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The tetrahedral character of the boron atom newly defined—a useful tool to evaluate the N → B bond

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Abstract

The tetrahedral character at the boron atom in boron complexes with a coordinative N → B bond has been evaluated on the basis of 144 solid state and gas phase molecular structures in order to obtain additional information on the van der Waals versus covalent relationship of the boron–nitrogen bond. The tetrahedral character has been calculated by a new formula that includes all six bond angles at the boron atom. Thereby, the N → B bond length and the tetrahedral character are correlated and permit the description of the reaction path for the formation of the N → B bond. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Boron complexes; Tetrahedral character; Coordinative N → B bond; Reaction path; Van der Waals interactions

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1. Introduction

Donor–acceptor complexes with a so-called coordinative or dative N → B bond have now been known for more than 100 years [1] and since G.N. Lewis successfully established his new revolutionary theory on acid–base systems [2] such complexes have been studied extensively. It soon became clear that the strength of the dative N → B bond depends greatly on the substituents on both atoms; i.e. the Lewis acidity of the boron atom is highest in the presence of electron withdrawing substituents and the Lewis basicity of the nitrogen atom is increased by electron releasing alkyl groups; however, in both cases steric requirements of the substituents can significantly counteract these stabilizing electronic contributions [3–8].

As a quantitative determination of the N → B bond energy by physical methods is associated with an enormous instrumental effort [9,10], different techniques like ^{11}B- and ^{14}N-NMR [11–17], dynamic NMR [6,8,18–23], theoretical calculations [24], microwave spectroscopy [24], electron diffraction [24] and X-ray crystallography [24] have been used more or less successfully to obtain at least some qualitative information on the strength of this bond. In most of the cases it is the N → B bond length that is used for an interpretation of the N → B bond strength that can vary in magnitudes of at least 100 kJ mol^{-1} (i.e. the gas phase dissociation enthalpies of the amine boranes studied by H.C. Brown vary from 52 to 152 kJ mol^{-1} [3,4]).

The N → B bond length can vary from 1.57 Å, the value for the covalent boron nitrogen bond in cubic boron nitride [25], to 2.91 Å, the sum of the van der Waals radii of nitrogen and boron [26]. Such a large variation in bond length permits the observation of the transition between covalent and van der Waals binding and several structural studies have shown that this continuous transition seems to be reasonable [26–31]. Comments on the transition from van der Waals to covalent bonding have been obtained first by X-ray analyses of tetra- and pentacoordinated molecules with representative elements as well as transition metal atoms. These studies have shown that bond lengths and bond angles involving the same elements span values from those characteristic of nonbonded, van der Waals type interactions through those suggestive of incipient and ultimately fully-developed chemical bonds [32–35].

With increasing N → B bond length the geometry of boron complexes changes from tetrahedral to trigonal

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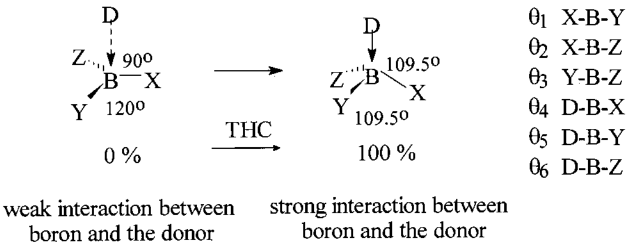
planar (Scheme 1). If one considers the general addition reaction $R_3B + \text{donor} \rightarrow R_3B - \text{donor}$ and defines a reaction path in terms of the coordinates N→B bond length and R–B–N bond angle, a Bürgi structural correlation diagram is obtained [32–35], in which each point on the logarithmic plot is represented by a crystallographic solid-state structure and can be regarded as a snapshot along the reaction path for the formation of the N→B dative bond. An explicit assumption in the use of this structural correlation method is that the perturbing effects in the crystal lattice are negligible from the point of view of displacing the system from the reaction path. This theory was confirmed recently by the description of boron complexes with large gas–solid structure differences [30,31]. In the case of $HCN \rightarrow BF_3$ the gas–solid differences of the N→B bond length and the N–B–F bond angles are 0.84 Å and 14°, respectively [31]. Nonetheless, both the gas-phase structure (obtained by microwave spectroscopy and theoretical calculations) and the solid-state structure lie on the same correlation plot.

