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Convenient direct syntheses of novel fused-ring CB_4N_5 systems by nitrile hydroboration†

Robert Coult,[a] Mark A. Fox,[a] Brian Rand,[b] Kenneth Wade *,[a] and Aidan V. K. Westwood[b]

[a] *Chemistry Department, Durham University Science Laboratories, South Road, Durham, UK DH1 3LE*
[b] *School of Materials, University of Leeds, Leeds, UK LS2 9JT*

Reactions between B_2H_6 or BH_3·thf (thf = tetrahydrofuran) and nitriles RC≡N (R = Me, Et, Bu^t or CH_2F), previously known to generate borazines $(RCH_2NBH)_3$ have been found to generate also 25–37% yields of novel carboraza bicyclic systems related to dihydronaphthalene, $H_3B_4N_5(RCH_2)_4CHR$, thus affording for the first time a direct route from commercially available acyclic reagents into mixed carbon–boron–nitrogen heterocyclic chemistry.

Bubbling diborane in nitrogen through refluxing acetonitrile was shown in 1968[1] to give the borazine $(EtNBH)_3$ **1** in 35–40% yield, together with what appeared (from mass spectroscopic studies) to be a complex mixture of derivatives of higher boron–nitrogen heterocyclic systems including B_5N_5 naphthalene analogue **5** and B_6N_6 biphenyl analogue **6**.

Re-examination of such reactions, using a wider range of nitriles and reaction conditions, has confirmed that borazines $(RCH_2NBH)_3$ **1**–**4**† are indeed major volatile products, but has also revealed that in all of the systems studied a second major product could be separated by low-pressure distillation from involatile residues. This second product, accounting for some 25–37% of the total mass of the products, was the unexpected novel fused-ring CB_4N_5 heterocyclic system **7**–**10**.

In all of the cases studied (R = Me, Et, Bu^t or CH_2F) the 'carboraza' (carbon–boron–nitrogen) products **7**–**10** were colourless liquids that decomposed slowly in moist air. They were characterized by multinuclear NMR, mass and infrared spectroscopy and elemental analyses. Their bicyclic structures and the identities and sites of substituents were deduced from their NMR spectra. Boron-11 NMR studies of **7** showed a group of doublets at δ 35.0, 33.8 and 32.4 and a singlet at δ 25.8 (intensity ratio 3:1) that could be assigned to the three unique BH groups and B^9 (the boron atom common to both rings, with no substituent hydrogen atom) respectively. The carbon-13 and proton NMR spectra of **7** showed peaks for the CHMe and non-equivalent CH_2Me units as expected.

The ^1H NMR spectra of **7** revealed two of the four CH_2 groups to host diastereotopic protons. This clearly means that the two CH_2 groups at N^1 and N^3 are closer to the centre of asymmetry, *i.e.* the ring carbon, than the other ones.[3] This enables us to distinguish **7** from the other possible isomer with the ring carbon in the 4 position. The structures of **8**–**10** were deduced similarly from their NMR spectra.

Further support for the structure of **7** which we have been unable to obtain in suitable crystalline form for X-ray crystallographic characterization is shown by proton nuclear Overhauser effect (NOE) and boron IGLO/NMR[4] studies (Fig. 1). The structure of **7** was optimized at the STO-3G level[5] to give the geometry shown in Fig. 2. Using the optimized geometry of **7** as the model, the minimum distances between the methine proton and the methylene protons are 1.99 Å for H^a and 2.17 Å for H^b, H^c and H^d in agreement with NOE showing the methine proton to be significantly closer to one methylene proton (H^a) than the others (H^b, H^c and H^d). The different values of H^a and H^b are due to the restriction in the rotation of the ethyl group at N^1 by the ethyl group at N^8 with an hypothetical distance of 3.5 Å between the methyl carbon at N^1 and the methylene carbon at N^8 as the minimum allowed.

