Chemistry of the B_5H_9-Assisted Trimerization of $(CH_3)_2NBH_2$[1]

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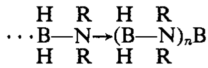
Abstract: Experimental results on the liquid-phase conversion of $(CH_3)_2NBH_2$ to its trimer by means of B_5H_9 are consistent with a mechanism beginning with the disruption of the B_5H_9 by $2(CH_3)_2NBH_2$ to form $(CH_3)_2NB_2H_5$ and $(CH_3)_2NBH_2 \cdot B_4H_6$. The latter then would react further in three ways: (1) to support the growth of a polymeric $[(CH_3)_2NBH_2]_n$ chain capable of rapid cyclization and re-formation of $(CH_3)_2NBH_2 \cdot B_4H_6$; (2) to lose H_2, forming nonvolatile $[(CH_3)_2NBH_2 \cdot B_4H_4]_x$; (3) to lose BH_3 to form a second $(CH_3)_2NB_2H_5$ and nonvolatile $[(CH_3)_2NBH_2 \cdot B_3H_3]_x$. The relative importance of each process depends upon the reactant ratios and concentrations; but (2) and (3) limit the repetition of (1). In connection with this study, an infrared technique for monitoring B^{10}–B^{11} exchanges was developed. The infrared effects of axial steric interference in $[(CH_3)_2NBH_2]_3$ are seen by comparison with $[(CH_3)_2PBH_2]_3$, and the infrared spectrum of the by-product $[(CH_3)_2N]_2B_4H_6$ is presented.

It was demonstrated some years ago that the cyclohexane-like ring compound $[(CH_3)_2NBH_2]_3$ can be formed in major yields by a most unusual process involving pentaborane(9) with an aminoboron hydride.[2-4] Next, it was suggested that the formation of this ring trimer, against severe mutual steric interference by the axial methyl groups,[4] might be explained by a mechanism in which the first step is the removal of a BH_3 group from B_5H_9.[5] Thus some of the $(CH_3)_2NBH_2$ would be converted to $(CH_3)_2NB_2H_5$,[6] or $[(CH_3)_2N]_2BH$ would go over to $2(CH_3)_2NBH_2$,[7] and the resulting B_4H_6 unit would be so electron-deficient as to support the growth of a dative-bonded chain



$$\cdots \underset{H}{\overset{H}{B}}—\underset{R}{\overset{R}{N}}\rightarrow(\underset{H}{\overset{H}{B}}—\underset{R}{\overset{R}{N}})_nB_4H_6$$

However, when $n = 3$ the quite empty boron orbital at the end of the chain could well gain electron density by breaking the chain to form $[(CH_3)_2NBH_2]_3$, leaving a $(CH_3)_2NBH_2 \cdot B_4H_6$ unit to react further in various ways, including the irreversible formation of nonvolatile amine-inclusive resins.[2] A full proof of such a mechanism would be very difficult, especially since the process occurs only in the liquid phase, but the following new facts become intelligible by reference to it.

1. A vapor-phase mixture of $(CH_3)_2NBH_2$ and B_5H_9, heated 14 hr at 103°, showed only the disproportionation equilibrium of $(CH_3)_2NBH_2$,[7] and 99% of the B_5H_9 was recovered. This result correlates with a general lack of complex formation by B_5H_9 vapor, whereas base adducts of B_5H_9 form readily enough in the liquid phase, as required for the suggested mechanism.

2. The trimerization is not catalyzed in the classical sense, for its extent is limited by the supply of B_5H_9, which is destroyed. For example, with $5(CH_3)_2NBH_2$ per B_5H_9 (95°, 21 hr), $4(CH_3)_2NBH_2$ was consumed, with 65% of this going to form the trimer.[2] But when only one B_5H_9 was used per 300 $(CH_3)_2NBH_2$ (6 hr, 142°), only $12(CH_3)_2NBH_2$ was consumed, with 35% conversion to the trimer. In terms of the suggested mechanism it would appear that the B_4H_6 complex could be used more than once to accomplish the trimerization, but that other reactions remove it fairly promptly.

3. Using $(CH_3)_2NBH_2$ in excess, we find that for each B_5H_9 consumed, the molar sum of the products $H_2 + (CH_3)_2NB_2H_5$ is invariably close to 2.

