Crystal and Molecular Structure of Cyclotriborazane, the Inorganic Analog of Cyclohexane

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Abstract: The crystal structure of cyclotriborazane, $(BH_2NH_2)_3$, has been determined at room temperature from X-ray diffraction data. The compound crystallizes in the orthorhombic space group *Pbcm*, with $a = 4.403$ (3), $b = 12.210$ (7), and $c = 11.227$ (10) Å. A set of 450 reflections was obtained by counter methods. The molecule has the chair form, with molecular symmetry very close to C_{3v}, one of the mirror planes being required by the space group, and the threefold axis lying along *a*. Conventional, full-matrix least-squares refinement of 59 variables converged with the weighted *R* factor 0.049. On including four extra variables describing the charge distribution in the molecule, this *R* factor fell to 0.035. The average partial charges found on each type of atom are as follows: B, +0.7 e; N, −0.3 e; H(B), −0.3 e; and H(N), +0.1 e. The relatively large charges on the hydrogen atoms are consistent with the high heat of sublimation. The calculated dipole moment based upon these point charges at the atomic positions is 3.0 D, which compares well with the experimental value. The ring atoms oscillate as a rigid group, and the corrected B–N bond distance is 1.576 (2) Å. The equatorial B–H distances average 1.11 (1) Å and appear to be longer than the axial B–H distances, which average 1.08 (1) Å.

Although species of empirical composition BH_2NH_2 have been encountered since the early studies of boron–nitrogen systems of some 45 years ago,[1] it was not until relatively recently that tractable, crystalline solids of such composition have been isolated.[2] The most extensively studied of these materials is cyclotriborazane, $(BH_2NH_2)_3$, formally the analog of cyclohexane in the boron–nitrogen system. However, its chemical and physical properties differ markedly from the hydrocarbon. It is a crystalline solid of low volatility at room temperature. The heat of sublimation is 25 ± 3 kcal/mol. Its dipole moment in *p*-dioxane is 3.2 ± 0.10 D.[3] The description of the crystal and molecular structure of cyclotriborazane presented here is of interest in comparison with cyclohexane. Although earlier studies of a methyl substituted derivative[4] and of a phosphorus analog[5] show these to have the chair conformation, there was some interest in a possible boat conformation due to transannular attraction arising from the polar character of the BH_2NH_2 units within the molecule. Indeed, the molecule $((CH_3)_2Al\cdot NHCH_3)_3$ has been shown to exist in both a chair form and a skew-boat form, although the latter conformation appears to arise from steric factors.[6] It was also of interest to investigate the molecular charge distribution in this molecule, in view of the high heat of sublimation and large dipole moment, which imply large charge separations in this molecule.

Experimental Section

Cyclotriborazane used in this study was prepared according to the method of Boddeker, Shore, and Bunting.[2] Crystals were grown from benzene solution at room temperature. They were obtained as plates elongated along the *a* axis.

Inspection of precession and Weissenberg photographs showed the crystal system to be orthorhombic. Reflections $0kl$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, were absent, indicating possible space groups *Pbcm* or $Pbc2_1$. These systematic absences were further confirmed during data collection by counter methods. Cell dimensions were first obtained from powder photographs using a camera calibrated with an NBS As_2O_3 sample. The observed parameters were $a = 4.44$ (2), $b = 12.26$ (3), $c = 11.23$ (3) Å, based upon a least-squares refinement of 20 θ values. At a later stage, parameters were redetermined by accurate alignment of 12 reflections on a Picker four-circle diffractometer. A least-squares refinement of these cell dimensions and of angular zeros gave $a = 4.403$ (3), $b = 12.210$ (7), and $c = 11.227$ (10) Å, where the standard deviations allow for random errors only. These latter cell dimensions were used in the final analysis of the structure. The density calculated on the basis of four molecules per unit cell is 0.95 g/cm³, which compares well with the experimental value of 0.96 (1) g/cm³, obtained using a density gradient.

Collection and Reduction of Intensity Data. Data were first obtained from multiple exposures by the equiinclination Weissenberg method. Unintegrated photographs were obtained for layers 0–3 about both the *a* axis and the *c* axis. Intensities were estimated visually with an intensity scale which was prepared from the same crystal used to collect data. After applying Lorentz and polarization factors, the data from different nets were placed on the same relative scale by the method of Nordman.[7] The 332 independent reflections so obtained were used in the determination and the initial refinement of the structure.

At a later stage, it became evident that a more precise set of intensities would be valuable. A fresh crystal approximately 0.5 × 0.4 × 0.3 mm was mounted in a thin-walled capillary tube on a Picker four-circle diffractometer controlled by an EMR 6130 computer. The six faces were normal to the cell axes and the mounting was close to the *a* axis. On examination using ω scans, peak widths at half-height varying over several tenths of a degree were found, indicating the mosaicity of the crystal to be highly anisotropic. This is consistent with our observations at the end of the refinement that the 020 plane appears to be affected by extinction while the 002 plane does not, though of similar intensity. Photographic examination of several other crystals unfortunately revealed none that were more suitable for structure determination.

Integrated intensities were obtained by the θ–2θ scan technique. The symmetrical scan range was 2.7° in 2θ, the scan rate 2°/min,

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(1) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Amer. Chem. Soc.*, 60, 2297 (1938); E. Wiberg, K. Hertwig, and A. Bolz, *Z. Anorg. Allg. Chem.*, **256**, 177 (1948); E. Wiberg, A. Bolz, and P. Buchheit, *ibid.*, 256, 285 (1948); G. W. Schaeffer, and L. J. Basile, *J. Amer. Chem. Soc.*, 77, 331 (1955); G. W. Schaeffer, M. D. Adams, and F. J. Koenig, *ibid.*, 78, 725 (1956); A. K. Holliday and N. R. Thompson, *J. Chem. Soc.*, 2695 (1960).

(2) G. H. Dahl and R. Schaeffer, *J. Amer. Chem. Soc.*, **83**, 3032 (1961); S. G. Shore and C. W. Hickam, *Inorg. Chem.*, **2**, 638 (1963); K. W. Boddeker, S. G. Shore, and R. K. Bunting, *J. Amer. Chem. Soc.*, **88**, 4396 (1966).