Theoretical calculations have shown that the potential energy surface of ammonia borane $H_3N \rightarrow BH_3$ is quite flat in a non polar environment and that embedding the adduct in the polar environment of a polar solvent or the crystal lattice results in a shortening of the dative N→B bond owing to stabilizing dipole–dipole interactions [36,37]. In the case of $H_3N \rightarrow BH_3$ the N→B bond is 0.1 Å longer in the gas-phase structure (microwave spectroscopy and theoretical calculations) than in the X-ray structure or a self consistent reaction field (SCRF) [36].

Up to now the structure correlation method could only be applied to a limited number of relatively symmetrical amine trifluoroborane complexes, and a correlation between the N→B bond length and the N–B–F bond angle was established [26,27]. It may be expected that in more unsymmetrical amine boranes, that may contain even chelates, this bond angle parameter is less adequate, because it may not reflect a quantitative measurement of the distorted tetrahedral shape in reference to the idealized geometry. The situation changes, if all six bond angles around the central boron atom are used as shape parameters and referenced to the two extreme cases, the trigonal planar and tetrahedral geometry.



Scheme 1. Change of bond angles on the approximation of a donor to a three-coordinated boron atom.

Table 1
Boron nitrides

Compound	Structure	$d(N \rightarrow B)$ (Å)	THC_{DA} (%)
β-BN [25]	Cubic	1.57	100
α-BN [43]	Hexagonal	3.33	0

In the present contribution an easy mathematical equation that imposes little additional burden on the crystallographer is presented, it also permits the quantitative measurement of distortion along the reaction path between a van der Waals and covalent boron–nitrogen bond. With this parameter the van der Waals versus covalent bonding relationship will be studied in more detail on the basis of gas-phase (microwave spectroscopy, electron diffraction and theoretical calculations) and solid-state (X-ray crystallography) molecular structures.

2. Results and discussion

Some years ago M. Ōki introduced a new parameter known as the tetrahedral character (THC) for the evaluation of the geometry of boron complexes with a dative N→B bond [22]. This parameter is calculated from the bond angles at the boron atom, if the molecular structure of the compound to be studied is known:

$$\mathrm{THC_{OKI}}[\%] = \frac{120° - \dfrac{(\theta_1 + \theta_2 + \theta_3)°}{3}}{120° - 109.5°} \times 100 = \frac{\sum_{n=1-3} (120 - \theta_n)}{31.5°} \times 100 \qquad (1)$$

θ_1, θ_2, θ_3 see Scheme 1.

The bond angles $\theta_1 - \theta_3$ used for the calculation of this parameter are all related to covalent bonds. It is supposed that the interaction between the boron and the donor changes the geometry at the boron atom from trigonal planar to tetrahedral. In the presence of a weak interaction the corresponding tetrahedral character is close to 0%, while a strong donor–acceptor interaction provides a value near 100% (Scheme 1).

One of the problems in the calculation of the tetrahedral character so far is, that there are also obtained values significantly higher than 100. This happens, because only the three bond angles at the boron atom with covalent bonds are considered. In what follows,