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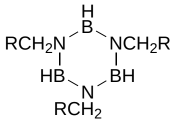
† Syntheses of **1**–**4** and **7**–**10**. In a typical experiment, B_2H_6 (5.5 g, 0.25 mol), generated by dripping BF_3·OEt_2 (50 cm^3, 0.40 mol) into a solution of $NaBH_4$ (12.5 g, 0.33 mol) in dry diglyme (2-methoxyethyl ether) (80 cm^3) over a period of 2 h, was swept in a stream of nitrogen into the nitrile RC≡N (51.3 cm^3, 1.0 mol) at 60 °C. Distillation through a short column allowed unchanged nitrile and the borazine $H_3B_3N_3R_3$ **1**–**4** to be removed separately. Subsequent distillation at <0.1 mmHg (1 mmHg = 133.322 Pa) afforded the carboraza heterocycle **7**–**10** as a colourless liquid distillate leaving a waxy involatile residue.

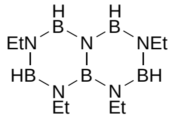
When BH_3·thf [as a molar solution in tetrahydrofuran (thf)] was used as the source of borane, the appropriate volume to generate ultimately a 1:2 molar ratio of BH_3 to RCN was added dropwise to the hot nitrile during 2 h. The volatility of the thf allowed it to be distilled, with unchanged nitrile, from the reaction mixture before the boron-containing products.

1,3,5-Triethylborazine **1**[2] (9.55 g, 36% based on consumed B_2H_6), b.p. 154–160 °C. 1,3,6,8-Tetraethyl-2-methyl-1,3,6,8,10-pentaaza-4,5,7,9-tetraboradihydronaphthalene **7** (11.88 g, 36%), b.p. 70–80 °C at 0.05 mmHg (Found: C, 44.7; H, 10.6; N, 26.6%; M^+ 260. $C_{10}H_{27}B_4N_5$ requires C, 46.1; H, 10.4; N, 26.9%; M 260); δ_B(164 MHz; solvent $CDCl_3$; standard BF_3·Et_2O) 35.0 (1 B, d, BH), 33.8 (1 B, d, BH), 32.4 (1 B, d, BH), 25.8 (1 B, s, B^9); δ_H(500 MHz; $CDCl_3$; $SiMe_4$) 4.43 (1 H, s, BH), 4.42 [1 H, q, ^3J(HH) 6, C^2H], 4.38 (1 H, s, BH), 4.09 (1 H, s, BH), 3.41 [2 H, q, ^3J(HH) 7, CH_2], 3.41 [1 H, dq, ^2J(HH) 14, ^3J(HH) 7, H^d/H^c], 3.23 [2 H, q, ^3J(HH) 7, CH_2], 3.19 [1 H, dq, ^2J(HH) 14, ^3J(HH) 7, H^c/H^d], 3.13 [1 H, dq, ^2J(HH) 14, ^3J(HH) 7, H^b], 2.95 [1 H, dq, ^2J(HH) 14, ^3J(HH) 7, H^a], 1.20 [3 H, d, ^3J(HH) 6, C^2CH_3], 1.15 [3 H, t, ^3J(HH) 7, CH_3], 1.12 [9 H, t, ^3J(HH) 7 Hz, 3 CH_3]; δ_C(100 MHz; $CDCl_3$; $SiMe_4$) 69.1 (d, C^2), 45.3 (t, CH_2), 44.5 (t, CH_2), 43.5 (t, CH_2), 42.2 (t, CH_2), 26.1 (q, C^2CH_3), 20.5 (q, CH_3), 20.1 (q, 2 CH_3), 16.6 (q, CH_3); *m*/*z* 260 (M^+, 0.8%), 245 ($M - CH_3$, 100). 1,3,5-Tripropylborazine **2**[2] 32%, b.p. 40–45 °C at 0.05 mmHg. 2-Ethyl-1,3,6,8-tetrapropyl-1,3,6,8,10-pentaaza-4,5,7,9-tetraboradihydronaphthalene **8** 37%, b.p. 120–125 °C at 0.1 mmHg; δ_B 33.8 (3 B, br, 3 BH), 26.1 (1 B, s, B^9); *m*/*z* 330 (M^+, 1.4%), 302 ($M^+ - C_2H_4$, 100). 1,3,5-Tri(*tert*-butylmethyl)borazine **3** 63%, b.p. 95–105 °C at 0.08 mmHg; δ_B 34.9; *m*/*z* 276 ($M^+ - CH_3$, 8%), 234 ($M^+ - C_4H_9$, 100). 2-*tert*-Butyl-1,3,6,8-tetra(*tert*-butylmethyl)-1,3,6,8,10-pentaaza-4,5,7,9-tetraboradihydronaphthalene **9** 26%, b.p. 145–155 °C at 0.02 mmHg; δ_B 34.3 (3 B, br, 3 BH), 27.8 (1 B, sh, B^9); *m*/*z* 471 (M^+, 0.2%), 456 ($M^+ - CH_3$, 2), 414 ($M^+ - C_4H_9$, 100). 1,3,5-Tri(2′-fluoroethyl)borazine **4** 46%; ($\frac{1}{4}$ scale) b.p. 55–65 °C at 0.04 mmHg; δ_B 34.3; *m*/*z* 218 (M^+, 3%), 185 ($M^+ - CH_2F$, 100). 2-Fluoromethyl-1,3,6,8-tetra(2′-fluoroethyl)-1,3,6,8,10-pentaaza-4,5,7,9-tetraboradihydronaphthalene **10** 28% ($\frac{1}{4}$ scale; **Caution**: it can decompose spontaneously to a non-volatile polymeric solid during vacuum distillation), b.p. 120–130 °C at 0.04 mmHg; δ_B 34.6 (3 B, br, 3 BH), 25.6 (1 B, s, B^9); *m*/*z* 350 (M^+, 0.8%), 317 ($M^+ - CH_2F$, 100).

