

Bis[4-(trimethylammonio)phenyl]  
disulfide diiodide acetone solvateZheng Zhang,<sup>a</sup> Xiao-Yan Tang,<sup>b</sup> Jian-Ping Lang<sup>b</sup> and  
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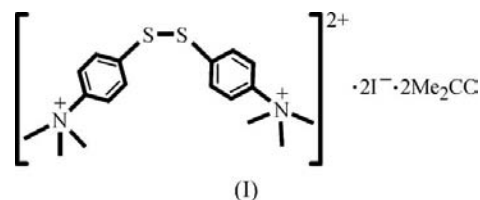
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The title compound,  $C_{18}H_{26}N_2S_2^{2+} \cdot 2I^- \cdot 2C_3H_6O$ , is an intermediate in the design of the zwitterionic thiolate 4-(trimethylammonio)benzenethiolate (Tab), in which a pair of aryl-substituted S atoms are linked by a covalent bond. The central S—S bond length is 2.020 (3) Å and the  $C_{ar}-S-S-C_{ar}$  torsion angle is  $-84.1(2)^\circ$ . The crystal structure is stabilized by nonclassical hydrogen bonds which occur as intramolecular C—H $\cdots$ I interactions and intermolecular C—H $\cdots$ S and C—H $\cdots$ O contacts. In the crystal structure, both the dication and the two symmetrically independent iodide counter-anions are located on twofold crystallographic axes, whereas the acetone solvent molecule occupies a general position.

## Comment

Over the last few decades, disulfides have stimulated intense interest owing to their donor capabilities towards metal ions (Bernal *et al.*, 1976; Haller & Treichel, 1983; Roesky *et al.*, 1984; Kitaura *et al.*, 2002) and their potential application in biological systems (Hald *et al.*, 1948; Ricci & Bernal, 1969).

However, structural information for aromatic disulfides is limited (Woodard *et al.*, 1976; Cannon *et al.*, 2000; Anaconda *et al.*, 2003; Nicholson *et al.*, 2006; Clegg & Coxall, 2005), especially as far as aromatic disulfides containing an ammonium ( $-NR_3$ ) group (Chen, Xu, Zhang, Zain *et al.*, 2004) are concerned.



Recently, we have engaged in the synthesis of metal complexes of the zwitterionic ammonium thiolate 4-(trimethylammonio)benzenethiolate (Tab) with different transition metals, such as  $Hg^{II}$ ,  $Au^I$  and  $Ag^I$  (Chen, Xu, Xu *et al.*, 2004; Chen, Xu, Zhang, Chen & Lang, 2004; Chen, Zhang, Tang, Ren, Li *et al.*, 2006; Chen, Zhang, Tang, Ren, Zhang & Lang, 2006). The title compound, (I), represents an intermediate in the design of Tab (DePamphilis *et al.*, 1974) and can be used as a large cation to form metal disulfides (Chen, Zhang, Ren & Lang, 2006; Chen *et al.*, 2005). In order to investigate its properties further, the title compound was synthesized and characterized.

The asymmetric unit of compound (I) contains one half of a dication and two symmetrically independent iodide anions, where each of these moieties sits on or about crystallographic twofold axes, and an acetone solvent molecule in a general position. A perspective view of (I) is shown in Fig. 1. The disulfide dication has positive charges formally located on the  $-NMe_3$  groups. The torsion angle about the S—S bond [ $C1^i-S1^i-C1-S1$ ; symmetry code: (i)  $-x - \frac{1}{2}, -y + 1, z$ ] is  $-84.1(2)^\circ$  and hence smaller than those reported for two other compounds containing the  $(Tab-Tab)^{2+}$  dication, *viz.*  $(Tab-Tab)[HgI_4]$  ( $92.1^\circ$ ; Chen *et al.*, 2005) and  $(Tab-Tab)[CuBr_4]$  [ $93.05(5)^\circ$ ; Tang *et al.*, 2006]. Comparable values have also been observed in  $(Tab-Tab)[CuBr_3]$  [ $82.1(4)^\circ$ ],  $(Tab-Tab)[CuI_3]$  [ $81.9(5)^\circ$ ] and  $\{(Tab-Tab)[Cu_2I_4]\}_n$  [ $80.34(4)^\circ$ ].