4. As the excess $(CH_3)_2NBH_2$ is increased, the molar ratio of formed $(CH_3)_2NB_2H_5$ to consumed B_5H_9 ranges from 1 to 2, with H_2 decreasing from 1 to 0.

Items 3 and 4 lead us to suggest a more detailed system of chemical processes, expressed by the following idealized equations.

$$2(CH_3)_2NBH_2 + B_5H_9 \longrightarrow (CH_3)_2NB_2H_5 + (CH_3)_2NBH_2 \cdot B_4H_6 \tag{1}$$

$$(CH_3)_2NBH_2 \cdot B_4H_6 + 3(CH_3)_2NBH_2 \longrightarrow [(CH_3)_2NBH_2]_4 \cdot B_4H_6 \tag{2}$$

$$[(CH_3)_2NBH_2]_4 \cdot B_4H_6 \longrightarrow [(CH_3)_2NBH_2]_3 + (CH_3)_2NBH_2 \cdot B_4H_6 \tag{3}$$

$$(CH_3)_2NBH_2 \cdot B_4H_6 \longrightarrow \frac{1}{x}[(CH_3)_2NBH_2 \cdot B_4H_4]_x + H_2 \tag{4}$$

$$(CH_3)_2NBH_2 \cdot B_4H_6 + (CH_3)_2NBH_2 \longrightarrow \frac{1}{x}[(CH_3)_2NBH_2 \cdot B_3H_3]_x + (CH_3)_2NB_2H_5 \tag{5}$$

Process 1 accounts for the fact that the yield of $(CH_3)_2NB_2H_5$ never is less than one per B_5H_9 consumed, while (5) accounts for higher yields, up to a limit of $2(CH_3)_2NB_2H_5$ related to the removal of no more than $2BH_3$ from B_5H_9 by a tertiary amine base.[2] Process 2 represents the formation of the polymeric $(CH_3)_2NBH_2$ chain, leading to the cyclization process 3; but processes 4 and 5 rapidly remove the supply of $(CH_3)_2NBH_2 \cdot B_4H_6$ units, thereby limiting their repeated use for processes 2 and 3. The nonvolatile products of (4) and (5) do not catalyze the trimerization of $(CH_3)_2$-

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(1) We are grateful for support by the Office of Naval Research through Contract No. Nonr-228(13), Task Order NR 052 050. Reproduction of this paper is permitted for any purpose of the United States Government. Fuller details of most of this work are presented by J. S. Sandhu, Ph.D. Dissertation, University of Southern California Libraries, 1966 (available on microfilm or photoprint).

(2) A. B. Burg, *J. Am. Chem. Soc.*, **79**, 2129 (1957). This paper showed the conversion process but erroneously gave the formula as $[(CH_3)_2N]_3B_3H_4$ because the very difficult alcoholytic analysis was inadequate.

(3) G. W. Campbell, Jr., and L. Johnson, *ibid.*, **81**, 3800 (1959). Here the ring trimer was proved by the nmr spectrum and confirmed by an alcoholysis which was more nearly complete because a lower temperature left less of the sample in the vapor phase.

(4) L. M. Trefonas, F. S. Matthews, and W. N. Lipscomb, *Acta Cryst.*, **14**, 273 (1961). X-Ray proof of the chair-form $(BN)_3$ ring.

(5) A. B. Burg, *Proc. Robert A. Welch Found. Conf. Chem. Res., VI, Houston, 1962*, 139 (1963).

(6) A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, **71**, 3451 (1949).

(7) A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 953 (1951).

