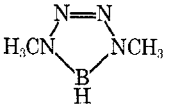
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

The Molecular Structure of Dimethylcyclotetrazenoborane, $(CH_3)_2N_4BH$

BY C. H. CHANG, R. F. PORTER, AND S. H. BAUER

Received October 23, 1968

The structure of $(CH_3)_2N_4BH$ in the gas phase has been verified to be



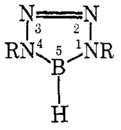
Although the electron diffraction patterns are not uniquely interpretable in terms of a planar structure, the acceptance of a planar conformation is supported by the observed magnitudes of the bonded distances and by theoretical arguments based on the electron-rich character of the four N atoms in the ring. The bond lengths and bond angles determined by least-squares fitting of the intensity data are: B—N = 1.413 ± 0.010 Å, N—N = 1.375 ± 0.005 Å, N=N = 1.291 ± 0.006 Å, N—C = 1.454 ± 0.009 Å, B—H = 1.195 Å (assumed), C—H = 1.096 ± 0.010 Å, ∠NBN = 101.8 ± 0.6°, and ∠CNN = 115.8 ± 0.3°. These values suggest the presence of extensive delocalization of the π electrons in the N_4B ring.

Introduction

An N_4B five-membered ring system which is isoelectronic with triazole was synthesized for the first time by Greenwood and Morris.[1] The 2,5-diphenylcyclotetrazenoborane, $(C_6H_5)_2N_4BH$, was prepared by the reaction of phenyl azide with either decaborane or aniline–borane. Morris and Perkins later succeeded in preparing the dimethyl and methylphenyl derivatives[2,3] and demonstrated the generality of the following scheme for preparing derivatives of this novel heterocyclic N_4B ring

$$RN{=}N{=}N + [R'N{=}BH] \longrightarrow RR'N_4BH$$

Of the three possible isomeric structures



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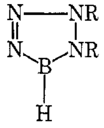

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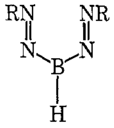

III

III appears to be the least likely since no absorptions characteristics of an RN=N– group were observed.[1,3] Assignment of infrared frequencies[4] and molecular orbital calculations[2] favored structure I, although the distinction between I (C_{2v}) and II (C_s) on the basis of the infrared data is not definitive.

Since $(CH_3)_2N_4BH$ is the simplest available derivative of cyclotetrazenoborane, an electron diffraction determination of its structure will resolve the ambiguity and should provide interesting quantitative information on the dimensions of the new N_4B ring. The results of such an investigation are reported below.

Experimental Section

A reasonably pure sample of $(CH_3)_2N_4BH$, as judged from its vapor-phase ir spectrum, was provided by Dr. John H. Morris, who stated that it was prepared *via* a slightly different route from above, *i.e.*, by heating dimethyl sulfate, methylammonium azide, and lithium borohydride together in ether at 120° for 48 hr, followed by a vacuum fractionation of the products.[5] A small amount of methyl azide, CH_3N_3, was detected as an impurity, in the mass spectrometer.

Sectored electron diffraction photographs were obtained with a 65-kV beam using the new Cornell electron diffraction apparatus, described previously.[6] The sample was kept at room temperature. Methods followed in this laboratory for measuring the plates and reducing the data have already been adequately described in the literature.[7]

Results

A listing of intensity–diffraction angle values is given in Table I. These are plotted in Figure 1, along with the refined background curves for two ranges of diffraction angles, covering $q = 6$–$123\ \text{Å}^{-1}$. Since the sample was found by mass spectrometry to contain a small amount of methyl azide, estimation of the impurity content was based on preliminary radial distribution and least-squares analyses.

We may write

$$M_1(q) = [M(q) - \chi_2 M_2(q)]/\chi_1 \tag{1}$$

where $M(q)$ is the total experimental molecular scattering as a function of q while $M_1(q)$ and $M_2(q)$ are theoretical scattering functions for $(CH_3)_2N_4BH$ and CH_3N_3; χ_1 and χ_2 are the corresponding mole fractions. We found that $\chi_2 = 4\%$ gave the best least-squares fit. $M_2(q)$ was calculated on basis of an early structure analysis.[8]

For the final structure determination, the experimental molecular intensity curve was corrected for the 4% impurity on the basis of eq 1. Figure 2 shows the resulting experimental molecular scattering curve for $(CH_3)_2N_4BH$ and that calculated for the converged least-squares planar model, illustrated in Figure 3.

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[1] N. N. Greenwood and J. H. Morris, *J. Chem. Soc.*, 6205 (1965).

[2] J. H. Morris and P. G. Perkins, *ibid.*, *A*, 576 (1966).

[3] J. H. Morris and P. G. Perkins, *ibid.*, *A*, 580 (1966).

[4] A. J. Downs and J. H. Morris, *Spectrochim. Acta*, **22**, 957 (1966).

[5] J. H. Morris, private communication.

[6] S. H. Bauer and K. Kimura, *J. Phys. Soc. Japan*, **17**, 300 (1962).

[7] (a) J. L. Hencher and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 5527 (1967); (b) W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1683 (1969).

[8] L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).

