Notes

X-ray Crystallographic Structure of a 7-Aza-*nido*-undecaborane Derivative: $(NB_2{}^tBu_3H)NB_{10}H_{12}$

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Introduction

7-Aza-*nido*-undecaborane, $NB_{10}H_{13}$,[1] is an isoelectronic analogue of the well-characterized 7,8-dicarba-*nido*-undecaborane, $C_2B_9H_{13}$.[2] The 2-fold deprotonation of both molecules makes anions $NB_{10}H_{11}{}^{2-}$ and $C_2B_9H_{11}{}^{2-}$, respectively, available, the open pentagonal faces of which may be closed by 14e-fragments of transition metal complexes to give a series of corresponding metalla-*closo*-clusters.[3,4] The two bridging H atoms of *nido*-7,8-$C_2B_9H_{13}$ connect adjacent B−B edges of the pentagonal C_2B_3 face, establishing C_s symmetry. The same symmetry was concluded for *nido*-7-$NB_{10}H_{13}$ from 2-D $^{11}B-^{11}B$ NMR spectra; nonadjacent B−B edges of the NB_4 face were considered to be bridged.[1] Crystals of *nido*-$NB_{10}H_{13}$, appropriate for a structural determination, could not be prepared. We recently reported on a derivative, $(NB_2{}^tBu_3H)NB_{10}H_{12}$ (**I**), in which a NB_2 three-membered ring is bonded to the N atom of the azaborane via a B−N bond.[5] This derivative **I** turned out to give appropriate crystals for a structural determination.

Experimental Section

Crystallographic data are collected in Table 1 . Crystals of **I** were obtained from hexane at −27 °C. The X-ray study was carried out on an ENRAF-Nonius CAD4 diffractometer using Cu Kα radiation (graphite monochromator). Data collection in the $\pm h,+k,+l$ quadrant of the diffraction sphere performed on a colorless parallelepiped (approximate dimensions 0.5 × 0.3 × 0.3 mm) resulted in 4433 reflections. The criterion of $I > \sigma(I)$ was satisfied by 3549 independent reflections, which were considered to be observed. For data reduction and refinement, the SDP package was used.[6] Structure solution with direct methods[7] allowed the location of all non-hydrogen atoms. In the course of the refinement, rotational disorder for the *tert*-butyl group C1, C2, C3, and C4 (with a minority conformer of occupancy 0.2) was taken into account. All C−C bond lenghts in this disordered moiety were constrained to a value of 1.53 ± 0.02 Å. The hydrogen atoms of the disordered group and two hydrogens at C8 were treated as riding on the corresponding carbon atoms. The atom H_c was located in a difference Fourier synthesis; its positional parameters were not refined, because the atom tended to approach B14 even closer on refinement. All other hydrogen atoms could be freely refined with isotropic displacement parameters, and anisotropic displacement paramters were assigned to all non-hydrogen atoms except the disordered methyl-carbon atoms of the minority conformer. The convergence results in Table 1 were obtained for 347 variables. As the displacement parameters of some atoms are probably affected by the above mentioned disorder and do not satisfy Hirshfeld's rigid bond test,[8] we cannot comment on a possible slight bond shortening in the three-membered ring or in other peripheric parts of the molecule due to large-amplitude movements.

Table 1. Crystal Data for $(NB_2{}^tBu_3H)NB_{10}H_{12}$ (**I**)[a]

chem formula	$C_{12}H_{40}B_{12}N$	Z	4
fw	342.2	D_x, g cm^{-3}	0.9938
space group	$P2_1/n$	T, K	203
a, Å	10.832(1)	μ (Cu Kα), cm^{-1}	3.2
b, Å	13.925(2)	λ, Å	1.5418
c, Å	15.937(3)	R	0.089
β, deg	107.95(6)	R_w	0.093
V, Å^3	2286.9(7)	Δ/ρ, e Å^{-3}	0.661

[a] The quantity minimized in the least square procedures is $\Sigma w(|F_o| - |F_c|)^2$. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

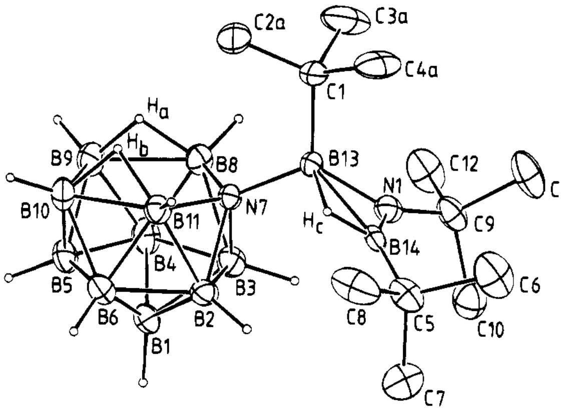

Figure 1. Molecular structure for $(NB_2{}^tBu_3H)NB_{10}H_{12}$ (**I**).

