$BH^{\delta-}$–$^{\delta+}HC$ Interactions in *N*-Borane and *N*-Chloroborane Adducts Derived from 1,3,5-Heterocyclohexanes

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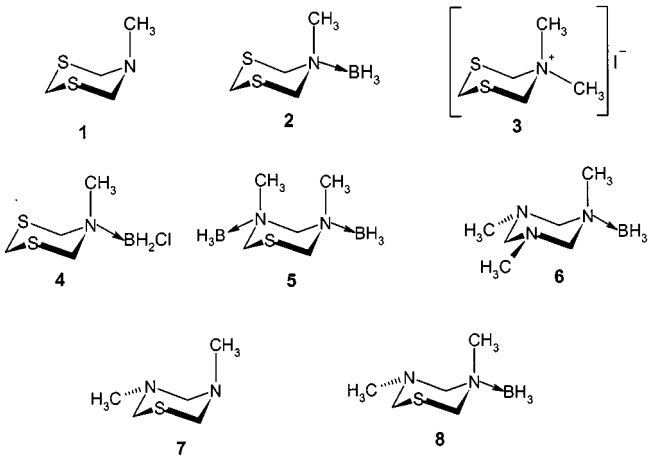
The molecular structures of 5-methyl-1,3-dithia-5-azinium-cyclohexane iodide, 5-chloroborane-5-methyl-1,3-dithia-5-azacyclohexane, 3,5-bis(borane)-3,5-dimethyl-1-thia-3,5-diazacyclohexane, and 1-borane-1,3,5-trimethyl-1,3,5-triazacyclohexane were determined by X-ray diffraction studies. Interactions between hydridic and protic hydrogen atoms are present when the distances between hydridic and protic hydrogen atoms are shorter than 265 pm and angles for B–N–C bonds are smaller than 107.6(3)°. These interactions explain the conformation of the borane adducts in the solid state.

Introduction

Six-membered 1,3,5-triheterocyclohexanes bearing N and O and/or S atoms are rich in lone pairs and are therefore expected to be versatile ligands.[1] We have been systematically studying the synthesis of 1,3,5-heterocyclohexanes bearing at least one nitrogen atom[1c,1d,2] and the coordination of these heterocyclohexanes to boranes.[1a–1c,1e–1h]

The *N*-borane adduct **2**, derived from *N*-methyldithiazacyclohexane (**1**), was shown by NMR methods to have a fixed conformation at room temp. in $CDCl_3$ or [D_8]THF. Its NMR spectrum at room temp. is similar to that of the free heterocycle **1** at −65°C (270-MHz ^1H), which, at room temp., in ring-conformational equilibrium, has its CH_3 group in the axial position ($\Delta G^{\geq} = 46.0 \pm 0.8$ kJ/mol). The remarkably static behavior of **2** needs to be explained because the BH_3 and CH_3 groups are expected to behave similarly with regard to ring inversion, and **2** would therefore be expected to be a fluxional cyclohexane like its isolobal compound 5,5-dimethyldithiazoniumcyclohexane iodide (**3**). To find an explanation, the solid-state molecular structures of **1**–**6** and the conformational behavior of **1**,[1a] **2**,[1a,1b] **3**,[1g] **4**,[1h] **5**,[1h] and **6**[1f] were studied. The conformations of **2** and **4**–**6** were shown by NMR spectroscopy to be fixed at room temp. and in solution. A dipolar interaction between the hydridic B–H and protic C–H groups, previously reported for some aminoboron hydrides,[3] could explain these frozen conformations. This possibility was confirmed by the results of the structure analyses of compounds **1**–**6**. The structure of **1** has already been reported,[1c] but is important for comparison with the data of **3** and **4**.



