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Molecular Structure and Two Crystal Structures of 6-Isothiocyano-decaborane, $6\text{-B}_{10}\text{H}_{13}\text{NCS}$

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Received March 7, 1973

The reaction of mercuric thiocyanate with $6,9\text{-B}_{10}\text{H}_{12}(\text{SMe}_2)_2$ or $6,9\text{-B}_{10}\text{H}_{12}(\text{SEt}_2)_2$ yields $\text{B}_{10}\text{H}_{13}\text{NCS}$. A new preparation from NaNCS and decaborane is described. X-Ray structure determinations prove that the NCS group is attached covalently at the N atom to B6 of decaborane. The B-N bond is 1.435 Å in length, too short for a pure single bond. Identical molecular structures of $\text{B}_{10}\text{H}_{13}\text{NCS}$ have been found in two crystal structures, both in space group $P2_1/n$ with four molecules per unit cell. The form found at 13° has unit cell parameters $a = 7.352$ (5), $b = 14.611$ (5), $c = 10.561$ (5) Å, and $\beta = 105.273$ (13) $^\circ$. Full-matrix, least-squares refinement gives $R = \Sigma \|F_o\| - |F_c| / \Sigma \|F_o\| = 0.063$ for 1181 X-ray diffraction maxima measured on a Picker four-circle diffractometer. Crystals grown at room temperature had unit cell parameters of $a = 7.93$ (1), $b = 14.78$ (1), $c = 9.47$ (1) Å, and $\beta = 101.68$ (2) $^\circ$. Full-matrix, least-squares refinement gives $R = 0.087$ for 716 reflections.

Several questions arise when SCN^- reacts with boranes: (a) Is the SCN attached at S or N, provided that a simple reaction occurs? (b) Is the SCN attached at a single boron atom or does it bridge between two boron atoms of a polyborane? (c) At which boron (or borons) does reaction occur? (d) Is there a contribution of π bonding to the pseudohalogen ligand?

The compound of this study $\text{B}_{10}\text{H}_{13}\text{NCS}$ was first prepared by the reaction of mercuric thiocyanate with 6,9-bis-(dimethyl sulfide)decaborane or with the analogous diethyl compound.¹ Infrared and nmr spectra indicated substitution at B6. However, migration of the substituent into the bridge position remained as a possibility. Also, preference was expressed,¹ correctly as we shall prove, for bonding from the boron cage to nitrogen of the SCN group on the basis of infrared spectra.

Infrared spectra also give strong support for the structure $\text{H}_3\text{N}\cdot\text{BH}_2\text{SCN}$ but do not exclude the alternative $\text{H}_3\text{N}\cdot\text{BH}_2\text{NCS}$. This compound and salts of BH_3NCS^- were prepared² by reaction of diborane with thiocyanates. We shall prove in the following paper³ that this neutral compound is $\text{H}_3\text{N}\cdot\text{BH}_2\text{NCS}$, an isothiocyanate.

The formation of $\text{B}_{10}\text{H}_{12}\text{SCN}^-$ has been reported² from decaborane and thiocyanate in dimethoxyethane. Although the structure was not established, favor was expressed for substitution at B6 on the basis of the X-ray study of $\text{B}_{10}\text{H}_{12}(\text{NCCH}_3)_2$,⁴ although a B6,B9 bridge was an alternative. In a later note⁵ this ion, revised as $\text{B}_{10}\text{H}_{12}\text{NCS}^-$, was shown to degrade in water to $\text{B}_9\text{H}_{13}\text{NCS}^-$. In the present study, we have isolated a compound identical with $\text{B}_{10}\text{H}_{13}\text{NCS}$, prepared from decaborane and mercury thiocyanate, by adding anhydrous HCl to $\text{B}_{10}\text{H}_{12}\text{NCS}^-$ in dimethoxyethane.

On the basis of the structure investigations described below we show that all of these compounds are isothiocyanates, in which the nitrogen of the SCN group is covalently bonded to boron.

Experimental Section

Preparation. Our first sample of $\text{B}_{10}\text{H}_{13}\text{NCS}$ was supplied by S. Hermanek. Additional material was synthesized by his method¹

(1) B. Stibr, J. Plešek, F. Hanousek, and S. Hermanek, *Collect. Czech. Chem. Commun.*, **35**, 1794 (1971).

(2) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **83**, 2471 (1961).

(3) D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2920 (1973).

(4) J. M. Reddy and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **81**, 754 (1959).

(5) E. L. Muetterties and W. H. Knoth, *Inorg. Chem.*, **4**, 1498 (1965).

in our laboratory. In order to relate this compound to the $\text{B}_{10}\text{H}_{12}\text{NCS}^-$ ion,^{2,5} we prepared $\text{B}_{10}\text{H}_{13}\text{NCS}$ from decaborane and sodium thiocyanate as follows. A 0.025-mol sample of NaNCS and 0.02 mol of $\text{B}_{10}\text{H}_{14}$ were stirred in 60 ml of dimethoxyethane until evolution of hydrogen ceased. Anhydrous HCl was bubbled in for 1 hr, and dimethoxyethane was removed. The sublimate was isolated in 27% yield. This product had an infrared spectrum identical with that published¹ for $\text{B}_{10}\text{H}_{13}\text{NCS}$ and a melting point (84–85 $^\circ$) close to that published earlier¹ (83–85 $^\circ$). Single crystals of this product gave the same unit cell parameters and the same $0kl$ and $1kl$ intensities as those of the authentic $\text{B}_{10}\text{H}_{13}\text{NCS}$. This relationship between $\text{B}_{10}\text{H}_{12}\text{NCS}^-$ and $\text{B}_{10}\text{H}_{13}\text{NCS}$ leads us to the conclusion that both the ion and neutral molecule have the same mode of binding of the NCS group to the boron cage, as discussed below.

