Thermal fragmentation reactions of 1,4,2-dithiazines and 1,4,2,5-dithiadiazines in the presence of dienophiles: synthesis of 1,4-dithiine derivatives. X-Ray crystal structures of a 1,4,2-dithiazine 1,1-dioxide and a 1,4,2,5-dithiadiazine derivative

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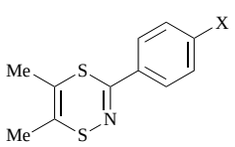
The reaction of 5,6-dimethyl-3-(4-bromophenyl)-1,4,2-dithiazine 1b with dimethyl acetylenedicarboxylate (DMAD) at 180 °C in *o*-dichlorobenzene affords a mixture of thiophene derivative 5 and isothiazole derivative 6: the former probably *via* the zwitterionic adduct 3 and dithiine derivative 4, neither of which are isolable; the latter by sulfur extrusion from 1b. Reaction of norbornene with 1b affords dithiine derivative 7. Oxidation of 1b with *meta*-chloroperoxybenzoic acid yields the 1,1-dioxide derivative 8, the X-ray crystal structure of which is reported. The efficient synthesis of 3-aryl-6-methylthio-1,4,2,5-dithiadiazine derivatives 12a–c by ring expansion of 1,4,2-dithiazolium salts 11a–c with an iodine–ammonia reagent is described. Reaction of 12c with DMAD at 180 °C affords the stable dithiine derivative 14, probably *via* the intermediate 1,4,2-dithiazine 13. Electrochemical oxidation of 12a–c is irreversible, yielding 1,4,2,5-dithiadiazinium cation radicals at potentials [E^{ox} = 1.55–1.73 V (*vs.* Ag/AgCl)] which are sensitive to the electronic nature of the *para*-substituent on the aryl ring. The X-ray crystal structure of 12b is reported.

Organic heterocycles which contain three or more heteroatoms have attracted considerable attention recently; they display a diverse range of chemical and physical properties.[1] The 1,4,2-dithiazine ring system **1** can be synthesised from readily



1 a X = OMe
b X = Br

available starting materials in a few steps.[2] Nakayama *et al.*[3] have shown that under forcing reaction conditions (refluxing *o*-dichlorobenzene at 180 °C) 1,4,2-benzodithiazines react with dienophiles such as dimethyl acetylenedicarboxylate (DMAD). The mode of reaction is unproven but seems to occur by one of two routes: (i) fragmentation of the heterocycle to yield a 1,2-benzodithiete intermediate, or its ring-opened *o*-dithiobenzoquinone tautomer, which is trapped by DMAD, or (ii) reaction of DMAD at one of the sulfur atoms in the ring and subsequent fragmentation of a zwitterionic species to yield a 1,4-benzodithiine. A consequence of using the 1,4,2-benzodithiazine derivative is that the 1,2-dithiete intermediate is stabilised by the benzene substituent prior to trapping with the dienophile. The resulting 1,4-benzodithiines are stable and isolable after column chromatography: modest yields have been reported (40%). It has been shown recently within our group[2] that 3-substituted 5,6-dimethyl-1,4,2-dithiazines **1** react under photochemical conditions in the presence of dienophiles to yield 1,4-dithiines, but significantly under thermal conditions, the derivative studied (compound **1a**) formed isothiazoles and not 1,4-dithiines, thereby providing a contrasting pattern of reactivity to the benzo-analogues studied by Nakayama's group.[3]

