

The dimer, trimer and 1,2,4-trithiolane of adamantanethione

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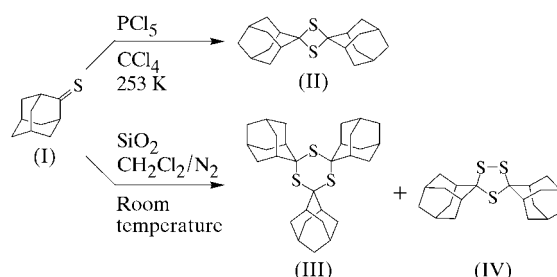
The molecules of dispiro[1,3-dithietane-2,2':4,2''-diadamantane], C₂₀H₂₈S₂, have crystallographic *C_i* symmetry, as well as local *D_{2h}* symmetry, and a planar 1,3-dithietane ring. The molecules of trispiro[1,3,5-trithiane-2,2':4,2'':6,2'''-triadamantane], C₃₀H₄₂S₃, have approximate *C₂* symmetry and the 1,3,5-trithiane ring has a twist-boat conformation. The C—S—C bond angles within the ring are about 8° larger than observed in most related 1,3,5-trithiane structures. In dispiro[1,2,4-trithiolane-3,2':5,2''-diadamantane], C₂₀H₂₈S₃, the molecules have local *C₂* symmetry and the 1,2,4-trithiolane ring has a half-chair conformation.

Comment

Interest in the chemistry of thiocarbonyl compounds has increased remarkably over the last few years. For example, thioketones have been used as 'superdipolarophiles' in 1,3-dipolar cycloadditions (Fisera *et al.*, 1996; Huisgen *et al.*, 2001) and as 'superdienophiles' in hetero-Diels–Alder reactions (Schatz & Sauer, 1994; Rohr *et al.*, 1998). Thiocarbonyl compounds are also starting materials for the generation of thiocarbonyl ylides (Mloston & Heimgartner, 2000) that are then used to prepare thia-heterocycles by 1,3-dipolar cycloadditions or by 1,3- as well as 1,5-dipolar electrocyclizations. In addition, thioketones and some other C=S-containing compounds have been shown to undergo Lewis acid-catalyzed reactions with oxiranes to yield 1,3-oxathiolanes (Blagoev *et al.*, 2000; Fu *et al.*, 2001).

In most of these studies, non-enolizable thioketones have been used as model compounds; for example, thiobenzophenone (Pedersen *et al.*, 1978), 1,1,3,3-tetramethylindane-2-thione (Klages & Voss, 1980; Langhals & Langhals, 1990), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (Elam & Davis, 1967) and adamantanethione (Greidanus, 1970). These thioketones proved to be relatively stable and they can be prepared conveniently by thionation of the corresponding ketones either by treatment with thionating reagents, such as

P₄S₁₀ and Lawesson's reagent, or with a mixture of H₂S and HCl. Several papers report the formation of dimers, trimers and other side products during the synthesis of thioketones (*cf.* Campaigne, 1946; Schönberg, 1955; Mayer *et al.*, 1964; Bleisch & Mayer, 1967; Scheibye *et al.*, 1982; Sachweh & Langhals, 1990). The first preparation of pure adamantanethione, (I), with P₄S₁₀ in pyridine, was described by Greidanus (1970). He also observed that (I) undergoes dimerization and trimerization to give compounds (II) and (III) when treated with methanesulfonic acid (*cf.* Ishii *et al.*, 1997). The dimer, (II), was also formed in high yields in reactions of (I) with α,β -unsaturated carbonyl compounds, which act as heterodienes (Katada *et al.*, 1984a), as well as with derivatives of 2-hydroxybenzyl alcohol and with hydrazoneyl chlorides (Katada *et al.*, 1984b).



As part of our ongoing studies of the synthesis and reactivity of α -chlorosulfonyl chlorides (Koch *et al.*, 1999; Mloston, Majchrzak *et al.*, 2002), we also tried to prepare 2-chloro-adamantyl-2-sulfonyl chloride by treatment of (I) with phosphorus pentachloride in tetrachloromethane at 353 K. Surprisingly, the 1,3-dithietane dimer, (II), was formed as the major product.