(3) D. R. Leavers, J. R. Long, S. G. Shore, and W. J. Taylor, *J. Chem. Soc. A*, 1580 (1969).

(4) L. M. Trefonas, F. S. Mathews, and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 273 (1961).

(5) W. C. Hamilton, *ibid.*, **8**, 199 (1955).

(6) K. Gosling, G. M. McLaughlin, G. A. Sim, and J. D. Smith, *J. Chem. Soc. D*, 1618 (1970).

(7) C. E. Nordman, *Acta Crystallogr.*, 13, 535 (1960).

and background counts were recorded for 20 sec at each edge of the scan. A copper target was used, and the diffracted beams were passed through 0.02-mm nickel foil (Cu Kα_1 = 1.5405 Å). The diffracted beams were attenuated by successive layers of 0.001-in. brass foil whenever the count rate exceeded about 9000 cps. The takeoff angle at the copper target was 1.8° at which angle the intensity of the 111 reflection was about 75% of its maximum. The intensities of three reflections were measured at approximate 6 hr intervals, and these standard intensities showed no significant variation with time. All reflections with sin θ/λ less than 0.55 in the two octants with h and k positive were measured. After subtraction of background, the intensities were corrected for Lorentz and polarization effects and reduced to structure factors. Standard deviations were obtained by the relation $\sigma^2(I) = C + 9 + g^2(B + 18) + p^2I^2$ where C represents the gross count, B is the total background count and g is the ratio of the time spent scanning to the time spent measuring background. $I = C - gB$ is the net integrated intensity. The numerical constants allow for the truncation of the last digit by the Picker instrument. The standard deviation on the structure factor F was assumed to be given by $\sigma(F^2)/2F$. In cases where I was zero or negative, the structure factor was taken as zero with a standard deviation of $\sigma(F^2)$. The factor p is the "ignorance factor,"[8] which is meant to allow for systematic errors, and a value of 0.05 was chosen in the present case. The intensities of 851 potentially observable reflections were recorded, of which 709 were greater than 3σ, while of 189 systematically absent reflections measured, only one had a net intensity greater than 3σ.

The linear absorption coefficient is 4.40 cm^{-1} for Cu Kα radiation. An absorption correction was applied using the method of Gaussian intervals described by Busing and Levy.[9] Corrections to F^2 varied from 1.12 to 1.18.

On averaging the data, the average deviation from the mean of equivalent structure factors was 1.3%. Standard deviations of the averaged values were obtained by normal error propagation. In about 75 out of the 399 reflections recorded twice, these standard deviations were less than those based on differences from the mean. After averaging, we had 451 independent structure factors, and all of these, including zeros, were used in the least-squares refinements of atomic parameters.

Determination and Refinement of the Structure. A three-dimensional sharpened Patterson function calculated using the photographic data revealed positions of the boron and nitrogen atoms consistent with the centrosymmetric space group *Pbcm*. After least-squares refinement, six of the hydrogen atoms were located on a difference Fourier synthesis, but the remaining two were incorrectly located. Least-squares refinements involving coordinates for all atoms, anisotropic thermal parameters for the heavier atoms, and isotropic thermal parameters for the hydrogen atoms converged with values of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ equal to 0.13 and 0.16, respectively. At this stage, standard deviations were about 0.01 and 0.05 Å for the coordinates of the heavy atoms and of the hydrogen atoms, respectively. The molecule was seen to have the chair conformation and symmetry close to C_{3v}. Only one of the mirror planes is required by the space group. The boron–nitrogen distances at this stage were 1.57, 1.62, and 1.58 Å.

The determination of the structure was now continued using the data obtained by counter methods. Calculation of structure factors using parameters from the photographic data for the boron and nitrogen atoms, and six hydrogen atoms, gave R_1 = 0.17. The remaining two hydrogen atoms were readily located as the highest two peaks on a difference Fourier synthesis. Full-matrix refinements of positional and isotropic thermal parameters for all the atoms now converted at R_1 = 0.061 and R_2 = 0.080, while with anisotropic thermal parameters for the heavy atoms convergence occurred when R_1 = 0.046 and R_2 = 0.053. These calculations and all others involving the counter data were performed with the EMR 6130 computer using locally written programs.[10] Scattering factors were obtained from the compilation of Ibers.[11] At this stage the average isotropic temperature factors for the hydrogen atoms were B = 1.4 for hydrogen atoms attached to boron and 1.9 for those attached to nitrogen. These values were considerably lower than the temperature factors for the boron and nitrogen atoms (B = 2.9–3.0). This phenomenon has been noted previously.[12] On using the spherical scattering factors for bonded hydrogen of Stewart, *et al.*,[13] the thermal parameters for the hydrogen atoms converted at the more reasonable values of B = 3.4 for the hydrogen atoms on boron and 4.0 for the hydrogen atoms on nitrogen and, rather unexpectedly, R_1 and R_2 fell from 0.046 and 0.053 to 0.043 and 0.049, respectively. This represents a very significant improvement of the model.

Estimation of the Partial Atomic Charges

An attempt was now made to determine atomic charge parameters from the diffraction data by least squares. Our procedures were based on the L-shell projection method suggested by Stewart[14] and on extensions to this method suggested by Coppens, *et al.*[15] This formalism involves the simplest possible extension to the conventional scattering model in X-ray crystallography, in which all atoms are assumed to have spherical symmetry and zero net charge (or an integral charge in the case of ions). In the L-shell projection model, the scattering is still assumed to be from spherical distributions, but is factored into contributions from the core electrons, which are assumed to be unperturbed by the bonding, and from the valence shell electrons, which carry a variable occupancy factor. The scattering factors used were those given by Stewart,[14] who concludes that the most appropriate valence-shell scattering factors are those calculated using Slater-type orbitals with coefficients for each atom averaged over different molecular environments.

