Complexes of 1-boraadamantane and its derivatives with 1-azaadamantanes: synthesis and molecular structure

Yu. N. Bubnov,[ab] M. E. Gurskii,[a] D. G. Pershin,[a] K. A. Lyssenko,[b] and M. Yu. Antipin[b]*

[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: bor@cacr.ioc.ac.ru

[b]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085

The reactions of 1-boraadamantane and 2-methyl-, 2-ethyl-, 2,2-dimethyl-, and 3,5-dimethyl-substituted 1-boraadamantanes with their 1-azaadamantane analogs afforded a series of 1 : 1 adducts, which are stable to atmospheric air and moisture. ^1H, ^{13}C, and ^{31}B NMR spectra as well as mass spectra of the compounds synthesized were investigated. Only the adduct of 2,2-dimethyl-1-boraadamantane with 2,2-dimethyl-1-azaadamantane readily dissociates into the initial components due to steric hindrances that prevent strong B←N coordination. The structure and geometric parameters of the 1-boraadamantane complex with 3,5-dimethyl-1-azaadamantane were established by X-ray diffraction analysis.

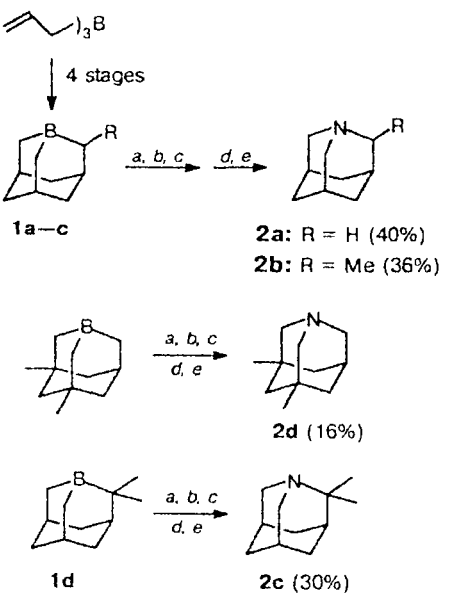
Key words: 1-boraadamantane, 1-azaadamantane; complexes of organoboranes with amines, X-ray diffraction analysis.

1-Boraadamantane (**1a**, R^1 = H), which was prepared by hydroboration of products of condensation of triallylborane with allene or acetylene derivatives,[1,2] exhibits high chemical reactivity. Compound **1a** was used as a starting compound in the synthesis of various derivatives of cyclohexane, bicyclo[3.3.1]nonane,[1–3] and many cage compounds, including 1-adamantanol,[1,2,4] remantadine,[5] derivatives of homoadamantane,[2,6] *etc.* Based on 1-boraadamantane and a series of its alkyl derivatives,[3,7] a preparative procedure has been developed for the synthesis of 1-azaadamantane[8,9] (**2**, R^2 = H) and its homologs[10] (the replacement of boron by nitrogen was carried out in five simple stages virtually in two flasks, the so-called two-pot procedure, Scheme 1).

It should be noted that 1-boraadamantanes **1** and their nitrogen analogs **2** are "electronic antagonists." The former are unique Lewis acids containing the sp^3-hybridized B atom, and they readily form air-stable 1 : 1 complexes with various amines.[1,2,11] On the contrary, 1-azaadamantanes are bases that possess a lone electron pair at the N atom. 1-Boraadamantane (**1a**), 2-alkyl- (**1b,c**), 2,2-dimethyl- (**1d**), and 3,5-dimethyl-substituted 1-boraadamantanes, and the corresponding nitrogen analogs of these compounds (**2a—d**)[8–10] are readily available. Therefore, we succeeded in synthesizing a series of 1 : 1 adducts of these two unique heterocage compounds (**3a—h**). We also studied their physicochemical properties and the effect of the steric factors on their stability.

Hexane solutions of complexes of compounds **1a,b** with THF or complexes of **1c,d** with NMe_3 were treated with the corresponding nitrogen bases **2a—d** (Scheme 2)

Scheme 1



Reagents: *a*. NaN_3; *b*. I_2; *c*. H_2O_2, OH^-; *d*. $SOCl_2$; *e*. NaOH.

