Multinuclear NMR Spectra, ^{1}H-T_1 Relaxation, Conformational Behavior, and Intramolecular $H^{\delta-}\cdots^{\delta+}H$ Contacts of N−Borane Cyclic Adducts in Solution

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Introduction

Short proton−hydride ($H^{\delta+}...^{\delta-}H$) contacts are organizing interactions which initiate chemical reactions. For example, dihydrogen bonding in transition metal hydrides causes proton transfer to yield dihydrogen complexes.[1] The dihydrogen bonds, $M-H^{\delta-}\cdots^{\delta+}H$ or even $B-H^{\delta-}...^{\delta+}H$,[2] are experimentally observed by convenient methods in solution and solid state. Intramolecular contacts $C-H^{\delta+}\cdots^{-\delta}H-B$ and $C-H^{\delta+}\cdots^{-\delta}F-B$ (2.2−2.5 Å), established in some cyclic borane adducts in solid state,[2b,3a] can affect conformational states of such molecules in solution.[3] The aim of the present work was to determine these $C-H^{\delta+}\cdots^{-\delta}H-B$ contacts in solutions by the ^{1}H-T_1 relaxation method.

Experimental Section

Solvents and amines were freshly distilled and dried before use according to convenient procedures. The NMR spectra were obtained with JEOL-400 and Bruker-300 spectrometers. The T_1 measurements were carried out by the standard inversion−recovery (180°−τ−90°) method with the use of a Bruker-300 NMR spectrometer in deoxygenated solutions. Calculations of the relaxation times were completed using the nonlinear three-parameter fitting routine of the spectrometer.

Adducts **1**−**4** were prepared by the room-temperature addition of 1.2 equiv of $BH_3{\cdot}S(CH_3)_2$ or $BF_3{\cdot}OEt_3$ solutions to 1.0 equiv of a dry amine under anhydrous conditions. An excess of $BH_3{\cdot}S(CH_3)_2$ was evaporated, and the resulting compounds were kept under N_2. The BH_3- and BF_3-adducts were obtained as white solids and viscous yellow liquids, respectively.

Adduct 1. ^{1}H NMR ($CDCl_3$): δ 3.20 (m, 2H, H-1, ^2J(H1−H2) = 11.5 Hz, ^3J(H1−H3) = 6.0 Hz, ^3J(H1−H4) = 5.0 Hz); 2.65 (m, 2H, H-2, ^3J(H2−H3) = 6.6 Hz, ^3J(H2−H4) = 7.0 Hz); 1.94 (m, 2H, H-3, ^2J(H3−H4) = 12.0 Hz); 1.80 (m, 2H, H-4); 4.6 (s, 1H, N−H); 1.4 (q, 3H, BH_3). ^{13}C NMR ($CDCl_3$): δ 54.2 (t, C-2,5, ^1J(C−H) = 142.2 Hz); 24.6 (t, C-3,4, ^1J(C−H) = 133.9 Hz). ^{11}B NMR ($CDCl_3$): δ −17.2 (q, BH_3, ^1J(B−H) = 94.2 Hz). ^{15}N NMR (C_6D_6): δ −331.3 (d, NH, ^1J(N−H) = 71.3 Hz).

Adduct 2. ^{1}H NMR ($CDCl_3$): δ 3.16 (m, 2H, H-1, ^2J(H1−H2) = 11.2 Hz), ^3J(H1−H3) and ^3J(H1−H4) = 5.7 Hz); 2.97 (m, 2H, H-2, ^3J(H2−H3) and ^3J(H2−H4) = 6.7 Hz); 1.87 (m, 4H, H-3,4); 5.1 (s, 1H, N−H). ^{13}C NMR ($CDCl_3$): δ 47.0 (t, C-2,5, ^1J(C−H) = 146.1 Hz); 24.3 (t, C-3,4, ^1J(C−H) = 134.2 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −1.0 (q, BF_3, ^1J(B−F) = 16.9 Hz).^{19}F NMR (C_6D_6): δ −156.9. ^{15}N NMR (C_6D_6): δ −324.0 (m, NH, ^1J(N−H) = 71.6 Hz, ^1J(N−B) = 19.5, ^2J(N−F) = 19.5 Hz).

