exo-9,10,11-Trithiatetracyclo[5.5.1.0²,⁶.0⁸,¹²]tridec-3-ene

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Abstract. $C_{10}H_{12}S_3$, $M_r = 228·40$, monoclinic, $P2_1/n$ $(2/m)$, $a = 12·461$ (3), $b = 9·023$ (2), $c = 9·346$ (3) Å, $\beta = 101·34$ (2)°, $V = 1030·3$ (5) Å³, $Z = 4$, $D_x = 1·472$, $D_m = 1·469$ g cm⁻³, $\lambda(Cu\,K\alpha) = 1·54178$ Å, $\mu = 60·7$ cm⁻¹, $F(000) = 480$, $T = 295$ K, $R = 0·032$ for 1219 independent observed reflections. The molecule has an *exo* trithiolane ring with an *anti* conformation with respect to the methylene bridge of 8,9,10-trinorbornane. The S—S and S—C distances average 2·045 (4) and 1·830 (3) Å respectively. The cyclopentene ring is almost planar with the maximum deviation from its least-squares plane being 0·008 (3) Å.

Introduction. At elevated temperatures (413–453 K) elemental sulfur in the presence of amines reacts with olefins to give complex mixtures of polysulfides (Naylor, 1947; Moore & Seville, 1954). The mechanism of this reaction has not been established and conflicting theories have been proposed (Pryor, 1962); however, free-radical mechanisms are favored (Davies, 1970). The trithiolanes of 8,9,10-trinorbornene (Shields & Kurtz, 1969) and of *endo*-dicyclopentadiene, *exo*-dicyclopentadiene and tricyclopentadiene (Emsley, Griffiths & Jayne, 1979) were prepared in high yields by heating the olefins and elemental sulfur in DMF. A similar result was obtained upon the irradiation of a solution of 8,9,10-trinorbornene and sulfur (Inoue, Tezuka & Oae, 1978). Recently, an extensive study of the thermal reactions of sulfur with olefins has been undertaken, and a variety of previously unreported two and three S-atom addition products has been found (Bartlett & Ghosh, 1985).

9,10,11-Trithiatetracyclo[5.5.1.0²,⁶.0⁸,¹²]tridec-3-ene (1) was obtained as the only product of the reaction between *exo*-dicyclopentadiene and sulfur. Although some cyclic 1,2,3-trithiolanes are solids, only the structures of 13,14,15-trithiahexacyclo[9.5.1.1³,⁹.0²,¹⁰.0⁴,⁸.-0¹²,¹⁶]octadec-5-ene (2) (Emsley, Griffiths & Osborn, 1979) and 1,2,3-trithian-5-yl *N*-methylcarbamate (Kato, Hashimoto, Otsuka & Nakatsu, 1978) have been reported. An interest in the conformation of the trithiolane ring, the stereochemistry of the addition, and

a comparison with the literature structures, led to an X-ray investigation of the title compound.

(1)

(2)
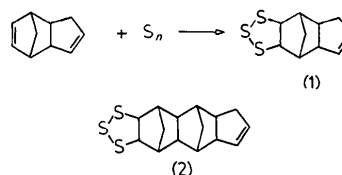
Experimental. 3·0 mmol of anhydrous NH_3 was bubbled into a suspension of 2·0 g (62·5 mmol) of amorphous sulfur in 50 ml of DMF. 2·00 g (15·1 mmol) of *exo*-dicyclopentadiene was added and the mixture stirred vigorously overnight at 383 K. The cooled dark-yellow reaction mixture was poured into 150 ml of ice-cold water and extracted twice with 30 ml of ether. The ether layer was washed with brine and dried over $MgSO_4$. Upon evaporation of the solvent 3·2 g (93%) of crude (1) was obtained. Sublimation followed by recrystallization from absolute ethanol gave a pale-yellow solid, m.p. 364–366 K. Analysis: calcd for $C_{10}H_{12}S_3$: C 52·6, H 5·3, S 42·1%; found: C 52·1, H 5·2, S 42·2%. IR (KBr): 3050, 2900, 1440, 1300 cm⁻¹. ¹H NMR (300 MHz): 5·74 (*m*, 1H), 5·46 (*m*, 1H), 3·70 (*m*, 2H), 2·50–2·80 (*m*, 2H), 2·28 (*m*, 2H), 2·16 (*s*, 1H), 1·98 (*d*, 2H), 1·78 (*d, J* = 12·0Hz, 1H), 1·26 (*d, J* = 12·0Hz, 1H). ¹³C NMR: 133·2 (*d*), 130·5 (*d*), 69·9 (*d*), 69·4 (*d*), 54·8 (*d*), 47·1 (*d*), 44·9 (*d*), 42·9 (*d*), 38·7 (*t*), 26·2 (*t*).