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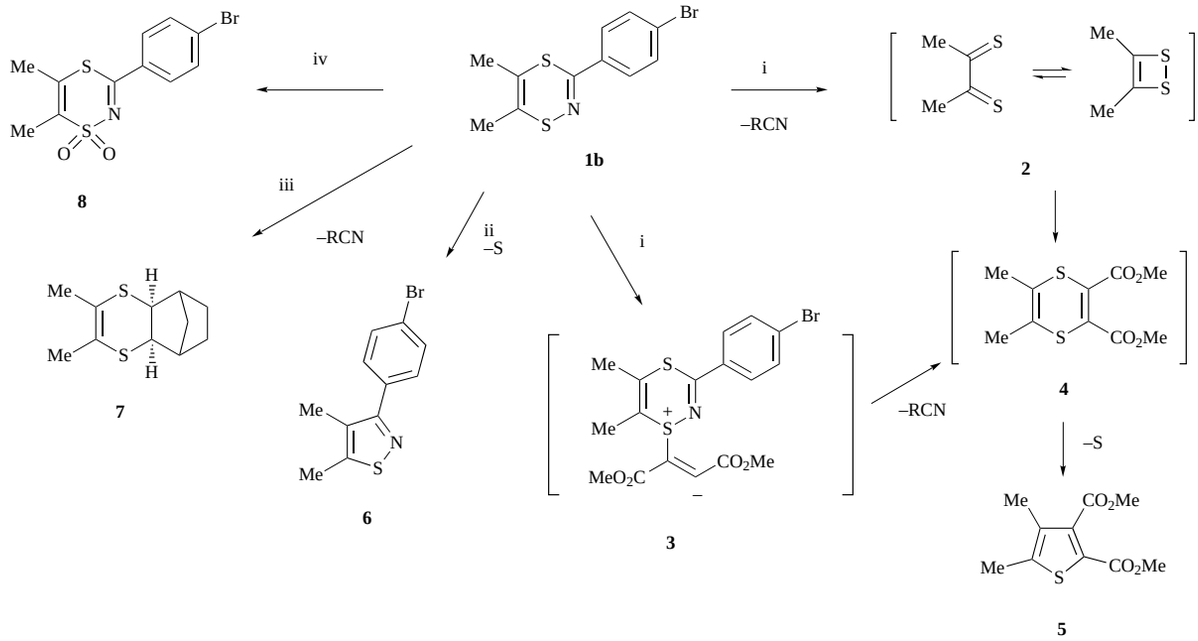
Results and discussion

Reactions of 1,4,2-dithiazines 1

We report new studies on compound **1b**: an important factor in influencing the reactivity of the 1,4,2-dithiazine ring system appears to be the electronic nature of the substituent at C(3). We had observed previously by UV–visible spectroscopy and by cyclic voltammetry that the electronic characteristics of the 1,4,2-dithiazine ring were sensitive to the electronic nature of substituent X (*e.g.* the oxidation potential is raised by the presence of the electron-withdrawing halogen substituent).[2a,b] With judicious choice of the aromatic substituent at C(3) and specific reaction conditions, 1,4,2-dithiazines **1** can be induced to fragment thermally by various pathways to give different products—namely isothiazoles or 1,4-dithiines.

We established that thermolysis of **1a**, which bears an electron-rich methoxyphenyl substituent at C(3), in the presence of dienophiles does not give 1,4-dithiine derivatives. Instead the only product was the isothiazole derivative formed by extrusion of S(4) from the ring. This is a known process for many 1,4,2-dithiazines and occurs typically between 120–130 °C, without the presence of a dienophile.[2c] We have now found that when substituent X in compound **1** is electron-withdrawing, *e.g.* bromo derivative **1b**, the reactivity of the ring system is abruptly changed.

Heating a solution of compound **1b** in *o*-dichlorobenzene to 180 °C in the presence of DMAD gave a complex mixture of products from which thiophene derivative **5** (15%) and isothiazole **6** (40%) were isolated (Scheme 1). The former product is presumably derived from sulfur extrusion[4] from dithiine **4**, which could be formed either *via* the zwitterionic intermediate **3** (akin to the zwitterionic adducts of 1,4,2-benzodithiazines proposed by Nakayama *et al.*)[3] or by Diels–Alder trapping of a transient 1,2-dithiete **2**. Isothiazole **6** is the expected product from thermal loss of S(4) from compound **1b**. Clearly, the effect of the bromine substituent is to reduce electron density in the dithiazine ring, which apparently favours the reaction with DMAD. This cannot readily be explained by a change in electron density at S(1), which presumably acts as the nucleophilic



Scheme 1 *Reagents and conditions:* i, DMAD, *o*-dichlorobenzene, reflux; ii, heat; iii, norbornene, *o*-dichlorobenzene, reflux; iv, peracetic acid, CH_2Cl_2, 20 °C

centre in reactions with DMAD. Rather, it must reflect a change in the overall electron distribution in the ring possibly related to the 8π (potentially anti-aromatic) nature of the heterocycle. Conversely, an electron-donating substituent on the benzene ring (derivative **1a**) promotes sulfur extrusion and isothiazole formation.

When a flask containing **1b** and DMAD in *o*-dichlorobenzene was immersed in an oil bath preheated to 180 °C a slightly increased yield of thiophene derivative **5** (20%), and correspondingly less isothiazole **6** (34%), was obtained. Although this is a relatively small change in the ratio of products, it was highly reproducible and indicates that the isothiazole is formed at lower temperatures than those needed for DMAD to react.