TABLE I

INTENSITY DATA FOR $(CH_3)_2N_4BH$

Set 1		Set 2			
Q	INTENSITY	Q	INTENSITY	Q	INTENSITY
6.	0.8939	28.	0.9341	80.	1.0262
7.	0.6800	29.	1.0017	81.	1.0331
8.	0.5292	30.	1.0033	82.	1.0479
9.	0.4245	31.	0.9815	83.	1.0651
10.	0.4038	32.	0.9296	84.	1.0838
11.	0.4182	33.	0.8909	85.	1.0995
12.	0.4328	34.	0.8667	86.	1.1102
13.	0.4367	35.	0.8511	87.	1.1216
14.	0.4197	36.	0.8337	88.	1.1290
15.	0.4488	37.	0.8122	89.	1.1400
16.	0.5471	38.	0.7930	90.	1.1485
17.	0.6786	39.	0.7877	91.	1.1595
18.	0.7791	40.	0.7877	92.	1.1722
19.	0.8135	41.	0.7809	93.	1.1847
20.	0.7697	42.	0.7717	94.	1.1983
21.	0.6849	43.	0.7820	95.	1.2109
22.	0.6065	44.	0.8089	96.	1.2218
23.	0.5570	45.	0.8445	97.	1.2373
24.	0.5300	46.	0.8711	98.	1.2520
25.	0.5191	47.	0.8796	99.	1.2701
26.	0.5220	48.	0.8720	100.	1.2898
27.	0.5550	49.	0.8466	101.	1.3080
28.	0.6191	50.	0.8239	102.	1.3244
29.	0.6781	51.	0.8066	103.	1.3412
30.	0.7057	52.	0.7995	104.	1.3570
31.	0.6996	53.	0.8000	105.	1.3718
32.	0.6837	54.	0.8073	106.	1.3844
33.	0.6713	55.	0.8251	107.	1.3981
34.	0.6678	56.	0.8473	108.	1.4123
35.	0.6656	57.	0.8718	109.	1.4314
36.	0.6592	58.	0.8863	110.	1.4529
37.	0.6475	59.	0.9004	111.	1.4740
38.	0.6413	60.	0.9084	112.	1.4964
39.	0.6448	61.	0.9115	113.	1.5174
40.	0.6539	62.	0.9139	114.	1.5396
41.	0.6558	63.	0.9139	115.	1.5602
42.	0.6546	64.	0.9122	116.	1.5804
43.	0.6685	65.	0.9109	117.	1.6010
44.	0.6948	66.	0.9105	118.	1.6210
45.	0.7238	67.	0.9177	119.	1.6413
46.	0.7436	68.	0.9256	120.	1.6622
47.	0.7523	69.	0.9337	121.	1.6844
48.	0.7446	70.	0.9443	122.	1.7056
49.	0.7319	71.	0.9554	123.	1.7259
50.	0.7186	72.	0.9703		
51.	0.7159	73.	0.9844		
52.	0.7174	74.	0.9997		
53.	0.7227	75.	1.0128		
54.	0.7346	76.	1.0241		
55.	0.7544	77.	1.0271		
56.	0.7763	78.	1.0278		
57.	0.7958	79.	1.0232		

The refined experimental radial distribution curve (Figure 4) was evaluated with a damping factor of $\gamma = 0.00154$. This figure also shows the difference curve between the experimental and theoretical radial distribution functions for several models. The first peak with its shoulder includes all six bonded distances: B—H = 1.195, C—H = 1.098, N=N = 1.290, N—N = 1.375, B—N = 1.413, and C—N = 1.453 Å. The second peak was resolved into 11 nonbonded distances of which only the heavy-atom pairs ($N_1\cdots N_3 = 2.173$, $N_1\cdots N_4 = 2.192$, $N_2\cdots B_5 = 2.284$, $N_2\cdots C_6 = 2.397$, and $B_5\cdots C_6 = 2.640$ Å) contribute significantly to the area. The peak centered at 3.54 Å was assigned to the nonbonded $N_2\cdots C_7 = 3.506$ and $N_1\cdots C_7 = 3.639$ Å. The only heavy nonbonded atom pair left is C···C at 5.078 Å. From this radial distribution curve, it is apparent that the compound used in this study cannot have structure II, since in that case the nonbonded C···C would produce a peak at about 2.85 Å, and there would be no single heavy atom pair distance at about 5.0 Å.

Details of the Analysis

To select structural parameters, we assumed that the molecule has a plane of symmetry and that the four N atoms are coplanar. This is justified by the demonstrated presence of N=N,[4] the elimination of structure II by the radial distribution curve, and the totality of evidence in favor of structure I. We then introduced ten parameters, six bonded distances and four angles; the latter are $\angle N_1BN_4$ and $\angle xN_1C_6$ projected onto the N_4 atom plane (Figure 3); the angle α is between the planes of N_1BN_4 and $N_1N_2N_3N_4$, and the angle ϵ is that which the C—N bonds make with the N_4 plane. We assumed that the B—H bond was in the N_1BN_4 plane and $\angle$NCH has the tetrahedral value 109.5°.

