An X-ray Crystallographic Determination of
5,6,7-Trithiahexacyclo[9.5.1.1^{3,9}.0^{2,10}.0^{4,8}.0^{12,16}]octadec-13-ene*

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Abstract

$C_{15}H_{18}S_3$, grown from $CHCl_3$ solution, is monoclinic, space group $P2_1/n$, $a = 12\cdot025$ (12), $b = 14\cdot349$ (15), $c = 8\cdot460$ (4) Å, $\beta = 112\cdot06$ (6)°, $U = 1353$ Å^3, $Z = 4$. The structure was refined to $R = 0\cdot047$. Three new pieces of information are supplied by the determination: the compound is shown to have an *exo* trithiolan ring, the conformation of this ring is *anti* and the bisnorbornyl part of the molecule is (*endo-exo*). The configuration of the whole molecule is *exo-(endo-exo)-endo*.

Introduction

There are 32 possible structural isomers of the sulphurized tricyclopentadiene compound $C_{15}H_{18}S_3$. The tricyclopentadiene part could have one of eight configurations, the pentene ring being either *exo* or *endo* to one of the four configurations of the bisnorbornyl portion. The three S atoms comprising the trithiolan ring could then be attached *exo* or *endo* to the hydrocarbon moiety, and the trithiolan ring itself, being non-planar, could orientate itself *anti* or *syn* with regard to the rest of the molecule.

As this paper will show, the isomer which crystallizes from $CHCl_3$ solution is the *anti* conformation of *exo-(endo-exo)-endo*.†

The structure is written (I) and a perspective view is given in Fig. 1.

(I)

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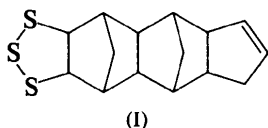
* Note: The atomic numbering used throughout this paper is arbitrary and does not correspond to the systematic chemical numbering given in the title.

† The first prefix refers to the trithiolan ring, the pair in parentheses to the bisnorbornyl system, and the last to the pentene ring.

When tricyclopentadiene was first synthesized and investigated its discoverers assumed it to be a mixture of the isomers (*exo-exo*)-*exo* and (*exo-exo*)-*endo* (Alder & Stein, 1932, 1934). This (*exo-exo*) supposition for the two norbornyl structures persisted in the literature (Littlehailes, 1969) despite well reasoned arguments for the (*exo-endo*) form being the more likely, with the pentene ring *endo* in the major fraction of tricyclopentadiene (Solloway, 1952; Stille & Frey, 1959). Strong support for the (*endo-exo*)-*endo* arrangement came from the ^1H NMR spectrum (Foster & McIvor, 1969). Although it is a solid, m.p. 341 K, tricyclopentadiene was not analysed by diffraction methods and its structure remained unconfirmed.

Trithiolans were first reported in a patent (US Pat. 3 586 700, 1971), but since their discovery only a few have been made, namely the trithiolans of norbornene (Kurtz & Shields, 1969; Inone, Tezuk & Oae, 1978), and *endo*-dicyclopentadiene, *exo*-dicyclopentadiene and tricyclopentadiene (Emsley, Griffiths & Jayne, 1979). They are made by heating together the olefin and elemental sulphur in the presence of an amine. The structure was deduced as an *exo* addition of the three S atoms across the norbornene double bond on the basis of ^1H NMR spectral analysis. The conformation of the trithiolan ring itself remained unresolved although one would naturally assume it to be *anti*.

Some of the trithiolans are solids but only that from tricyclopentadiene, $C_{15}H_{18}S_3$, gave crystals suitable for a full X-ray crystallographic structure determination. A preliminary report of this has been published (Emsley,
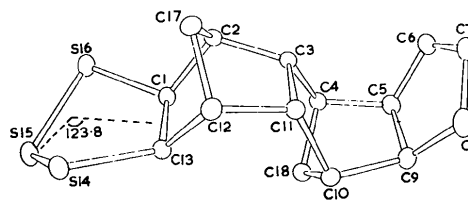

Fig. 1. Structure of the title compound, *exo-(endo-exo)-endo-* $C_{15}H_{18}S_3$.

Griffiths & Osborn, 1978); here we give the complete data.

Experimental

Crystals of the title compound are yellow prisms, elongated along a. A crystal was cut to $0.3 \times 0.5 \times 0.2$ mm and mounted about a.

