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2-Phenyl-1,3-dithian-5-one

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Abstract. $C_{10}S_2O_2H_{10}$, $M_r = 210.3$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 14.258$ (5), $b = 5.217$ (3), $c = 15.374$ (5) Å, $\beta = 117.92$ (6)°, $R = 0.046$. The carbonyl group is more puckered than in cyclohexanones.

Introduction. The structure of 2-phenyl-1,3-dithian-5-one (PTO)* has been determined by X-ray diffraction in order to determine the deformation of the ring caused by substitution of the ring C atoms by S.

The reflexion data were collected by a Philips PW 1100 X-ray diffractometer with graphite-mono-

chromated Cu $K\alpha$ radiation. The structure factors of 1731 independent reflexions were obtained within $\theta = 3 \sim 78^\circ$. The structure was solved by the three-

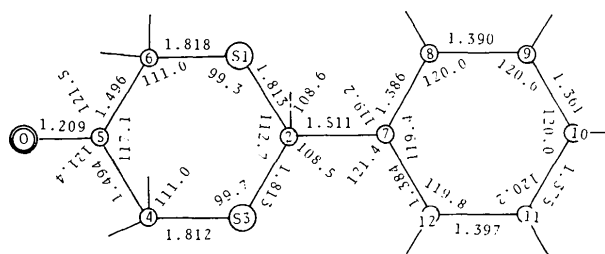


Fig. 1. Bond lengths and bond angles in PTO.

Table 1. *Positional* ($\times 10^4$ for S, O and C and $\times 10^3$ for H atoms) and *thermal* ($\times 10^4$ for S, O and C) parameters

The form of the anisotropic temperature factor is: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	813 (2)	1460 (5)	-2251 (2)	93 (2)	780 (15)	63 (1)	-32 (4)	32 (1)	-88 (4)
S(1)	1141 (1)	1647 (2)	212 (0)	57 (0)	432 (3)	43 (0)	-31 (1)	17 (0)	20 (1)
S(3)	2858 (1)	4337 (2)	-64 (1)	60 (0)	759 (5)	44 (0)	-68 (1)	20 (0)	11 (1)
C(2)	2129 (2)	4174 (5)	635 (2)	58 (2)	350 (11)	41 (1)	-8 (4)	19 (1)	0 (3)
C(4)	1773 (3)	4985 (7)	-1277 (2)	81 (2)	615 (17)	46 (2)	-59 (5)	21 (2)	24 (4)
C(5)	954 (2)	2919 (6)	-1589 (2)	59 (2)	469 (14)	40 (1)	1 (4)	14 (1)	3 (4)
C(6)	319 (2)	2727 (6)	-1045 (2)	57 (2)	521 (15)	43 (1)	-18 (4)	15 (1)	9 (4)
C(7)	2909 (2)	3684 (5)	1701 (2)	50 (2)	391 (12)	41 (1)	-9 (4)	18 (1)	0 (3)
C(8)	2921 (2)	5317 (7)	2417 (2)	74 (2)	506 (15)	51 (2)	21 (5)	21 (2)	-27 (4)
C(9)	3634 (3)	4899 (8)	3402 (2)	96 (3)	730 (21)	46 (2)	9 (6)	21 (2)	-35 (5)
C(10)	4337 (2)	2922 (8)	3672 (2)	71 (2)	701 (20)	45 (2)	-6 (5)	12 (2)	19 (5)
C(11)	4329 (3)	1274 (8)	2970 (2)	71 (2)	632 (19)	67 (2)	53 (5)	18 (2)	42 (5)
C(12)	3607 (2)	1638 (7)	1977 (2)	75 (2)	499 (15)	52 (2)	36 (5)	23 (2)	9 (4)

	x	y	z	B		x	y	z	B
H(1)	174 (2)	588 (6)	55 (2)	6 (1)	H(6)	240 (3)	683 (7)	221 (2)	7 (1)
H(2)	149 (3)	657 (6)	-125 (2)	6 (1)	H(7)	362 (3)	612 (8)	392 (3)	9 (1)
H(3)	211 (3)	510 (8)	-171 (3)	8 (1)	H(8)	487 (3)	255 (8)	435 (3)	8 (1)
H(4)	1 (2)	444 (6)	-103 (2)	5 (1)	H(9)	483 (3)	-12 (8)	311 (3)	8 (1)
H(5)	-27 (2)	149 (6)	-133 (2)	5 (1)	H(10)	363 (3)	43 (8)	148 (3)	9 (1)

* The crystals were prepared by Dr Jochims, University of Konstanz, West Germany.