X-Ray Data. Single crystals of both the low-temperature form and the room-temperature form were grown by slow sublimation after $\text{B}_{10}\text{H}_{13}\text{NCS}$ was sealed into evacuated glass tubes. All work on the low-temperature form was done in a room at 13 $^\circ$, but the use of this temperature below in identifying this form does not imply that this is a transition temperature. This form was grown into fairly thick plates, usually elongated along the a axis, by placing one end of the glass tube in water at 38 $^\circ$. Each single crystal was mounted in a glass capillary for X-ray study.

Weissenberg photographs of the $0kl$ and $1kl$ levels and precession photographs of the $h0l$, $h1l$, $hk0$, and hkl levels showed Laue symmetry $C_{2h}-2/m$. Extinctions were consistent with the space group $P2_1/n$. A least-squares fit, from two crystals, of 28 Bragg angles measured on a Picker diffractometer yielded cell parameters of $a = 7.352$ (5), $b = 14.611$ (5), $c = 10.561$ (5) Å, and $\beta = 105.27$ (1) $^\circ$. Assumption of four molecules per unit cell gave a calculated density of 1.09 g/cm³.

Intensities of several check reflections gradually declined on exposure of the crystal to X-rays. Therefore, three crystals were used for the data collection. A crystal was discarded when intensities of check reflections dropped by 10%. All crystals, ranging in length from 0.4 to 0.7 mm, were mounted so that the a axis coincided with the goniometer axis. Three-dimensional data were collected on a four-circle Picker automated diffractometer, using $\text{Cu K}\alpha$ radiation filtered through Ni foil. Each diffraction maximum having $2\theta < 118.0^\circ$ was scanned through ω over a range of 2.2 $^\circ$ at a rate of 1 $^\circ$ /min. We used a takeoff angle of 3.5 $^\circ$ and 1-mm collimators for both incident and diffracted beams.

Because $\mu = 20.2$ cm⁻¹, transmission coefficients were required, for which we used a gaussian quadrature method.⁶ These coefficients ranged from 0.499 to 0.728 for the first crystal, from 0.561 to 0.716 for the second, and from 0.564 to 0.682 for the third. Data from the three crystals, including almost two complete asymmetric units, were placed on a common scale by Rae's method,⁷ giving $R = \Sigma H_i |S_i| / \Sigma H_i - \bar{I}_H / \Sigma H_i \bar{I}_H = 0.03$, where H is hkl , $I_{H,i}$ is the intensity of reflection H in data set i , \bar{I}_H is the average value of reflection H , and S_i is the scale factor for set i . Several reflections which were obvious victims of extinction were removed before correlation. The final data set included 1181 reflections with $I > 2\sigma(I)$, where $\sigma(I) = (C + (T_c/2T_b)^2(B_1 + B_2))^{1/2}$. Here, C is the total count for the scan, B_1 and B_2 are the background counts, T_c

(6) C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

(7) A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

Table I. B, C, N, and S Coordinates and Anisotropic Thermal Parameters of the 13° Form^{a, b}

	<i>x</i>	<i>y</i>	<i>z</i>	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
S	0.7521 (2)	0.0037 (1)	-0.1540 (1)	312 (2)	84 (7)	93 (1)	-76 (3)	148 (2)	-82 (2)
C	0.7437 (5)	0.0419 (3)	-0.0156 (3)	208 (9)	40 (2)	86 (4)	-24 (7)	59 (9)	-13 (5)
N	0.7414 (5)	0.0680 (3)	0.0867 (3)	311 (9)	47 (2)	75 (3)	37 (7)	95 (8)	-29 (5)
B1	0.8362 (7)	0.1377 (3)	0.4856 (4)	279 (12)	60 (3)	58 (4)	75 (11)	12 (11)	7 (6)
B2	0.9233 (6)	0.1354 (4)	0.3434 (5)	203 (10)	68 (3)	92 (4)	24 (12)	66 (11)	-29 (8)
B3	0.8860 (7)	0.2418 (4)	0.4150 (4)	202 (11)	66 (4)	97 (5)	-63 (13)	70 (10)	-43 (7)
B4	0.7137 (6)	0.2391 (4)	0.5035 (4)	275 (12)	47 (3)	68 (5)	-2 (10)	66 (11)	-24 (6)
B5	0.7356 (7)	0.0643 (3)	0.3583 (4)	324 (13)	41 (3)	88 (4)	76 (12)	108 (11)	19 (6)
B6	0.7439 (6)	0.1145 (3)	0.2068 (4)	210 (10)	40 (3)	84 (4)	-7 (10)	88 (10)	-5 (6)
B7	0.8104 (7)	0.2298 (4)	0.2453 (4)	306 (13)	48 (3)	97 (4)	-81 (10)	175 (10)	-13 (6)
B8	0.6702 (7)	0.2979 (3)	0.3517 (4)	348 (13)	40 (3)	81 (4)	-5 (13)	96 (12)	-15 (6)
B9	0.4910 (7)	0.2384 (4)	0.4000 (4)	250 (11)	60 (3)	93 (5)	31 (10)	102 (11)	-20 (7)
B10	0.5936 (7)	0.1330 (4)	0.4632 (4)	342 (15)	51 (3)	97 (5)	-22 (11)	185 (12)	-2 (7)

