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Structure of a Functionalized Tetrahydrobenzothiophene

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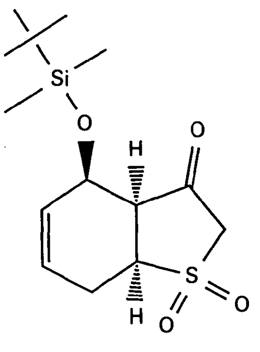
Abstract. (±)-4-(*tert*-Butyldimethylsiloxy)-3a,4,7,7a-tetrahydrobenzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide, $C_{14}H_{24}O_4SSi$, $M_r = 316{\cdot}49$, monoclinic, $P2_1/n$, $a = 7{\cdot}1431\ (7)$, $b = 19{\cdot}643\ (2)$, $c = 12{\cdot}528\ (1)$ Å, $\beta = 104{\cdot}810\ (8)°$, $V = 1699{\cdot}4\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}24$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 2{\cdot}597$ cm^{-1}, $F(000) = 680$, $T = 298$ K, $R = 0{\cdot}0566$ for 2733 reflections [$F_o \geq 4\sigma(F_o)$]. The two rings are *cis*-fused with the cyclohexene ring in the half-chair conformation while the thiophene moiety has the envelope conformation. The endocyclic bond angles of the cyclohexene ring are enlarged, especially at the bridgehead C atoms, C3a and C7a, which have angles 116·0 (2) and 116·8 (2)°, respectively. There are several close intramolecular contacts: C3···O11 2·614 (3), O10···O11 3·137 (3), O10···C7 3·073 (4) Å. Adjacent molecules related by $1-x$, $1-y$, $2-z$ stack so that the carbonyl O and C atoms of one molecule lie directly over the carbonyl C and O atoms of the second molecule. The C···O distance is 3·023 (3) Å in this intermolecular interaction.

Experimental. (1) was synthesized *via* an intermolecular Diels–Alder reaction of the *tert*-butyldimethylsiloxydiene of crotonaldehyde and the appropriate enone obtained from 3-sulfolene. The structure was obtained to confirm the regiochemistry and the stereochemistry of this process. Full details will be described elsewhere (Martin & Daniel, 1989). Crystals of (1) were obtained by slow evaporation from ethyl acetate. The data crystal was a colorless needle of approximate dimensions 0·18 × 0·23 × 0·76 mm. The data were collected on a Nicolet *P*3 diffractometer using a graphite monochromator. Lattice parameters were obtained from the least-squares refinement of 50 reflections with $21{\cdot}3 < 2\theta < 29{\cdot}2°$. The data were collected using the ω-scan technique (8446 reflections, of which 3913 were unique, $R_{\text{int}} = 0{\cdot}0185$), with a 2θ range from 4·0–55·0° and a 1·2° ω scan at 5–10° min^{-1} ($h = 0\to10$, $k = -26\to26$, $l = -17\to17$). Four reflections ($\bar{2}0\bar{2}$, 080, 112, $\bar{2}\bar{3}1$) were remeasured every 196 reflections to monitor instrument and crystal stability (maximum correction on I was <2%). The data were also corrected for Lp effects and absorption (based on crystal shape; transmission-factor range 0·9315–0·9615). Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (1180 reflections). Data reduction, absorption and decay correction were performed using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick, 1987). The structure was solved by direct methods (Sheldrick, 1987) and refined by full-matrix least squares (Sheldrick, 1976). In all, 277 parameters were refined. The non-H atoms were refined with anisotropic thermal parameters. All H-atom positions were obtained from a ΔF map and refined with isotropic thermal parameters. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0{\cdot}5kI^{-1/2}\{[\sigma(I)]^2 + (0{\cdot}02I)^2\}^{1/2}$. The intensity,



(1)

0108-2701/89/122018-03$03.00

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* ($Å^2$) *for non*-H *atoms of* (1)

$U_{eq} = 1/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{A}_{ij}$ where $\mathbf{A}_{ij}$ is the dot product of the *i*th and *j*th direct-space unit-cell vectors.