Table I. Data on the Trimerization of $(CH_3)_2NBH_2$

Expt no.	Initial reactants		Consumed reactants		$(DMAB)_3$			H_2	DMAD	H_2 + DMAD per used B_5H_9	Formula of nonvolatile $(DMAB \cdot B_xH_y)_z$		
	DMAB	B_5H_9	DMAB	B_5H_9	mmoles	%	Per B_5H_9				x	y	y/x
1	5.993	4.010	3.608	1.010	0.402	33	40	0.593	1.380	1.95	3.67	3.95	1.076
2	9.929	4.010	4.165	1.120	0.444	32	40	0.488	1.709	1.96	3.48	3.61	1.037
3	15.333	4.010	4.761	1.240	0.460	30	37	0.338	2.140	2.00	3.26	3.27	1.003
4	15.025	3.040	3.726	1.001	0.336	27	34	0.241	1.740	1.98	3.29	3.34	1.015
5	15.315	2.150	2.794	0.720	0.268	29	37	0.158	1.350	2.09	3.10	2.90	0.935
6	4.464	1.034	0.914	0.327	0.043	14	13	0.146	0.480	1.91	3.80	3.90	1.026
7	10.790	1.034	1.269	0.376	0.044	10	12	0.084	0.667	2.00	3.30	3.30	1.00
8	14.955	1.034	1.279	0.391	0.050	12	13	0.065	0.733	2.04	3.12	3.12	1.00
9	23.258	1.034	1.432	0.443	0.052	11	12	0.066	0.835	2.03	3.05	3.00	0.984
10	10.721	0.776	1.097	0.324	0.033	9	10	0.070	0.575	1.99	3.22	3.25	1.009
11	10.289	0.517	0.861	0.240	0.027	9	11	0.037	0.458	2.06	3.08	3.00	0.974

NBH_2, although this component can be displaced by a stronger base such as $[(CH_3)_2N]_2BH$ or $(CH_3)_3N$. Apparently $(CH_3)_2NBH_2$ is only superficially attached to the boron hydride polymer, whereas in all other known resins derived from base + B_5H_9[8] the base is so firmly incorporated into the structure as never to be recovered as such under any circumstances.

It should not be assumed that experimental reality is fully expressed by our five equations, for the ratio of H_2 + $(CH_3)_2NB_2H_5$ to the consumed B_5H_9 can deviate as much as 4.5% from the exact average 2.00 (mean deviation, 2.0%). Also, a mean deviation of 2.5% in the H:B ratios for the polyborane polymer aspect of the nonvolatile product (from the average ratio of 1.01) is not wholly attributable to experimental error, for there were minor by-products such as $[(CH_3)_2N]_2B_4H_6$.[2]

The structure of this bisaminotetraborane remains a mystery, for all reasonable suggestions require B–H–B bridging, which could not be recognized in the vapor-phase infrared spectrum (nor could conclusive information be gained from a B^{11} nmr scan by Dr. J. R. Spielman of California State College at Los Angeles). However, a high polarity in the B–N bonds would mean a small relative variation of polarity during the B–H–B bridge vibrations, leading to poor intensity, especially if the structure has some symmetry.

The hope for yet more understanding of the role of B_5H_9 in the trimerization, through B^{10}–B^{11} exchange studies, was frustrated by the relatively high rate of exchange of $(CH_3)_2NB_2H_5$ with $(CH_3)_2NBH_2$ and with B_5H_9 itself.

Experiments on the Trimerization. Mixtures of $(CH_3)_2NBH_2$ and B_5H_9 in small sealed tubes were kept for 14 hr in an oil bath at 103 ± 0.2°. Then each tube was opened to the high-vacuum system, and H_2 was removed (through a trap at −196°) by an automatic Sprengel pump[9] delivering to a calibrated measuring tube. The other components were separated by high-vacuum fractional condensation and measured as gases or weighed, with results determining the composition of the nonvolatile residue. The fraction B_5H_9 + $(CH_3)_2NB_2H_5$ passed a trap at −70° and was resolved by repeated sublimation from a tube at −78°. The unconsumed $(CH_3)_2NBH_2$ was trapped as the solid dimer at −35°, while any minute trace of $[(CH_3)_2N]_2BH$ went through to condense at −70°. Traces of $[(CH_3)_2N]_2B_4H_6$ were removed from $[(CH_3)_2NBH_2]_3$ by passage through a trap at −5°, for condensation at −10°

The main quantitative results are shown in Table I. For the first five experiments the tube volume was 10.0 ml and for the others, 16.0 ml. All quantities of substances are in millimoles. For convenience, DMAB = $(CH_3)_2NBH_2$ and DMAD = $(CH_3)_2NB_2H_5$. The yields of $(DMAB)_3$ are given as millimoles, as per cents of consumed DMAB, and as moles per mole of consumed B_5H_9. These yields decrease with decreasing B_5H_9 as more of the consumed DMAB goes to other products. The sharp drop in the per cent yield for expt 6 and beyond relates to a sharp decrease of B_5H_9 in the liquid phase.

