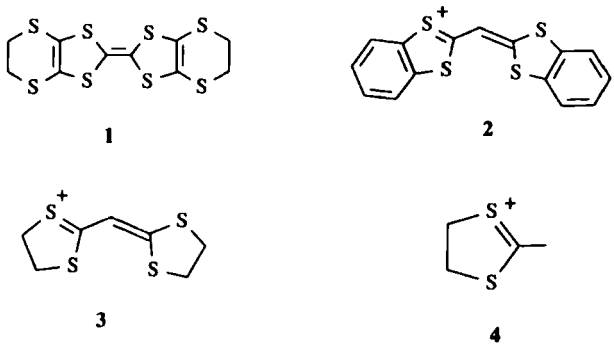


FIGURE 1 Approximate representation of orbitals occupied by a sulfide sulfur atom's lone pairs of electrons.



SCHEME 1

In connection with studies on organic conductors and superconductors we have synthesized salts of two cations **2** and **3** which are derived from the 2-(1,3-dithiol-2-ylidenemethyl)-1,3-dithiolium system. Both these cations could be stabilised in a planar conformation which allows the positive charge to be delocalised over the four sulfur atoms and the three central carbon atoms. However, an undistorted structure (Fig. 2) would require an exceptionally short intramolecular (1,5) sulfur...sulfur contact of ca. 2.5 Å between the two heterocyclic rings, which would be 0.7 Å within the sum of two 'in-plane' effective atomic radii for bonded sulfide sulfur. These symmetrical systems provide a good test for determining the lower limit for the approach of two divalent sulfur atoms. To investigate this in more detail we have measured the structures of these cations by X-ray diffraction.

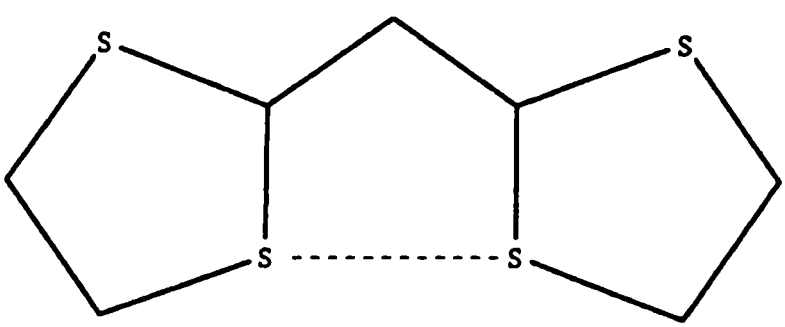


FIGURE 2 Undistorted molecular skeleton of cation **3**

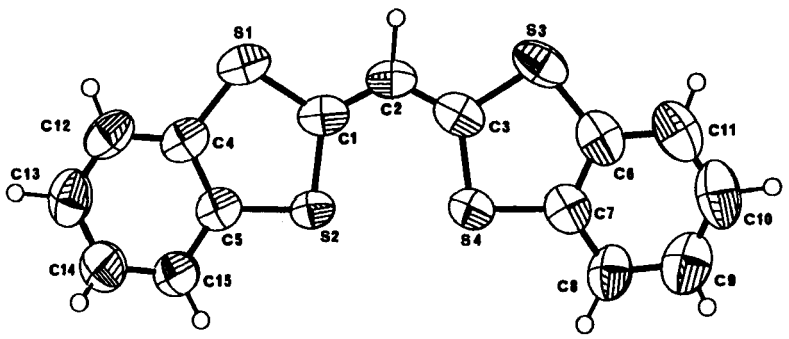


FIGURE 3 Molecular structure of cation **2** with displacement parameters drawn at the 50% level (PLATON[27]).

