Derivatives of Cyclotetrazenoborane. Part II.¹ Preparation and Properties of Dimethyl- and Methylphenyl-cyclotetrazenoborane

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A synthesis of two new derivatives of the type RR'N₄BH has been achieved which confirms the generality of the reaction of organic azides with primary amine boranes, and the prediction of their existence. The physical properties are in agreement with earlier calculations.

BORON-NITROGEN ring systems have been of interest since Stock first prepared borazine,² but it is only in the last four years that other systems have been described.^{3,4} Boron-nitrogen rings are of particular importance in view of the possibility of electron delocalisation, and calculations ¹ on the recently described ⁵ ring system (I)

have indicated that the N_4B ring is intrinsically stable and predicted that derivatives such as H_2N_4BH and $(CH_3)_2N_4BH$ should be preparable. The calculations also lead to the conclusions that, in the case of the dimethyl derivative, (a) the boron-11 n.m.r. should be shifted from that in 2,5-diphenylcyclotetrazenoborane, (b) the first electronic absorption band should occur near 191 m μ , and (c) the barrier to rotation of the methyl groups should be low.

We have been able to confirm the prediction 1 that (CH₃)₂N₄BH should be preparable, and have established

$$RN_3 + R'NH_2 \cdot BH_3 \longrightarrow RR'N_4 BH + 2H_2$$
(1)

$$3RN_3 + B_{10}H_{14} \longrightarrow R_2N_4BH + H_2 + 2N_2 + [R,N,B_9,H_{11}] (2)$$

the generality of reactions (1) and (2). The physical properties of (CH₃)₂N₄BH are consistent with those predicted, and in agreement with the proposed structure.

RESULTS AND DISCUSSION

2,5-Dimethylcyclotetrazenoborane was prepared by treating methyl azide with either methylamine-borane or decaborane. Treatment of aniline-borane with methyl azide yielded 2-methyl-5-phenylcyclotetrazenoborane. The physical properties of the two compounds are recorded in Table 1 together with the previously obtained data for 2,5-diphenylcyclotetrazenoborane.

The structure of the dimethyl derivative is strongly indicated by its physical properties. Elemental analysis ascertained its chemical constitution and the molecular weight was established by examining the mass spectrum over a range of ionising voltages, when the ratio of the intensities of the peaks at m/e 97 and 98 remained

constant. The vibrational spectra of this molecule are reported in detail elsewhere,⁶ and, in particular, support a model of C_{2v} symmetry with a low barrier to rotation

TABLE 1

Physical properties of cyclotetrazenoborane derivatives

Physical property	Ph ₂ N ₄ BH ^a	Me_2N_4BH	$MePhN_4BH$	
M. p.	117°	11°	32°	
N.m.r. ¹¹ B δ (p.p.m.) (BCl ₃)	+29.9	+26.1	$\sim +29$	
J_{B-H} (c./sec.)	164 ± 5	165 ± 3	Broad	
1H δ _{Ph} (p.p.m.) (TMS)	-7.5		-7.2	
δ _{Me}		-3.59	-3.45	
δ _{B-H}		-4.10		
J _{в-н} (с./sec.)		166 ± 1		
U.v. absorption $\lambda_{max.}~(m\mu)$	242, end absn.	198	242, end absn.	
$\varepsilon_{\text{max.}}$ (l. cm. ⁻¹ mole ⁻¹)	$2{\cdot}56 imes 10^4$	$\stackrel{({\sim}6\cdot3}{ imes10^3}{}_b$	$1.25 imes 10^4$	
I.r. absorption ¹¹ B-H str.				
(cm1)	2651	2636 °	2656	
¹⁰ B-H str. (cm. ⁻¹)	2661sh	2655 °	2670	
^a Ref. 5. ^b This appro	ximate valu	e was obta	ined by cali-	

brating a vapour spectrum from the visible side of a solution of known concentration. . Ref. 6.

of the methyl groups, in agreement with the predicted 1 value of ~ 1 kcal. mole⁻¹. The presence of a single B-H bond is suggested by a sharp infrared absorption at 2636 cm.⁻¹ with its associated shoulder at 2644 cm.⁻¹, and these have been assigned to the ¹¹B and ¹⁰B boronhydrogen stretching vibrations. Further confirmation is obtained from the nuclear magnetic resonance (n.m.r.) spectra; thus, a single methyl peak in the proton spectrum and a doublet in the boron-11 spectrum demonstrates the equivalence of the methyl groups and reveals the single hydrogen atom attached to boron. The coupling constant of ~ 166 c./sec. is consistent with that obtained for Ph₂N₄BH, and the ¹¹B chemical shift is at lower field than the diphenyl derivative.⁵

The ultraviolet absorption maximum at 198 m μ in 2,5-dimethylcyclotetrazenoborane agrees with the value calculated for the lowest-energy electronic transition.¹

Analogous reasoning leads to the conclusion that the structure of the compound MePhN₄BH is similar to the dimethyl and diphenyl derivatives. It is interesting to compare the apparent ε_{max} of the 242-m μ transitions in 2,5-diphenylcyclotetrazenoborane and 2-methyl-5phenylcyclotetrazenoborane. That these are in the

Part I, preceding Paper.
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⁴ H. Nöth and G. Abeler, Angew. Chem., 1965, 77, 506.
⁵ N. N. Greenwood and J. H. Morris, J., 1965, 6205.
⁶ A. J. Downs and J. H. Morris, Spectrochim. Acta, in the press

approximate ratio 2:1 suggests that interaction between the phenyl ring and the heterocyclic part of the molecules is weak and that this transition virtually stems from the phenyl rings alone.