Syntheses

Compound **3** was obtained by conventional methods from **1** and CH_3I, and was crystallized from H_2O. The 1:1 reaction of a commercial mixture of BH_2Cl, $BHCl_2$, and BH_3 in DMS (in a ratio of 90:8:2, respectively) with **1** produced the adducts in the same ratio.[1h] Compound **4** was isolated from this mixture by crystallization from $CHCl_3$ and was characterized by NMR spectroscopy. Its ^{13}C-NMR chemical-shift data indicate that the *N*-methyl group (δ = 39.2) is present in an axial position.[1h]

The N–BH_3 adduct **6** was prepared from the reaction between BH_3·THF and 1,3,5-trimethyl-1,3,5-triazacyclohexane.[1f] It was also a byproduct of the reaction of the same heterocycle with $LiBH_4$ in boiling hexane, and it was isolated by sublimation and recrystallization from the same solvent.

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The reaction of 3,5-dimethyl-1-thia-3,5-diazacyclohexane (**7**) with 1 or 2 equiv. of BH_3·THF gave the monoadduct **8** and the bisadduct **5**, as deduced from their NMR spectra.[1h] In both compounds, the $N-BH_3$ groups are in the equatorial positions, as indicated by the ^{13}C-NMR chemical shifts of the $N-CH_3$ groups (close to $\delta = 45$).[1a]

Molecular Structures

The molecular structure of compound **3** is depicted in Figure 1. Crystallographic data and bonding parameters are summarized in Tables 1−2. The formation of the cation is accompanied by a shortening of the S−C bonds (on average 0.03 Å) compared with those of compound **1**. There are intermolecular S···S contacts (2.99 Å) as well as four comparatively short C−H···I contacts ranging from 3.04 to 3.28 Å.

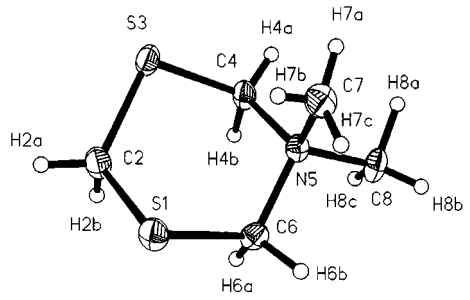


Figure 1. Molecular structure of the cation of **3**

The ring of **4** is also in the chair conformation (Figure 2). The methyl groups are in axial positions and the BH_2Cl moiety is in an equatorial position. The chlorine atom stands antiperiplanar to the methyl group. The molecular structure of **4** compared with that of the free heterocycle **1**[1d] (Table 2) has C−S bonds that are on average shorter by 0.015 Å, a consequence of the ammonium-type N atom in **4**. The BH_3 coordination changes the bond lengths in the ring: The N−C4 [1.502(5) Å], N−C6 [1.496(5) Å], and N−C7 [1.495(5) Å] bonds are expectedly longer in the adduct than in **1** [N−C4: 1.428(4); N−C6: 1.433(4); N−C7: 1.466(5) Å]. On the other hand, in the adduct, the angles C7−N5−C4 [111.0(3)°], C7−N5−C6 [111.0(3)°], and C6−N5−C4 [110.3(3)°] are closer to the angles in the free 1,3,5-dithiazacyclohexane [C7−N5−C4: 114.6(3)°; C7−N5−C6: 114.2(3)°; C6−N5−C4: 113.1(3)°], in accordance with the increased sp^3 character of the nitrogen atom. It is interesting to note the narrow angle C7−N5−B [105.4(3)°] which allows the hydridic atom to be closer to the CH hydrogen atom. Steric repulsion instead of an attractive force between the borane and the methyl group would have resulted in a wider angle.

