589. *Boron–Carbon Heterocyclic Compounds. Part I. Synthesis and Reactions of Perhydro-9b-boraphenalene.*

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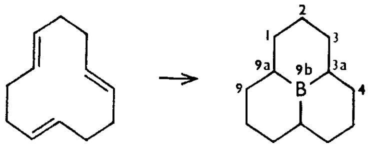
The tricyclic structure of perhydroboraphenalene (II) has been established and the physical and chemical properties of this compound have been compared with those of the tributylborons. Adducts of perhydroboraphenalene with ammonia, pyridine, and piperidine were studied and the infrared spectra of perhydroboraphenalene, cyclododecane, cyclododeca-1,5,9-triene, and cyclododecanetriol have been recorded.

Alkylborons were first prepared one hundred years ago[1] and have since then been extensively studied.[2] However, cyclic organic compounds including boron in the ring have only recently been prepared and no systematic study of their properties has been reported. The present work was initiated to study the effect of ring size and ring substituents on the reactivity of the boron atom and to compare the properties of selected heterocyclic compounds with those of the corresponding open-chain compounds. At that time, only six compounds containing boron–carbon rings were known[3-6] and these were distributed equally between 5-, 6-, and 7-membered rings. Further examples have since appeared[7-11] but little is known of the chemistry and information on physical properties is also meagre.

In most cyclic boron–carbon compounds each boron atom occurs in one ring only. Lithium bis(diphenyleno)borate[5] is the sole example in which a boron atom is common to two rings, and one tricyclic compound (II) has been mentioned.[6] This compound, now named perhydro-9b-boraphenalene, was stated to be formed by addition of borine–triethylamine to cyclododeca-1,5,9-triene (I); it boiled at 131°/16 mm., was thermally stable, unreactive towards hydrogen and olefins, and extremely sensitive to air, and formed an addition compound with ammonia.[6] We have confirmed the existence of perhydroboraphenalene and report details of its synthesis and certain of its physical and chemical properties.



(I) (II)

Reaction between cyclododeca-1,5,9-triene (obtained by trimerising butadiene) and diborane yields a polymer and the tricyclic monomer (II). The yield of perhydroboraphenalene was poor when diborane was added directly to cyclododecatriene at temperatures between 20° and 100°, the main product being polymer. Yields increased when the reaction was carried out in carbon tetrachloride or trimethylamine, and considerable improvement resulted when triethylamine was used as solvent. The yield of perhydroboraphenalene increased still further when cyclododecatriene was treated with separately

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[1] Frankland and Duppa, *Proc. Roy. Soc.*, 1860, **10**, 568.
[2] Lappert, *Chem. Rev.*, 1956, **56**, 959.
[3] Torssell, *Acta Chem. Scand.*, 1954, **8**, 1779.
[4] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 5176.
[5] Wittig and Herwig, *Chem. Ber.*, 1955, **88**, 962.
[6] Köster, *Angew. Chem.*, 1957, **69**, 684.
[7] Clark, Jones, and Stange, Abs. Papers, 133rd Meeting, Amer. Chem. Soc., 1958, p. 45L.
[8] Winternitz, Abs. Papers, 135th Meeting Amer. Chem. Soc., 1959, p. 19M.
[9] Köster and Reinert, *Angew. Chem.*, 1959, **71**, 521.
[10] Köster, *Angew. Chem.*, 1959, **71**, 520.
[11] Davidson and French, *J.*, 1960, 191.

prepared borine–triethylamine in carbon tetrachloride, and almost quantitative hydroboronation occurred at 110° in light petroleum or 2,2′-dimethoxydiethyl ether.

The structure of the product was established by analysis, by molecular-weight determination (cryoscopically in cyclohexane), and as follows. It had no infrared bands near 715 and 795 cm.$^{-1}$ characteristic of the *cis*- and *trans*-double bonds of cyclododecatriene, but a new doublet appeared at 1129—1140 cm.$^{-1}$ close to the expected frequencies for the ^{11}B–C and ^{10}B–C asymmetric vibrations. Hydrolysis with alkaline hydrogen peroxide yielded cyclododecanetriol.