Synthesis of **11**. Compound **7** (2.36 g, 9 mmol) in Et_2O (10 cm^3) was treated with MeLi (35 mmol in 30 cm^3 hexane) and heated under reflux for 70 h. Diethyl ether was removed. The product was filtered and distilled to afford a fraction b.p. 140–160 °C at 0.05 mmHg identified as **11**. 2,4,5,7-Tetramethyl-1,3,6,8-tetraethyl-1,3,6,8,10-pentaaza-4,5,7,9-tetraboradihydronaphthalene **11** (2.26 g, 7.5 mmol, 83%); δ_B 37.8 (1 B, s, BMe), 35.9 (2 B, s, 2 BMe), 29.1 (1 B, s, B^9); *m*/*z* 302 (M^+, 0.6%), 288 ($M^+ - CH_2$, 100).



	R
1	Me
2	Et
3	Bu^t
4	CH$_2$F



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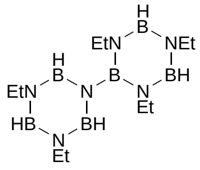

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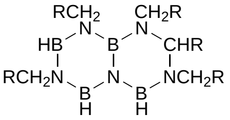
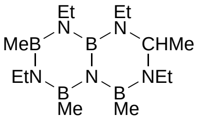


	R
7	Me
8	Et
9	Bu^t
10	CH$_2$F



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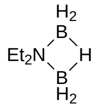

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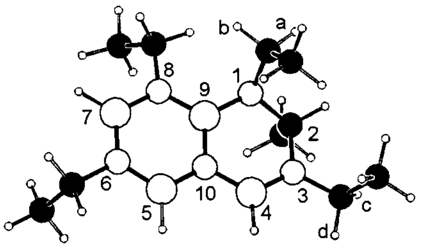

Calculated boron NMR chemical shifts at the IGLO (or GIAO) level from static *ab initio* or experimentally determined geometries of boron compounds are known to fit well with the observed shifts in solution.[6,7] The IGLO(DZ)[8] calculated shifts are δ 32.0 (35.0) for B^5, 31.8 (33.8) B^7, 30.2 (32.4) B^4 and 23.8 (25.8) B^9 for the static STO-3G optimized geometry of **7**. These values are some 2–3 ppm upfield compared to the experimental data shown in parentheses.‡

Compound **7** rapidly forms NHEt$_2$, NH$_2$Et and NH$_3$ with water at ambient temperature. With an excess of methyllithium in diethyl ether, it gives the B-methylated derivative, Me$_3$B$_4$N$_5$Et$_4$(CHMe) **11**.

