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Studies of Boron-Nitrogen Compounds. V.<sup>1</sup> Two Isomers of 1,3,5-Trimethylcycloborazane

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The compound 1,3,5-trimethylcycloborazane,  $B_3H_5N_3H_3(CH_3)_3$ , previously prepared from methylamine and diborane, now has been prepared also from (a) methylamine hydrochloride and sodium borohydride and from (b) 1,3,5-trimethylborazine by the reaction  $2B_3H_2N_3(CH_3)_3 \cdot 3HCl + 6NaBH_4 \rightarrow 2B_3H_5N_3H_3(CH_3)_3 + 6NaCl + 3B_2H_6$ . Two isomers, I and II, have been isolated both by fractional sublimation under high vacuum and by fractional recrystallization from benzene and methanol. Isomer I is the least soluble and sublimes at a higher temperature. Both isomers probably are in the chair form and physical and chemical evidence indicates that I has all methyl groups equatorial and II has two methyl groups equatorial and one axial.

## Introduction

Compounds of the class characterized by a six-membered ring of alternating tetracoordinated boron and nitrogen atoms have in the past been assigned names as trimeric aminoboranes,<sup>2,3,4</sup> saturated<sup>5</sup> or hexahydro borazole,<sup>6</sup> and borazole adducts.<sup>7</sup> Since none of these names can be systematized easily to apply to all compounds of this class, confusion can be avoided by naming them as derivatives of the parent  $B_3H_6N_3H_6$ , which would be called cycloborazane. Substitutions would be indicated as they are for the borazines,<sup>8</sup> nitrogen atoms being in the 1,3,5 positions. This system has been used throughout the present paper.

The compound 1,3,5-trimethylcycloborazane,  $B_3H_5N_3H_3(CH_3)_3$ , first prepared by Bissot and Parry,<sup>2</sup> also can be prepared by the method of Dahl and Schaeffer<sup>6</sup> and now has been isolated as an intermediate in the preparation of 1,3,5-trimethylborazine by the method of Schaeffer and Anderson.<sup>9</sup> Two isomers (I and II) have been separated and their structures deduced by chemical and physical means.

## Experimental

**A. Preparation from Methylamine Hydrochloride and Sodium Borohydride.**—In a typical preparation, 28.4 g. (0.421 mole) of methylamine hydrochloride and 19.0 g. (0.500 mole) of sodium borohydride were mixed in a 200-cc. flask fitted with a reflux condenser and a drying tube. About 30 cc. of dry monoglyme was added through the condenser. When the initial gas evolution had ceased, the reaction mixture was heated to reflux (about 85°) for 5 hours. The solvent was evaporated and the solid subjected to high vacuum sublimation at about 100°. The sublimed material, mixed isomers of 1,3,5-trimethylcycloborazane, was collected on a cold finger at 0° and amounted to 9.4 g., a yield of 52%. When the initial reaction was carried out at 0°, the solvent evaporated at 0°, and high vacuum sublimation carried out at room temperature, methylamineborane ( $BH_3NH_2CH_3$ ) was collected on a 0° cold finger. The compound was identified by its 53–55° melting point (lit.<sup>10</sup> 54°) and by its n.m.r. spectrum.<sup>11</sup>

**B. Preparation from 1,3,5-Trimethylborazine.**—Following the method of Schaeffer and Dahl,<sup>6</sup> about 5 cc. of dry diethyl ether was condensed under vacuum into a 50-cc. flask at -196° and 0.44 g. (3.58 mmole) of 1,3,5-trimethylborazine (prepared by the method of Schaeffer and Anderson<sup>9</sup>) condensed on the ether. Excess hydrogen chloride was condensed in and the flask was warmed to room temperature and stirred until precipitation appeared complete. The ether and excess hydrogen chloride were removed under vacuum and the solid residue,  $B_3H_5Cl_3N_3H_3(CH_3)_3$ , was subjected to continuous evacuation for several

hours at room temperature to remove all volatile materials. The flask was cooled to -196°, filled with dry nitrogen, and 1.0 g. of sodium borohydride was introduced. The flask was stoppered and evacuated, and 10 cc. of dry monoglyme was condensed under vacuum onto the solid. Upon warming to room temperature, most of the solid dissolved. After 36 hours of stirring at room temperature, a 70% yield of diborane was found to have been produced based on the reaction  $2B_3H_5Cl_3N_3H_3(CH_3)_3 + 6NaBH_4 \rightarrow 2B_3H_5N_3H_3(CH_3)_3 + 3B_2H_6 + 6NaCl$ .