^a Anisotropic temperature factors are of the form $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}]$. ^b Standard deviations are from full-matrix, least-squares refinement.

is the scan time, and T_b is the time for a single background.⁸

Procedures for study of the room-temperature form were nearly identical with those described above, except that the crystals were grown at about 23°. The space group is also $P2_1/n$, and cell parameters are $a = 7.93$ (1), $b = 14.78$ (1), $c = 9.47$ (1) Å, and $\beta = 101.68$ (2)°. One single crystal, $0.34 \times 0.16 \times 0.10$ mm in dimensions, was used for data collection on the Picker diffractometer, with a takeoff angle of 3.3° and an ω scan of 2.0°. Periodic check of two reflections indicated a linear decline of intensities with time, which was due primarily to sublimation of the crystal, not to deterioration in the X-ray beam. The maximum decline was approximately 50%. Hence, a linear correction was applied to the complete data set. Transmission coefficients, ranging from 0.71 to 0.84, were also applied. In the final refinement we used 716 reflections having $I > 3\sigma(I)$.

Solution of Structures and Refinement. The low-temperature form was solved by initial location of sulfur coordinates in a Patterson function. Its y coordinate of zero led to phases for only half of the reflections and to a false mirror plane in the electron density map based upon phases of sulfur only. At this stage the value of $R = \sum |F_o| - |F_c| / \sum |F_o|$ was 0.65. However, the carbon bonded to sulfur was found in both the Patterson and electron density maps. Its inclusion in the structure factors led to an R value of 0.56 and to an electron density showing all nonhydrogen atoms. Straightforward least-squares refinement, using block and full matrices including anisotropic thermal parameters, reduced R to 0.11. An electron density map from which all nonhydrogen atoms were subtracted revealed the 13 unique hydrogen atoms. In the subsequent refinements the isotropic temperature factors of the hydrogens were fixed at 5.0 Å². All other thermal parameters, coordinates, and a secondary extinction correction factor were refined. The secondary extinction factor, g , was applied to the calculated structure factors using the expression $F_c^{2*} = F_c^2 / (1 + \beta g F_c^2)$, where F_c^{2*} is the corrected value of F_c^2 and β is an angular factor.⁹ The final value of g is 34.3×10^{-6} . In addition, eight reflections which were much affected by extinction were removed. The final full-matrix, least-squares cycle gave an R value of 0.063 and $R_w = [\sum w(k^2 |F_o|^2 - |F_c|^2)^2 / \sum w(k |F_o|)^4]^{1/2} = 0.089$. These refinements minimized $\sum w(k^2 |F_o|^2 - |F_c|^2)^2$, where k is the scale factor and $w = 1/F_o^2$ for $F_o \geq 17.4$ and $w = 1/17.4 F_o$ for $F_o \leq 17.4$.

A final difference electron density map from which all atoms were subtracted had highest peaks at about 0.2 e/Å³, at the sulfur position (anomalous scattering by the sulfur atom was neglected). In a final Fourier map 12 of the 13 hydrogens had peak densities in the range 0.56–1.35 e/Å³. The H5 atom, which is in the $y = 0.0$ plane, as are two of the sulfur atoms, had a maximum height of only 0.20 e/Å³. The B, C, N, and S atomic scattering factors are from the "International Tables for X-Ray Crystallography." The H atomic scattering factor was especially prepared for covalent hydrogen for use in the CRYRM computing system,⁹ which was used for all refinements and electron density maps.

The room-temperature form was solved and refined by these same procedures. The final cycles of full-matrix, least-squares refinement reduced R to 0.087 and R_w to 0.145. Hydrogen atoms were assigned fixed values of 6.0 Å² for isotropic temperature factor

constants in these refinements. No corrections for secondary extinction were required. In a final electron density difference map the peak heights of the hydrogen atoms were in the range 0.49–0.91 e/Å³. The two highest peaks in the final difference map from which all atoms, including hydrogen, had been subtracted were on opposite sides of sulfur at peak heights of 0.30 e/Å³.

Results

This molecule, B₁₀H₁₃NCS, is an isothiocyanate. The nitrogen atom is bonded to atom B6 of the decaborane framework (Figure 1).