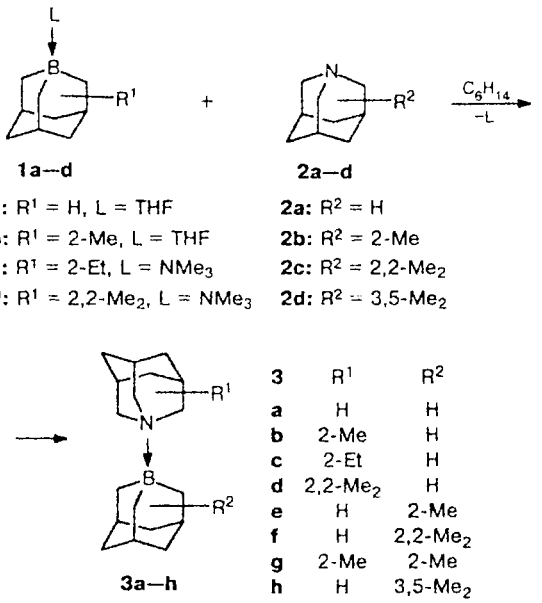
to obtain adducts of 1-boraadamantanes with 1-azaadamantanes **3a—h** in 40—80% yields (Table 1).

The resulting adducts are white crystalline compounds stable to atmospheric moisture and oxygen. Their structures were confirmed by physicochemical methods

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1818—1824, September, 1998.

1066-5285/98/4709-1771 $20.00 © 1998 Plenum Publishing Corporation

Scheme 2



3	R^1	R^2
a	H	H
b	2-Me	H
c	2-Et	H
d	2,2-Me_2	H
e	H	2-Me
f	H	2,2-Me_2
g	2-Me	2-Me
h	H	3,5-Me_2

(high-resolution mass spectrometry and ^1H, ^{11}B, and ^{13}C NMR spectroscopy; see Tables 1 and 2). The molecular structure of complex **3h** was established by X-ray diffraction analysis.

Due to high stability of adducts **3a—h,** their mass spectra have a pronounced molecular ion peak $[M]^+$ (the relative intensity was ~50%). In addition, the mass spectra have intense peaks of ions $[M-C_4H_9]^+$ (100%) and peaks of the corresponding 1-azaadamantanes and 1-boraadamantanes (the intensities were 55—60%) that were formed as a result of partial dissociation of adducts **3a—h.**

Table 1. Yields, melting points, and the data of high-resolution mass spectrometry for compounds **3a—h**

1-Boraadamantane	1-Azaadamantane	Adduct	Yield (%)	M.p. /°C	$[M]^+$, experiment / calculation
1a	**2b**	**3a**	61	323—325 (decomp.)	271.24581 / 271.24697
1b	**2b**	**3b**	72	223—226	285.26181 / 285.26261
1c	**2a**	**3c**	40	129—133 (decomp.)	299.27724 / 299.27825
1d	**2a**	**3d**	79	187—189	299.27688 / 299.27825
1a	**2b**	**3e**	55	170—172 (decomp.)	285.26165 / 286.24261
1a	**2c**	**3f**	59	113—116 (decomp.)	299.27524 / 299.27825
1b	**2b**	**3g**	65	135—138 (decomp.)	299.27625 / 299.27825
1a	**2d**	**3h**	42	159—161 (decomp.)	299.27644 / 299.27825

The chemical shifts in the ^{11}B NMR spectra of compounds **3** (see Table 1) are in the δ region from 4 to −4, which is typical of complexes of trialkylboranes with amines (for example, δ ^{11}B are −4.0 and +0.1 for 1-boraadamantane pyridinate[12] and the adduct of Me_3B with trimethylamine,[13] respectively). The parameters of the ^1H and ^{13}C NMR spectra of the compounds under study are given in Table 2.

Interestingly, the signal in the ^{11}B NMR spectrum is shifted downfield and the relative intensity of the molecular ion peak in the mass spectra substantially decreases as the number of alkyl groups at position 2 of each of the 1-heteroadamantane nuclei increases. This indicates that the B←N coordination bond is weakened as steric hindrances increase. As a result, the adduct of 2,2-dimethyl-1-azaadamantane with 2,2-dimethyl-1-boraadamantane readily dissociates into the initial components, and we failed to isolate it.

The results of X-ray diffraction analysis reported below also confirm the fact that in complexes **3** the substituents at the α positions with respect to the boron and nitrogen atoms are in close proximity.

