2-Phenyl-1-boraadamantane complexes. Synthesis and intramolecular dynamics

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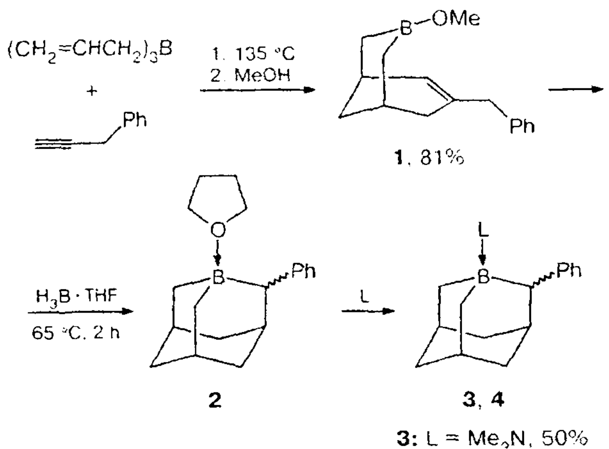
The reaction of triallylborane with 3-phenylprop-1-yne at 135—140 °C followed by treatment of the reaction mixture with MeOH afforded 7-benzyl-3-methoxy-3-borabicyclo[3.3.1]non-6-ene (**1**) in 81% yield. Hydroboration of compound **1** with a solution of BH_3 in THF yielded the tetrahydrofuran complex of 2-phenyl-1-boraadamantane (**2**). The reactions of trimethylamine or pyridine with compound **2** afforded the trimethylamine (**3**) or pyridine (**4**) complexes of 2-phenyl-1-boraadamantane, respectively. Hindered rotation about the C(2)—Ph bond in adduct **3** was observed by ^{1}H and ^{13}C NMR spectroscopy. The activation energy of this process is 58.6 kJ mol^{-1} (determined by 2D ^{1}H—^{1}H EXSY spectroscopy).

Key words: triallylborane, allylboron-acetylenic condensation, 1-boraadamantane compounds, amine complexes, hindered rotation, dynamic NMR.

1-Boraadamantane derivatives occupy a special place among organoboron compounds.[1,2] Owing to a combination of unique geometry, a high strain energy, and a number of useful properties, these compounds are of great interest for theoretical and experimental studies. In particular, 2-substituted 1-boraadamantanes are ideal models for solving some classical problems of the chemistry of adamantane, such as interactions of nonbonded atoms through space or within the adamantane core.

In the present work, 2-phenyl-1-boraadamantane was synthesized for the first time and the dynamic behavior of its complexes was studied.

The reaction of triallylborane with 3-phenylprop-1-yne at 135—140 °C (allylboron-acetylenic condensation[1,2]) followed by treatment of the products with MeOH afforded 7-benzyl-3-methoxy-3-borabicyclo[3.3.1]non-6-ene **1** in 81% yield. Hydroboration of the latter (with $H_3B \cdot THF$) followed by refluxing for 2 h according to a procedure reported previously[3] gave (after removal of the solvent and highly volatile products) the tetrahydrofuran complex of 2-phenyl-1-boraadamantane (**2**). The trimethylamine (**3**) and pyridine (**4**) complexes were synthesized by the reactions of compound **2** with Me_3N and Py, respectively.



1, 81%

2

3, 4

3: L = Me_3N, 50%

4: L = Py, 16%

The presence of the phenyl group leads to a decrease in the stability of these complexes compared to that of the corresponding complexes of unsubstituted 1-boraadamantane, which results in a substantial decrease in the yield of compounds **3** and **4** after recrystallization from hexane. In the mass spectra of compounds **3** and **4**, the peaks $[M - L]^+$ of free 2-phenyl-1-boraadamantane predominate (100%), while the relative intensities of the molecular ion peaks M^+ comprise only ~3% in both

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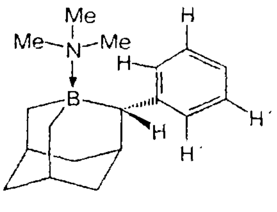
cases. This distribution of the intensities of the M^+ and $[M - L]^+$ peaks is very typical of amine complexes of polyhedral boron compounds (3-borahomoadamantane[4] and 2,2-dimethyl-1-boraadamantane[5]) with a reduced strength of the B←N coordination bond.