Single crystals of **5** were obtained from a chloroform solution of **8**. The crystals were obviously formed by disproportionation of the monoborane **8** into **7** and bisborane adduct **5**. The molecular structure of **5** is shown in Figure 3, and its bonding parameters are summarized in Table 2. The C−S bond lengths in **5** match the average C−S bond

Table 1. Crystallographic data for compounds **3**−**6**

Compound	**3**	**4**	**5**	**6**
Empirical formula	$C_5H_{12}INS_2$	$C_4H_{11}BClNS_2$	$C_5H_{18}B_2N_2S$	$C_6H_{18}BN_3$
Molecular mass	277.18	183.52	159.89	143.04
Crystal size [mm]	0.45 × 0.21 × 0.16	0.3 × 0.2 × 0.1	0.4 × 0.2 × 0.1	0.1 × 0.1 × 0.10
Crystal color	colourless	colourless	colourless	colourless
Crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
Space group	*P*−1	*Cc*	*Pca*2(1)	*Aba*2
a [Å]	7.211(1)	5.948(1)	10.366(2)	22.014(9)
b [Å]	7.368(1)	14.618(3)	9.966(2)	15.135(6)
c [Å]	9.248(2)	9.862(2)	9.818(2)	5.552(1)
α [°]	89.23(3)	90	90	90
β [°]	77.58(3)	102.22(3)	90	90
γ [°]	80.56(3)	90	90	90
V [Å^3]	473.2(1)	838.1(3)	1014.3(3)	1850(1)
Z	2	4	4	8
ρ (calcd.) [mg/m^3]	1.945	1.455	1.047	1.027
μ [mm^{-1}]	3.752	0.869	0.258	0.063
F(000)	268	384	352	640
Temperature [K]	293(2)	204	204	183(2)
2θ range for data collection	4.52 to 53.92	5.58 to 43.96°	5.68 to 49.96	3.70 to 55.10
Index ranges	$-9 \le h \le 0$	$0 \le h \le 6$	$-12 \le h \le 12$	$-27 \le h \le 27$
	$-9 \le k \le 9$	$-15 \le k \le 15$	$0 \le k \le 11$	$-18 \le k \le 18$
	$-11 \le l \le 11$	$-10 \le l \le 10$	$0 \le l \le 11$	$-3 \le l \le 3$
Reflections collected	2225	1125	1835	4987
Reflections unique	2057	578	949	1348
Reflections observed (4σ)	1912	571	866	1228
R(int)	0.0108	0.0366	0.0452	0.0346
Number of variables	131	82	91	106
Weighting scheme[a] x/y	0.1365/0.1030	0.0573/0.3046	0.1312/0.000	0.0373/0.6919
GOOF	1.118	0.982	0.985	1.138
Final *R* (4σ)	0.0676	0.0280	0.0529	0.0352
Final *R* *wR*2	0.1592	0.0692	0.1335	0.0816
Largest residual peak [e/Å^3]	4.290	0.334	0.320	0.141

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Bond lengths [Å] and bond angles [°] for **1**−**6**