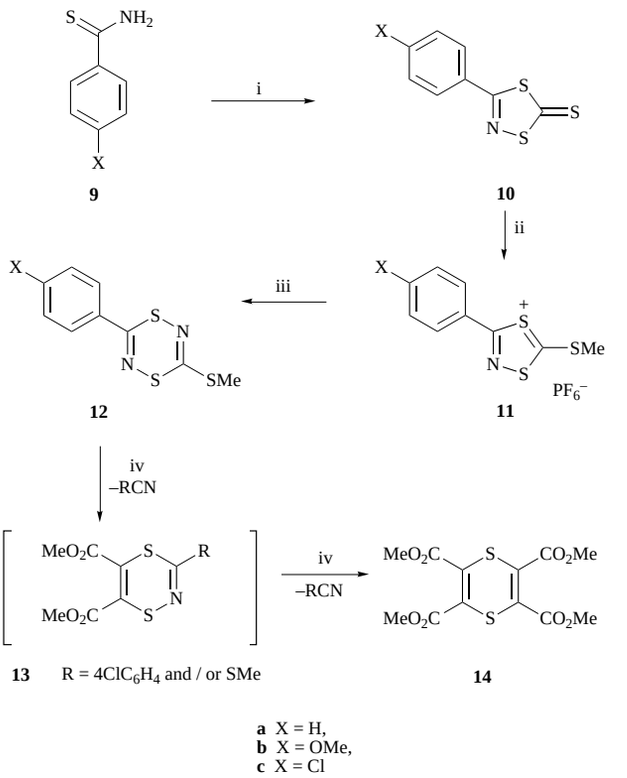
We have explored the thermal reactions of other dienophiles with **1b**. The best yield came from heating **1b** in the presence of norbornene at 180 °C. Dithiine **7** (55%) was isolated, rather than the derived thiophene, presumably because there would be no gain in aromaticity from loss of sulfur from **7** (*cf.* the formation of **5** from **4**). No adducts were obtained from attempted reactions of **1b** with either dimethyl maleate or tetracyanoethene (TCNE): only isothiazole **6** and unreacted starting materials were isolated.

We suggest that the thermal reactions of 1,4,2-dithiazine **1b** with DMAD and with norbornene proceed *via* zwitterionic intermediates, *e.g.* **3**, as Nakayama proposed for 1,4,2-benzodithiazines,[3] and other workers postulated for cycloaddition-elimination reactions between 1,4-dithiine 1,1-dioxides and DMAD.[5] The developing anion on the dienophile is available for intramolecular attack at S(4) of the 1,4,2-dithiazine. However, for reaction with dimethyl maleate or TCNE, the anion will delocalise onto the ester carbonyl or nitrile groups, respectively, thereby reducing its nucleophilicity and suppressing dithiine formation: at the relatively high temperatures used in the reaction, sulfur extrusion to form the isothiazole **6** (up to 53% yield) occurs instead. An intense blue solution, which formed when the mixture of **1b** and TCNE in *o*-dichlorobenzene was heated between *ca.* 120–160 °C, is consistent with the formation of a zwitterionic species akin to **3**, but this compound decomposed upon attempted isolation. We considered that the coloured solution could be due to charge-transfer complex formation between **1b** and TCNE: however, we believe this is unlikely as decomplexation to starting materials would be expected, rather than decomposition to unidentified products, as was observed.

We have explored, for the first time, reactions of the 1,4,2-dithiazine heterocycle with oxidising agents. Complex product mixtures, including insoluble polymeric materials, were obtained by treating **1b** with magnesium monoperoxyphthalate, *m*-chloroperbenzoic acid, mercury oxide–I_2 reagent or Oxone® (potassium peroxymonosulfate) under standard conditions. However, when peracetic acid (1 or 2 equiv.) was used, a pale yellow crystalline product was isolated. Mass spectrometry established that two oxygen atoms had added to compound **1b** and a prominent fragment corresponding to $(M + H - SO_2)^+$ implied that the compound was a sulfone derivative: the ^{1}H NMR spectrum was consistent with a single compound, and the chemical shift difference between the two methyl groups ($\Delta\delta$ 0.11 ppm) was significantly greater than that of the starting material **1b** ($\Delta\delta$ 0.05 ppm).[2b] Taken together, these data clearly suggested that oxidation had occurred at only one of the sulfur atoms of **1b**, but they did not differentiate between the S(1) and S(4) sulfones. The structure was established by X-ray analysis to be the novel 1,4,2-dithiazine 1,1-dioxide **8** (see below). It is noteworthy that the oxidation of the sulfur atoms of 1,4-dithiine derivatives also generally yields the sulfone, rather than the sulfoxide or disulfoxide product.[4] Attempted reaction of **8** with dienophiles (DMAD, TCNE and dimethyl maleate) resulted in formation of polymeric material and several products (TLC evidence) which could not be purified.