RESULTS AND DISCUSSION

The cations **2** and **3** were synthesized as their tetrafluoroborate salts by reaction of benzene-1,2-dithiol or ethane-1,2-dithiol with malonyl dichloride in the presence of ethereal fluoroboric acid following a procedure of Klaveness and Undheim for preparing dithiolanium salts such as **4**[9] from dithiols and acid chlorides. The ^{1}H and ^{13}C NMR data for **2**.BF_4 and **3**.BF_4 indicate that in solution the cations have structures which are symmetrical about the carbon atom which connects the heterocycles. The chemical shift of this carbon atom in **2** and **3** (δ: 109.5 & 113.7 respectively) is much lower than that of its bonded neighbours which are attached to two sulfur atoms (δ: 174.0 and 198.8) suggesting that the positive charge is mainly localised on the heterocyclic rings. The hydrogen atom on each of the central carbon atoms is significantly deshielded (δ: 8.76 & 7.76). X-Ray measurements were made at 293 K for **2**.BF_4, but at 150K for **3**.BF_4 since the ambient temperature crystal structure showed substantial molecular thermal motion.[10]

The structures and atomic numbering systems for both cations are illustrated in Fig. 3 and Fig. 4. (There are two cations with very similar conformations in the asymmetric unit of **3**.BF_4.) Selected molecular geometry is given in Table I. The conformations of cations **2** and **3** are similar. The central portions of each cation (the four sulfur atoms and three intervening carbon atoms) show three particular features: they have an almost planar structure with approximate *mm* symmetry, there is a short intramolecular sulfur...sulfur contact, and there are in-plane angular distortions at the three carbon atoms. Thus, each cation has maximised the possibility of delocalising the positive charge via the π-system, but shows in-plane angular distortions which increase the intramolecular sulfur...sulfur contact to 2.894(2) Å in **2** and 3.036(1) and 3.061(1) Å in **3**. The structure of **2**.BF_4 will be described in detail first.

TABLE I Selected Molecular Geometry for Cations **2** and **3** (molecules A and B) with estimated standard deviations in parentheses.

			Interatomic Distances (Å)				
	2	**3(A)**	**3(B)**		**2**	**3(A)**	**3(B)**
S(1)-C(1)	1.722(4)	1.718(3)	1.729(3)	S(3)-C(3)	1.718(4)	1.731(3)	1.716(3)
S(1)-C(4)	1.724(6)	1.804(4)	1.803(4)	S(3)-C(6)	1.734(5)	1.817(4)	1.809(4)
S(2)-C(1)	1.710(5)	1.712(3)	1.725(3)	S(4)-C(3)	1.709(5)	1.724(3)	1.717(3)
S(2)-C(5)	1.738(5)	1.819(4)	1.808(4)	S(4)-C(7)	1.726(4)	1.835(4)	1.834(3)
C(1)-C(2)	1.392(6)	1.400(5)	1.384(4)	C(2)-C(3)	1.396(6)	1.374(5)	1.397(4)
C(4)-C(5)	1.396(7)	1.517(5)	1.483(5)	C(6)-C(7)	1.382(6)	1.494(6)	1.496(5)
S(2)...S(4)	2.894(2)	3.036(1)	3.061(1)				
			Bond Angles (°)				
	2	**3(A)**	**3(B)**		**2**	**3(A)**	**3(B)**
C(1)-S(1)-C(4)	96.9(2)	96.3(2)	96.1(2)	C(3)-S(3)-C(6)	96.5(2)	95.4(2)	95.8(2)
C(1)-S(2)-C(5)	97.5(2)	95.7(2)	96.1(2)	C(3)-S(4)-C(7)	96.7(2)	96.1(2)	95.3(2)
S(1)-C(1)-S(2)	114.6(3)	115.9(2)	115.8(2)	S(3)-C(3)-S(4)	115.0(3)	115.9(2)	116.2(2)
S(1)-C(1)-C(2)	120.4(3)	119.0(2)	118.6(2)	S(3)-C(3)-C(2)	120.7(3)	118.4(3)	118.1(2)
S(2)-C(1)-C(2)	125.0(4)	125.1(3)	125.6(2)	S(4)-C(3)-C(2)	124.3(3)	125.7(3)	125.7(2)
C(1)-C(2)-C(3)	124.9(4)	127.5(3)	127.5(3)				
S(1)-C(4)-C(5)	116.4(4)	106.8(3)	109.4(3)	S(3)-C(6)-C(7)	115.5(5)	108.1(3)	108.4(2)
S(2)-C(5)-C(4)	114.7(4)	107.6(2)	110.2(3)	S(4)-C(7)-C(6)	116.2(4)	108.9(3)	106.8(3)

