

The Crystal Structure of *trans*-2,5-Dibromo-7-thiabicyclo-[4.2.0]-1(6)-octene 7,7-Dioxide

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The structure of *trans*-2,5-dibromo-7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide has been determined by single crystal X-ray methods. The unit cell is monoclinic, space group No. 14 $P2_1/c$. The structure was solved by means of Patterson and electron density calculations and refined by least squares methods to a final R -value of 0.08. The bromine atoms are in a *trans* position and the cyclohexene ring takes a half-chair conformation.

In connection with the synthesis of the four-membered ring sulfone 2*H*-benzo[*b*]thiete 1,1-dioxide,^{1,2} the photobromination of 7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide was studied. The main product in this reaction is *trans*-2,5-dibromo-7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide obtained as colour-less crystals from a benzene-ether solvent mixture. The stereochemistry of this compound has been discussed in a previous paper² where arguments favouring the *cis* configuration were given. A single crystal diffraction investigation has now been completed, the result of which shows that the configuration is *trans*. It may also be noted that the crystallized compound contains benzene of crystallization.

EXPERIMENTAL

The compound was prepared according to Ref. 2 and the crystals were isolated as transparent needles. In order to obtain accurate cell dimensions powder photographs were taken with a Guinier focusing camera using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) and lead nitrate as internal standard. Refinement of the cell dimensions using the program POWDER³ and 33 indexed reflexions yielded the following values:

$$a = 10.8140 \pm 0.0009 \text{ \AA}, b = 7.9623 \pm 0.0007 \text{ \AA}, \\ c = 17.298 \pm 0.002 \text{ \AA} \quad \beta = 99.233 \pm 0.009^\circ, V = 1470.1 \text{ \AA}^3 \quad (t = 23^\circ \text{ C}).$$

The experimental density of 1.76 g/cm³, determined by flotation in thallium formate, agrees well with the theoretical value of 1.783 g/cm³, assuming four formula units and four benzene molecules of crystallization per unit cell (F.W. = 316.6).

Weissenberg photographs were taken for layers 0–6 about the *b*-axis using the equi-inclination multiple film technique and Ni-filtered Cu radiation. The intensities were estimated visually by comparison with a standard scale prepared from one of the strong reflexions from the crystal. The intensities from the different films in each set were scaled together and corrected for Lorentz and polarisation effects (SCALE and DATAP2).⁴ The intensities from the different layers were scaled together approximately, assuming a linear relationship between intensity and time of exposure. A total of 1333 independent reflexions was measured. The linear absorption coefficient is 89.8 cm⁻¹ and an absorption correction was applied.

The presence of benzene of crystallization was indicated early by loss of weight of the compound when stored² and a strong smell of benzene even after prolonged drying.

The crystal used in the investigation was of size 0.18 × 0.26 × 0.35 mm and was mounted in a 0.3 mm glass capillary to prevent efflorescence due to loss of benzene of crystallization.

STRUCTURE DETERMINATION

From the unobserved reflexions $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ the space group was found to be $P2_1/c$.

A three dimensional Patterson synthesis was calculated (DFR)⁴ from which the positions

of the two bromine atoms were easily found. Successive electron density calculations revealed the rest of the atoms including the benzene carbon atoms. After three cycles of block diagonal least squares refinement (BLOCK)⁴ in which atomic coordinates, isotropic temperature factors and individual scale factors for each layer were allowed to vary, the weighting scheme of Cruickshank⁵ [$w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$] with $a = 18$, $c = 0.008$ and $d = 0$ and the X-ray scattering factor tables of Doyle and Turner⁶ being used an R -value of 0.13 was obtained. At this stage a difference synthesis was calculated which did not show any new atoms but indicated anisotropic thermal motion of the bromine atoms. Consequently allowance for anisotropic thermal motion of the bromine atoms was made in the final refinement. Six cycles of full

matrix least squares refinement (LALS)⁴ in which atomic coordinates, thermal parameters and individual scale factors for each layer were allowed to vary (in all 89 parameters) gave a final R -value of 0.08. All the last shifts in the parameters were less than 5 % of the estimated standard deviation of the corresponding parameter. A difference synthesis calculated after the last refinement showed no peaks higher than about 0.8 e/Å³. No attempts were made to locate the hydrogen atoms.

A list of measured and calculated structure factors can be obtained from the author on request.

