

1,4,6-Tris(di-isopropylamino)-1,4,6-triborospiro[4.4]nona-2,8-diene from the Reaction of Benzene with Subvalent Boron Species

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Reaction of benzene with sodium/potassium alloy and dichloro(di-isopropylamino)borane (1 : 2) in 1,2-dimethoxyethane gives, in addition to other products, the title compound, characterised by its mass (EI, FI) and NMR (^1H , ^{11}B , ^{13}C) spectra and X-ray crystallography.

Recently we reported the formation of 1,4-bis(di-isopropylamino)-1,3a,4,6a-tetrahydroborolo[3,2-*b*]borole (A) and 2,8,9-tris(di-isopropylamino)-2,8,9-triborabicyclo[3.3.1]-nona-3,6-diene (B) from the reaction of benzene with subvalent species obtained by dehalogenation of $\text{Cl}_2\text{BNPr}_2^i$ with Na/K alloy.¹ Likewise novel polycyclic species (C) and (D) were obtained starting from toluene or *m*-xylene with Na/K and $\text{F}_2\text{BNPr}_2^i$.² All products characterised so far contain neither spiro centres nor CH_2 groups. When the reaction between C_6H_6 , Na/K, and $\text{Cl}_2\text{BNPr}_2^i$ was conducted using only one third of a molar equivalent of benzene, a new species was isolated and characterised as 1,4,6-tris(di-isopropylamino)-1,4,6-triborospiro[4.4]nona-2,8-diene (1).^{†‡} The spiro

[†] For the preparation of (1), Na/K alloy (1 mol: 7.7 g of Na + 26.0 g of K) was dispersed in a solution of C_6H_6 (0.17 mol) dimethoxyethane (DME; 500 ml) and the mixture stirred at 20 °C for 30 h. $\text{Cl}_2\text{BNPr}_2^i$ (0.5 mol) was added dropwise with vigorous stirring, and the mixture stirred for 24 h at reflux temperature. Insoluble material (alloy and salts) was filtered off under N_2 . Solvent was distilled off and the residue distilled at 0.2 mbar (125–215 °C). After redistillation at 0.005 mbar (105–155 °C), short-path distillation ($\times 2$) gave 9.8 g of a yellow viscous oil (b.p. 132 °C at 0.002 mbar, air bath temp.) which consisted mainly of (1) (field ionization MS and ^1H NMR intensity relationships). From this fraction colourless crystals of (1), m.p. 181 °C, separated after standing for several weeks. As losses are very high upon fractionating highly viscous melts and considerable amounts of (1) are also contained in a higher boiling fraction we assume that the amount of (1) formed in the reaction exceeds 11 g (about 20%).

Spectroscopic data for (1), $\text{C}_{24}\text{H}_{48}\text{B}_3\text{N}_3$: MS: EI (70 eV), m/z 411 (4%) (M^+); FI, m/z 411 (100%); M^+ calc.: 411.41274; found: 411.41274; NMR (250 MHz, CDCl_3 , vs. internal SiMe_4 or external $\text{BF}_3\cdot\text{OEt}_2$): $\delta(^{11}\text{B})$ 44.9 ($w_{1/2}$ 420 Hz) and 51.5 ($w_{1/2}$ 480 Hz) ppm; $\delta(^1\text{H})$ 0.93, 0.94, and 1.03 (all d, $^3J_{\text{HH}}$ 6.70 Hz); 1.21, 1.28, and 1.32 (all d, $^3J_{\text{HH}}$ 6.90 Hz) (total 36H); 3.19 (2H) and 3.23 (1H) (both sept., $^3J_{\text{HH}}$ 6.90 Hz); 3.29 (2H) and 3.57 (1H) (both sept., $^3J_{\text{HH}}$ 6.70 Hz); 1.83 (dd, $^3J_{\text{HH}}$ 1.5, $^4J_{\text{HH}}$ 1.5 Hz, 2H, 7-H₂); 5.65–5.69 (m, 2H, 8-, 9-H); and 7.49 (s, 2H, 2-, 3-H); $\delta(^{13}\text{C})$: 21.5, 21.8, 22.4, 23.8, 25.5, and 26.4 (all Me); 44.5 (1C), 44.9 (2C), 50.7 (2C), and 25.3 (1C) (all CHMe_2); 26.8 (br., 7-C); 125.8 and 141.8 (8-, 9-C); and 161.6 (br., 2-, 3-C). No ^{13}C signal could be recorded for C-5 (connected to three boron atoms).

