

Kurzzmitteilung / Short Communication

9-Diisopropylamino-9-borabicyclo[4.2.1]nona-2,4,7-triene from the Reaction of Cyclooctatetraene with Sodium-Potassium Alloy and Dihalogeno(diisopropylamino)boranes

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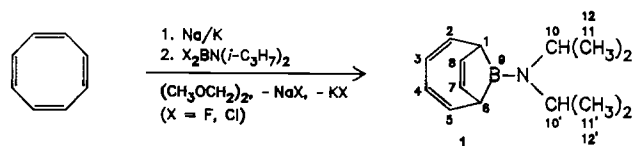
Key Words: 1,3,5,7-Cyclooctatetraene / 9-Borabicyclo[4.2.1]nona-2,4,7-triene, 9-(diisopropylamino)- / Borane, dihalogeno(diisopropylamino)-

The reaction of 1,3,5,7-cyclooctatetraene with sodium-potassium alloy and dihalogeno(diisopropylamino)boranes in 1,2-dimethoxyethane gives the title compound, characterized by

elemental analysis, MS (EI, FI), NMR (^1H , ^{11}B , ^{13}C), and X-ray crystallography.

Recently, we have reported on reactions of aromatic compounds with subvalent boron species^{1,2}. The formation of compounds $\text{C}_6\text{H}_6 \cdot x \text{BN}(i\text{-C}_3\text{H}_7)_2$ ($x = 1-6$) from the reaction of dichloro(diisopropylamino)borane with sodium-potassium alloy in 1,2-dimethoxyethane has been detected by mass-spectrometric studies. Among these, 1,4-bis(diisopropylamino)-1,3a,4,6a-tetrahydroborolo[3.2-*b*]borole and 2,8,9-tris(diisopropylamino)-2,8,9-triborabicyclo[3.3.1]nona-3,6-diene have been isolated. By varying the reaction conditions, 1,4,6-tris(diisopropylamino)-1,4,6-triborasp[4.4]nona-2,8-diene has also been obtained³. In the case of naphthalene two formal borane units are added to the same ring to yield a 1,5-dihydro-1,5-epiboranobenzo[*c*]borepine derivative¹. Acenaphthylene adds one "diisopropylaminoborene" unit to give 2,3-dihydro-1*H*-naphtho[1,8-*cd*]borine².

We report here on the synthesis of 9-diisopropylamino-9-borabicyclo[4.2.1]nona-2,4,7-triene (**1**) involving treatment of 1,3,5,7-cyclooctatetraene with sodium-potassium alloy in 1,2-dimethoxyethane and subsequent addition of dichloro- or difluoro(diisopropylamino)borane to the 10π -aromatic dianion.



Boron species formed upon dehalogenation of dihalogeno(diisopropylamino)boranes — however they might be formulated — apparently react in a somewhat different way as compared with carbenes^{1,2}. It is known, that cyclooctatetraene reacts with carbenes by 1,2 addition to give the bicyclo[6.1.0]nona-2,4,6-triene system^{4,5}. In contrast, subvalent boron species undergo 1,4 addition leading to the bicyclo[4.2.1]nona-2,4,7-triene system. There is some evidence from ^{13}C -NMR spectra of the isomer fraction (see Experimental) that one of the isomers formed is the boracyclononatriene with sp^2 carbon atoms bonded to boron. **1** is quite stable towards hydrolysis in boiling water. However, it is hydrolyzed by boiling aqueous KOH (30%, 12 h) to give a mixture of cyclooctatriene isomers.

Crystal Structure of 1

The molecular structure of **1** is depicted in Figure 1. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 1, selected bond lengths and angles in Table 2.