A pale-yellow crystal was ground to an approximate sphere of size 0·30 × 0·28 × 0·28 mm, Syntex $P2_1$ diffractometer system, $\theta:2\theta$ scan, $2\theta_{max} = 114·2°$, variable scan rate, graphite-monochromated Cu $K\alpha$ radiation; lattice parameters from least-squares refinement of 15 reflections (19·7 ≤ 2θ ≤ 74·5°) with angles measured by a centering routine associated with the diffractometer system; density of 1·469 g cm⁻³ (flotation using aqueous CsCl); systematic absences $(h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0)$ consistent with space group $P2_1/n$, monitored reflection (032) showed no intensity variation greater than 1%; 1403 independent reflections measured (0 ≤ h ≤ 13, 0 ≤ k ≤ 9, −9 ≤ l ≤ 9); 1219 had intensities greater than $3\sigma(I)$; Lorentz and polarization corrections; 48

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sets of equivalent reflections $(10 \leq 2\theta \leq 100°)$ measured accurately yielding $R_{int} = 0.018$; no absorption correction made; direct methods (*MULTAN*78: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); after several cycles of refinement H atoms located in difference density map, full-matrix refinement with anisotropic thermal parameters (H atoms isotropic) was followed by two cycles of refinement with H atoms fixed, $R = 0.032$, $wR = 0.037$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$ (derived from counting statistics), 136 parameters refined, $(\Delta/\sigma)_{max} = 0.016$ (coordinate), $S = 1.40$, $10.27| e Å^{-3}$ largest peak in final difference Fourier map.

Locally written programs used for data reduction, *MULTAN*78 for direct-methods calculations, and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all others; atomic scattering factors for C, O and S from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), real and imaginary contributions to the anomalous dispersion applied (*International Tables for X-ray Crystallography*, 1974). Table 1 gives atomic positional parameters and U_{eq} values while Table 2 gives interatomic distances, valence angles, and selected torsion angles.*

Discussion. Fig. 1 is an *ORTEP*II drawing (Johnson, 1971) of the title compound. The three S atoms have added to the *exo* face of the 8,9,10-trinorbornene unit forming a nonplanar five-membered ring exhibiting an envelope conformation. S(3) forms the flap of the envelope and is bent away (*anti*) from the methylene bridge with a 126·4 (3)° folding angle. This is the configuration and conformation found in the trithiolane derivative of tricyclopentadiene (2) (Emsley, Griffiths & Osborn, 1979) which has a folding angle of 123·4°. The average S—S and S—C distances of 2·045 (4) and 1·830 (3) Å are equivalent to the 2·047 (2) and 1·836 (4) Å average values for (2). The S—S distance is equivalent to the 2·039 (4) Å average value reported for a six-membered trithiolane ring (Kato *et al.,* 1978) but the S—C distance differs significantly from the average value of 1·921 (5) Å. In compound (1) the two chemically equivalent S—C distances are statistically equal while the two S—S distances deviate by more than 3σ; however, this may reflect an underestimate of the standard deviation. The structurally equivalent bonds of the 8,9,10-trinorbornene unit are statistically equivalent.

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42573 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* $(\times 10^4)$ *for non-*H *atoms and their equivalent isotropic thermal parameters* $(Å^2 \times 10^3)$

	x	y	z	U_{eq}*
C(1)	6426 (2)	−308 (3)	−406 (3)	39 (2)
S(2)	5739 (1)	−1909 (1)	−1394 (1)	49 (1)
S(3)	5400 (1)	−875 (1)	−3373 (1)	54 (1)
S(4)	6960 (1)	−77 (1)	−3198 (1)	58 (1)
C(5)	7063 (2)	649 (3)	−1351 (3)	38 (2)
C(6)	8242 (2)	577 (3)	−475 (3)	38 (2)
C(7)	8280 (2)	1508 (3)	912 (3)	36 (1)
C(8)	9408 (2)	1696 (3)	1836 (3)	47 (2)
C(9)	9512 (2)	954 (3)	3121 (3)	45 (2)
C(10)	8487 (2)	193 (3)	3259 (3)	51 (2)
C(11)	7662 (2)	539 (3)	1854 (3)	41 (2)
C(12)	7319 (2)	−816 (3)	862 (3)	41 (2)
C(13)	8295 (2)	−997 (3)	125 (3)	40 (2)

* $U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$.