After the solvent had been removed, the solid was heated to about 100° under high vacuum. The material that sublimed was collected on a 0° cold finger and amounted to 0.22 g., or a yield of 48%.

**C. Separation of Isomers.**—1,3,5-trimethylcycloborazane can be separated into two isomers, I and II, by fractional sublimation under high vacuum and by fractional crystallization from benzene or from methanol, isomer I amounting to about 70% of the mixture. Isomer I sublimes readily at about 70°, whereas II sublimes readily at about 50°. Isomer II is the more soluble in all solvents investigated, including chloroform, acetonitrile, monoglyme, methanol, and benzene.

*Anal.* Calcd. for  $B_3H_5N_3H_3(CH_3)_3$ : C, 28.00; H, 14.10; B, 25.23; N, 32.66. Found (I): C, 28.24; H, 13.93; B, 25.49; N, 32.88. Found (II): C, 28.11; H, 13.81; B, 25.26; N, 32.40.

Molecular weights were determined in chloroform solution using a vapor pressure osmometer (Mechrolab Mdl. 30). Calcd. for  $B_3H_5N_3H_3(CH_3)_3$ : 128.7. Found: I, 138; II, 133.

**D. Thermal Stabilities.**—Samples of I and II were heated for 4.5 hours at 200°. The results are summarized in Table I. It is apparent that the thermal stability of I is somewhat greater than that of II.

TABLE I  
DECOMPOSITION OF 1,3,5-TRIMETHYLCYCLOBORAZANES AT 200°

Reactants		Products		
Isomer	mmole	$B_3H_5N_3Me_3$ mmole	$H_2$ mmole	Ratio of $H_2:B_3H_5N_3Me_3$
I	0.432	0.360	92.7	1.11
II	0.450	0.417	83.3	1.31

**E. Spectral Studies.**—The <sup>1</sup>H and <sup>11</sup>B spectra of I and II in acetone-*d*<sub>6</sub> solution were obtained at 60 and 19.3 Mc./sec., respectively, with a Varian model 4300B high resolution spectrometer. The <sup>11</sup>B spectra of I and II are identical and consist of symmetrical 1:2:1 triplets with  $J = 101 \pm 2$  c.p.s. and  $\delta = +6.2 \pm 1$  p.p.m. ( $BF_3 \cdot O(C_2H_5)_2 = 0$ ).

Infrared spectra of I and II were obtained using Perkin-Elmer Infracord spectrometers (Models 137 and 137-G). In a potassium bromide pellet, the N-H band of II is resolved into two peaks at 3.05 and 3.08 microns, but is a single sharp peak at 3.10 microns for I. The B-H band at 4.2 to 4.4 microns is broad and unresolved. In monoglyme solution, the N-H band for both I and II is a sharp single peak at 3.08 microns, but B-H bands are resolved into several peaks in the 4.1–4.5 region. The most striking difference in the spectra of the two isomers occurs in the 6.5–15.0 micron region. The spectrum of II contains all the lines observed for I (about 12) plus about ten additional lines, indicating that II has lower symmetry than I.

The X-ray powder patterns of I and II were obtained with a Phillips Geiger Counter Spectrometer using copper K $\alpha$  radiation. Characteristic  $d$  spacings for I and II are recorded in Table II. The powder pattern of I has been satisfactorily indexed on the basis of an orthorhombic unit cell. The unit cell dimensions are  $a = 8.11$ ,  $b = 12.60$ , and  $c = 8.01$  Å., and the crystal density is 1.03 g./cc. assuming four molecules per unit cell. The density by flotation is in the range 0.98–1.07.

Crystals of 1,3,5-hexamethylcycloborazane<sup>4</sup> are orthorhombic with four molecules per unit cell of dimensions  $a = 11.20$ ,  $b = 13.17$ , and  $c = 8.07$  Å. The crystal density is 0.945 g./cc. Observed reflections do not permit isomer I to belong to the same space group as the compound above. It is interesting to observe

(1) For paper IV in this series see G. H. Dahl and R. O. Schaeffer, *J. Am. Chem. Soc.*, **83**, 3034 (1961).

