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Synthetic, Structural and Electrochemical Studies on the 1,2-Dithiole-3-thione System: Preparation and Reactions of the 5,6-Dihydro-1,2-dithiolo[4,5-*b*][1,4]dithiin-3-ium Cation

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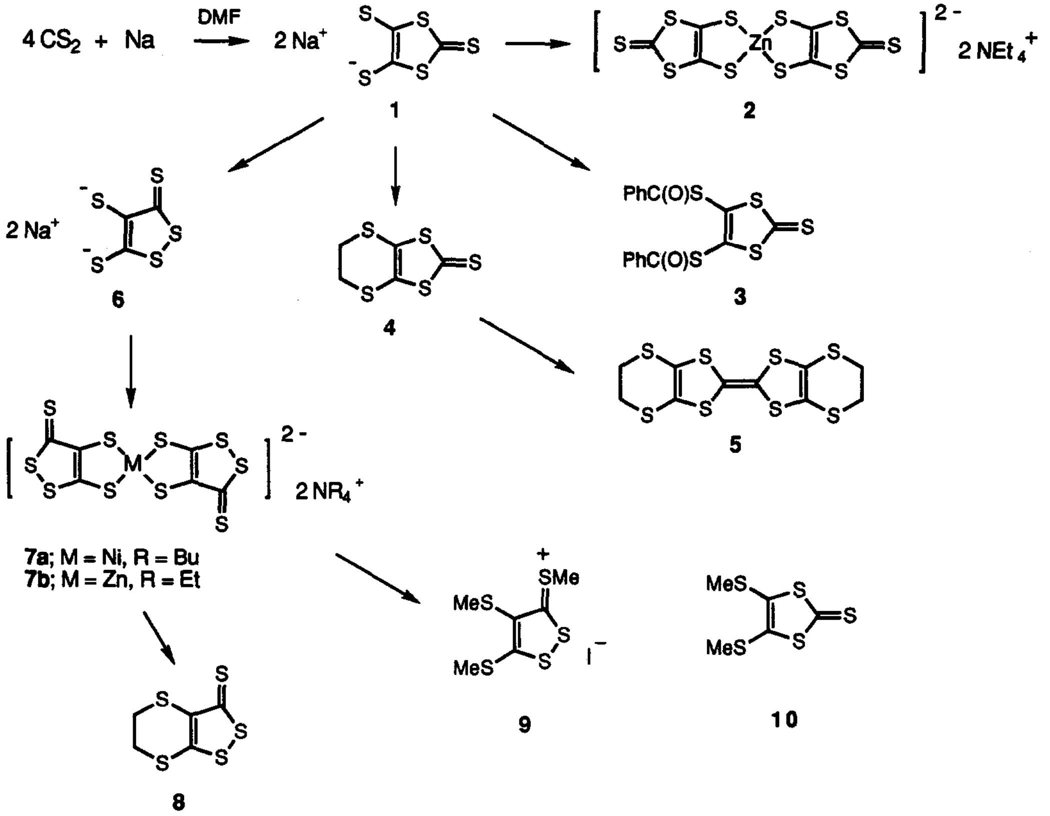
Abstract: The synthesis, X-ray crystal structure and some reactions of 1,2-dithiole-3-thione derivative **8** are reported. The structure of thione **8** is characterised by a remarkable three-dimensional network of close, non-bonded, S---S interactions. Compound **8** is efficiently converted into the 1,2-dithiolium cation salt **11** by sequential reaction with *meta*-chloroperoxybenzoic acid and sodium iodide. Cation salt **11** reacts with aqueous ammonia in the presence of iodine to afford isothiazole derivative **18** in high yield; the mechanism proposed for this reaction proceeds *via* 1,2,3-dithiazine derivative **17**. The solution electrochemistry of the title thione, and related compounds, has been studied by cyclic voltammetry.

