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The Crystal Structure of 7-Hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]pyridine, $C_6H_7N_2BSO$

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The crystal and molecular structure of 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]-pyridine has been studied by the aid of three-dimensional X-ray integrated film data. The symmetry is monoclinic, space group $P2_1/c$. The unit cell contains 4 molecules $C_6H_7N_2BSO$ and the cell dimensions are $a=7.732(4)$, $b=10.059(4)$, $c=11.946(6)$ Å, $\beta=124.56(6)°$. The structure has been refined to an R-value of 0.080 (1135 independent reflections). The fused rings, C_5H_2BS, are approximately planar. Neglecting the substituents, the largest deviation from the best plane is 0.03 Å. The average of the various distances within the pyridine-like skeleton C_3N_2B is close to 1.40 Å.

Gronowitz and coworkers [1] have investigated several organoboron compounds from physicochemical and synthetic points of view. The aim of the present study was to investigate the planarity of the borazaropyridine ring which is isoelectronic with the pyridine ring, and also to determine its bond lengths. The substance chosen for this investigation was the compound 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]pyridine. A study of the crystal structure of a related monocyclic compound, *e.g.* 5-ethyl-3-hydroxy-3,2-borazaropyridine,[2] would have been more appropriate for our purposes, but we have hitherto not succeeded in protecting these single crystals from deteriorating during the X-ray work.

7-Hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]pyridine, $C_6H_7N_2BSO$, was first synthesized by Gronowitz and Namtvedt.[3] Single crystals suitable for this study were kindly supplied by Dr. A. Maltesson. X-Ray powder diffraction photographs were recorded in a Guinier-Hägg focusing camera with Cu$K\alpha_1$ radiation and potassium chloride ($a=6.2909$ Å) added as an internal standard. The following lattice parameters were obtained with the aid of least-squares calculations: $a=7.732(4)$, $b=10.059(4)$, $c=11.946(6)$ Å, $\beta=124.56(6)°$, $V=768$ Å^3. The density observed by flotation methods was 1.40 g cm^{-3}. Assuming 4 formula units $C_6H_7N_2BSO$ per unit cell, the calculated density is 1.43 g cm^{-3}. The needle-shaped single crystals used for the X-ray work were enclosed in a Lindemann capillary over a saturated solution of the substance in water. The reason is that the substance decomposes in air of normal relative humidity. The capillary was mounted on an integrating Weissenberg camera, in such a way that the needle axis [001] was parallel to the rotation axis. The layers $hk0$ to $hk10$ were registered with Cu$K\alpha$ radiation. The multiple film technique was used, and the intensities of the reflections were measured with the aid of a Nonius Mark II micro densitometer. The following conditions limiting possible reflections were found: hkl, no conditions; $h0l$, $l=2n$; $0k0$, $k=2n$. These extinctions are characteristic of the space group $P2_1/c$ (No. 14). The intensities were corrected for Lorentz and polarization effects, but not for the absorption effects ($\mu=31.3$ cm^{-1}).

The crystal structure was solved by means of symbolic addition methods, using the program GAASA.[4] The program worked automatically, and peaks corresponding to the 11 non-hydrogen atoms in the asymmetric part of the unit cell could be recognized in the first E-map. The positions thus obtained were refined by means of least-squares calculations

using anisotropic temperature factors for all atoms. Difference Fourier maps revealed the positions of all hydrogen atoms except the one attached to the oxygen atom. A final refinement including all atoms but one hydrogen atom gave a conventional R value of 0.080 for all observed 1135 reflections. The R value for the 1121 reflections actually used in the refinement was 0.068. The reflections given non-zero weight in the refinement had $|F_o|$ values according to $0.5 \leq |F_o|/|F_c| \leq 2.0$. Cruickshank's weighting scheme with $A=1.5$, $C=0.17$ and $D=0$ was used. The S value (goodness of fit) was 0.17, and thus deviated heavily from 1, which is not unusual using film data. The final weighting scheme gave for ten $|F_o|$ intervals values of $\overline{w\Delta^2}$ between 0.6 and 1.6. The final positional and thermal parameters of the atoms are given in Table 1. Lists of observed and calculated $|F|$ values can be obtained on request from the Division of Inorganic Chemistry 2, Lund.