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(3) D. T. Haworth, "Syntheses and Studies of B and N Substituted Borazines," Thesis, St. Louis University, 68 (1959).

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(7) J. C. Sheldon and B. C. Smith, *Quart. Rev.*, **14**, 200 (1960).

(8) Preliminary Report of the Advisory Committee on the Nomenclature of Organic Boron Compounds, 1958, Chemical Abstracts.

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(10) E. R. Alten, R. D. Brown, J. C. Carter and R. C. Taylor, *ibid.*, **81**, 3550 (1959).

(11) To be published.

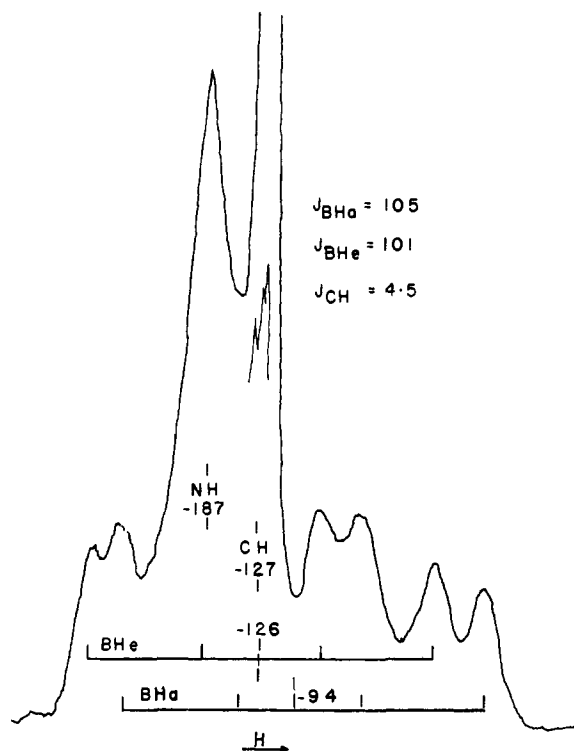


Fig. 1.—Proton n.m.r. spectrum of  $B_3H_6N_3H_3(CH_3)_3$  (isomer I) in acetone- $d_6$  at 60 Mc./sec. with positions in c.p.s. from the zero reference as tetramethylsilane (internal).

that removal of an axial methyl group from 1,3,5-hexamethylcycloborazane would probably allow closer packing along the  $a$  axis (which is 3.09 Å. longer in this compound than in I). Some shortening occurs along the  $b$  axis where primary interactions are between the two equatorial methyl groups in the hexamethyl

TABLE II  
X-RAY POWDER PATTERNS FOR TWO ISOMERS OF  
1,3,5-TRIMETHYLCYCLOBORAZANE

I			II			
$d$	$I$ (rel.)	$hkl$	$d$	$I$ (rel.)	$d$	$I$ (rel.)
8.07	1	100	6.88	11	3.57	12
7.98	1	001	6.37	32	3.26	3
6.83	100	110	6.26	100	3.16	7
5.69	1	101	4.86	4	2.95	3
4.22	20	030, 121	4.53	36	2.89	11
4.06	9	200	4.34	24	2.65	2
4.00	14	002	4.21	7	2.41	3
3.41	11	220	4.16	7	2.39	3
3.09	1	122	3.76	23	2.25	3
2.28	5	330	3.63	20	2.22	3

derivative. Thus, no conclusive argument concerning the structures of the two materials appears possible despite the relationship between the two unit cells. Single crystal studies would undoubtedly be of greater value, but as yet all crystals examined have been unsuitable owing to extensive twinning.

**F. Interconversion Studies.**—Isomers I and II interconvert slowly in liquid ammonia solution at room temperature. The only method found to be suitable for determination of the equilibrium constant for this interconversion was proton n.m.r. analysis of ammonia- $d_3$  solutions of equilibrated mixtures of I and II. Ammonia- $d_3$  exchanges very rapidly with the nitrogen protons of I and II, so that in ammonia- $d_3$  solutions, in which the ammonia- $d_3$  is in large excess, the only N-H resonance observed is that of ammonia at  $-42$  c.p.s. (TMS = 0). The result of this complete exchange is the collapse of the multiplet structure of the methyl group resonances so that only two lines are observed corresponding to the two types of methyl groups. Known mixtures of I and II were made up in ammonia- $d_3$  for calibration purposes and kept frozen at  $-196^\circ$  except when spectra were being run. A calibration curve was made by plotting percentage II versus the ratio of the low field to high field C-H resonance intensities. It was found that for each analysis a new calibration curve had to be prepared because of the fluctuation of instrument characteristics. A sample mixture of I and II in am-