In the present refinements, a "double atom" was placed at the position of each ring atom, with total scattering power given by $(f_c + pf_v)$, where f_c and f_v represent the core and valence scattering factors, respectively. The occupancy of the valence shell was found by refining the variable parameter, p. For the hydrogen atoms, of course, the core scattering is zero. The results of several refinements are presented in Table I. In all cases except refinement F, the molecular charges were assumed to have C_{3v} symmetry, and no distinction was made between axial and equatorial substituents. In refinement A, the occupancy factors alone were allowed to vary, while in refinement B, the scale factor was also refined, and in refinement C, an overall temperature factor was also varied. There seemed to be little correlation of the L-shell populations with the scale factor, but rather more correlation than expected with the overall temperature factor. This prompted us to allow all of the positional and thermal parameters to vary which led to drastic improvement in the agreement factors, R_2 dropping from 0.0491 to 0.0354.

At this stage, the 111 and 020 planes, which are very strong, had F_o less than F_c by 7 and 19%, respectively. These are two of the three strongest planes, and it seemed likely that the differences were due to secondary extinction. While secondary extinction is apparently not a large factor for the crystal under study, we were

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(8) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(9) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957).

(10) Structure factor least-squares calculations and the determination of errors in derived parameters follow the general algorithms described by Busing, Martin, and Levy in ORFLS and ORFFE; Corfield's program for Fourier synthesis uses the symmetry operations of the space group to optimize calculation times.

(11) "International Tables of Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, p 202.

(12) L. H. Jensen and A. J. Mabis, *Acta Crystallogr.*, 21, 770 (1966); L. H. Jensen and M. Sundaralingham, *Science*, **145**, 1185 (1964).

(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(14) R. F. Stewart, *ibid.*, **53**, 205 (1970).

(15) P. Coppens, D. Pautler, and J. F. Griffiths, *J. Amer. Chem. Soc.*, **93**, 105 (1971).

Table I. Least-Squares Refinements Involving Valence Shell Occupancy Factors[a]

	Refinement A	B	C	D	E	F	G	H	I
No. of variables	4	5	6	63	63	71	62	62	56
$R_1 \times 100$	4.23	4.23	4.27	3.11	2.67	2.73	2.69	2.71	2.76
$R_2 \times 100$	5.20	5.16	5.03	3.54	3.37	3.42	3.38	3.38	3.49
Scale factor	(1.16)	1.15	1.07	1.14	1.12	1.12	1.10	1.11	1.12
% total charge	87	89	98	93	97	97	(100)	(100)	(100)
Charge on B, e	0.59 (4)[b]	0.55 (4)	0.33 (6)	0.85 (6)	0.77 (6)	0.74 (8) 0.81 (9)	0.73 (5)	0.84 (5)	0.76 (5)
Charge on N	−0.39 (3)	−0.40 (3)	−0.41 (3)	−0.30 (5)	−0.27 (5)	0.28 (6) 0.33 (7)	−0.25 (5)	−0.16 (5)	−0.10 (5)
Charge on H(B)	−0.13 (1)	−0.12 (2)	−0.04 (2)	−0.39 (3)	−0.37 (3)	−0.34 to −0.40	−0.36 (3)	−0.46 (3)	−0.40 (2)
Charge on H(N)	0.03 (1)	0.05 (1)	0.08 (2)	+0.11 (2)	+0.12 (2)	0.13 to 0.15	+0.12 (2)	+0.12 (2)	0.07 (2)
Point charge dipole moment[c]	−0.7 (2)	−0.6 (2)	−0.6 (2)	4.0 (4)	4.1 (4)	3.8 (8)	4.1 (4)	5.5 (4)	4.4 (3)

[a] In each column is summarized the results of least-squares refinement of valence shell occupancy factors: A, alone; B, with overall scale factor; C, with overall scale and temperature factors; D, with all conventional parameters; E, with all conventional parameters, 111 and 020 planes being omitted; F, as E, without symmetry constraints on valence shell parameters; G, as E, with least-squares constraint of neutrality; H, as G, with $\zeta = 1.08$ for boron hydrogen atoms; I, as H, with constraints on thermal motion of hydrogen atoms. [b] In this table and in all subsequent tables, the figures in parentheses refer to the estimated standard deviations in terms of the least significant digit. [c] The dipole moment lies along the threefold axis and is given a positive value when the negative pole points in the direction of decreasing x.

Table II. Fractional Coordinates and Thermal Parameters for $(BH_2NH_2)_3$

Atom	x	y	z	$10^5\beta_{11}$[a]	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
B(1)	0.1483 (3)	0.11588 (11)	0.25	2988 (91)	399 (10)	722 (13)	−30 (21)		
N(2)	0.2546 (2)	0.05002 (7)	0.36258 (7)	3066 (65)	522 (8)	515 (9)	−79 (12)	−88 (5)	−23 (13)
B(3)	0.1500 (3)	−0.07308 (8)	0.36844 (8)	3227 (70)	532 (9)	479 (9)	−63 (16)	57 (6)	−43 (16)
N(4)	0.2564 (3)	−0.12935 (9)	0.25	2823 (81)	379 (9)	643 (10)	40 (16)		

[a] Thermal parameters are expressed in the form $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2lh\beta_{31})]$.

concerned that the valence shell occupancy parameters might be sensitive to errors in the low order planes. In a further refinement, E, the 111 and the 020 planes were deleted from the data. None of the occupancy factors changed by more than two estimated standard deviations.

In refinement F, the symmetry constraints on the valence shell occupancy parameters were relaxed, and a separate valence occupancy factor for each atom was refined. No improvement in the values of R_1 and R_2 was noted by the introduction of eight extra parameters, and the ranges found for individual occupancy factors, which had been constrained equally in the earlier refinements, were well within the ranges expected on the basis of the standard deviations.

During refinements A–F, no least-squares constraint was imposed that the molecule remain neutral. After convergence, the occupancy factors, p, were all normalized so as to make the molecule neutral. A model using spherical scattering factors for the valence electrons would not be expected to account for the total electronic charge, and in harmony with this, the per cent total charge found is consistently less than 100%. The renormalization corresponds to partitioning the electrons in each bond in proportion to the atomic numbers of the atoms forming the bond, which does not seem unreasonable on the basis of electronegativities. In refinement G the neutrality of the molecule was introduced as a linear constraint on the occupancy factors, using the technique of Lagrange multipliers.[16] This technique has the advantage of reducing the correlation between the valence shell population parameters,[15] although the use of this constraint has been questioned.[17] In the present case, the valence shell population parameters do not seem to be sensitive to the particular method of normalization used. Two further refinements are discussed in a later part of the paper.

