

Brenner, 1965; Riche & Pascard-Billy, 1976). The six C—C bond lengths in the benzene ring average 1.387 Å.

The bonds about the S atom form a distorted tetrahedron as in other sulphone groups (Giuseppetti, Tadini, Bettinetti & Giordano, 1977; Hamodrakas, Filippakis & Sheldrick, 1977; Hamodrakas & Filippakis, 1977). The S—C distance lies within the range of reported values (Calleri, Chiari, Villa, Manfredotti, Guastini & Viterbo, 1976; Tranqui, Vicat & Fillion, 1976). The O(A)—S(1)—N(2) angle is increased to 120.6°, while the N(2)—S(1)—C(13) angle is decreased to 103.0°; dihedral angles C(12)S(1)C(13)—N(2)S(1)O(A), O(A)S(1)C(13)—N(2)S(1)C(12) and O(A)S(1)C(12)—N(2)S(1)C(13) are 84.4, 84.4 and 90.0° respectively. The S(1)—N(2) bond, 1.565 (1) Å, is slightly longer than double-bond values previously observed for compounds containing this group (Tickle & Prout, 1971; Cameron & Duncanson, 1976; Wieggers & Vos, 1963). Following the conformational criterion of Altona, Geise & Romers (1968) we calculated the pseudo-rotation phase angles: $\Delta = -8.51^\circ$, $\varphi_m = 4.54^\circ$. The conformation of the ring can be considered as a distorted half chair. The shorter intermolecular distances are contained in Table 3.

We gratefully thank Professor M. Lora Tamayo and coworkers for suggesting the problem and supplying the material, and the Centro de Proceso de Datos del Ministerio de Educación y Ciencia (Madrid) for the facilities required in the use of the Univac 1108 computer. Most of the computations were performed with the XRAY system of crystallographic programs (Stewart, Kundell & Baldwin, 1970).

Acta Cryst. (1977), B33, 3913–3915

2-Phenylcyclopropane-1-spiro-4'-(2'-benzylthio-4',5'-dihydro-6'H-1',3'-thiazine)-5'-spiro-2''-oxirane (CTO)

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(Received 30 June 1977; accepted 27 July 1977)

Abstract. C₂₀H₁₉ONS₂, monoclinic, $P2_1/c$, $Z = 4$, $a = 18.193$ (3), $b = 5.584$ (1), $c = 17.563$ (2) Å, $\beta = 101.55$ (2)°, μ (Mo $K\alpha$) 2.92 cm⁻¹, $\rho_c = 1.34$, $\rho_m = 1.31$ g cm⁻³ (floatation). Final R and R_w values for the observed reflections are 0.054 and 0.049. The heterocyclic six membered ring has an 'overall' half-chair conformation.

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Introduction. The title compound is used as the base in the preparation of synthetic cephalopurines. It presented, when examined by IR and NMR spectroscopy, some structural ambiguities, namely the existence of either a six-membered or a five-membered ring.

A crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was used. 3089 independent reflections up

Table 1. Fractional atomic coordinates, with the least-squares e.s.d.'s in parentheses