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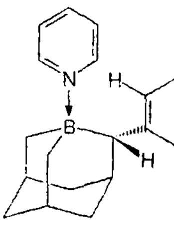

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The ^1H NMR spectrum of trimethylamine complex **3** at room temperature (293 K) has two broad signals in the aromatic region at δ 7.84 and 7.14 (for *o*-H and *o*-H′, respectively) (Fig. 1). The ^{13}C NMR spectrum of compound **3** at 313 K has two broadened signals belonging to the *m*-C (δ 130.2) and *o*-C (δ 127.7) atoms of the phenyl ring (Fig. 2). This fact indicates that dynamic processes occur in the molecule. A decrease in the temperature to 253 K leads to the complete nonequivalence of two *ortho* and two *meta* positions of the phenyl ring, which is clearly manifested both in the ^1H and ^{13}C NMR spectra. An increase in the temperature leads to averaging of pairs of the signals for the protons and the carbon atoms at the *ortho* and *meta* positions (see Figs. 1 and 2). The observed phenomenon is a consequence of the hindered rotation of the phenyl group about the C(2)—Ph bond due to steric interactions between the substituent and the trimethylamine ligand, which is unambiguously confirmed by the presence of the nuclear Overhauser effect between the *o*-H atoms of the aromatic ring and the hydrogen atoms of the Me groups of the trimethylamine ligand.

The rate of this process was estimated by 2D $^1H-^1H$ EXSY spectroscopy[6] for two nonequivalent signals for the *o*-H atoms (Fig. 3). The rate constant was calculated according to Eq. (1) from the experimentally measured intensities of the diagonal peaks and cross-peaks corresponding to the exchange between the *o*-H and *o*-H′ atoms:

$$k = (1/t_m)\log_e((r+1)/(r-1)), \qquad (1)$$
$$r = (I_{AA} + I_{BB})/(I_{AB} + I_{BA}),$$

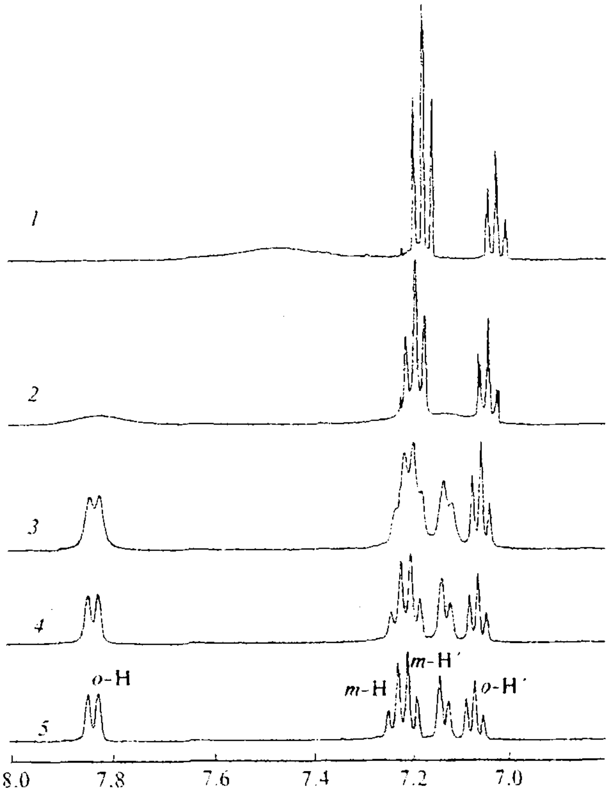

Fig. 1. Temperature dependence of the ^1H NMR spectrum of the 2-phenyl-1-boraadamantane complex (**3**) (400.13 MHz for ^1H, $CDCl_3$, the region of signals for the phenyl group) at different temperatures, K: 323 (*1*), 293 (*2*), 273 (*3*), 263 (*4*), and 253 (*5*).