The atomic parameters at the end of refinement G are given in Tables II and III.[18] R_1 and R_2 for the 387 structure factors with $F^2 > 3\sigma$ were 0.0224 and 0.0328, respectively, and a refinement restricting the data to

Table III. Fractional Coordinates and Thermal Parameters for the Hydrogen Atoms

Atom	x	y	z	B	B_{calcd}[a]
H(1A)	−0.098 (3)	0.1185 (10)	0.25	6.3 (3)	3.0
H(1E)	0.248 (3)	0.1991 (13)	0.25	7.0 (4)	3.5
H(2A)	0.454 (3)	0.0531 (9)	0.3692 (8)	3.3 (3)	2.9
H(2E)	0.184 (2)	0.0829 (10)	0.4273 (12)	4.2 (3)	3.4
H(3A)	−0.096 (2)	−0.0758 (7)	0.3722 (6)	5.9 (2)	2.7
H(3E)	0.255 (2)	−0.1144 (8)	0.4469 (9)	6.6 (3)	3.6
H(4A)	0.454 (4)	−0.1363 (12)	0.25	3.1 (3)	2.9
H(4E)	0.184 (3)	−0.1971 (15)	0.25	3.5 (4)	3.1

[a] These figures were calculated assuming the entire molecule vibrates as a rigid body; the T and ω tensors used were those given in Table IV.

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(16) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 137.

(17) R. F. Stewart, personal communication.

(18) A list of observed structure factors and those calculated at the end of refinement G will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1480. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

these planes gave no change in the parameters greater than 0.3σ. The error in an observation of unit weight is 1.4, based on all data. The average value of $w\Delta^2$, where $\Delta = |F_o| - |F_c|$, was reasonably constant over different ranges of magnitudes of the structure factors (1.7–1.8) except that the 38 weakest planes were clearly underweighted ($\overline{w\Delta^2} = 0.13$). The values of $\overline{w\Delta^2}$ averaged over different ranges of sin θ/λ vary from 1.0 to 1.7, except for those ranges which include the contribution of four weak, high-angle planes.

A difference Fourier calculated at the end of refinement G had, as its most significant features, areas of density near the centers of bonds between ring atoms, as well as negative regions at the extremities of the bonds. Sections through various three-atom segments are shown in Figure 1, where the contours in each case represent the difference density averaged over two crystallographically independent three-atom fragments of the molecule. The average standard deviation of this function is estimated to be 0.02 e/Å^3, by application of the formula $\sigma = (\Sigma\Delta^2)^{1/2}/V$. The maximum peak heights in the B–N bonds are 0.10 e/Å^3, values somewhat lower than those often found in comparable difference syntheses. Each of the ring atoms lies in a slight well with a density of about −0.03 e/Å^3. It is interesting that there is a slight residual positive density in the N–H and B–H bonds and also a slight negative region at the extremities of these bonds.

The appearance of a difference Fourier calculated at the end of the conventional refinement, where the scattering factors had been taken from ref 11, was remarkably similar to the difference density represented in Figure 1. There were similar peaks of height 0.1 e/Å^3 between the boron and nitrogen atoms, but there were in addition several other peaks of similar height near the hydrogen atoms and in unoccupied regions in the unit cell.

Analysis of the Thermal Motion

Busing and Levy[19] have pointed out that bond lengths calculated from atomic positions obtained by least-squares refinement are always underestimated. The correct bond length requires a knowledge of the joint probability density function for the pair of atoms forming the bond, but this information is not available from conventional least-squares refinements. A reasonable assumption in many cases is that one atom "rides" on the other, when an exact expression is possible. This assumption seemed inappropriate for the boron–nitrogen distances in the present molecule, and an analysis of the rigid body librations was carried out. There were two principal motives for this analysis. First, although the thermal motion in the crystal was small, even a slight correction to the boron–nitrogen bond lengths would be many times the estimated standard deviations of 0.0015 Å; and secondly, there appeared to be a significant difference between the lengths of the equatorial and axial boron–hydrogen distances, and it was necessary to explore whether this was an artifact due to the thermal motion. Accordingly, the vibration and libration tensors T and ω for the ring part of the molecule were obtained by the method of Cruickshank.[20] The β values for N(2) and B(3) were given unit weight, and those of B(1) and N(4) were given half-weight. With the restrictions on T and ω due to the molecule lying on a crystallographic mirror plane, there are eight tensor elements to be found from 20 β values. The center of libration need not be at the center of gravity of the molecule,[21] and the T and ω tensors were calculated at each of a series of origins systematically spaced near the center of gravity. The form of the ω tensor is not very sensitive to the position of the origin of librations in this crystal. The rigid body thermal parameters are shown in Table IV. The rigid body vibrations are remarkably isotropic with an average root-mean-square amplitude of 0.17 Å. The root-mean-square libration amplitudes are 4.6, 2.6, and 1.6° about axes fairly close to the crystallographic axes a, b, and c, with the principal libration of the molecule about a direction 16° away from the threefold axis. Individual atomic anisotropic terms calculated from the tensors in Table IV are compared with those calculated from the atomic thermal parameters in Table V. The agreement is very satisfactory, and the