Table 2
Amine boranes

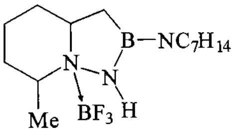
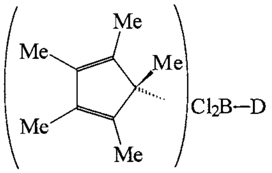
Compound	Structure	$d(N \rightarrow B)$[a] (Å)	THC$_{DA}$[a] (%)
1 [44,45]	$H_3N \rightarrow BF_3$	1.60 (2) 1.599 (7)[b]	87 91.3[b]
2 [46]	$MeH_2N \rightarrow BF_3$	1.58 (2)	90
3 [47–49]	$Me_3N \rightarrow BF_3$	1.585 (15) 1.674 (4)[c] 1.636 (4)[d]	83 78.4[c,e] 79.7[d]
4 [50]	Pyridine → BF_3	1.603 (5)	87.1
5 [51]	Imidazole → BF_3	1.544 (7)	95.7
6 [30,31,37]	$HCN \rightarrow BF_3$	1.638 (2) 2.47 (3)[d] 2.441[f,g]	75.2 5.2[d,e] 11.3[e,f,g]
7 [52,26,37]	$MeC{\equiv}N \rightarrow BF_3$	1.630 (4) 2.011 (7)[d] 2.277[f,g]	75.4[e] 21.8[d,e] 18.3[e,f,g]
8 [29]	$NCCN \rightarrow BF_3$	2.647 (3)[d] 2.570[f,g]	0[d] 6.3[e,f,g]
9 [28,37]	$N_2 \rightarrow BF_3$	2.875 (2)[d] 2.725[f,g]	1.7[d,e] 2.7[e,f,g]
10 [53]		1.66 (1)	83
11 [54]	$Me_3N \rightarrow BH_2F$	1.633 (6)	71.9[e]
12 [55,56]	$Me_3N \rightarrow BCl_3$	1.609 (6) 1.659 (6)[c]	100.0 91.0[c]
13 [57]	Pyridine → BCl_3	1.592 (3)	93.6
			
14 [58]	D = pyridine	1.606 (7)	80.8
15 [58]	D = isoqinoline	1.601 (6)	81.0
16 [55,48]	$Me_3N \rightarrow BBr_3$	1.60 (2) 1.663(13)[c]	92 94[c,e]
17 [59]	Pyridine → BBr_3	1.59 (2)	92
18 [60]	$Me_3N \rightarrow BI_3$	1.663(13)[c]	94[c,e]
19 [61,62]	$H_3N \rightarrow BH_3$	1.658[d] 1.689[f,h] 1.664[f,i]	69.6[d] 67.3[e,f,h] 69.1[e,f,i]

Table 2 (*Continued*)

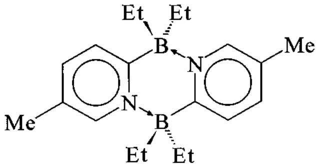
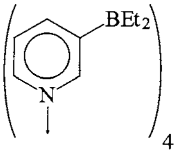
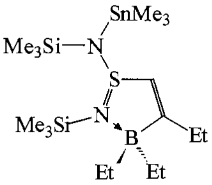
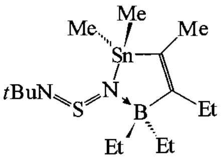
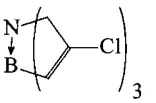
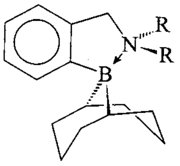
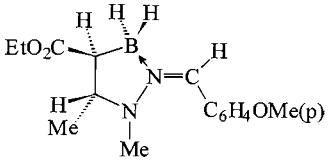
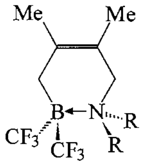
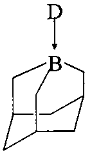
Compound	Structure	*d*(N → B)[a] (Å)	THC$_{DA}$[a] (%)
20 [60,63]	$Me_3N \rightarrow BH_3$	1.656 (2)[c] 1.638(10)[d]	77.0[c,e] 74.1[d]
21 [64]	$H_3N \rightarrow BMe_3$	1.605 (11)	81
22 [65]	$Me_2HN \rightarrow BMe_3$	1.656 (4)	81.8
23 [54,66]	$Me_3N \rightarrow BMe_3$	1.698(10)[d] 1.836[f,h]	90.3[d] 81.3[f,h]
24 [67]	$Me_2HN \rightarrow B(CF_3)_2(1\text{-}C_3H_4CN)$	1.607 (3)	91.2
25 [68]		1.611(2)	95.0
26 [69]		1.638 (5)	80.1
27 [70]		1.638 (7)	77.8
28 [71]		1.636 (2)	83.0
29 [72]		1.626	56.4
			
30 [22]	R = Me	1.746 (2)	58.3
31 [22]	R = Et	1.764 (3)	57.0

Table 2 (*Continued*)

Compound	Structure	$d(N \rightarrow B)^a$ (Å)	$THC_{DA}{}^a$ (%)
32 [73]		1.600 (7)	76.4
			
33 [74]	R = Me	1.621 (3)	88.3
34 [74]	R = Et	1.633 (6)	86.6
			
35 [75]	D = pyridine	1.642 (6)	96.7
36 [75]	D = quinoline	1.722 (7) Mean value: ø 1.638[j]	90.7 ø 82.9[j]

[a] The molecular structures have been determined by X-ray crystallography unless otherwise mentioned. Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

[b] $H_3N \rightarrow BF_3$ is complexed with 18-crown-6.

