

C12b	0.3670 (5)	0.8013 (2)	0.7979 (2)	0.0458 (8)
C13b	0.2527 (6)	0.8191 (2)	0.8777 (3)	0.0656 (11)
C14b	0.3402 (6)	0.8541 (2)	0.7260 (3)	0.0554 (10)
C15b	0.4870 (5)	0.8482 (2)	0.6558 (3)	0.0512 (9)
C16b	0.7008 (6)	0.8737 (2)	0.6771 (3)	0.0732 (12)
C17b	0.4357 (5)	0.8206 (2)	0.5791 (2)	0.0495 (9)
C18b	-0.0888 (5)	0.7296 (2)	0.4781 (3)	0.0633 (10)
C19b	0.3273 (6)	0.7321 (2)	0.3951 (2)	0.0647 (10)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55244 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1008]

Table 2. Selected bond lengths (Å) and angles (°)

Sia—O1a	1.630 (4)	Sib—O1b	1.633 (2)
Sia—O2a	1.644 (4)	Sib—O2b	1.641 (3)
Sia—C18a	1.846 (4)	Sib—C18b	1.853 (4)
Sia—C19a	1.845 (4)	Sib—C19b	1.835 (4)
O1a—C1a	1.435 (4)	O1b—C1b	1.439 (4)
O2a—C17a	1.372 (4)	O2b—C17b	1.384 (4)
C1a—C2a	1.512 (5)	C1b—C2b	1.508 (4)
C1a—C8a	1.536 (5)	C1b—C8b	1.531 (4)
C2a—C3a	1.378 (6)	C2b—C3b	1.378 (5)
C2a—C7a	1.390 (6)	C2b—C7b	1.374 (5)
C3a—C4a	1.379 (7)	C3b—C4b	1.391 (6)
C4a—C5a	1.383 (8)	C4b—C5b	1.375 (7)
C5a—C6a	1.350 (8)	C5b—C6b	1.352 (7)
C6a—C7a	1.378 (7)	C6b—C7b	1.384 (6)
C8a—C9a	1.518 (5)	C8b—C9b	1.520 (5)
C8a—Na	1.472 (4)	C8b—Nb	1.474 (4)
Na—C10a	1.463 (4)	Nb—C10b	1.462 (4)
Na—C11a	1.351 (4)	Nb—C11b	1.348 (4)
C11a—O3a	1.240 (4)	C11b—O3b	1.235 (4)
C11a—C12a	1.517 (5)	C11b—C12b	1.532 (5)
C12a—C13a	1.518 (5)	C12b—C13b	1.523 (5)
C12a—C14a	1.548 (5)	C12b—C14b	1.536 (5)
C14a—C15a	1.489 (5)	C14b—C15b	1.501 (5)
C15a—C16a	1.515 (6)	C15b—C16b	1.507 (6)
C15a—C17a	1.319 (5)	C15b—C17b	1.314 (5)
O2a—Sia—O1a	110.8 (2)	O2b—Sib—O1b	111.1 (1)
C18a—Sia—O1a	111.8 (2)	C18b—Sib—O1b	112.4 (1)
C19a—Sia—O1a	106.1 (2)	C19b—Sib—O1b	105.3 (2)
C18a—Sia—O2a	104.4 (2)	C18b—Sib—O2b	103.3 (2)
C19a—Sia—O2a	109.8 (2)	C19b—Sib—O2b	110.4 (2)
C19a—Sia—C18a	114.1 (2)	C19b—Sib—C18b	114.5 (2)
C1a—O1a—Sia	126.1 (2)	C1b—O1b—Sib	125.7 (2)
C17a—O2a—Sia	124.0 (2)	C17b—O2b—Sib	125.0 (2)
C2a—C1a—O1a	108.9 (3)	C2b—C1b—O1b	109.0 (2)
C8a—C1a—O1a	108.6 (2)	C8b—C1b—O1b	108.5 (2)
C8a—C1a—C2a	111.3 (3)	C8b—C1b—C2b	110.9 (2)
C9a—C8a—C1a	112.6 (3)	C9b—C8b—C1b	113.0 (3)
Na—C8a—C1a	112.8 (3)	Nb—C8b—C1b	113.2 (2)
Na—C8a—C9a	112.1 (3)	Nb—C8b—C9b	111.7 (3)
C10a—Na—C8a	114.5 (2)	C10b—Nb—C8b	114.6 (2)
C11a—Na—C8a	120.2 (3)	C11b—Nb—C8b	119.4 (2)
C11a—Na—C10a	125.3 (3)	C11b—Nb—C10b	125.9 (3)
O3a—C11a—Na	120.9 (3)	O3b—C11b—Nb	121.3 (3)
C12a—C11a—Na	120.6 (3)	C12b—C11b—Nb	120.4 (3)
C12a—C11a—O3a	118.5 (3)	C12b—C11b—O3b	118.4 (3)
C13a—C12a—C11a	109.7 (3)	C13b—C12b—C11b	109.3 (3)
C14a—C12a—C11a	109.7 (3)	C14b—C12b—C11b	108.6 (3)
C14a—C12a—C13a	110.6 (3)	C14b—C12b—C13b	111.4 (3)
C15a—C14a—C12a	114.5 (3)	C16b—C15b—C14b	117.4 (3)
C16a—C15a—C14a	117.8 (3)	C17b—C15b—C14b	122.2 (3)
C17a—C15a—C14a	122.2 (3)	C17b—C15b—C16b	120.4 (3)
C17a—C15a—C16a	120.0 (4)	C15b—C17b—O2b	123.6 (3)
C15a—C17a—O2a	123.4 (3)		