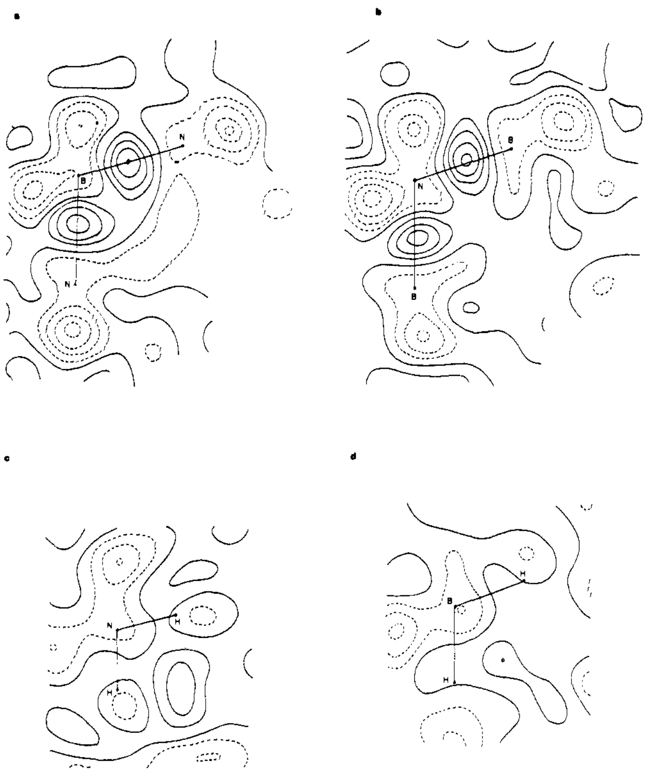

Figure 1. Averaged difference densities calculated in the planes of various three-atom segments in the molecule. The structure factors used were those calculated at the end of refinement G.

Table IV. Vibration and Libration Tensors for $(BH_2NH_2)_3$[a]

T, Å^2	0.0265 (10)	0.0001 (4)	0
		0.0293 (4)	0
			0.0284 (4)
ω, deg^2	19.7 (7)	3.7 (7)	0
		7.7 (15)	0
			2.7 (14)

[a] Fractional coordinates of center of libration: 0.12, −0.026, 0.25.

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(19) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

(20) D. W. J. Cruickshank, *ibid.*, **9**, 754 (1956).

(21) G. S. Pawley, *ibid.*, **16**, 1204 (1963).

Table V. Observed and Calculated Tensor Components

		U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
B(1)	From individual β values	293 (9)	301 (7)	461 (9)	−8 (6)		
	From rigid body parameters	290	295	460	−1		
N(2)	From individual β values	301 (6)	395 (6)	329 (5)	−22 (3)	−61 (3)	−6 (3)
	From rigid body parameters	310	393	332	−22	−62	−4
B(3)	From individual β values	317 (7)	402 (6)	306 (6)	−17 (4)	39 (4)	−11 (4)
	From rigid body parameters	309	401	306	−19	48	−13
N(4)	From individual β values	277 (9)	286 (6)	410 (7)	11 (4)		
	From rigid body parameters	278	297	405	7		

[a] The tensor U is defined so that the mean square amplitude of vibration in a direction l is given by $l'Ul$, where the components of l are on a set of Cartesian axes parallel to the crystallographic axes. The values given have been multiplied by 10^4.

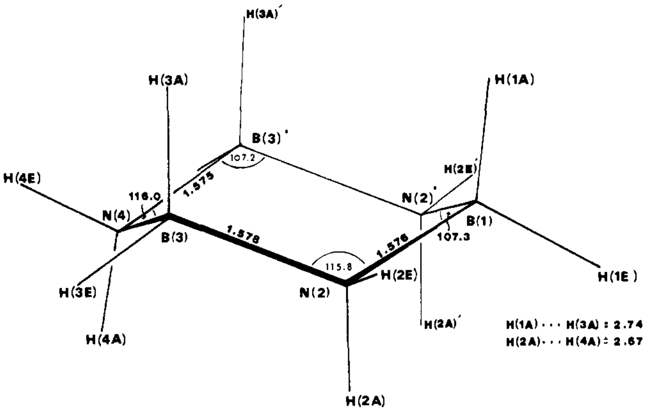

Figure 2. Perspective view of the molecule, showing the numbering system and some of the bond lengths and angles.

Table VI. Bond Lengths and Angles in $(BH_2NH_2)_3$

(a) Bond Lengths (A)

	Uncorrected	Corrected[a]
B(1)–N(2)	1.570 (2)	1.576
N(2)–B(3)	1.573 (2)	1.578
B(3)–N(4)	1.568 (2)	1.575
B(1)–H(1A)	1.08 (1)	1.12
B(3)–H(3A)	1.08 (1)	1.12
B(1)–H(1E)	1.11 (1)	1.15
B(3)–H(3E)	1.12 (1)	1.16
N(2)–H(2A)	0.88 (1)	0.89
N(4)–H(4A)	0.88 (2)	0.88
N(2)–H(2E)	0.89 (1)	0.91
N(4)–H(4E)	0.89 (2)	0.90

Bond Angles (deg)

N(4)′–B(1)–N(4)	107.3 (1)	H(1A)–B(1)–N(2)	108.3 (4)
N(2)–B(3)–N(4)	107.2 (1)	H(3A)–B(3)–N(2)	108.9 (5)
B(1)–N(2)–B(3)	115.8 (1)	H(3A)–B(3)–N(4)	108.6 (5)
B(3)–N(4)–B(3)′	116.0 (1)	H(1E)–B(1)–N(2)	110.6 (4)
		H(3E)–B(3)–N(2)	110.1 (5)
		H(3E)–B(3)–N(4)	110.3 (5)
H(1A)–B(1)–H(1E)	111.7 (10)	H(2A)–N(2)–B(1)	110.0 (6)
H(3A)–B(3)–H(3E)	111.7 (7)	H(2A)–N(2)–B(3)	109.2 (7)
H(2A)–N(2)–H(2E)	105.1 (10)	H(4A)–N(4)–B(3)	109.9 (5)
H(4A)–N(4)–H(4E)	105.4 (13)	H(2E)–N(2)–B(1)	108.9 (8)
		H(2E)–N(2)–B(3)	109.2 (7)
		H(4E)–N(4)–B(3)	107.6 (5)

[a] The B–N distances were corrected assuming that the six-membered ring oscillated as a rigid group, and the B–H and N–H distances were corrected assuming riding motion.

six atoms forming the chair in the molecule appear to vibrate as a rigid group.

The isotropic temperature factors for the hydrogen atoms calculated from the T and ω tensors are compared with the least-squares values in Table III. The least-squares values are in every case larger, especially for the boron hydrogen atoms. This is probably partly because the hydrogen atoms will tend to "ride" on the ring atoms, and partly because the thermal parameters for the boron hydrogen atoms do seem artificially high. The rigid body parameters predict that the equatorial hydrogen atoms should have B values about 0.5 Å^2 higher than the axial hydrogen atoms, and this discrepancy is also found in the least-squares values, where the difference averages 0.7 Å^2.