Steimecke and coworkers have reported the remarkable reaction of carbon disulfide with sodium metal in DMF to yield the dithiolate salt **1**, which is conveniently isolated and stored as the zincate salt **2**.[1] Compound **1** readily forms the di(thioester) **3**, from which it can be regenerated under basic conditions. Dithiolate **1** has been 'capped' with a range of difunctional electrophiles, *eg.* reaction with dibromoethane yields derivative **4**, thus providing key intermediates in the synthesis of substituted tetrathiafulvalene (TTF) derivatives which are components of organic metals and organic superconductors.[2-6] Notably, BEDT-TTF **5** is prepared *via* **1** as precursor.[3] Reactions of **1** have also been used to synthesise macrocyclic structures.[7,8] It has been shown that the 1,3-dithiole-2-thione derivative **1** is converted into the 1,2-dithiole-3-thione isomer **6** upon refluxing in DMF.[9] The structure of nickelate salt **7a**, which was obtained from dithiolate **6**, was proved by X-ray analysis.[9]

In contrast to the 1,3-dithiole system **1**,[2-8] the chemistry of the 1,2-dithiole isomer **6** is virtually unexplored; notably a few reactions of compounds **8** and **9**, obtained therefrom, have been reported.[10,11] In this paper we describe the X-ray crystal structure of compound **8**, and new reactions of this compound which yield the bicyclic 1,2-dithiolium cation salt **11** and the novel isothiazole derivative **18**.

RESULTS AND DISCUSSION

Preparation of Compound **8**. Several approaches to the 1,2-dithiole-3-thione derivative **8** have been explored with the aim of finding the most expedient route. When zincate salt **2** was heated at 130°C in DMF for 4 h, followed by addition of dibromoethane, the only isolated product was the 1,3-dithiole derivative **4**, suggesting that isomerisation of zincate salt **2** to salt **7b** did not occur under the conditions which isomerised the disodium salt **1** into salt **6**.[9] Likewise, product **8** was not obtained when disodium salt **1** was formed *in situ* from di(thioester) **3**,[3] and the mixture then refluxed in DMF for 4 h, followed by addition of dibromoethane; only low yields of the 2-thione isomer **4** were obtained. Direct thermal isomerisation of 2-thione **4** into 3-thione **8** did not occur: refluxing thione **4** in DMF resulted in progressive destruction of the compound, although isomerisation is reported to occur under photochemical conditions.[12] We therefore resorted to using zincate salt **7b**, which was obtained in 62% yield from **1**, as the precursor to **8**. Alkylation of zincate salt **7b** with dibromoethane in refluxing acetonitrile afforded compound **8** in 69% yield.



X-Ray Crystal Structure Analysis of 1,2-Dithiole-3-thione Derivative **8**. The X-ray crystal structure of compound **8** was obtained for two reasons. Firstly, attention is currently focussed on organosulfur heterocycles which form intermolecular S---S networks in the solid state,[13-15] and compound **8**, with several peripheral sulfur atoms, was seen as a prime candidate in this respect. The study of non-bonded close contacts between chalcogen atoms is crucial to the development of electron donors which form organic metals.[16,17] Secondly, a comparison of the molecular dimensions in the neutral compound **8** with those of the related anionic nickelate salt **7a**,[9] cationic 1,2-dithiolium salt **9**,[18] and related 1,3-dithiole structures, *eg*. **10**,[19] would provide new information on the electron distribution in 1,2-dithiole systems in general.

Needle-shaped crystals of compound **8** were obtained from chloroform solution. X-ray analysis showed there are two symmetry independent molecules in the structure of compound **8** (molecules **8A** and **8B**). The atom numbering scheme is shown in Figure 1, and the bond lengths and angles are presented in Table 1. The 1,2-dithiole ring in both molecules **8A** and **8B** is essentially planar: the maximum deviations from a least squares plane defined by the 1,2-dithiole ring atoms are 0.04 and 0.01 Å, respectively. Both molecules **8A** and **8B** have very similar bond lengths and angles, except for the dithioethylene bridge, the carbon atoms of which, in molecule **B**, show large displacement factors, which explains the apparent shortening of the C(3')-C(4') bond [1.375(10) Å, *cf.* C(3)-C(4) = 1.511(8) Å]. Similar features in dithioethylene bridges of related structures have been reported previously.[17,20] The conjugated C=C and C=S bonds within structure **8** are all significantly longer [C(5)-C(2) = 1.369(6), C(5')-C(2') = 1.375(7), C(1)-S(1) = 1.662(6) and C(1')-S(1') = 1.659(7) Å] than the non-conjugated C=C and C=S bonds of the related 1,3-dithiol-2-thione structure **10** [which are 1.352(4) and 1.647(3), respectively][19] implying that there is intramolecular π–electron delocalisation in the α,β–unsaturated thione portion of compound **8**. The S-S bond lengths of compound **8** [2.047(4) and 2.049(4) Å, for molecules **A** and **B**, respectively] are very similar to those observed in 1,2-dithiolium cation salt **9** (2.024 Å)[18] and other 1,2-dithiolium cation salts[21] and are entirely consistent with that expected for a sulfur-sulfur single bond.