[c] Data obtained from gas electron diffraction.

[d] Data obtained from MW spectroscopy.

[e] Not all bond angles at the boron atom have been published, so that the missing β value for the mean X–B–Y, X–B–Z and Y–B–Z bond angle was calculated by the following equation: $\beta = 2\sin^{-1}[\sin(180° - \alpha)\cdot(\sin 60°)]$, where α corresponds to the mean N–B–(X,Y,Z) bond angle. In the same way, α can be calculated if β is known.

[f] Data obtained from theoretical calculations.

[g] (RMP2/6-31G**).

[h] (HF/6-31G*).

[i] (MP3/6-31G*).

[j] Mean value from X-ray crystallographic data only. A correction of 0.023 and 0.060 Å has been appliesd to $N_{sp^2} \rightarrow B$ and $N_{sp} \rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value.

an improved formula for the calculation of the tetrahedral character is proposed that includes all six bond angles at the boron atom. This has two advantages, first the THC values are all between 0 and 100%, and second the inclusion of the bond angles with the donor atom can compensate to some extent for steric effects between substituents at the boron atom, that may alter the geometry.

The THC_{OKI} value calculated by Eq. (1) can also be calculated with Eq. (2) under the condition that $\theta_n \geq 109.5°$:

$$THC_{OKI}[\%] = \left[1 - \frac{\sum_{n=1-3} |109.5 - \theta_n|°}{31.5°}\right] \times 100 \qquad (2)$$

As it has been explained in the introduction, it would be useful to calculate the tetrahedral character at the boron atom with all six bond angles around the central atom. This can be done, if it is considered that bond angles θ_1–θ_3 normally range from 109.5–120° and bond angles θ_4–θ_6 from 90–109.5°. With this assumption the following equation can be proposed:

$$\mathrm{THC_{DA}}[\%] = \left[1 - \frac{\sum_{n=1-6} |109.5-\theta_n|^\circ}{3(120-109.5)^\circ + 3(109.5-90)^\circ}\right] \times 100 = \left[1 - \frac{\sum_{n=1-6} |109.5-\theta_n|^\circ}{90^\circ}\right] \times 100 \qquad (3)$$

The equation can be tested for the two extreme cases: With $\theta_1 = \theta_2 = \theta_3 = 120°$ and $\theta_4 = \theta_5 = \theta_6 = 90°$ the $\mathrm{THC_{Donor-Acceptor}}$ value is 0%, while $\theta_{n=1-6} = 109.5°$ gives a value of 100%.

In order to evaluate this new equation the molecular structures of 144 different boron complexes with a coordinative N → B bond including amine boranes, borinate, boronate, borate and aminoborane adducts have been examined. The N → B length (Å) and tetrahedral character $\mathrm{THC_{DA}}$ [%] of various boron complexes are resumed in Tables 1–8. Data have been included from gas electron diffraction studies, microwave spectroscopy, theoretical calculations and X-ray crystallography. For a comparison of these data it is assumed that the shortening of bond length on going from $C(sp^3)$–$C(sp^3)$ to $C(sp^3)$–$C(sp^2)$ and from $C(sp^3)$–$C(sp^3)$ to $C(sp^3)$–$C(sp)$ of about 0.023 and 0.060 Å [38], respectively, applies to N → B bonds as well, so that this correction was applied to the data in the realization of Figs. 1–5.