The best planes of the two heterocyclic rings in cation **2** are almost coplanar (interplanar angle: 2.1(3)°). The two C,C bonds from C(1) and C(3) to the central atom C(2) are very similar in length (1.392(6) & 1.396(6) Å) and are ca. 0.5 Å longer than a typical C,C double bond. The four C-S bonds to C(1) and C(3) lie in the range 1.709(5)–1.722(6) Å. The most important factors in increasing the distance between S(2) and S(4) are the in-plane angular distortions at trigonal carbons C(1), C(2) and C(3). Angles S(2)-C(1)-C(2), C(1)-C(2)-C(3)

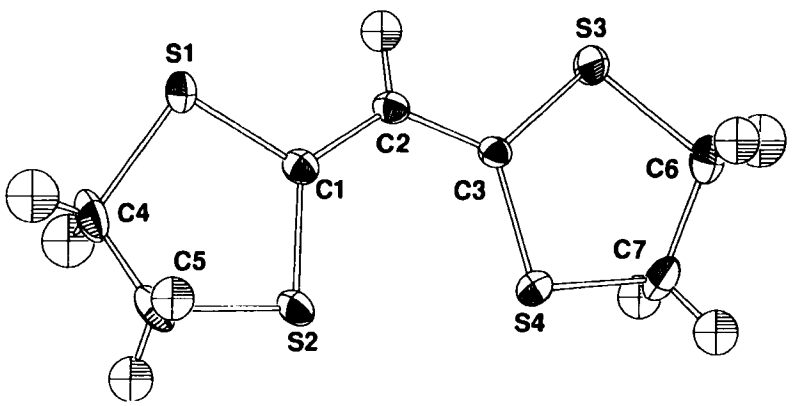
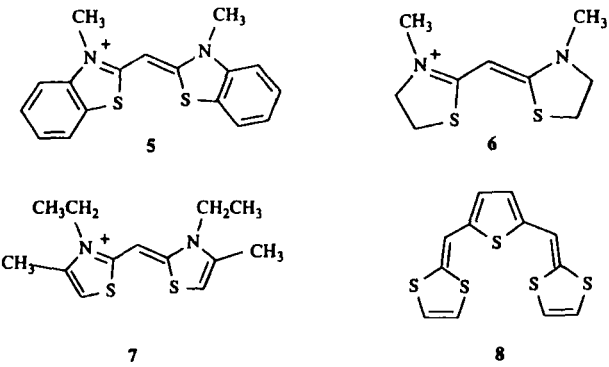


FIGURE 4 Molecular structure of cation **3** (molecule A) with displacement parameters drawn at the 50% level (PLATON[27]).

and C(2)-C(3)-S(4) are widened to 125.0(4), 124.9(4) and 124.3(3)°, so that the S(2)...S(4) contact is 2.894(2) Å. The atoms C(5), S(2), S(4) and C(7) are nearly collinear; the S(2)...S(4) vector makes angles of 179.5° and 179.0° with the S(2)-C(5) and S(4)-C(7) bonds. (It has been noted that short contacts from sulfide sulfur to electron-rich species tend to lie along the extension of a C-S bond.[11]) The bonds to sulfur from the benzene rings (1.724–1.738 Å) are ca. 0.015 Å longer than those to C(1) and C(3), indicative of the significant involvement of the sulfur atoms in the delocalisation of the positive charge.