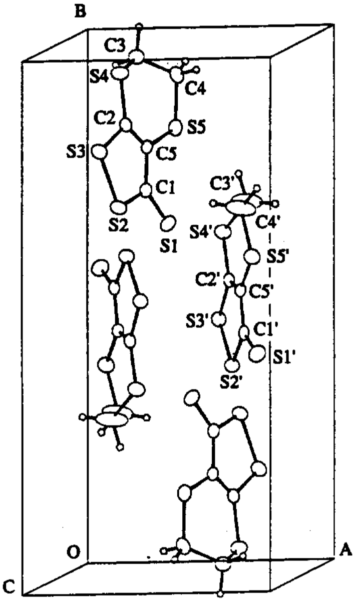


Figure 1. X-ray crystal structure of compound **8** showing the atom numbering scheme.

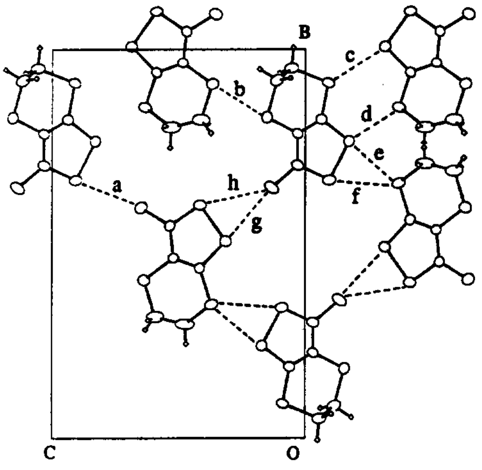


Figure 2. X-ray crystal structure of **8** viewed down the *a* axis. Intermolecular S--S distances (Å) are as follows: a, 3.786; b, 3.447; c, 3.506; d, 3.668; e, 3.385; f, 3.827; g, 3.357; h, 3.766. Additional unique contacts (not shown) are: S(1)--S(5') 3.719; S(1')--S(3) 3.725; S(1')--S(4) 3.731.

A comparison of the bond lengths of structure **8** with those reported for the dithiolate ligand in nickelate salt **7a**[9] reveals significant differences only in the C=C and C-S lengths; the C=S lengths are closely comparable in both structures. The C-S bond lengths in salt **7a** are shortened, relative to **8**, to 1.68-1.73 Å, by coordination to the nickel atom, and the C=C bond distance is lengthened to 1.42 Å,[9] which is consistent with more extended π–electron delocalisation in the bis(dithiolate) structure **7a**.