	x	y	z		x	y	z
C(1)	0.3233 (1)	0.3154 (5)	0.3184 (1)	C(18)	0.1105 (2)	0.6670 (6)	0.1666 (2)
C(2)	0.2482 (1)	0.4039 (5)	0.3343 (1)	C(19)	0.1749 (2)	0.6267 (6)	0.2222 (2)
C(3)	0.2793 (2)	0.1645 (6)	0.3639 (2)	H(2)	0.254 (1)	0.527 (4)	0.375 (1)
S(1')	0.43656 (4)	0.54446 (1)	0.22475 (4)	H(3A)	0.302 (1)	0.151 (5)	0.421 (1)
C(2')	0.3662 (1)	0.3221 (5)	0.2007 (1)	H(3B)	0.256 (1)	0.019 (5)	0.338 (2)
N(3')	0.3221 (1)	0.2369 (4)	0.2404 (1)	H(3''A)	0.500 (2)	0.368 (6)	0.428 (2)
C(5')	0.3927 (1)	0.4412 (5)	0.3590 (1)	H(3''B)	0.441 (2)	0.139 (6)	0.434 (2)
C(6')	0.4143 (1)	0.6480 (6)	0.3147 (2)	H(6'A)	0.463 (1)	0.724 (5)	0.340 (2)
O(1'')	0.3965 (1)	0.4883 (4)	0.4401 (1)	H(6'B)	0.373 (2)	0.772 (5)	0.302 (2)
C(3'')	0.4489 (2)	0.3182 (7)	0.4173 (2)	H(7A)	0.340 (1)	0.167 (5)	0.076 (2)
S(2)	0.36669 (4)	0.22726 (1)	0.10423 (4)	H(7B)	0.307 (1)	0.082 (4)	0.151 (1)
C(7)	0.3116 (2)	-0.0454 (5)	0.0969 (2)	H(9)	0.240 (2)	0.344 (6)	0.009 (2)
C(8)	0.2337 (1)	-0.0273 (5)	0.0484 (1)	H(10)	0.119 (2)	0.324 (6)	0.081 (2)
C(9)	0.2072 (2)	-0.2102 (5)	-0.0029 (2)	H(11)	0.038 (2)	0.006 (6)	0.074 (2)
C(10)	0.1350 (2)	-0.2011 (7)	-0.0471 (2)	H(12)	0.083 (2)	0.295 (5)	0.015 (2)
C(11)	0.0889 (2)	-0.0143 (7)	-0.0408 (2)	H(13)	0.205 (2)	0.287 (5)	0.091 (2)
C(12)	0.1143 (2)	0.1674 (6)	0.0111 (2)	H(15)	0.123 (2)	0.143 (6)	0.299 (2)
C(13)	0.1859 (2)	0.1605 (5)	0.0549 (2)	H(16)	0.011 (2)	0.206 (6)	0.207 (2)
C(14)	0.1807 (1)	0.4330 (5)	0.2723 (2)	H(17)	0.004 (2)	0.534 (5)	0.123 (2)
C(15)	0.1197 (2)	0.2789 (6)	0.2645 (2)	H(18)	0.107 (2)	0.796 (5)	0.130 (2)
C(16)	0.0555 (2)	0.3188 (6)	0.2090 (2)	H(19)	0.217 (2)	0.737 (5)	0.224 (2)
C(17)	0.0514 (2)	0.5132 (6)	0.1601 (2)				

to 25° in θ were collected in the $\omega/2\theta$ mode on a Philips PW 1100 diffractometer with Mo radiation monochromated by graphite. 2540 data had intensities greater than their standard deviations estimated from counting statistics, and were considered as observed. No crystal decay was detected. The cell parameters come from a least-squares fit of the diffractometer angular settings of 30 reflections. The data were corrected for Lorentz and polarization effects but not for absorption.

A phasing model was sought by a Patterson analysis and the model was confirmed and completed by a Fourier synthesis. Least-squares calculations refined the structure to give the H atoms in a difference synthesis. They were included in the final refinement with isotropic thermal factors while the nonhydrogen atoms were treated anisotropically. Owing to the number of variables this refinement had to be carried out using the free blocking option of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970), which was used in most of the calculations, on a Univac 1108 computer. The weighting scheme was chosen to give no trends in $\langle w\Delta^2 \rangle$ (Cano & Martinez-Ripoll, 1975). A final difference synthesis had no significant peaks, the noise range being $\pm 0.28 e \text{ \AA}^{-3}$, with final unweighted and weighted R factors of 0.054 and 0.044 respectively.*

