1156. *Derivatives of Cyclotetrazenoborane (Boratetrazole),* N_4H_2BH

By N. N. GREENWOOD and J. H. MORRIS

A new five-membered ring system containing one boron and four nitrogen atoms has been synthesised by the reaction of phenyl azide with either decaborane or aniline–borane. The structure of 2,5-diphenylcyclotetrazenoborane, Ph_2N_4BH, has been established and its spectroscopic and other properties investigated.

DURING a systematic study of the reactions of decaborane with a variety of ligands, it was found that phenyl azide reacted to give a five-membered ring system containing one boron and four nitrogen atoms. The reaction is doubly interesting since cleavage of decaborane by ligands is relatively rare,[1] and also because the product of the reaction is a novel heterocycle. The reaction proceeds smoothly in a solvent such as boiling toluene, and also occurs in the absence of solvent when decaborane and phenyl azide are warmed to 50° in a sealed tube. Nitrogen and hydrogen are evolved in approximately the molar ratio 2 : 1:

$$B_{10}H_{14} + 3PhN_3 \longrightarrow Ph_2N_4BH + H_2 + 2N_2 + [Ph, N, B_9, H_{11}]$$

The nature of the polyborane residue has not yet been established.

The molecular formula and structure of diphenyltetrazenoborane (I) were established by the experiments indicated below, and the compound was independently synthesised in 70% yield by the direct reaction of phenyl azide with aniline–borane in ether at room temperature.

$$PhNH_2BH_3 + PhN_3 \longrightarrow Ph_2N_4BH + 2H_2$$

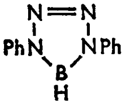
---

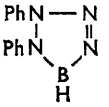
[1] " Boron, Metallo-boron Compounds, and Boranes," ed. R. M. Adams, Interscience, New York, 1964; M. F. Hawthorne, *Adv. Inorg. Chem. Radiochem.*, 1963, **5**, 307; W. N. Lipscomb, " Boron Hydrides," Benjamin, New York, 1963.

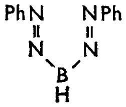
The reaction can be considered to proceed by elimination of hydrogen from aniline–borane to give the monomeric precursor of triphenylborazene, [PhNBH], which then adds on a molecule of phenyl azide. The reaction can readily be extended to other organic azides and primary-amine–boranes.

Diphenylcyclotetrazenoborane is a white crystalline compound, m. p. 117°, density 1·30 g. cm.$^{-3}$. It is volatile and sublimes readily under reduced pressure at temperatures near 100°. It is stable to mechanical shock and is thermally stable at least to the melting point. The crystals are stable in air for prolonged periods, but in a moist atmosphere they slowly become coated with boric acid during a period of months. Diphenylcyclotetrazenoborane is highly soluble in benzene and toluene but less soluble in light petroleum, cyclohexane, carbon disulphide, diethyl ether, chloroform, and carbon tetrachloride.

Structure (I) was established in the following manner. Elemental analysis and molecular weight led to the formula $C_{12}H_{11}BN_4$. The infrared spectrum indicated the presence of phenyl groups and a boron–hydrogen bond, and also suggested the absence of BH_2, CH_2, CH_3, NH, and NH_2 groups. The presence of phenyl groups was confirmed by proton n.m.r. measurements, and the ^{11}B n.m.r. spectrum showed just one doublet 29·9 p.p.m. upfield from boron trichloride and with a coupling constant J_{B-H} of 164 c./sec. typical of a single B–H group.


(I)


(II)


(III)

There are three possible isomeric structures for a molecule of the type Ph_2N_4BH, namely (I), (II), and (III). The ultraviolet absorption spectrum was similar to that obtained for phenyl-substituted triazoles and tetrazoles,[2] and it is significant that the heterocyclic structures (I) and (II) are formally analogous to triazoles in which the two carbon atoms have been replaced by the isoelectronic B–N grouping. Structure (III) is least likely since the groups Ph–N=N– would be expected[3] to absorb near 33,000 cm.$^{-1}$ and further delocalisation involving the boron atom might be expected to shift the absorption to even lower energy whereas the lowest energy band in the observed absorption spectrum was at 41,200 cm.$^{-1}$ ($\varepsilon_{max.}$ 2·56 × 10^4 l. cm.$^{-1}$ mole^{-1}). End absorption was also observed. A more detailed theoretical discussion of the electronic absorption spectrum and stability of cyclotetrazenoborane derivatives will shortly be published.[4]

Further structural evidence comes from a crystallographic investigation, for which we are indebted to Dr. H. P. Stadler. This shows that the unit cell contains two molecules and has the dimensions 13·0 × 5·92 × 7·35 Å. Molecular models indicate that structure (I) can be planar and that a unit cell comprising two such molecules, stacked with the planes approximately parallel and with a centre of symmetry, has just the observed dimensions. By contrast, structure (II) cannot be planar because of steric interference of the adjacent phenyl groups and the minimum dimensions of a unit cell for this structure are approximately 13·3 × 6·0 × 9·3 Å.