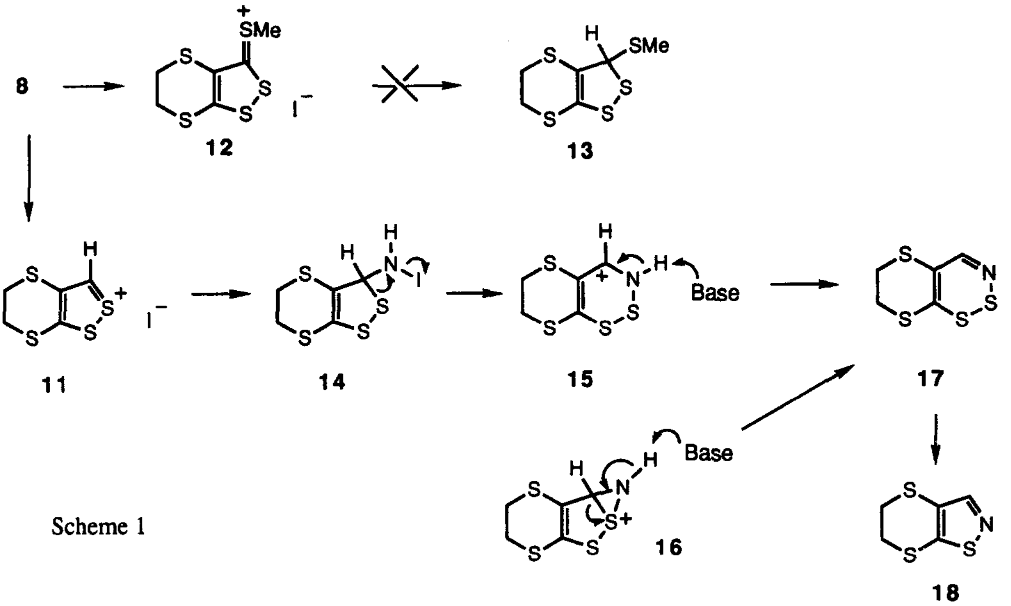
The structure of compound **8** reveals several intermolecular S---S contact distances that are significantly shorter than the accepted Van der Waals distance of 3.7-3.8 Å.[22] The shortest non-bonded contact is 3.357 Å, between S(1) and S(3'). The close S---S interactions in structure **8** are identified in Figure 2 (only the unique contacts are indicated). Compound **8** is, therefore, a good example of a growing family of organosulfur heterocycles which have solid state structures that are characterised by a three-dimensional network of non-bonded S---S interactions.[13-15]

Preparation and Reactions of 1,2-Dithiolium Cation Salt **11**. We wanted to obtain the 1,2-dithiolium cation salt **11**, which is unsubstituted at C(3), with a view to preparing Wittig and Wittig-Horner reagents therefrom, which, by analogy with the isomeric 1,3-dithiole derivatives reported recently,[23,24] should be versatile reagents. A very inefficient, multi-step route to cation **11** from thione **8**, which proceeded *via* compounds **12** and **13**, has been reported recently by Papavassiliou and coworkers.[11,25] We have reinvestigated this route. Compound **8** was *S*-methylated with iodomethane, using the literature procedure,[11] to afford 1,2-dithiolium cation salt **12** (82% yield). However, in our hands, numerous attempts to reduce salt **12** with sodium borohydride did not provide compound **13**; a complex, multi-component mixture (TLC and NMR evidence), probably containing ring-opened products, was obtained and could not be purified using the reported procedure.[11] Notably, we did not observe the protons of the dithioethylene group, which should resonate at δ 3.4-3.2 ppm, suggesting that major degradation of the heterocyclic system had occurred. Therefore, we explored an alternative approach to cation **11**, and have developed a straightforward route from thione **8**. Reaction of compound **8** with *meta*-chloroperoxybenzoic acid yielded the crude hydrogensulfate salt of **11**, which upon addition to aqueous sodium iodide[26,27] furnished the desired compound **11**, as the iodide salt, in 34% yield. Salt **11**, which is highly insoluble in water and in common organic solvents, is stable when stored under ambient conditions, whereas the isomeric 1,3-dithiolium cation requires storage at <0°C.[23]

The reactions of phosphorus and nitrogen nucleophiles towards compound **11** have been examined. Addition of either triphenylphosphine or trimethylphosphite to a suspension of cation **11** in acetonitrile at 20°C (which are standard conditions for the 1,3-dithiolium isomer)[23,24] gave intractable product mixtures, with no evidence for the formation of the desired phosphonium salt or phosphonate ester, respectively. Likewise, the reaction of hydrazine hydrate with cation **11** failed to give an isolable product, despite literature precedents for other 1,2-dithiolium cations.[26]

Conversely, the reaction of cation **11** with an excess of aqueous ammonia in the presence of iodine, at room temperature in acetonitrile, cleanly furnished the novel isothiazole derivative **18** in 84% yield. It is notable that salt **11** is insoluble in acetonitrile prior to the addition of iodine, whereupon rapid dissolution takes place. This is a particularly interesting reaction which we believe proceeds *via* the intermediacy of 1,2,3-dithiazine derivative **17** (Scheme 1). Initial reaction at C(3) of cation **11** would yield an electron-deficient nitrogen species **14**, which could lose iodide ion with S-N bond formation, to give cationic intermediate **15**.