The mass spectrum of 2,5-dimethylcyclotetrazenoborane (Table 2) is also best interpreted on the basis of the proposed structure. The peaks at m/e 97—100 can be satisfactorily assigned to the isotopic variations of the parent ion $(CH_3)_2N_4BH^+$, and only minor discrepancies are observed from the calculated intensities using the peak at 97 as a single species, and assuming literature values of isotopic masses.⁷

It is curious that negligible fragmentation corresponding to the loss of one proton from the boron was identified. The first significant loss appears to be that of 28, 29, 30, or 31 mass units, with the major peak occurring at m/e 69. This is probably best understood as loss of N₂ or CH₂N; CH₃N or N₂ + H; 2CH₃; 2CH₃ + H, resulting in fragments (CH₃)₂N₂BH⁺;

TABLE 2

Mass spectrum of 2,5-dimethylcyclotetrazenoborane

<i>m e</i> Intensity	$\begin{array}{c} 100 \\ 0{\cdot}10 \end{array}$	$99 \\ 4.29$	98 100·00	$97 \\ 24.26$	96 0·03	$\begin{array}{c} 82 \\ 0 \cdot 08 \end{array}$	71 0·06
<i>m e</i> Intensity	$70 \\ 1 \cdot 12$	$69 \\ 13.12$	$68 \\ 4.27$	$\begin{array}{c} 67 \\ 1 \cdot 87 \end{array}$	66 0·47	$\begin{array}{c} 65 \\ 0 \cdot 08 \end{array}$	64 0·04
<i>m e</i> Intensity	$\begin{array}{c} 63 \\ 0 \cdot 94 \end{array}$	$\begin{array}{c} 62 \\ 0{\cdot}03 \end{array}$	$\begin{array}{c} 58 \\ 0.08 \end{array}$	$57 \\ 2 \cdot 04$	$56 \\ 0.12$	55 4·63	$54 \\ 1 \cdot 50$
<i>m e</i> Intensity	$53 \\ 1.89$	$\begin{array}{c} 52 \\ 0.89 \end{array}$	$51 \\ 0.15$	$\begin{array}{c} 50 \\ 0{\cdot}02 \end{array}$	49 0·10	$48.5 \\ 0.08$	48 0·07
<i>m e</i> Intensity	$\begin{array}{c} 47 \\ 0.01 \end{array}$	$\begin{array}{c} 46 \\ 0{\cdot}05 \end{array}$	$45 \\ 0.12$	$44 \\ 1.75$	$43 \\ 3.00$	$\begin{array}{c} 42 \\ 44 \cdot 84 \end{array}$	41 14·93
<i>m e</i> Intensity	40 19·46	39 6·05	$\begin{array}{c} 38 \\ 2\cdot 30 \end{array}$	37 0∙90	36 0·13	$34 \\ 1 \cdot 13$	${}^{33\cdot 5}_{0\cdot 62}$
<i>m e</i> Intensity	33 3∙63	${}^{32\cdot 5}_{1\cdot 24}$	$32 \\ 0.59$	$31 \\ 0.26$	$30 \\ 1 \cdot 32$	$\begin{array}{c} 29 \\ 1 \cdot 26 \end{array}$	$28 \\ 30.13$
<i>m e</i> Intensity	$\begin{array}{c} 27 \\ 8{\cdot}52 \end{array}$	$rac{26}{3\cdot 21}$	$25 \\ 0.77$	$\begin{array}{c} 24 \\ 0{\cdot}30 \end{array}$	$18 \\ 1.58$	17 0·30	$16 \\ 0.13$
<i>m e</i> Intensity	$15 \\ 4.82$	14 0·81	$13 \\ 1.93$	$12 \\ 1 \cdot 24$	$11 \\ 2.28$	$10 \\ 0.57$	

 $(CH_3)_2N_2B^+$; $CH_3N_3BH^+$; N_4BH^+ ; N_4B^+ . Alternative cleavage seems to yield the fragments $CH_3N_3^+$ and CH_3NBH^+ since a peak at m/e 57 (possibly due to $CH_3N_3^+$) does not appear to have a ¹⁰B satellite, and peaks corresponding to CH_3NBH^+ are observed at m/e 41 and 40, although the major peak in this area occurs at m/e 42.

The parent-ion peaks are just observed when an ionising voltage of 10 ev is used, and this may be taken as an approximate value of the ionisation potential of the molecule. The valence state ionisation potential of a non-bonding electron of an "azo" nitrogen atom is ca. 12 ev,⁸ whereas the removal of an electron from the highest filled molecular orbital would require ca. 14.5 ev;¹ hence, the first electron lost by the molecule most probably originates from one of the nitrogen atoms.