With the aim of determining the geometric characteristics, possible distortions of the 1-heteroadamantane frameworks, and the B—N bond length, which characterizes the stability of the complex, we carried out X-ray diffraction analysis of the adduct of 1-boraadamantane with 3,5-dimethyl-1-azaadamantane **3h** (Fig. 1). The

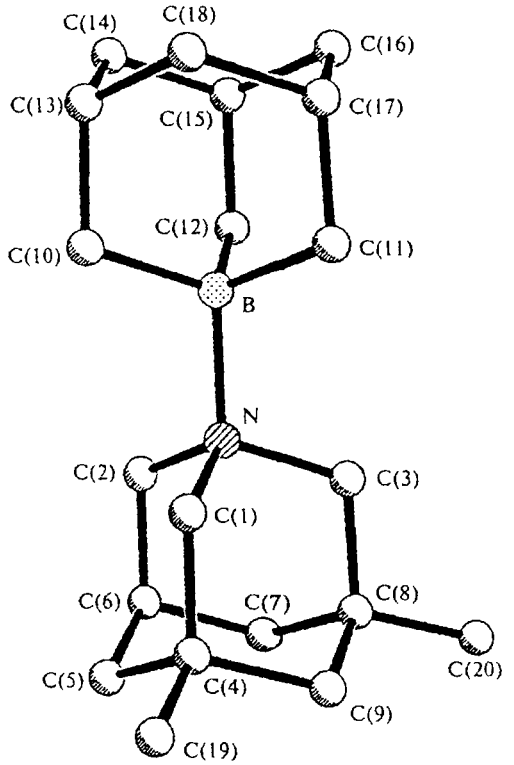
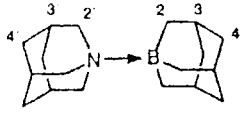
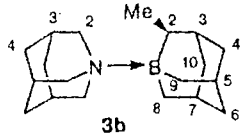
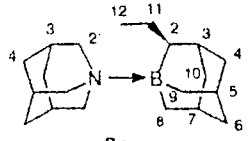
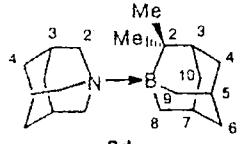


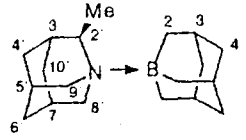
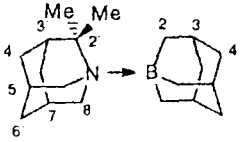
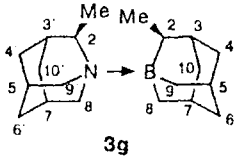
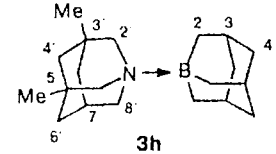
Fig. 1. Overall view of molecule **3h** and the atomic numbering scheme.

Table 2. ^{11}B, ^{1}H, and ^{13}C NMR spectra of compounds **3a—h**

Compound	δ ^{11}B	δ ^{1}H (200 Mz) (*J*/Hz)		δ ^{13}C	
		1-Boraadamantane	1-Azaadamantane	1-Boraadamantane	1-Azaadamantane
 **3a**	−3.9	0.97 (d, 2 H, CH_2B, J = 3.5); 2.89 (br.s, 3 H, C(3)H); 2.20 (AB spectrum, 6 H, C(4)H, J_{AB} = 39.8)	2.69 (s, 6 H, CH_2N); 1.24 (s, 3 H, C(3')H); 1.18 (s, 6 H, C(4')H)	34.3 (C(2)); 34.1 (C(3)); 41.75 (C(4))	27.25 (C(3')); 34.9 (C(4')); 56.2 (C(2'))
 **3b**	−0.6	0.68—1.24 (m, 5 H, C(2,8,9)H); 1.42 (d, 3 H, CH_3, J = 7.0); 1.88 (d, 1 H, C(3)H, J = 11.2); 2.00—2.35 (m, 6 H, C(4,6,10)H); 2.75 (br.s, 2 H, C(5,7)H)	2.80 (s, 6 H, CH_2N); 1.34 (s, 3 H, C(3')H); 1.31 (s, 6 H, C(4')H)	22.6 (CH_3); 34.3 (C(5));* 34.5 (C(7));* 35.4 (C(4)); 42.2 (C(10)); 43.1 (C(6)); 44.5 (C(3))	27.4 (C(3')); 34.9 (C(4')); 56.95 (C(2'))
 **3c**	−1.05	0.67—1.24 (m, 5 H, C(2,8,9)H); 1.29 (t, 3 H, CH_3, J = 6.7); 2.58 (br.s, 1 H, C(3)H); 1.95—2.31 (m, 6 H, C(4,6,10)H); 1.62—1.88 (m, 2 H, C(11)H); 2.76 (br.s, 2 H, C(5,7)H)	2.83 (s, 6 H, CH_2N); 1.37 (s, 3 H, C(3')H); 1.32 (s, 6 H, C(4')H)	22.6 (CH_3); 34.3 (C(5));* 34.5 (C(7));* 35.4 (C(4)); 42.2 (C(10)); 43.1 (C(6)), 44.5 (C(3))	27.4 (C(3')); 34.9 (C(4')); 56.95 (C(2'))
 **3d**	+1.5	0.65 (d, 2 H, $C(8,9)H_\beta$, J = 12.0); 1.09 (d, 2 H, $C(8,9)H_\alpha$, J = 12.0); 1.36 (s, 6 H, CH_3); 1.45 (br.s, 1 H, C(3)H); 1.82 (d, 2 H, $C(4,10)H_\beta$, J = 12.8); 1.99 (AB spectrum, 2 H, C(6)H, J_{AB} = 61.3); 2.38 (d, 2 H, $C(4,10)H_\alpha$, J = 12.8); 2.66 (br.s, 2 H, C(5,7)H)	2.78 (s, 6 H, CH_2N); 1.22 (s, 3 H, C(3')H); 1.20 (d, 6 H, C(4')H, J = 2.6)	31.6 (CH_3); 33.8 (C(5,7)); 36.4 (C(4,10)); 41.8 (C(6)); 53.1 (C(3))	26.7 (C(3')); 34.1 (C(4')); 57.6 (C(2'))