Deprotonation of **15** could then yield the 8-π electron 1,2,3-dithiazine system **17**, which would be unstable to loss of sulfur with formation of the observed isothiazole **18**. It is also conceivable that thiaziridine system **16** is involved as an intermediate. Previous workers have obtained isothiazole products from reactions of monocyclic 1,2-dithiolium cations with ammonia: however, as iodine was not present, a completely different mechanism was proposed for the reaction, involving initial cleavage of the disulfide bond by the amine.[28] We favour a mechanism for the ammonia / iodine reaction *via* the 1,2,3-dithiazine system **17** (Scheme 1) in the light of our recent work on the ring expansion of 1,3-dithiolium cation salts, which occurs under identical conditions, to yield related 1,4,2-dithiazine derivatives (X-ray proof of structure).[29] 1,2,3-Dithiazine derivatives are very rare,[30,31] and although we have been unable to isolate intermediate **17**, we have isolated and characterised analogues of **17** possessing the 1,2,3-dithiazine structure (NMR and MS evidence) from reactions of other 1,2-dithiolium cations with the iodine/ammonia system under identical conditions.[32]



Scheme 1

Electrochemical Studies. The redox properties of the neutral and cationic 1,2-dithiole derivatives **8** and **12** have been studied by cyclic voltammetry in dichloromethane solution and the data compared with 1,3-dithiole analogues. Compound **8** shows a broad, poorly-defined irreversible oxidation wave at $E^{ox} = 1.3V$, whereas isomer **4** shows a well-defined oxidation peak at $E^{ox} = 1.25V$ (*cf.* BEDT-TTF **5** is considerably easier to oxidise, undergoing two reversible single-electron oxidations at $E_1{}^{1/2} = 0.59$ and $E_2{}^{1/2} = 0.99V$).[20] The instability of the cation radical of compound **8** is possibly the result of ring opening due to cleavage of the S-S bond. Cation **12** is harder to reduce than the isomeric 2-methylthio-1,3-dithiolium system: the former compound undergoes a quasi-reversible reduction at $E^{red} = -0.38V$, while the latter compound is reduced irreversibly at -0.26V. Isothiazole derivative **18** is significantly harder to oxidise to the radical cation than compound **8** (an irreversible wave is seen for **18** at $E^{ox} = 1.6V$) which reflects the stability of the 6-π electron isothiazole ring.

Cation salt **12** reacted with two equivalents of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) in acetonitrile to yield a salt of stoichiometry **12**-$(TCNQ)_2$ in 32% yield. The salt is an organic semiconductor ($\sigma_{rt} = 2 \times 10^{-3}$ Scm^{-1}, two-probe, compressed pellet measurement) and contains the TCNQ anion radical as judged by IR spectroscopy [ν (CN) = 2186 cm^{-1} which is diagnostic of anionic TCNQ].[33]

EXPERIMENTAL

General. Details of equipment and general procedures used in this work have been reported recently.[34] Electrochemical studies were performed using a BAS 100 Electrochemical Analyser. Data were recorded versus Ag/AgCl, Pt button working electrode, Pt wire counter electrode, scan rate 100 mVs^{-1}, 5×10^{-4} mol dm^{-3} compound, 0.1 mol dm^{-3} $Bu_4N^+PF_6^-$ in dry dichloromethane at 20°C under argon.