The boron–nitrogen bond lengths corrected for the rigid body thermal motion[19] are given in Table VI, the average extension being 0.006 Å. The range of bond lengths is 0.0051 Å before correction and 0.0036 Å after correction, and the latter range is more consistent with the average standard deviation in the B–N bond distance of 0.0011 Å, which is the value calculated without the contribution of the errors in the cell dimensions. (The standard deviations in Table VI include contributions from errors in the cell dimensions.)

The corrections to the boron–hydrogen bond lengths are very slight, 0.004 Å for the equatorial and 0.001 Å for the axial bonds. Note that these corrections increase the difference between axial and equatorial bond lengths. Corrections to the boron–hydrogen bond lengths assuming a "riding" model were larger but were equal for both types of bonds. A fuller treatment of these bonds lengths would require anisotropic refinement of the hydrogen atoms, and it was not felt that the data justified this. In fact, we did carry out one refinement where anisotropic coefficients were assigned to the hydrogen atoms attached to boron. There was a negligible change in R_2, and the B–H bond lengths corrected with the assumption that the hydrogen atom "rides" on the boron atom showed an even greater difference in length between the axial and equatorial bonds.

Discussion

Structure and Conformation. The numbering of the atoms is shown in a perspective view of the molecule in Figure 2. The molecule has the chair conformation, and the molecular symmetry is very close to C_{3v}, with the mirror plane through B_1 and N_4 being imposed by the space group.

The mean B–N distance after correction for thermal librations is 1.576 (2) Å. This is very close to that found in cubic boron nitride, 1.565 (1) Å.[22] Other measurements of the length of a B–N single bond average 1.58 Å.[23] Thus, in $H_3NB_3H_7$ the distance is

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1.581 (3) Å,[24] in $C_2H_5NH_2B_6H_{11}NHC_2H_5$ it is 1.574 (7) Å,[23] and in a study of the N-methylated derivative of the present compound Lipscomb, *et al.*, report a B–N distance of 1.59 (3) Å.[4] There does not appear to be clear evidence of bond shortening on ring formation as in the case of cyclohexane,[25] where the C–C bond length is 1.528 (5) Å, compared to 1.5445 (1) Å in diamond.[26] However, the bond distances in several halogenated boranes R_3NBX_3 appear slightly longer, varying from 1.58–1.61 Å.[27] The bond lengths in two dimers appear also to be longer, with B–N distances of 1.60 (1) and 1.59 (1) Å quoted for $[(CH_3)_2NBF_2]_2$[28] and $[(CH_3)_2NBCl_2]_2$,[29] respectively.

There is a very clear difference between the ring angles at boron, averaging 107.2 (1)°, and those at nitrogen, which average 115.9 (1)°. There is a complementary difference in the angles subtended by the hydrogen atoms, the H–B–H angles averaging 111.7 (6)° and the H–N–H angles 105.3 (8)°. A similar pattern is seen in other trimers involving group III and group V atoms. Thus, in $[(CH_3)_2AlC_2H_4N]_3$,[30] the angles at the aluminum and nitrogen atoms are respectively 102 and 120°, and in $[H_2B(CH_3)_2P]_3$,[5] the angles at the boron and phosphorus atoms are respectively 112 and 118°. Interestingly enough, in the compound $[(CH_3)_2NBCH_2]_3$, the ring angle at the boron atom is *larger* than that at carbon, 115 *vs.* 111°. The earlier study[4] on the methylated derivative of the present compound did not show such an alternation, the N–B–N and B–N–B angles being 114 (2) and 113 (1)°, respectively, although the external angle at the group V atom was small (104 (3)°), as is found in the present case.

The average uncorrected N–H distance is 0.88 (1) Å, while the uncorrected B–H distances average 1.10 (1) Å. These distances are typical for N–H and B–H bond lengths found by X-ray methods and are shorter than those found by spectroscopic methods or by electron diffraction. For comparison, the terminal B–H distances in diborane were found to be 1.08 (2) Å by X-ray methods and 1.196 (8) Å by electron diffraction.[31] An interesting feature of the present structure is the 0.03 Å difference between the axial and equatorial B–H distances, which is significant at the 1% level. This difference has persisted in all of our refinements and is not reduced on correcting for thermal motion according to any of our models. Thermal corrections to the B–H distances are extremely difficult to arrive at, because the thermal parameters for the hydrogen atoms appear to be unreliable, owing to strong correlation with the charge parameters. Our estimates vary from 0.001–0.004 Å, assuming the entire molecule librates as a rigid group, to 0.04–0.05 Å assuming the hydrogen thermal parameters are real and the hydrogen atoms ride on the boron atoms. The riding model corrections to the N–H distances are much smaller.

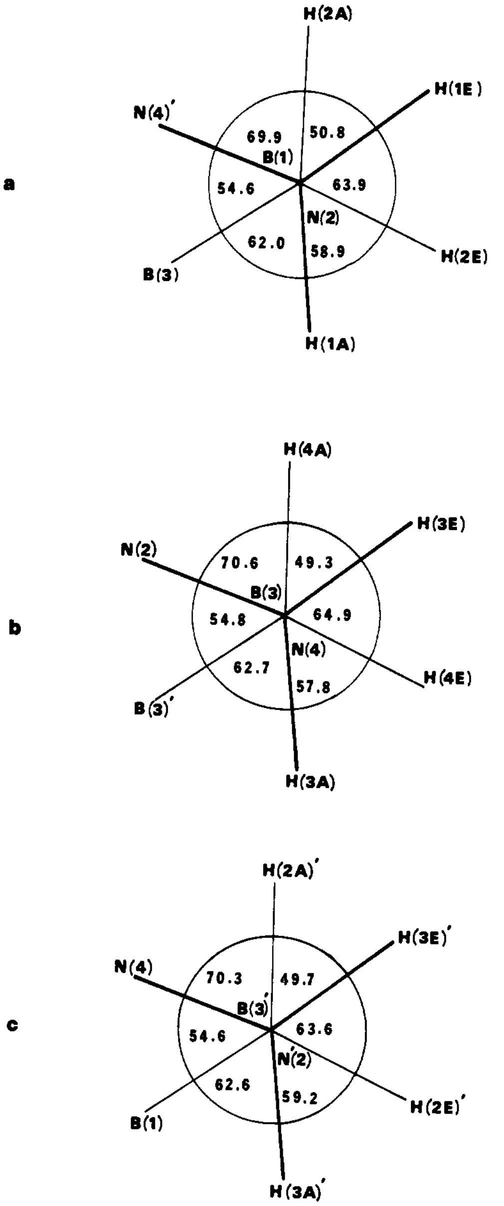

Figure 3. The dihedral angles associated with each of the three independent B–N bonds in the molecule. All views are in the same direction around the ring.