Compd.	**1**[1d]	**3** (X = C8)	**4** (X = B9)	Compd. **5**		Compd. **6**	
S1-C6	1.836(4)	1.790(5)	1.810(4)	S1-C2	1.792(3)	B1-N3	1.623(3)
S1-C2	1.794(4)	1.797(6)	1.810(5)	S1-C6	1.792(4)	N1-C6	1.447(2)
S3-C4	1.836(3)	1.786(5)	1.800(4)	N5-C7	1.492(4)	N1-C4	1.456(2)
S3-C2	1.803(4)	1.792(6)	1.785(4)	N5-C4	1.494(4)	N1-C1	1.465(2)
N5-C7	1.466(5)	1.494(7)	1.496(5)	N5-C6	1.509(4)	N2-C4	1.451(2)
N5-C4	1.428(4)	1.517(6)	1.502(5)	N5-B9	1.644(5)	N2-C5	1.452(2)
N5-C6	1.433(4)	1.519(6)	1.493(5)	N3-C2	1.485(4)	N2-C2	1.462(3)
N5-X	−	1.512(6)	1.627(6)	N3-C4	1.492(4)	N3-C5	1.487(2)
Cl-B9	−	−	1.868(5)	N3-C8	1.495(5)	N3-C6	1.492(2)
		N3-B10	1.640(5)	N3-C3	1.492(3)		
Compd.	**1**[1d]	**3** (X = C8)	**4** (X = B9)	Compd. **5**		Compd. **6**	
C2−S3−C4	97.3(2)	98.6(3)	97.9(2)	C2−S1−C6	94.8(2)	C6−N1−C4	109.9(2)
C2−S1−C6	97.8(2)	99.0(2)	97.1(2)	C7−N5−C4	114.9(3)	C6−N1−C1	109.7(1)
N5−C4−S3	115.7(2)	114.4(3)	115.6(3)	C7−N5−C6	110.4(2)	C4−N1−C1	111.2(1)
N5−C6−S1	116.0(2)	114.4(3)	116.1(3)	C4−N5−C6	110.6(2)	C4−N2−C5	109.5(1)
C6−N5−C7	114.2(3)	112.6(3)	111.6(3)	C7−N5−B9	107.7(3)	C4−N2−C2	111.1(1)
C6−N5−C4	113.1(3)	109.6(4)	110.5(3)	C4−N5−B9	106.0(3)	C5−N2−C2	110.0(2)
C7−N5−C4	114.6(3)	112.5(4)	110.9(3)	C6−N5−B9	106.8(3)	C5−N3−C3	110.1(1)
S3−C2−S1	113.7(2)	113.0(3)	112.7(2)	C2−N3−C4	110.0(3)	C6−N3−C3	110.0(2)
C6−N5−X	−	106.6(4)	109.1(3)	C2−N3−C8	111.3(3)	C5−N3−C6	108.0(1)
C7−N5−X	−	109.0(4)	105.0(3)	C4−N3−C8	114.3(3)	C5−N3−B1	109.3(2)
C4−N5−X	−	106.2(4)	109.6(3)	C2−N3−B10	107.2(3)	C6−N3−B1	109.7(1)
N5−X−Cl	−	−	109.6(3)	C4−N3−B10	106.1(2)	C3−N3−B1	109.7(1)
				C8−N3−B10	107.6(3)	N2−C4−N1	109.2(1)
				N5−C6−S1	113.2(2)		
				N3−C2−S1	113.0(2)		
				N3−C4−N5	118.9(3)		