Lattice parameters were calculated by least squares from θ values of 21 high-angle reflections (measured on a Siemens off-line four-circle diffractometer).

Crystal data

Monoclinic, $P2_1/n$, uniquely determined from systematic absences; $a = 12.025$ (12), $b = 14.349$ (15), $c = 8.460$ (4) Å, $\beta = 112.06$ (6)°; $U = 1353$ Å^3; $Z = 4$, $D_c = 1.443$ Mg m^{-3}; $F(000) = 624$; $\mu = 4.6$ mm^{-1} (for Cu $K\alpha$, $\lambda = 1.5418$ Å).

Intensities of 2008 reflections ($\theta_{max} = 65°$), of which 105 were classed as unobserved [$I < 2.58\sigma(I)$] (Allen, Rogers & Troughton, 1971), were measured with the five-value method (Stewart, 1972). These were corrected for Lorentz–polarization factors (but not for absorption) and then used with MULTAN (Germain, Main & Woolfson, 1971) to obtain a preliminary view of the structure. From this, approximate positions for the S and 12 of the C atoms were obtained which, after isotropic least-squares refinement, gave a $\Delta\rho$ map from which the other three C atoms were located. Anisotropic refinement of all non-hydrogen atoms led to $R = 0.076$.

The H atoms were included in subsequent refinement with fixed coordinates (obtained with a program by Dr D. J. Williams) and fixed isotropic temperature factors. Nine low-angle reflections, which seemed to be affected by extinction, were excluded from the last cycles which gave a final $R = 0.047$.* Scattering factors for S and C were taken from Doyle & Turner (1968), those for H from Stewart, Davidson & Simpson (1965).

Results and discussion

Table 1 lists the coordinates for the non-hydrogen atoms, Table 2 those for the H atoms,* and Table 3 bond lengths. Fig. 2 shows the valence angles and Fig. 3 the peripheral torsion angles of the molecule.

Fig. 1 shows a perspective view of the molecule, and displays the exo-(endo-exo)-endo configuration. Fig. 4

* Lists of structure factors, anisotropic thermal parameters and H atom positions (Table 2) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34474 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

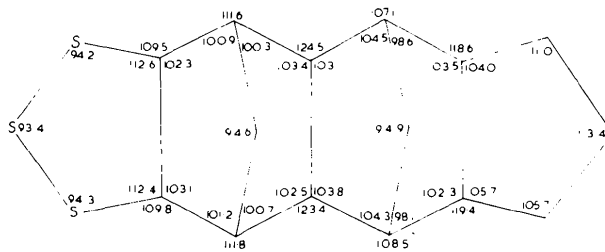|			
C(1)–C(2)	1.554 (5)	C(8)–C(9)	1.532 (6)
C(1)–C(13)	1.572 (4)	C(9)–C(10)	1.558 (5)
C(2)–C(3)	1.545 (5)	C(10)–C(18)	1.542 (6)
C(2)–C(17)	1.535 (6)	C(10)–C(11)	1.530 (6)
C(3)–C(4)	1.528 (6)	C(11)–C(12)	1.550 (5)
C(3)–C(11)	1.557 (4)	C(12)–C(17)	1.527 (5)
C(4)–C(18)	1.538 (5)	C(12)–C(13)	1.541 (5)
C(4)–C(5)	1.560 (5)	C(13)–S(14)	1.839 (4)
C(5)–C(6)	1.510 (6)	S(14)–S(15)	2.047 (2)
C(5)–C(9)	1.571 (5)	S(15)–S(16)	2.046 (1)
C(6)–C(7)	1.350 (7)	S(16)–C(1)	1.833 (3)
C(7)–C(8)	1.465 (6)		

Fig. 2. Valence angles (°) of the title compound, C$_{15}$H$_{18}$S$_3$. E.s.d.'s are $\pm0.3°$ for all valence angles except those involving S atoms, for which $\sigma = \pm0.1°$.

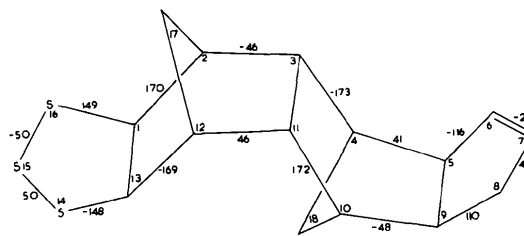Fig. 3. Peripheral torsion angles (°) of C$_{15}$H$_{18}$S$_3$. The e.s.d. for all angles is 1°.