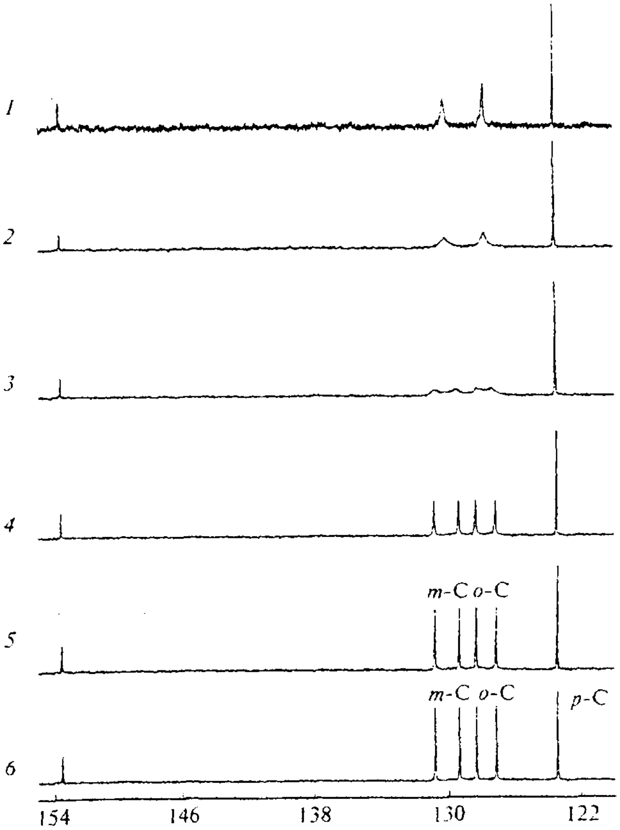

Fig. 2. Temperature dependence of the ^{13}C NMR spectrum of the 2-phenyl-1-boraadamantane complex (**3**) ($CDCl_3$, the region of signals for the phenyl group) at different temperatures, K: 323 (*1*), 313 (*2*), 293 (*3*), 273 (*4*), 263 (*5*), and 253 (*6*).

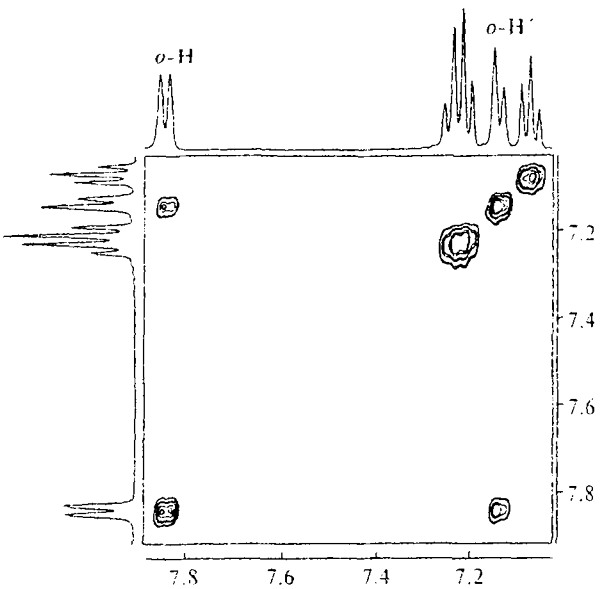

Fig. 3. 2D $^1H-^1H$ EXSY spectrum of compound **3** (400.13 MHz for ^1H, $CDCl_3$, 238 K): the mixing time is 1 s; the relaxation delay is 2 s.

where I_{AA} and I_{BB} are the intensities of diagonal peaks. I_{AB} and I_{BA} are the intensities of cross-peaks, and t_m is the mixing time.