Table 2. *Interatomic distances* (Å)*, valence angles* (°) *and selected torsion angles* (°)

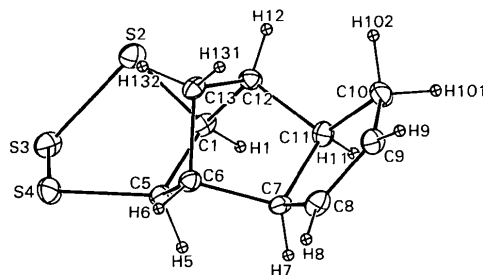|			
S(2)—S(3)	2·041 (1)	C(6)—C(13)	1·524 (4)
S(2)—C(1)	1·833 (3)	C(7)—C(8)	1·508 (3)
S(3)—S(4)	2·049 (1)	C(7)—C(11)	1·549 (4)
S(4)—C(5)	1·827 (3)	C(8)—C(9)	1·359 (4)
C(1)—C(5)	1·559 (4)	C(9)—C(10)	1·477 (4)
C(1)—C(12)	1·528 (3)	C(10)—C(11)	1·532 (4)
C(5)—C(6)	1·537 (3)	C(11)—C(12)	1·543 (4)
C(6)—C(7)	1·538 (4)	C(12)—C(13)	1·520 (4)
S(3)S(2)C(1)	95·1 (1)	C(6)C(7)C(11)	103·6 (2)
S(2)S(3)S(4)	93·7 (1)	C(8)C(7)C(11)	104·5 (2)
S(3)S(4)C(5)	95·2 (1)	C(7)C(8)C(9)	111·5 (2)
S(2)C(1)C(5)	113·0 (2)	C(8)C(9)C(10)	111·9 (2)
S(2)C(1)C(12)	110·6 (2)	C(9)C(10)C(11)	106·1 (2)
C(5)C(1)C(12)	103·4 (2)	C(7)C(11)C(10)	106·1 (2)
S(4)C(5)C(1)	112·8 (2)	C(7)C(11)C(12)	102·5 (2)
S(4)C(5)C(6)	111·8 (2)	C(10)C(11)C(12)	114·4 (2)
C(1)C(5)C(6)	102·4 (2)	C(1)C(12)C(11)	107·6 (2)
C(5)C(6)C(7)	107·1 (2)	C(1)C(12)C(13)	101·9 (2)
C(5)C(6)C(13)	101·7 (2)	C(11)C(12)C(13)	101·9 (2)
C(7)C(6)C(13)	101·9 (2)	C(6)C(13)C(12)	95·0 (2)
C(6)C(7)C(8)	114·5 (2)		
C(1)S(2)S(3)S(4)	48·0 (1)	C(7)C(11)C(12)C(1)	−70·6 (2)
S(2)S(3)S(4)C(5)	−48·2 (1)	C(11)C(12)C(1)C(5)	72·4 (3)
S(3)S(4)C(5)C(1)	33·6 (2)	C(12)C(1)C(5)C(6)	−0·8 (2)
S(4)C(5)C(1)S(2)	−0·1 (2)	C(7)C(8)C(9)C(10)	−0·9 (3)
C(5)C(1)S(2)S(3)	−33·6 (2)	C(8)C(9)C(10)C(11)	0·0 (4)
C(1)C(5)C(6)C(7)	−71·0 (2)	C(9)C(10)C(11)C(7)	0·9 (3)
C(5)C(6)C(7)C(11)	73·0 (2)	C(10)C(11)C(7)C(8)	−1·3 (3)
C(6)C(7)C(11)C(12)	−1·5 (2)	C(11)C(7)C(8)C(9)	1·4 (3)

Fig. 1. *ORTEP* drawing of compound (1). Thermal ellipsoids are drawn at the 35% probability level. H atoms are drawn as spheres of arbitrary radius.