It was found during the preliminary least-squares calculations that allowing arbitrary variation of the l_{ij}'s (root-mean-square amplitudes of vibration) for the bonded atom pairs led to converged solutions with physically unacceptable distances. This is consistent with general experience when several interatomic distances are within 0.15 Å. The least-squares program incorporates no criteria for distinguishing between spreading similar distances apart and decreasing the corresponding l_{ij}'s, or *vice versa*. Hence we found it necessary to constrain the following mean amplitudes to values reported for similar molecules: $l_{N=N} = 0.044$, $l_{N-N} = 0.048$, $l_{B-N} = 0.052$, $l_{C-N} = 0.052$, $l_{B-H} = 0.084$, and $l_{C-H} = 0.078$ Å, in the final least-squares runs. The values for B—H = 1.195 Å and $l_{C\cdots C} = 0.088$ Å are average magnitudes obtained after several cycles of the preliminary calculations. All of the constrained l_{ij}'s and their assumed magnitudes are listed in Table II. These were obtained by preliminary least-squares fitting of the intensity curve, alternately constraining distances and l_{ij}'s. The variables used in the final least-squares calculation and the corresponding results are given in Table III.

TABLE II

CONSTRAINED l_{ij}'S FOR LEAST-SQUARES ANALYSES[a]

	l_{ij}, Å	
Atom pair	For models A, B, C	For model D
N=N	0.044	Unconstrained but all set equal
N—N	0.048	
B—N	0.052	
C—N	0.052	
B—H	0.084	0.084
C—H	0.078	0.078
C···C	0.088	0.088
B···H	0.150	0.150
$N_1\cdots H_8$	0.090	0.090
$N_1\cdots H_9$	0.120	0.120
$N_1\cdots H_{12}$	0.120	0.120
$N_2\cdots H_8$	0.100	0.100
$N_2\cdots H_9$	0.170	0.170
$N_2\cdots H_{12}$	0.190	0.190
$C_6\cdots H_8$	0.095	0.095
$C_6\cdots H_{12}$	0.130	0.130
$H_9\cdots H_{10}$	0.090	0.090
$H_9\cdots H_{12}$	0.170	0.170

[a] A number of tests were made, in which the nonbonded $l_{M\cdots H}$'s were varied over a total range of 20% with no significant effect on the least-squares geometrical values. The values listed in this table did give the lowest standard deviation.

The planar structure with C_{2v} symmetry was first examined by setting the two out-of-plane angles equal

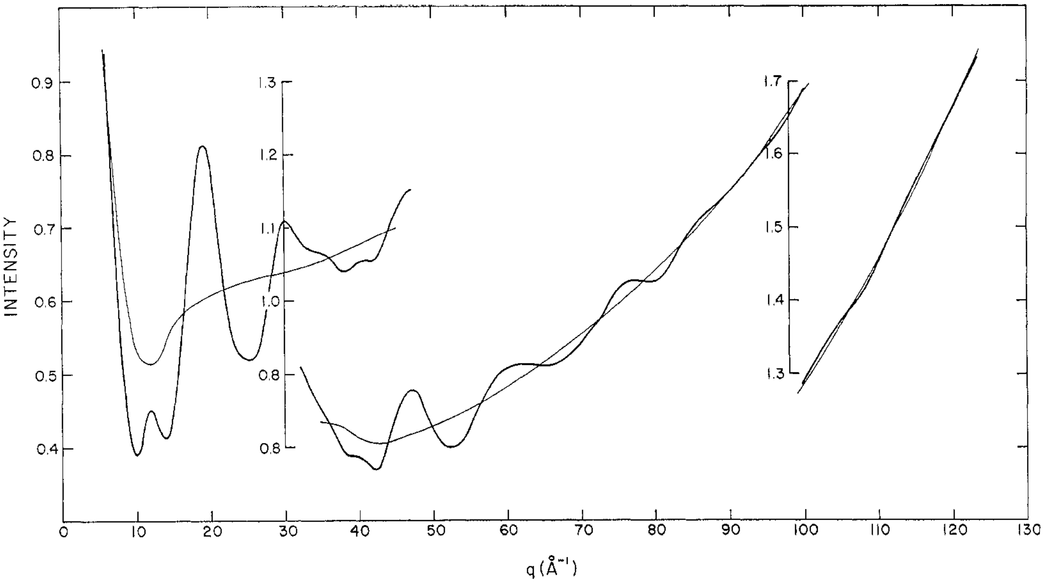


Figure 1.—The experimental intensity and background curves.