Synthesis and reactivity of 1,4,2,5-dithiadiazines 12

We next focussed our attention on the 1,4,2,5-dithiadiazine ring system, which had previously been prepared by a variety of routes. These include reaction between thiobenzamide *S*-oxide and $Et_3O^+BF_4^-$ (the first reported synthesis),[6] and most recently, the insertion of a nitrogen atom, derived from *S*-dimethylthiocarbamoyl-substituted sulfenamides[7] or an iodine–ammonia reagent,[8] into the 1,4,2-dithiazolium ring. In view of our experience in synthesising system **1** from 1,3-dithiolium cations and iodine–ammonia reagent,[2] we opted to explore a similar route to compounds **12** (Scheme 2). We identified two points of special interest: (i) would the reaction of cations **11**[9] with iodine–ammonia reagent give 1,4,2,5-dithiadiazines by nitrogen insertion into the S(4)–C(5) bond, or isomers by insertion into the S(1)–C(5) or C(5)=S bonds? (ii)



9 **10** **11** **12** **13** **14**

a X = H,
b X = OMe,
c X = Cl

Scheme 2 *Reagents and conditions:* i, CCl_3SCl, $CHCl_3$, reflux; ii, Me_2SO_4, reflux, then HPF_6, Et_2O, 0 °C; iii, I_2, NH_4OH, MeCN, 20 °C; iv, DMAD, *o*-dichlorobenzene, reflux

How would system **12** fragment or react in the presence of dienophiles?

Following the general procedure of Greig *et al.*,[9a] thiobenzamides **9a–c** reacted with trichloromethanesulfenyl chloride to afford the corresponding 3-aryl-1,4,2-dithiazole-5-thione derivatives **10a–c**, which were *S*-methylated in high yield with dimethyl sulfate and isolated as the hexafluorophosphate salts **11a–c**. Reaction of **11a–c** with iodine (3 equiv.) followed by aqueous NH_4OH (10 equiv.) furnished 1,4,2,5-dithiadiazine derivatives **12a–c** as the only isolable products (46–59% yields). ^{1}H and ^{13}C NMR spectra of these products were consistent with either the 1,4,2,5-dithiadiazine system **12** (as reported by Shibuya and co-workers)[7,8] or the 1,4,2,6-isomer. (Thermally very stable derivatives of this ring system have been synthesised by entirely different routes.[10]) An X-ray crystal structure analysis of **12b** unambiguously established the former structure. The reasons for the regiospecificity in this formation of **12a–c** are unclear. The initial step is presumably addition at C(5) of cation **11** of a nucleophilic nitrogen species derived from the iodine–ammonia reagent—the relative stability of the ensuing intermediates may then dictate the exclusive formation of isomer **12**.

We have explored the reactions of **12a–c** with DMAD. If the system reacted in an analogous manner to **1b**, the 1,4,2,5-dithiadiazine ring could eliminate two possible nitrile fragments to give two different 1,4,2-dithiazines [containing either the SMe or aryl substituent at C(3)]. Refluxing a solution of **12a** or **12b** and DMAD in either toluene or *o*-dichlorobenzene (180 °C) resulted in no reaction: notably, no sulfur extrusion to form dithiazoles was seen, in contrast to isothiazole formation from the analogous 1,4,2-dithiazines. However, when compound **12c** was refluxed in *o*-dichlorobenzene in the presence of DMAD (5 equiv.), tetramethyl 1,4-dithiine-2,3,5,6-tetracarboxylate **14** (12%) was isolated. We have considered two possible ways in which compound **14** could be formed in this reaction. Firstly, there are documented examples[11] of DMAD reacting directly with sulfur to form compound **14**, but it is unlikely that this would occur to such an extent in our case, where the only source of sulfur could be that extruded from compound **12c**, and, moreover, we have not observed the formation of compound **14** in reactions where 1,4,2-dithiazines, *e.g.* **1a** or **1b**, are known to extrude sulfur in the presence of DMAD.[2b] A second, and far more likely, scenario is that the 1,4,2,5-dithiadiazine ring of **12c** reacts with DMAD with loss of a nitrile fragment (MeSCN and/or *p*-ClC_6H_4CN) to form 1,4,2-dithiazine derivative **13**, which, as would be expected from the reactions of **1b** (Scheme 1), reacts further with DMAD to yield the isolated product **14** and a nitrile fragment. It is notable that the four electron-withdrawing ester groups stabilise 1,4-dithiine derivative **14** to the extent that its decomposition to the corresponding thiophene was not observed, in contrast to analogue **4**. The formation of **14** from **12c** provides the first evidence for the reactivity of the 1,4,2,5-dithiadiazine ring in the presence of dienophiles. It is interesting to note that, as with compound **1b**, an electron-withdrawing *para*-substituent on the aryl group increases the reactivity of the heterocycle.