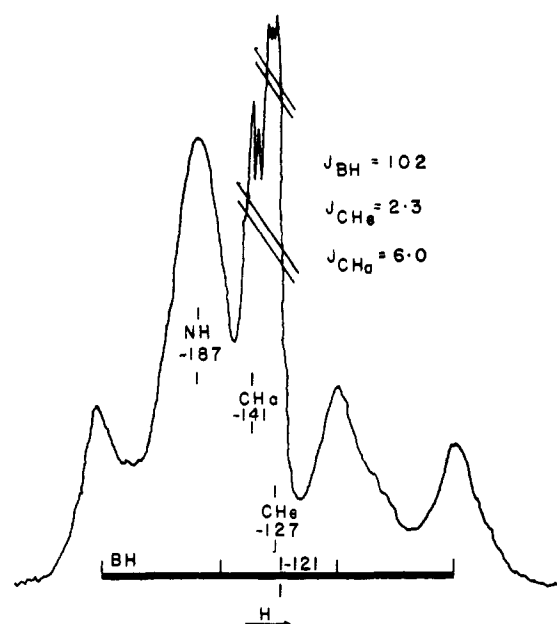
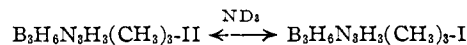


Fig. 2.—Proton n.m.r. spectrum of  $B_3H_6N_3H_3(CH_3)_3$  (isomer II) in acetone- $d_6$  at 60 Mc./sec. with positions in c.p.s. from the zero reference as tetramethylsilane (internal).

monia- $d_3$  was kept at  $31 \pm 1^\circ$  for 45 days. After the thirty-fifth day there was no further change in the sample. The equilibrium constant for the interconversion



is  $2.28 \pm 0.10$  at  $31^\circ$ , corresponding to a free energy change of  $-0.51 \pm 0.03$  kcal.

## Discussion

The structures of I and II have been assigned on the basis of the above data along with analogies drawn from conformational analysis of the cyclohexanes. Thermodynamic data for the cyclohexanes indicates that the most stable isomer should have the chair conformation with all three methyl groups in equatorial positions ( $C_{3v}$  symmetry), whereas the next most stable isomer should have only two methyl groups in equatorial positions, the third being axial ( $C_s$  symmetry). The proton n.m.r. spectrum of I (Fig. 1) shows only one species of C-H and two species of B-H. The B-H resonances have been tentatively assigned axial and equatorial positions in accordance with assignments made for substituted cyclohexanes and related compounds.<sup>12-14</sup> Their different chemical shifts and coupling constants undoubtedly arise primarily from non-bonded interactions with the methyl groups. It has been shown that I has more thermal stability and only about half as many infrared active vibrations as II. These observations are consistent with a structure in which the ring is in a chair shape, as is 1,3,5-hexamethylcycloborazane,<sup>4</sup> and all methyl groups are in equatorial positions. The proton n.m.r. spectrum of II (Fig. 2) shows two C-H resonances, one twice as intense as the other. The more intense resonance has a chemical shift identical with that for I. The other C-H resonance is shifted downfield as expected<sup>12</sup> for an axial substitution. The different types of B-H for isomer II are not resolved as there are four different species possible if one methyl group is axial.

(12) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 387.

(13) S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp. 115-119.

The results of the equilibrium studies are in agreement with the structures assigned the isomers. The free energy change of  $-0.51$  kcal. is much less than the  $-1.6$  kcal. observed for an axial-to-equatorial interconversion of a methyl group on a cyclohexane,<sup>15</sup> but the lower free energy difference observed in this study is in part a result of the lower non-bonded interaction resulting from the somewhat longer B-N bond distance (expected to be about  $1.60$  Å. as in similar compounds).<sup>4</sup> The slow rate of methyl group interconversion in the

(15) C. W. Beckett, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2488 (1947).

presence of rapid N-H exchange indicates that the energy barrier to interconversion is fairly large even though the energy difference between an axial and an equatorial methyl group is small.