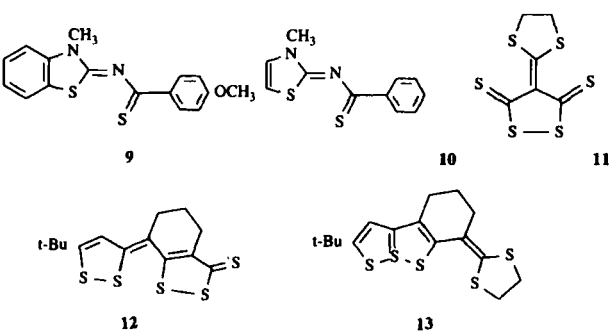
The structure of cation **3** differs from that of **2** in several ways. The S(2)...S(4) contact distances in the cations of **3** are larger than that in **2** by 0.15–0.17 Å. The in-plane angular distortions at C(1), C(2) and C(3) are more severe than in **2**, especially at the central atom with angle C(1)-C(2)-C(3) wider by 2.6°. The conformation of each heterocyclic ring is a half chair with the methylene carbons displaced in opposite directions out of the plane defined by the other three ring atoms by 0.22–0.28 Å. For molecule A, carbon atoms C(4) and C(7) are displaced to one side of the molecular plane and carbon atoms C(5) and C(6) are displaced to the opposite side; but for molecule B, carbon atoms C(4) and C(6) (and C(5) and C(7)) are displaced to the same side of the molecular plane. The ring conformations cause the axes of *s* type lone pairs on atoms S(2) and S(4) to be displaced from the best planes of the corresponding heterocyclic rings in opposite directions for cation A, but in the same direction for cation B, which may account for the small difference in S...S separations (by 0.025(2) Å).

The fusion of benzene rings to the heterocyclic structure in cation **2** would be expected to stabilise the cation by donation of π electron density and development of aromatic character in the heterocyclic rings, and indeed there is a notable reduction (by 25 p.p.m.) in the chemical shifts of the most deshielded carbon atoms, C(1) and C(3), in **2** compared with **3**. It should be noted that the whole cation **2** could be considered as a 22 π electron system with the potential for some degree of aromatic stabilisation, albeit with a long S,S link. This may contribute to the slightly shorter S...S contact in cation **2** than in cation **3** (by ca 0.15 Å). The greater conjugation in **2** is indicated by the position of the u.v. maximum at 503 nm., (cf. 420 nm. in **3**), and the increased downfield shift of the central methine hydrogen atom (by 1.0 p.p.m.) may be related to an aromatic ring current effect. A search of the Cambridge Crystallographic Database revealed similar short S...S contacts in species with approximate *mm* symmetry: the cations **5**–**7**[12–14] (as their TCNQ salts) (**5**: 2.964, **6**: 2.992, **7**: 3.065 Å) and the neutral molecule **8**[15] (3.065 Å). Molecules **9**–**11**[6,16], which show similar short S...S contacts (2.906(1), 2.926(1) and 2.93(1) Å), are also formally 10 π or 14 π heterocyclic systems. (In the latter cases, the delocalisation of charge from one sulfur to the other could lead to an attractive electrostatic component



SCHEME 2

to the S,S interaction.) Similar short intramolecular contacts have been observed in **12** where the S,S contact distance is 2.86 Å[17] and **13** where the distance is 2.96 Å[18], though neither structure possesses the extra symmetry of **2** and **3**. For in-plane intramolecular sulfur...sulfur contacts between sulfide groups the effective atomic radius is ca. 1.45 Å, about 0.15 Å smaller than the corresponding effective radius in intermolecular S...S contacts. That is to say, that at separations below ca. 2.9 Å the interatomic repulsion becomes intolerably high. Apart from reference to a possible aromatic contribution to stabilisation of the short S...S contact we have avoided deliberately the question of whether there is indeed some weak S,S bonding present, which could be envisaged if the sulfur atoms in contact adopted a higher valence state. Accurate electron density measurements may provide further evidence for this. (Such a study on a S...O=C showed no increase in charge density between the heteroatoms[19]). An analysis of