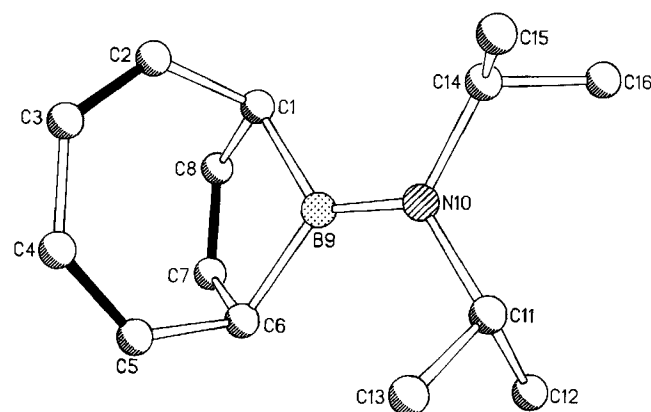


Figure 1. Molecular structure of 1

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) [\AA^2]; equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
N(10)	2590(4)	1066(1)	8137(3)	40(1)
B(9)	1655(7)	1428(2)	6884(5)	43(1)
C(1)	1591(6)	2085(1)	6996(4)	45(1)
C(2)	-423(7)	2266(2)	7327(5)	54(2)
C(3)	-2396(6)	2051(1)	6708(4)	46(1)
C(4)	-3038(6)	1607(1)	5627(4)	42(1)
C(5)	-1932(7)	1275(1)	4947(5)	54(2)
C(6)	367(6)	1305(1)	5029(4)	46(1)
C(7)	859(5)	1822(1)	4282(4)	38(1)
C(8)	1487(5)	2231(1)	5304(4)	42(1)
C(11)	2712(5)	467(1)	7938(4)	39(1)
C(12)	4008(7)	315(1)	6768(5)	57(2)
C(13)	546(6)	201(2)	7516(5)	60(2)
C(14)	3678(5)	1268(1)	9757(4)	39(1)
C(15)	6050(6)	1165(1)	10171(5)	51(1)
C(16)	2677(7)	1058(2)	11033(5)	61(2)

Table 2. Selected bond lengths [Å] and angles [°]

N(10)-B(9)	1.408 (5)	B(9)-C(1)	1.615 (5)
B(9)-C(6)	1.631 (5)	C(1)-C(2)	1.482 (6)
C(1)-C(8)	1.487 (5)	C(2)-C(3)	1.363 (5)
C(3)-C(4)	1.423 (5)	C(4)-C(5)	1.322 (6)
C(5)-C(6)	1.482 (6)	C(6)-C(7)	1.492 (5)
C(7)-C(8)	1.328 (5)		
B(9)-N(10)-C(11)	124.0(3)	B(9)-N(10)-C(14)	121.4(3)
N(10)-B(9)-C(1)	126.5(3)	N(10)-B(9)-C(6)	130.4(3)
C(1)-B(9)-C(6)	103.1(3)	B(9)-C(1)-C(2)	110.4(3)
B(9)-C(1)-C(8)	100.2(3)	C(2)-C(1)-C(8)	107.5(3)
C(1)-C(2)-C(3)	126.9(3)	C(2)-C(3)-C(4)	129.7(4)
C(3)-C(4)-C(5)	131.4(3)	C(4)-C(5)-C(6)	127.5(3)
B(9)-C(6)-C(5)	108.2(3)	B(9)-C(6)-C(7)	98.9(3)
C(5)-C(6)-C(7)	110.5(3)	C(6)-C(7)-C(8)	114.6(3)
C(1)-C(8)-C(7)	113.5(3)		

The molecule obtained by the reaction described above contains one five-membered ring and one seven-membered ring. Both rings contain the atoms C1, B9, and C6 and are formed by bridging of the BN(*i*Pr)₂ unit to the former eight-membered ring. Three remaining double bonds could be located in the molecule.

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Experimental

Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen. — NMR [¹H, ¹³C (TMS int.), ¹¹B (Et₂O-BF₃ ext.): Bruker AM 250. — MS (EI, 70 eV; FI): Varian MAT CH5. — Cl₂BN(*i*Pr)₂⁶, F₂BN(*i*Pr)₂^{7,8}. — All reactions are performed in a dry atmosphere of N₂ and in dry solvents.