RESULTS

The final atomic parameters are given in Table 1. A list of interatomic distances and

Table 1. Atomic coordinates as fractions of the cell edges (standard deviations within parentheses). The anisotropic temperature coefficient is $\exp - [\frac{1}{4} (a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + a^*b^*U_{12}hk + a^*c^*U_{13}hl + b^*c^*U_{23}kl)]$. The primed atoms are benzene carbon atoms.

Atom	x	y	z	$B(\text{Å}^2)$
Br(1)	0.4364(2)	0.0944(2)	0.2595(1)	
Br(2)	0.1551(2)	-0.0526(3)	-0.0468(1)	
S	0.3929(3)	0.3130(5)	0.0020(2)	3.35
C(1)	0.427(1)	-0.011(2)	0.155(1)	3.60
C(2)	0.311(1)	-0.125(2)	0.140(1)	3.67
C(3)	0.189(1)	-0.023(2)	0.119(1)	4.08
C(4)	0.189(1)	0.088(2)	0.048(1)	3.23
C(5)	0.315(1)	0.159(2)	0.050(1)	2.89
C(6)	0.417(1)	0.124(2)	0.099(1)	2.84
C(7)	0.518(1)	0.245(2)	0.077(1)	3.63
O(1)	0.411(1)	0.264(1)	-0.074(1)	5.06
O(2)	0.352(1)	0.481(1)	0.012(1)	4.64
C(1)'	-0.002(2)	0.351(3)	0.230(3)	7.51
C(2)'	0.118(2)	0.370(3)	0.233(1)	8.11
C(3)'	0.171(2)	0.455(3)	0.174(1)	6.51
C(4)'	0.098(2)	0.517(3)	0.113(1)	6.16
C(5)'	-0.032(2)	0.501(3)	0.107(1)	8.09
C(6)'	-0.087(3)	0.413(3)	0.170(2)	8.24

Atom	Br(1)	Br(2)
U_{11}	0.0846	0.0520
U_{22}	0.0534	0.0887
U_{33}	0.0404	0.0583
U_{12}	-0.0107	-0.0042
U_{13}	0.0002	-0.0039
U_{23}	-0.0023	-0.0479

Table 2. Interatomic distances with standard deviations. The primed atoms are benzene carbon atoms. The atomic numbering is in accordance with Fig. 1.

Bond	Distance, Å	Bond	Distance, Å
Br(1)–C(1)	1.98(1)	C(7)–S	1.80(2)
Br(2)–C(4)	1.98(1)	O(1)–S	1.41(1)
C(1)–C(2)	1.54(2)	O(2)–S	1.43(1)
C(2)–C(3)	1.54(2)	C(1)'–C(2)'	1.30(4)
C(3)–C(4)	1.51(2)	C(2)'–C(3)'	1.42(3)
C(4)–C(5)	1.47(2)	C(3)'–C(4)'	1.30(3)
C(5)–C(6)	1.32(2)	C(4)'–C(5)'	1.39(3)
C(6)–C(1)	1.44(2)	C(5)'–C(6)'	1.49(4)
C(6)–C(7)	1.54(2)	C(6)'–C(1)'	1.36(4)
C(5)–S	1.76(1)		

Table 3. Bond angles with standard deviations. The primed atoms are benzene carbon atoms. The atomic numbering is in accordance with Fig. 1.

Angle	A, °	Angle	A, °
Br(1)–C(1)–C(2)	109(1)	C(6)–C(7)–S	84(1)
Br(1)–C(1)–C(6)	106(1)	C(5)–S–C(7)	79(1)
Br(2)–C(4)–C(3)	109(1)	C(5)–S–O(1)	113(1)
Br(2)–C(4)–C(5)	106(1)	C(5)–S–O(2)	114(1)
C(6)–C(1)–C(2)	111(1)	C(7)–S–O(1)	113(1)
C(1)–C(2)–C(3)	112(1)	C(7)–S–O(2)	114(1)
C(2)–C(3)–C(4)	113(1)	O(1)–S–O(2)	118(1)
C(3)–C(4)–C(5)	110(1)	C(1)'–C(2)'–C(3)'	123(2)
C(4)–C(5)–C(6)	127(1)	C(2)'–C(3)'–C(4)'	119(2)
C(5)–C(6)–C(1)	124(1)	C(3)'–C(4)'–C(5)'	120(2)
C(4)–C(5)–S	141(1)	C(4)'–C(5)'–C(6)'	120(2)
C(6)–C(5)–S	92(1)	C(5)'–C(6)'–C(1)'	115(2)
C(5)–C(6)–C(7)	105(1)	C(6)'–C(1)'–C(2)'	123(2)
C(1)–C(6)–C(7)	131(1)		