Physical Properties.—Perhydroboraphenalene, n_D^{21} 1·5107, is a colourless, moderately viscous liquid, immiscible with de-aerated water but miscible with carbon tetrachloride, benzene, carbon disulphide, or cyclohexane. In the range 0—50° the density $d^t_4 = 0{\cdot}9619 - 7{\cdot}69 \times 10^{-4}t$. Its vapour pressure (Table 1) can be represented by the relation $\log p$ (mm.) $= 7{\cdot}848 - 2625/T$. The heat of vaporisation is 12·0 kcal. mole^{-1}, the extrapolated b. p. ~255°, and the Trouton constant 22·7 cal. deg.$^{-1}$ mole^{-1}.

TABLE 1. *Vapour pressure of perhydro-9b-boraphenalene.*

t	20·7°	39·5°	50·5°	60·2°	71·2°	79·8°	90·8°	101·4°	109·9°	120·1°	130·2°
p (mm.)	0·06	0·32	0·53	0·98	1·57	2·26	4·07	6·47	10·29	15·65	22·58

The electron-acceptor strength of perhydroboraphenalene towards a variety of ligands was investigated. No complex with tetrahydrofuran could be detected by vapour-pressure measurements even at −40°. Water and triethylamine also failed to form complexes but 1 : 1 adducts were obtained with ammonia, pyridine, and piperidine. The vapour pressure–composition curve for the system perhydroboraphenalene–ammonia at 20° is shown in Fig. 1 and the dissociation vapour pressure of the viscous, liquid 1 : 1 complex is given in Table 2. The data led to a linear plot, $\log p$ (mm.) $= 6{\cdot}835 - 1680/T$, but the corresponding enthalpy change 7·69 kcal. mole^{-1} cannot be taken as the heat of dissociation of the liquid complex into liquid perhydroboraphenalene and gaseous ammonia since it also incorporates the heat of mixing of perhydroboraphenalene with the complex and the heat of solution of ammonia in the liquid mixture. The complex solidified below 10°.

TABLE 2. *Dissociation pressure of the complex* $C_{12}H_{21}B{-}NH_3$.

t	−10·0°	0·0°	10·0°	16·2°	20·0°	34·0°	40·0°
p (mm.)	2·73	4·79	7·52	10·26	12·47	22·53	29·63

The vapour pressure–composition curve for the system perhydroboraphenalene–pyridine at 20° is also given in Fig. 1. The system exhibits an increasing dissociation pressure of pyridine at compositions above a mole ratio of about 0·7 and at the equimolar ratio this pressure is 4·5 mm. The 1 : 1 complex is a white solid which melts over a range of temperature near 60°. The variation of its dissociation pressure as a function of temperature is given in Table 3.

TABLE 3. *Dissociation pressure of the complex* $C_{12}H_{21}B{-}C_5H_5N$.

t	−20·0°	−15·0°	−10·0°	−5·0°	0·0°	+5·0°	10·0°	15·0°	21·1°
p (mm.)	0·64	0·90	1·17	1·66	2·02	2·43	3·01	3·49	5·13
t	31·5°	48·5°	56·6°	66·2°	76·0°	82·4°	89·0°	99·7°	
p (mm.)	6·79	11·60	16·25	23·25	36·5	45·5	62·3	94·3	

The Arrhenius plot has two limbs intersecting at 60°. The slope in the low-temperature region corresponds to 6·5 kcal. mole^{-1} and that in the high temperature region to 11·0 kcal. mole^{-1}. The higher value for the liquid complex presumably implies that the heat of solution of the solid complex in liquid perhydroboraphenalene is greater than the heat of mixing of the liquid complex with perhydroboraphenalene by an amount which exceeds the heat of fusion of the complex.

