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X-Ray Structure of 5-Chloro-1-thia-5-boracyclooctane

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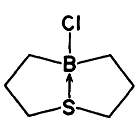
Synopsis. 5-Chloro-1-thia-5-boracyclooctane has been prepared by the hydroboration of diallyl sulfide with a chloroborane–dimethyl sulfide complex and its structure containing a sulfur-boron dative bond has been examined in detail by an X-ray crystallographic analysis.

As a part of a study on the development of useful cyclic hydroborating agents such as 9-borabicyclo-[3.3.1]nonane, 5-chloro-1-thia-5-boracyclooctane (**1**)



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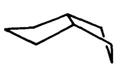

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was synthesized. In the present paper, we wish to report on the X-ray structure determination and molecular geometry of this new heterocyclic compound.

Experimental

Preparation of 5-Chloro-1-thia-5-boracyclooctane. In a 300-ml flask cooled in a Dry Ice–acetone bath was placed a mixture of diallyl sulfide (23.0 g, 201 mmol) and pentane (100 ml). A chloroborane–dimethyl sulfide complex (200 mmol) prepared by Brown's procedure[1)] was added dropwise to the vigorously-stirred solution over a period of 2 h, the temperature being kept below −20 °C. The reaction mixture was warmed to 20 °C and was stirred for another 2 h at this tempeature. After removal of the solvent, the residue was heated to 150 °C and was then distilled under reduced pressure to give 5-chloro-1-thia-5-boracyclooctane (27.56 g, 84.8% yield) as colorless crystals: Mp 50.5—51.5 °C; IR (CCl_4) 864, 1034, 1052, 1140, 1283, 1423, and 2590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (4H, t, J=7 Hz), 1.99 (4H, q, J=7 Hz), 2.59 (2H, t, J=7 Hz), and 3.02 (2H, t, J=7 Hz); MS (70 eV) m/z (%) 164 (2.85, M$^+$ for $BC_6H_{12}SCl^{37}$), 162 (7.65, M$^+$ for $BC_6H_{12}SCl^{35}$), 127 (9.85, M$^+$-Cl), 122 (9.94, $BC_6H_{12}SCl^{37}$-42), 120 (27.9, $BC_6H_{12}SCl^{35}$-42), and 42 (100, $CH_2CH_2CH_2$). The absence of any peak in the m/z 250—900 region indicates that this product is a monomer. Found: C, 43.70; H, 7.53; S, 19.63; Cl, 21.67%. Calcd for $BC_6H_{12}SCl$: C, 44.35; H, 7.44; S, 19.73; Cl, 21.82%.

X-Ray Measurement. A single crystal with dimensions of about 0.3×0.4×0.5 mm^3 was used. Because of the instability to air, the sample was sealed in a glass capillary tube filled with nitrogen gas. The crystallographic data were as follows: $BC_6H_{12}SCl$, mol wt 162.48, monoclinic, space group $P2_1/n$, a=11.383(7), b=11.055(5), c=6.586(5) Å, β=90.97(5)°, Z=4, D_c=1.302 g cm^{-3}, μ(Mo $K\alpha$)=6.15 cm^{-1}. The unit-cell dimensions and diffraction intensities were measured on a Rigaku four-circle diffractometer at the High-Brilliance X-Ray Laboratory of Hokkaido University, using graphite-monochromated Mo $K\alpha$ radiation. The ω—2θ scan technique was applied at an ω scan rate of 4° min^{-1}; the background was counted for 10 s at each end of the scan range. Three standard reflections, measured at intervals of every 100 reflections, showed a slight decrease in intensity with the course of data collection; the final-intensity/initial-intensity ratios were 0.93—0.94. The intensities were corrected for this damage to the sample as well as for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 50°, 1138 independent structure factors above the $3\sigma(F)$ level were selected for the structure determination.

Structure Determination

The structure was solved by the Monte Carlo direct method,[2)] using the 10 reflections with the greatest $|E|$ values as the starting set. The fourth-generated random-phase set led to the correct solution; an E-map based on 301 phases revealed the locations of all the non-hydrogen atoms. The structure was refined by the block-diagonal least-squares method with anisotropic thermal parameters. After all the hydrogen atoms had been located in a difference Fourier map, further full-matrix least-squares refinements were performed including the hydrogen atoms with isotropic temperature factors and the anomalous dispersion effects of the chlorine and sulfur atoms. For these refinements, the following weighting scheme was used:

$$w=1/\{\sigma(F)^2\exp(c_1X^2+c_2Y^2+c_3XY+c_4X+c_5Y)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The c_1, c_2, c_3, c_4, and