Table 1 Selected bond distances in **8**, **12b** and **1a**[a]

Bond	Length/Å		
	12b	**8**	**1a**
S(1)–N(2)	1.709(5)	1.622(3)	1.709(2)
S(1)–C(6)	1.754(6)	1.754(4)	1.752(2)
N(2)–C(3)	1.282(8)	1.287(5)	1.274(3)
C(3)–S(4)	1.765(6)	1.739(4)	1.785(2)
S(4)–E(5)[b]	1.709(5)	1.751(4)	1.762(2)
E(5)–C(6)[b]	1.282(8)	1.336(5)	1.336(3)
S(1)–O(1)		1.434(3)	
S(1)–O(2)		1.433(3)	
C(6)–S(61)	1.746(6)		

[a] Ref. 2(*b*). [b] E = N (**12b**), C (**8** and **1a**).

Solution UV spectra of **12a–c** in acetonitrile demonstrate that the aryl substituent is conjugated with the heterocyclic ring: the value of λ_{max} shifts hypsochromically along the series **12b** (391 nm), **12a** (385–375 nm, broad band) and **12c** (371 nm). Cyclic voltammetric data in acetonitrile solution show that the *para*-substituent on the aryl ring of **12** exerts a significant influence on the oxidation potential of the system. [These data are consistent with the solid-state conformation of **12b**, discussed below, in which the phenyl ring is almost coplanar with the S(1)–N(2)–C(3)–S(4) plane.] Compounds **12a–c** undergo a single irreversible oxidation (the corresponding cathodic reduction peak is not observed) at a potential which increases along the series **12b** (E^{ox} 1.55 V), **12a** (E^{ox} 1.59 V) and **12c** (E^{ox} 1.73 V) (all *versus* Ag/AgCl, in acetonitrile), *i.e.* the OMe substituent stabilises the oxidised species more than H and much more than Cl at the same position. By analogy with our previous studies on 1,4,2-dithiazines,[2a,b] we presume that the oxidation process corresponds to formation of the 1,4,2,5-dithiadiazinium cation radical. The presence of the additional nitrogen atom in ring system **12** raises the oxidation potential (*i.e.* the cation radical is destabilised) relative to **1**, by *ca.* 400 mV for the same substituents X. This is a logical progression, as compounds **1** are harder to oxidise than 1,4-dithiine derivatives.[4]

X-Ray crystal structures of 8 and 12b

In the structure of sulfone **8** (Fig. 1) all non-hydrogen atoms except O(1) and O(2) are coplanar to within ±0.04 Å, in contrast with the folded (by 50°) conformation of **1a**.[2b] The 1,4,2-dithiazine ring of **1a** is an 8π-electron system, and a planar ring would be destabilised by anti-aromaticity, which is not possible for sulfone **8** for which there are no lone pairs on S(1). Comparison of the bond distances (Table 1) indicate increased π-delocalisation in **8**. It is noteworthy that oxidation of 1,4-dithiines leads to no such planarisation: the heterocyclic rings in 2,5-diphenyl-1,4-dithiine 1-oxide[12] and 3-bromo-2,5-diphenyl-1,4-dithiine 1,1-dioxide[13] are folded by 38 and 51°,

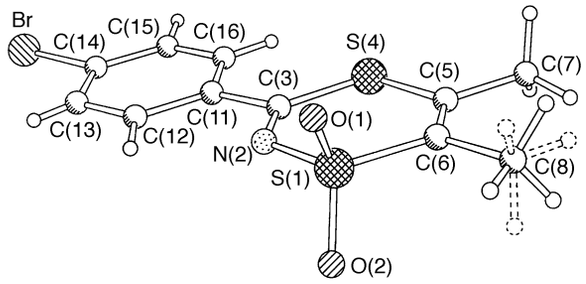


Fig. 1 Molecular structure of **8** (showing the disorder of one methyl group)

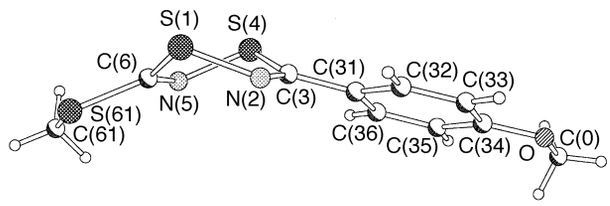


Fig. 2 Molecular structure of **12b**

respectively, which are similar to the parent (unoxidised) 1,4-dithiine derivatives.