(to be continued)

Table 2. (*continued*)

Compound	δ ^{11}B	δ ^{1}H (200 Mz) (*J*/Hz)		δ ^{13}C	
		1-Boraadamantane	1-Azaadamantane	1-Boraadamantane	1-Azaadamantane
 **3e**	−1.15	1.04 (d, 2 H, CH_2B, J = 3.0); 2.83 (br.s, 3 H, C(3)H); 2.15 (m, 6 H, C(4)H)	0.96 (br.s, 1 H, C(3′)H); 1.08 (br.s, 2 H, C(5′,7′)H); 1.28 (d, 3 H, CH_3, J = 6.9); 1.57 (d, 1 H, C(4′)H_α, J = 12.2); 2.45—3.02 (m, 5 H, C(2′,8′,9′)H)	29.8 (C(2)); 34.5 (C(3)); 41.75 (C(4))	19.55 (Me); 27.4 (C(5′,7′)); 29.5 (C(4′)); 34.5 (C(3′)); 35.9 (C(6′)); 36.5 (C(10′)); 50.0 (C(9′)); 59.7 (C(2′)); 62.5 (C(8′))
 **3f**	+3.9	1.14 (d, 6 H, C(2)H, J = 3.2); 2.12 (m, 6 H, C(4)H); 3.05 (br.s, 3 H, C(3)H)	1.26 (s, 6 H, CH_3); 1.35 (br.s, 3 H, C(3′,5′)H); 1.38—1.82 (m, 6 H, C(4′,6′)H); 2.78 (d, 4 H, CH_2N, J = 13.0)	35.15 (C(3)); 41.5 (C(4))	27.0 (CH_3); 27.4(C(5′,7′)); 32.7 (C(3′)); 31.45 (C(4′)); 37.15 (C(6′)); 53.55 (C(8′)); 55.8 (C(2′))
 **3g**	+0.65	0.72—1.12 (m, 5 H, C(8,9)H); 1.46 (t, 3 H, CH_3, J = 6.4); 1.84 (d, 1 H, C(3)H, J = 10.6); 1.93—2.35 (m, 6 H, C(4,6,10)H); 2.70 (br.s, 2 H, C(5,7)H)	1.29 (d, 3 H, CH_3, J = 6.2); 1.12—1.48 (m, 9 H, C(3′,5′,7′)H, C(4′,6′,10′)H); 2.54—3.12 (m, 5 H, C(2′,8′,9′)H)	22.6 (CH_3); 34.7 (C(5));* 34.8 (C(7));* 35.4 (C(4)); 41.95 (C(6)); 43.1 (C(10)); 44.5 (C(3))	19.7 (Me); 27.5 (C(5′,7′)); 29.5 (C(4′)); 34.5 (C(3′)); 35.7 (C(6′)); 36.7 (C(10′)); 58.85 (C(9′)); 59.05 (C(2′)); 62.4 (C(8′))
 **3h**	−4.1	0.56 (d, 6 H, C(2)H, J = 4.5); 2.15 (br.s, 3 H, C(3)H); 1.45—1.62 (AB spectrum, 6 H, J_{AB} = 42.2)	0.82 (s, 6 H, CH_3); 1.26 (AB spectrum, 2 H, C(4′)H, J_{AB} = 37.0); 1.45 (br.s, 4 H, C(6′,10′)H); 2.04 (m, 1 H, C(7′)H); 2.57 (AB spectrum, 4 H, C(2′,9′)H, J_{AB} = 31.9); 2.82 (br.s, 2 H, C(8′)H)	26.2 (C(2)); 32.85 (C(3)); 40.4 (C(4))	27.2 (CH_3); 27.7 (C(7′)); 29.3 (C(3′,5′)); 40.95 (C(4′,10′)); 48.9 (C(4′)); 54.45 (C(8′)); 60.5 (C(2′,9′))