Table 1. Final positional and thermal parameters for 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-c] pyridine. Standard deviations are given in parentheses. The anisotropic thermal parameters are based on the expression: exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

Atom	x	y	z	B(Å^2)
S(1)	0.66581(14)	0.05643(10)	0.17299(9)	For β_{ij},
C(2)	0.5365(6)	−0.0695(4)	0.1926(4)	see below
C(3)	0.5707(6)	−0.0684(4)	0.3173(5)	
C(4)	0.7715(6)	0.0737(4)	0.5335(4)	
N(5)	0.8941(4)	0.1720(3)	0.6025(3)	
N(6)	0.9701(4)	0.2480(3)	0.5442(3)	
B(7)	0.9218(6)	0.2304(4)	0.4102(4)	
C(8)	0.7695(5)	0.1162(3)	0.3330(3)	
C(9)	0.7018(5)	0.0394(3)	0.3972(3)	
C(10)	1.1121(7)	0.3527(4)	0.6355(4)	
O	1.0158(4)	0.3131(3)	0.3707(3)	
H(21)	0.448(7)	−0.134(4)	0.117(4)	2.3(8)
H(31)	0.516(8)	−0.126(5)	0.346(5)	3.3(10)
H(41)	0.729(6)	0.022(4)	0.582(4)	1.6(7)
H(101)	1.046(13)	0.425(8)	0.662(9)	8.7(22)
H(102)	1.177(8)	0.400(5)	0.594(5)	3.2(10)
H(103)	1.217(8)	0.312(6)	0.732(5)	3.9(11)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.02703(28)	0.01074(11)	0.00885(13)	−0.00142(12)	0.00712(14)	−0.00154(7)
C(2)	0.0260(10)	0.0119(5)	0.0118(5)	−0.0020(5)	0.0071(5)	−0.0021(3)
C(3)	0.0238(9)	0.0099(4)	0.0144(6)	−0.0020(5)	0.0096(6)	−0.0009(3)
C(4)	0.0274(9)	0.0099(4)	0.0115(4)	0.0002(4)	0.0112(5)	0.0006(3)
N(5)	0.0274(8)	0.0094(3)	0.0098(3)	0.0004(4)	0.0097(4)	0.0002(2)
N(6)	0.0247(7)	0.0079(3)	0.0099(3)	0.0000(3)	0.0086(4)	−0.0006(2)
B(7)	0.0228(9)	0.0081(4)	0.0095(4)	0.0020(4)	0.0077(5)	0.0002(3)
C(8)	0.0203(7)	0.0078(3)	0.0092(4)	0.0017(4)	0.0067(4)	0.0006(2)
C(9)	0.0218(8)	0.0089(3)	0.0092(4)	0.0003(4)	0.0081(4)	−0.0003(2)
C(10)	0.0344(11)	0.0091(4)	0.0113(5)	−0.0024(5)	0.0099(6)	−0.0020(3)
O	0.0379(9)	0.0103(3)	0.0123(3)	−0.0047(4)	0.0138(5)	−0.0011(2)

DISCUSSION OF THE STRUCTURE

Intramolecular distances. One molecule of 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-c]-pyridine is projected on its best plane in Figs. 1a – 1c, where distances, angles, and deviations from the best plane are given. *E.s.d.*'s for distances between non-hydrogen atoms are 0.004 Å for carbon-sulfur interactions and

0.005 – 0.006 Å for other distances. *E.s.d.*'s for carbon-ring hydrogen bond lengths are 0.04 – 0.05 Å, and for carbon-methyl hydrogen distances 0.05 – 0.09 Å. *E.s.d.*'s for angles between non-hydrogen atoms are 0.2 – 0.3° and for angles involving only one hydrogen atom 3 – 5°.

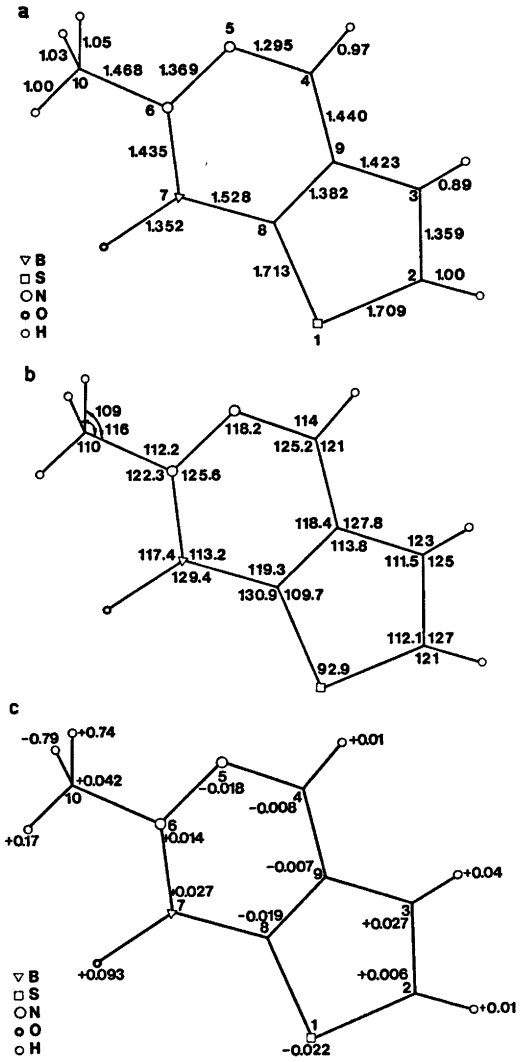

Fig. 1. Projection of one molecule of 7-hydroxy-6-methyl-7,6-borazarothieno[3,2-*c*]pyridine on its best plane. Fig. 1a shows the numbering of the atoms together with the intermolecular distances, Fig. 1b gives pertinent angles within the molecule, and Fig. 1c gives the deviations (Å) of the various atoms from a best plane calculated using only the nine ring atoms.