It is significant that the preparation of diphenylcyclotetrazenoborane from aniline–borane and phenyl azide is directly analogous to the synthesis of triazoles and tetrazoles by the addition of azides to carbon–carbon or carbon–nitrogen triple bonds:[2,5]

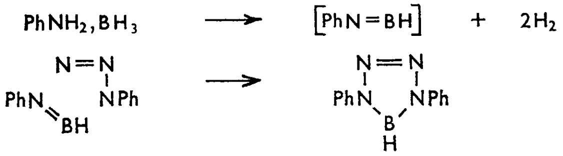
---

[2] W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, 1953, **18**, 1269; B. Elpern and F. C. Nachod, *J. Amer. Chem. Soc.*, 1950, **72**, 3379; J. H. Boyer, "Heterocyclic Compounds," ed. R. C. Elderfield, vol. 7, Wiley, New York, 1961, p. 384.

[3] C. N. R. Rao, "Ultraviolet and Visible Spectroscopy. Chemical Applications," Butterworths, London, 1961.

[4] J. H. Morris and P. G. Perkins, unpublished work.

[5] E. Hoggarth, in "Chemistry of Carbon Compounds," ed. E. H. Rodd, vol. IVA, ch. 6, Elsevier, London, 1957.



This reaction may give an indication of the mechanism of cleavage of decaborane by phenyl azide. It is thought that the reaction proceeds by the initial elimination of hydrogen from decaborane and 2 moles of phenyl azide to give a typical di-ligand adduct which then eliminates 2 moles of nitrogen to form an unstable intermediate; this cleaves to give the monomeric phenylborazene and an unstable polyborane fragment which reacts further.

$$B_{10}H_{14} + 2PhN_3 \longrightarrow (PhN_3)_2B_{10}H_{12} + H_2$$
$$(PhN_3)_2B_{10}H_{12} \longrightarrow [(PhN)_2B_{10}H_{12}] + 2N_2$$
$$[(PhN)_2B_{10}H_{12}] \longrightarrow [PhN{=}BH] + [PhNB_9H_{11}]$$

The phenylborazene intermediate then reacts with a third mole of phenyl azide as above.

The hydrolysis of 2,5-diphenylcyclotetrazenoborane with a concentrated aqueous ethanolic solution of hydrochloric acid at 60° has been investigated. The boron is eliminated as boric acid with evolution of hydrogen, and the azo-intermediate then reacts further to give anilinium chloride and nitrogen:

$$Ph_2N_4BH + 3H_2O \longrightarrow B(OH)_3 + H_2 + PhNH{\cdot}N{:}N{\cdot}NHPh \xrightarrow{HCl} 2PhNH_3Cl + N_2$$

Boric acid was determined by a standard procedure using mannitol, hydrogen and nitrogen were identified by mass spectrometry, and anilinium hydrochloride was recovered by evaporation of the reaction mixture and identified by infrared spectroscopy.

Infrared Spectra.—The infrared spectrum of 2,5-diphenylcyclotetrazenoborane in the range 20—4000 cm.$^{-1}$ has been obtained using carbon tetrachloride, carbon disulphide, and benzene solutions, discs in potassium bromide and Polythene, and pressed discs of the pure compound. The results are given in the Table together with suggested assignments.

A molecule of 28 atoms having C_{2v} symmetry has 78 normal modes of vibration of which 66 are active in the infrared. Fifty-one modes are associated primarily with the phenyl groups though most of these are effectively degenerate pairs since the vibrations internal to each phenyl group are essentially independent of the other phenyl group. The phenyl bands are easily recognised and are labelled in the accepted way.[6] The Ph–N stretches occur at 1291 and 1311 cm.$^{-1}$.

The ^{11}B–H and ^{10}B–H stretches are at relatively high frequencies (2651 and 2661 cm.$^{-1}$); the B–H in plane deformation is assigned to the unresolved band at 1045 cm.$^{-1}$ and the B–H out-of-plane deformation occurs at 811, 822 cm.$^{-1}$. The planar 5-membered heteroring is expected to give rise to eight infrared-active modes [7] all of which have been identified. Comparison with the spectrum of 2,5-dimethylcyclotetrazenoborane [4] and phenylboracyclopentane [7] aided the assignments. Two of the modes, an A_1 stretch and the B_1 deformation, do not involve motion of the boron atom and are assigned to the sharp bands at 1062 and 968 cm.$^{-1}$, respectively. The ring-breathing mode occurs as a ^{11}B, ^{10}B doublet at 1091, 1109 cm.$^{-1}$, and the third A_1 stretch is at 905 and 915 cm.$^{-1}$. The two B_1 stretching modes occur at the highest wave-numbers and are predominantly B–N stretches: 1405, 1418 and 1190, 1200 cm.$^{-1}$. The A_1 deformation is unresolved at 668 cm.$^{-1}$, and the lowest of the ring modes is the B_2 deformation which occurs at 420 cm.$^{-1}$. It is noteworthy that, although the sequence of frequencies of the ring modes for the N_4B and $[CH_2]_4B$ rings are similar, the individual modes of the cyclotetrazenoborane ring, with the exception of the B_2 deformation, all occur at frequencies higher than those of the corresponding boracyclopentane ring. This presumably reflects the increased rigidity of the boron–nitrogen