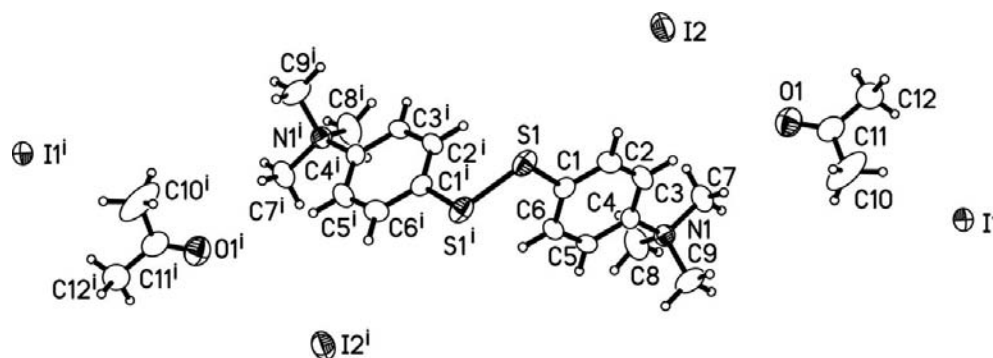
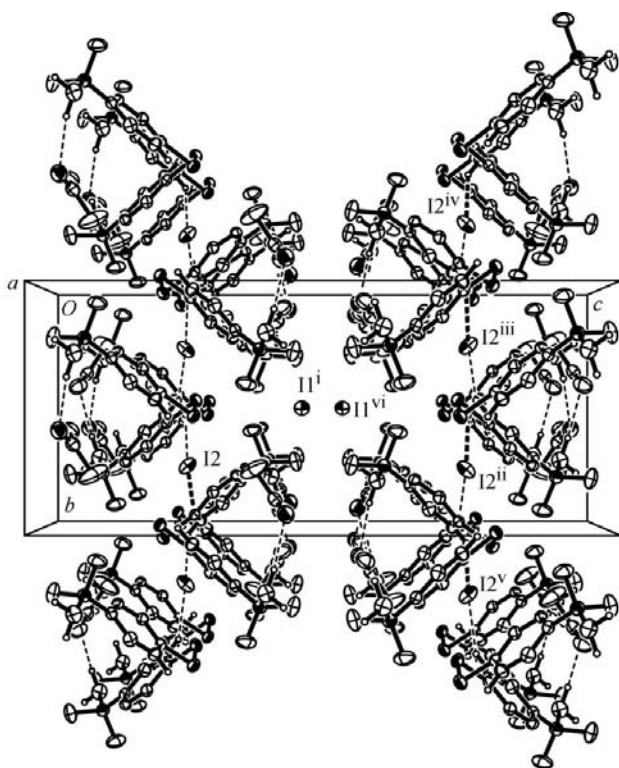


Figure 1

A plot of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i)  $-x - \frac{1}{2}, -y + 1, z$ .]



**Figure 2**

A packing diagram for (I), viewed approximately down the *a* axis. All H atoms have been omitted for clarity, except for those involved in the hydrogen-bonding interactions (shown as dashed lines). [Symmetry codes: (i)  $x - 1, \frac{1}{2} - y, \frac{1}{2} - z$ ; (ii)  $\frac{1}{2} + x, y, 1 - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $\frac{1}{2} + x, -1 + y, 1 - z$ ; (v)  $1 - x, 2 - y, 1 - z$ ; (vi)  $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$ .]

(Chen, Zhang, Ren & Lang 2006), and (Tab–Tab)<sub>2</sub>[Hg<sub>3</sub>Cl<sub>10</sub>] [81.47 (4)°; Chen, Zhang, Tang, Ren, Zhang & Lang, 2006]. The different torsion angles about the S–S bonds in these compounds may be due to the steric requirements of the anions or solvents. The S–S bond is 2.030 (3) Å, which is similar to the values observed in (Tab–Tab)[HgI<sub>4</sub>] [2.030 (3) Å], (Tab–Tab)[CuBr<sub>3</sub>] [2.0538 (17) Å], (Tab–Tab)[CuI<sub>3</sub>] [2.049 (3) Å], [(Tab–Tab)[Cu<sub>2</sub>I<sub>4</sub>]]<sub>n</sub> [2.026 (2) Å], (Tab–Tab)[CuBr<sub>4</sub>] [2.020 (3) Å] and (Tab–Tab)<sub>2</sub>[Hg<sub>3</sub>Cl<sub>10</sub>] [2.034 (2) Å].