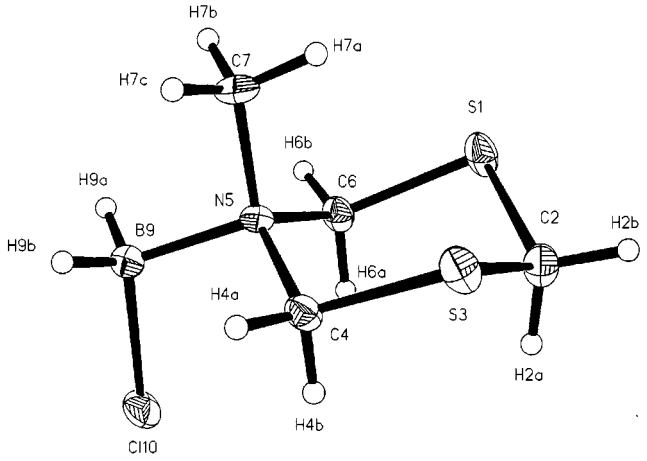


Figure 2. Molecular structure of **4**

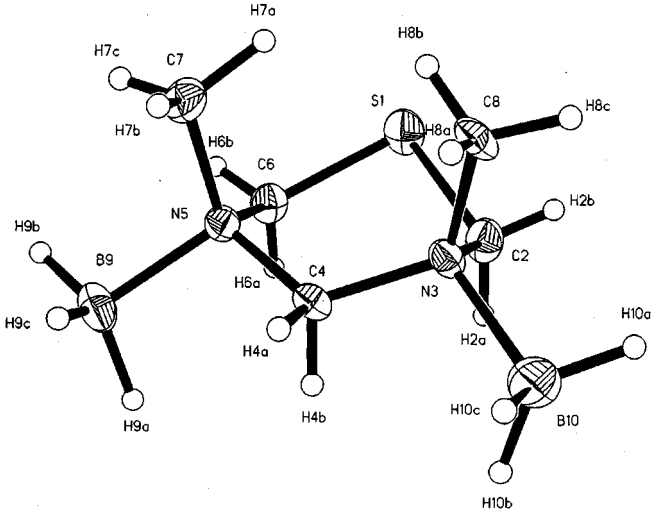


Figure 3. Molecular structure of **5**

lengths of **4**, therefore the two CH_3NBH_3 units must have the same inductive effect on the C−S bond as the ammonium character of the N atom in **4**. Moreover, the N−B bond lengths in **5** are longer than the N−B bond length in **4**. We explain this by the missing inductive effect of the chlorine atom. Compound **5** shows a chair conformation (Figure 3). The two BH_3 groups are in equatorial positions and the two CH_3 groups are in axial positions; the open angles C8−N3−C4 114.6(3)° and C7−N5−C4 114.8(3)° indicate the steric compression suffered by the methyl groups.

The molecular structure of **6** is depicted in Figure 4 and its crystallographic data are presented in Tables 1−3. The heterocycle adopts a chair conformation. The angles around N1, N2, and N3 indicate sp^3 hybridization of these atoms. Two CH_3 groups and BH_3 occupy equatorial positions, and the N3−CH_3 group occupies an axial position.

Interactions between Hydridic and Protic Hydrogen Atoms

The van der Waals radius for the hydrogen atom in a methyl group is reported to be 120 pm.[3] Larger radii have been calculated (145 and 165 pm).[4] In metallic hydrides,

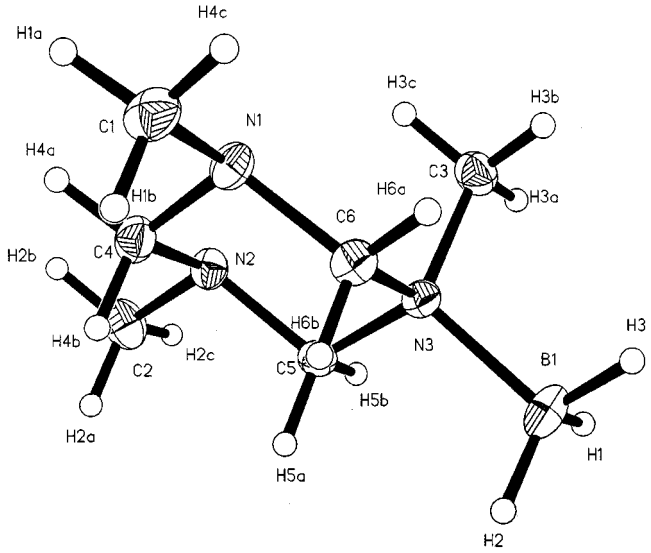


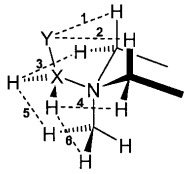
Figure 4. Molecular structure of **6**

the hydrogen ionic radii were found to range from 137 to 154 pm.[5] If an average of 145 pm is assumed, the sum of the van der Waals radii of a protic and an ionic hydridic hydrogen atom is 265 pm. Since the van der Waals radius of the C−H species is 90 pm larger than the hydrogen atomic radius one can estimate that the van der Waals radius of a hydridic hydrogen atom is 145 + 90 = 235 pm. The sum of these van der Waals radii is therefore even larger than that assumed for *r*(H) (van der Waals) + *r*(H^-).

The C−H···H−B atomic distances for **3**−**6** are summarized in Table 3. The distances that are shorter than 265 pm are considered to be the sum of the van der Waals radii, and indicate a strong stabilizing H^+-H^- interaction.[6] The distances in the *N*-methyldithiazinium iodide are all larger than 265 pm.