SCHEME 3

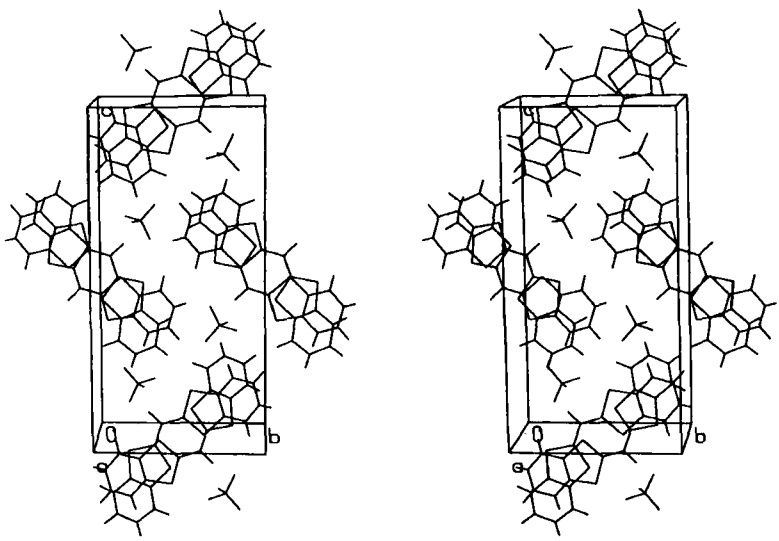


FIGURE 5 Molecular packing arrangement for $2.BF_4$ (PLUTON[28]); only one orientation of the disordered tetrafluoroborate ion is shown.

the electron density distribution using the 'theory of atoms in molecules' developed by Bader and colleagues,[20] may determine whether there is a bonding interaction between the sulfur atoms.

The crystal packing arrangements for $2.BF_4$ and $3.BF_4$ are shown in Fig. 5 and Fig. 6. The tetrafluoroborate ions in $2.BF_4$ show some orientational disorder [21]. In the crystal structure of $2.BF_4$ the cations are arranged in stacks along the *a* axis with centres of symmetry between each pair of neighbours in the stack. There are no sulfur...sulfur contacts less than 3.75 Å between cations, and the shortest sulfur...fluorine contacts, from S(2) and S(4) to the anion, are ca. 3.0 Å. In the crystal packing of $3.BF_4$ one dithiole ring from each cation, A and B, form ABAB type stacks along the *a* axis, in which the longest molecular axes of A and B lie roughly perpendicular. The anions are well ordered at this lower measurement temperature. One tetrafluoroborate ion lies in the space between the second dithiole rings of the A cations. There are three short intermolecular sulfur...sulfur contacts in the range 3.57–3.61 Å (S(1A)...S(3A, 2 − x, 1 − y, 1 − z), S(3A)...S(3B, 1.5 − x, 0.5 + y, 0.5 − z), S(1B)...S(3B), 1.5 − x, 0.5 + y, 0.5 − z). The shortest S...F contacts are 3.03 (S(4A)...F(1B, 1.5 − x, y − 0.5, 0.5 − z), and 3.04 (S(1B)...F(3B, x, y, z).

Cations **2** and **3** are attractive precursors for preparation of allenes **14** and **15**. Other workers have reported that treatment of these salts with sodium hydride in DMF gave **16** and **17** which they claimed was due to head to head dimerisation