The y coordinate of Sia was fixed to define the origin. The absolute configuration of the molecule about the C1—C2 bond was known so only the relative configurations at other chiral sites had to be determined. f'' was ignored for all atoms, but f' was used for Si.

Computer programs of the CRYM Crystallographic Computing System (Duchamp, 1964) were used, together with MULTAN (Main *et al.*, 1980) and ORTEP (Johnson, 1976).

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endo-2-Phenyl-exo-3,4,5-trithiatricyclo-[5.2.1.0^{2,6}]decane exo-4-Oxide

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Abstract

The three S atoms add to the *exo* face of norbornene forming a slightly distorted envelope conformation for the trithiolane ring. The sulfoxide is *exo* with respect to the ring, and the O atom is 2.41(2) Å from an H on the bridging C atom. The two C—S bonds differ by 0.047(2) Å while AM1 calculations predict a difference of 0.029 Å.

Comment

Sulfur reacts with norbornene in *N,N*-dimethylformamide at 373 K to produce the *exo*-trithianorbornane and the *exo*-pentathiene (Ghosh, 1986). Oxidation of the trithiane

with *m*-chloroperbenzoic acid produces the 1'-sulfoxide and exclusively the *endo*-2'-sulfoxide (1) whose structure was confirmed by X-ray diffraction (Ghosh, 1986). When 2-phenylnorbornene reacts with sulfur the *exo*-trithiane is also produced but subsequent oxidation produces only the 1'-sulfoxide. The 2'-sulfoxide could be prepared by the reaction of SOCl_2 with 2-phenyl-2,3-dithianorbornane in the presence of pyridine (Ghosh & Bartlett, 1988). The 2'-*exo/endo*-trithiane sulfoxides are produced in a 3:1 ratio. The assignment of the *exo*-2'-sulfoxide (2) was confirmed by a single-crystal X-ray diffraction study.

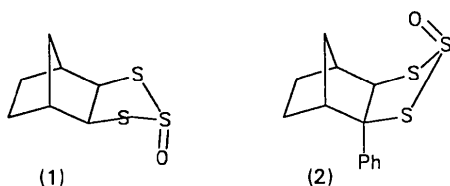


Table 1 lists coordinates for the non-H atoms while Table 2 lists non-H-atom bond lengths and angles. Fig. 1 is a thermal ellipsoid drawing of the molecule. The trithiolane ring is *exo* with respect to the norbornyl ring to which it is attached. The central sulfur, S2, is bent in the *exo* direction with the oxygen of the sulfoxide occupying an *exo* site. The trithiolane ring is twisted away from the envelope conformation due to the differences in bond angles and bond lengths associated with the addition of the phenyl ring at C6. The S1—C5—C6—S3 and C1—C6—C5—C4 torsion angles are 15.9(1) and 5.7(2)°. The bonds C5—S1 = 1.810(2) and C6—S3 = 1.857(2) Å are statistically inequivalent which may be related to the phenyl substitution at C6.

