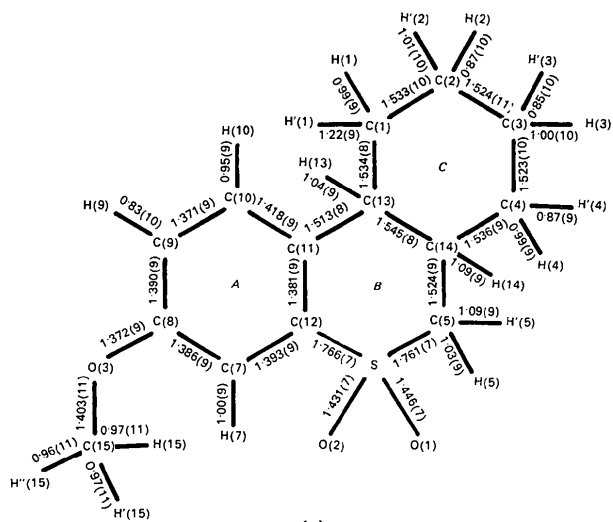*Acta Cryst.* (1975). B31, 2743

The crystal structure of 8-methoxy-1,2,3,4,5,6-*cis*-4a,10b-octahydro-6-thiaphenanthrene-6,6-dioxide.* By

N. N. DHANESHWAR, S. S. TAVALE and L. M. PANT, *National Chemical Laboratory, Poona, India*

The crystals are orthorhombic, space group *Pbnb*, with $a = 30 \cdot 60$ (2), $b = 10 \cdot 56$ (1), $c = 8 \cdot 03$ (1) Å; $D_m = 1 \cdot 355$ g cm^{-3}; D_c for $Z = 8$, $1 \cdot 351$ g cm^{-3}. The structure, solved with the help of a sulphur-phased Fourier map, has been refined to an R of $0 \cdot 105$ for 1635 F_o's. The molecular dimensions are all normal. The bonds around the sulphur atom have a slightly distorted tetrahedral configuration suggesting a greater *s* character of the S=O bonds than of the S–C bonds.

The X-ray analysis of 8-methoxy-1,2,3,4,5,6-*cis*-4a,10b-octahydro-6-thiaphenanthrene-6,6-dioxide

---

was undertaken to confirm the structure and, in particular, the *cis* relatiohsnip of the *B/C* ring junction in order to support the conclusions of the chemical work on the mechanism of the stereo-selective hydride transfer in the thia series of compounds (Tilak, Desai, Deshpande, Jain & Vaidya, 1966; Tilak, Mitra & Muljiani, 1969).

The crystals are orthorhombic, space group *Pbnb* (a nonstandard version of *Pccn*, No. 56) with $a = 30 \cdot 60$ (2), $b =$
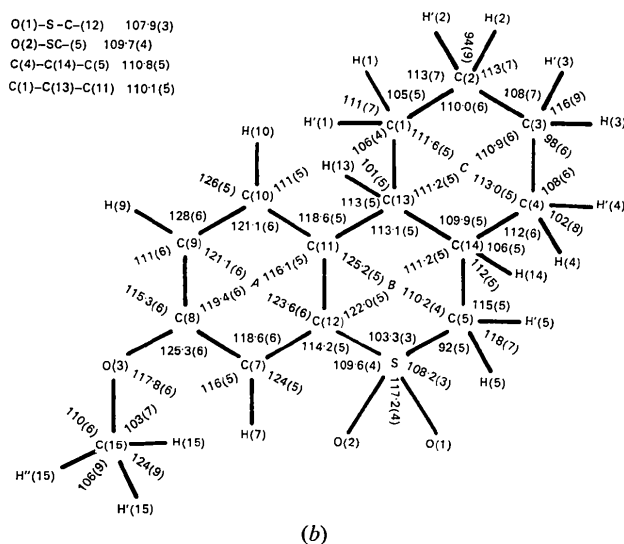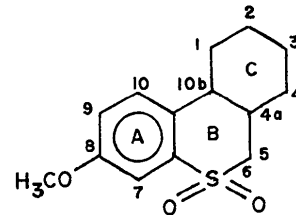