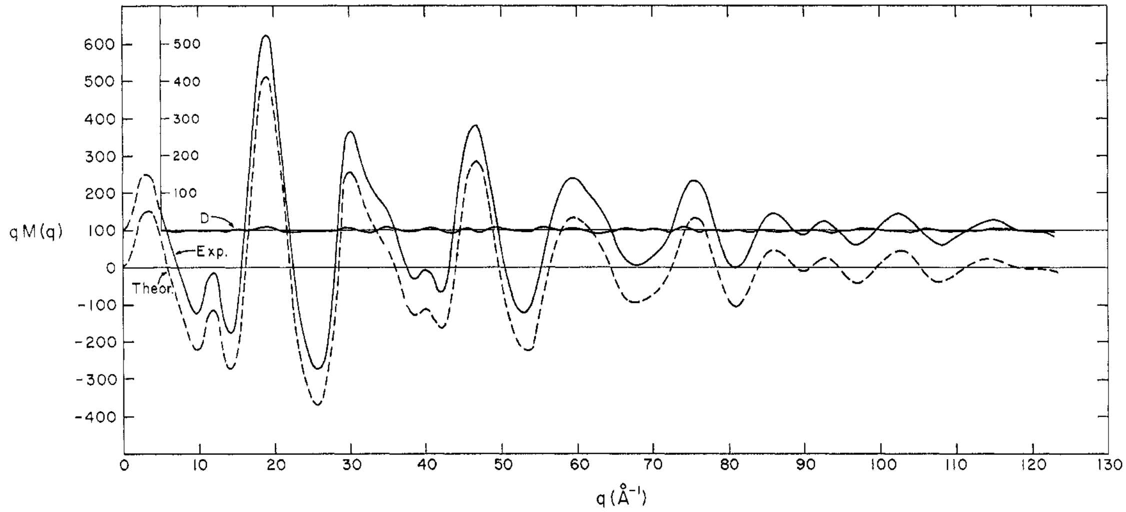


Figure 2.—The reduced molecular scattering curve for $(CH_3)_2N_4BH$ and that calculated from the converged least-squares planar model. Curve D is the difference curve.

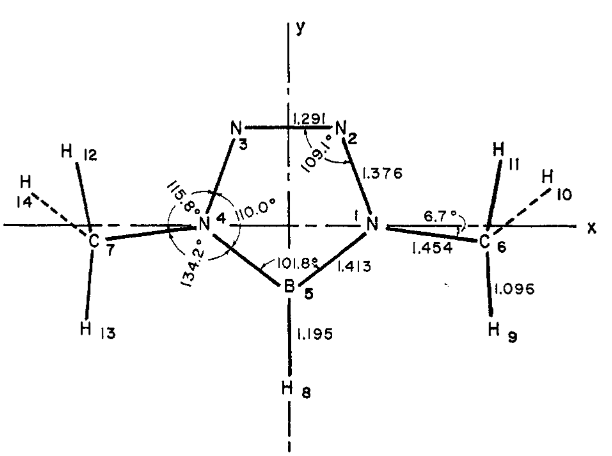


Figure 3.—Projection of $(CH_3)_2N_4BH$ onto the plane of N_4B.

to zero. The converged values for the parameters and the l_{ij}'s for the planar model (A) are listed in the second column of Table III. In the error matrix no strong correlations were indicated for the chosen parameters while the calculated uncertainties (standard deviations as listed in Table III) are reasonably small.

Two types of nonplanar models were also considered. In one set of calculations the out-of-plane angles were successively constrained in the least-squares analyses at $\alpha = -\epsilon = 2$–$10°$. As shown in Figure 5, standard deviations for the converged sets of parameters show a very slight minimum at $\alpha = 3.5°$ which is not statistically significant. The corresponding values for the parameters on the basis of $\alpha = 3.0°$ (model B) are tabulated in Table III. In the next case, α and ϵ were allowed to vary independently (model C); this led to the lowest standard deviation. To determine whether

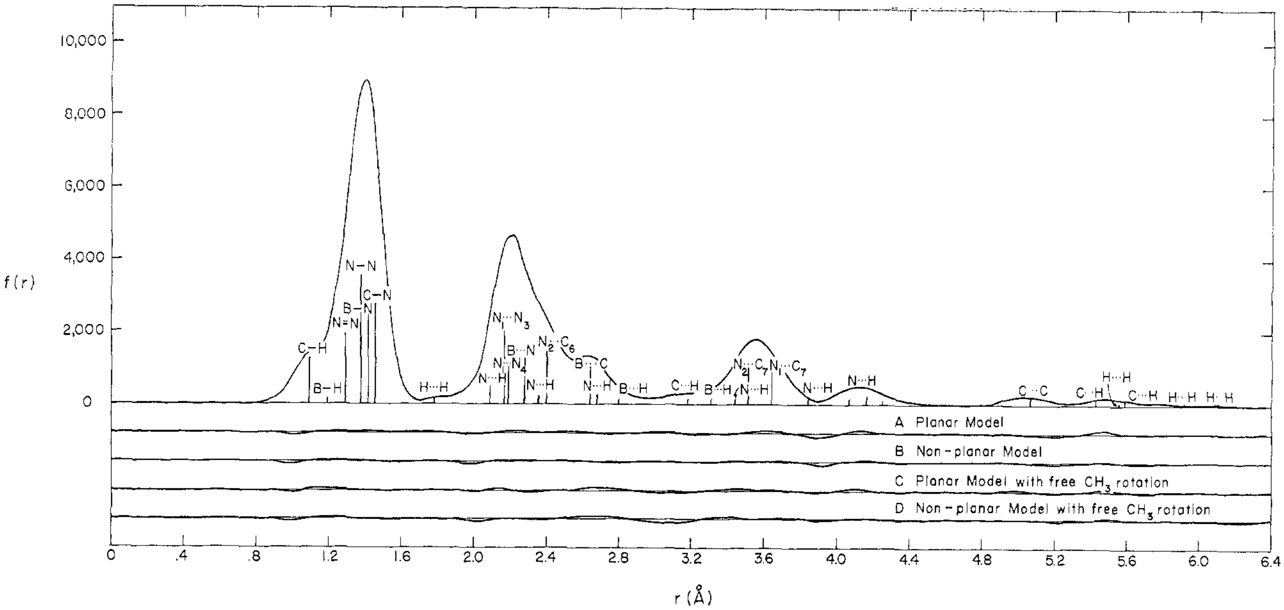


Figure 4.—The refined radial distribution curve for $(CH_3)_2N_4BH$ and the difference curves between the experimental and theoretical functions for different models.

