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# Structures of Sulfur Analogues of Precocenes. II. 6,7-Dimethoxy-2,2-dimethyl-3,4-epoxy-3,4-dihydro-2*H*-1-benzothiopyran 1,1-Dioxide

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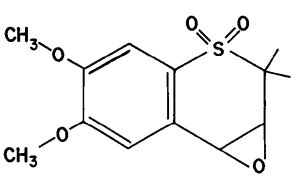
**Abstract.** $C_{13}H_{16}O_5S$, $M_r = 284{\cdot}33$, monoclinic, $P2_1/n$, $a = 12{\cdot}180\ (5)$, $b = 6{\cdot}535\ (2)$, $c = 16{\cdot}893\ (7)$ Å, $\beta = 91{\cdot}27\ (4)°$, $V = 1344{\cdot}3\ (9)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}405$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 2{\cdot}42$ cm$^{-1}$, $F(000) = 600$, $T = 298$ K, $R = 0{\cdot}053$ for 1242 observed reflections. The S atom is tetrahedral with a dihedral angle between planes C—S—C and O—S—O of 90·3 (2)°. The S—C($sp^2$) and S—C($sp^3$) bond distances are 1·756 (4) and 1·827 (5) Å respectively.

**Experimental.** The synthesis of compound (1) has been reported previously (Ferreira & Catani, 1987). The data-collection and refinement parameters are summarized in Table 1. The structure was solved using standard direct methods and difference Fourier techniques. In final cycles of full-matrix least-squares refinement all non-H atoms anisotropic. H atoms included, as fixed contributors, at positions found in difference synthesis, all with a common isotropic temperature factor that refined to $U = 0{\cdot}083$ Å$^2$. Scattering factors for non-H atoms from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970), for H from Stewart, Davidson & Simpson (1965); programs used: *SHELX*76 (Sheldrick, 1976), *ORTEP* (Johnson, 1965). Most of the calculations were performed on a VAX 11/780 computer of the Instituto de Física e Química de São Carlos.



(1)

Atomic coordinates are listed in Table 2,* bond lengths and angles in Table 3. Shortest intermolecular distances: O(1)···C(3)($x,y-1,z$) = 3·315 (6), and O(2)···C(13)($1-x,-y,-z$) = 3·294 (6) Å. Fig. 1 is a perspective drawing of the molecule illustrating atom labeling.

**Related literature.** Structural data of several cyclic sulfones have been published by Yasuoka, Kasai,

* Lists of H-atom positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51656 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/89/060961-02$03.00

Table 1. *Crystallographic summary for* (1)

| | |
|---|---|
| (*a*) Data collection[i,ii] | |
| Mode | $\omega$–$2\theta$ |
| Scan rate (°min$^{-1}$) | 2·6–6·7 |
| $\theta$ range (°) | 0–25 |
| Range of *hkl* | $-12 < h < 12$ |
| | $-1 < k < 6$ |
| | $l < 17$ |
| Total reflections measured | 2653 |
| Unique reflections | 2165 |
| $R_{int}$ | 0·02 |
| Approximate crystal dimensions (mm) | 0·15 × 0·20 × 0·25 |
| (*b*) Structure refinement[iii] | |
| Reflections used $\|I > 3\sigma(I)\|$ | 1242 |
| No. of variables | 173 |
| *R*, *wR* | 0·053,0·060 |
| Max. shift/e.s.d. | 0·003 |
| Max., min. density in final difference map (e Å$^{-3}$) | 0·25, −0·27 |
| *S* | 21·9 |

Notes: (i) Unit-cell parameters by least-squares refinement of the setting angles of 25 reflections with $10·2 < \theta < 21·5°$. (ii) Enraf–Nonius CAD-4 diffractometer with graphite monochromator was used. Two standard reflections (0,$\bar{1}$,12, 7$\bar{1}$9) measured every hour showed no significant variation. No correction for absorption. (iii) Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = [\sigma^2(F_o) + 0·002F_o^2]$.