Adduct 3. ^{1}H NMR ($CDCl_3$): δ 3.12 (m, 2H, H-1); 2.71 (m, 2H, H-2); 2.07 (m, 2H, H-3); 1.89 (m, 2H, H-4), 2.60 (s, 3H, Me−N). ^{13}C NMR ($CDCl_3$): δ 62.8 (t, C-2,5, ^1J(C−H) = 145.3 Hz); 23.0 (t, C-3,4, ^1J(C−H) = 131.5 Hz); 51.2 (q, Me−N, ^1J(C−H) = 141.4 Hz). ^{11}B NMR ($CDCl_3$): δ −11.2 (q, BH_3, ^1J(B−H) = 96.8 Hz).

Adduct 4. ^{1}H NMR ($CDCl_3$): δ 3.45 (m, 2H, H-2); 2.77 (m, 2H, H-1); 1.97 (m, 4H, H-3, H-4); 2.60 (s, 3H, Me−N). ^{13}C NMR ($CDCl_3$): δ 56.9 (t, C-2,5, ^1J(C−H) = 143.0 Hz); 23.1 (t, C-3,4, ^1J(C−H) = 133.4 Hz); 44.6 (q, Me−N, ^1J(C−H) = 140.7 Hz). ^{11}B-{^{1}H} NMR ($CDCl_3$): δ 0.1 (q, BF_3, ^1J(B−F) = 15.7 Hz).^{19}F NMR ($CDCl_3$): δ −162.2.

Adduct 7. ^{1}H NMR ($CDCl_3$): δ 3.04 (m, 2H, H-2, ^2J(H1−H2) = 13.5 Hz, ^3J(H2−H4) = 11.0 Hz, ^3J(H2−H3) = 4.6 Hz); 2.81 (m, 2H, H-1, ^3J(H1−H3) and ^3J(H1−H4) = 3.9 Hz); 1.71 (m, 1H, H-5), 1.68 (m, 2H, H-3,4), 1.41 (m, 1H, H-6); 2.56 (m, 3H, CH_3, ^3J(H−^{11}B) = 1.5 Hz). ^{13}C NMR ($CDCl_3$): δ 52.4 (t, C-2,6, ^1J(C−H) = 140.7 Hz); 19.0 (t, C-3,5, ^1J(C−H) = 129.1 Hz); 22.3 (t, C-4, ^1J(C−H) = 128.4 Hz); 39.1 (q, Me−N, ^1J(C−H) = 141.4 Hz). ^{11}B{^{1}H} NMR ($CDCl_3$): δ 0.3 (q, BF_3, ^1J(B−F) = 15.8 Hz).^{19}F NMR ($CDCl_3$): δ −163.4.

Results and Discussion

Borane adducts **1**−**4** were characterized by multinuclear NMR spectra (Experimental Section). Simulation procedures, {^{1}H}-, {^{11}B}-, and ^{1}H-NOESY experiments provided the assignments in Table 1.

The ^{1}H NMR spectrum of adduct **1** ($CDCl_3$, 25 °C) shows four nonequivalent methylene protons, supporting the structure in Chart 1. Protons 1 and 2 exhibit the different ^3J(HCNH) constants. Finally, the line of 2 is remarkably broadened ($\Delta\nu$ = 2.5−3.0 Hz) due to a three-bond ^{1}H−^{11}B coupling. This effect, by analogy with the ^3J(H−H) coupling rule,[4] results from different dihedral angles H(1)−C−N−B and H(2)−C−N−B (Chart 2). The same spectral features are detected in adduct **2**. In contrast, the "frozen" (ring−chair) conformations of the cycles in **5**−**8**[3] (Chart 1) show the equally broadened lines of protons 1 and 2 due to their symmetrical location with respect

