Acta Cryst. (1976). B**32**, 3157

The Crystal Structure of *trans*-1-Thioniabicyclo[4.4.0]decane Bromide

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(*Received* 31 *March* 1976; *accepted* 19 *May* 1976)

The crystal structure of the title compound has been determined by single-crystal X-ray analysis. The crystal is orthorhombic, space group $Cmc2_1$, with $a=13{\cdot}217$ (4), $b=9{\cdot}784$ (3), $c=8{\cdot}083$ (3) Å, $Z=4$. The structure was solved by heavy-atom methods and refined by full-matrix least-squares calculations to $R=0{\cdot}044$ for 603 observed reflexions. The structure is ionic and can be taken as belonging to the NaCl type, composed of Br^- ions and *trans*-1-thioniabicyclo[4.4.0]decane (TBD) cations. The TBD ring has mirror symmetry with a symmetrical *trans*-chair conformation. A distinct difference is found in the two S–C bond lengths (1·806, 1·872 Å).

Introduction

1-Thioniabicyclo[4.4.0]decane (TBD) bromide was first synthesized by Eastman & Kritchevsky (1959), but no discussion has been given on the conformation of the TBD ring. The authors synthesized TBD bromide by the method of Eastman & Kritchevsky, and succeeded in separating two isomers by column chromatography on silica gel. Both were recrystallized from ethanol solutions to give colourless plates (crystal *a*) and colourless needles (crystal *b*). ^{13}C-NMR spectra suggest that (*a*) is the *cis* and (*b*) the *trans* form (Miyoshi, Tokuno, Arata, Hiroki & Ohashi, 1976). In order to extend these studies, a single-crystal X-ray analysis of (*b*) has been attempted.

Experimental

The crystals are colourless needles elongated along **c**. Weissenberg photographs showed orthorhombic symmetry with systematic absences $h+k=2n+1$ for hkl, $l=2n+1$ for $h0l$, which correspond to the space groups $Cmcm$, $C2cm$ and $Cmc2_1$. The lattice parameters and intensities were measured on a Philips four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å), with a crystal of dimensions $0{\cdot}15\times0{\cdot}10\times0{\cdot}17$ mm. The crystal data are: $C_9H_{17}SBr$, F.W. 237·2, orthorhombic, space group $Cmc2_1$, $a=13{\cdot}217$ (4), $b=9{\cdot}784$ (3), $c=8{\cdot}083$ (3) Å, $V=1045{\cdot}3$ Å^3, $Z=4$, $D_x=1{\cdot}51$ g cm^{-3}, μ(Mo $K\alpha$)$=44{\cdot}2$ cm^{-1}.

The intensities were measured by the θ–2θ scan technique with a scan interval $\Delta\omega=0{\cdot}9°+0{\cdot}5°\tan\theta$, a scan speed 0·04° s^{-1}, and the maximum $2\theta=55°$. The background was measured at each side of the reflexion for half the scan time. 675 independent reflexions were collected, and of these 68 were considered to be unobserved according to the criterion $I\leq\sigma(I)$, where the $\sigma(I)$'s were calculated from counting statistics. Some of the $(\bar{h}k\bar{l})$ reflexions were also measured. The intensities were corrected by the Lorentz and polarization factors, but no absorption correction was made.