Fig. 1 shows the plot of the N → B bond length against the corresponding $\mathrm{THC_{DA}}$ value for the amine trifluoroboranes **1**–**10**, some of which have been studied before in order to examine the transition between typical van der Waals and covalent nitrogen–boron interactions [26–31]. In the graphics only experimental values have been included. The two extremes of the plot are formed by α- (hexagonal) and β-boron nitride (cubic) with $\mathrm{THC_{DA}}$ values of 0 and 100%, respectively. Thereby, in the case of α-boron nitride a trigonal planar geometry is assumed for the boron atoms considering that the interplanar interactions between the boron and the nitrogen atoms are weak and only of electrostatic nature. The corresponding N–B distances are 3.33 and 1.57 Å. The correlation between the N → B bond length and the $\mathrm{THC_{DA}}$ value is straightforward, although data of different instrumental methods (X-ray crystallography, gas electron diffraction and microwave spectroscopy) have been included in this graphic. In this way the results of Leopold et al. are confirmed, who found a similar correlation between the N → B bond length and the N–B–F bond angle [26,27]. It can also be seen that the gas-phase points connect smoothly with those points representing solid-state structures. This indicates, as proposed by Leopold et al. [26], that although the formation of the crystal lattice perturbs the system significantly (i.e. consider the differences in N → B bond length of $HCN \rightarrow BF_3$ in the gas-phase and the solid state), the perturbation is one which drives the system along the reaction path but does not cause it to deviate from it.

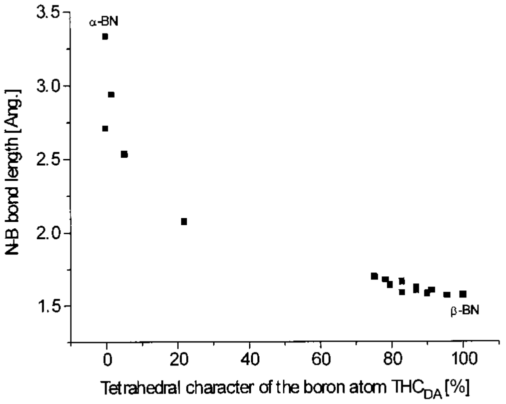


Fig. 1. Correlation between the tetrahedral character of the boron atom and the N → B bond length for compounds **1**–**10**. Molecules with an N_{sp2}–B and an N_{sp}–B bond have been corrected by + 0.023 and + 0.060 Å, respectively.

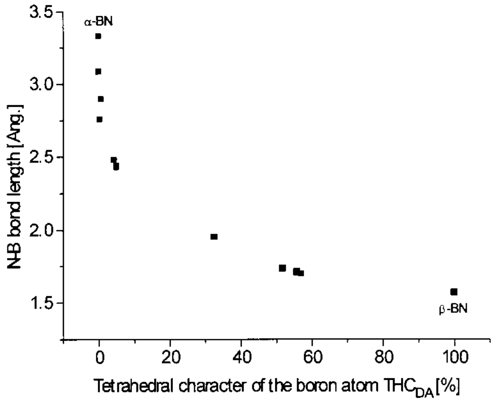


Fig. 2. Correlation between the tetrahedral character of the boron atom and the N → B bond length for compounds **94**–**99**.

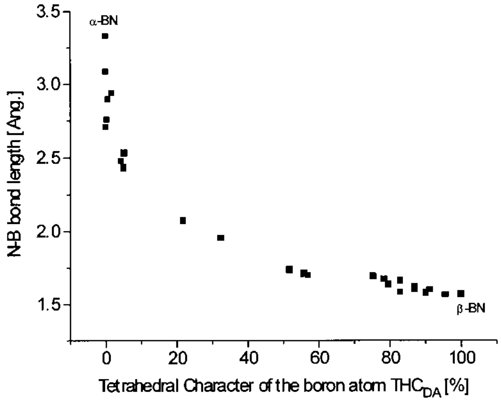


Fig. 3. Correlation between the tetrahedral character of the boron atom and the N → B bond length for compounds **1**–**10** and **94**–**99**.