The S–S bonds in the dications lie at an angle of 18.2 (2)° to the [100] direction. The shortest distance between the S atoms of neighbouring dications is 4.669 (2) Å for S1<sup>i</sup>⋯S1(x,  $-y + \frac{3}{2}, -z + \frac{1}{2}$ ). Iodide anions and acetone solvent molecules are located between the dications. Looking down the *a* axis, it appears that each pair of I1 anions acts as an anionic template, with four symmetry-related quaternary ammonium ions arranged around them as shown in Fig. 2. With the nonclassical hydrogen-bonding interactions between atom I2 and the adjacent benzene ring containing atom C2 or the methyl group containing atom C7, the I2 anions are positioned near the benzene rings. The I2 anions are arranged in strands along the *b* axis. The solvent molecules are situated between the dications near the –NMe<sub>3</sub> groups, with nonclassical intermolecular hydrogen-bonding interactions between the acetone atom O1 and atom C7 of the methyl group (Table 1).

## Experimental

Bis[4-(dimethylamino)phenyl] disulfide (dads) was prepared according to the literature procedure of Clegg & Coxall (2005). MeI (2 ml) was added to a solution containing dads (60.6 mg, 0.2 mmol) in Me<sub>2</sub>CO (5 ml). The mixture was stirred at room temperature for 1 d and a large amount of precipitate of (I) was formed, collected by filtration, washed with Et<sub>2</sub>O and dried *in vacuo*. To a glass beaker containing (I), obtained directly from the above preparation, was added 5 ml MeCN and 1 ml Me<sub>2</sub>CO, forming a homogeneous yellow solution. After standing the yellow solution at ambient temperature for several days, light-yellow block-shaped crystals of (I) were formed (yield: 0.118 g; 84%, based on S). The crystal used for the crystal structure determination was obtained directly from the above preparation. Analysis found: C 40.52, H 5.31, N 4.02%; calculated for C<sub>24</sub>H<sub>38</sub>I<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 40.90, H 5.44, N 3.98%. IR (KBr, cm<sup>-1</sup>): 1585 (*s*), 1465 (*m*), 1406 (*m*), 1120 (*m*), 1007 (*s*), 956 (*s*), 744 (*m*).

### Crystal data

C <sub>18</sub> H <sub>26</sub> N <sub>2</sub> S <sub>2</sub> <sup>2+</sup> ·2I <sup>-</sup> ·2C <sub>3</sub> H <sub>6</sub> O	<i>V</i> = 3003.4 (10) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 704.48	<i>Z</i> = 4
Orthorhombic, <i>Pnna</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.398 (2) Å	<i>μ</i> = 2.26 mm <sup>-1</sup>
<i>b</i> = 10.1902 (19) Å	<i>T</i> = 193 K
<i>c</i> = 23.773 (5) Å	0.13 × 0.12 × 0.10 mm

### Data collection

Rigaku Mercury diffractometer	31366 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	3437 independent reflections
<i>T</i> <sub>min</sub> = 0.758, <i>T</i> <sub>max</sub> = 0.806	3348 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.039

### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.056	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.099	Δρ <sub>max</sub> = 0.63 e Å <sup>-3</sup>
<i>S</i> = 1.15	Δρ <sub>min</sub> = -0.80 e Å <sup>-3</sup>
3437 reflections	
201 parameters	

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H⋯ <i>A</i>	<i>D</i> –H	H⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> –H⋯ <i>A</i>
C7–H7C⋯I2 <sup>i</sup>	1.05 (7)	3.03 (7)	4.038 (7)	162 (5)
C7–H7B⋯O1 <sup>i</sup>	0.97 (7)	2.54 (7)	3.463 (8)	158 (5)
C2–H2⋯I2	0.98 (5)	2.93 (5)	3.818 (5)	151 (4)

Symmetry code: (i)  $-x + \frac{1}{2}, -y + 1, z$ .

The H atoms of the Tab–Tab group were determined by Fourier synthesis [the range of refined C–H distances for the benzene rings is 0.86 (5)–0.98 (5) Å and for the methyl groups is 0.93 (7)–1.05 (7) Å], while the H atoms of the methyl groups of the acetone solvent molecule were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.98 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3006). Services for accessing these data are described at the back of the journal.

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