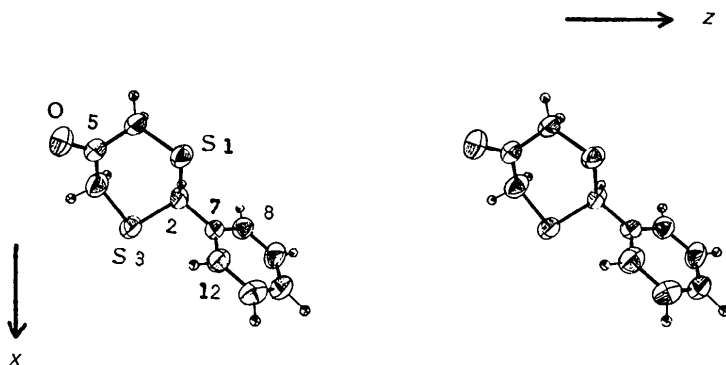
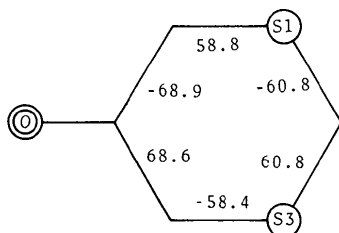
Fig. 2. Stereoscopic view of the PTO molecule drawn by *ORTEP*

Fig. 3. Endocyclic torsional angles in PTO.

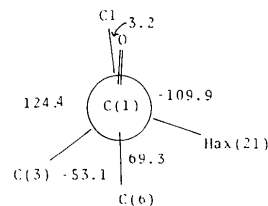
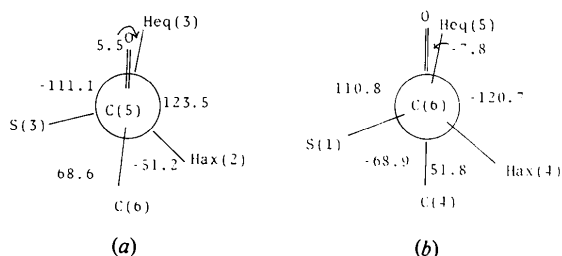
Fig. 5. Newman projection along the bond C(1)–C(2) in *cis*-2-chloro-4-*tert*-butylcyclohexanone.

Fig. 4. Newman projections along the bonds (a) C(4)–C(5) and (b) C(5)–C(6), respectively, in PTO; Hax and Heq denote the hydrogen atoms at axial and equatorial positions respectively.

dimensional Patterson function and the multi-solution method (Germain, Main & Woolfson, 1971) using reflexions with $E \geq 2.0$. All the positions of the H atoms were obtained from a three-dimensional difference Fourier map. The final refinement was carried out by the block-diagonal least-squares method [program by Okaya & Ashida (1967)] including H atoms with isotropic temperature factors. The final R value was 0.046.*

Discussion. The molecular structure of PTO is shown in Fig. 1 and the bond lengths and angles in Fig. 2. The

Table 2. Bond lengths (\AA) and angles ($^\circ$) involving hydrogen atoms

C(2)–H(1)	1.02 (3)	C(8)–H(6)	1.02 (4)
C(4)–H(2)	0.93 (4)	C(9)–H(7)	1.03 (5)
C(4)–H(3)	0.99 (5)	C(10)–H(8)	0.98 (3)
C(6)–H(4)	1.00 (3)	C(11)–H(9)	0.97 (4)
C(6)–H(5)	0.99 (3)	C(12)–H(10)	1.00 (5)
C(7)–C(2)–H(1)	112 (2)	C(5)–C(6)–H(5)	114 (2)
S(1)–C(2)–H(1)	108 (2)	C(9)–C(8)–H(6)	121 (2)
S(3)–C(2)–H(1)	108 (2)	C(7)–C(8)–H(6)	119 (2)
C(5)–C(4)–H(2)	111 (2)	C(10)–C(9)–H(7)	121 (2)
S(3)–C(4)–H(2)	108 (2)	C(8)–C(9)–H(7)	119 (2)
C(5)–C(4)–H(3)	113 (2)	C(11)–C(10)–H(8)	115 (2)
S(3)–C(4)–H(3)	104 (2)	C(9)–C(10)–H(8)	125 (2)
H(2)–C(4)–H(3)	110 (3)	C(12)–C(11)–H(9)	116 (2)
S(1)–C(6)–H(4)	109 (2)	C(10)–C(11)–H(9)	124 (2)
C(5)–C(6)–H(5)	110 (2)	C(7)–C(12)–H(10)	122 (2)
H(4)–C(6)–H(5)	108 (3)	C(11)–C(12)–H(10)	118 (2)
S(1)–C(6)–H(5)	105 (2)		