3-Thio-5,6-dihydro-1,2-dithiolo[4,5-b][1,4]dithiin **8**. To a stirred mixture of sodium (11.5 g, 0.5 mol) (which was conveniently cut into small pieces using a cheese grater)[35] in carbon disulfide (135 mL, 2.2 mol) at 0°C, dimethylformamide (150 mL, 1.9 mol) was added dropwise with stirring over 15 min. The mixture was allowed to warm to 20°C and stirred for a further 115 h under nitrogen. A small amount of residual sodium was then removed by filtration through a glass wool plug. Excess carbon disulfide was removed by distillation and the remaining mixture was then heated at 130-140°C for 2 h. The mixture was cooled and methanol (200 mL) then water (250 mL) were added with stirring. A solution of zinc chloride (10.0 g, 0.07 mol) in ammonia solution (33%, 250 mL) and methanol (250 mL) was then added to the reaction mixture with stirring. A solution of tetraethylammonium bromide (26.5 g, 0.13 mol) in water (125 mL) was then added dropwise with stirring over 10 min. This caused the crude zincate salt **7b** to precipitate as a dark oil which was separated and allowed to solidify. It was then purified by stirring in ether (1 L) overnight whereupon it broke up into a fine brown precipitate. This precipitate was filtered off and washed consecutively with water (1 L), propan-2-ol (200 mL) and ether (300 mL). Drying *in vacuo* yielded zincate salt **7b**[9] as a brown powder (27.7 g, 62%) from which thione **8** was prepared as follows. Zincate salt **7b** (8.7 g, 12.1 mmol) was dissolved in dry acetonitrile (100 mL) and dibromoethane (4.1 mL, 48 mmol) was added. The mixture was refluxed under nitrogen for 22 h. Solvent was then removed *in vacuo* and the residue chromatographed on a short silica column eluting all coloured material with dichloromethane. *In vacuo* removal of solvent gave the crude thione **8**. This product was purified by column chromatography on silica with dichloromethane : cyclohexane (1:2 v/v) as eluent. The fastest running yellow elution band was collected and identified as the isomeric thione **4** (<5% yield) by comparison with authentic material.[3] The major orange elution band was then collected and evaporated to yield analytically pure thione **8** as a ruddy crystalline solid (3.75 g, 69%) m.pt. 125-127°C (lit.[10] 126°C). Recrystallisation was achieved from chloroform.

5,6-Dihydro-1,2-dithiolo[4,5-b][1,4]dithiin-3-ium Iodide **11**. Thione **8** (0.5 g, 2.2 mmol) was dissolved in acetone (150 mL) and cooled to 0°C. A solution of *m*-chloroperoxybenzoic acid (50%, 2.3 g, 6.7 mmol) in acetone (20 mL) was added dropwise with stirring over 2 min. Stirring at 0°C was maintained for 0.5 h whence the precipitate which formed was filtered off and washed with ether (3 x 30 mL). After drying *in vacuo* the crude product was converted directly into iodide salt **11** as follows. The solid was dissolved in water (100 mL), the solution was filtered and the filtrate added with stirring to sodium iodide (1.7 g, 11 mmol) in water (20 mL). The resulting precipitate was filtered off and washed with acetone (2 x 30 mL) and then with ether (3 x 30 mL). Drying *in vacuo* yielded salt **11** (0.24 g, 34%) as an orange solid, m.p. 181-184°C (Found: C, 18.82; H, 1.54. $C_5H_5S_4I$ requires C, 18.75; H, 1.57%); ν_{max}(KBr)/cm^{-1} 3045, 2945, 1405, 1335, 1280, 1175, 1020 and 865; δ_H (250 MHz; DMSO) 10.1 (1H, broad s) and 3.55-3.27 (4H, m).

5,6-Dihydro-1,2-thiazolo[4,5-b][1,4]dithiin **18**. To a stirred solution of salt **11** (240 mg, 0.75 mmol) and iodine (190 mg, 1.5 mmol) in acetonitrile (100 mL) was added ammonia solution (33%, 0.44 mL, 7.5 mmol). Stirring was continued for 3 h at 20°C after which time water (200 mL) was added. The solution was extracted with dichloromethane (3 x 60 mL), the organic layers combined and washed with water (200 mL). After drying ($MgSO_4$) and filtering, the solvent was removed *in vacuo* and the residue chromatographed on a silica column eluting with dichloromethane:cyclohexane (1:1 v/v). *In vacuo* evaporation of solvent afforded isothiazole **18** (110 mg, 84%) as an orange crystalline solid, m.p. 44-46°C [Found: C, 34.18; H, 2.79; N, 7.31%; m/z (EI) 174.95676. $C_5H_5NS_3$ requires C, 34.26; H, 2.88; N, 7.99%; m/z 174.95846]; ν_{max}(KBr)/cm^{-1} 2920, 1415, 1365, 1285, 1180, 855, 770 and 485; λ_{max} (hexane:dichloromethane 1:1)/nm 226, 250, 258 and 310; δ_H (250 MHz, $CDCl_3$) 8.07 (1H, s) and 3.30 (4H, AA'BB'); δ_C (250 MHz, $CDCl_3$) 155.2, 146.2, 120.5, 28.4 and 26.0; m/z (EI) 175, (CI) 176.