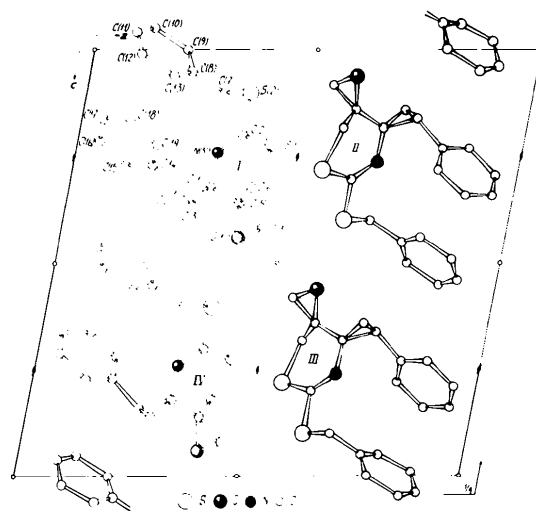


Fig. 1. Molecular packing and atomic numbering.

The atomic scattering factors used for all atoms except H are from *International Tables for X-ray Crystallography* (1962), and from Stewart, Davidson & Simpson (1965) for H.

Discussion. Table 1 shows the atomic fractional coordinates referred to the atomic numbering given in Fig. 1. Table 2 is a list of the main geometrical parameters.

The mean bond distance in the phenyl rings is 1.379 Å, with a maximum atomic deviation from the plane of 0.007 Å. The geometry around the S atoms

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32900 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Geometrical parameters with the least-squares e.s.d.'s in parentheses

(a) Bond distances (Å)

C(8) C(9)	1.383 (4)	C(7) S(2)	1.813 (2)
C(9) C(10)	1.386 (4)	S(2) C(2')	1.776 (3)
C(10) C(11)	1.357 (5)	S(1') C(2')	1.773 (3)
C(11) C(12)	1.380 (5)	S(1') C(6')	1.804 (3)
C(12) C(13)	1.374 (4)	C(6') C(5')	1.488 (4)
C(13) C(8)	1.382 (4)	C(5') C(1)	1.495 (4)
C(14) C(15)	1.390 (4)	C(1) N(3')	1.434 (3)
C(15) C(16)	1.380 (4)	C(1) C(2)	1.531 (4)
C(16) C(17)	1.377 (5)	C(2) C(3)	1.503 (4)
C(17) C(18)	1.363 (5)	C(3) C(1)	1.500 (4)
C(18) C(19)	1.385 (4)	C(5') O(1'')	1.437 (3)
C(19) C(14)	1.385 (4)	O(1'') C(3'')	1.458 (4)
C(2) C(14)	1.477 (3)	C(3'') C(5')	1.465 (4)
C(7) C(8)	1.504 (4)		

(b) Bond angles (°)

C(7) C(8) C(9)	119.1 (3)	C(2')-S(1')-C(6')	98.9 (1)
C(7) C(8) C(13)	122.7 (2)	S(1') C(6') C(5')	109.8 (2)
C(9) C(8) C(13)	118.1 (2)	C(6') C(5') C(1)	113.6 (2)
C(8) C(13) C(12)	121.1 (3)	C(5') C(1) N(3')	116.8 (2)
C(13) C(12) C(11)	120.3 (3)	C(1) N(3') C(2')	121.6 (2)
C(12) C(11) C(10)	119.3 (3)	N(3') C(2') S(1')	130.1 (2)
C(11) C(10) C(9)	120.9 (3)	N(3') C(1) C(2)	115.4 (2)
C(10) C(9) C(8)	120.4 (3)	N(3') C(1) C(3)	115.5 (2)
C(2) C(14) C(19)	120.1 (3)	C(2) C(1) C(5')	117.4 (2)
C(2) C(14) C(15)	122.3 (3)	C(5') C(1) C(3)	120.0 (2)
C(19) C(14) C(15)	117.5 (2)	C(1) C(5') C(3'')	58.9 (2)
C(14) C(15) C(16)	121.1 (3)	C(1) C(5') O(1'')	115.4 (2)
C(15) C(16) C(17)	120.0 (3)	C(6') C(5') C(3'')	120.6 (3)
C(16) C(17) C(18)	120.0 (3)	C(6') C(5') O(1'')	114.3 (2)
C(17) C(18) C(19)	119.9 (3)	C(1) C(2) C(3)	59.3 (2)
C(18) C(19) C(14)	121.4 (3)	C(2) C(3) C(1)	61.3 (2)
C(8) C(7) S(2)	115.4 (2)	C(3) C(1) C(2)	59.4 (2)
C(7) S(2) C(2')	102.1 (1)	C(5') O(1'') C(3'')	60.8 (2)
S(2) C(2') S(1')	107.2 (1)	O(1'') C(3'') C(5')	58.9 (2)
S(2) C(2') N(3')	122.8 (2)	C(3'') C(5') O(1'')	60.3 (2)