---

[6] R. R. Randle and D. H. Whiffen, *J. Mol. Spectroscopy*, 1955, 111.

[7] N. N. Greenwood and J. C. Wright, *J.*, 1965, 448.

Infrared spectrum of 2,5-diphenylcyclotetrazenoborane (for description of phenyl modes *a–y* and hetero-ring modes I—VIII see refs. 6 and 7, respectively).

ν (cm.$^{-1}$)	Rel. ε	Assignment
72	<1	Lattice or torsional modes (?)
108	<1	
140	<1	
175	3	PhX ring out-of-plane deform. (*x* mode)
227	1	
247	<1	
254	<1	
300	1	PhX in-plane deform. (*u* mode)
420	3	Hetero-ring out-of-plane deform. (mode VIII)
473	3	PhX ring out-of-plane deform. (*y* mode)
548	17	PhX ring in-plane deform. (*t* mode)
620	4	Ph ring in-plane deform. (*s* mode)
668	8	Hetero-ring in-plane deform. (mode IV)
689	131	Ph ring out-of-plane deform. (*v* mode)
708	44	PhX ring in-plane deform. (*r* mode)
753	160	CH out-of-plane deform. (*f* mode)
811	41	^{11}B–H out-of-plane deform.
822	17	^{10}BH out-of-plane deform.
905	28	^{11}B hetero-ring sym. stretch (mode III)
915	16	^{10}B hetero-ring sym. stretch (mode III)
968	47	Hetero-ring in-plane deform. (mode VII)
1002	6	Ph ring in-plane deform. (*p* mode)
1031	19	CH in-plane deform. (*b* mode)
1045	8	BH in-plane deform.
1062	200	Hetero-ring A_1 stretch (mode I)
1077	17	CH in-plane deform. (*d* mode)
1091	65	^{11}B hetero-ring breathing (mode II)
1109	18	^{10}B hetero-ring breathing (mode II)
1159	13	CH in-plane deform. (*c* mode)
1177	20	CH in-plane deform. (*a* mode)
1190	60	^{11}B hetero-ring B_1 stretch (mode VI)
1200	20	^{10}B hetero-ring B_1 stretch (mode VI)
1291	7	PhN antisym. stretch (*q* mode)
1311	16	PhN sym. stretch (*q* mode)
1331	14	CC(Ph) B_1 stretch (*o* mode)
1379	20	(2 × 689)
1405	125	^{11}B hetero-ring antisym. stretch (mode V)
1418	41	^{10}B hetero-ring antisym. stretch (mode V)
1471	20	CC(Ph)B_1 stretch (*n* mode)
1505	170	CC(Ph) A_1 stretch (*m* mode)
1511sh	31	CC(Ph) A_1 stretch (*m* mode)
1600	70	CC(Ph) B_1 stretch (*l* mode)
1609	124	CC(Ph) A_1 stretch (*k* mode)
1664	4	(753 + 905) and (753 + 915)
1735	5	The four combination bands of CH out-of-plane deformations (1 + 3 pairs)
1793	6	
1811	5	
1868	6	
1887	6	
1944	4	
1963	5	
2651	18	^{11}B–H stretch
2661sh	7	^{10}B–H stretch
3046sh	16	C–H stretches
3053	21	
3073	13	
3083sh	8	
3102	5	
3115	4	

heterocycle as a result of the 6-electron π-bonding system in the planar ring. This involvement of boron in π-bonding also explains the position of the ^{11}B n.m.r. resonance which is at quite high field for three-co-ordinate boron and is close to the resonance in trimethyl borate.