The activation parameters thus determined are as follows: E_a = 58.6±2.6 kJ mol^{-1}, ln$A$ = 28±0.6, and $\Delta G^{\neq}$ = 60.6±2.9 kJ mol^{-1}. The barriers ($\Delta G^{\neq}$) of the aryl group are 53.2 and 60.2 kJ mol^{-1} for *cis,cis*-2,6-dimethyl-1-phenylcyclohexanol[7] and (2,6-dimethylphenyl)cyclohexane,[8] respectively. These values are close to the data obtained in this work.

When studying the temperature dependence of the ^1H and ^{13}C NMR spectra of the pyridine complex of 2-phenyl-1-boraadamantane **4** in a solution of Py-d_5 at temperatures of up to 233 K, no effects of molecular dynamics were observed. This fact is attributable to weaker steric interactions between the phenyl substituent and the pyridine ligand, which possesses a plane symmetry (unlike the three-dimensional structure of the trimethylamine ligand in compound **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 AC-200P (operating at 200.13 MHz for ^1H) and Bruker AMX-400 (operating at 400.13 MHz for ^1H) instruments. The mass spectra (EI) were obtained on a KRATOS MS30 instrument (200 eV). The solvents were prepared according to a standard procedure.[9]

7-Benzyl-3-methoxy-3-borabicyclo[3.3.1]non-6-ene (1). 3-Phenylprop-1-yne[10] (10.3 g, 89 mmol) was added dropwise to triallylborane[2] (15 g, 110 mmol) at 135—140 °C for 30 min. Then the reaction mixture was kept at this temperature for 1 h. Methanol (30 mL) was added carefully to the resulting mixture at 20 °C and the mixture was refluxed for 1 h. Then the methanol was evaporated *in vacuo* and distillation of the residue afforded compound **1** in a yield of 17.4 g (81%), b.p. 140—143 °C (0.03 Torr). n_D^{20} 1.5390. Found (%): C, 80.29; H, 8.78; B, 4.21. $C_{16}H_{21}OB$. Calculated (%): C, 80.02; H, 8.81; B, 4.51. ^1H NMR ($CDCl_3$), δ: 0.60—2.50 (m, 10 H, a complex multiplet of aliphatic protons); 3.12 (d, 1 H, CH_APh, J_{AB} = 14 Hz); 3.22 (d, 1 H, CH_BPh, J_{AB} = 14 Hz); 3.51 (s, 3 H, MeO); 5.53 (br.d, 1 H, HC=C, J = 6.4 Hz); 7.00—7.39 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 24.9 and 25.0 (C(2) and C(4)); 27.3 and 29.4 (C(1) and C(5)); 32.5 and 36.7 (C(8) and C(9)); 44.1 (C—Ph); 52.8 (Me—O); 125.6 (*p*-Ph); 128.4 and 127.9 (*o*- and *m*-Ph); 130.1 ($\underline{C}$H=O); 133.1 (CH=$\underline{C}$); 140.1 (Ph^i).

The tetrahydrofuran complex of 2-phenyl-1-boraadamantane (2). Compound **1** (12.46 g, 52 mmol) was added dropwise to a solution of diborane[2] (0.55 mol L^{-1}, 53 mmol) in THF (98 mL) at 0 °C and the reaction mixture was refluxed for 1 h. Low-boiling compounds were removed *in vacuo* and compound **2** was obtained as an yellowish oil in a yield of 14.4 g (~98% by weight). ^{11}B NMR ($CDCl_3$), δ: 10.7. ^1H NMR ($CDCl_3$), δ: 0.70—2.50, a complex spectrum of the protons of the 1-boraadamantane core (m, 14 H) with a pronounced multiplet at δ 1.85 (m, C(3)H_2 and C(4)H_2 in THF); 3.91 (m, 4 H, CH_2OCH_2 in THF); 7.10—7.40 (m, 3 H, *m*- and *p*-Ph); 7.62 (d, 2 H, *o*-Ph, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 24.4 (the C(3)—C(4) fragment in THF); 26.8 (C(9)); 28.6 (C(8)); 33.4 and 33.9 (C(5) and C(7)); 33.6 (C(4)); 40.3 and 41.8 (C(6) and C(10)); 41.4 (C(3)); 46.3 (C(2)); 68.5 (CH_2OCH_2 in THF); 123.3 (*p*-Ph); 127.3 (*o*-Ph); 129.5 (*m*-Ph); 150.6 (Ph^i).