Discussion.—There are four possible *cis-trans*-isomers of cyclododeca-1,5,9-triene. Molecular models indicate that all can react to give perhydroboraphenalene but the all-*trans*-configuration (I) is the most convenient to use when representing the reaction in plane projection. As the length [12] of a normal B–C bond (1·56 Å) is almost identical with

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[12] "Tables of Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, 1958.

that of a C–C bond (1·54 Å) the most stable conformation of perhydroboraphenalene should be that shown in Fig. 2. Each ring is in the chair configuration and the boron atom is 0·5 Å above the plane of the three adjacent carbon atoms. In this conformation the distance between neighbouring axial hydrogen atoms is 2·5 Å. Appreciable strain is required to force the boron atom into the plane of the adjacent carbon atoms and, if this is done, the distance between axial hydrogen atoms is reduced to 2·35 Å (provided that tetrahedral symmetry is maintained around each carbon atom). Another configuration of the molecule is possible in which the three-carbon bridge shown as between the two equatorial positions *eq* in Fig. 2 is attached at the axial positions *ax*. The chair conformation can be retained in each ring but the shortest H–H distance is only 1·8 Å, implying considerable steric interference.

FIG. 1. *Dissociation pressure, at* 20°, *of* (*A*) *perhydro-9b-boraphenalene–ammonia and* (*B*) *–pyridine.*

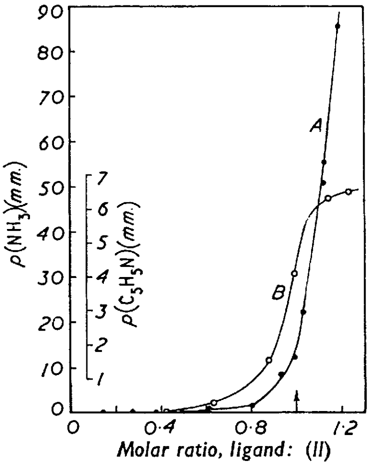
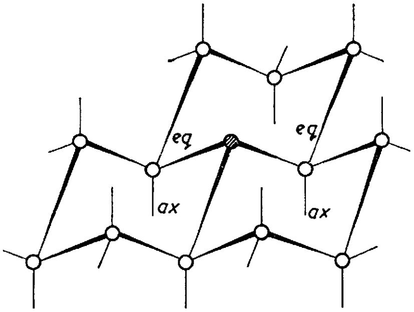


FIG. 2. *Steric model of perhydro-9b-boraphenalene.*



The tricyclic perhydroboraphenalene (II) can be transformed into tri-n-butylboron by breaking three carbon–carbon bonds (3–3a, 6–6a, 9–9a) and adding six hydrogen atoms. The properties of the heterocycle might therefore be expected to resemble those of the trialkyl. Perhydroboraphenalene has a higher b. p. (255°) than has tri-n-butylboron (210°),[13] and is less volatile at all temperatures above —30° ($p \sim 10^{-3}$ mm.) despite its lower heat of vaporisation:

perhydroboraphenalene: $\log p$ (mm.) $= 7{\cdot}848 — 2625/T$; $-\Delta H_{\text{vap.}} = 12{\cdot}0_1$ kcal. mole^{-1}

tri-n-butylboron:[14] $\log p$ (mm.) $= 8{\cdot}797 — 2857/T$; $-\Delta H_{\text{vap.}} = 13{\cdot}0_7$ kcal. mole^{-1}

Perhydroboraphenalene is the more stable to heat and does not decompose below 150° (at least), whereas the trialkyl yields[15] *trans*-2-butene or but-1-ene and tetra-n-butyldiborane above 100°. The electron-acceptor strength of tri-n-butylboron has not been investigated quantitatively but, like perhydroboraphenalene, it does not react with water or triethylamine.[16]

Scission of the three carbon–carbon bonds at positions 1–2, 4–5, and 7–8 leads to tri-s-butylboron but no properties of this compound have been reported. Though structurally less closely related to perhydroboraphenalene, tri-isobutylboron and tri-t-butylboron are known and have properties resembling those of the tricyclic compound to some extent.