[‡] **Crystal data for $\text{C}_{24}\text{H}_{48}\text{B}_3\text{N}_3$:** monoclinic, space group $P2_1/c$, $a = 1716.8(3)$, $b = 1084.4(2)$, $c = 1584.1(3)$ pm, $\beta = 114.31(1)^\circ$, $U = 2.688$ nm³, $Z = 4$, $D_c = 1.016$ g/cm³, $\mu = 0.05$ mm⁻¹, $F(000) = 912$. A crystal (0.8 × 0.7 × 0.6 mm) was mounted on a Stoe-Siemens four-circle diffractometer. 5100 reflections were measured at -85 °C using Mo- K_α radiation (λ 71.073 pm), giving 3484 independent data, of which 2987 with $F > 3\sigma(F)$ were employed for all calculations. The structure was determined by direct methods (SHELXS-86). All non-hydrogen atoms were refined anisotropically; a riding model starting from calculated positions was employed for the hydrogen atoms; 271 parameters were refined with a weighting scheme [$w^{-1} = \sigma^2(F) + g F_o^2$; $g = 0.0004$]. The final values for R and R_w were 0.042 and 0.045 respectively; the final difference electron density map showed a maximum of 170 and a minimum of -150 e nm⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

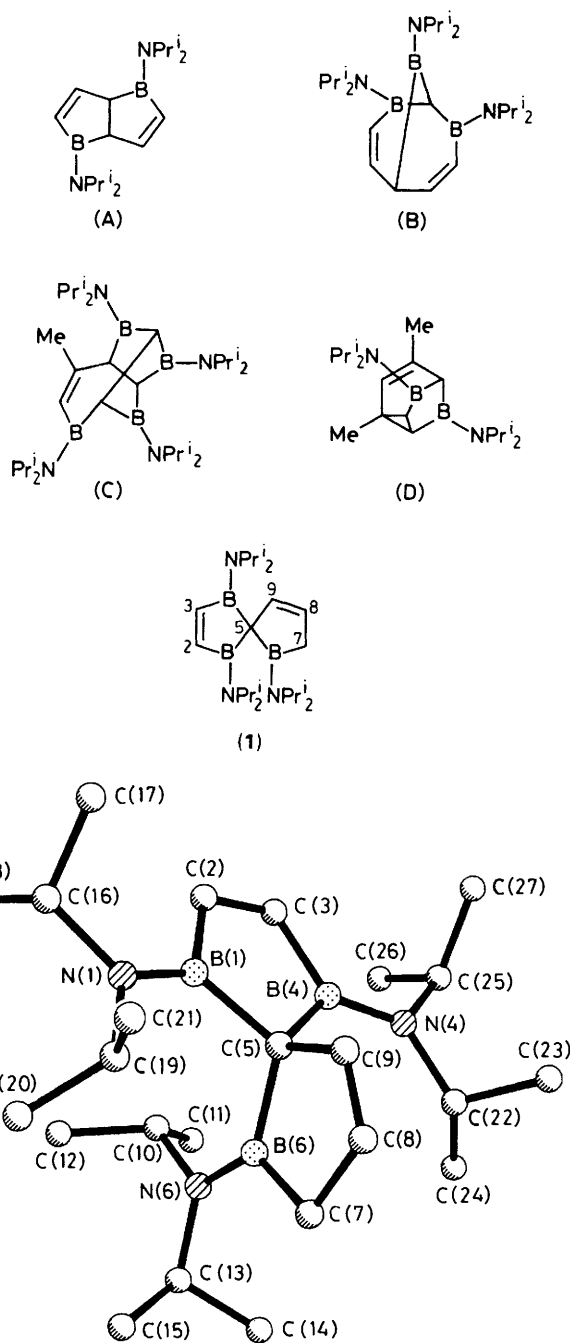


Figure 1. Molecular structure of (1); selected bond lengths (pm) and angles ($^\circ$): C(5)–B(1) 162.2(2), C(5)–C(9) 151.9(3), C(7)–C(8) 150.0(3), C(8)–C(9) 132.0(2), C(2)–C(3) 133.6(3), B(1)–C(2)–C(3) 111.7(1), B(6)–C(7)–C(8) 102.6(1), C(5)–C(9)–C(8) 116.7(2), C(7)–C(8)–C(9) 113.0(2).

compound (1) is formed by the formal insertion of 'borene' units 'BNPr₂' into the benzene ring, as for the species previously reported.^{1,2} Apparently this occurs *via* carbene type intermediates. The complexity of the process (in the liquid phase) makes a sequential mechanistic interpretation impracticable.

The single crystal *X*-ray structure of (1) (Figure 1) shows spiro, planar, five-membered rings containing one and two boron atoms, respectively. Both the bond lengths and hydrogen atoms (all could be located in difference electron density syntheses) clearly identified C(8)–C(9) and C(2)–C(3) as double bonds.

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