* Signals can be interchanged.

Table 3. Bond lengths (d) and bond angles (ω) in molecule **3h**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
N—C(3)	1.499 (3)	C(6)—C(7)	1.529 (4)	C(17)—C(18)	1.531 (3)	C(5)—C(6)	1.528 (4)
N—C(1)	1.506 (3)	C(8)—C(20)	1.520 (3)	N—C(2)	1.503 (3)	C(7)—C(8)	1.539 (3)
B—C(11)	1.625 (3)	C(10)—C(13)	1.539 (3)	N—B	1.690 (3)	C(8)—C(9)	1.533 (3)
B—C(10)	1.628 (3)	C(12)—C(15)	1.545 (3)	B—C(12)	1.625 (3)	C(11)—C(17)	1.545 (3)
C(2)—C(6)	1.524 (3)	C(13)—C(18)	1.533 (3)	C(1)—C(4)	1.534 (3)	C(13)—C(14)	1.531 (3)
C(4)—C(19)	1.523 (4)	C(15)—C(16)	1.534 (3)	C(3)—C(8)	1.529 (3)	C(14)—C(15)	1.534 (3)
C(4)—C(9)	1.531 (3)			C(4)—C(5)	1.534 (3)	C(16)—C(17)	1.531 (3)

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(3)—N—C(2)	108.1 (2)	C(4)—C(9)—C(8)	110.8 (2)	C(5)—C(4)—C(1)	107.8 (2)
C(2)—N—C(2)	107.8 (2)	C(17)—C(11)—B	107.7 (2)	C(5)—C(4)—C(9)	109.2 (2)
C(2)—N—B	110.6 (2)	C(14)—C(13)—C(18)	109.2 (2)	C(6)—C(5)—C(4)	109.2 (2)
C(11)—B—C(12)	108.5 (2)	C(18)—C(13)—C(10)	109.6 (2)	C(2)—C(6)—C(5)	109.6 (2)
C(12)—B—C(10)	109.2 (2)	C(14)—C(15)—C(16)	109.4 (2)	C(6)—C(7)—C(8)	108.9 (2)
C(12)—B—N	110.7 (2)	C(16)—C(15)—C(12)	110.6 (2)	C(20)—C(8)—C(7)	111.4 (2)
N—C(1)—C(4)	112.9 (2)	C(18)—C(17)—C(16)	108.9 (2)	C(20)—C(8)—C(9)	110.7 (2)
N—C(3)—C(8)	113.1 (2)	C(16)—C(17)—C(11)	109.8 (2)	C(7)—C(8)—C(9)	108.9 (2)
C(19)—C(4)—C(1)	109.2 (2)	C(3)—N—C(1)	108.1 (2)	C(13)—C(10)—B	108.0 (2)
C(19)—C(4)—C(9)	110.8 (2)	C(3)—N—B	111.6 (2)	C(15)—C(12)—B	107.6 (2)
C(1)—C(4)—C(9)	108.2 (2)	C(1)—N—B	110.5 (2)	C(14)—C(13)—C(10)	110.5 (2)
C(2)—C(6)—C(7)	109.5 (2)	C(11)—B—C(10)	108.1 (2)	C(15)—C(14)—C(13)	111.0 (2)
C(7)—C(6)—C(5)	110.1 (2)	C(11)—B—N	109.8 (2)	C(14)—C(15)—C(12)	109.6 (2)
C(20)—C(8)—C(3)	109.2 (2)	C(10)—B—N	110.4 (2)	C(15)—C(16)—C(17)	110.7 (2)
C(3)—C(8)—C(7)	108.5 (2)	N—C(2)—C(6)	111.4 (2)	C(18)—C(17)—C(11)	111.0 (2)
C(3)—C(8)—C(9)	108.0 (2)	C(19)—C(4)—C(5)	111.5 (2)	C(17)—C(18)—C(13)	110.9 (2)