Treatment of (I) with silica gel in dichloromethane at room temperature resulted in a mixture of the trithiane trimer, (III), the 1,2,4-trithiolane, (IV), and unreacted (I) in the ratio 9:25:62, respectively. The trimer was successfully crystallized for the first time (*cf.* Greidanus, 1970) from dichloromethane/hexane. The main product, (IV), is a well known compound previously obtained as a side product in several reactions, such as the reaction of (I) with nitrile sulfides or sulfur (Wai & Sammes, 1991), with sodium thiophenolate (Huisgen & Rapp, 1997), with phosphorous pentasulfide (Okuma, Shibata *et al.*, 2000) or with elemental sulfur (Okuma, Kojima *et al.*, 2000). In each case, the sulfur-containing reagent can be envisaged as

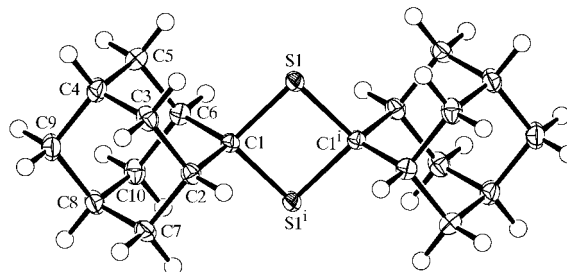


Figure 1

View of the molecule of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) 2 - x, -y, -z.]

being the source of the additional S atom. However, compound (IV) has also been obtained when (I) was the only sulfur compound present in the reaction mixture, such as in reactions of (I) with organic azides (Mloston, Romanski & Heimgartner, 1996; Mloston, Romanski, Linden *et al.*, 1996) and with tributylammonium fluoride (Mloston, Prakash *et al.*, 2002). A reaction mechanism for the formation of 1,2,4-trithiolanes from thioketones and organic azides has been proposed (Mloston & Heimgartner, 1995; Mloston, Romanski *et al.*, 1995). As part of their full characterization, low-temperature X-ray crystal structure determinations of compounds (II), (III) and (IV) were carried out.

The molecule of compound (II) sits across a crystallographic centre of inversion and, as a consequence, the 1,3-dithietane ring is planar (Fig. 1). In addition, the molecule has local D_{2h} symmetry, with an r.m.s. fit of 0.015 Å. The C—S—C bond angles are significantly less than 90°, while the S—C—S angles are correspondingly larger than 90° (Table 1). The literature reports only five other structures that have a 1,3-dithietane ring with unsubstituted-S and sp^3 C atoms. The structure of 1,1,3,3-tetrachloro-2,4-dithiacyclobutane (Krebs & Beyer, 1969; Boese *et al.*, 1993) is the only one where the molecule has crystallographic C_i symmetry, although the molecule of *trans*-2,4-dimethyl-2,4-bis(thioacetylthio)-1,3-dithietane (Mikołajczyk *et al.*, 1977) has pseudo- C_i symmetry and a planar 1,3-dithietane ring. In both *anti*-bis(camphor)-1,3-dithietane (Back *et al.*, 1995) and 2,4-bis(cymantrenyl)-2,4-dimethyl-1,3-dithietane (Batsanov *et al.*, 1992), the molecules have local C_2 symmetry about an axis perpendicular to the plane of the 1,3-dithietane ring. In the former compound, the 1,3-dithietane ring is almost planar, being folded about the S···S and C···C axes by approximately 4°, while in the latter compound, the ring is folded more significantly, the fold being approximately 12° about both the S···S and C···C axes. In 1,4-diphenyl-2,2,3,3-tetramethyl-5,6-dithiabicyclo[2.1.1]hexane (Block *et al.*, 1997), the two dithietane ring C atoms are