Table 1. The Final Atomic Parameters and Estimated Standard Deviations

Atom	10^4x	10^4y	10^4z	B_{eq}[a)]/Å^2
S(1)	1860(1)	4775(1)	1804(1)	3.87
C(2)	3197(4)	4092(5)	856(8)	5.17
C(3)	4085(5)	4147(7)	2539(10)	7.09
C(4)	3544(4)	3767(5)	4498(8)	5.33
B(5)	2274(4)	4371(4)	4755(6)	3.51
C(6)	1192(4)	3520(4)	5302(7)	4.56
C(7)	912(5)	2759(5)	3426(8)	5.34
C(8)	764(4)	3571(5)	1639(7)	5.08
Cl	2315(1)	5843(1)	6195(2)	5.37

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the i-th principal axis of the thermal ellipsoid.

c_5 coefficients were evaluated from the $(\Delta F)^2$ distribution; $c_1=-0.418\times10^{-3}$, $c_2=29.8$, $c_3=0.241$, $c_4=0.388\times10^{-2}$, and $c_5=-35.9$. The final R value was 0.050. The final atomic parameters are listed in Table 1.3)

The calculations were done on a HITAC M-280H computer at the Hokkaido University Computing Center using our own programs. The atomic scattering factors and anomalous dispersion corrections were taken from the International Tables.4)

Results and Discussion

The obtained molecular structure is depicted in Fig. 1. The molecule has a bicyclo[3.3.0]octane skeleton where an eight-membered ring is bridged by a dative bond formed between the S(1) and B(5) atoms. As Fig. 2 shows, of the two five-membered rings, one (S(1), C(2), C(3), C(4), and B(5)) adopts an envelope conformation; the C(3) atom deviates remarkably from the C(2)–S(1)–B(5)–C(4) mean plane onto the opposite side to the C(6) and C(8) atoms. On the other hand, the remaining ring has a half-chair conformation with an approximate two-fold rotation axis through the S(1) atom; however, this conformation is not very different from the envelope one where the C(7) atom deviates from the C(8)–S(1)–B(5)–C(6) plane onto the same side as the C(2) and C(4) atoms. Accordingly, it may be said that the conformation of the present bicyclic system as a whole resembles the most stable C_s conformation of *cis*-bicyclo[3.3.0]octane (**2**).5)

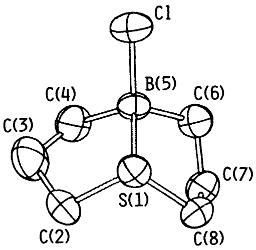

Fig. 1. A perspective view of the 5-chloro-1-thia-5-boracyclooctane molecule. Each non-hydrogen atom is represented as a thermal ellipsoid enclosing a 50% probability.

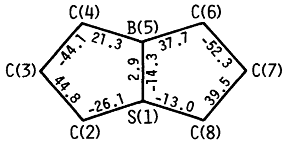

Fig. 2. The torsion angles (ϕ/°). The torsion angles relevant to atoms which form the same ring are given in the ring. The e.s.d.'s are 0.3—0.7°.

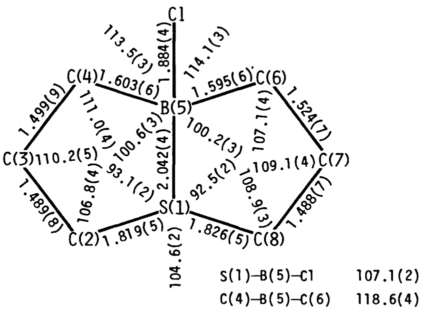

Fig. 3. The bond distances (l/Å) and angles (θ/°) and estimated standard deviations.

As Fig. 3 shows, the S(1)–B(5) bond distance is considerably longer than the S–B distances (av. 1.927 Å) in the adamantane-like compound $[CH_2(SBH_2)_2]_2$6) in which each of the sulfur and boron atoms forms two equivalent S–B bonds. Such a long bond distance (2.04(2) Å) has already been found for the S–B dative bonds by which the two 3,4-diethyl-2,5-diiodo-1,2,5-thiadiborolene molecules form a centrosymmetric dimer.7) The average (1.599 Å) of the B(5)–C(4) and B(5)–C(6) bond ditances lies midway between the B(sp^2)–C(sp^3) distance (1.570(4) Å) in dimethyl(methylthio)borane8) and the B(sp^3)–C(sp^3) distance (av 1.632 Å) in lithium tetramethylborate,9) whereas the B(5)–Cl bond distance is somewhat longer than the B(sp^3)–Cl distance (av. 1.864 Å) in boron trichloride-trimethylamine complex.10) The S(1)–C(2) and S(1)–C(8) bond distances are almost equal to the standard S–C(sp^3) distance (1.82 Å).

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