bond lengths and bond angles in molecule **3h** are given in Table 3. The atomic coordinates are listed in Table 4. The C—C bond angles and bond angles at most of the carbon atoms in both parts of the molecule are in the ranges of 1.528(4)—1.545(3) Å and 108.0(2)—111.0(2)°, respectively (the average values are 1.534(3) Å and 109.6(2)°, respectively). These values are close to the corresponding parameters for the complexes of 1-boraadamantane (d_{aver} = 1.537(4) Å, ω_{aver} = 110.1(8)°)[14,15] and 4-(*p*-chlorobenzoyl)-1-azaadamantane hydrochloride **4** (d_{aver} = 1.527(4) Å, ω_{aver} = 109.4(8)°)[16] and for the crystal structure of the ordered phase of adamantane (at 188 K) in which the corresponding bond lengths and bond angles are 1.529(3) Å and 109.5(4)°, respectively.[17]

The exceptions are the C—C—N bond angles. Their average value (112.4(4)°) is 3.5° larger than that in the molecule of hydrochloride **4**.[16] In addition, the endocyclic C—N—C bond angles in complex **3h** are 2—3° smaller than those in compound **4**. In our opinion, the above-mentioned facts indicate that the 1-azaadamantane nucleus in the structure under consideration is somewhat strained.

The B—C and N—C bond lengths vary within rather narrow ranges (1.625—1.628(3) and 1.499—1.506(3) Å, respectively), which is typical of symmetrical 1-heteroadamantane structures.[14—16] The B and N atoms are characterized by the tetrahedral configuration. The deviations of the B and N atoms from the planes through the adjacent atoms are 0.564 and 0.536 Å, respectively. The $C_3B—NC_3$ fragment adopts a skewed conformation relative to the B—N bond (Fig. 2).

The length of the dative B←N bond in the structure under study is 1.690(3) Å, which is substantially larger than the corresponding values in complexes of boranes with amines in which the N atom is not sterically

Table 4. Coordinates of nonhydrogen atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($U_{eq} \times 10^4$) for compound **3h**

Atom	x	y	z	U_{eq}/Å^2
N	585(2)	8267(1)	7574(1)	19(1)
B	−557(2)	9070(2)	7471(2)	19(1)
C(1)	1731(2)	8664(2)	7090(2)	24(1)
C(2)	876(2)	7996(2)	8854(2)	27(1)
C(3)	249(2)	7391(2)	6887(2)	22(1)
C(4)	2802(2)	7966(2)	7160(2)	28(1)
C(5)	3067(2)	7705(2)	8476(2)	35(1)
C(6)	1915(2)	7282(2)	8967(2)	32(1)
C(7)	1544(3)	6390(2)	8275(2)	33(1)
C(8)	1261(2)	6648(2)	6955(2)	26(1)
C(9)	2407(2)	7083(2)	6457(2)	28(1)
C(10)	−91(2)	10070(2)	8043(2)	24(1)
C(11)	−983(2)	9245(2)	6077(2)	21(1)
C(12)	−1731(2)	8704(2)	8162(2)	24(1)
C(13)	−1167(2)	10767(2)	7931(2)	27(1)
C(14)	−2257(2)	10391(2)	8581(2)	29(2)
C(15)	−2733(2)	9467(2)	8018(2)	26(1)
C(16)	−3099(2)	9631(2)	6693(2)	27(1)
C(17)	−2009(2)	9993(2)	6032(2)	24(1)
C(18)	−1557(2)	10915(2)	6609(2)	29(1)
C(19)	3909(2)	8241(2)	6633(2)	41(1)
C(20)	842(2)	5794(2)	6226(2)	38(1)

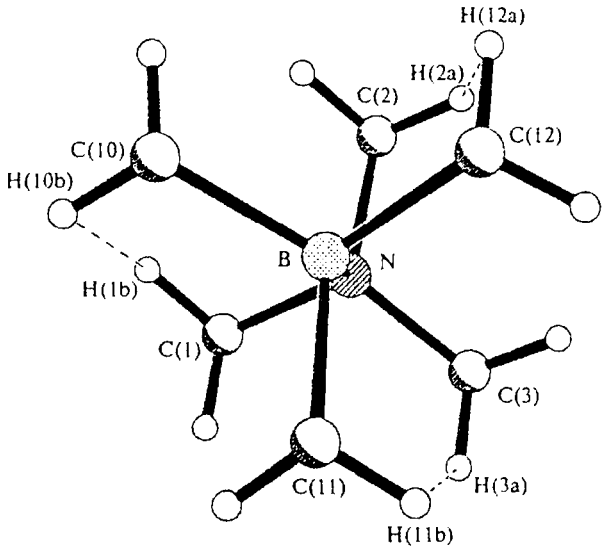


Fig. 2. Projection of the structure **3h** along the B←N bond.