In the structure of **12b** (Fig. 2, Table 1), the dithiadiazine ring is folded by 48.3(2)° along the S(1)···S(4) vector. A similar conformation has been observed previously in other 1,4,2,5-dithiadiazines,[6b,7] as well as in isoelectronic 1,4,2-dithiazines[2a,b] and most 1,4-dithiines.[4] The benzene ring of **12b** forms a dihedral angle of 26.4(2)° with the S(1)–N(2)–C(3)–S(4) plane, while the N(5)–C(6)–S(61)–C(61) torsion angle of −9.1(6)° implies conjugation between the methylthio group and the N(5)=C(6) bond.

Experimental

General procedures are the same as those reported previously.[2c]

Dimethyl 4,5-dimethylthiophene-2,3-dicarboxylate 5 and 3-(4-bromophenyl)-4,5-dimethyl-1,2-thiazole 6

1,4,2-Dithiazine **1b**[2b] (500 mg, 1.66 mmol) was dissolved in *o*-dichlorobenzene (50 cm^3) and dimethyl acetylenedicarboxylate (0.82 cm^3, 6.6 mmol) was added. The flask was immersed in an oil bath preheated to 180 °C, and the mixture was refluxed with stirring under argon for 6 h. Volatile materials were removed *in vacuo* and the resultant black tarry residue was chromatographed on a silica column, initially with diethyl ether–hexane (3:1, v/v) as eluent and then with diethyl ether–hexane (1:1, v/v). The first product obtained was **6** (151 mg, 34%) as a light brown solid, mp 62–63 °C (from ethanol) (this mp is decisively different from that of the isomeric 1,3-thiazole, lit.,[14] mp 106–107 °C) (Found: C, 49.19; H, 3.74; N, 4.89. $C_{11}H_{10}BrNS$ requires C, 49.27; H, 3.73; N, 5.22%); *m/z* (CI) 270 [M + H^+ (^{81}Br)]; δ_H(200 MHz, $CDCl_3$), 7.61–7.45 (4 H, 2 d, *J* 8.9, Ph), 2.47 (3 H, s, Me), 2.21 (3 H, s, Me); δ_C(100 MHz, $CDCl_3$) 166.9, 158.7, 135.3, 131.4, 129.8, 129.0, 122.7, 12.4, 12.0; ν_{max}(KBr)/cm^{-1} 1589, 1491, 1398, 1147, 1067, 1002, 811, 538.

The second product to elute was compound **5** (75 mg, 20%) which was spectroscopically identical with a sample synthesised previously in 4% yield.[2b]

Following the above procedure, a mixture of the dithiazine **1b** (400 mg, 1.33 mmol) and dimethyl maleate (0.67 cm^3, 5.3 mmol) was dissolved in *o*-dichlorobenzene (100 cm^3) and refluxed for 4 h. After concentration *in vacuo* and flash column chromatography, the only product to be isolated was the isothiazole **6** (190 mg, 53%).

4a,5,6,7,8,8a-Hexahydro-2,3-dimethyl-5,8-methano-1,4-benzodithiine 7

Following the above procedure, a mixture of the dithiazine **1b** (300 mg, 1 mmol) and norbornene (940 mg, 10 mmol) was refluxed in *o*-dichlorobenzene (80 cm^3) for 4 h. Column chromatography on silica yielded the product **7** (118 mg, 56%) as a light brown solid, mp 51–52 °C (HRMS: found, 212.0685. $C_{11}H_{16}S_2$ requires *M*, 212.0693); δ_H(200 MHz, $CDCl_3$) 3.29 (2 H, m), 2.47 (1 H, m), 2.43 (1 H, m), 2.31 (2 H, m), 2.08 (6 H, s), 1.63 (2 H, m), 1.26 (2 H, m); δ_C(100 MHz, $CDCl_3$) 132.2, 57.9, 44.5, 34.8, 29.4, 22.1. Isothiazole **6** (61 mg, 23%) was also isolated.