Table III

Structure Parameters for $(CH_3)_2N_4BH$[a]

	Model					
	A, planar	B, nonplanar: $\alpha = \epsilon$	C, nonplanar: α, ϵ independent	D, nonplanar: α, ϵ independent		
B—N, Å	1.4127 (0.0033)	1.4141 (0.0031)	1.4126 (0.0033)	1.4176		
N—N, Å	1.3754 (0.0016)	1.3747 (0.0016)	1.3763 (0.0017)	1.3706		
N=N, Å	1.2904 (0.0017)	1.2875 (0.0017)	1.2914 (0.0017)	1.2982		
N—C, Å	1.4527 (0.0022)	1.4531 (0.0022)	1.4537 (0.0022)	1.4505		
C—H, Å	1.0976 (0.0035)	1.0964 (0.0034)	1.0957 (0.0032)	1.0998		
B—H, Å	1.195 {assumed}	1.195 {assumed}	1.195 {assumed}	1.195 {assumed}		
$0.5\angle N_1BN_4$, radian	0.8882 (0.0020)	0.8885 (0.0019)	0.8932 (0.0043)	0.8855		
$\angle xN_1C_6$, radian	−0.1168 (0.0041)	−0.1179 (0.0040)	−0.1184 (0.0039)	−0.1191		
α, radian	0.0 {assumed}	−0.0524 {assumed}	0.0978 (0.0358)	0.0452		
ϵ, radian	0.0 {assumed}	0.0524 {assumed}	−0.0136 (0.0101)	−0.0416		
$l_{B\cdots N} = l_{N_2\cdots C_6}$, Å	0.0739 (0.0044)	0.0705 (0.0044)	0.0741 (0.0047)	0.0798		
$l_{B\cdots C}$, Å	0.0638 (0.0028)	0.0636 (0.0029)	0.0638 (0.0028)	0.0655		
$l_{N_1\cdots C_l}$, Å	0.0791 (0.0051)	0.0812 (0.0053)	0.0761 (0.0047)	0.0738	←	$l_{N_1\cdots C_7} = l_{N_2\cdots C_7}$, Å
$l_{N_1\cdots N_3} = {}_{N_1\cdots N_4}$, Å	0.0561 (0.0011)	0.0556 (0.0012)	0.0565 (0.0012)	0.0559		
$l_{N_2\cdots C_7}$,	0.0670 (0.0037)	0.0699 (0.0040)	0.0668 (0.0036)	0.0523	←	$l_{B—N} = l_{N—N} = l_{N=N}$, Å
Std dev	0.02085	0.02251	0.02069	0.02311		
Residual	0.04625	0.05504	0.04386	0.05183		
Error	0.04625	0.05504	0.04386	0.05188		

[a] Refer to the text and to ref 7b for a discussion of correlations and error limits. Standard deviations are given in parentheses.

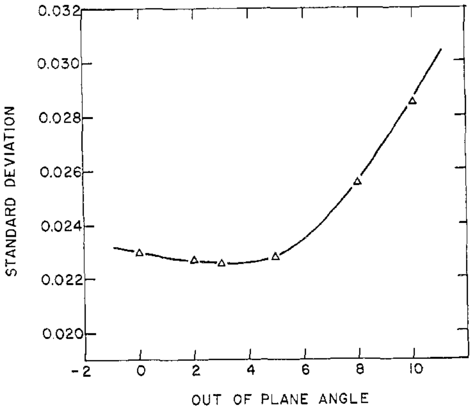


Figure 5.—Standard deviations for the converged sets of parameters for a sequence of out-of-plane angles.

the constrained values for l_{ij}'s for the bonded atom pairs and whether the assumed equality of the two pairs of nonbonded l_{ij}'s in models A, B, and C had a significant effect on the least-squares magnitudes for the geometric parameters, we tested model D. (Refer to Tables II and III.) While the standard deviation for this model is not quite as low as A, B, and C, the best values for the bonded distances changed insignificantly; to optimize the fit, the program settled on $\langle l_{ij}\rangle_{av} = 0.052$ Å for all of the bonded heavy-atom pairs. The largest fractional change occurred for α and ϵ, the nonplanarity parameters. It is evident from Table III that the bonded distances in the planar and the best nonplanar models differ only in the third decimal place. Since the constraint of planarity forces adjustment in the bonded distances in order to provide the best fit for the complete pattern and since the bonded values remain essentially unchanged, it follows that in $(CH_3)_2N_4BH$: B—N = 1.413 ± 0.010, N—N = 1.375 ± 0.005, N=N = 1.291 ± 0.006, N—C = 1.454 ± 0.009, and C—H = 1.096 ± 0.010 Å. The error limits were assigned to be the larger of the estimated systematic errors[7b] or three times the calculated standard deviations. For the planar model, the least-squares analysis converged to $\angle N_1B_5N_4 = 101.8 \pm 0.6°$ and $\angle xN_1C_6 = 6.7 \pm 0.3°$. The other angles were calculated to be $\angle N_1N_2N_3 = 109.1°$, $\angle N_3N_4N_5 = 110.0°$, $\angle N_2N_1C_6 = 115.8°$, and $\angle B_5N_1C_6 = 134.2°$.