The various distances within the pyridine-like skeleton C_3N_2B differ significantly, but as expected their average is close to 1.40 Å. The C(4) – N(5) distance of 1.295(5) Å corresponds to a partial double bond and according to the curve given by Donohue, Lavine and Rollett [5] the π bond order is 0.67. The N(5) – N(6) distance of 1.369(4) Å is shorter than a single bond N – N and its length corresponds to π bond order of 0.45 according to calculations made by Sabesan and Ventkatesan.[6] The B(7) – N(6) distance of 1.435(5) Å is about the same as the B – N distance 1.424(1) Å found in hexachloroborazine in a recent refinement.[7] The B(7) – C(8) distance of 1.528(5) Å may be compared to the B – C distances in derivatives of the pyridine-like compound borin, C_5H_5B. Thus Huttner, Krieg and Gartzke,[8] in their paper on π complexes between cobolt(0) and two substituted borins, found an average B – C (ring) distance of 1.519(5) Å. The B – OH distance in the present compound is 1.352(5) Å. It is appreciably shorter than the value 1.395(7) Å given for a boron-ether oxygen distance in Ref. 8 but agrees fairly well with the value of 1.366 Å given for a formal single bond between three-coordinated boron and oxygen in a number of borates.[9] One noteworthy thing about the angles in the pyridine-like skeleton C_3BN_2 is that those around boron deviate appreciably from 120°. The distances and angles within the thiophene ring are normal. The fused rings C_5N_2BS are approximately planar. Neglecting the substituents, the best plane was calculated for the nine atoms of the ring skeleton. The largest deviations of the ring atoms from the plane occurred for the B(7) and C(3) atoms and amounted to +0.03 Å in both cases. The substituents O and C(10) were at distances of +0.09 and +0.04 Å, respectively, from the best plane (*cf.* Fig. 1c). The dihedral angle between the thiophene ring and the borazaropyridine ring is 178(6)° and does thus not deviate significantly from zero. The respective least-squares planes were calculated using only ring atoms. It may also be noted that one of the methyl hydrogen atoms is situated nearly in the ring plane, whereas the other two hydrogen atoms of the same group are situated at equal distances above and below the best plane.

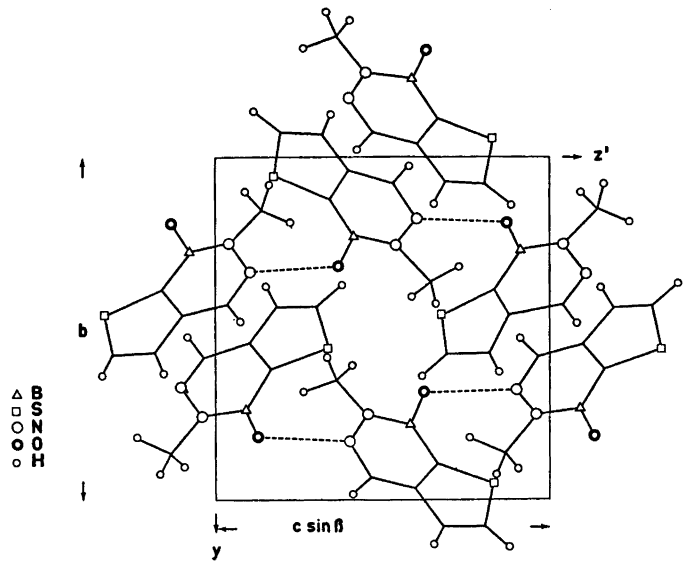

Fig. 2. Projection of the structure on a plane perpendicular to the *a*-axis.

Intermolecular distances. Fig. 2 shows the projection of the crystal structure on a plane perpendicular to the *a* axis. The molecules are joined by O–H···N hydrogen bonds to two chains, identical by centrosymmetry. The corresponding O–N distances are 2.789(4) Å.

A final difference map showed a peak corresponding to 0.24 of the height of a hydrogen atom at the expected position of the H(OH) atom. However, the map also revealed peaks and pits, which measured in the same scale amounted to 0.3 and 0.6 units, respectively.

Except for the hydrogen bond just mentioned no other intermolecular distances shorter than the corresponding sums of the van der Waals radii occur.

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