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1-Benzothiepin 1,1-Dioxide

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Abstract. $C_{10}H_8O_2S$, monoclinic, $P2_1/n$ (No. 14), $a = 7.597$ (2), $b = 17.897$ (4), $c = 6.855$ (2) Å, $\beta = 108.84$ (1)° [$\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å], $Z = 4$, $D_c = 1.45$ g cm $^{-3}$, $F.W. = 192.3$, $\mu(\text{Mo } K\alpha) = 3.2$ cm $^{-1}$. The thiepin ring takes a boat form and shows bond alternation, while the benzo ring maintains a conjugated structure.

Introduction. Crystals were supplied by Professor I. Murata and his co-workers at Osaka University. A crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was mounted on a Rigaku automated, four-circle, single-crystal diffractometer. The Rigaku software system for a FACOM-R-controlled diffractometer was used to find low-order reflexions and to calculate unit-

cell parameters. The orientation and the unit-cell dimensions of the crystal were confirmed by a θ - 2θ scan along several reciprocal lattice axes and a preliminary intensity data collection within a full sphere of a small radius in the reciprocal lattice. Systematic absences were: $h0l$, $h+l=2n+1$ and $0k0$, $k=2n+1$. The good quality of the crystal was established by an ω -scan of several reflexions. (These procedures show that intensity data can be collected without preliminary photographic investigation.)

The θ - 2θ scan technique was employed for data collection. The integrated intensity was determined by scanning over the peak at a rate of 4° min $^{-1}$, and subtracting the background obtained by averaging the two values measured for 5 s at both ends of a scan. The scan range in 2θ was from -0.9° from the $K\alpha_1$ peak to 0.9° from the $K\alpha_2$ peak. 1548 unique reflexions were measured out to a 2θ (Mo $K\alpha_1$) value of 50° , and of these, 215 reflexions were less than $\sigma(F)$ and recorded as zero. Five standard reflexions were measured after every 59 reflexions; their intensities remained constant throughout the data collection. Graphite-monochromatized Mo $K\alpha$ radiation was used.

The heavy-atom method was used for the structure solution. The most plausible location of the sulphur atom was chosen by interpreting a three-dimensional Patterson map. Subsequent Fourier syntheses revealed all the non-hydrogen atoms. All the H atoms were located on a difference Fourier synthesis after anisotropic refinement of the model. The least-squares refinement was carried out with the *FMLS* program (Ashida, 1973). Atomic scattering factors for C, O and

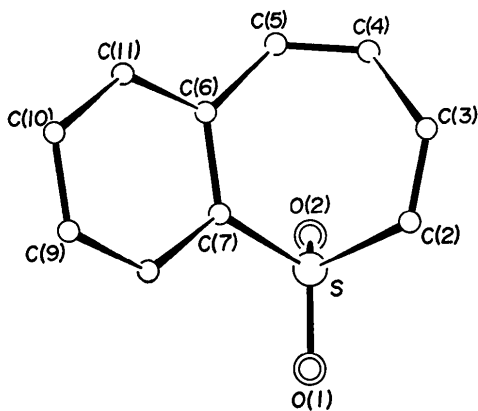


Fig. 1. The molecular structure of 1-benzothiepin 1,1-dioxide projected onto the plane passing through the atoms C(2), C(3), C(6) and C(7).