TCNQ Salt of Cation **12**. A mixture of the iodide salt of cation **12** (50 mg, 0.14 mmol) and 7,7,8,8-tetracyano-*p*-quinodimethane (58 mg, 0.28 mmol) were dissolved in boiling acetonitrile (15 mL). The solution was cooled to room temperature to give a precipitate of salt **12**-$(TCNQ)_2$ as a black powder (28 mg, 32%). (Found: C, 55.31; H, 2.26; N, 17.75. $C_{30}H_{15}N_8S_5$ requires C, 55.57; H, 2.33; N, 17.36%); ν_{max} (KBr) 2186 cm^{-1}; the remainder of the spectrum comprises a series of broad bands, typical of an organic conductor.

X-Ray Crystal Structure Analysis of Compound **8**. Crystal data: $C_5H_4S_5$, monoclinic space group $P\ 2_1/a$, $a = 8.205(1)$, $b = 17.610(4)$, $c = 12.086(1)$ Å, $\beta = 108.36(1)°$, $U = 1657.41$ Å^3, $Z = 8$, $F(000) = 912$, Mo-K_α radiation, $\lambda = 0.71069$ Å. The structure was solved by direct methods (SHELXS 86)[36] and refined by least-squares analysis[37] (anisotropic for non-hydrogens) to $R = 0.046$ for 2479 observed ($F_o > 3\sigma F_o$) reflections from 4106 unique data. The data were collected on an Enraf-Nonius FAST area detector diffractometer positioned at the window of a rotating anode generator. Bond lengths and bond angles are given in Table 1. Full details of data collection and refinement, atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Table 1. Bond Lengths (Å) and Angles (°) for Compound **8**.

Molecule **8A**		Molecule **8B**	
C(1)-S(1)	1.662(6)	C(1')-S(1')	1.659(7)
S(3)-S(2)	2.047(4)	S(3')-S(2')	2.049(4)
C(1)-S(2)	1.731(7)	C(1')-S(2')	1.731(7)
C(2)-S(3)	1.736(6)	C(2')-S(3')	1.731(6)
C(2)-S(4)	1.728(6)	C(2')-S(4')	1.738(6)
C(3)-S(4)	1.824(7)	C(3')-S(4')	1.779(9)
C(4)-S(5)	1.786(7)	C(4')-S(5')	1.794(9)
C(5)-S(5)	1.753(6)	C(5')-S(5')	1.748(6)
C(5)-C(1)	1.423(7)	C(5')-C(1')	1.433(7)
C(5)-C(2)	1.369(6)	C(5')-C(2')	1.375(7)
C(4)-C(3)	1.511(8)	C(4')-C(3')	1.375(10)
C(1)-S(2)-S(3)	97.0(3)	C(1')-S(2')-S(3')	97.5(3)
C(2)-S(3)-S(2)	94.1(3)	C(2')-S(3')-S(2')	93.9(3)
C(3)-S(4)-C(2)	100.9(3)	C(3')-S(4')-C(2')	100.8(4)
C(5)-S(5)-C(4)	102.9(3)	C(5')-S(5')-C(4')	102.4(4)
S(2)-C(1)-S(1)	119.1(4)	S(2')-C(1')-S(1')	119.9(4)
C(5)-C(1)-S(1)	126.9(4)	C(5')-C(1')-S(1')	126.4(5)
C(5)-C(1)-S(2)	114.0(4)	C(5')-C(1')-S(2')	113.7(4)
S(4)-C(2)-S(3)	113.1(3)	S(4')-C(2')-S(3')	113.2(4)
C(5)-C(2)-S(3)	117.6(4)	C(5')-C(2')-S(3')	118.1(4)
C(5)-C(2)-S(4)	129.3(4)	C(5')-C(2')-S(4')	128.7(5)
C(4)-C(3)-S(4)	113.5(4)	C(4')-C(3')-S(4')	120.8(7)
C(3)-C(4)-S(5)	114.7(4)	C(3')-C(4')-S(5')	120.3(7)
C(1)-C(5)-S(5)	115.6(4)	C(1')-C(5')-S(5')	116.0(4)
C(2)-C(5)-S(5)	127.1(4)	C(2')-C(5')-S(5')	127.2(4)
C(2)-C(5)-C(1)	117.3(5)	C(2')-C(5')-C(1')	116.8(5)

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