Table 3
Borinate adducts

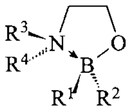
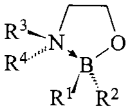
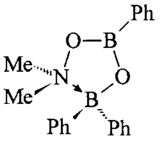
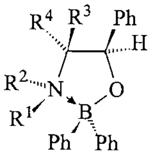
Compound	Structure				$d(N \rightarrow B)^a$ (Å)	$THC_{DA}{}^a$ (%)
						
	R^1	R^2	R^3	R^4		
37 [76,77]	C_6H_5	C_6H_5	H	H	1.654 (3)	74.4
38 [78]	p-FC_6H_4	p-FC_6H_4	H	H	1.652 (4)	76.0
39 [77]	p-MeC_6H_4	p-MeC_6H_4	H	H	1.657 (3)	75.0
40 [79]	C_6H_5	C_6H_5	Me	Me	1.684 (3)	75.8
41 [80]	C_6H_5	C_6H_5O	Me	Me	1.676 (3)	59.6
						
	R^1	R^2	R^3	R^4		
42 [7]	H	H	H	H	$1.759^{b,c}$	$56.4^{b,c}$
43 [7]	H	H	Me	H	$1.703^{b,c}$	$58.7^{b,c}$
44 [7]	H	H	Me	Me	$1.704^{b,c}$	$59.8^{b,c}$
45 [7]	Me	Me	H	H	$1.809^{b,c}$	$58.4^{b,c}$
46 [7]	Me	Me	Me	H	$1.746^{b,c}$	$63.2^{b,c}$
47 [7]	Me	Me	Me	Me	$1.804^{b,c}$	$63.4^{b,c}$
48 [81]					1.717 (3)	73.0
						
	R^1	R^2	R^3	R^4		
49 [8]	H	H	Me	H	1.65 (2)	76
50 [8]	H	H	H	Me	1.661 (9)	69.4
51 [8]	Me	H	Me	H	1.68 (2)	67
52 [8]	Me	H	H	Me	1.66 (1)	79
53 [8]	Me	Me	Me	H	1.744 (8)	76.3
54 [8]	Me	Me	H	Me	1.74 (1)	78

Table 3 (*Continued*)

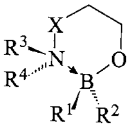
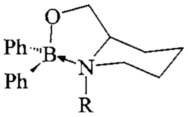
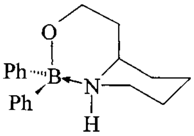
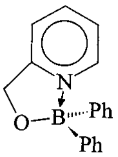
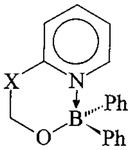
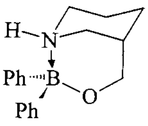
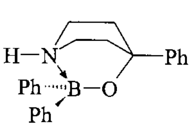
Compound		Structure				$d(N \rightarrow B)^a$ (Å)	$THC_{DA}{}^a$ (%)
							
	X	R^1	R^2	R^3	R^4		
55 [79]	CH_2	Ph	Ph	H	H	1.638 (3)	82.4
56 [82]	CH_2	$(Ph_2Me)SiO$	Ph	H	H	1.639 (4)	74.2
57 [83]	O	Ph	Ph	Me	Me	1.715 (6)	73.6
							
58 [23]		R = H				1.648 (3)	74.1
59 [23]		R = Me				1.73 (1)	73
60 [23]						1.673 (2)	84.8
61 [84]						1.642 (3)	72.0
							
62 [84]		X = CH_2				1.685 (4)	78.4
63 [85]		X = NH				1.642 (3)	78.4
64 [23]						1.674 (5)	85.1
65 [23]						1.646 (8)	82.1

Table 3 (*Continued*)

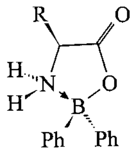
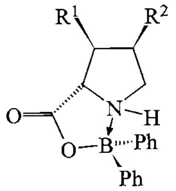
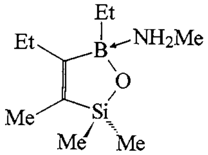
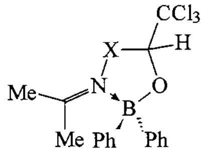
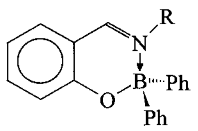
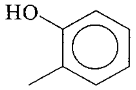
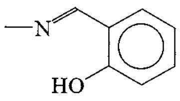
Compound	Structure	$d(\mathrm{N}\rightarrow\mathrm{B})^{a}$ (Å)	$\mathrm{THC}_{\mathrm{DA}}{}^{a}$ (%)
			