Table 1. Atomic parameters and their estimated standard deviations

Positional parameters are expressed as fractions of cell edges. Anisotropic temperature factors are expressed as: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ and isotropic temperature factors are of the form: $\exp(-B \sin^2 \theta/\lambda^2)$ with B values in \AA^2 . E.s.d.'s are listed in parentheses with respect to the least significant digit of any parameter.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0.13260 (9)	0.15221 (4)	0.32480 (11)	0.01377 (13)	0.00233 (18)	0.02544 (18)	-0.00025 (9)	0.0192 (3)	0.00272 (10)
O(1)	-0.0562 (3)	0.14990 (13)	0.3230 (4)	0.0183 (5)	0.00404 (9)	0.0457 (8)	0.0005 (3)	0.0352 (10)	-0.0020 (4)
O(2)	0.2707 (3)	0.17809 (12)	0.5098 (3)	0.0234 (5)	0.00375 (8)	0.0269 (6)	-0.0022 (3)	0.0196 (9)	-0.0069 (4)
C(2)	0.1399 (4)	0.20675 (16)	0.1184 (5)	0.0175 (6)	0.00216 (9)	0.0333 (9)	0.0013 (4)	0.0139 (12)	0.0020 (5)
C(3)	0.2902 (4)	0.21439 (17)	0.0619 (5)	0.0215 (7)	0.00259 (10)	0.0285 (9)	-0.0027 (4)	0.0150 (13)	0.0023 (5)
C(4)	0.4654 (4)	0.17576 (18)	0.1411 (5)	0.0176 (6)	0.00369 (11)	0.0261 (8)	-0.0025 (4)	0.0208 (12)	-0.0011 (5)
C(5)	0.4982 (4)	0.10747 (18)	0.2204 (4)	0.0133 (5)	0.00422 (12)	0.0220 (7)	0.0014 (4)	0.0142 (10)	-0.0000 (4)
C(6)	0.3692 (4)	0.05024 (15)	0.2412 (4)	0.0186 (6)	0.00287 (9)	0.0145 (6)	0.0034 (4)	0.0095 (10)	0.0000 (5)
C(7)	0.1969 (4)	0.06237 (14)	0.2698 (4)	0.0168 (5)	0.00220 (8)	0.0164 (6)	0.0005 (3)	0.0113 (9)	-0.0000 (4)
C(8)	0.0781 (4)	0.00386 (17)	0.2744 (5)	0.0241 (7)	0.00282 (10)	0.0209 (7)	-0.0036 (4)	0.0148 (12)	-0.0005 (4)
C(9)	0.1327 (6)	-0.06873 (18)	0.2566 (5)	0.0415 (11)	0.00261 (10)	0.0242 (9)	-0.0049 (5)	0.0222 (16)	0.0009 (5)
C(10)	0.3041 (6)	-0.08240 (18)	0.2353 (5)	0.0487 (13)	0.00251 (10)	0.0251 (9)	0.0066 (6)	0.0247 (17)	0.0019 (5)
C(11)	0.4197 (5)	-0.02472 (18)	0.2277 (5)	0.0300 (8)	0.00328 (11)	0.0211 (8)	0.0082 (5)	0.0179 (13)	0.0015 (5)

Table 1 (cont.)

	x	y	z	B
H(2)	0.027 (5)	0.2304 (19)	0.057 (5)	5.3 (8)
H(3)	0.282 (4)	0.2521 (18)	-0.055 (5)	4.4 (7)
H(4)	0.575 (5)	0.1996 (20)	0.119 (5)	5.4 (8)
H(5)	0.621 (4)	0.0920 (17)	0.251 (5)	4.3 (7)
H(8)	-0.045 (4)	0.0174 (18)	0.289 (5)	4.5 (7)
H(9)	0.042 (5)	-0.104 (2)	0.262 (6)	6.4 (9)
H(10)	0.344 (5)	-0.129 (2)	0.222 (6)	6.5 (9)
H(11)	0.539 (5)	-0.0367 (20)	0.211 (5)	5.6 (8)

Table 2. Selected bond distances (\AA) and bond angles ($^\circ$) with estimated standard deviations

S—O(1)	1.431 (3)	O(1)—S—O(2)	117.5 (2)
S—O(2)	1.436 (3)	O(1)—S—C(2)	107.8 (2)
S—C(2)	1.735 (4)	O(1)—S—C(7)	108.6 (2)
S—C(7)	1.756 (3)	O(2)—S—C(2)	109.4 (2)
C(2)—C(3)	1.326 (5)	O(2)—S—C(7)	108.1 (2)
C(3)—C(4)	1.441 (5)	C(2)—S—C(7)	104.8 (2)
C(4)—C(5)	1.328 (5)	S—C(2)—C(3)	123.6 (3)
C(5)—C(6)	1.456 (4)	C(2)—C(3)—C(4)	128.2 (4)
C(6)—C(7)	1.402 (4)	C(3)—C(4)—C(5)	128.6 (4)
C(7)—C(8)	1.389 (4)	C(4)—C(5)—C(6)	130.1 (4)
C(8)—C(9)	1.381 (5)	C(5)—C(6)—C(7)	126.4 (3)
C(9)—C(10)	1.378 (6)	C(5)—C(6)—C(11)	117.3 (3)
C(10)—C(11)	1.367 (6)	C(7)—C(6)—C(11)	116.3 (3)
C(11)—C(6)	1.406 (5)	S—C(7)—C(8)	117.2 (3)
C(2)—H(2)	0.93 (4)	S—C(7)—C(6)	120.6 (3)
C(3)—H(3)	1.03 (4)	C(6)—C(7)—C(8)	121.9 (3)
C(4)—H(4)	0.99 (4)	C(7)—C(8)—C(9)	119.4 (4)
C(5)—H(5)	0.93 (4)	C(8)—C(9)—C(10)	119.8 (4)
C(8)—H(8)	1.00 (4)	C(9)—C(10)—C(11)	120.7 (5)
C(9)—H(9)	0.94 (4)	C(10)—C(11)—C(6)	121.7 (4)
C(10)—H(10)	0.90 (4)		
C(11)—H(11)	0.98 (4)		

S were from Hanson, Herman, Lea & Skillman (1964) and for H from Stewart, Davidson & Simpson (1965). The following weighting scheme was applied: $w = (8.0/|F_o|)^2$ for $|F_o| > 8.0$, $w = 1.0$ for $8.0 \geq |F_o| \geq 1.4$ and $w = 0.2$ for $|F_o| < 1.4$. The final conventional R is 0.063 for 1548 reflexions, and 0.045 for 1333 non-zero reflexions.*

Discussion. The molecular structure projected onto the plane passing through C(2), C(3), C(6) and C(7) is shown in Fig. 1. An ORTEP plot is shown in Fig. 2. The final atomic parameters, and bond distances and angles are listed in Tables 1 and 2 respectively.