The trimethylamine complex of 2-phenyl-1-boraadamantane (3). Gaseous Me_3N (9.8 g, 0.166 mol) was introduced into a solution of compound **2** (8.5 g, 0.03 mol) in pentane (60 mL) at 20 °C. The solvent and THF were removed *in vacuo* and trimethylamine complex **3** was obtained in a yield of 4.01 g (95%). Crystallization from hexane afforded compound **3** in a yield of 2.11 g (7.83 mmol) (50%), m.p. 98—100 °C. Found (%): C, 79.99; H, 10.51; B, 3.94. $C_{18}H_{28}BN$. Calculated (%): C, 80.29; H, 10.48; B, 4.02. ^{11}B NMR ($CDCl_3$), δ: −1.28. ^1H NMR ($CDCl_3$), δ: 0.66—2.75 (m, 14 H, a complex set of multiplets of the protons of the 1-boraadamantane core); 2.18 (s, 9 H, MeN); 7.05 (t, 2 H, *p*-Ph, J = 7.4 Hz); 7.19 (t, 2 H, *m*-Ph, J = 7.4 Hz); 7.14 and 7.83 (both br.s, 2 H, *o*-Ph). ^{13}C NMR ($CDCl_3$), δ: 23.4 (C(9)); 29.2 (C(8)); 32.7 and 33.4 (C(5) and C(7)); 33.9 (C(4)); 40.0 (C(2)); 41.1 (C(3)); 41.0 and 42.6 (C(6) and C(10)); 48.5 (Me_3N); 123.5 (*p*-Ph); 129.6 (*o*-Ph); 130.2 (*m*-Ph); 153.7 (Ph^i). MS, m/z (I_{rel} (%)): 269 $[M]^+$ (4), 210 $[M - Py]^+$ (100).

The pyridine complex of 2-phenyl-1-boraadamantane (4). Pyridine (0.8 mL, 8.59 mmol) was added to a solution of adduct **2** (2.53 g, 8.53 mmol) in pentane (15 mL) and the reaction mixture warmed up. Evaporation of low-boiling compounds *in vacuo* afforded pyridine adduct **4** (2.2 g). Crystallization of the latter gave compound **4** in a yield of 0.40 g (16.2%), m.p. 100—102 °C. Found (%): C, 82.79; H, 8.45; B, 3.45. $C_{20}H_{24}BN$. Calculated (%): C, 83.04; H, 8.36; B, 3.47. ^{11}B NMR (Py-d_5), δ: −3.8. ^1H NMR (Py-d_5), δ: 0.80—2.70, a complex multiplet of the protons of the 1-boraadamantane core (m, 14 H); 7.10 (m, 5 H, C_6H_5); 7.39 (t, 2 H, *m*-Py, J = 6.6 Hz); 7.77 (t, 1 H, *p*-Py, J = 6.6 Hz); 8.45 (d, 2 H, *o*-Py, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.8 (C(9)); 36.7 (C(8)); 33.1 and 34.0 (C(5) and C(7)); 35.0 (C(4)); 40.6 (C(3)); 41.5 and 43.3 (C(6) and C(10)); 49.6 (C(2)); 123.9 (*m*-Py); 139.6 (*p*-Py); 144.8 (*o*-Py); 125.6 (*p*-Ph); 128.7 (*o*-Ph); 130.0 (*m*-Ph); 151.6 (Ph^i). MS, m/z (I_{rel} (%)): 289 $[M]^+$ (3), 210 $[M - Py]^+$ (100).

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