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Table 1. The ^{1}H-T_1 NMR Data (300 MHz) for Adducts **1**−**8** in $CDCl_3$ at 25 °C[a]

comp	proton	δ (ppm)	T_1 (s)
	1	3.20 (br), ^3J(HNCH) = 6.3 Hz	3.1, 7.3, [b]0.24[c]
	2	2.65 (sbr),	3.4, 7.3, [b]0.27[c]
1		^3J(HNCH) = 8.6 Hz	3.7, 7.9, [b]0.31[c]
	3	1.94	
	4	1.80	3.8, 8.7, [b]0.36[c]
	BH_3	1.40	1.5, 3.4, [b]0.11[c]
	1	3.16 (br), ^3J(HNCH) =5.3 Hz	1.1, 2.0[b]
2	2	2.97 (sbr), ^3J(HNCH) = 7.3 Hz	1.2, 2.1[b]
	3	1.87	1.7, 2.0[b]
	4	1.87	1.7, 2.0[b]
	1	3.12	5.6, 10.5,[b]0.93[c]
	2	2.71	6.0, 10.6,[b]0.94[c]
3	3	2.07	5.9, 13.0,[b]0.96[c]
	4	1.89	5.9, 11.0,[b]0.97[c]
	CH_3	2.60(br)	3.6, 6.3,[b]0.50[c]
	BH_3	1.50	2.5, 4.0,[b]0.39[c]
	1	2.85, ($^3J(^1H-^{11}B)$ = 0.8 Hz)	4.8
	2	3.45, ($^3J(^1H-^{11}B)$ = 1.5 Hz)	5.1
4	3	2.06	5.9
	4	2.06	5.9
	CH_3	2.60, ($^3J(^1H-^{11}B)$ = 1.4 Hz)	2.7
	1	3.17, ^3J(HNCH) = 2.3 Hz	1.6
	2	2.45, ^3J(HNCH) = 12.4 Hz	1.7
5	3, 4, 5, 6	1.70, 1.50, 1.30	1.8, 1.6, 1.7
	BH_3	1.40, ($^3J(^1HBN^1H)$ = 2.3 Hz)[d]	0.95
	1	3.25 (br), ^3J(HNCH) = 3.0 Hz	0.94
6	2	2.59 (br), ^3J(HNCH) = 12.9 Hz	0.93
	3, 4, 5, 6	1.76, 1.57, 1.33	0.90, 0.75, 0.95
	1	2.82 (br)	2.5
	2	3.05 (br)	1.8
7	3, 4, 5, 6	1.75, 1.69, 1.41	2.7, 2.6
	CH_3	2.56, ($^3J(^1H-^{11}B)$ = 1.5 Hz)	2.3
	1	3.85	3.4
	2	4.37	3.0
	3	4.03	3.8
8	4	3.40	3.6
	CH_3	2.87	2.7
	BH_3	1.65	1.5

[a] Broadened due to a $^1H-^{11}B$ coupling (br), strongly broadened (sbr), respectively [b] CD_2Cl_2 at 25 °C. [c] CD_2Cl_2 at −90 °C. [d] Measured by $\{^{11}B\}$ − experiments.

to $^{11}BR_3$ (Chart 2). On the basis of the data, one can conclude that adducts **1** and **2** exist in solutions as envelope conformations[5] with the equatorial BR_3 groups (Chart 1). Note that equatorial protons 1 are high-frequency shifted by the equatorial BR_3 groups.[6] Six-membered cyclic adducts **5** and **6** show the same spectral feature.[3] In contrast, adducts **4** and **7**, containing the $N(CH_3)BF_3$ fragments, demonstrate the opposite tendency;