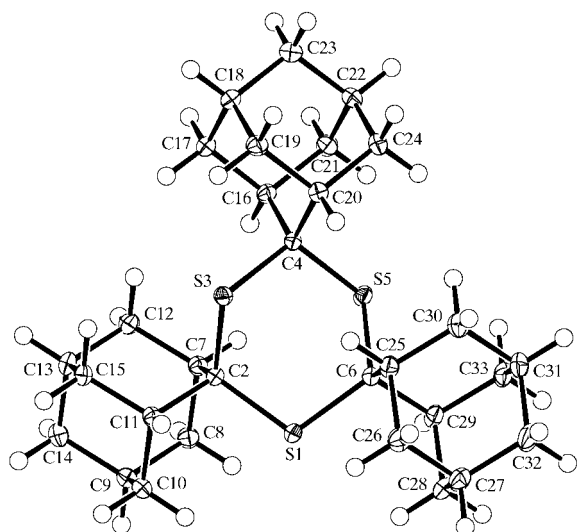


Figure 2
View of the molecule of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

bridged by an ethylene group, which constrains the C—S—C bonds to be part of a five-membered ring. This produces severe folding of the 1,3-dithietane ring into a V-shape about both the S···S and C···C axes, the folds being 61.7 and 52.8°, respectively. The C—S bond lengths and C—S—C and S—C—S angles in the 1,3-dithietane ring of (II) are similar to those in all of the related compounds, with the exception of the highly puckered ring of 1,4-diphenyl-2,2,3,3-tetramethyl-5,6-dithiabicyclo[2.1.1]hexane, where the ring strain reduces the C—S—C angles to a mean value of 73.4 (1)°.

The molecule of compound (III) has approximate C_2 symmetry about an axis passing through S1 and C4, with an r.m.s. fit of 0.17 Å (Fig. 2). The 1,3,5-trithiane ring has an almost perfect twist-boat conformation, with puckering parameters (Cremer & Pople, 1975) $Q = 0.990$ (1) Å, $q_2 = 0.990$ (1) Å, $q_3 = 0.003$ (1) Å, $\varphi_2 = 90.26$ (6)° and $\theta = 89.8$ (1)° for the atom sequence S1—C2—S3—C4—S5—C6. The Cambridge Structural Database (CSD, October 2001 release; Allen & Kennard, 1993) contains 19 entries covering 12 compounds that have a 1,3,5-trithiane ring with unsubstituted-S and sp^3 C atoms, excluding those where the ring is part of a hexathiaadamantane moiety. Of these, the only structure in which the 1,3,5-trithiane ring has a twist-boat conformation is that of *trans*-2,4,6-tris(trichloromethyl)-1,3,5-trithiane (Irving & Irving, 1987), while a chair conformation is found in all of the remaining structures. The overall mean C—S bond length and C—S—C and S—C—S angles in the 1,3,5-trithiane ring of these 19 literature structures are 1.818 (6) Å, 100.3 (8)° and 113.7 (5)°, respectively. The C—S bond lengths of (III) have a mean value of 1.837 (2) Å and are similar to the mean value for the other structures, although the S1—C2 and S1—C6 bonds are slightly longer (Table 2). More significant are the C—S—C angles of (III), whose mean value of 108.73 (9)° is over 8° larger than the overall mean value for the other structures, while the S—C—S angles for (III) have a mean value of 110.8 (1)°, which is about 3° smaller than the mean value for the other structures. This variation in the angles within the 1,3,5-trithiane ring might be a result of each C atom of the ring being disubstituted. The only other reported 1,3,5-trithiane structure with disubstituted ring C atoms is that of β -2,4,6-triphenyl-2,4,6-tris(trimethylsilyl)-1,3,5-trithiane (Bonini *et al.*, 1988), and this structure also has enlarged C—S—C and contracted S—C—S angles similar to those observed for compound (III).