Results and Discussion

The structure of **I** is shown in Figure 1; selected bond distances and angles are given in Table 2. The cluster unit NB_{10} clearly forms a *nido*-fragment derived from an icosahedral *closo*-structure. The open pentagonal face NB_4 turns out to be nonplanar, but planes through B8−B9−B10−B11 and through N7−B8−B11 include an interplanar angle of only 9.4(6)°. The three B−B bonds in that NB_4 face, two of which are bridged by H_a and H_b, are the longest bonds in the skeleton (1.82−1.88 Å), whereas the B−N bonds in the open face are distinctly shorter (1.62, 1.63 Å) than those in the skeletal backbone (1.71, 1.72 Å). The N atom is closer to the center M of the cluster (M−N7 = 1.544 Å) than the B atoms (M−B = 1.63−1.76 Å with an average value of 1.684 Å), the center M being defined by the arithmetic mean of the coordinates for the skeletal atoms, B1, B5, and N7 excepted. Such a penetration of the N-atom toward the polyhedral center had already been detected in the *closo*-skeletons of $(PhCH_2)NB_{11}H_{11}$[9] and NB_9H_{10}[10] . Among

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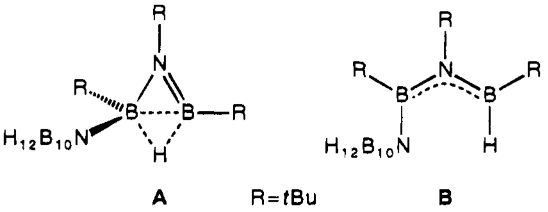
Table 2. Selected Bond Distances (Å) and Angles (deg) for **I**

N7−B2	1.709(2)	B5−B10	1.745(2)
N7−B3	1.722(2)	B6−B10	1.764(3)
N7−B8	1.620(2)	B6−B11	1.767(2)
N7−B11	1.625(2)	B8−B9	1.833(2)
B1−B2	1.739(2)	B9−B10	1.876(3)
B1−B3	1.733(2)	B10−B11	1.819(2)
B1−B4	1.788(3)	B13−B14	1.801(2)
B1−B5	1.749(2)	N1−B13	1.574(2)
B1−B6	1.795(2)	N1−B14	1.304(2)
B2−B3	1.743(2)	B13−N7	1.610(2)
B2−B6	1.746(2)	B13−C1	1.619(2)
B2−B11	1.800(2)	B14−C5	1.595(2)
B3−B4	1.750(2)	N1−C9	1.533(2)
B3−B8	1.820(2)	B8−H_a	1.31(2)
B4−B5	1.781(3)	B9−H_a	1.19(2)
B4−B8	1.779(2)	B11−H_b	1.31(1)
B4−B9	1.770(3)	B10−H_b	1.26(1)
B5−B6	1.775(2)	B13−H_c	1.35
B5−B9	1.746(3)	B14−H_c	0.98
B8−N7−B11	112.0(1)	B13−N1−C9	144.5(1)
N7−B8−B9	110.6(1)	B14−N1−C9	138.2(1)
B8−B9−B10	102.6(1)	N1−B14−C5	145.7(1)
B9−B10−B11	103.1(1)	B13−B14−C5	155.7(1)
B10−B11−N7	110.7(1)	B8−H_a−B9	94(1)
B13−N1−B14	76.9(1)	B10−Hb−B11	90(1)
N1−B13−B14	44.83(7)	B13−Hc−B14	100(1)
N1−B14−B13	58.31(9)		

the 15 deltahedral faces, 12 do not deviate largely from regularity with angles in the range of 58−62°. In the triangles N7−B2−B11 and N7−B3−B8, however, the short bonds N7−B11 and N7−B8 and the penetration of N7 toward the cluster center cause large angles at N7 (65.3 and 65.9°, respectively) and small ones at B2, B3 (55.1 and 54.3°, respectively). The extralong bond B9−B10 corresponds to an expanded angle B9−B5−B10 (65.0°). The small deviations of the NB_{10} unit from C_s symmetry can be attributed to the chiral ligand at N7. It looks reasonable that the parent compound $NB_{10}H_{13}$ exhibits C_s symmetry in solution.[1]

The structure of the N-bonded cluster ligand has been discussed in principle.[5] The structure of **I** again demonstrates that a B−N 2c2e-π-bond and a B−H−B 3c2e bond (structure **A**) are more favorable than a B−N−B 3c2e-π-bond and a B−H 2e bond (structure **B**). A B−H−B bridge containing a B atom as low coordinated as B14 in **I** constitutes a novel bonding situation.[5,11] The hydrogen bridge B13−H_c−B14 is rather unsymmetric, certainly. The bond distance N1−B14 of 1.304(2) Å seems to be particularly short for a B−N double bond. The estimated standard deviation of this distance, however, must be considered to be too optimistic (see Experimental Section).



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Supporting Information Available: Tables of data collection and refinement parameters, positional and thermal parameters for all atoms, anisotropic displacement parameters for non-hydrogen atoms, bond distances and bond angles (9 pages). Ordering information is given on any current masthead page.

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