Structure determination and refinement

The maximum attainable symmetry of the TBD ring is *m*, so that the centrosymmetric space group $Cmcm$ with $Z=4$ was excluded. The approximate position of the Br atom was easily obtained from the Patterson synthesis. From the interpretation of the Patterson map, it was assumed that the space group $Cmc2_1$ was correct, and this was confirmed by successive structural analyses. The Fourier map phased by the Br atom showed a pseudo mirror plane perpendicular to *z*. The approximate positions of S, C(1), C(3) and C(4) were uniquely obtained, and these atoms were found to lie almost on the pseudo mirror plane at $z=\frac{1}{2}$. Two pairs of peaks, lying symmetrically above and below the pseudo mirror plane, appeared. Two peaks (one from each pair) must be the C(2) C(5) atoms, and the rest their ghosts. From these peculiar conditions, there were four possibilities for the sets of the positional parameters. However, two of these should give the same structure if one neglects the terms for anomalous scattering, and the same should apply to the remaining two models. Hence two models remained at this stage; one implied the *cis*-boat and the other the *trans*-chair conformation for the TBD ring. At an early stage of the refinement, these two models differed only in the *z* parameter of the C(5) atom. Five cycles of isotropic full-matrix least squares, with the minimization of $\sum w(|F_o|-|F_c|)^2$, based on the two models were applied. The refinement went smoothly and no abnormal temperature parameters were found for any of the atoms of the two models. The R_0, R and R_w values were: $R_0=0{\cdot}079$, $R=0{\cdot}108$, $R_w=0{\cdot}120$ for the *trans* model and $R_0=0{\cdot}094$, $R=0{\cdot}124$, $R_w=0{\cdot}142$ for the *cis* model, where $R_0=\sum||F_o|-|F_c||/\sum|F_o|$ for non-zero reflexions, $R=\sum||F_o|-|F_c||/\sum|F_o^2|$ for all reflexions, and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$ for all reflexions. Bond distances and angles were calculated with the parameters obtained for the two structures. The results showed that the *trans* model was reasonable, whereas the *cis* model gave quite abnormal values for certain

bond distances and angles [C(2)–C(3) = 1·35 Å, C(1)–C(2)–C(3) = 131°]. Moreover, the difference Fourier map for the *cis* model revealed distinct peaks at the places where the C(2) and C(5) atoms should lie for the *trans* model, but no such peaks appeared in the difference Fourier map for the *trans* model. Thus the *trans* model was considered to be correct, and this was confirmed by successive structural analyses. Five cycles of anisotropic refinement reduced R_0 to 0·060 and R to 0·085. At this stage the absolute structure of the crystal was determined by the Bijvoet relations. A further three cycles of anisotropic full-matrix least squares including all the H atoms with fixed parameters, C–H = 1·04 Å, the tetrahedral angle for C–C–H, and an isotropic thermal factor $B_H = 5·0$ Å^2, excluding four reflexions with small scattering angles and large $|F_o|$, reduced R_0 to 0·044, R to 0·063, and R_w to 0·063. The weighting scheme applied in the final cycle was $w = 15·0/|F_o|$ for $|F_o| \geq 15·0$, $w = 1$ for $0 < |F_o| < 15·0$, $w = 0$ for $|F_o| = 0$. The scattering factors for the Br^- ion, S and C atoms were taken from *International Tables for X-ray Crystallography* (1974), while those for the H atoms were from the table given by Stewart, Davidson & Simpson (1965), and the anomalous scattering factors for the Br and S atoms from the values given by Cromer & Liberman (1970). The refinements were performed with a modified *HBLS*-IV program (Okaya & Ashida, 1967). All the calculations were performed on an NEAC 2200-250B computer at this University. The final atomic parameters are listed in Table 1.*

Results and discussion

Fig. 1 shows the crystal structure projected along **c**. The structure is ionic and can be taken as belonging to the NaCl type, composed of Br^- ions and TBD cations. The shortest intermolecular atomic distances are shown in Fig. 1. No interatomic distances shorter than their respective van der Waals separations are found. The TBD ring is found to have a mirror plane with a symmetrical *trans*-chair conformation, as shown in Fig. 2. The bond distances and angles are given in Fig. 3. The S–C(5) bond length (1·806 Å) agrees well with

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31924 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

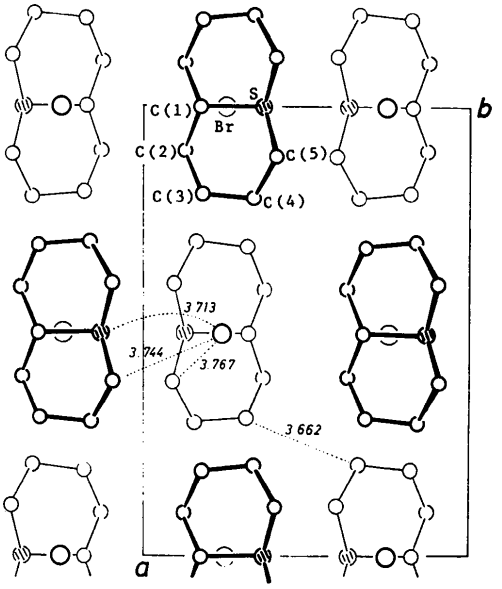


Fig. 1. The crystal structure projected along **c**.