Table 1. *Fractional coordinates* ($\times 10^4$) *for the non-hydrogen atoms, with e.s.d.'s in parentheses*

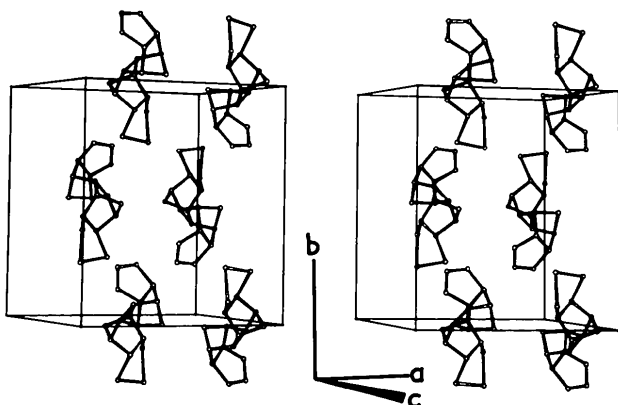|	x	y	z
S(14)	2523 (1)	2716 (1)	3370 (1)
S(15)	712 (1)	2532 (1)	2150 (1)
S(16)	438 (1)	3868 (1)	1242 (1)
C(1)	1264 (3)	4395 (2)	3329 (4)
C(2)	1868 (3)	5313 (2)	3089 (4)
C(3)	2395 (3)	5870 (2)	4771 (4)
C(4)	1735 (3)	6054 (2)	5972 (5)
C(5)	2523 (4)	6744 (3)	7370 (5)
C(6)	3126 (4)	7542 (3)	6841 (5)
C(7)	4332 (4)	7463 (3)	7555 (5)
C(8)	4737 (4)	6650 (3)	8672 (6)
C(9)	3596 (4)	6121 (3)	8522 (5)
C(10)	3318 (3)	5167 (2)	7576 (4)
C(11)	3490 (3)	5272 (2)	5882 (4)
C(12)	3446 (3)	4441 (2)	4688 (4)
C(13)	2372 (3)	3794 (2)	4450 (4)
C(17)	3026 (3)	4934 (3)	2963 (4)
C(18)	1946 (3)	5169 (3)	7070 (5)

Fig. 4. Packing arrangement of $C_{15}H_{18}S_3$.

shows the packing arrangement: there are no unusually close intermolecular contacts.

The trithiolan ring is *exo* with respect to the norbornyl ring to which it is attached, as expected from the likely free-radical mechanism of its formation (Davies, 1970) and the ^{1}H NMR spectral data (Kurtz & Shields, 1969). The expected *anti* conformation is confirmed. The dihedral angle of the trithiolan ring is 123·8° (Fig. 1) which compares well with that calculated by Jørgensen (1978) for the trithiolan formed by norbornene which was 127·7°. This value came from molecular-mechanics calculations, using the Allinger force field, which also indicated that the *anti* conformer was favoured over the *syn* conformer by 10·0 kJ mol^{-1}.

Allinger and co-workers have applied the method to thiols, thioethers including S-bridged molecules (Allinger & Hickey, 1975), and disulphides (Allinger, Hickey & Kao, 1976). S—S lengths (2·02 Å) and the S—S—S angle (90·8°) calculated by Jørgensen (1978) for the trithiolan ring agree reasonably well with those found in this analysis: 2·046 Å and 93·4° respectively. In linear trisulphides larger values (*ca* 105°) are encountered for the S—S—S angle (Foss, 1960; Rahman, Safe & Taylor, 1970).

But for the double bond, the molecule could have a central plane of symmetry. The double bond is, however, unambiguously assigned, for the bond lengths C(6)—C(7), 1·350 Å, and C(7)—C(8), 1·465 Å, differ significantly (16σ), clearly indicating its location.

The S—S lengths in the trithiolan ring, 2·046 Å, are the same as those found in other cyclic and linear poly-sulphide systems, and there is nothing unusual in the

bonding parameters to suggest that the stability of the trithiolans stems from structural uniqueness.

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