The question remains as to whether it is best to consider $(CH_3)_2N_4BH$ as having a planar minimum energy configuration but with large out-of-plane amplitudes of the boron and carbon atoms [$l_{B\cdots N}$, $l_{N\cdots C}$ are considerably larger than $l_{N_1\cdots N_2}$, $l_{N_1\cdots N_4}$] due to a flat potential function or to accept model C, as representative of the minimum in Figure 5. Since the difference between the standard deviations for A and C are insignificant, while there are pertinent theoretical arguments in favor of a planar structure, we favor that alternative.

Shrinkage effects for nonbonded distances were estimated from[9]

$$-\delta \equiv (r^g{}_{A\cdots B})_{obsd} - (r^g{}_{A\cdots B})_{calcd}$$

where

$$(r^g{}_{A\cdots B})_{obsd} \equiv (r^e{}_{A\cdots B})_{obsd} + \left[\frac{(l_{A\cdots B})^2}{r^e{}_{A\cdots B}}\right]_{obsd}$$

$r^e{}_{A\cdots B}$ and $l_{A\cdots B}$ are the least-squares converged values for the nonplanar model (C) and $(r^g{}_{A\cdots B})_{calcd}$ was obtained from the planar model, with $\angle N_1BN_4 = 0.8868$ and $\angle xN_1C_6 = 0.1168$ radian. As shown in Table IV the very small values of δ for $N_1\cdots N_3$ and $N_1\cdots N_4$ are consistent with the assumption that the four nitrogen atoms are coplanar. The remaining values are comparable in magnitude to the shrinkages calculated for benzene from spectroscopic data:[10] $\delta_{C_1\cdots C_3} = 0.00342$ and $\delta_{C_1\cdots C_4} = 0.00485$ Å.

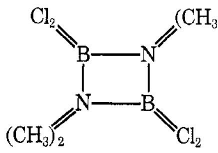
TABLE IV
SHRINKAGE EFFECT

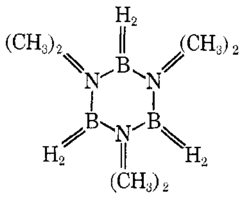
A···B	$(r^g{}_{A\cdots B})_{calcd}$, Å	$(r^g{}_{A\cdots B})_{obsd}$, Å	δ, Å
$N_1\cdots N_3$	2.1742	2.1748	−0.0006
$N_1\cdots N_4$	2.1936	2.1920	0.0016
$N_2\cdots B_5$	2.2860	2.2831	0.0029
$N_2\cdots C_6$	2.3988	2.3981	0.0007
$B_5\cdots C_6$	2.6405	2.6391	0.0014
$N_2\cdots C_7$	3.5078	2.5069	0.0009
$N_1\cdots C_7$	3.6406	3.6359	0.0047
C···C	5.0793	5.0706	0.0087

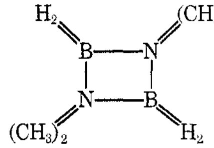
During the least-squares runs, it was found that in order to obtain reasonable values for the root-mean-square amplitudes for the nonbonded heavy-atom pairs, the l_{ij}'s for the nonbonded $B\cdots H$ and $N_2\cdots H$ had to be constrained to particularly large values, as shown in Table II. This is a strong indication that the methyl groups rotate essentially freely about the N—C bonds. The two CH_3 groups were assumed to have C_{3v} symmetry and to rotate in the same direction in a 3-minimum potential, with a barrier height of 1 kcal, as estimated by Morris and Perkins.[2] The $qM(q)$ functions were calculated for 10 different positions of the CH_3 groups and were averaged, appropriately weighted. The resultant $qM(q)$ was transformed to f(r). Differences between the experimental and theoretical curves are shown in Figure 4, C and D, where C corresponds to the planar and D to the nonplanar models. The difference curves are not significantly improved as compared with A and B, because of the small contributions to the total from $B\cdots H$ and $N_2\cdots H$ atom pairs. Hence, the large l_{ij}'s for $B\cdots H = 0.130$, $N_2\cdots H_9 = 0.130$, and $N_2\cdots H_{12} = 0.150$ Å used in these calculations are reasonable.