	x	y	z	U_{eq}
S1	0·78665 (10)	0·49019 (4)	0·80233 (6)	0·0436 (2)
C2	0·7219 (5)	0·4378 (2)	0·9026 (3)	0·0490 (12)
C3	0·5094 (4)	0·45076 (14)	0·8951 (2)	0·0404 (10)
C3a	0·4158 (4)	0·49965 (13)	0·8039 (2)	0·0375 (9)
C4	0·2931 (4)	0·45920 (14)	0·7047 (2)	0·0401 (10)
C5	0·2790 (5)	0·4942 (2)	0·5975 (3)	0·0557 (12)
C6	0·3826 (5)	0·5459 (2)	0·5821 (3)	0·0569 (13)
C7	0·5325 (5)	0·5803 (2)	0·6693 (3)	0·0567 (13)
C7a	0·5769 (4)	0·54413 (14)	0·7804 (2)	0·0402 (10)
O8	0·4268 (3)	0·42509 (11)	0·9575 (2)	0·0578 (9)
O9	0·9593 (3)	0·52826 (12)	0·8514 (2)	0·0664 (9)
O10	0·7850 (3)	0·45156 (12)	0·7051 (2)	0·0585 (8)
O11	0·3760 (3)	0·39260 (9)	0·70299 (14)	0·0387 (6)
Si12	0·24400 (11)	0·32211 (4)	0·68307 (7)	0·0443 (3)
C13	0·1559 (9)	0·3042 (3)	0·8082 (5)	0·087 (2)
C14	0·0325 (7)	0·3315 (3)	0·5625 (5)	0·082 (2)
C15	0·4120 (4)	0·2541 (2)	0·6600 (3)	0·0514 (11)
C16	0·4746 (10)	0·2686 (4)	0·5548 (5)	0·104 (3)
C17	0·5935 (8)	0·2518 (3)	0·7552 (5)	0·094 (2)
C18	0·3103 (11)	0·1856 (3)	0·6506 (11)	0·131 (4)

I, is given by ($I_{peak} - I_{background}$) × (scan rate); 0·02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects, absorption and decay. $\sigma(I)$ was estimated from counting statistics: $\sigma(I) = [(I_{peak} + I_{background})^{1/2} \times \text{(scan rate)}]$. Final $R = 0·0566$ for 2733 reflections, with $wR = 0·0540$ ($R_{all} = 0·0902$, $wR_{all} = 0·0608$) and a goodness-of-fit = 1·497. The maximum $|\Delta/\sigma|$ was $<0·1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were $-0·27$ and 0·39 e $Å^{-3}$, respectively. The scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with the anomalous-dispersion corrections taken from the work of Cromer & Liberman (1970). The scattering factors for the H atoms were obtained from Stewart, Davidson & Simpson (1965). Values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974).* Figures were generated using *SHELXTL-Plus* (Sheldrick, 1987). The positional and equivalent isotropic thermal parameters for non-H atoms are listed in Table 1, while the bond lengths and angles for the non-H atoms are listed in Table 2. The atom-labeling scheme is shown in Fig. 1. Other computer programs used in this work are listed in reference 11 of Gadol & Davis (1982).

Table 2. *Bond lengths* (Å) *and angles* (°) *for non*-H *atoms of* (1)

1	2	3	1—2	1—2—3
C2	S1	C7a	1·773 (4)	95·3 (2)
C2	S1	O9		110·40 (14)
C7a	S1	O9	1·798 (3)	110·40 (14)
C7a	S1	O10		110·93 (12)
O9	S1	O10	1·439 (2)	117·29 (14)
O10	S1	C2	1·433 (2)	110·4 (2)
C3	C2	S1	1·518 (5)	107·3 (2)
C3a	C3	O8	1·511 (4)	124·1 (3)
C3a	C3	C2		113·3 (3)
O8	C3	C2	1·204 (4)	122·5 (3)
C4	C3a	C7a	1·545 (4)	116·0 (2)
C4	C3a	C3		109·4 (2)
C7a	C3a	C3	1·532 (4)	107·3 (2)
C5	C4	O11	1·489 (4)	109·9 (3)
C5	C4	C3a		112·4 (2)
O11	C4	C3a	1·438 (3)	109·2 (2)
C6	C5	C4	1·299 (5)	125·9 (3)
C7	C6	C5	1·483 (5)	125·3 (3)
C7a	C7	C6	1·523 (4)	113·8 (3)
S1	C7a	C3a		105·8 (2)
S1	C7a	C7		112·7 (2)
C3a	C7a	C7		116·8 (2)
Si12	O11	C4	1·658 (2)	122·8 (2)
C13	Si12	C14	1·866 (7)	108·9 (3)
C13	Si12	C15		111·3 (2)
C13	Si12	O11		109·4 (2)
C14	Si12	C15	1·852 (5)	111·6 (2)
C14	Si12	O11		110·7 (2)
C15	Si12	O11	1·867 (3)	104·91 (12)
C16	C15	C17	1·522 (8)	107·7 (4)
C16	C15	C18		109·8 (6)
C16	C15	Si12		110·1 (3)
C17	C15	C18	1·522 (6)	109·2 (5)
C17	C15	Si12		110·6 (3)
C18	C15	Si12	1·520 (7)	109·4 (4)