standard deviations are estimated to be 0.003–0.006 \AA and 0.1–0.3 $^\circ$, but 0.03–0.05 \AA and 2–3 $^\circ$ for those involving H atoms. The C–S, C–C and C–H bond lengths are similar to the values for 2-phenyl-1,3-dithiane (PT) (Kalf & Romers, 1966). In PTO as well as in PT, the dithiane ring has the chair form with the phenyl ring in an equatorial position. The plane of the benzene ring almost bisects the dithiane ring [torsional angle: S(1)–C(2)–C(7)–C(12) = 68.9 $^\circ$]. The angles C(6)–S(1)–C(2) and C(2)–S(3)–C(4) are 99.3 and 99.7 $^\circ$, which agree with those in PT. The angles

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32281 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

C(5)—C(6)—S(1) and C(5)—C(4)—S(3) are both 111.0° which is significantly smaller than in PT (114.9 and 116.1°) but comparable with the values in cyclohexane itself (Geise, Buys & Mijlhoff, 1971). The angle S(1)—C(2)—S(3) (112.7°) is also smaller than in PT (115.3°). C(5) forms an sp^2 hybrid orbital, with C(4)—C(5)—C(6) 117.1° , similar to the values of 116 and 117° in cyclohexane-1,4-dione (Mossel & Romers, 1964; Groth & Hassel, 1964). The mean of the absolute values of the torsional angles S(3)—C(4)—C(5)—C(6) and S(1)—C(6)—C(5)—C(4) is 68.8° (Fig. 3), indicating that the C(4)—C(5)—C(6) part is more puckered than in PT (61.6°) or *cis*-2-chloro-4-*tert*-butylcyclohexanone (57.3°) (de Graaff, Giesen, Rutten & Romers, 1972). In 1,3-dioxane derivatives, the O—C—O part is more puckered than the C—C—C part (de Kok & Romers, 1970; Kobayashi & Iitaka, 1977) whereas in 1,3-dithiane derivatives, the C—C—C part is more puckered than the S—C—S part. In Figs. 4 and 5, the torsional angles along the C(4)—C(5) and C(5)—C(6) bonds of PTO and the C(1)—C(2) bond of *cis*-2-chloro-4-*tert*-butylcyclohexanone are given. In PTO, the carbonyl O atom lies between the S atom and the equatorial H atom while in the cyclohexanone derivative it lies between the equatorial Cl atom in the 2-position and the axial H atom. The average of the

torsional angles O—C(5)—C(4)—S(3) and O—C(5)—C(6)—S(1) is 111.0° for PTO but the O—C(1)—C(2)—C(3) angle in *cis*-2-chloro-4-*tert*-butylcyclohexanone is 127.6° .

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(Z)-5-Isopropyl-2-phenyl-1,3-dioxan-5-ol*

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Abstract. $C_{13}O_3H_{18}$, $M_r = 222.3$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 9.558$ (4), $b = 11.336$ (5), $c = 5.835$ (3) Å, $\alpha = 92.61$ (4), $\beta = 107.15$ (6), $\gamma = 89.89$ (4) $^\circ$. The final R value was 0.094. No intramolecular hydrogen bond was found in the crystal.

Introduction. The existence of intramolecular hydrogen bonds in 1,3-dioxan-5-ols in CCl_4 solution has been shown by IR spectra (Brimacombe, Foster & Stacey, 1958; Baker, Brimacombe, Foster, Whiffen & Zweifel, 1959; Bagget, Brimacombe, Foster, Stacey & Whiffen, 1960; Kobayashi, 1974). It has also been demonstrated by NMR that the OH group at C(5) in (Z)-2-phenyl-1,3-dioxan-5-ol is bonded equally to two

ring O atoms by a bifurcated hydrogen bond in dilute CCl_4 solution (Kobayashi, 1974; Jochims & Kobayashi, 1976).

In order to clarify the results of such studies, the crystal and molecular structure of (Z)-5-isopropyl-2-phenyl-1,3-dioxan-5-ol (Fig. 1) was determined by X-ray analysis. The reflexion data were collected on a Philips PW 1100 X-ray diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The intensities of 2227 independent reflexions were obtained within $\theta = 3 \sim 78^\circ$. The crystal structure was solved by the multi-solution method (Germain, Main & Woolfson, 1971) based on 152 reflexions with $E \geq 2.00$. The positions of all non-hydrogen atoms were located on an E map. The atomic parameters were refined by the block-diagonal least-squares method including anisotropic temperature factors. The positions of all the H atoms

* This work forms part of the PhD thesis of Y. Kobayashi at the University of Konstanz, West Germany.