overcrowded[14,18–20] (1.589(5) Å in $(CF_3)_3BNH_2Et$,[18] 1.596(8) Å in $(CF_3)_3BNHEt_2$,[18] 1.578(1) Å in F_3BNH_3,[19] and 1.642(4) Å in 1-boraadamantane pyridinate[14]). However, in the case of adducts of R_3B with bulky amines and when the B—N bond is involved in the ring, an elongation of the B—N bond is rather typical (1.722(8) Å in 1-boraadamantane quinolinate,[14] 1.746(2) Å in 9-[2-(dimethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane,[21] and 1.698 Å in Me_3BNMe_3 according to the data of IR spectroscopy[22]).

We believe that the elongation of the B—N bond and the slight distortion of the 1-azaadamantane nucleus in the structure of **3h** are due to repulsion between the hydrogen atoms of the methylene groups bonded to the N and B atoms (see Fig. 2). The corresponding intramolecular distances H(2a)...H(12a), H(3a)...H(11b), and H(10b)...H(1b) (2.18(2) Å) are shorter than the sum of the van der Waals radii of two hydrogen atoms (2.31 Å).[23] As mentioned above, the replacement of one and all the more two hydrogen atoms by the bulky methyl groups at positions 2 in both the 1-boraadamantane and 1-azaadamantane fragments leads to an increase in repulsion and hence, to weakening of stability of complexes **3**.

Experimental

All operations with organoboron compounds were carried out under an atmosphere of dry argon. The ^1H, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker-AM-200 instrument relative to Me_4Si (^1H and ^{13}C) and $BF_3 \cdot Et_2O$ (^{11}B). The mass spectra were measured on a Varian-CH6 spectrometer.

Synthesis of compounds 3 from complexes of 1-boraadamantane and its derivatives with THF (typical procedure). A solution of sublimated 1-azaadamantane **2a** (0.155 g, 1.13 mmol) in anhydrous hexane (2.5 mL) was added with stirring using a magnetic stirrer to a solution of the complex of 2-methyl-1-boraadamantane **1b** with THF (0.26 g, 1.13 mmol) in anhydrous hexane (4 mL) at 20 °C, and a white precipitate of adduct **3b** formed. The reaction mixture was stirred at 20 °C for 0.5 h. The precipitate was filtered off, washed with anhydrous hexane (2.5 mL), and dried *in vacuo* (12 Torr). Compound **3b** was obtained in a yield of 0.23 g (72%), m.p. 223—226 °C.

Adducts **3a,e—h** were synthesized analogously.

Synthesis of compounds 3 from complexes of derivatives of 1-boraadamantane with NMe_3 (typical procedure). A solution of 1-azaadamantane **2a** (0.185 g, 1.34 mmol) in a mixture of dry ether (1 mL) and hexane (2 mL) was added dropwise with stirring to a solution of the complex of **1d** with NMe_3 (0.30 g, 1.21 mmol) in hexane (6 mL) at 20 °C. Within 1—2 min after completion of the addition, a white precipitate of adduct **3d** began to form. The reaction mixture was stirred at 20 °C for 0.5 h. Then the solvents were distilled off *in vacuo* (12 Torr). The residue was suspended in anhydrous hexane (10 mL) and filtered off. Then the residue was dried *in vacuo* (1 Torr, 30 °C, 0.5 h), and compound **3d** was obtained in a yield of 0.32 g (79%), m.p. 187—189 °C.

Adduct **3c** was prepared analogously.