Chart 1

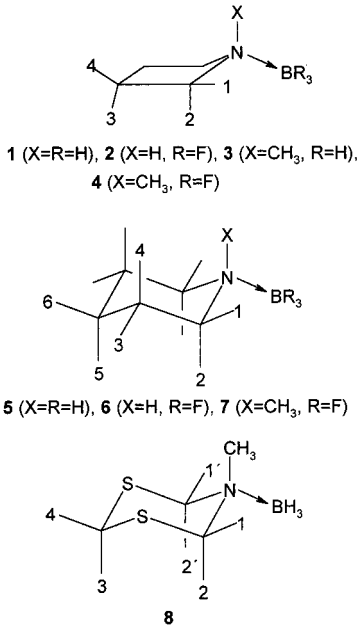
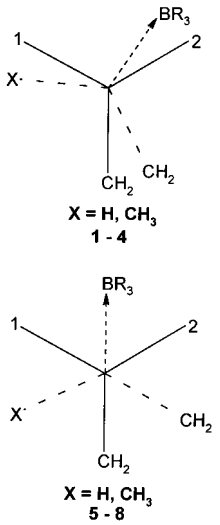


Chart 2



here axial protons 2 are high-frequency shifted (Table 1).

Usually five-membered cycles are flexible in solutions.[5] However, the ^{1}H and ^{13}C NMR spectra of **1** (CD_2Cl_2) were temperature independent, and the ^{1}H-NOESY experiments (25° and −90 °C) revealed the cross-peaks 1-2, 3-4, 1-4, 2-3, and 1-NH. The VT ^{1}H-NOESY spectra of adduct **2** (CD_2Cl_2) were similar to that of **1**.

The "frozen" conformations of **1**, **2**, and **8**[3] are convenient to use to determine contacts $H^{\delta+}\cdots\cdots{}^{-\delta}H$ in solution by the ^{1}H-T_1 relaxation method. The method provides a high accuracy when ^{1}H-T_1 times reach minimal values (T_{1min}) at low temperatures.[8] Unfortunately, such measurements are not possible for the investigated adducts because of their small inertia moments. Actually, protons 1 and 2 in adduct **1** (CD_2Cl_2, −90 °C) show the T_1 values of 0.24 and 0.26 s, respectively, which are

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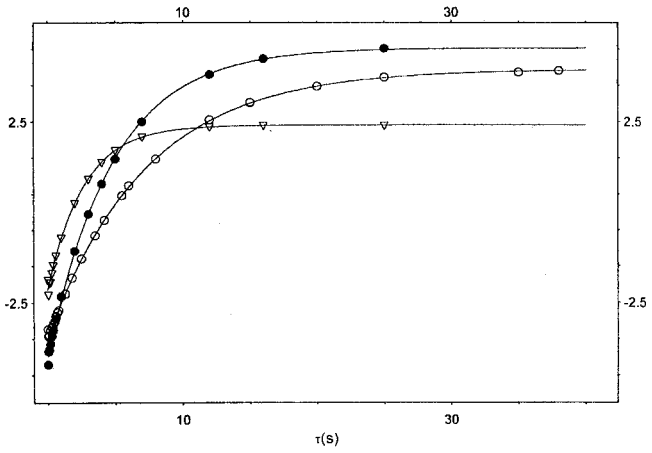

Figure 1. Inversion−recovery curves (Intensities *I* versus delay times τ in sec), obtained for CH_3 (▽) and α-protons (●) in adduct **4** ($CDCl_3$, 25 °C) and α-protons (o) in adduct **1** (CD_2Cl_2, 25 °C).

significantly greater than those calculated by eq 1, where ν is the ^{1}H NMR frequency. [8b]

$$r(\mathrm{H-H})^6 = 5.815^6\,(T_{1\min}/\nu) \qquad (1)$$

The calculation leads to $T_{1\min} = 0.10-0.15$ s if r(H...H) = 1.54−1.64 Å and ν = 300 MHz.

