

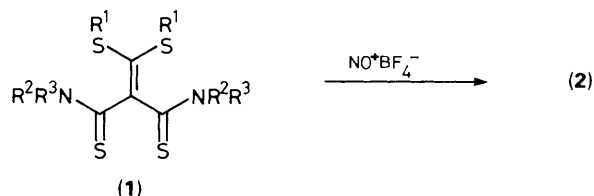
## Dications of the 1,2-Dithiole Series and a Stable Thiete

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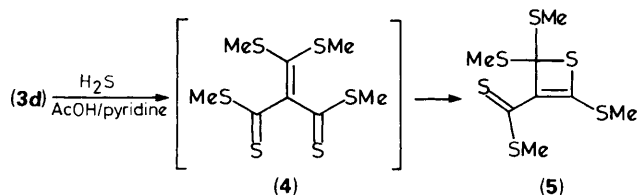
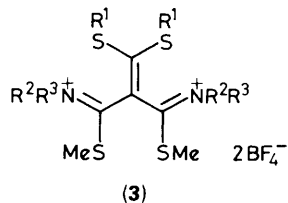
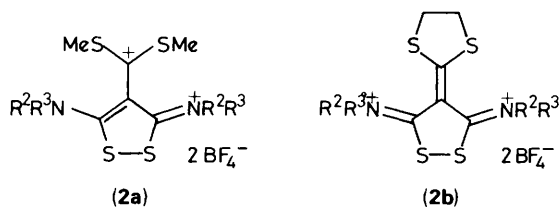
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Oxidation of methylenedithiomalonamides gives rise to 3,5-bis(dimethylamino)-4-methyl-1,2-dithiolium salts, and thiolysis of a dimethyl methylenemalonodithioimidate leads to a stable thiete.

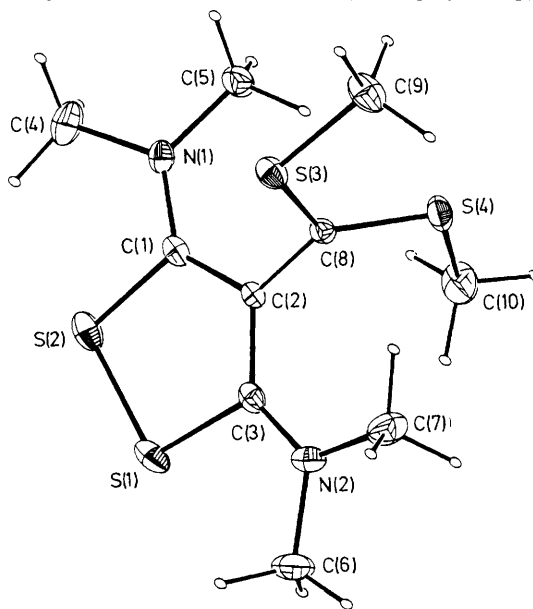
Triplet trimethylenemethanes<sup>1</sup> are potential components of organic ferromagnets and ferromagnetic organic metals.<sup>2</sup> Stabilization of these notoriously unstable 4π-electron 'anti-Y-aromatic' systems can be achieved by donor-acceptor substitution,<sup>3</sup> but trimethylenemethane derivatives of this type have singlet ground states. Thio groups also are supposed to stabilize the trimethylenemethane system.<sup>4,5</sup> Thus, the electrochemical reduction of hexathiotrimethylenemethane dications in which the thio groups are incorporated in 1,3-dithiole rings indicates the formation of stable trimethylenemethane derivatives.<sup>4</sup> Reduction of trimethylenemethane dication derivatives of the 1,2-dithiole[3,4-c]1,2-dithiole series, however, gives rise to products from the opening of one of the 1,2-dithiole rings.<sup>6</sup> In order to get more information on the properties and structures of 1,2-dithiole dication salts we tried to synthesize 1,2-dithiolium salts (2) as precursors of trimethylenemethane diradicals.



- a;  $R^1 = R^2 = R^3 = \text{Me}$   
 b;  $R^1 - R^1 = -\text{CH}_2\text{CH}_2-$ ,  $R^2 = R^3 = \text{Me}$   
 c;  $R^1 - R^1 = -\text{CH}=\text{C}(\text{Ph})-$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{Me}$   
 d;  $R^1 = \text{Me}$ ,  $R^2 = R^3 = -(\text{CH}_2)_5-$