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[13] Booth and Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1415.
[14] Skinner and Tees, *J.*, 1953, 3378.
[15] Rosenblum, *J. Amer. Chem. Soc.*, 1955, **77**, 5016.
[16] Johnson, Snyder, and Van Campen, *J. Amer. Chem. Soc.*, 1938, **60**, 115.

Thus, tri-isobutylboron[17,18] boils at 188° and has d_4^{25} 0·7380, $n_D^{22\cdot5}$ 1·41882 (perhydroboraphenalene, b. p. 255°, d_4^{25} 0·9427, n_D^{21} 1·5107), and tri-t-butylboron boils[18] at 181·5° and forms no complex with triethylamine,[19] but forms a liquid 1 : 1 adduct with ammonia[20] which has a dissociation pressure of 1·5 mm. at 0° and 13·3 mm. at 25° (perhydroboraphenalene–ammonia: p_0 4·8 mm., p_{25} 15·5 mm.). These comparisons indicate that perhydroboraphenalene resembles trialkyl borons of comparable molecular weight and that the main effect of placing the boron atom in a heterocyclic ring is to restrict the movement of the butyl groups, making the boron atom slightly less accessible for complex-formation.

EXPERIMENTAL

Intermediates and Solvents.—Solvents and reagents were dried by the usual procedures, fractionated in an atmosphere of dry, oxygen-free nitrogen, and handled subsequently either in a nitrogen-filled glove-box or by cold distillation in a vacuum-line.

Diborane was obtained in 85% yield by addition of boron trifluoride–ethyl ether to lithium aluminium hydride in ether, in an apparatus similar to that described by Schlesinger *et al.*[21] The gas had *M* 30·8 (calc., 27·7) and was pure (infrared spectrum) except for a trace of silicon tetrafluoride.

Borine–triethylamine was prepared by direct addition of the stoicheiometric amount of diborane to triethylamine or by a modification of the method used to prepare borine–trimethylamine, namely:[22] Triethylamine hydrochloride (30 g.), dried by warming at 100° under reduced pressure, was placed with 50 ml. of ether in a three-necked flask, the apparatus flushed with oxygen-free nitrogen, and lithium borohydride (4 g. in 200 ml. of ether) added with stirring. Hydrogen was evolved according to the equation, $Et_3NHCl + LiBH_4 = LiCl + BH_3,NEt_3 + H_2$. After 1 hr. under reflux the solvent was distilled off and the product fractionated in the vacuum-line. The yield was almost quantitative. Borine–triethylamine was a colourless liquid, m. p. −3°, n_D^{21} 1·4427, stable in air, miscible with carbon tetrachloride and carbon disulphide but immiscible with water. Because of its ready preparation, stability, and ease of handling either as liquid or as vapour, borine–triethylamine is a convenient laboratory source of the BH_3 radical.

Cyclododeca-1,5,9-triene was synthesised from butadiene by Ziegler's method,[23] the catalyst being prepared from titanium tetrachloride and diethylaluminium chloride.[24] After the product had been fractionated, pure cyclododecatriene was obtained having b. p. 99°/11 mm., m. p. −20° (lit.,[23,25] b. p. 100°/11 mm., m. p. −18°) (Found: C, 88·8; H, 11·0%; *M*, 165. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%; *M*, 162); it had d_4^{22} 0·8925 and n_D^{20} 1·5062. The infrared spectrum (see below) was identical with that obtained from authentic samples of cyclododeca-1,5,9-triene kindly supplied by Koninklijke/Shell Laboratorium, Amsterdam, and by Imperial Chemical Industries Limited, Billingham.

Cyclododecane.—Catalytic hydrogenation of 1·574 g. of cyclododecatriene over palladised charcoal resulted in absorption of 714 ml. of H_2 (3C⁚C = 722 ml.). During the hydrogenation, crystals of cyclododecane were deposited; after recrystallisation from carbon tetrachloride they had m. p. 61·0° (lit.,[26] 61·0°).