At room temperature, the dipole−dipole relaxation of ^{1}H is described as:

$$1/T_1 = (4/3)(\mu_o/4\pi)^2\,\hbar^2\gamma_H{}^2\gamma_{NS}{}^2 S(S+1)\tau_c r(\mathrm{H-S})^{-6} \qquad (2)$$

where μ_o, S, and γ are known physical constants, and τ_c is a correlation time of molecular reorientations.[7] The equation transforms to:

$$1/T_1(\mathrm{H-H}) = 8.55 \times 10^{11}\tau_c r(\mathrm{H-H})^{-6} \qquad (3a)$$

$$1/T_1(\mathrm{H-{}^{11}B}) = 2.38 \times 10^{11}\tau_c r(\mathrm{H-B})^{-6} \qquad (3b)$$

for the ^{1}H−^{1}H and ^{1}H−^{11}B (in account for the natural abundance of ^{11}B) interactions, respectively. Here T_1 and τ_c are measured in sec, and r is expressed in Å. In the solid cyclic N−BH_3 adducts, the C−$H^{\delta+}\cdots{}^{-\delta}$H−B contacts (between the α-methylene and BH_3 protons) are elongated up to 2.2−2.5 Å.[2b,3a,c] Taking τ_c as 1×10^{-11} s, calculation by eq 3a leads to ^{1}H-T_1 ≥ 13.3 s when a proton−hydride distance, r(H...H), is ≥2.2 Å. The same τ_c value predicts T_1 = 1.54 s for two methylene protons separated by 1.54 Å. Hence proton−hydride interactions can be contributed to a total relaxation rate of the methylene protons by ≤10%. Note that in a common case, T_1 values are determined with errors ≈5%.[8a] Thus, proton−hydride contributions (which can be quantitatively interpreted) are quite small and correspond to 5−10% of measured magnitudes.

Eqs. (3) are valid for isotropic molecular motions, while the adducts in Chart 1 are nonspherical. However, inversion−recovery curves collected, for example, in solutions of **1** and **4** (Figure 1), do not reveal the features typical of anisotropic motions.[9a] Table 1 shows that the T_1(1) and T_1(2) values in **5** and **6** are identical, corresponding well to the locations of protons 1 and 2 with respect to BR_3 (Chart 2). In contrast, adducts **1** and **2** show the remarkable difference in T_1 of H(1) and H(2) ($CDCl_3$, 25 °C). It is interesting that the T_1 values are more elongated for the axial protons which are closer to BH_3 or BF_3 (Chart 2). However, the difference disappears in CD_2Cl_2 at 25 °C and appears again at low temperatures (Table 1). We assume that such effects (see also **3**) are caused by anisotropic motions and cannot be interpreted in distance terms.

Adducts **1**, **2**, and **8** show that averaged relaxation rates ($R_1(1,2) = 1/T_1(1,2)$), characterizing α-methylene protons, are constantly higher than R_1(3,4). This observation can be used to determine contacts C−$H^{\delta+}\cdots{}^{-\delta}$H−B. According to the X-ray structures of the cyclic NBH_3 adducts[2b,3a,c,9b] (similar to **1**, **2**, and **8**), distances H...H in the NCH_2 and SCH_2 groups are measured as 1.55−1.57 Å. These distances in the BH_3 groups are remarkably longer (1.84−1.93 Å). Finally, the B−H bond lengths are lying between 1.10 and 1.15 Å. On the basis of the structural data, the T_1(3,4) value in adduct **8** gives, using eq 3a, $\tau_c = 0.44\ 10^{-11}$ s ($CDCl_3$, 25 °C). In turn, this value predicts T_1 of the BH_3 protons, relaxing by proton−proton and proton−boron dipolar interactions (eq 4), as 1.30 s; this is in accord with 1.54 s in

$$1/T_1(\mathrm{BH_3}) = 2(8.55 \times 10^{11})(0.44 \times 10^{-11})(1.84)^{-6} + (2.38 \times 10^{11})(0.44 \times 10^{-11})(1.10)^{-6} \qquad (4)$$

Table 1. One can think that BH_3 in **8** is not a fast-spinning group about the N−B bond because the rotation with $\tau \ll \tau_c$ strongly elongates ^{1}H-T_1 times.[10] The same approach to **1** results in the τ_c value of 0.43×10^{-11} s ($CDCl_3$, 25 °C), 0.19×10^{-11} s (CD_2Cl_2, 25 °C), and 4.9×10^{-11} s (CD_2Cl_2, −90 °C). Again, the $T_1(BH_3)$ time in **1** is well predicted as 1.4, 3.2, and 0.12 s, respectively.