It was already known that adducts RC≡N·BH$_3$ can be isolated by reactions between nitriles and diborane at low temperatures.[9] Such adducts spontaneously rearrange at or above ambient temperature to borazines (RCH$_2$NBH)$_3$ presumably *via* aldiminoboranes (RCH=NBH$_2$)$_n$ which are known[10] as dimers (RCH=NBR′$_2$)$_2$ when alkylated or arylated on boron.

Formation of the carboraza heterocycles **7**–**10** in these reactions [and in similar reactions at 40–50 °C, or using BH$_3$·thf as the source of borane instead of B$_2$H$_6$] is intriguing. Nucleophilic attack by the nitrile nitrogen atom on the co-ordinated nitrile carbon of RC≡N·BH$_3$ or aldimino carbon of (RCH=NBH$_2$)$_2$ could generate the C–C–N–C–C skeletal unit found as the R–CH–N–CH$_2$R residue in **7**–**10** along with C–N bond cleavage. A previous indication that such nitrile coupling and C–N bond cleavage can occur was provided by the isolation of traces of B$_2$H$_5$NEt$_2$ **12** from the diborane–acetonitrile reaction.[1]

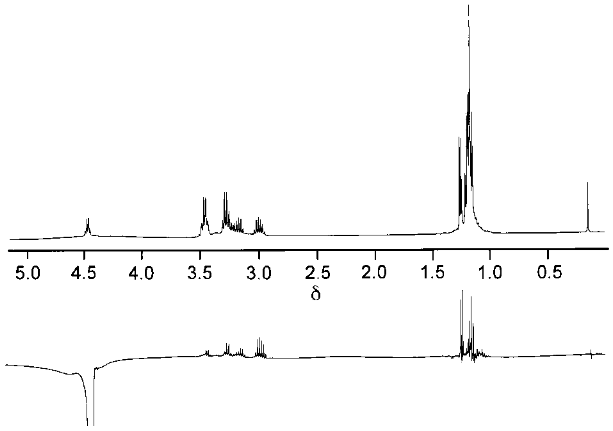

Fig. 1 Proton and NOE spectra of complex **7**

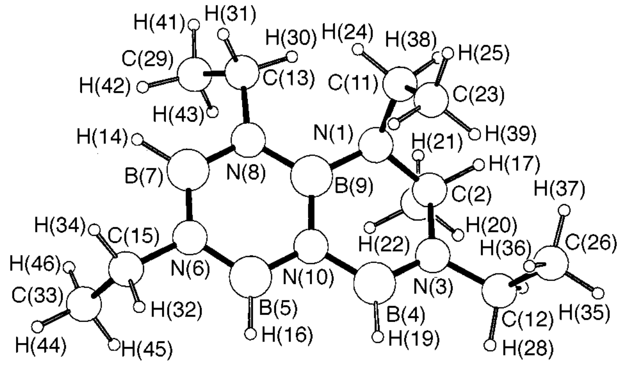

Fig. 2 The STO-3G optimized geometry of the fused-ring CB$_4$N$_5$ system **7**

Boron–nitrogen heterocycles incorporating some carbon atoms are also accessible from reactions of organoboranes with nitriles[11] or hydrogen cyanide,[12] though they require higher temperatures or hazardous materials (HCN). Other mixed carbon–boron–nitrogen ring systems are known, including borazarenes containing even numbers of carbon atoms in their rings, though these have normally required multi-step syntheses.[13] The reactions we describe here are the first to provide direct easy access to fused-ring 'carboraza' systems from commercially available acyclic precursors.

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‡ Calculated NMR chemical shifts [STO-3G/IGLO(DZ)] of the alternative isomer of **7**, where the ring carbon is at the 4 position, are δ 31.9, 30.4, 27.7 and 21.7.

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