Discussion

The results of this study are in accord with the proposed C_{2v} planar symmetry for $(CH_3)_2N_4BH$ by Morris and his coworkers.[3,4] The boron–nitrogen bond length of 1.413 ± 0.010 Å is very short compared with that expected for unit B—N bond, 1.59 Å, as observed in IV[11] and V[12] and 1.61 Å in VI.[13] It is slightly less than the B—N distance in VII[7b] (1.436 Å), in VIII (1.42 Å), in IX[14] (1.41 Å), and in X[15] (1.426 Å) and the ring B—N bond in XI[16] (1.415 Å), all of which are pseudo-


IV


V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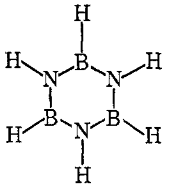
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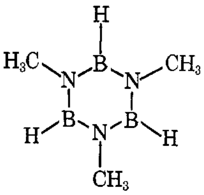
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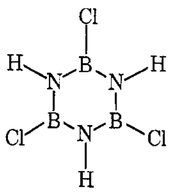
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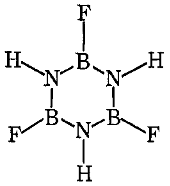
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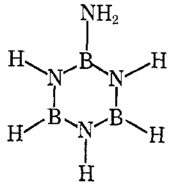
XI

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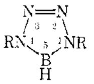
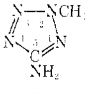
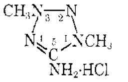
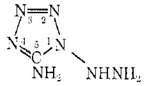
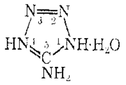
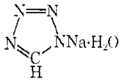
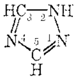
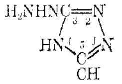
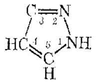
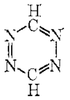
Table V

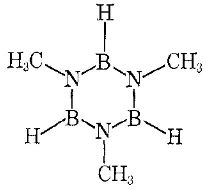
Reported Structures of 6π-Electron Systems Which Have N—N Bonds and Results of MO Calculations

Molecule	Structure	Stretching freq, $\nu_{N=N}$, cm^{-1}	Bond length, r_{N-N}, Å	Bond order, η
Dimethylcyclotetrazenoborane (I)		1360[a]	$r_{12} = 1.376 \pm 0.005$[b] $r_{23} = 1.283 \pm 0.005$[b]	0.24[c] 0.94[c]
2-Methyl-5-aminotetrazole (XV)		1435[d]	$r_{12} = 1.34 \pm 0.017$[e] $r_{23} = 1.29 \pm 0.017$[e] $r_{34} = 1.32 \pm 0.017$[e]	0.46[f] 0.58[f] 0.69[f]
HCl salt of 1,3-dimethyl-5-imino-tetrazole (XVI)			$r_{12} = 1.35 \pm 0.02$[g] $r_{23} = 1.30 \pm 0.02$[g] $r_{34} = 1.31 \pm 0.02$[g]	0.54[f] 0.67[f] 0.46[f]
Hydrazine salt of 5-aminotetrazole (XVII)		1439[d]	$r_{12} = 1.356 \pm 0.008$[h] $r_{23} = 1.295 \pm 0.007$[h] $r_{34} = 1.346 \pm 0.006$[h]	
5-Aminotetrazole monohydrate (XVIII)		1443	$r_{12} = 1.381 \pm 0.015$[i] $r_{23} = 1.255 \pm 0.015$[i] $r_{34} = 1.373 \pm 0.015$[i]	
Sodium tetrazole monohydrate (XIX)			$r_{12} = 1.348 \pm 0.002$[j] $r_{23} = 1.310 \pm 0.002$[j]	
2H-1,2,4-Triazole (XX)			$r_{12} = 1.354 \pm 0.014$[k]	
3-Hydrazino-5-mercapto-1,2,4-triazole (XXI)			$r_{12} = 1.40 \pm 0.013$[l]	
Pyrazole (XXII)			$r_{12} = 1.361 \pm 0.016$[m]	0.26[o]
s-Tetrazine (XXIII)			$r_{12} = 1.321 \pm 0.010$[n]	0.66[o]

[a] See ref 4. [b] This work. [c] See ref 2. [d] H. B. Jonassen, T. Paukert, and R. A. Henry, *Appl. Spectry.*, **21,** 89 (1967). [e] J. H. Bryden, *Acta Cryst.*, **9,** 874 (1956). [f] A. J. Owen, *Tetrahedron*, **14,** 237 (1961). [g] J. H. Bryden, *Acta Cryst.*, **8,** 211 (1955). [h] J. H. Bryden, *ibid.*, **11,** 31 (1958). [i] K. Britts and I. L. Karle, *ibid.*, **22,** 308 (1967). [j] G. J. Palenik, *ibid.*, **16,** 596 (1963). [k] H. Deuschl, *Ber. Bunsenges. Physik. Chem.*, **69,** 550 (1965). [l] M. E. Senko and D. H. Templeton, *Acta Cryst.*, **11,** 808 (1958). [m] H. W. W. Ehrlich, *ibid.*, **13,** 946 (1960). [n] F. Bertinotti, G. Giacomello, and A. M. Liquori, *ibid.*, **9,** 510 (1956). [o] M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44,** 759 (1966).

aromatic, in that 6π electrons may be assigned to the $(B—N)_3$ ring. The N—N bond length of 1.375 ± 0.005 Å is also considerably shorter than a typical unit N—N bond such as is present in hydrazine (1.449 Å).[17] These suggest extensive delocalization of the π electrons in the N_4B ring and provide a rational basis for the N═N bond of 1.291 ± 0.006 Å which is longer than the separation found for nitrogen–nitrogen double bonds. A compilation of N═N bond lengths has been published,[18] and it is interesting to note that these distances correlate well with the corresponding N═N stretching frequencies. The $\nu_{N=N}$ is 1636 cm^{-1} in N_2F_2 (N═N = 1.230 Å),[18,19] 1626 cm^{-1} in F_2CN_2 (diazirine) (1.228 Å),[20,21] and 1360 cm^{-1} in $(CH_3)_2N_4BH$ (1.291 Å);[4] others are tabulated in Table V.