Crystal and molecular parameters of the low-temperature form (Tables I–IV) and of the room-temperature form (Tables V and VI) include coordinates, thermal parameters, bond distances, and bond angles. Observed and calculated structure factors are available for both forms.¹⁰ In Table VII we assume C_{2v} symmetry for the boron framework and then compare average B–B distances in each of these two forms with those in decaborane.¹¹ Because the B₁₀H₁₃NCS molecules in these two crystal structures are identical within experimental errors, we refer only to the more precise results of the low-temperature form in the remainder of this paragraph. The B(6)···B(9) distance is 3.59 Å in B₁₀H₁₃NCS and 3.57 Å in B₁₀H₁₄. The B(2)B(6)N angle of 131° and the less reliable B(4)B(9)H(9) angle of 134° in B₁₀H₁₃NCS compare with 132° in B₁₀H₁₄. These results, and those in Table VII, indicate only small distortions of decaborane upon reaction with thiocyanate. X-Ray values of the average BH (terminal) bond distance of 1.08 (8) Å and the BH (bridge) bond distance of 1.25 (7) Å are less than those of the neutron diffraction study¹¹ by the expected amount (almost 0.1 Å).¹² The BNCS group is almost linear, having a B(6)NC angle of 171° and an NCS angle of 178°. Also the N, C, and S atoms are 0.02, 0.21, and 0.45 Å from the well-defined plane of B(2), B(4), B(6), and B(9). This plane makes an angle of 84° with respect to the planes of B(6), N, C, and S, which are coplanar within 0.014 Å. We comment on these results in the Discussion.

Packing in the two crystalline forms of B₁₀H₁₃NCS (Figures 2 and 3) is similar in the placement of the boron cage near the screw axis. The isothiocyanate group is extended away from this axis in a direction opposite to that of a screw-related molecule in both crystal forms. However, there are differences as follows.

In the low-temperature form, the packing around the screw axis involves reasonable van der Waals contact between H(8)

(8) C. W. Burnham, Y. Ohashi, S. Hafner, and D. Virgo, *Amer. Mineral.*, **56**, 850 (1971).

(9) D. J. Duchamp of the Upjohn Co., R. E. Marsh and his research group at the California Institute of Technology, and coworkers at Harvard University.

(10) See paragraph at end of paper regarding supplementary material.

(11) A. Tippe and W. C. Hamilton, *Inorg. Chem.*, **8**, 464 (1969).

(12) T. A. Halgren, R. J. Anderson, D. S. Jones, and W. N. Lipscomb, *Chem. Phys. Lett.*, **8**, 547 (1971).

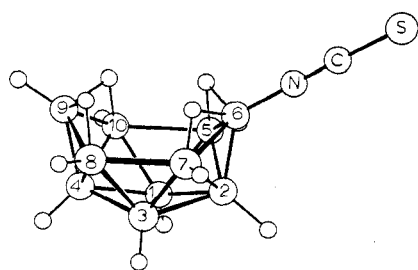


Figure 1. The molecular structure and numbering system for $B_{10}H_{13}NCS$.

Table II. Hydrogen Coordinates of the 13° Form

	x	y	z
H1	0.9154 (45)	0.1062 (23)	0.5717 (30)
H2	1.0845 (44)	0.1069 (26)	0.3537 (36)
H3	1.0029 (43)	0.2851 (25)	0.4473 (30)
H4	0.7529 (44)	0.2712 (30)	0.6033 (39)
H5	0.7498 (48)	-0.0019 (26)	0.3739 (28)
H7	0.8669 (44)	0.2663 (28)	0.1835 (33)
H8	0.6445 (44)	0.3685 (27)	0.3324 (31)
H9	0.3504 (45)	0.2673 (25)	0.4070 (32)
H10	0.5483 (55)	0.0929 (27)	0.5319 (31)
H5-6 ^a	0.6080 (44)	0.0824 (24)	0.2540 (31)
H6-7	0.6760 (45)	0.1912 (26)	0.1845 (29)
H8-9	0.5048 (46)	0.2655 (27)	0.2987 (29)
H9-10	0.4636 (59)	0.1497 (24)	0.3671 (37)

^a H5-6 means a bridge hydrogen between B(5) and B(6).

Table III. Bond Distances (Å) of the 13° Form

B1-B2	1.781 (8)	B6-B7	1.773 (8)
-B3	1.773 (8)	-N	1.435 (6)
-B4	1.769 (8)	-H5-6	1.31 (4)
-B5	1.727 (6)	-H6-7	1.23 (4)
-B10	1.737 (8)	B7-B8	1.981 (8)
-H1	1.05 (3)	-H7	1.01 (4)
B2-B3	1.781 (8)	-H6-7	1.17 (3)
-B5	1.768 (8)	B8-B9	1.763 (8)
-B6	1.707 (6)	-H8	1.06 (4)
-B7	1.793 (8)	-H8-9	1.29 (3)
-H2	1.23 (3)	-B9-B10	1.768 (8)
B3-B4	1.762 (8)	-H9	1.14 (4)
-B7	1.740 (6)	-H8-9	1.17 (4)
-B8	1.754 (7)	-H9-10	1.34 (4)
-H3	1.05 (3)	B10-H10	1.05 (4)
B4-B8	1.773 (7)	-H9-10	1.22 (4)
-B9	1.713 (6)	N-C	1.149 (5)
-B10	1.779 (8)	C-S	1.581 (4)
-H4	1.12 (4)		
B5-B6	1.776 (7)		
-B10	1.983 (8)		
-H5	0.98 (4)		
-H5-6	1.27 (3)		