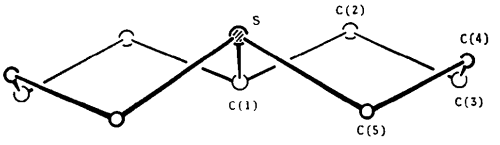


Fig. 2. A perspective drawing of the TBD ring, showing the conformation and the numbering system.

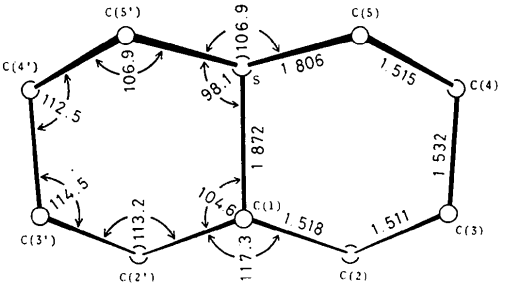


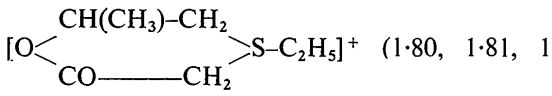
Fig. 3. Bond lengths (Å) and angles (°) in the TBD ring. The e.s.d.'s range from 0·008 to 0·013 Å and from 0·4 to 0·7°.

Table 1. *Fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* ($\times 10^4$)

The temperature factor has the form: $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. E.s.d.'s are in parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0	2540 (1)	0	64 (0)	88 (1)	139 (2)	0	0	13 (3)
S	0	3666 (2)	4864 (7)	38 (1)	72 (2)	117 (4)	0	0	45 (6)
C(1)	0	1767 (8)	5141 (22)	29 (4)	64 (7)	132 (18)	0	0	−72 (27)
C(2)	981 (6)	1294 (8)	4350 (12)	53 (5)	93 (8)	180 (15)	22 (10)	12 (12)	2 (17)
C(3)	1912 (5)	1826 (8)	5223 (23)	44 (4)	105 (8)	251 (30)	35 (9)	−18 (20)	28 (29)
C(4)	1997 (5)	3387 (8)	5272 (19)	36 (3)	111 (7)	238 (29)	−10 (8)	12 (16)	86 (27)
C(5)	1098 (5)	4053 (7)	6109 (11)	47 (4)	86 (7)	150 (12)	−11 (9)	−21 (13)	−9 (16)

average literature values: 1·817 Å (Sutton, 1965), 1·822 Å for cyclic compounds and 1·795 Å for non-cyclic compounds (Tamura, 1971). This value can also be compared with those in alkylsulphonium compounds as found in $[(CH_3)_2S(C_6H_5)]^+$ (1·81, 1·82, 1·83 Å; López-Castro & Truter, 1964) and in



Kelstrup & Kjaer, 1975). On the other hand, the S–C(1) bond (1·872 Å) is significantly longer than the S–C(5) bond (1·806 Å). Barns & Sundaralingam (1973) have reported that the S–C distances in the 2,3-dimethyl-2-butenyl-1,1,2-trimethylpropylsulphonium ion increase with increasing bulkiness of the alkyl groups attached to the S atom (1·799, 1·830, 1·882 Å). Long S–C bonds have also been reported in *meso*-3,3′-dithiobisvaline (1·853, 1·858 Å; Warner, Ottersen & Seff, 1974) and in 3,3,3′,3′-tetramethyl-D-cystine (1·865, 1·866 Å; Rosenfield & Parthasarathy, 1975). The values of the angles C(1)–C(2)–C(3), C(2)–C(3)–C(4) and C(3)–C(4)–C(5), larger than the tetrahedral angle, are not unusual for cyclic molecules containing one or more S atoms, as has been pointed out by Valle, Busetti, Mammi & Carazzolo (1969). On the other hand, both the angles S–C(1)–C(2) and S–C(5)–C(4) are found to be smaller than the tetrahedral angle. This is caused, presumably, by the formation of a fused-ring system. The angle C(2)–C(1)–C(2′) shows the maximum deviation (7·8°) from the ideal angle, where the largest ring strain is expected. A significant difference in the two C–S–C angles is also observed (98·1, 106·9°).

The authors wish to thank Professor S. Sugiura, Kanazawa University, for the use of the diffractometer.

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