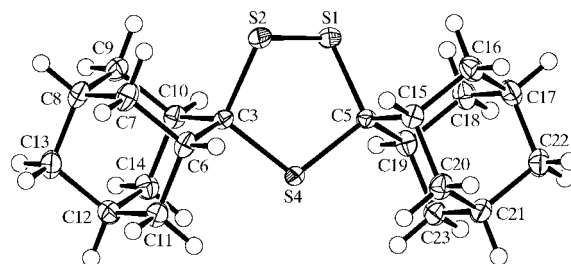


Figure 3
View of the molecule of (IV) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The molecule of compound (IV) has local C_2 symmetry about an axis passing through S4 and the midpoint of the S1–S2 bond, with an r.m.s. deviation of 0.028 Å (Fig. 3). The 1,2,4-trithiolane ring has a half-chair conformation twisted on the S1–S2 bond, with puckering parameters $q_2 = 0.692$ (1) Å and $\varphi_2 = 15.95$ (8)° for the atom sequence S1–S2–C3–S4–C5. Atoms S1 and S2 deviate from the plane defined by atoms C3, S4 and C5 by 0.630 (1) and –0.512 (1) Å, respectively. The CSD contains 17 entries for reported structures that have a 1,2,4-trithiolane ring with unsubstituted-S and sp^3 C atoms, but geometrical data are available for only eight of these. The bond lengths and angles within the 1,2,4-trithiolane ring of compound (IV) (Table 3) are consistent with those of these related structures. There does not seem to be a preference for the conformation of the 1,2,4-trithiolane ring, as an envelope conformation or a distorted variant thereof is found in four of the eight related structures for which data are available.

Experimental

For the preparation of (II), phosphorus pentachloride (765 mg, 3.6 mmol) was added to a solution of adamantanethione, (I) (300 mg, 1.8 mmol), in tetrachloromethane (10 ml) and the mixture was heated under reflux (353 K) for 7 h. The mixture was then poured onto ice, the organic phase was extracted with aqueous NaHCO_3 solution ($\times 3$) and water ($\times 3$), dried over MgSO_4 , filtered, and the solvent evaporated. The crude residue (256 mg) was recrystallized from hexane/dichloromethane, yielding 169 mg (56.3%) of (II) as colourless prisms (m.p. 578–580 K). Single crystals of (II) were obtained by slow evaporation of a solution in hexane/dichloromethane.

For the preparation of (III) and (IV), silica gel (4.0 g) was added to a solution of (I) (66 mg, 0.4 mmol) in dry dichloromethane (10 ml) under a nitrogen atmosphere at room temperature. After stirring the mixture for 3 d at room temperature, the suspension was filtered, the residue was washed with dichloromethane ($\times 4$), and the filtrate was evaporated. Chromatographic separation (SiO_2 , hexane/ CH_2Cl_2 10:1) and crystallization gave 6 mg (9%) of (III) as colourless needles [m.p. 618.9–619.4 K (decomposition)] and 12 mg (25%) of (IV) as colourless prisms (m.p. 468.4–469.7 K). In addition, 41 mg (62%) of (I) were recovered. Single crystals of (III) and (IV) were obtained by slow evaporation of solutions in dichloromethane/hexane and chloroform/dichloromethane/methanol, respectively.

Compound (II)

Crystal data

$\text{C}_{20}\text{H}_{28}\text{S}_2$	$D_x = 1.330 \text{ Mg m}^{-3}$
$M_r = 332.56$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 17 358 reflections
$a = 6.4567$ (1) Å	$\theta = 2.0\text{--}30.0^\circ$
$b = 12.0271$ (2) Å	$\mu = 0.32 \text{ mm}^{-1}$
$c = 10.7163$ (2) Å	$T = 160$ (1) K
$\beta = 93.8719$ (5)°	Prism, colourless
$V = 830.28$ (2) Å ³	$0.25 \times 0.25 \times 0.20 \text{ mm}$
$Z = 2$	

Table 1

Selected geometric parameters (Å, °) for (II).

S1–C1	1.8411 (10)	S1–C1 ¹	1.8432 (10)
C1–S1–C1 ¹	85.76 (4)	S1–C1–S1 ¹	94.24 (4)

Symmetry code: (i) $2 - x, -y, -z$.