and the C-N bond of the molecule above it. Atom H(8) of one molecule is 3.09 Å from N and 3.16 Å from C of an adjacent molecule. Atom H(9) is 3.29 Å from N and 3.07 Å from C in a neighboring molecule, and, similarly, H(3) is 2.91 Å from N and 3.05 Å from C of another molecule. These contacts between the CN pair and hydrogen atoms of a different molecule are an important feature of the packing. The closest intermolecular S...H approach is 2.87 Å, close to the van der Waals contact, and there are five longer S...H contacts less than 3.5 Å. The shortest intermolecular H...H contact is 2.44 Å, and there are ten more up to 3.0 Å. None of these distances involve screw-related molecules, for which 3.13 Å is the shortest H...H distance. Antiparallel NCS units have opposed atom distances of 3.73-3.89 Å. These units also have the closest S...S approaches, at 4.20 Å.

In the room-temperature form, there are differences in detail, but similar intermolecular contacts are observed. Molecules related by a screw axis have H(9) 3.32 Å from N and

Table IV. Bond Angles (deg) of the 13° Form

B2-B1-B3	60.1 (4)	B2-B6-H5-6	104 (2)
B2-B1-B4	114.3 (5)	B2-B6-H6-7	101 (2)
B2-B1-B5	60.5 (4)	B5-B6-B7	105.0 (5)
B2-B1-B10	118.0 (5)	B5-B6-N	127.3 (5)
B2-B1-H1	119 (3)	B5-B6-H5-6	46 (2)
B3-B1-B4	59.6 (4)	B5-B6-H6-7	116 (2)
B3-B1-B5	107.4 (5)	B7-B6-N	126.3 (5)
B3-B1-B10	107.2 (5)	B7-B6-H5-6	116 (2)
B3-B1-H1	128 (3)	B7-B6-H6-7	41 (2)
B4-B1-B5	118.5 (5)	N-B6-H5-6	109 (2)
B4-B1-B10	61.0 (4)	N-B6-H6-7	111 (2)
B4-B1-H1	117 (3)	H5-6-B6-H6-7	95 (3)
B5-B1-B10	69.9 (4)	B2-B7-B3	60.5 (4)
B5-B1-H1	115 (3)	B2-B7-B6	57.2 (4)
B10-B1-H1	115 (3)	B2-B7-B8	106.8 (5)
B1-B2-B3	59.7 (4)	B2-B7-H7	125 (3)
B1-B2-B5	58.2 (4)	B2-B7-H6-7	98 (3)
B1-B2-B6	110.3 (5)	B3-B7-B6	109.0 (5)
B1-B2-B7	105.0 (5)	B3-B7-B8	55.8 (4)
B1-B2-H2	119 (3)	B3-B7-H7	123 (3)
B3-B2-B5	105.3 (5)	B3-B7-H6-7	127 (3)
B3-B2-B6	110.1 (5)	B6-B7-B8	117.0 (5)
B3-B2-B7	58.3 (4)	B6-B7-H7	119 (3)
B3-B2-H2	121 (3)	B6-B7-H6-7	43 (3)
B5-B2-B6	61.5 (4)	B8-B7-H7	118 (3)
B5-B2-B7	104.5 (5)	B8-B7-H6-7	94 (3)
B5-B2-H2	123 (3)	H7-B7-H6-7	109 (4)
B6-B2-B7	60.8 (4)	B3-B8-B4	59.9 (4)
B6-B2-H2	122 (3)	B3-B8-B7	55.1 (4)
B7-B2-H2	127 (3)	B3-B8-B9	109.2 (5)
B1-B3-B2	60.2 (4)	B3-B8-H8	129 (3)
B1-B3-B4	60.1 (4)	B3-B8-H8-9	130 (2)
B1-B3-B7	107.6 (5)	B4-B8-B7	105.8 (5)
B1-B3-B8	107.2 (5)	B4-B8-B9	58.0 (4)
B1-B3-H3	129 (3)	B4-B8-H8	129 (3)
B2-B3-B4	114.8 (5)	B4-B8-H8-9	98 (2)
B2-B3-B7	61.2 (4)	B7-B8-B9	117.2 (5)
B2-B3-B8	118.1 (5)	B7-B8-H8	118 (3)
B2-B3-H3	117 (3)	B7-B8-H8-9	98 (2)
B4-B3-B7	117.7 (6)	B9-B8-H8	115 (3)
B4-B3-B8	60.6 (4)	B9-B8-H8-9	42 (2)
B4-B3-H3	119 (3)	H8-B8-H8-9	100 (4)
B7-B3-B8	69.1 (4)	B4-B9-B8	61.3 (4)
B7-B3-H3	114 (3)	B4-B9-B10	61.5 (4)
B8-B3-H3	115 (3)	B4-B9-H9	134 (3)
B1-B4-B3	60.3 (4)	B4-B9-H8-9	106 (3)
B1-B4-B8	106.6 (5)	B4-B9-H9-10	103 (3)
B1-B4-B9	110.8 (5)	B8-B9-B10	105.2 (5)
B1-B4-B10	58.6 (4)	B9-B9-H9	127 (3)
B1-B4-H4	116 (3)	B8-B9-H8-9	47 (3)
B3-B4-B8	59.5 (4)	B8-B9-H9-10	118 (3)
B3-B4-B9	111.2 (5)	B10-B9-H9	127 (3)
B3-B4-B10	105.9 (5)	B10-B9-H8-9	121 (3)
B3-B4-H4	117 (3)	B10-B9-H9-10	44 (3)
B8-B4-B9	60.7 (4)	H9-B9-H8-9	104 (4)
B8-B4-B10	104.3 (5)	H9-B9-H9-10	107 (4)
B8-B4-H4	126 (3)	H8-9-B9-H9-10	98 (4)
B9-B4-B10	60.8 (4)	B1-B10-B4	60.4 (4)
B9-B4-H4	125 (3)	B1-B10-B5	54.8 (4)
B10-B4-H4	125 (3)	B1-B10-B9	109.7 (5)
B1-B5-B2	61.3 (4)	B1-B10-H10	115 (3)
B1-B5-B6	109.6 (5)	B1-B10-H9-10	131 (3)
B1-B5-B10	55.3 (4)	B4-B10-B5	105.9 (5)
B1-B5-H5	119 (3)	B4-B10-B9	57.8 (4)
B1-B5-H5-6	128 (2)	B4-B10-H10	123 (3)
B2-B5-B6	57.6 (4)	B4-B10-H9-10	105 (3)
B2-B5-B10	106.9 (5)	B5-B10-B9	117.8 (5)
B2-B5-H5	123 (3)	B5-B10-H10	114 (3)
B2-B5-H5-6	102 (2)	B5-B10-H9-10	93 (3)
B6-B5-B10	116.3 (5)	B9-B10-H10	124 (3)
B6-B5-H5	122 (3)	B9-B10-H9-10	49 (3)
B6-B5-H5-6	48 (2)	H10-B10-H9-10	111 (4)
B10-B5-H5	117 (3)	B6-N-C	171.0 (6)
B10-B5-H5-6	90 (2)	N-C-S	178.1 (6)
H5-B5-H5-6	112 (4)	B5-H5-6-B6	87 (3)
B2-B6-B5	61.0 (4)	B6-H6-7-B7	95 (4)
B2-B6-B7	62.0 (4)	B8-H8-9-B9	92 (2)
B2-B6-N	131.3 (6)	B9-H9-10-B10	87 (4)