EXPERIMENTAL

Solvents and Intermediates.—Diethyl ether was dried over sodium and distilled *in vacuo* from lithium borohydride before use. Methyl azide was prepared by treating aqueous sodium azide with dimethyl sulphate and was dried over potassium hydroxide pellets. Methylamine-borane was prepared by treating methylammonium chloride with lithium borohydride in diethyl ether.⁹

2,5-Dimethylcyclotetrazenoborane.—A heavy-wall Pyrex tube was charged with methylamine-borane (0.466 g., 10.4 mmoles) dissolved in 10 ml. of diethyl ether, and methyl azide (0.69 g., 12.0 mmoles) was condensed in from the vacuum line. The tube was sealed and heated to 140° for 16 hr. in a Carius-tube furnace. The tube was cooled and opened on the vacuum line through traps at -30, -78. and -196° to yield 555 ml. of non-condensable gas which was shown by mass spectrometry to consist of H_2 , 86%; N_2 , 13%; and O_2 , 1%. This corresponded to a yield of 477 ml. of hydrogen (theor., 466 ml.). The -30° trap contained dimethylcyclotetrazenoborane (0.65 g., 60%), m. p. 11° (Found: C, 24.8; H, 7.2; B, 11.0; N, 57.2. C₂H₇BN₄ requires C, 24.5; H, 7.2; B, 11.1; N, 57.2%). The vapour pressure of the compound was ca. 8 mm. at 20° . A small quantity of a white crystalline material remained in the tube at room temperature, and is being investigated further.

Reaction of Decaborane with Methyl Azide.—A heavywalled Pyrex tube was charged with decaborane (0.26 g., 2.13 mmoles), and methyl azide (1.14 g., 24.0 mmoles) was condensed in under vacuum. The mixture was left at room temperature for 6 weeks, during which time the solution became yellow. The non-condensable gases were removed and the mixture was pumped under vacuum through traps at -78 and -196° . A yellow, non-volatile, oily borane residue remained in the tube and ca. 0.2 g. of dimethylcyclotetrazenoborane was isolated from the -78° trap. The product was identified by its infrared spectrum and melting point.

2-Methyl-5-phenylcyclotetrazenoborane.—Aniline (1.8 g.), excess of diborane, methyl azide (0.8 g.), and ca. 10 ml. of diethyl ether were sealed together in vacuo in a heavywalled Pyrex tube, which was kept at room temperature for 2 weeks. The volatile materials were removed and the oily residue was distilled under vacuum. The product (ca. 1 ml.) was a colourless liquid, b. p. $80^{\circ}/10^{-2}$ mm., which crystallised on cooling and subsequently melted at 23° . After redistillation, the product melted at 32° (Found: C, 52·1; H, 6·1; B, 6·4; N, 35·0. C₇H₉BN₄ requires C, 52·5; H, 5·7; B, 6·8; N, 35·0%).

Methylphenylcyclotetrazenoborane was also prepared by refluxing together aniline hydrochloride, lithium borohydride, and methyl azide in diethyl ether solution.

Infrared Spectra.—The infrared spectra of dimethylcyclotetrazenoborane⁶ and methylphenylcyclotetrazenoborane were recorded on a Perkin-Elmer model 125 spectrophotometer as liquid films. Methylphenylcyclotetrazenoborane showed bands at 506, 542, 616, 669, 691, 718, 768, 815, 826, 906, 916, 922sh, 937, 974, 987, 1006, 1025, 1035, 1077, 1107sh, 1119, 1127, 1143, 1162, 1175, 1217sh, 1235, 1295, 1315, 1331, 1375, 1392, 1400, 1412, 1437, 1467, 1509, 1617, 1744, 1797, 1877, 1952, 2656, 2670, 2940sh, 2954, 2987, 3054, 3067, 3078, 3088sh cm.⁻¹.

⁸ J. Hinze and H. H. Jaffé, J. Amer. Chem. Soc., 1962, 84, 540.
 ⁹ H. Nöth and H. Beyer, Chem. Ber., 1960, 93, 928.

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Ultraviolet Spectra.—These were recorded on Perkin-Elmer model 137, Unicam S.P. 500 and 700 spectrophotometers in the vapour phase or as solutions in cyclohexane.

Mass Spectra.—Mass spectra were obtained on an A.E.I. model M.S.2. spectrometer using an ionising voltage of 70 ev and the spectrum of Me_2N_4BH is recorded in Table 2. In addition, the parent-ion peaks of Me_2N_4BH were examined using ionising voltages of 70, 18, 11, and 10 ev.

N.m.r. Spectra.—The ¹H and ¹¹B spectra of dimethylcyclotetrazenoborane and methylphenylcyclotetrazenoborane were recorded at 60 and 20 Mc./sec., respectively, on an A.E.I. model R.S.2. n.m.r. spectrometer, and the spectra were calibrated by the side-band technique using internal tetramethylsilane and capillary boron trichloride standards.

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