The conformation of the ring in the $(BH_2NH_2)_3$ molecule is rather close to that in cyclohexane,[25] in spite of the alternating bond angles in the ring. Presumably this is because the average ring angle in the present molecule is 111.5°, which is identical with the ring angle in cyclohexane found by Davis and Hassel.[25] The dihedral angles around the three independent B–N bonds are shown in Figure 3. The agreement between the dihedral angles for the different bonds indicates the molecular symmetry is very close to C_{3v}. The average ring dihedral angle is 54.7 (1)°, indicating that the chair is slightly flattened, as in cyclohexane, where dihedral angles of 54.5 (4) and 55.9 (4)° have been quoted.[25] The mean dihedral angle between axial hydrogen atoms is 172.7°, and that between equatorial hydrogen atoms is 64.1°.

The symmetrical nature of the triborazane molecule makes the silhouette representation of the chair ap-

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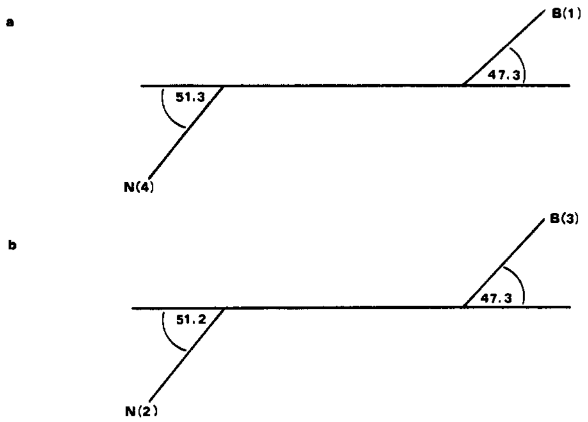

Figure 4. The two independent silhouette views of the molecule.

propriate.[32] In this representation, the molecule is projected onto a plane which passes through two opposing ring atoms and is normal to the best plane through the other four "base" atoms. The conformation is described in terms of the angles γ between the four-atom plane and each of two three-atom planes. The two independent silhouette representations for the triborazane molecule are shown in Figure 4. The four base atoms are strictly coplanar in Figure 3a and are close to being coplanar in Figure 3b. The silhouette angles are 51.4° at the nitrogen end of the molecule and 47.2° at the boron end. Distortions are slight, but real. The mean of the two values, however, is the same as the tilt angle in cyclohexane, assuming the ring bond angle is 111.6° as found by Davis and Hassel.[25] A more recent value for this bond angle is 111.1°[25] which leads to $\gamma = 50.6°$ in cyclohexane.

Table VII lists some of the more important intermolecular distances. All the shortest contacts are between oppositely charged hydrogens. There are three H · · ·H contacts less than the van der Waals distance of 2.4 Å, and these are shown in the packing diagram in Figure 5. The shortest contacts between molecules related by the short a axis are 2.51 Å, a somewhat surprising result, since the molecular dipoles are stacked end-to-end along the a axis.

Table VII. Intermolecular Distances between Hydrogen Atoms

Atom in molecule at xyz	Atom		Distance, Å[a]
H(1A)	H(4E)	$-x, \frac{1}{2} + y, z$	2.29
H(1E)	H(4E)	$-x, \frac{1}{2} + y, z$	2.29
H(2E)	H(3A)	$-x, -y, 1 - z$	2.29
H(1E)	H(4A)	$1 - x, \frac{1}{2} + y, z$	2.40
H(2E)	H(3E)	$-x, -y, 1 - z$	2.43
H(1A)	H(2A)	$-1 + x, y, z$	2.51
H(3A)	H(4A)	$-1 + x, y, z$	2.52
H(2A)	H(3A)	$1 + x, y, z$	2.53
H(2A)	H(3E)	$1 - x, -y, 1 - z$	2.54
H(1E)	H(4E)	$1 - x, \frac{1}{2} + y, z$	2.80
H(2E)	H(3E)	$1 - x, -y, 1 - z$	2.87

[a] The standard deviations average 0.02 Å.

Charge Refinements. The least-squares refinements including valence shell occupancy factors as adjustable parameters are apparently valid improvements of the scattering model, judging from the large drop in the values of R_1 and R_2. The geometry of the molecule remained unchanged on refining the occupancy factors, except that the bond lengths and angles involving the hydrogen atoms were more consistent after these refinements. While there are variations in the magnitudes of the partial charges in Table I, it is pleasing that the average values correspond to what one might have expected on the basis of the relative electronegativities of boron and nitrogen. The charge distribution appears not to be grossly sensitive to extinction errors (comparing refinements D and E) nor to the exact technique used to ensure overall neutrality (comparing refinements E and G). The distribution of charges follows the molecular symmetry (refinement F). The main effect of allowing for correlations of the charge parameters with the positional and thermal parameters (refinements D onwards) was that the charge on the hydrogen atoms attached to boron became much larger. In addition, the values found for the isotropic temperature factors for these hydrogens atoms were artificially high. One reason for the high temperature factors on the boron hydrogen atoms might be the use of an incorrect Slater coefficient, ζ. The wave function for the hydrogen atom is represented by $\phi = N \exp(-\zeta r)$ in this formalism, where ϕ is the value of the wave function at distance r from the nucleus and N is a normalizing constant. The value of ζ used for both types of hydrogen atoms had been 1.24, as suggested by