Table V. B, C, N, and S Coordinates and Thermal Parameters of the Room-Temperature Form

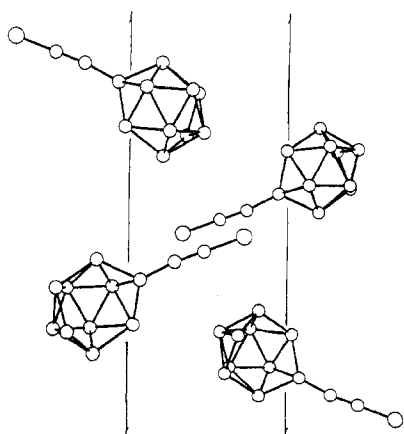
	<i>x</i>	<i>y</i>	<i>z</i>	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
S	0.8192 (4)	-0.0679 (2)	0.8926 (4)	175 (5)	57 (2)	175 (5)	53 (6)	38 (8)	36 (6)
C	0.6653 (12)	-0.0055 (7)	0.8376 (11)	197 (20)	44 (6)	111 (14)	-35 (20)	44 (32)	-12 (16)
N	0.5476 (11)	0.0420 (6)	0.7961 (9)	259 (19)	57 (6)	176 (15)	79 (18)	-54 (33)	-14 (16)
B1	0.2181 (16)	0.2055 (8)	0.4944 (12)	203 (24)	48 (7)	96 (15)	-37 (24)	78 (31)	-13 (19)
B2	0.2827 (15)	0.0963 (7)	0.5575 (12)	190 (23)	37 (6)	111 (16)	21 (23)	11 (34)	-45 (18)
B3	0.0713 (16)	0.1343 (8)	0.5585 (14)	197 (24)	36 (6)	151 (21)	19 (22)	22 (36)	9 (20)
B4	0.0523 (16)	0.2524 (8)	0.5715 (13)	203 (24)	34 (6)	122 (18)	14 (24)	33 (36)	7 (19)
B5	0.4219 (14)	0.1927 (10)	0.6079 (13)	196 (26)	44 (6)	105 (17)	-6 (24)	71 (32)	-21 (20)
B6	0.4063 (16)	0.0978 (9)	0.7283 (13)	260 (27)	42 (7)	127 (18)	36 (25)	69 (37)	-17 (20)
B7	0.1845 (16)	0.0752 (9)	0.7027 (13)	218 (28)	37 (7)	140 (18)	10 (24)	84 (31)	-44 (20)
B8	0.0269 (15)	0.1780 (9)	0.7154 (14)	151 (22)	53 (8)	151 (17)	43 (23)	82 (32)	49 (21)
B9	0.1255 (17)	0.2868 (10)	0.7455 (14)	226 (28)	45 (7)	160 (22)	33 (26)	40 (42)	-8 (23)
B10	0.2632 (16)	0.2949 (8)	0.6194 (15)	248 (26)	31 (6)	125 (19)	-35 (22)	75 (36)	-12 (19)