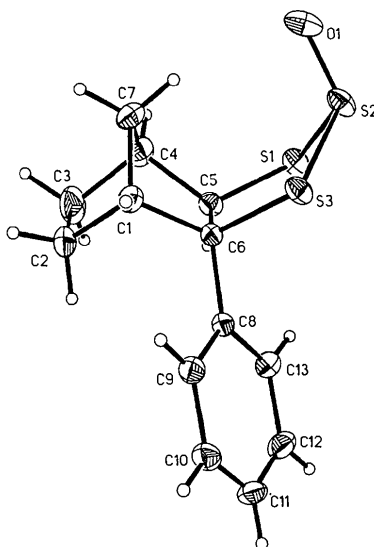


Fig. 1. View of a molecule of $\text{C}_{13}\text{H}_{14}\text{OS}_3$ showing the labeling of the non-H atoms. Thermal ellipsoids are shown at 30% probability levels; H atoms are drawn as spheres of arbitrary radius.

These distances may be compared with the average C—S distance of 1.833(5) Å in the unoxidized trithiolane rings of *exo*- (Watson, Jain, Bartlett & Ghosh, 1986) and *endo*-9,10,11-trithiatetracyclo[5.5.1.0^{2,6}.0^{8,12}]tridec-3-ene (Emsley, Griffiths & Osborn, 1979). The S1—S2 and S2—S3 distances of 2.088(1) and 2.090(1) Å are equivalent and may be compared with the average distance of 2.046(3) Å for the unoxidized trithiolane rings. Oxidation leads to rehybridization of the central S atom [S=O = 1.470(2) Å] and S—S bond elongation. The remainder of the bonds are normal for norbornyl systems. AM1 geometry optimization (Dewar, Zoebisch, Healy & Stewart, 1985) leads to a 0.029 Å difference in the C5—S1 and C6—S3 bonds and a 0.010 Å difference between the two S—S bonds. The O1···H7a intramolecular separation is 2.41(2) Å.

Experimental

Crystal data

$\text{C}_{13}\text{H}_{14}\text{OS}_3$
 $M_r = 282.42$
 Monoclinic
 $P2_1/n$
 $a = 14.232(3)$ Å
 $b = 5.973(1)$ Å
 $c = 14.980(2)$ Å
 $\beta = 93.52(1)^\circ$
 $V = 1270.8(3)$ Å³
 $Z = 4$
 $D_x = 1.48$ Mg m⁻³

Mo $K\alpha$ radiation, graphite
 monochromator
 $\lambda = 0.71073$ Å
 Cell parameters from 25
 reflections
 $\theta = 11.57$ – 14.46°
 $\mu = 5.40$ cm⁻¹
 $T = 295$ K
 Prism
 $0.38 \times 0.29 \times 0.09$ mm
 Colorless

Data collection

R3M/ μ update of Syntex P2₁
 diffractometer
 ω scans, scan rate
 4 – 29.3° min⁻¹
 Absorption correction:
 ψ scan
 $T_{\min} = 0.761$, $T_{\max} =$
 0.930
 4103 measured reflections
 2922 independent reflections

2551 observed reflections
 $[I \geq 3\sigma(I)]$
 $R_{\text{int}} = 0.008$
 $\theta_{\max} = 27.5^\circ$
 $h = -18 \rightarrow 18$
 $k = 0 \rightarrow 7$
 $l = -3 \rightarrow 19$
 2 standard reflections
 monitored every 100
 reflections
 intensity variation: $< \pm 2\%$

Refinement

Refinement on F
 Final $R = 0.0346$
 $wR = 0.0388$
 $S = 1.737$
 2551 reflections
 211 parameters
 All H-atom parameters re-
 fined
 $w = [\sigma^2(F_o) + 0.00014F_o^2]^{-1}$
 $(\Delta/\sigma)_{\max} = 0.008$