EXPERIMENTAL

Solvents were dried, and purified by standard procedures. Phenyl azide was prepared by treating phenylhydrazine with nitrous acid.[8]

Reaction of Decaborane with Phenyl Azide.—A 25-ml. flask, fitted with a reflux condenser and nitrogen by-pass, was charged with decaborane (0·88 g., 7·2 mmoles), phenyl azide (5·41 g., 45·5 mmoles), and toluene (14·8 g.), and the mixture was heated under reflux for 48 hr. Gas was evolved during the reaction and the mixture darkened in colour. At room temperature a slight turbidity developed, and at −78° crystals were deposited; these were filtered off and washed with a small quantity of light petroleum. The *product* (0·86 g., 4·6 mmoles) could be recrystallised from benzene–petroleum, toluene–petroleum, or light petroleum (b. p. 100—120°); it had m. p. 116—117° and density 1·30 as measured by flotation in a mixture of $CF_2Cl{\cdot}CFCl_2$ and light petroleum (b. p. 60—80°) [Found: C, 65·2; H, 5·2; B, 4·6; N, 23·1%; *M* (single-crystal *X*-ray method), 221. $C_{12}H_{11}BN_4$ requires C, 64·9; H, 5·0; B, 4·9; N, 25·2%; *M*, 222]. Addition of a further 50 ml. of light petroleum (b. p. 30—40°) to the filtrate yielded a precipitate of an air-reactive, curdy, yellow product and a red oil which could not readily be isolated.

When the reaction was carried out in a sealed tube in the absence of solvent, the same crystalline product was obtained and the non-condensable gas produced was collected on the vacuum line. Thus, decaborane (0·351 g., 2·88 mmoles) and phenyl azide (1·22 g., 10·2 mmoles) after 5 days at 50° yielded 201·6 ml. of non-condensable gas which was shown by mass spectrometry (A.E.I. Model MS2) to be 28·7% hydrogen and 71·3% nitrogen. This corresponds to a

---

[8] R. O. Lindsay and C. F. H. Allen, *Org. Synth.*, 1942, **22**, 96.

yield (based on the first equation in the text) of 90% hydrogen and 111% nitrogen, suggesting that some decomposition or further reaction of the excess of phenyl azide had occurred.

Preparation of 2,5-*Diphenylcyclotetrazenoborane*.—A flask (B24; 100 ml.) fitted with a vacuum-line attachment was charged with aniline (1·29 g., 13·9 mmoles) and diethyl ether (10 ml.) which had been cold-distilled from lithium borohydride on the vacuum line. Diborane (150 ml., 6·7 mmoles) was condensed in, and the mixture allowed to warm slowly to about 10°. Phenyl azide (1·55 g., 13·0 mmoles) was added and the mixture allowed to stand at room temperature for 60 hr. The product separated as large crystals which were filtered off, and the mother-liquor continued to deposit crystals until a total of 1·94 g. (70%) was obtained. The crystals were shown to be identical with the product obtained from decaborane by their infrared spectrum, *X*-ray diffraction pattern, and mixed melting point.

X-*Ray Data*.—Standard single-crystal rotational and Weissenberg photographs of 2,5-diphenylcyclotetrazenoborane led to cell dimensions of 13·0 × 5·92 (*b*-axis) × 7·35 Å. In conjunction with the density, this yields a unit-cell mass of 442. The patterns also indicated a centre of symmetry with at least two molecules per unit cell, and were consistent with a planar molecule of the structure proposed.

Nuclear Magnetic Resonance Spectra.—Measurements were made on an A.E.I. model R.S.2. spectrometer using a frequency of 60 Mc./sec. for ^{1}H and 20 Mc./sec. for ^{11}B. The proton spectrum of 2,5-diphenylcyclotetrazenoborane in carbon tetrachloride showed only the complex pattern typical of the phenyl grouping, with four main peaks, which were multiplets, at 7·25, 7·39, 7·61, and 7·72 p.p.m. downfield from tetramethylsilane. The ^{11}B spectrum in toluene showed only a doublet at +29·9 p.p.m. from a capillary of boron trichloride with $J_{\text{B–H}} = 164 \pm 5$ c./sec.

Ultraviolet Absorption Spectra.—These were recorded on a Perkin-Elmer model 137 spectrometer using solutions in cyclohexane.

Infrared Spectra.—A Perkin-Elmer model 125 high-resolution spectrometer was used to study spectra of solutions in carbon tetrachloride, and carbon disulphide in the range 4000—400 cm.$^{-1}$. The far-infrared region (450—200 cm.$^{-1}$) was investigated by means of a Grubb–Parsons DM4 spectrometer; pressed discs of the pure compound, or of the compound dispersed in powdered Polythene were used. The strongest bands in this region were also observed in benzene solution. A pressed disc of the pure compound was also examined by interferometric techniques in the range 400—20 cm.$^{-1}$ using a Research and Industrial Instrument Company's Fourier spectrophotometer FS520.

The authors acknowledge financial support from the United States Air Force through the European Office of Aerospace Research, and thank Dr. H. P. Stadler for assistance with the single-crystal *X*-ray investigation.

DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF NEWCASTLE UPON TYNE.

[*Received, April 5th*, 1965.]