5,6-Dimethyl-3-(4-bromophenyl)-1,4,2-dithiazine 1,1-dioxide 8

To a rapidly stirred solution of dithiazine **1b** (100 mg, 3.3 mmol) in dry dichloromethane (20 cm^3) at room temperature was added, in one portion, peracetic acid (32% in ethyl acetate; 1.38 cm^3, 6.6 mmol) in ethyl acetate (5 cm^3). The mixture was left to stir for 8 min before pouring into water. The organic phase was washed with water (3 × 20 cm^3), dried ($MgSO_4$) and concentrated to *ca.* 3 cm^3. Cold hexane (15 cm^3) was added and the mixture immediately cooled in ice. A crystalline pale yellow precipitate of **8** (25 mg, 23%) was isolated by filtration, mp 218 °C (from ethanol); *m/z* (EI) 333 $(M + H)^+$, 269 $(M + H - SO_2)^+$, 238, 183, 150; δ_H(200 MHz, $CDCl_3$) 7.89 (2 H, d, *J* 8), 7.65 (2 H, d, *J* 8), 2.38 (3 H, s), 2.27 (3 H, s); ν_{max}(KBr)/cm^{-1} 1580, 1528, 1479, 1120, 1069, 1009, 827.

Synthesis of 1,4,2-dithiazolium salts 11. General procedure

The corresponding 3-aryl-1,4,2-dithiazole-5-thione derivative **10a–c**[9] (0.4 mmol) was dissolved in dimethyl sulfate (100 cm^3) and the solution was refluxed under argon for 3 h or until TLC analysis showed complete consumption of starting material. After cooling to 0 °C, diethyl ether (20 cm^3) and hexafluorophosphoric acid (65% in diethyl ether; 0.25 cm^3, 2 mmol) were added dropwise sequentially and the mixture was stirred for 15 min, then poured into dry diethyl ether (300 cm^3) at 0 °C to give a pale brown precipitate. This was filtered, washed with diethyl ether and dried to give the hexafluorophosphate salt as a pale brown solid, which was used directly, without further purification, in the next step. There was thus obtained: salt **11a** (127 mg, 86%), mp 129–130 °C; salt **11b** (154 mg, 94%), mp 123–124 °C; salt **11c** (145 mg, 88%), mp 119.5–120.5 °C.

Synthesis of 3-aryl-6-methylthio-1,4,2,5-dithiadiazines 12. General procedure

To a solution of the hexafluorophosphate salt **11a–c** (0.50 mmol) in dry acetonitrile (30 cm^3) was added iodine (191 mg, 0.75 mmol) and the mixture was stirred until homogeneous. Aqueous ammonia solution (35%; 3.5 cm^3, 31.5 mmol) was added dropwise and the mixture stirred for 4 h at room temperature before pouring into water (30 cm^3). The aqueous mixture was extracted with dichloromethane (3 × 20 cm^3) and the combined organic extracts were dried ($MgSO_4$), evaporated to dryness and then chromatographed on a silica column using hexane–dichloromethane (1:1, v/v) as eluent. The yellow solid thereby obtained was recrystallised from ethanol to yield compounds **12a–c** as pale yellow crystals.

3-Phenyl-6-methylthio-1,4,2,5-dithiadiazine 12a. (68 mg, 55%), mp 32–33 °C (HRMS: found, 239.9831. $C_9H_8N_2S_3$ requires *M*, 239.9838); δ_H(200 MHz, $CDCl_3$) 7.96 (2 H, d, *J* 4.2), 7.45 (3 H, m), 2.57 (3 H, s); δ_C(100 MHz, $CDCl_3$) 171.3, 168.1, 134.4, 132.2, 128.9, 127.9, 15.7; ν_{max}(KBr)/cm^{-1} 3000–2900, 1507, 1472, 1434, 1308, 1241, 985, 926; λ_{max}(MeCN)/nm 375–385 (br); E^{ox} (MeCN) +1.79 V (*vs.* Ag/AgCl).

3-(4-Methoxyphenyl)-6-methylthio-1,4,2,5-dithiadiazine 12b. (63 mg, 46%), mp 83–85 °C (HRMS: found, 269.9950. $C_{10}H_{10}N_2OS_3$ requires *M*, 269.9955); δ_H(200 MHz, $CDCl_3$) 7.87 (2 H, d, *J* 9), 6.92 (2 H, d, *J* 9), 3.85 (3 H, s), 2.56 (3 H, s); δ_C(100 MHz, $CDCl_3$) 170.8, 168.8, 162.9, 129.7, 126.9, 114.2, 55.4, 15.6; ν_{max}(KBr)/cm^{-1} 2950–2800, 1602, 1516, 1501, 1251, 1172,