Perhydro-9b-boraphenalene.—Borine–triethylamine (10·93 g., 0·1 mole) was dissolved in 100 ml. of light petroleum in a 500 ml., 3-necked flask fitted with a mercury-sealed stirrer, reflux condenser, and dropping funnel. The apparatus was flushed with oxygen-free nitrogen and heated under reflux during the dropwise addition (2 hr.) of 15·62 g. (0·1 mole) of cyclododecatriene in light petroleum (50 ml.). This minimised the possibility of polymerisation during hydroboronation. (It is not necessary to isolate borine–triethylamine; *e.g.*, a solution of

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[17] Krause and Nitsche, *Ber.*, 1921, **54**, 2784.
[18] Hurd, *J. Amer. Chem. Soc.*, 1948, **70**, 2053.
[19] Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 1452.
[20] Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 374.
[21] Schlesinger, Brown, Gilbreath, and Katz, *J. Amer. Chem. Soc.*, 1953, **75**, 195.
[22] Schaeffer and Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.
[23] Belgian Pat. 555,180.
[24] Ziegler and Martin, *Makromol. Chem.*, 1956, **18/19**, 186.
[25] Wilke, *Angew. Chem.*, 1956, **69**, 397.
[26] Ruzicka, Plattner, and Wild, *Helv. Chim. Acta*, 1946, **29**, 1611.

lithium borohydride in 2,2′-dimethoxydiethyl ether can be added to a suspension of triethylamine hydrochloride in the same solvent; the mixture is heated to 110° and a solution of cyclododecatriene in the same solvent is added slowly.) The product was then fractionated at reduced pressure to give a quantitative yield of perhydroboraphenalene (Found: C, 80·1; H, 12·1; B, 6·15%; *M*, 185. Calc. for $C_{12}H_{21}B$: C, 81·9; H, 12·0; B, 6·15%; *M*, 176) (this boron analysis was the mean of 6·3% based on the weight of ash after combustion and 6·0% obtained by conductimetric titration of a solution prepared by vigorous oxidation of perhydroboraphenalene with concentrated nitric acid). The molecular weight was determined cryoscopically in cyclohexane (k_f 20·2); rigorous exclusion of oxygen was essential.

Cyclododecanetriol.—Perhydroboraphenalene (5 g.) was hydrolysed with alkaline hydrogen peroxide,[27] then extracted with ether, and the ether layer was re-extracted with water. Slow evaporation of the aqueous extract during several days yielded white crystals of *cyclododecanetriol*, m. p. 185° after recrystallisation [Found: C, 66·6; H, 11·2%; *M* (Rast), 246. $C_{12}H_{24}O_3$ requires C, 66·6; H, 11·2%; *M*, 216]. The *triacetate*, recrystallised from aqueous alcohol, had m. p. 95° [Found: C, 62·8; H, 8·6; Ac, 36·7%; *M* (Rast), 330. $C_{18}H_{30}O_6$ requires C, 63·1; H, 8·8; Ac, 37·8%; *M*, 342].

Vapour-pressure Measurements.—Conventional vacuum-line techniques are inconvenient for handling a liquid such as perhydroboraphenalene which is involatile at room temperature (p = 0·06 mm. at 20°), and they were supplemented by use of a nitrogen-filled glove box. A known weight of perhydroboraphenalene was transferred to the manometer system, and successive amounts of ligand were then condensed in from a weighing tube or calibrated bulb. Pressure differences were measured with a cathetometer (0·01 mm.). For measurements above room temperature, where condensation was a problem, the whole apparatus was immersed in an electrically heated oil-bath in a transparent vacuum-flask, the mercury having previously been degassed *in vacuo* at 180°. Observed pressure differences at each temperature were corrected for the changing density of mercury.

Infrared Spectra.—The infrared spectra of cyclododecatriene, perhydroboraphenalene, and cyclododecanetriol have not previously been recorded. The spectra of solutions of cyclododecane agree with that recently published for the molten compound [28] at 81°. Spectra were obtained in the range 375—8000 cm.$^{-1}$ by use of a Unicam S.P. 100 Spectrometer.