66 [86]	$R = (CH_2)_3NH_3^+OAc^-$	1.624 (6)	75.9
67 [86]	$R = (CH_2)_3N{=}CMe_2$	1.606 (5)	74.3
68 [86]	$R = (CH_2)_2Sme$	1.613 (6)	75.2
			
69 [87]	$R^1 = H$, $R^2 = H$	1.626 (3)	76.6
70 [86]	$R^1 = CH_2COOH$, $R^2 = C(Me){=}CH_2$	1.646 (6)	66.9
71 [88]		1.638 (3)	75.4
			
72 [89]	X = O	1.631 (3)	66.6
73 [90]	X = NEt	1.603 (1)	69.7
			
74 [91]	R = OH	1.602 (2)	79.7
75 [92]	R = 	1.634 (5)	75.0
76 [93]	R = 	1.651 (3)	81.9

Table 3 (*Continued*)

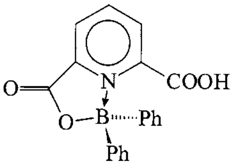
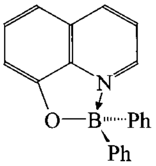
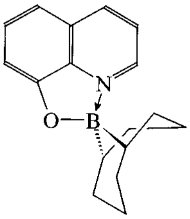
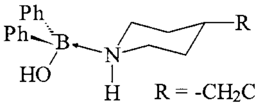
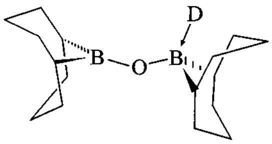
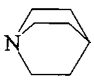
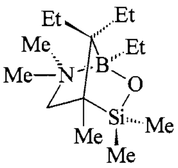
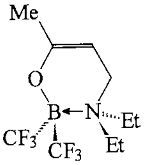
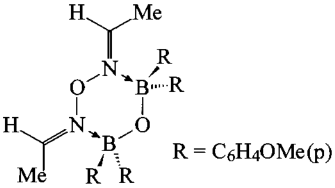
Compound	Structure	*d*(N→B)[a] (Å)	THC$_{DA}$[a] (%)
77 [86]		1.658 (6)	64.4
78 [94]		1.61 (1)	73
79 [94]		1.637 (3)	71.2
80 [23]	 R = -CH$_2$CH$_2$OH	1.665 (4)	83.1
			
81 [95]	D = pyridine	1.661 (4)[d]	83.7[d]
82 [95]	D = 	1.717 (2)[e] 1.713 (4)[f] 1.665 (2)[g]	73.0[e] 68.3[f] 59[g]

Table 3 (*Continued*)

Compound	Structure	$d(N\rightarrow B)^a$ (Å)	$THC_{DA}{}^a$ (%)
83 [96]		1.720 (3)	57.0
84 [74]		1.64 (1)	84
85 [97]			
		Mean value: ø 1.665[h]	ø 74.8[h]

[a] Mean value from X-ray crystallographic data only. A correction of 0.023 and 0.060 Å has been applied to $N_{sp^2}\rightarrow B$ and $N_{sp}\rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value. Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

[b] Data obtained from theoretical calculations.

[c] (HF/6-31G**).

[d] $T = 128$ K.

[e] $T = 110$ K.

[f] $T = 298$ K.

[g] $T = 323$ K.

[h] Mean value from X-ray crystallographic data only. A correction of 0.023 and 0.060 Å has been applied to $N_{sp^2}\rightarrow B$ and $N_{sp}\rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value.

An even better correlation is obtained, when the N–B bond distances of the solid-state boronate adducts **94**–**99** with different substituents at the nitrogen atom are plotted against their corresponding THC_{DA} values. From Fig. 2 it can be seen that there is nearly no deviation from the idealized curve due to the similar chemical environment around the N → B bond. The equation of the curves in Figs. 1 and 2 are nearly identical as can be seen from Fig. 3, where the values of both figures have been joined in one plot. This may indicate that there exists only one general reaction path for the formation of a coordinative N → B bond.