9-(Diisopropylamino)-9-borabicyclo[4.2.1]nona-2,4,7-triene (**1**): 30 ml (0.26 mol) of 1,3,5,7-cyclooctatetraene is added slowly to 0.53 mol of sodium-potassium alloy (4.1 g Na, 14 g K) in 500 ml of 1,2-dimethoxyethane. The formation of the dianion proceeds moderately exothermically. After stirring for 12 h, 0.26 mol of dichloro- or difluoro(diisopropylamino)borane (48.2 g or 38.7 g) are slowly added, and the mixture is heated at reflux for 5 h. The slurry is then filtered through a glass frit, 1,2-dimethoxyethane is removed under reduced pressure, and the residue distilled. About half of the fraction, collected at 72°C/0.001 mbar, solidified to give crystals of **1** which are filtered off. The viscous filtrate appears to be a mixture of isomers of **1** as indicated by FI-MS, showing only [M⁺] at *m/z* = 215, and NMR which proves the existence of at least two isomers which could not be separated so far. After recrystallization from 1,2-dimethoxyethane, the yield of **1** is 18 g (31%) or 17 g (30%) for the reaction with dichloro- or difluoro(diisopropylamino)borane. — MS (EI): *m/z* (%) = 215 (40) [M⁺]; (FI): *m/z* (%) = 215 (100). — NMR (CDCl₃): δ¹¹B = 47.4 (*h*_{1/2} = 190 Hz); δ¹H = 2.33 (dd, ³J_{1,2} = ³J_{6,5} = 9.1 Hz, ³J_{1,8} = ³J_{6,7} = 1.8 Hz, 1-, 6-H), 5.55 (d, ³J_{7,1} = ³J_{8,6} = 1.8 Hz, 7-, 8-H), 5.97 (AA'MM'XX', ³J_{2,1} = ³J_{5,6} = 9.1 Hz, ³J_{2,3} = ³J_{5,4} = 11.2 Hz, ⁴J_{2,4} = ⁴J_{5,3} = 0.6 Hz, ⁵J_{2,5} = ⁵J_{5,2} = 0.7 Hz, 2-, 5-H), 5.63 (AA'XX', ³J_{3,4} = ³J_{4,3} = 7.5 Hz, ³J_{3,2} = ³J_{4,5} =

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11.2 Hz, ⁴J_{3,5} = ⁴J_{4,2} = 0.6 Hz, 3-, 4-H), 3.60 (sept, ³J_{10,11/12} = ³J_{10,11/12'} = 6.9 Hz, 10-, 10'-H), 1.15 (d, ³J_{12,10} = ³J_{12,10'} = 6.9 Hz, 12-, 12'-H), 1.14 (d, ³J_{11,10} = ³J_{11,10'} = 6.9 Hz, 11-, 11'-H); δ¹³C = 35.66 (br. C-1, -6), 127.56 (s, C-7, -8), 135.21 (s, C-2, -5), 124.02 (s, C-3, 4), 48.24 (s, C-10, -10'), 23.26 (s, C-11, 11'), 24.29 (s, C-12, -12').

C₁₄H₂₂BN (215.14) Calcd. C 78.16 H 10.31 B 5.02 N 6.51
Found C 78.09 H 10.40 B 5.20 N 6.60

Crystal Data for C₁₄H₂₂BN (**1**)⁹: A crystal (0.8 × 0.3 × 0.7 mm) was mounted on a Stoe-Siemens four-circle diffractometer. — Monoclinic, space group P2(1)/n with *a* = 6.513(1), *b* = 24.503(4), *c* = 8.632(1) Å, β = 105.06(1)°, *V* = 1330.3 Å³, *M* = 215.1, *Z* = 4, *D*_{calc.} = 1.074 g/cm³, μ = 0.06 mm⁻¹, *F*(000) = 472. — Data were collected at -85°C using Mo-K_α radiation (λ = 0.7107 Å) in the 2θ range of 8–45°. Intensities of 2066 reflections were measured of which 1710 were independent and 1454 considered as observed with *F* > 3σ(*F*). They were used in the refinement. Absorption corrections were not applied. The structure was solved by direct methods (SHELXS-86¹⁰). All non-hydrogen atoms were refined anisotropically. A riding model with idealized geometry was employed for H atom refinement, and the hydrogen thermal parameters were refined isotropically with those of atoms bonded to the same carbon atom constrained to be equivalent. 145 parameters were refined, and a weighting scheme (*w*⁻¹ = σ²*F*_o + 0.0005 · *F*_o²) was used. The final values for *R* and *R*_w were 0.074 and 0.083, respectively, with the final Fourier difference map showing a maximum of 0.54 and a minimum of -0.24 e Å⁻³. The relatively high *R* values and residual electron densities indicate a slight disorder of the molecule involving a pseudo mirror plane in the mean plane of the seven-membered ring.

CAS Registry Numbers

1: 124686-64-2 / Cl₂BN(*i*-C₃H₇)₂: 44873-49-6 / F₂BN(*i*-C₃H₇)₂: 38751-90-5 / 1,3,5,7-cyclooctatetraene: 629-20-9

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