Fig. 1. (*a*) Bond lengths (Å) and (*b*) angles (°) with e.s.d.'s in parentheses. The following angles are not marked in the diagram: O(1)–S–C(12), 107·9 (3); O(2)–S–C(5), 109·7 (4); C(4)–C(14)–C(5), 110·8 (5); C(1)–C(13)–C(11), 110·1 (5).
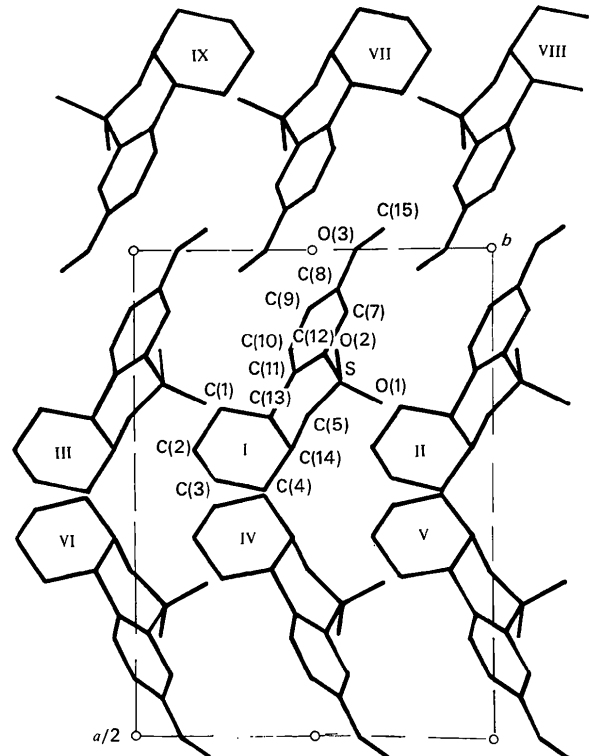
Fig. 2. Structure projected on (001). Symmetry code: (I) x,y,z; (II) $x,\frac{1}{2}+y,\frac{1}{2}-z$; (III) $x,y-\frac{1}{2},\frac{1}{2}-z$; (IV) $\frac{1}{2}-x,y,\frac{1}{2}-z$; (V) $\frac{1}{2}-x,\frac{1}{2}+y,z$; (VI) $\frac{1}{2}-x,y-\frac{1}{2},z$; (VII) $\bar{x}, 1-y,\bar{z}$; (VIII) $\bar{x},\frac{3}{2}-y,\frac{1}{2}+z$; (IX) $\bar{x},\frac{1}{2}-y,\frac{1}{2}+z$.

Table 1. *Final atomic and thermal parameters and their estimated standard deviations (in parentheses)*

Anisotropic thermal parameters are of the form $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{23}kl + 2b_{13}hl)]$.

(a) Non-hydrogen atoms ($\times 10^4$)

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	1500 (2)	2414 (6)	6023 (7)	6 (1)	41 (6)	50 (8)	3 (1)	10 (5)	5 (2)
C(2)	1918 (3)	1629 (8)	5823 (9)	10 (1)	65 (7)	83 (11)	8 (2)	25 (7)	9 (3)
C(3)	2212 (2)	2226 (7)	4508 (8)	7 (1)	69 (8)	73 (9)	10 (2)	13 (7)	5 (2)
C(4)	2317 (2)	3595 (8)	4948 (7)	2 (1)	112 (9)	41 (8)	-2 (2)	-2 (6)	3 (2)
C(5)	1672 (2)	4621 (6)	3543 (7)	6 (1)	40 (5)	21 (7)	2 (1)	13 (5)	4 (2)
C(7)	598 (2)	5953 (7)	5888 (8)	7 (1)	60 (7)	54 (8)	2 (2)	-2 (6)	4 (2)
C(8)	378 (2)	5741 (7)	7371 (8)	5 (1)	67 (8)	54 (8)	1 (2)	0 (6)	3 (2)
C(9)	561 (2)	4942 (7)	8557 (8)	7 (1)	81 (8)	36 (8)	-3 (2)	-2 (6)	16 (2)
C(10)	954 (2)	4356 (6)	8280 (7)	7 (1)	50 (6)	32 (8)	1 (2)	12 (5)	10 (2)
C(11)	1182 (2)	4519 (6)	6758 (7)	5 (1)	38 (6)	31 (7)	-4 (1)	-9 (5)	4 (2)
C(12)	994 (2)	5335 (6)	5621 (7)	6 (1)	45 (6)	20 (7)	2 (1)	5 (5)	7 (2)
C(13)	1602 (2)	3791 (5)	6490 (7)	4 (1)	37 (5)	27 (7)	-1 (1)	8 (5)	-1 (2)
C(14)	1907 (2)	4413 (6)	5194 (7)	5 (1)	49 (6)	27 (7)	-2 (1)	-10 (5)	2 (2)
C(15)	-230 (2)	7014 (9)	6607 (13)	6 (1)	113 (11)	198 (16)	9 (2)	-21 (12)	3 (3)
O(1)	1476 (2)	6988 (5)	4066 (9)	21 (1)	34 (5)	245 (15)	-1 (2)	27 (7)	55 (3)
O(2)	966 (2)	5716 (8)	2398 (7)	16 (1)	185 (10)	53 (7)	31 (3)	41 (7)	-2 (2)
O(3)	-17 (2)	6263 (6)	7797 (7)	6 (1)	130 (7)	130 (9)	9 (2)	7 (7)	15 (2)
S	1264 (1)	5785 (2)	3769 (2)	9 (0)	56 (2)	51 (2)	11 (0)	29 (2)	15 (0)