The C—N bond length (1.454 ± 0.009 Å) is within experimental error (1.48 ± 0.02 Å) equal to that reported for XII[14] and for XIII. The value 1.096 ± 0.01 Å is in good agreement with C—H bond lengths in alkanes while the B—H bond distances are close to that found in boroxine.[22] The reported frequencies for B—H asymmetric stretching vibration (E′ type) also correlate well with the bond lengths in $(CH_3)_2N_4BN$ (ν_{B-H} = 2636 cm^{-1}, B—H = 1.195 Å),[4] $B_3O_3H_3$ (2620 cm^{-1}, 1.192 Å),[22,23] and $B_3N_3H_6$ (2520 cm^{-1}, 1.258 Å).[7b,24]



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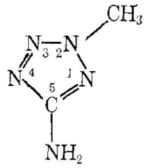

XIII

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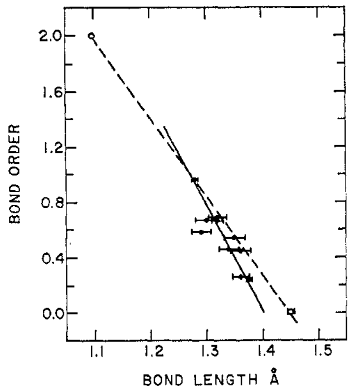

Figure 6.—Bond order as a function of bond length: - - -, predicted on the basis of N≡N = 1.097 Å and N—N = 1.449 Å; —, empirical relation.

A rationalization may be presented for the observed N—N bond lengths. The bond order (η) for the π system for two N—N bonds in the N_4B ring was calculated by a simple Hückel LCAO-MO method, with ω technique, to be 0.94 and 0.24. Results of similar MO calculations for other 6π-electron rings which contain N—N bonds are tabulated in Table V. While one may question the quantitative significance in these calculations, it is interesting to note that the empirical relation

$$\text{N-N} = 1.403 - 0.128\eta_{\text{N-N}}\ \text{Å}$$

correlates the N—N bond lengths and the bond orders within the experimental error. As shown in Figure 6 the bond lengths in these rings are shorter than predicted on a basis of N≡N = 1.097 Å in N_2[25] and N—N = 1.449 Å in N_2H_4[17] (broken line in the figure). The $(2 + 4n)$ rule is satisfied by $(CH_3)_2N_4BH$ for $n = 1$ if one does not count the nonbonding electron pairs on the doubly bonded N atoms and for $n = 2$ if one does include them.

Acknowledgments.—The authors wish to thank Dr. J. H. Morris for providing samples of this new compound, Mr. M. Cardillo for help in taking the photographs, and Mr. R. Hilderbrandt for developing some of the computer programs. The electron diffraction study was supported by the Advanced Research Projects Agency, the Army Research Office (Durham), and the National Science Foundation.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

The Structure of Borazine

BY W. HARSHBARGER, G. LEE, R. F. PORTER, AND S. H. BAUER

Received January 8, 1969

The molecular structure of borazine ($B_3N_3H_6$) was reinvestigated by electron diffraction. A planar D_{3h} model and two nonplanar (C_{3v} and C_2) models were fitted to the diffraction data. For two sets of data the nonplanar models statistically fit the observed diffraction data better than did the planar model. Owing to the absence of a permanent dipole moment for borazine, the C_2 model or a D_{3h} model with very large vibrational motion is preferred; the choice between these is not unambiguous. The bonded distances are B–N = 1.4355 ± 0.0021 Å, B–H = 1.258 ± 0.014 Å, and N–H = 1.050 ± 0.012 Å. The ring angles are ∠NBN = 117.7 ± 1.2° and ∠BNB = 121.1 ± 1.2°.

Introduction

The molecular structure of borazine in the gas phase was investigated previously by electron diffraction.[1,2] The conclusion of those studies, in which the visual technique was used, was that the molecule consisted of a planar ring with a B–N bond distance of 1.44 ± 0.02 Å.[2] A redetermination of the structure of borazine was undertaken to obtain more precise values for the interatomic distances, utilizing the greatly improved techniques which have been developed during the past three decades.

A large number of data, relevant to a discussion of its molecular structure, are now available on the physical properties of borazine. Since this compound is isoelectronic with and structurally similar to benzene, many investigators considered the question of the degree of electron delocalization which should be used to describe the p–π electron system of borazine. The B–N bond length is significantly shorter in $B_3N_3H_6$ than the 1.56 Å found in crystalline borazane, H_3BNH_3,[3] pointing to a higher bond order in borazine. Polarization measurements[4,5] appeared to indicate that this compound has a finite electric dipole moment, contradicting the symmetric planar structure deduced by electron diffraction. The first study was made with the gas phase, but the author did not place much reliance on his results owing to the instability of his sample.[4] The second investigation was made in a solution of benzene; this led to a value of 0.50 D.[5] However, a recent unsuccessful search for microwave absorption in the gas phase places an upper limit at 0.1 D for this molecule.[6]

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