X-ray diffraction study of compound 3h was carried out on an automated four-circle Synthex $P2_1$ diffractometer (−120 °C, Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $2\theta \leq 50°$). Crystals of **3h**, which were prepared by crystallization from hexane, are monoclinic, at −120 °C a = 10.947(4) Å, b = 14.208(4) Å, c = 11.218(3) Å, β = 93.39(2)°, V = 1741(9) Å^3, d_{calc} = 1.141 g cm^{-3}, Z = 4, space group $P2_1/n$, M = 299.29; $F(000)$ = 664, μ = 0.064 mm^{-1}. A total of 2877 reflections were measured. The structure was solved by the direct method and refined by the full-matrix least-squares method based on F^2. The positions of the hydrogen atoms were located from difference electron density syntheses and refined isotropically. The structure was refined using 2209 independent reflections with $I > 2\sigma(I)$. The final values of the R factors were as follows: R_1 = 0.0466 and wR_2 = 0.1466, GOF = 0.875 for 2709 independent reflections. Analysis of anisotropic thermal parameters within the framework of the rigid body model (LTS)[24] demonstrated that in the crystal molecule **3h** can be considered as a rigid body. The correspondence between the values of U_{ij} calculated with the use of the LTS model is characterized by the R factor R_U = 0.069. The correction for the bond lengths was no more than 0.004 Å. All calculations were carried out on a PC/AT computer with the use of the SHELXTL PLUS program package (Version 5). The coordinates of the nonhydrogen atoms are given in Table 4.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-03-32555, 97-03-33783, and 98-03-32993a) and by the Russian Federation Government (Program "Leading Scientific Schools," Project Nos. 96-15-97289 and 96-15-97367).

References

1. Yu. N. Bubnov, M. E. Gurskii, and I. D. Gridnev, in *Comprehensive Heterocyclic Chemistry*, 2nd Ed., 1996, **8**, Ed. G. Jones, Ch. 34, 889.
2. B. M. Mikhailov and Yu. N. Bubnov, *Organoboron Compounds in Organic Synthesis*, Harwood Acad. Sci. Publ., London—New York, 1984, 645 pp.
3. Yu. N. Bubnov, *Pure Appl. Chem.*, 1987, **59**, 895.

4. M. E. Gurskii, T. V. Potapova, B. M. Mikhailov, A. V. Ignatenko, and Yu. N. Bubnov, *Metalloorg. Khim.*, 1990, **3**, 1195 [*Organomet. Chem. USSR*, 1990, **3** (Engl. Transl.)].
5. M. E. Gurskii, T. V. Potapova, and Yu. N. Bubnov, *Mendeleev Commun.*, 1993, 56.
6. M. E. Gurskii, D. G. Pershin, and Yu. N. Bubnov, *Mendeleev Commun.*, 1992, 153.
7. Yu. N. Bubnov, M. E. Gurskii, A. I. Grandberg, and D. G. Pershin, *Tetrahedron*, 1986, **42**, 1079.
8. Yu. N. Bubnov, M. E. Gurskii, and D. G. Pershin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 952 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 857 (Engl. Transl.)].
9. Yu. N. Bubnov, M. E. Gurskii, and D. G. Pershin, *J. Organomet. Chem.*, 1991, **412**, 1.
10. Yu. N. Bubnov, M. E. Gurskii, and D. G. Pershin, *Mendeleev Commun.*, 1994, 43.
11. Yu. N. Bubnov, T. V. Potapova, and M. E. Gurskii, *J. Organomet. Chem.*, 1991, **412**, 311.
12. B. M. Mikhailov, V. N. Smirnov, and V. A. Kasparov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2302 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
13. H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 1974, **13**, 3070.
14. L. G. Vorontsova, O. S. Chizhov, V. N. Smirnov, and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 595 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].
15. M. V. Sergeeva, A. I. Yanovsky, Yu. T. Struchkov, B. M. Mikhailov, M. E. Gurskii, and D. G. Pershin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2483 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2296 (Engl. Transl.)].
16. M. J. Fernandes, E. Galvez, A. Lorente, J. A. Solver, F. Florencio, and J. Sanz, *J. Heterocycl. Chem.*, 1989, **26**, 349.
17. J. P. Amoreux and M. Foulon, *Acta Crystallogr.*, 1987, **43B**, 470.
18. D. J. Bruer, H. Burger, F. Dorrenbach, G. Pawelke, and W. Weuter, *J. Organomet. Chem.*, 1990, **161**, 385.
19. M. Yu. Antipin, Yu. L. Slovokhotov, A. I. Yanovsky, and Yu. T. Struchkov, *Dokl. Akad. Nauk SSSR*, 1985, **281**, 340 [*Dokl. Chem.*, 1985 (Engl. Transl.)].
20. *Cambridge Crystallographic Database, Release 1995*, Cambidge (England), 1995.
21. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1995, **64**, 446 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].
22. P. M. Kusnetsof and R. L. Kuczkowskii, *Inorg. Chem.*, 1978, **17**, 2308.
23. S. Toyota and M. Oki, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1832.
24. V. S. Shomaker and K. N. Trueblood, *Acta Crystallogr.*, 1968, **24B**, 63.

Received February 23, 1998;
in revised form April 6, 1998