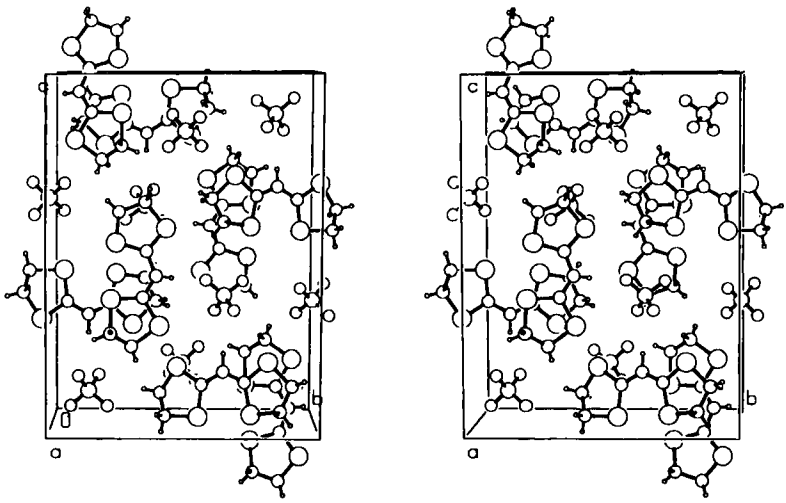
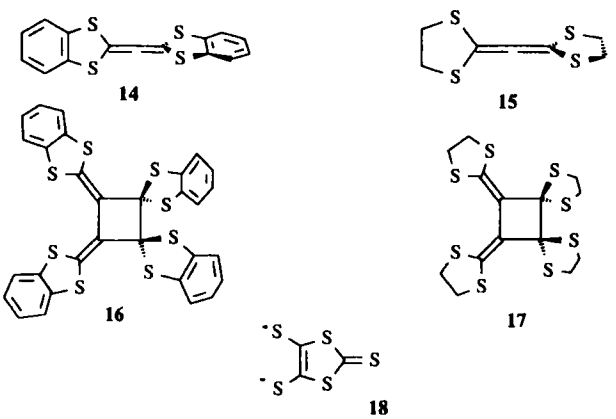


FIGURE 6 Molecular packing arrangement for $3.BF_4$ (PLUTON[28]); hydrogen atoms are excluded, and only one orientation of the disordered tetrafluoroborate ion is shown.

of the preformed allene.[22] This is rather surprising and an alternative explanation of the regiochemistry of these reactions is that the allene has reacted with the unreacted cation and not with another allene molecule. Attempts to form analogues of **5** from 2-thioxo-1,3-dithioledithiolate **18** and malonyl dichloride for preparation of electroactive organic materials have been unsuccessful.



SCHEME 4

EXPERIMENTAL

2-(1,3-Benzodithiol-2-ylidenemethyl)-1,3-benzodithiol-1-ium Tetrafluoroborate. 2.BF_4

A solution of fluoroboric acid in ether (0.3 ml, 40%) was added dropwise over 10 min. to a stirred solution of benzene-1,2-dithiol (0.35 g, 2.46 mmol) and malonyl dichloride (0.18 g, 1.28 mmol) in ether (7 ml) at 0°, and left stirring for 15 min. during which time an oil separated. After stirring for 1 h at room temperature, trituration with addition of further ether (10 ml) gave 2.BF_4 (0.25 g, 50%), as red needles, m.p. 248–250 °C (from acetonitrile/ether) (Found: C, 44.6; H, 1.9%. $C_{15}H_9S_4BF_4$ requires C, 44.6; H, 2.2%); δ_H: (100 MHz, DMSO-d_6): 8.76 (1H, s, methine-H), 8.32 (4H, dd, J 6, 3 Hz, 4-,7-,4′-7′-H); 7.70 (4H, J 6, 3 Hz, 5-,6-,5′-,6′-H); δ_C (67.6 Hz, DMSO-d_6): 174.0 (2-,2′-C), 137.5 (3a-,7a-,3a′-,7a′-C), 128.9 (4-,4′-,7-,7′-C), 125.0 (5-,5′-,6-,6′-C), 109.5 (methine-C); $\nu_{max.}$ 1626, 1303, 1060, 746 cm^{-1}, $\lambda_{max.}$ 286 (10,900), 375 (6,000), 502 (21,000) nm.