Hydridic and protic hydrogen atoms have been found to deform the angles of their molecular backbones.[6] $H^{\delta-}-H^{\delta+}$ interactions can therefore also be deduced from the angles between the methyl and the borane groups. For

Table 3. Non-bonding distances $H^{\delta+}-^{\delta-}H$ for **3**−**6**



3: X = C, Y= H; **5**: X = B, Y= H
4: X = B, Y= Cl; **6**: X = B, Y= H

Compd.		1	2	3	4	5	6
3		2.858	2.858	3.514	3.533	2.972	2.352
4		2.730	2.730	2.509	2.448	2.417	2.461
5	N^3	2.563	2.212	2.508	2.523	2.420	2.499
	N^5	2.584	2.311	2.470	2.493	2.313	2.617
6		2.464	2.486	2.544	2.537	2.524	2.445

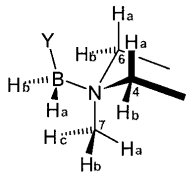
example, B9−N5−C7 [105.0(3)°] in **4**, and B9−N5−C7 and B10−N3−C8 [107.6(3)°] in **5** are smaller than the angle C7−N5−C8 [109.0(4)°] in **3**, thus allowing the close approach of the hydridic and the protic hydrogen atoms as expected for dipolar forces. The torsional angles C5−H5A−H2−B1 (−3.1°), C6−H6B−H2−B1 (4.9°), C5−H5B−H1−B1 (2.2°), and C6−H6A−H3−B1 (−0.5°) are close to 0°, showing that the H^+-H^- interaction is almost at an optimum.

In conclusion, we propose that this kind of intramolecular H^+-H^- interaction[6] is a dominating factor in stabilizing the conformation of boron hydride adducts of azacyclohexanes. It seems to be as important as the intermolecular N−H···H−B interactions that are characteristic for amine−boranes in the solid state, which has recently been pointed out by Crabtree et al.[7]

Experimental Section

The X-ray diffraction studies of **3**−5 were performed with an Enraf−Nonius CAD4 diffractometer (Mo-K_α = 71.069 pm, monochromator: graphite, ω-2θ scan). Cell parameters were determined

Table 4. Torsion angles $C-H^{\delta+}-^{\delta-}H-B$ for **4**−**6**



3, **5** and **6**: Y= H; **4**: Y= Cl

Compd.		$BY-H_aC^6(C^2)$	$BY-H_bC^4$	$BH_b-H_bC^6(C^2)$	$BH_a-H_bC^4$	$BH_b-H_cC^7$	$BH_a-H_bC^7(C^8)$
3		8.42	18.61	9.12	14.79	28.63	7.64
4		3.82	8.51	3.71	1.23	7.78	0.71
5	N^3	20.97	8.51	6.31	36.86	15.08	12.24
	N^5	13.33	12.36	2.66	35.68	10.40	7.73
6		4.92	3.15	0.53	2.18	2.44	3.85

by least-squares refinement of diffractometer angles for 24 automatically centered reflections. Absorption corrections were not necessary; corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution. The SHELXL[8] software package was used for refinement and data output. All hydrogen atoms in structures were found in the difference Fourier map. Data was collected for compound **6** with a Siemens P4 instrument with a CCD area detector and a low-temperature device LTP2. The unit cell was determined from the data on 75 frames and data collection was performed in the hemisphere mode with $\Delta\varphi = 0.3°$ and 10 s/frame exposures. Data reduction used the program SAINT. The structure was solved by direct methods (SHELXL-86). Experimental parameters are listed in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data as supplementary publications nos. CCDC-133313 (**3**), -133314 (**4**), -133315 (**5**) and -133316 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat). + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

5-Methyl-1,3,5-dithiazoniacyclohexane Iodide (3): To a solution of 5-methyl-1,3,5-dithiazacyclohexane (**1**) (1 mmol) in 20 mL of dry THF, CH_3I (1.2 mmol) was added at room temp. The mixture was stirred for 3 h; compound **3** precipitated from the solution. It was filtered and crystallized from H_2O.

Acknowledgments

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