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

| | *x* | *y* | *z* | $B_{iso}$* |
|---|---|---|---|---|
| S | 0·6883 (1) | 0·2280 (2) | 0·0498 (1) | 2·74 (4) |
| O(1) | 0·7745 (2) | 0·0845 (5) | 0·0683 (2) | 3·9 (1) |
| O(2) | 0·6101 (3) | 0·1681 (5) | −0·0105 (2) | 3·9 (1) |
| O(3) | 0·4320 (3) | 0·3945 (6) | 0·3325 (2) | 4·5 (1) |
| O(4) | 0·3795 (3) | 0·0905 (5) | 0·2451 (2) | 4·3 (1) |
| O(5) | 0·8475 (2) | 0·4661 (5) | 0·1545 (2) | 4·1 (1) |
| C(2) | 0·7484 (4) | 0·4728 (7) | 0·0215 (3) | 3·2 (2) |
| C(3) | 0·7957 (4) | 0·5826 (7) | 0·0927 (3) | 3·5 (2) |
| C(4) | 0·7447 (4) | 0·5733 (7) | 0·1699 (3) | 3·5 (2) |
| C(5) | 0·5855 (4) | 0·4866 (7) | 0·2520 (3) | 3·2 (2) |
| C(6) | 0·4966 (4) | 0·3674 (8) | 0·2691 (3) | 3·1 (2) |
| C(7) | 0·4666 (4) | 0·2010 (8) | 0·2209 (3) | 3·1 (2) |
| C(8) | 0·5254 (3) | 0·1631 (7) | 0·1536 (2) | 2·7 (2) |
| C(9) | 0·6158 (3) | 0·2848 (7) | 0·1358 (2) | 2·5 (2) |
| C(10) | 0·6482 (3) | 0·4456 (7) | 0·1853 (2) | 2·5 (2) |
| C(11) | 0·6562 (4) | 0·6037 (7) | −0·0162 (3) | 4·9 (2) |
| C(12) | 0·8391 (4) | 0·4184 (7) | −0·0376 (3) | 4·6 (2) |
| C(13) | 0·3490 (4) | −0·0837 (8) | 0·1998 (3) | 4·8 (2) |
| C(14) | 0·4527 (4) | 0·5697 (8) | 0·3817 (3) | 5·2 (2) |

* $B_{iso} = \frac{4}{3}\sum_i\sum_j B_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

Table 3. *Interatomic bond distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| S–O(1) | 1·437 (3) | C(2)–C(11) | 1·538 (7) |
| S–O(2) | 1·434 (3) | C(2)–C(12) | 1·547 (7) |
| S–C(2) | 1·827 (5) | C(3)–C(4) | 1·458 (7) |
| S–C(9) | 1·756 (4) | C(4)–C(10) | 1·469 (6) |
| O(3)–C(6) | 1·355 (6) | C(5)–C(6) | 1·370 (6) |
| O(3)–C(14) | 1·434 (6) | C(5)–C(10) | 1·401 (6) |
| O(4)–C(7) | 1·354 (6) | C(6)–C(7) | 1·402 (7) |
| O(4)–C(13) | 1·417 (6) | C(7)–C(8) | 1·379 (6) |
| O(5)–C(3) | 1·428 (6) | C(8)–C(9) | 1·396 (6) |
| O(5)–C(4) | 1·463 (6) | C(9)–C(10) | 1·394 (6) |
| C(2)–C(3) | 1·504 (7) | | |

| | | | |
|---|---|---|---|
| O(1)–S–O(2) | 116·6 (2) | O(5)–C(4)–C(3) | 58·5 (3) |
| O(1)–S–C(2) | 109·5 (2) | O(5)–C(4)–C(10) | 116·8 (4) |
| O(1)–S–C(9) | 109·7 (2) | C(3)–C(4)–C(10) | 122·7 (4) |
| O(2)–S–C(2) | 108·5 (2) | C(6)–C(5)–C(10) | 120·6 (4) |
| O(2)–S–C(9) | 107·9 (2) | O(3)–C(6)–C(5) | 124·6 (4) |
| C(2)–S–C(9) | 104·1 (2) | O(3)–C(6)–C(7) | 114·3 (4) |
| C(6)–O(3)–C(14) | 117·7 (4) | C(5)–C(6)–C(7) | 121·0 (4) |
| C(7)–O(4)–C(13) | 117·6 (4) | O(4)–C(7)–C(6) | 115·7 (4) |
| C(3)–O(5)–C(4) | 60·6 (3) | O(4)–C(7)–C(8) | 125·3 (4) |
| S–C(2)–C(3) | 110·9 (3) | C(6)–C(7)–C(8) | 119·0 (4) |
| S–C(2)–C(11) | 107·6 (3) | C(7)–C(8)–C(9) | 120·1 (4) |
| S–C(2)–C(12) | 105·3 (3) | S–C(9)–C(8) | 118·1 (3) |
| C(3)–C(2)–C(11) | 109·2 (4) | S–C(9)–C(10) | 121·0 (3) |
| C(3)–C(2)–C(12) | 111·1 (4) | C(8)–C(9)–C(10) | 120·9 (4) |
| C(11)–C(2)–C(12) | 112·7 (4) | C(4)–C(10)–C(5) | 119·1 (4) |
| O(5)–C(3)–C(2) | 119·0 (4) | C(4)–C(10)–C(9) | 122·6 (4) |
| O(5)–C(3)–C(4) | 60·9 (3) | C(5)–C(10)–C(9) | 118·3 (4) |
| C(2)–C(3)–C(4) | 122·1 (4) | | |

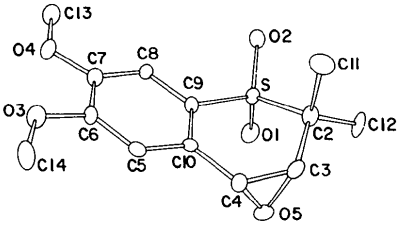



Fig. 1. Perspective view of the molecule showing atom labeling.

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