2-(1,3-Dithiolan-2-ylidenemethyl)-1,3-dithiolanium Tetrafluoroborate. 3.BF_4

Reaction of ethane-1,2-dithiol, malonyl dichloride and fluoroboric acid following the method above gave 3.BF_4 (46%), as a yellow precipitate, m.p. 229–230°C. (Found C: 27.0, H: 2.6% $C_7H_9S_4BF_4$ requires C: 27.3, H: 2.9%) δ_H (270 MHz, CD_3NO_2): 7.76 (1H, s, methine-H); 4.21 & 4.05 (2 × 2H, 2 × br, CH_2CH_2); δ_C (67.6MHz, CD_3NO_2): 198.8 (2-,2′-C), 113.7 (C-H), 46.0 & 41.3 (4,-4′,5-,5′-C); $\nu_{max.}$ 1315, 1278, 1160, 1034 cm^{-1}, $\lambda_{max.}$ (CH_3OH) 286 (1,300), 366 (1,200), 420 (7,500) nm.

X-Ray Crystal Structure Determination of 2.BF_4 and 3.BF_4

Crystal data for 2.BF_4

$C_{15}H_9S_4.BF_4$, M_r = 404.2, monoclinic, a = 7.246(3), b = 10.716(3), c = 12.122(6), β = 92.41(2)°, V = 1638.7 Å^3, $P2_1/c$, Z = 4, $D_{calc.}$ 1.59 g cm^{-3}, T = 293K, μ(MoKα) 5.9 cm^{-1}, 2614 unique reflections, 2141 with $I > 3\sigma(I)$, F(000) = 816, 292 parameters refined, final R 0.051, R_w 0.056.

Crystal data for 3.BF_4

$C_7H_9S_4.BF_4$, M_r = 308.2, monoclinic, a = 8.557(2), b = 14.553(2), c = 19.081(4) Å, β = 90.21(1)°, V = 2376 $Å^3$, $P2_1/n$, Z = 8, $D_{calc.}$ = 1.72 g cm^{-3}, T = 150 K, μ(MoKα) = 8.2 cm^{-1}, 3648 unique reflections, 2284 $F_0 > 4\sigma(F_0)$ F(000) 1248, 361 parameters refined, final R_1 0.040, wR_2 0.094.

The salt **2**.BF_4 forms very long and thin red crystals by diffusion of ether into an acetonitrile solution; needles grow to lengths greater than 1 cm with cross-sections of about 0.15 × 0.15 mm. Diffraction intensities were measured at room temperature using MoKα radiation on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Structures were solved with SHELXS-86,[23] and refined by full-matrix least-squares using SHELX 76.[24] Isotropic hydrogen atoms, located from difference Fourier maps, were included and two orientations of the tetrafluoroborate ion were refined (final ratio 62:38). It was necessary to include restraints to the B,F bonds (1.351(5) Å) and F,F bonds (2.206(5) Å). The refinement converged at R = 0.051 and R_w = 0.056 using weighting scheme $w^{-1} = [\sigma^2F + 0.0005F^2]$, and with maximum and minimum peaks in final difference Fourier maps of +0.39 & −0.34 e $Å^{-3}$. The maximum values of Δ/σ for atomic coordinates and anisotropic displacement parameters of non-hydrogen atoms were 0.15 and 0.15 for the cation, and 0.26 and 0.35 for the anion.

For **3**.BF_4 diffraction intensities were measured at 150K on an Enraf Nonius FAST system. The structure was solved with SHELXS-86[23] and refined with SHELXL-93[25]. Hydrogen atom positions were located in difference Fourier maps and included in the refinement. An empirical absorption correction based on ΔF using DIFFABS[26] was applied. The model converged at R = 0.040 and R_w = 0.068 with weighting scheme $w^{-1} = [\sigma^2(F_0^2) + 0.0383P]$ where P is [(larger of F^2 or 0) + 2 F_0^2]/3 and with maximum and minimum peaks in final difference Fourier maps of 0.56 & −0.38 e $Å^{-3}$. The maximum values of Δ/σ for atomic coordinates and displacement parameters are 0.10 and 0.01 for the cations and 0.04 and 0.004 for the anions. Final atomic coordinates have been submitted to the Cambridge Crystallographic Data Centre, and anisotropic displacement parameters and structure factor tables are deposited as Supplementary Data.

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