Table VI. Hydrogen Coordinates of the Room-Temperature Form

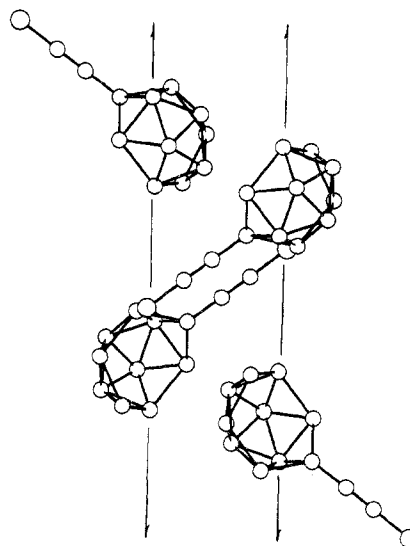
	<i>x</i>	<i>y</i>	<i>z</i>
H1	0.217 (10)	0.222 (7)	0.382 (8)
H2	0.337 (11)	0.049 (6)	0.489 (8)
H3	-0.028 (11)	0.103 (7)	0.502 (11)
H4	-0.064 (11)	0.284 (6)	0.506 (10)
H5	0.536 (10)	0.205 (7)	0.564 (9)
H7	0.112 (11)	0.018 (7)	0.737 (9)
H8	-0.086 (11)	0.165 (6)	0.764 (10)
H9	0.077 (11)	0.339 (6)	0.836 (10)
H10	0.304 (12)	0.356 (6)	0.588 (9)
H5-6	0.445 (10)	0.184 (6)	0.731 (9)
H6-7	0.292 (10)	0.098 (6)	0.815 (10)
H8-9	0.125 (13)	0.224 (6)	0.835 (10)
H9-10	0.259 (11)	0.292 (6)	0.740 (10)

Table VII. Bond Distances (Å) Assuming C_{2v} Symmetry

	$B_{10}H_{13}NCS$		$B_{10}H_{14}$
	13°	Room temp	
B1-B2	1.773	1.765	1.778
B1-B3	1.773	1.766	1.772
B1-B5	1.740	1.740	1.756
B2-B5	1.778	1.775	1.786
B2-B6	1.710	1.712	1.715
B5-B6	1.770	1.788	1.775
B5-B10	1.982	1.985	1.973

Figure 2. A view of the unit cell of the 13° form perpendicular to the *bc* plane. The *b* axis is vertical.

3.22 Å from C and have closest H···H contacts of 2.92 Å. Molecules related otherwise have H(2)···N = 3.31 Å, H(2)···C = 3.16 Å, H(8)···N = 3.49 Å, H(8)···C = 3.36 Å, H(10)···N = 3.43 Å, and H(10)···C = 3.27 Å. Also, there are six S···H contacts less than 3.5 Å, and eleven H···H contacts less than 3.0 Å, of which the shortest is 2.34 Å. The closest S···S approach is 3.75 Å. No other N, C, or S atoms are within 4 Å of one another.

Figure 3. A view of the unit cell of the room temperature form from the perpendicular to planes containing the *b* axis and the NCS groups. The *b* axis is vertical.

Discussion

The low melting point of the room-temperature form (84–85°) and ready sublimation under vacuum at about 38° suggest that intermolecular forces are not strong. Also, the intermolecular packing shows evidence of only weak forces. In both crystalline forms, the unit cell contains two pairs of molecules in which each pair is related by a twofold screw axis. The NCS "tail" points in a direction opposite to that of the "tail" on a screw-related molecule. In the low-temperature form the projection of the "tails" onto the *ac* plane is parallel to the *c* axis, while in the room-temperature form the "tails" make an angle of 25° with respect to the *a* axis. In spite of these formal differences the overall arrangements in three dimensions are rather similar, as illustrated in Figure 4. This is a stereoview of the low-temperature form, but the room-temperature form would look almost the same although with respect to the crystal axes the direction of view would be different. One feature of the low-temperature form not shared by the room-temperature form is the antiparallel arrangement of NCS groups about 3.8 Å apart.

Substitution at B(6) in the present study and at B(1) in 1-ethyldecaborane¹³ and in 1-iododecaborane¹⁴ produces very small distortions only, most noticeable in the iodo derivative. On the other hand, the bond distances are significantly changed when $B_{10}H_{14}$ is converted to $B_{10}H_{14}^{2-}$,

(13) A. Perloff, *Acta Crystallogr.*, **17**, 332 (1964).(14) A. Sequeira and W. C. Hamilton, *Inorg. Chem.*, **6**, 1281 (1967).