(c) Some dihedral and torsional angles (°) (mean e.s.d. = 0.3°)
(The usual Klyne & Prelog criterion has been used.)

(14 to 19) (8 to 13)	62.8
(14 to 19) (1, 2, 3)	51.0
(1, 2, 3) (3, 4, 5, 6)	79.6
(1, 2, 3) (8, 9, 10)	60.1
(8, 9, 10) (3, 4, 5, 6)	82.6
(8, 9, 10) (7, 8, 3)	89.6
C(3) C(1) C(5') O(1'')	-24.0
N(3') C(2') S(2) C(7)	-14.1
C(2') S(2) C(7) C(8)	106.2
S(2) C(7) C(8) C(13)	-46.2
C(1) C(2) C(14) C(15)	107.8
C(1) N(3') C(2') S(1')	-0.4
N(3') C(2') S(1') C(6')	9.9
C(2') S(1') C(6') C(5')	38.8
S(1') C(6') C(5') C(1)	-63.3
C(6') C(5') C(1) N(3')	53.5
C(5') C(1) N(3') C(2')	-18.7

seems to be normal (Lin & Sundaralingam, 1971; Depmeier & Jarchow, 1975). The geometry of the oxirane group agrees with the mean geometry for epoxy groups reported elsewhere (Foces-Foces, Cano & García-Blanco, 1977), its area being 0.914 Å². The

cyclopropane ring has quite a regular geometry with an area of 0.989 Å², a value which is between the theoretical values for cyclopropylidene and cyclopropane (Lathan, Radon, Hariharan, Hehre & Pople, 1973), its bent bonds shortening the C(2)-C(14) distance.

The six-membered ring has an overall half-chair conformation [with distances to the plane through the other ring atoms of 0.43 and 0.32 Å for C(6') and C(5') respectively]. More specifically it has the conformational parameters: $\pi_m = 30.6^\circ$, $q = 32.6^\circ$ and $\Sigma = 336.0^\circ$ ($\alpha_1 = 188.2^\circ$, $\alpha_2 = 147.8^\circ$), while the 'perfect half-chair' should have $\tau_m = q = 31.6^\circ$ and $\Sigma = 360^\circ$, which gives an angular sequence of 0, $-\phi_3/4$, $3\phi_3/4$, $-\phi_3$, $3\phi_3/4$, $-\phi_3/4$ and $\phi_3 = 63.2^\circ$. So it seems that the three-membered rings could be affecting the normal half-chair conformation (Cano, Foces-Foces & García-Blanco, 1977).

The H atoms are bonded normally, the geometry ranging between (0.92, 1.03 Å), (117, 122°) and (0.95, 1.04 Å), (100, 121°) for the phenyl and tetrahedral H atoms respectively.

There are no short intermolecular contacts and no non-bonding interactions within the molecule, the two phenyl rings being separated sufficiently.

We thank Drs Fernández-Alvarez and M. Bernabé (Itt^o Química Organica General, CSIC, Madrid) for suggesting the problem and providing the crystal. We also thank the Centro de Calculo del Ministerio de Educación Ciencia (Madrid) for computing facilities, and one of us (MLM) is grateful to the Ministerio de Ciencia for financial support.

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