In the thiopyran ring, the bond alternation is clearly recognized. C(2)—C(3) and C(4)—C(5) are double bonds, while the C(3)—C(4) and C(5)—C(6) bond distances are similar to those expected for C(sp^2)—C(sp^2) single bonds. S—C(2) and S—C(7) distances are also normal for a S^{IV}—C(sp^2) bond, although Ammon, Watts & Stewart (1970) have indicated that there is strong evidence for π -electron delocalization between the S and the sub-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31239 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

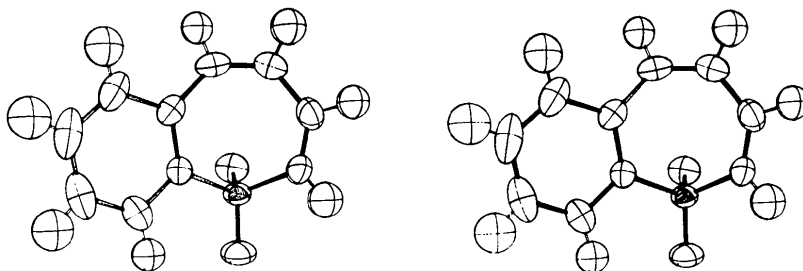


Fig. 2. An ORTEP plot of 1-benzothiepin 1,1-dioxide.

stituent C atoms in thiepin 1,1-dioxide. The C(6)–C(7) bond takes part in the conjugation of the benzene group [C(6) to C(11)], and slightly distorts the C_s symmetry of the thiepin ring.

The thiepin ring takes the boat form, and the dihedral angle between 'bow' atoms [the plane through C(2), S and C(7)] and 'stern' atoms [the plane through C(3), C(4), C(5) and C(6)] is 70.4° . The SO_2 plane almost bisects the plane through C(2), C(3), C(6) and C(7), the angle being 88.9° .

The distances and angles for probable hydrogen

Table 3. Distances and angles in probable hydrogen bonding

Key for superscripts			
None	x	y	z
(i)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
(ii)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
	O...C	O...H	O...H-C
O(2)···H(2 ⁱ)-C(2 ⁱ)	3.365 (4) Å	2.48 (4) Å	159 (3)°
O(1)···H(3 ⁱⁱ)-C(3 ⁱⁱ)	3.343 (4)	2.44 (3)	145 (3)

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Tris-(1-pyrazoly)phosphine

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Abstract. $P(C_3H_3N_2)_3$, $M=232.19$, hexagonal, space group $P6_3$, $a=8.443$ (4), $c=8.946$ (5) Å, $V=552.3$ Å³, $Z=2$, $D_c=1.396$ g cm⁻³. The structure was determined from diffractometer intensity measurements (Mo $K\alpha$ radiation) and refined by full-matrix least-squares calculations to an R of 0.043 for 267 observed reflexions. The molecule is pyramidal with the P atom lying on a crystallographic threefold axis. The pyrazolyl ring is planar and coordinated asymmetrically with respect to the P–N bond [1.714 (4) Å], the P–N–C and P–N–N angles being 135.4 (4) and 115.0 (3)° respectively.

bonding are listed in Table 3. They do not indicate strong bonding, but similar schemes are found in other sulphones (Ammon, Watts & Stewart, 1970; Boelema, Visser & Vos, 1967; Yasuoka, Kasai, Tanaka, Nagai & Tokura, 1972).

The authors thank Professor I. Murata and his co-workers for supplying the crystals.

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Introduction. The crystals are extremely sensitive to traces of water and were sealed in Lindemann glass capillaries in a dry box. Preliminary photographs (Cu $K\alpha$ radiation) showed the crystals to have Laue symmetry $6/m$ and systematic absences $00l$, $l=2n+1$, indicating space groups $P6_3$ or $P6_3/m$.

A crystal, $0.3 \times 0.3 \times 0.3$ mm, cut from a large acicular crystal, was used in the measurement of cell dimensions and collection of intensities on a Picker FACS-I diffractometer. Nb-filtered Mo $K\alpha$ radiation ($\lambda K\alpha_1=0.70926$ Å) and a scintillation counter with