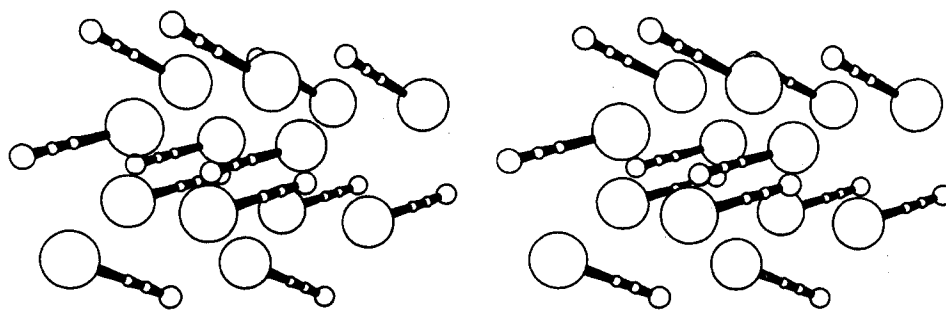


Figure 4. A stereoview of the low-temperature form. Thirteen molecules are shown to illustrate the packing. The N, C, and S atoms are shown explicitly; the decaborane "baskets" are represented by large circles.

perhaps largely because of the changes in hydrogen positions.¹⁵

The B-N distance of 1.435 Å in $B_{10}H_{13}NCS$ is far too short to be a "normal" single B-N bond, if there is such a thing. A survey¹⁶ indicates distances in the range 1.58 ± 0.02 Å for a number of compounds, including 1.57 Å in cubic BN.¹⁷ Thus, the distances of 1.52 Å in $B_{10}H_{12}(NCCCH_3)_2$ ⁴ and of 1.51 Å in $B_9H_{13}NCCH_3$ ¹⁸ were believed to be shortened by some conjugation. In fact, this very short 1.435-Å distance is comparable with that found between trigonal boron and trigonal nitrogen where the lone pair probably introduces substantial double-bond character. For example, the BN distance is 1.42 Å in $(CH_3)_2NB(CH_3)_2$.¹⁹ In tetra-*B*-isothiocyanotetra-*N*-*tert*-butylborazocine,²⁰ *i. e.*, $(t-BuNBNCs)_4$, where bonds to the boron atom are essentially coplanar, the B to N (of NCS) distance is 1.43 Å. Very likely, therefore, the BN distance of 1.435 Å in $B_{10}H_{13}NCS$ involves multiple bonding. The 80.2-MHz ¹¹B nmr spectrum of $B_{10}H_{13}NCS$ also provides evidence of substantial electronic interaction between electrons of the B_{10} unit and the NCS ligand. This spectrum is quite different from that usually seen in a substituted $B_{10}H_{14}$.¹ Ligand adducts, like $B_{10}H_{12}(py)_2$,²¹ are quite different because formal reduction of the cage orbitals has occurred,²² making these compounds derivatives of $B_{10}H_{14}^{2-}$. Nevertheless, the ultraviolet and visible spectra of these substituted pyridine derivatives show evidence of interactions between the electrons of the cage and those of the π system of the pyridine.²¹ These same pyridine derivatives are unreactive in ligand displacement reactions.²³

(15) D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, **12**, 546 (1973).

(16) W. N. Lipscomb and R. Lewin, *Advan. Chem. Ser.*, No. 42, 312 (1964).

(17) R. A. Wentdorf, Jr., *J. Chem. Phys.*, **26**, 956 (1957).

(18) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961).

(19) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).

(20) P. T. Clarke and H. M. Powell, *J. Chem. Soc. B*, 1172 (1966).

(21) (a) B. M. Graybill and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 2673 (1961); (b) M. F. Hawthorne and P. A. Wegner, *Inorg. Chem.*, **3**, 774 (1964).

(22) J. M. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

With respect to interaction with N or S of SCN^- , it seems clear from the short B-N distance in $B_{10}H_{13}NCS$ that the observed mode of bonding would be much more stable than bonding through B-S. This effect would enhance the known preference for bonding of B to N rather than to S in ligand displacement reactions where various amines are compared with dimethyl sulfide as ligands in $B_{10}H_{12}L_2$ compounds.²⁴ This preference may be related to a comparable polarization between B and N in the initial stages of bond formation, as compared with that between B and S.

The mechanism of substitution is not known, but it is probably nucleophilic in nature. Substitution at B(6) is expected from molecular orbital^{25,26} theories if indeed the initial ground state charge distribution is also dominant in the transition complex. We guess, therefore, that other $B_{10}H_{12}X^-$ salts^{2,5} are also substituted at B(6).

Acknowledgment. We thank the Office of Naval Research for support, the National Science Foundation for a predoctoral fellowship to D. S. K., and F. E. Scarbrough for help in the early stages of this study. We wish to thank Professor S. Hermanek for suggesting this problem to us and for supplying the initial samples of material.

Registry No. $NaSCN$, 540-72-7; $B_{10}H_{14}$, 17702-41-9; $B_{10}H_{13}NCS$, 32490-15-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2915.

(23) M. F. Hawthorne, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 276.

(24) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

(25) E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4467 (1972).

(26) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971).