For liquid *cis,cis,trans*-cyclododeca-1,5,9-triene,* the frequency (cm.$^{-1}$) and, in parentheses, apparent ε values of bands having ε > 15 were: 713 (61), 953 (38), 975 (93), 1017 (23), 1441 (56, sh), 1447 (61), 2847 (66), 2912 (107), 2930 (87), 2999 (40), 3030 cm.$^{-1}$ (17). There were no bands between 3050 and 8000 cm.$^{-1}$ but several weak bands (with ε 3—7) occurred between 375 and 1700 cm.$^{-1}$ in addition to those listed above, *viz.*, at 407, 606, 784, 796, 809, 870, 927, 1087, 1141, 1197, 1216, 1312, 1345, 1410, 1470(sh), 1661, and 1675 cm.$^{-1}$.

Cyclododecane was dissolved in carbon tetrachloride and in carbon disulphide in order to obtain a spectrum over the whole frequency range. The principal bands were at 722 (ε 68), 768 (23), 788 (41), 822 (10), 964 (13), 1044 (12), 1247 (13), 1308 (16), 1345 (25), 1362 (13), 1445 (83), 1470 (130), 2679 (11), 2849 (140), 2862 (160), 2905 (170), 2932 cm.$^{-1}$ (340).

Liquid perhydro-9b-boraphenalene had absorption bands (ε > 15) at 831 (21), 937 (19), 1090 (20), 1129 (49), 1140 (39), 1247 (17), 1272 (17, sh), 1280 (20), 1301 (35, sh), 1312 (55), 1329 (42), 1349 (60), 1360 (59), 1368 (58), 1447 (58), 1459 (58), 2766 (28), 2844 (250), 2890 (200, sh), and 2915 cm.$^{-1}$ (290). In addition there was a large number of weaker bands (ε 8—15): 673, 790, 839 (sh), 857, 889, 981, 995, 1010, 1025, 1048, 1080(sh), 1148 (sh), 1178, 1197, 1222, 1600, 2659, and 3001 cm.$^{-1}$.

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* It has been stated [25] that the titanium-containing catalyst used in the present work gives the *cis,trans,trans*-isomer though no evidence was cited to support this configuration. On the basis of infrared intensity measurements we believe that the product is *cis,cis,trans*. Thus, the C–H out-of-plane deformation in *trans*-substituted olefins which occurs at 975 cm.$^{-1}$ has a fairly constant intensity [29] of 132—141 l. cm.$^{-1}$ mole^{-1}, and polybutadienes formed by *trans*-addition have an intensity [30] of 133 in CS_2. Our ε values were 93 for a liquid film and 138 for solutions in CS_2. The corresponding band in *cis*-substituted olefins (713 cm.$^{-1}$) is more variable in intensity but is always weaker than the *trans*-band.[29] The observed intensity (ε 61) therefore indicates that two of the three double bonds in cyclododecatriene have the *cis*-configuration.

[27] Brown and Subba Rao, *J. Amer. Chem. Soc.*, 1956, **78**, 5694.
[28] Billeter and Gunthard, *Helv. Chim. Acta*, 1958, **41**, 338.
[29] Bellamy, " The Infra-Red Spectra of Complex Molecules," London, Methuen, 2nd edn., 1958.
[30] Silas, Yates, and Thornton, *Analyt. Chem.*, 1959, **31**, 529.

The spectrum of cyclododecanetriol (KBr disc) showed bands at 396 (6), 457 (7), 483 (6), 513 (7), 530 (5), 538 (5), 756 (16), 849 (10), 901 (18), 933 (20), 952 (18), 962 (20), 996 (16), 1024 (22), 1054 (19), 1082 (18), 1112 (14, sh), 1125 (18), 1157 (15), 1197 (16), 1264 (12), 1304 (14), 1352 (16), 1372 (16), 1427 (17), 1450 (20), 1472 (23), 2679 (10), 2859 (27), 2920 (32, sh), 2948 (37), 3308 cm.$^{-1}$ (broad 36).

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