The equal T_1(3) and T_1(4) times in adduct **8** show that dipole−dipole interactions 3−2(2') are negligible. Hence, an additional contribution to the total relaxation rate of α-protons, ($R_1(1,2) - R_1(3,4)$), calculated as 0.0412 s^{-1}, can be attributed to dipole−dipole interactions with BH_3.[11] Then, 0.0412 s^{-1} and the τ_c value of 0.44×10^{-11} s leads to a distance $H^{\delta+}\cdots{}^{-\delta}$H of 2.12 ± 0.12 Å[12a] to account for one C−$H^{\delta+}\cdots{}^{-\delta}$H−B contact.

The faster relaxation of H(1,2) with respect to H(3,4) in **1** can be expressed as $(R_1(1,2) - R_1(3,4))/R_1(1,2)$ that is 16% of $R_1(1,2)$. Thus, this contribution is higher than 10%, as discussed above. The same approach to the T_1 times in pirrolidine ($T_1(1,2)$ = 7.4 s, $T_1(3,4)$ = 8.0 s, $CDCl_3$, 25 °C) leads to 9%. Hence the N−H proton also accelerates the relaxation of H(1,2).[12b] Then, a proton−hydride contribution to the total relaxation rate of H(1,2) in **1** is estimated as 7% or as 0.0228 s^{-1} ($CDCl_3$, 25 °C), 0.0101 s^{-1} (CD_2Cl_2, 25 °C), and 0.291 s^{-1} (CD_2Cl_2, −90 °C). In turn, these values give distances C−$H^{\delta+}\cdots{}^{-\delta}$H−B between 2.33 ± 0.14 and 2.29 ± 0.14 Å. Thus, 2.30 Å can be taken as a good estimation. Finally, it should be emphasized that the spectral parameters and the relaxation in adducts **1** and **2** are very similar. Therefore, the short C−$H^{\delta+}\cdots{}^{-\delta}$F−B contacts can be also expected in solutions of **2**.

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(11) This is reasonable because contacts between NCH_3 and CH_2 are not shortened in the X-ray structures of the NCH_3 heterocyclic derivatives.[3a] In addition, α- and β-protons in *N*-methyl- pirrolidine showed the practically equal T_1 times (5.5 and 5.3 s, $CDCl_3$, 25 °C) despite the presence of the CH_3 group.

(12) (a) The error is estimated on the basis of the averaged $T_1(1,2)$ values. (b) The NH contribution is calculated as 0.0107 s^{-1}. The r(H...H) distance in the CH_2 groups, taken as 1.57−1.55 Å (see the text), gives $\tau_c = 0.22-0.20 \times 10^{-11}$ s. Then the contribution of 0.0107 s^{-1} corresponds to a very reasonable CH...HN distance of 2.4−2.3 Å.

Conclusions

Borane adducts **1**−**4** and **7** were characterized by ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{11}B NMR spectra in $CDCl_3$. The VT ^{1}H NMR and ^{1}H-NOESY studies revealed "frozen" envelope conformations in solutions of **1** and **2**. The BR_3 groups occupy equatorial positions.

The relaxation study allowed the determination the $H^{\delta+}\cdots{}^{-\delta}H$ contacts in solutions of **1** (2.30± 0.14 Å) and **8** (2.12 ± 0.12 Å), which are similar to those found in the solid state. These contacts are close (or even shorter) to the sum of the van der Waals radii of H. One can think that such contacts can control the conformational states.

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