The chemistry of both isomers of 1,3,5-trimethylcycloborazane is being investigated at the present time, and the results will be published in the near future.

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## Configurations and Magnetic Properties of the Nickel(II) Aminotroponeimineates

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The magnetic moments, electronic spectra and frequencies of n.m.r. absorption of the bis-nickel(II) chelates of aminotroponeimines are found to depend markedly on temperature, solvent and the structure of the ligand. It is shown that all these chelate characteristics are compatible with an intramolecular diamagnetic  $\rightleftharpoons$  paramagnetic equilibrium. The diamagnetic form of these chelates is identified with a square planar configuration about nickel, and the paramagnetic form, with an approximately tetrahedral configuration. Values of  $\Delta G$ ,  $\Delta E$  and  $\Delta S$  for the solution equilibria of several of these chelates derived from temperature dependences of n.m.r. contact shifts, magnetic susceptibilities and spectral intensities are presented.

### Introduction

The ground electronic state of nickel(II) coordination compounds (singlet, diamagnetic or triplet, paramagnetic) is exceptionally sensitive to geometry and/or strength of the ligand field.<sup>1</sup> While it has been generally accepted that the four-coordinated diamagnetic compounds of nickel(II) have a square planar structure corresponding to an electronic configuration  $3d_4s_4p^2$  for the bonding orbitals of the nickel atom, the structures and configurations of the four-coordinated paramagnetic complexes are by no means well established. The earlier theory of Pauling<sup>2</sup> assigned to these compounds the configuration  $4s_4p^3$  corresponding to a structure of tetrahedral symmetry, but more recent applications of ligand field theory<sup>1</sup> suggest that the square planar configuration may be retained in the triplet state. In view of this uncertainty, nickel(II) complexes in which the diamagnetic and paramagnetic forms (or states) are of sufficiently similar energies to permit thermal population of both are of particular interest.

Several examples have been reported<sup>3-8</sup> of formally four-coordinated nickel(II) complexes which in solution exhibit temperature dependent magnetic moments in the range  $0 < \mu_{\text{eff}} < 3.3$  BM. The best characterized of these is the nickel(II) bis-acetylacetonate which X-ray studies have shown<sup>9</sup> to exist as a discrete trimer in the solid. Here, nickel is surrounded by an octahedron of oxygen atoms and  $\mu_{\text{eff}} = 3.2$  B.M.<sup>10</sup> This

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(3) J. B. Willis and D. P. Mellor, *J. Am. Chem. Soc.*, **69**, 1237 (1947).

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(8) R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

(9) G. J. Bullen, R. Mason and P. Pauling, *Nature*, **189**, 291 (1961).

(10) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

same moment is observed for the acetylacetonate in benzene solution where it has been established that the chelate also is trimeric.<sup>11</sup> Nickel(II) chelates of  $\beta$ -diketones containing bulky substituents are found to exhibit in solution temperature dependent magnetic moments which can be understood on the basis of a

monomeric  $\rightleftharpoons$  polymeric  
(square planar, diamagnetic) (octahedral, paramagnetic)

equilibrium.<sup>6</sup> Similarly, Holm and co-workers<sup>4,8</sup> have established the existence of an associative equilibrium for the nickel(II) bis-salicylaldimines which would appear to account for the anomalous magnetic properties of solutions of this class of chelates.

While it is thus clear that the temperature dependent magnetic moments observed in solutions of certain classes of formally four-coordinated nickel(II) chelates can be attributed to associative equilibria, it is by no means certain that such equilibria are universally the cause of such effects.<sup>12</sup> Recently, new classes of four-coordinated non-chelated nickel(II) complexes have been reported which are paramagnetic and for which tetrahedral or approximately tetrahedral structures have been established.<sup>13-15</sup>

In earlier work,<sup>16</sup> we pointed out the existence of a solution equilibrium for bis-nickel(II) aminotropone-

square planar  $\rightleftharpoons$  tetrahedral  
(diamagnetic) (paramagnetic)

imineates. In this paper, we will present results of the n.m.r., susceptibility and spectral studies of this phenomenon.

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(12) Here we are classifying together solute-solute interactions such as occur in the  $\beta$ -diketone<sup>6</sup> and salicylaldimine<sup>7</sup> nickel(II) chelates, and solvent-solute interactions of the type postulated by Ballhausen and Liehr<sup>18</sup> and Maki.<sup>15</sup>

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