Data collection

Nonius KappaCCD diffractometer	2098 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{\text{int}} = 0.040$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{\text{max}} = 30.0^\circ$
$T_{\text{min}} = 0.769, T_{\text{max}} = 0.830$	$h = -9 \rightarrow 9$
29 949 measured reflections	$k = -16 \rightarrow 16$
2410 independent reflections	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.2667P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.34 \text{ e Å}^{-3}$
2409 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e Å}^{-3}$
100 parameters	
H-atom parameters constrained	

Compound (III)

Crystal data

$\text{C}_{30}\text{H}_{42}\text{S}_3$	$Z = 2$
$M_r = 498.84$	$D_x = 1.366 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.6436$ (1) Å	Cell parameters from 47 672 reflections
$b = 12.3102$ (2) Å	$\theta = 2.0\text{--}30.0^\circ$
$c = 15.6057$ (2) Å	$\mu = 0.32 \text{ mm}^{-1}$
$\alpha = 77.0671$ (5)°	$T = 160$ (1) K
$\beta = 86.7263$ (6)°	Needle, colourless
$\gamma = 77.1671$ (7)°	$0.25 \times 0.12 \times 0.10 \text{ mm}$
$V = 1212.81$ (3) Å ³	

Data collection

Nonius KappaCCD diffractometer	5854 reflections with $I > 2\sigma(I)$
φ and ω scans with κ offsets	$R_{\text{int}} = 0.053$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{\text{max}} = 30.0^\circ$
$T_{\text{min}} = 0.914, T_{\text{max}} = 0.970$	$h = -9 \rightarrow 9$
50 920 measured reflections	$k = -17 \rightarrow 17$
7114 independent reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.4675P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.42 \text{ e Å}^{-3}$
7113 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e Å}^{-3}$
298 parameters	
H-atom parameters constrained	

Table 2

Selected geometric parameters (Å, °) for (III).

S1–C2	1.8501 (12)	S3–C4	1.8341 (12)
S1–C6	1.8511 (12)	S5–C6	1.8270 (13)
S3–C2	1.8245 (12)	S5–C4	1.8370 (12)
C2–S1–C6	108.59 (5)	S3–C2–S1	110.51 (6)
C2–S3–C4	108.70 (5)	S3–C4–S5	111.26 (6)
C6–S5–C4	108.91 (5)	S5–C6–S1	110.52 (6)

Compound (IV)

Crystal data

$\text{C}_{20}\text{H}_{28}\text{S}_2$	$D_x = 1.359 \text{ Mg m}^{-3}$
$M_r = 364.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5453 reflections
$a = 13.3264$ (2) Å	$\theta = 2.0\text{--}30.0^\circ$
$b = 11.5166$ (1) Å	$\mu = 0.41 \text{ mm}^{-1}$
$c = 12.9233$ (1) Å	$T = 160$ (1) K
$\beta = 116.0645$ (5)°	Prism, colourless
$V = 1781.69$ (3) Å ³	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.044$
φ and ω scans with κ offsets	$\theta_{\text{max}} = 30.1^\circ$
50 637 measured reflections	$h = -18 \rightarrow 16$
5220 independent reflections	$k = -16 \rightarrow 0$
4190 reflections with $I > 2\sigma(I)$	$l = 0 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.6782P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{\AA}^{-3}$
5217 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{\AA}^{-3}$
208 parameters	
H-atom parameters constrained	

Table 3

Selected geometric parameters (\AA , $^\circ$) for (IV).

S1—C5	1.8334 (12)	S4—C3	1.8532 (12)
S1—S2	2.0281 (5)	S4—C5	1.8554 (12)
S2—C3	1.8378 (12)		
C5—S1—S2	96.13 (4)	S2—C3—S4	106.08 (6)
C3—S2—S1	96.22 (4)	S1—C5—S4	105.40 (6)
C3—S4—C5	104.53 (5)		

For each structure, all H atoms were placed in geometrically idealized positions (C—H = 0.99–1.00 \AA) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2002).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1020). Services for accessing these data are described at the back of the journal.

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