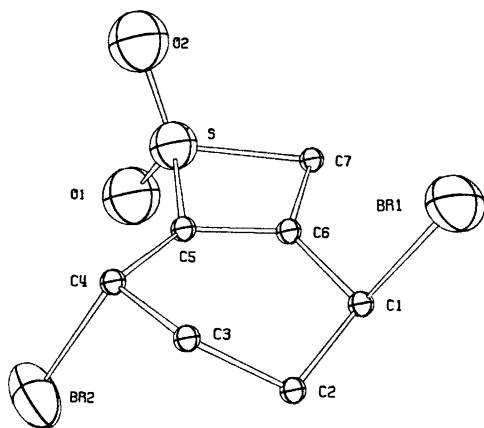


Fig. 1. Spatial drawing of the *trans*-2,5-dibromo-7-thiabicyclo[4.2.0]-1(6)-octene 7,7-dioxide molecule.

angles is given in Tables 2 and 3, respectively. A spatial drawing of the molecule is shown in Fig. 1 (ORTEP).⁴ Note that a different numbering system for the atoms is used than that dictated by organic nomenclature, cf. Ref. 2. As shown in Fig. 1 the bromine atoms are in a *trans* position and the cyclohexene ring takes a half-chair conformation.

The bond lengths found in the cyclohexene part of this molecule are in good agreement with those found in the cyclohexene molecule except for the C(4)–C(5) and C(6)–C(1) bonds which are shorter in this work [1.47(2) Å and 1.44(2) Å compared to 1.504(6) Å].⁷ The structure of the four membered ring C₃H₄O₂S has been determined by the microwave technique.⁸ The bond lengths and angles of the four mem-

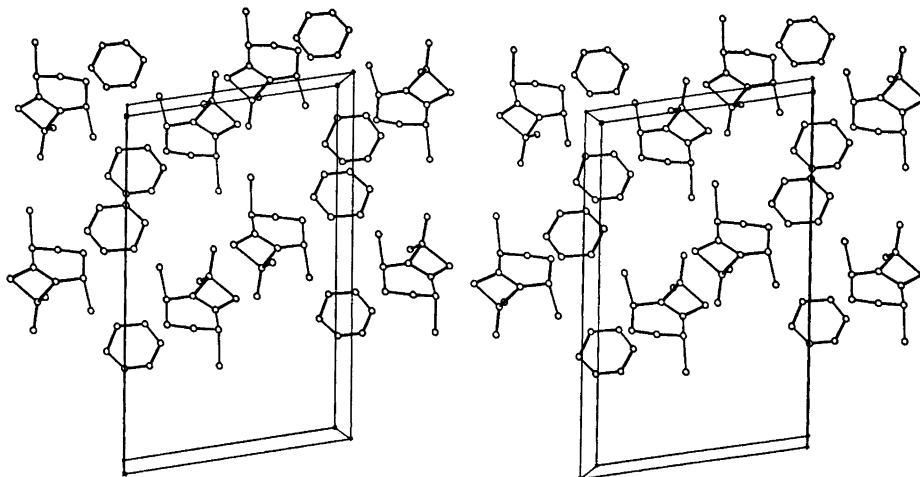


Fig. 2. Stereoscopic drawing of the packing in the crystal. The b -axis is directed upwards perpendicular to the plane of the paper and the c -axis is vertical.

bered ring part of the present molecule compare well with those found in Ref. 8 except for the double bond which is significantly longer in Ref. 8 (1.39 Å).

The high temperature factors and the comparatively large standard deviations in the coordinates of the benzene carbon atoms are to be expected since the benzene molecules are obviously weakly bonded.

The molecular packing of the crystal is shown in Fig. 2 and can be described as consisting of layers of molecules parallel to the $y-z$ plane. The layers are packed two by two, the benzene molecules lying cross-wise between these double layers, thus separating them but allowing the Br(2) atoms of neighbouring double layers to be in van der Waals contact (4.0 Å). The distance between the Br(1) atom of one molecule and the O(1) atom of its equivalent related by the glide plane is 3.15(1) Å which is somewhat shorter than expected from pure van der Waals interaction (3.35 Å).

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