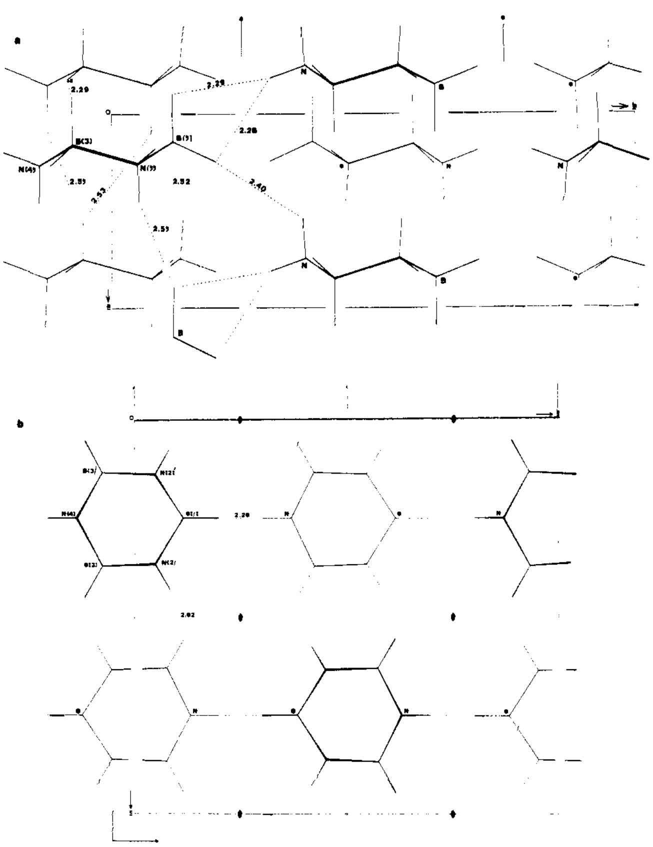

Figure 5. Projections of the structure, showing the packing and some of the intermolecular contacts. (a) Projection down the c axis. The molecules in bold outline are at $z = \frac{1}{4}$ and those in light outline at $z = \frac{3}{4}$. (b) Projection down the a axis. The molecules in bold outline have positive x coordinates, the others negative x coordinates.

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(32) J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, 91, 3567 (1969).

Hehre, Stewart, and Pople.[33] However, a lower value for this coefficient might be expected in the case of the boron hydrogen atoms, and by interpolating published coefficients for hydrogen in various molecules,[33,34] we chose a value of $\zeta = 1.08$ for these atoms. This coefficient was used for the boron hydrogen atoms in refinement H of Table I. The isotropic temperature factors on the boron hydrogen atoms decreased by an average of 1.6 Å^2 in this refinement, but were still higher than expected. The partial charges on the boron hydrogen atoms became even more negative, and there appears to be strong correlation between the charges and the temperature factors for these atoms. In a further refinement, the temperature factors on all axial hydrogen atoms were constrained to be equal, and also those on all equatorial hydrogen atoms. While the boron hydrogen atoms are certainly expected to vibrate more than the nitrogen hydrogen atoms, it was felt that this refinement would average the correlations in a way which would lead to more realistic partial charges. The results are presented in Table I, column I. The general distribution of electronic charge is very similar to all the other refinements, except that the charge on the nitrogen atoms has become very low. The value of R_2 is significantly higher than in refinement G. Further refinements involving adjustments of the ζ coefficients were not successful, owing to high correlation with both the thermal and the valence occupancy parameters.

Evaluation of the Partial Charges. The average charges found over all the refinements are +0.7 e for boron, −0.3 e for nitrogen, and −0.3 and +0.1 e for the respective hydrogen atoms. The large values for the charges on the ring atoms are in agreement with the calculations of Hoffmann,[35] who obtained +0.48 and −0.77 e for the boron and nitrogen atoms, respectively, using an extended Hückel LCAO–MO method. However, the relative magnitudes differ substantially. In all of Hoffmann's calculations on boron–nitrogen compounds, the nitrogen carries a very substantial negative charge compared with the boron atom, while in the present work, the boron atom carries the larger charge. Recently, Ermler, Corliss, and Kern[36] have calculated the electronic charge distribution in this molecule by SCF methods[37] using a minimal basis set of Slater orbitals. The net charges found, by the Mulliken[38] procedure, were: B; +0.17 e; N; −0.14 e; H(B), −0.18 e; H(N); +0.17 e. The SCF calculations agree with the present work in assigning relatively large charges to the hydrogen atoms and in the signs of the charges on all the atoms, but differ significantly in the charge assigned to the boron atoms. Further studies by X-ray methods of the charge distribution in molecules of this type would be valuable. The average negative charge of −0.3 e obtained for the boron hydrogen atoms, and the slight positive charge of 0.1 e for the nitrogen hydrogen atoms are consistent with the geometry of the BH_2 and the NH_2 groups. Thus the mutual repulsion of the negatively charged boron hydrogen atoms might be expected to make the H–B–H angle wider and the B–H distance longer.

It is pleasing that the dipole moments calculated on the basis of point charges bear some resemblance to the observed dipole moment of 3.2 D, but the inversion of direction which occurs between refinements C and D emphasizes that extreme caution should be applied to such calculations. The calculated dipole moment is the difference between a dipole due to the ring atoms and an opposite dipole due to the hydrogen atoms. The large values for the partial charges on the ring atoms found in this present study and predicted by Hoffmann imply that there should be a substantial opposite dipole due to the hydrogen atoms in order to account for the observed dipole moment, and this is consistent with the charges found for the hydrogen atoms in the present study. We note that the average values for the atomic charges (given in the preceding paragraph) would lead to a value of 3.0 D for the dipole moment based on point charges.

Further support for the rather substantial charges found for the hydrogen atoms in this study comes from the high heat of sublimation of 25 (3) kcal/mol. Parry and Weaver have postulated that electrostatic attraction between oppositely charged hydrogen atoms is a major contributor to the heat of sublimation in BH_3-NH_3.[39] The same would appear to be true in the present compound, since all the shortest intermolecular contacts involve hydrogen atoms of opposite charge.

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