Methylene dithiomalonamides (1a),<sup>5</sup> (1b, d) (prepared, like (1a), from *N,N,N',N'*-tetramethyldithiomalonamide and dithiomalonopiperidine, respectively, CS<sub>2</sub>, NaH and treatment of the so formed disodium dithiocarboxylates with ethylene bromide and methyl iodide, respectively), and (1c) (prepared from the sodium salt of *N,N'*-dimethyldithiomalonamide and 2-methylthio-4-phenyl-1,3-dithiolium tetrafluoroborate), can readily be oxidized with nitrosyl tetrafluoroborate to produce dication salts (2a-d) in high yields [(2a)†

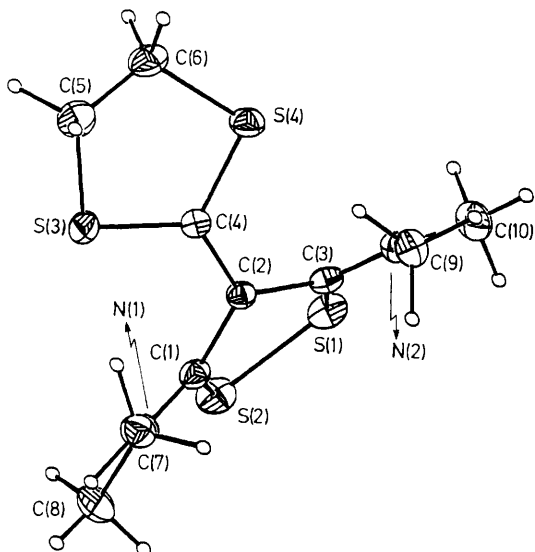


**Figure 1.** ORTEP view of the structure of (2a), showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): C(1)-S(2) 1.744, S(1)-S(2) 2.038, C(3)-S(1) 1.753, C(1)-N(1) 1.331, C(3)-N(2) 1.323, C(1)-C(2) 1.410, C(2)-C(3) 1.399, C(2)-C(8) 1.477; S(1)-C(3)-C(2) 113.6, C(1)-C(2)-C(3) 118.1, S(1)-S(2)-C(1) 95.0, S(2)-S(1)-C(3) 96.2, S(2)-C(1)-C(2) 116.9; dihedral angle between planes [C(1)-C(2)-C(3)-S(1)-S(2)]-[S(3)-C(8)-S(4)] 73.62 ± 0.53.

† Crystal data for (2a): C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>S<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub>, *M* = 468.13, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.676(2), *b* = 14.609(3), *c* = 10.977(2) Å, β = 112.41(2)°, *U* = 1879.3 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.654 g cm<sup>-3</sup>, *F*(000) = 952, *T* = 294 ± 1 K, μ(Mo-Kα) = 5.57 cm<sup>-1</sup>. Refinement of 242 parameters using 2546 observables with *F*<sup>2</sup> > 3σ(*F*<sup>2</sup>) gave residuals *R* and *R*<sub>w</sub> of 0.073 and 0.066, respectively.

Crystal data for (2b): C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>S<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub>, *M* = 466.12, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.428(2), *b* = 12.100(3), *c* = 13.006(3) Å, β = 106.00(2)°, *U* = 1879.9 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.642 g cm<sup>-3</sup>, *F*(000) = 944, *T* = 294 ± 1 K, μ(Mo-Kα) = 5.57 cm<sup>-1</sup>. Refinement of 238 parameters using 2515 observables with *F*<sup>2</sup> > 3σ(*F*<sup>2</sup>) gave residuals *R* and *R*<sub>w</sub> of 0.058 and 0.055, respectively.

Crystal data for (5): C<sub>8</sub>H<sub>12</sub>S<sub>6</sub>, *M* = 300.57, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 7.183, *b* = 12.727(3), *c* = 14.628(3) Å, β = 99.19(2)°, *U* = 1320.1 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.511 g cm<sup>-3</sup>, *F*(000) = 624, *T* = 294 ± 1 K, μ(Mo-Kα) = 9.59 cm<sup>-1</sup>. Refinement of 127 parameters using 2044 observables with *F*<sup>2</sup> > 3σ(*F*<sup>2</sup>) gave residuals *R* and *R*<sub>w</sub> of 0.028 and 0.025, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 2.** ORTEP view of the structure of **(2b)**, showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): C(1)–S(2) 1.746, S(1)–S(2) 2.072, C(3)–S(1) 1.752, C(1)–C(2) 1.442, C(2)–C(3) 1.442, C(1)–N(1) 1.305, C(3)–N(2) 1.291, C(2)–C(4) 1.394, C(4)–S(3) 1.718, C(4)–S(4) 1.706; C(3)–S(1)–S(2) 94.4, C(1)–S(2)–S(1) 95.8, C(2)–C(1)–S(2) 114.7, C(3)–C(2)–C(1) 111.4, C(2)–C(3)–S(1) 114.9; dihedral angle between planes [C(1)–C(2)–C(3)]–[C(4)–S(3)–C(5)–C(6)–S(4)]  $24.20 \pm 0.67$ .