Table 1 (*cont.*)

(b) Hydrogen atoms ($\times 10^3$)

	x	y	z
H(1)	134 (3)	201 (9)	694 (11)
H'(1)	128 (3)	247 (8)	476 (11)
H(2)	205 (3)	156 (10)	679 (12)
H'(2)	186 (3)	69 (10)	573 (13)
H(3)	252 (3)	192 (9)	439 (12)
H'(3)	207 (3)	227 (9)	360 (12)
H(4)	250 (3)	371 (10)	596 (10)
H'(4)	249 (3)	390 (10)	418 (10)
H(5)	144 (3)	395 (9)	319 (11)
H'(5)	187 (3)	506 (9)	257 (12)
H(7)	44 (3)	643 (9)	502 (11)
H(9)	41 (3)	493 (9)	942 (11)
H(10)	107 (3)	367 (9)	890 (10)
H(13)	178 (3)	367 (9)	759 (11)
H(14)	202 (3)	530 (9)	574 (11)
H(15)	-22 (3)	651 (11)	560 (14)
H'(15)	-50 (3)	716 (11)	724 (13)
H''(15)	-9 (3)	782 (11)	652 (14)

10·56 (1), $c = 8·03$ (1) Å; $D_m = 1·355$ g cm^{-3}; D_c for $Z = 8$, 1·351 g cm^{-3}. Data were collected and processed in the usual way from the zero to ninth-layer Weissenberg photographs about the b axis and from zero to third-layer photographs about the c axis; the crystals used for the two sets of photographs had the cross-sections $1·0 \times 0·9$ and $0·5 \times 1·5$ mm^2 respectively. The structure was obtained from a sulphur-phased three-dimensional Fourier map and refined by the block-diagonal least-squares method to an $R = 0·105$ for 1635 F_o's. Final atomic and thermal parameters together with their e.s.d.'s are given in Table 1 and the molecular dimensions in Fig. 1. The packing of the molecules is shown in Fig. 2.

The observed molecular dimensions are all normal. As expected, H(13) and H(14) at the B/C ring junction are *cis* to each other. The aromatic ring A is planar within 0·02 Å. The bond lengths and angles around the sulphur atom agree well with those in other similar structures (Chu & Chung; 1973, 1974; Dhaneshwar, Kulkarni, Tavale & Pant, 1975); the contraction of the C–S–C angle and the expansion of the O–S–O angle from the tetrahedral value is observed in all these compounds and probably implies more s character in the two S=O bonds than in the two S–C bonds.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31193 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

References

CHU, S. S. C. & CHUNG, B. (1973). *Acta Cryst.* B29, 2253–2259.

CHU, S. S. C. & CHUNG, B. (1974). *Acta Cryst.* B30, 1616–1618.

DHANESHWAR, N. N., KULKARNI, A. G., TAVALE, S. S. & PANT, L. M. (1975). *Acta Cryst.* B31, 750–754.

TILAK, B. D., DESAI, H. S., DESHPANDE, C. V., JAIN, S. K. & VAIDYA, V. M. (1966). *Tetrahedron*, 22. 7–23.

TILAK, B. D., MITRA, R. B. & MULJIANI, Z. (1969). *Tetrahedron*, 25, 1939–1946.