Boron Isotopic Exchanges. Although not very useful for a study of the mechanism of $(CH_3)_2NBH_2$ trimerization, our B^{10}–B^{11} exchange experiments have some interest *per se*, and the same techniques proved valuable in relation to the isomerization of $1\text{-}CH_3B_5H_8$.[10]

For the determination of the ratio of B^{10} to B^{11}, it was convenient to convert some of the sample to BCl_3 and to use the intensities of the well-separated asymmetric stretching peaks, at 995 and 953 cm^{-1}, as well-calibrated measures of B^{10} and B^{11}, respectively. The reason for the good separation of frequencies is that nearly all of the oscillation is motion by boron, so that the square-root rule, $\nu^{10}/\nu^{11} = \sqrt{11/10} = 1.049$, almost describes the observed ratio, 1.044.

Virtually all volatile boron compounds are easily converted to BCl_3 by one means or another; for our purposes direct chlorination was effective. However, the action of Cl_2 upon $(CH_3)_2NBH_2$ did not lead immediately to BCl_3 because the amine group held it in nonvolatile form. The results of one typical attempt are explained by the following equations with millimole stoichiometry.

$$\underset{0.40}{(CH_3)_2NBH_2} + \underset{0.80}{2Cl_2} \longrightarrow \underset{0.40}{(CH_3)_2NH_2^+BCl_4^-}$$

$$\underset{0.12}{(CH_3)_2NBH_2} + \underset{0.24}{2Cl_2} \longrightarrow \underset{0.12}{(CH_3)_2NH \cdot BCl_3} + \underset{0.12}{HCl}$$

Treatment of these nonvolatiles with the very strong Lewis acid $SbCl_5$ (12 hr, 100°) displaced 0.44 mmole of BCl_3 and brought the total HCl to 0.44 mmole.

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[8] A. B. Burg, "XVIIth International Congress of Pure and Applied Chemistry," Butterworths, London, 1960, p 57; *Angew. Chem.*, **72**, 191 (1960); see also ref 2.

[9] B. Bartocha, W. A. G. Graham, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **6**, 119 (1958).

[10] A. B. Burg and J. S. Sandhu, *J. Am. Chem. Soc.*, **87**, 3788 (1965).

The same process served as well for $[(CH_3)_2NBH_2]_3$; for $(CH_3)_2NB_2H_5$ or pentaborane derivatives, chlorination alone was sufficient.

The boron exchange between 95% B^{10}-enriched $(CH_3)_2NBH_2$ and normal $(CH_3)_2NB_2H_5$ was studied by heating four vapor-phase mixtures, each containing 4.4 mmoles of each component, in 25-ml sealed tubes at 103°. In the $(CH_3)_2NBH_2$, B^{11} rose from 5 to 37% in 3 hr, to 44% in 5 hr, to 47% in 9.6 hr, and to 50% in 12 hr (theoretical limit, 55%). Thus the exchange in the vapor phase was at least as fast as the trimerization would have been in the liquid phase. During that liquid-phase process, the $(CH_3)_2NBH_2$–$(CH_3)_2NB_2H_5$ exchange doubtless would have been much faster.

A mixture of 0.409 mmole each of 95% B^{10}-enriched $(CH_3)_2NB_2H_5$ and normal B_5H_9 was kept in a 24-ml sealed tube for 113 hr at 101°, producing 0.82 mmole of H_2 and nonvolatile material formulated approximately as $[(CH_3)_2NB_5H_4]_x$. The boron in this was 44% B^{10}, corresponding to exchange of about 3B per B_5H_9. The recovered $(CH_3)_2NB_2H_5$ had about 46% B^{10}, while the recovered B_5H_9 had 35% B^{10} (theoretical limit for both, 41% B^{10}).