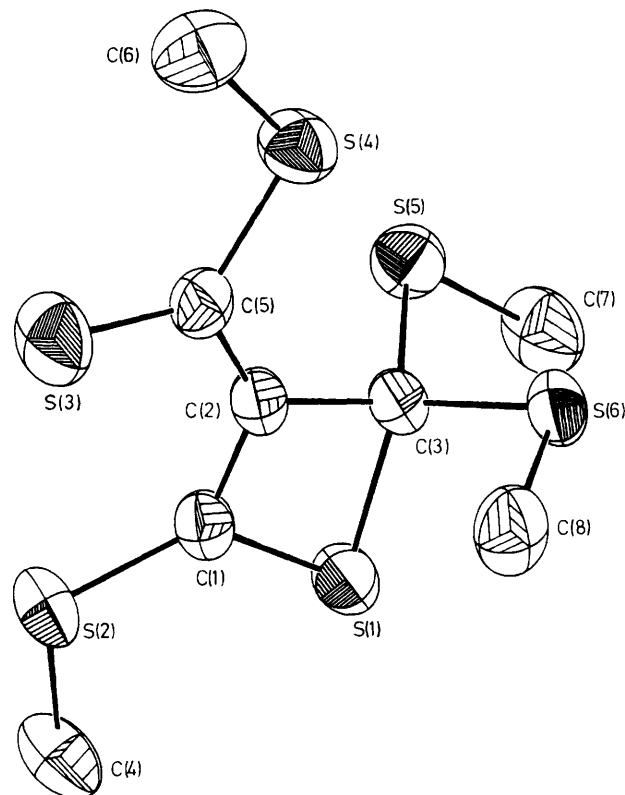
bright orange crystals,  $\lambda_{\max}$  (MeCN) 475 nm; **(2b)**<sup>+</sup> yellow crystals,  $\lambda_{\max}$  374 nm; **(2c)** yellow crystals,  $\lambda_{\max}$  452 nm; **(2d)** yellow platelets,  $\lambda_{\max}$  387 nm].

Single crystal X-ray analyses demonstrate that there is a marked difference in the structures of **(2a)** and **(2b)**. Both compounds are not planar. As shown in Figure 1, **(2a)** displays a dihedral angle of  $73.62^\circ$  between the planes of the dithiole ring and the bis(methylthio)methylene moiety. Figure 2 demonstrates that in the folded structure **(2b)** the twisted 1,3-dithiolane ring is tilted by  $24.20^\circ$  to the plane of the 1,2-dithiole ring.

Cyclic voltammetry of **(2a–c)** reveals that there are no stable trimethylenemethane diradical intermediates. The reduction is irreversible in terms of cyclic voltammetry, and the starting materials **(1)** are formed exclusively. The situation is somewhat different with **(3a, b, d)**, obtained from **(1a, b, d)** by warming with trimethyloxonium tetrafluoroborate. Cyclic voltammetry of **(3a, b)** exhibits a reversible wave followed by an irreversible wave.

With the object of preparing a 1,2-dithiolium salt of type **(2)** with methylthio groups instead of dimethylamino groups, we tried to synthesize the tetrathiomalonate **(4)**. Upon thiolysis of **(3d)**, however, instead of **(4)**, the stable crystalline thiete **(5)**<sup>†</sup>, m.p.  $91\text{--}93^\circ\text{C}$ , is formed in 69% yield. The parent thiete and its alkyl derivatives are thermally unstable.<sup>7</sup> 3-Aryl groups stabilize the system<sup>7</sup> and in a few photochemically synthesized spiro compounds<sup>8</sup> donor groups at position 2 increase the stability further.

Thermal ring opening to the thermodynamically more stable thioacroleins<sup>9</sup> is characteristic for thietes.<sup>7</sup> Therefore, the spontaneous formation of **(5)** is unexpected [in CDCl<sub>3</sub> solution, the <sup>1</sup>H n.m.r. spectrum does not allow a clear distinction between **(5)** and **(4)**]. As shown in Figure 3, bond distances in the planar thiete ring of **(5)** are basically the same as those in the parent compound (microwave spectrum),<sup>10</sup> although the difference in the C–S bond lengths is more pronounced.



**Figure 3.** ORTEP view of the structure of **(5)**, showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): C(3)–S(1) 1.898, C(1)–S(1) 1.747, C(1)–C(2) 1.362, C(2)–C(3) 1.512; C(3)–S(1)–C(2) 73.9, C(1)–C(2)–S(1) 99.0, C(3)–C(1)–C(2) 99.4, C(1)–C(3)–S(1) 87.7.

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