$\Delta\rho_{\max} = 0.39$ e Å⁻³
 $\Delta\rho_{\min} = -0.35$ e Å⁻³
 Extinction correction:
 $F_{\text{corr}} = F_o/[1 + 2.6(2) \times$
 $10^{-7} F_o^2/\sin^2\theta]^{1/4} \times$
 Atomic scattering factors
 from *International Tables*
 for X-ray Crystallography
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
S1	-0.2537 (1)	0.1774 (1)	0.3850 (1)	0.036 (1)
S2	-0.2058 (1)	0.4876 (1)	0.3423 (1)	0.038 (1)
S3	-0.1372 (1)	0.5569 (1)	0.4666 (1)	0.033 (1)
O1	-0.2844 (1)	0.6423 (2)	0.3214 (1)	0.052 (1)
C1	-0.2695 (1)	0.5517 (3)	0.5981 (1)	0.036 (1)
C2	-0.3154 (2)	0.4154 (4)	0.6712 (1)	0.048 (1)
C3	-0.3874 (2)	0.2665 (5)	0.6180 (2)	0.060 (1)
C4	-0.3705 (1)	0.3267 (4)	0.5207 (1)	0.046 (1)
C5	-0.2729 (1)	0.2297 (3)	0.5015 (1)	0.031 (1)
C6	-0.2017 (1)	0.3966 (3)	0.5497 (1)	0.027 (1)
C7	-0.3514 (1)	0.5769 (4)	0.5279 (1)	0.047 (1)
C8	-0.1231 (1)	0.2923 (3)	0.6084 (1)	0.027 (1)
C9	-0.0822 (1)	0.4078 (3)	0.6814 (1)	0.035 (1)
C10	-0.0069 (1)	0.3165 (4)	0.7321 (1)	0.044 (1)
C11	0.0287 (1)	0.1117 (4)	0.7108 (1)	0.047 (1)
C12	-0.0099 (1)	-0.0028 (4)	0.6382 (2)	0.044 (1)
C13	-0.0852 (1)	0.0862 (3)	0.5870 (1)	0.035 (1)

Table 2. Geometric parameters (\AA , $^\circ$)

S1—S2	2.088 (1)	C4—C5	1.549 (3)
S1—C5	1.810 (2)	C4—C7	1.522 (3)
S2—S3	2.090 (1)	C5—C6	1.566 (2)
S2—O1	1.470 (2)	C6—C8	1.513 (2)
S3—C6	1.857 (2)	C8—C9	1.390 (2)
C1—C2	1.542 (3)	C8—C13	1.389 (2)
C1—C6	1.550 (2)	C9—C10	1.388 (3)
C1—C7	1.528 (3)	C10—C11	1.369 (3)
C2—C3	1.542 (3)	C11—C12	1.372 (3)
C3—C4	1.534 (3)	C12—C13	1.385 (3)
S2—S1—C5	102.3 (1)	S3—C6—C1	110.7 (1)
S1—S2—S3	92.7 (1)	S3—C6—C5	110.6 (1)
S1—S2—O1	111.4 (1)	C1—C6—C5	101.1 (1)
S3—S2—O1	111.9 (1)	S3—C6—C8	102.9 (1)
S2—S3—C6	105.8 (1)	C1—C6—C8	115.7 (1)
C2—C1—C6	108.6 (2)	C5—C6—C8	116.1 (1)
C2—C1—C7	101.7 (2)	C1—C7—C4	94.5 (2)
C6—C1—C7	102.0 (1)	C6—C8—C9	120.7 (1)
C1—C2—C3	103.6 (2)	C6—C8—C13	121.0 (1)
C2—C3—C4	102.6 (2)	C9—C8—C13	118.1 (2)
C3—C4—C5	106.5 (2)	C8—C9—C10	120.5 (2)
C3—C4—C7	101.6 (2)	C9—C10—C11	120.5 (2)
C5—C4—C7	102.8 (2)	C10—C11—C12	119.6 (2)
S1—C5—C4	115.7 (1)	C11—C12—C13	120.5 (2)
S1—C5—C6	115.0 (1)	C8—C13—C12	120.7 (2)
C4—C5—C6	103.8 (1)		

Data collection and cell refinement: Syntex $P2_1$ diffractometer control program. Programs used for data reduction, to solve and refine structure: *SHELXTL* (Nicolet Instrument Corporation, 1986). Refinement was by block-cascade least-squares methods. All computer programs were supplied by Nicolet for Desktop 30 Microclipse and NOVA 4/C configurations.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55335 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1012]

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Diammonium Cyclopropane-1,1-dicarboxylate

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Abstract

Diammonium cyclopropane-1,1-dicarboxylate was prepared by neutralizing an aqueous solution of cyclopropane-1,1-dicarboxylic acid (Fluka) with 2 equivalents ammonium hydroxide. Each ammonium cation bridges two pairs of cyclopropane-1,1-dicarboxylate anions *via* hydrogen bonds; each anion is bridged to eight other anions in this way. The planes of the two carboxyl groups subtend an angle of 44.6° and the minimum $\text{COO}\cdots\text{OOC}$ distance is $2.839(3) \text{\AA}$. The OOC—C—COO bond angle is $120.4(2)^\circ$ which may be accounted for by the sp^2 hybridization of the cyclopropyl C atoms.

Comment

We have recently reported that the kinetic labilities of platinum complexes of 1,1-cycloalkyldicarboxylato and dialkylmalonato ligands may be related to their molecular structure (Bréhin, Kozelka, Bois &