Table 2 Crystal data for compounds **8** and **12b**

	12b	**8**
Formula	$C_{10}H_{10}N_2OS_3$	$C_{11}H_{10}BrNO_2S_2$
M	270.38	332.23
T/K	293	150
Symmetry	monoclinic	monoclinic
a/Å	4.0140(5)	6.933(1)
b/Å	7.396(1)	14.355(2)
c/Å	20.085(3)	12.274(1)
β (°)	94.57(1)	95.54(1)
U/Å^3	594.4(1)	1215.8(4)
Refl./unit cell	217	486
θ Range (°)	12–23	12–21
Space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
Z	2	4
μ (Mo-Kα)/cm^{-1}	6.0	37.1
D_c/g cm^{-3}	1.51	1.815
F(000)	280	664
Crystal size/mm	0.03 × 0.3 × 0.5	0.1 × 0.3 × 0.32
$2\theta_{max}$ (°)	51	51.5
Data total	2679	5156
Data unique	1755	2112
Data observed, $I > 2\sigma(I)$	1529	1977
R_{int}	0.047	0.054
Absorption correction	semi-empirical [a]	integration [b]
Transmission min, max	0.71, 1.00	0.32, 0.52
No. of refined variables	153	186
$wR(F^2)$, all data	0.146	0.110
Goodness-of-fit	1.12	1.09
$R(F)$, obs. data	0.051	0.039
$\Delta\rho_{max}$/e Å^{-3}	0.28	0.51
$\Delta\rho_{min}$/e Å^{-3}	−0.29	−0.50

[a] Based on equivalents of all reflections with $I > 5\sigma(I)$. [b] 6-Face primary pinakoid; $R_{int} = 0.082$ before correction.

1111, 1022, 936; λ_{max}(MeCN)/nm 391; E^{ox} (MeCN) +1.55 V (*vs.* Ag/AgCl).

3-(4-Chlorophenyl)-6-methylthio-1,4,2,5-dithiadiazine 12c. (81 mg, 59%), mp 111–112 °C (Found: C, 39.47; H, 2.55; N, 10.05. $C_9H_7ClN_2S_3$ requires C, 39.34; H, 2.55; N, 10.20%) (HRMS: found, 273.9463. $C_9H_7ClN_2S_3$ requires M, 273.9460); δ_H(200 MHz, $CDCl_3$) 7.87 (2 H, d, J 9), 7.42 (2 H, d, J 9), 2.57 (3 H); δ_C(100 MHz, $CDCl_3$) 174.5, 170.0, 168.4, 138.6, 132.8, 129.1, 15.7; ν_{max}(KBr)/cm^{-1} 2950–2800, 1648, 1588, 1510, 1502, 1377, 1250, 1100, 944, 910; λ_{max}(MeCN)/nm 371; E^{ox} (MeCN) +1.73 V (*vs.* Ag/AgCl).

Tetramethyl 1,4-dithiine-2,3,5,6-tetracarboxylate 14

Compound **12c** (300 mg, 1.09 mmol) and dimethyl acetylenedicarboxylate (0.67 cm^3, 5.45 mmol) were dissolved in *o*-dichlorobenzene (100 cm^3) and the mixture was heated at reflux for 8 h. The solvent and unreacted DMAD were removed *in vacuo* and the residue chromatographed on a silica column using a diethyl ether–hexane mixture (1:1, v/v) as eluent. The first compound to elute was unreacted **12c** (95 mg, 32%), followed by an oily orange solid which was washed with ice-cold diethyl ether to form a pale yellow solid which was filtered from the orange oil. The solid was identified as compound **14** (46 mg, 12%), by mp and NMR spectral comparison with literature values.[11]

X-Ray crystallography

Single-crystal X-ray diffraction experiments were carried out on a Siemens three-circle diffractometer with a CCD area detector (graphite monochromated Mo-Kα radiation, λ = 0.710 73 Å, ω scan mode) and Oxford Cryosystems open-flow N_2 gas cryostats. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 on all data (empirical extinction correction for **8**), using SHELXTL software.[15] Non-hydrogen atoms were refined anisotropically for both **8** and **12b**. Hydrogen atoms in **12b** were treated as 'riding'; methyl groups were refined as rigid bodies. In **8** all hydrogen atoms were refined isotropically, except in the 'ideally disordered' C(8)H_3 methyl group which was treated as a rigid body. The absolute configuration of the structure **12b** was determined by refining the Flack parameter,[16] which converged to −0.15(18) (*cf.* 0 for the correct and +1 for the inverted enantiomorph). Crystal data and experimental details are listed in Table 2. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/96.

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