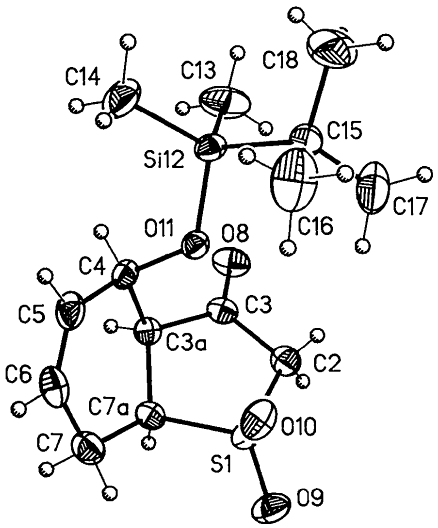


Fig. 1. View of (1) showing the atom-labeling scheme. Ellipsoids are scaled to the 30% probability level. H atoms are drawn to an arbitrary size. One H atom on C17 and one on C18 are obscured from view.

Related literature. The benzothiophene structure is a component of many known biologically active compounds. It is a component of breynins A and B

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* Tables of anisotropic thermal parameters, H-atom positional parameters, bond distances and angles involving the H atoms, structure-factor amplitudes, a view of the close C···O contacts between adjacent molecules and a unit-cell-packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52123 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Sakai, Ohkuma, Koshiyama, Naito & Kawaguchi, 1976; Nishiyama, Ikeda, Yoshida & Yamamura, 1989). Breynins A and B exhibit significant hypocholesterolemic activity in mammals (Koshiyama, Hatori, Ohkuma, Sakai, Imanishi, Ohbayashi & Kawaguchi, 1976).

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Structure of Eugenine, an Alkaloid from *Narcissus eugeniae*

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Abstract. (5*R**,6a*S**,11a*R**,11b*R**)-5-Ethoxy-6a,7,11a,11b-tetrahydro-2-methoxy-*N*-methyl-5*H*-[2]benzopyran[3,4-g]indolin-3-ol, $C_{19}H_{25}NO_4$, $M_r = 331{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}585\ (5)$, $b = 13{\cdot}527\ (2)$, $c = 15{\cdot}429\ (8)$ Å, $V = 1791\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}229$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}90$ cm^{-1}, $F(000) = 712$, room temperature. The structure was solved by direct methods and refined to a final R value of 0·045 ($wR = 0{\cdot}042$) for 950 observed reflections. In the structure there is one weak intermolecular hydrogen bond C(10)—H(10*a*)···O(*m*) = 2·34 (8) Å forming an infinite chain along the twofold axis. The molecule is far from planar and the assignment of an ethyl radical in position C(5) has been confirmed in the X-ray analysis. Only the benzene ring is planar and the C—C bond distances and C—C—C bond angles have average values of 1·383 (19) Å and 119·9 (1)° respectively. Distances and angles elsewhere in the molecule are not unusual.

Experimental. Platy white crystals of eugenine, crystallized from acetone, 0·11 × 0·07 × 0·06 mm. Enraf–Nonius CAD-4 computer-controlled single-crystal diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan. Cell parameters from setting angles of 25 reflections having $1 \le \theta \le 25°$. Data collection at 293 K: index range $-10 \le h \le 10$, $0 \le k \le 16$, $0 \le l \le 18$ with $2\theta \le 50°$, three standard reflections (444, $\bar{4}44$, $4\bar{4}4$) measured every 60 min showed only random deviations from mean intensity, 1810 unique measured reflections of which 950 observed with $I(hkl) \ge 2\sigma(I)$.

Structure solved by *MULTAN*80 (Main *et al.*, 1980). The least-squares refinement used *SHELX*76 (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1{\cdot}355/|\sigma^2(F) + 0{\cdot}001125\,(F)^2|$. 317 parameters refined: atom coordinates, anisotropic temperature factors for all non-H atoms, positions of H atoms calculated; $R = 0{\cdot}045$, $wR = 0{\cdot}042$, $(\Delta/\sigma)_{\max} = 0{\cdot}86$, max and min. in final $\Delta\rho$ map 0·20 and $-0{\cdot}21$ e Å^{-3}.