The exchange between 95% B^{10}-enriched $(CH_3)_2$-NB_2H_5 and normal 1-$CH_3B_5H_8$ (0.409 mmole of each in a 25-ml sealed tube) occurred during 113 hr at 101°. The recovered $(CH_3)_2NB_2H_5$ had gone from 5 to 28% B^{11} while the $CH_3B_5H_8$ had gone from 19.5 to 27% B^{10}. These results correspond approximately to a one-boron exchange between the two components, whereas the nonvolatile by-product had 45% B^{10}, representing completely random isotopic mixing. The infrared spectrum of the recovered $CH_3B_5H_8$ (0.376 mmole) showed a 4% appearance of the isolated 1154-cm^{-1} peak for 2-$CH_3B_5H_8$, with a corresponding small decrease of intensity for the isolated 1232-cm^{-1} peak for 1-$CH_3B_5H_8$.[11] As mentioned before, the one-boron exchange during only 4% isomerization indicates that the isomerization is not accomplished by BH_3-group exchange.[10]

Infrared Spectra. The steric interference among the axial methyl groups in $[(CH_3)_2NBH_2]_3$ has interesting effects upon the vibrational modes involving these methyl groups. By the usual rule that the frequency increases when the amplitude of oscillation is limited by collision with nearby atoms, we may expect some C–H stretching frequencies above those for the undisturbed equatorial methyl groups. However, each hindered C–H bond means a weakened force constant on the free side of the same methyl group, so that some lower frequencies also should be expected. Accordingly, we find no less than seven distinct peaks for C–H stretching in $[(CH_3)_2NBH_2]_3$, in contrast to only two for the sterically free trimer $[(CH_3)_2PBH_2]_3$. The axial B–H stretching also seems to be affected, for we find three B–H stretching peaks for $[(CH_3)_2NBH_2]_3$, including one at a frequency higher than expected in relation to the normal pair of B–H stretching peaks for $[(CH_3)_2$-$PBH_2]_3$. Other, less assignable bands also seem to be affected.

Table II presents the vapor-phase spectra of the two trimers and the diaminotetraborane. In order to develop sufficient vapor pressures, the samples were in 8-cm cells within a box heated by a hot-air blower (with window condensation avoided), all inside the cell chamber of the Beckman IR7 instrument. The relative intensities of the peaks (shown in parentheses after the frequencies) were calculated from the arbitrary definition $k = (100/PL) \log I_0/I$ for pressure P (cm, reduced to 25°) and path length L (cm) and with the intensity I read directly from the chart without correction for band superposition. Peaks possibly assignable to sterically hindered oscillations are marked "S," and the least certain assignments are indicated by question marks. Shoulders without intensities are weakly sigmoid. Most peaks are sharply defined, but an exception is the wide, shallow, and ragged absorption centered at 2810 cm^{-1} for the diaminotetraborane.

Table II. Infrared Frequencies (cm^{-1})

Assignment	$(Me_2NBH_2)_3$	$(Me_2PBH_2)_3$	$(Me_2N)_2B_4H_6$
C–H stretching	S3045 (5)		
	S3038 (6)		3033 (2.7)
	S3028 (4)		3023 sh (2.4)
	2990 (8)	2987 (6)	2982 (6)
	2950 (7)	2922 (7)	2953 (6)
	2935 sh		2899 sh (1.5)
	S2900 (2)		
	S2860 (1)		2858 (1.2)
	2820 (0.1)	2824 (0.7)	2810 (0.5)
B–H stretching	S2428 (7)		2540} (9)
	2400 (9)	2399 (21)	2537}
	2324 (6)	2361 (17)	2507 sh
			2484 (9)
			2459 sh (4)
			2406 (7)
			2336 (2.8)
CH_3 deformation	S1485 (4)		1481 (4.0)
	S1455 sh	1423 (5)	1443 (3.5)
	1441 (5)	1298} (4)	1410 (0.7)
	1236 (2)	1291}	1235 (7)
	?1206 (2)		?1205 (12)
BH_2 bending	1180 (1.4)	1111 (2)	1183 sh (5)
	1171 (1.5)	?998 (3)	1152 (4)
			1109 (4)
B–N stretching	1068 (1.2)	. . .	1035 (3)
CH_3 rocking and wagging; BH_2 rocking in and out of plane	S998 (2)		1000 (3)
	936 (9)	938 (24)	974 (3)
	S897 (2)		934 (5)
	850 (2)	853 (2.3)	896 (2)
	826 (4)	812 (1.2)	829 (2)
. . ? . .		750 (7)	?777 (0.4)
		742 sh (3)	
	?621	665 (2.5)	
		575 (0.15)	

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[11] For the full infrared spectra of these isomers see J. S. Sandhu, ref 1, pp 77, 78.