The cyclopentene ring is almost planar with the largest internal torsion angle being 1·4 (3)° and the maximum deviation from the least-squares plane being 0·008 (3) Å. The interplanar angle between the cyclopentene ring and C(6)C(7)C(11)C(12) is 120·2 (2)°. C(6)C(13)C(12) symmetrically bridges the six-membered ring forming interplanar angles of 124·4 (2) and 124·0 (2)° with C(6)C(7)C(11)C(12) and C(6)-C(5)C(1)C(12), respectively. This bridge is significantly asymmetric in 8,9,10-trinorbornene molecules exhibiting pyramidalization of the sp^2 C atoms. The 119·9 (2)° interplanar angle between the 8,9,10-trinorbornane unit C(6)C(5)C(1)C(12) and C(1)S(2)-S(4)C(5) is the same as that between the cyclopentene ring and the 8,9,10-trinorbornane moiety.

The intramolecular distances between *endo* H atoms, H(1)···H(11) and H(5)···H(7), are 2·38 (3) and 2·37 (3) Å respectively. H(132) lies 3·00 (3) and 2·95 (2) Å from S(2) and S(4) and 3·95 (2) Å from S(3). The only significant intermolecular contact is 2·27 (4) Å between H(1) atoms of adjacent molecules. The X-ray structural data are consistent with the addition of the S$_3$ unit to the *exo* face of the 8,9,10-trinorbornene molecule forming a nonplanar five-membered trithiolane ring with the central sulfur *anti* with respect to the methylene bridge. The *exo* addition is consistent with the pyramidalization of the sp^2 C atoms of 8,9,10-trinorbornene (Watson, 1983).

References

BARTLETT, P. D. & GHOSH, T. (1985). In preparation.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

DAVIES, D. I. (1970). *Essays on Free-Radical Chemistry*, Spec. Publ. No. 24, edited by W. A. WATERS & D. H. HEY, pp. 201–237. London: The Chemical Society.

EMSLEY, J., GRIFFITHS, D. W. & JAYNE, G. J. J. (1979). *J. Chem. Soc. Perkin Trans.* 1, pp. 228–232.

EMSLEY, J., GRIFFITHS, D. W. & OSBORN, R. (1979). *Acta Cryst.* B35, 2119–2121.

INOUE, S., TEZUKA, T. & OAE, S. (1978). *Phosphorus Sulfur*, 4, 219–221.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

KATO, A., HASHIMOTO, Y., OTSUKA, I. & NAKATSU, K. (1978). *Chem. Lett.* pp. 1219–1222.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOORE, C. G. & SEVILLE, R. W. (1954). *J. Chem. Soc.* pp. 2082–2089.

NAYLOR, R. F. (1947). *J. Chem. Soc.* pp. 1532–1539.

PRYOR, W. A. (1962). *Mechanisms of Sulfur Reaction*, pp. 97–116. New York: McGraw-Hill.

SHIELDS, T. C. & KURTZ, A. N. (1969). *J. Am. Chem. Soc.* 91, 5415–5416.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

WATSON, W. H. (1983). In *Stereochemistry and Reactivity of Systems Containing π Electrons.* Deerfield Beach, Florida: Verlag Chemie International.

Structure of 1,2'-Spirobiindan-1',3'-dione, a Key Intermediate in the Total Synthesis of Fredericamycin A*

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Abstract. $C_{17}H_{12}O_2$, $M_r = 248·3$, monoclinic, $P2_1/n$, $a = 12·544$ (2), $b = 7·507$ (1), $c = 13·480$ (2) Å, $\beta = 97·09$ (1)°, $V = 1259·7$ Å^3, $Z = 4$, D_m(flotation in aq. KI) $= 1·312$, $D_x = 1·309$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·94$ mm^{-1}, $F(000) = 520·0$, $T = 293$ K, $R = 0·050$ for 651 observed reflections. The [4.4]nonane system is characteristic of fredericamycin A. The angle between the two aromatic portions at the spiro C [89·9 (6)°] imposes the necessary spatial requirements and the C=O bond lengths [1·216 (9) and 1·202 (9) Å] indicate that they are properly positioned for synthesis of fredericamycin A. The internal angles at the spiro C atom average 102·4 (6)°.