Fig. 4 shows the correlation between the N → B bond length and the THC_{DA} value for all 144 boron complexes in Tables 2–8. The vast majority of this boron complexes shows a solid state N → B bond length between 1.54 and 1.76 Å. The corresponding THC_{DA} values are between 50 and 100%. Molecules studied with a N–B distance between 1.8 and 3.3 Å and THC_{DA} values between 50 and 0% are rare, but interesting. While the molecules at the right side of the THC_{DA} scale may still present some covalent interaction between nitrogen and boron, this is less probable for molecules at the left extreme, where the interaction should result mostly from the opposite partial charges at the boron (δ^+) and the nitrogen atom (δ^-). Indeed, an electrostatic interaction should predominate in compounds with N → B bond lengths over 2.91 Å, that is considered the sum of van der Waals radii for boron and nitrogen [26]. Up to now only two solid state structure types in the THC_{DA} range of 0–50% with corresponding N → B bond lengths of 1.8–3.3 Å are

Table 4
Boronate adducts

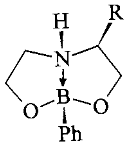
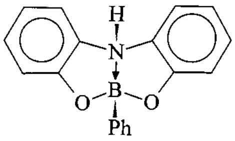
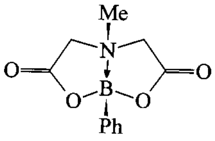
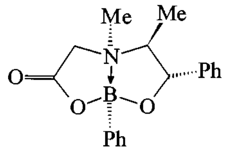
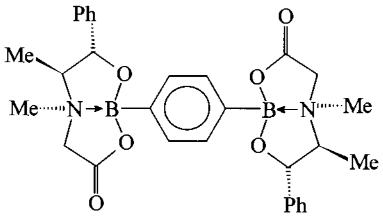
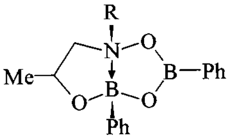
Compound	Structure	$d(\mathrm{N} \rightarrow \mathrm{B})^{a}$ (Å)	$\mathrm{THC_{DA}}^{a}$ (%)
			
86 [98]	R = H	1.661 (3)	65.7
87 [99]	R = Ph	1.666 (7)	64.3
88 [100]		1.699 (5)	64.4
89 [101]		1.668 (3)	63.1
90 [102]		1.713 (6)	62.6
91 [102]		1.718 (10)	62.8
92 [103]	 R = $CH_2C_6H_5$	1.750 (2)	53.9

Table 4 (*Continued*)

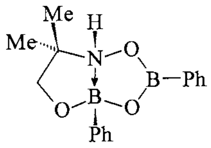
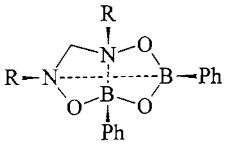
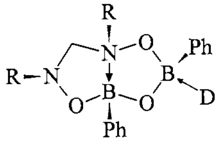
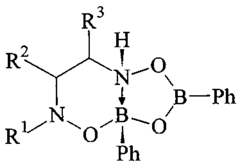
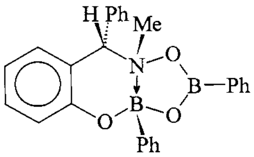
Compound	Structure	*d*(N→B)[a] (Å)	THC$_{DA}$[a] (%)
93 [104]		1.688 (2)	57.4
			
94 [105]	$R = CMe_2COOEt$	2.433 (3) 2.433 (3)[b]	5.1[c] 5.1[c]
95 [106]	$R = CMe_2CN$	2.475 (3) 2.755 (3)[b]	4.4[c] 0.3[c]
96 [107]	$R = Me$	1.733 (3) 3.082 (3)[b]	51.7 0.0[c]
97 [105]	$R = {}^tBu$	1.953 (3) 2.897 (3)[b]	32.6 0.6[c]
			
98 [108]	$R = Me,\ D = ONHEt_2$	1.712 (4) 3.318 (5)[b]	55.8 –
99 [109]	$R = Et,\ D = ONH_2Et$	1.698 (4) 3.409 (5)[b]	57.0 –
			
100 [110]	$R^1 = CH_2CH(OEt)_2$ $R^2 = H,\ R^3 = H$	1.759 (3) 2.981 (4)[b]	61.0 0.0[c]
101 [111]	R^1 = cyclohexyl $R^2 = Ph,\ R^3 = Me$	1.706 (2) 2.855 (2)[b]	63.0 0.6[c]
102 [112]		1.755 (2)	66.2

Table 4 (*Continued*)

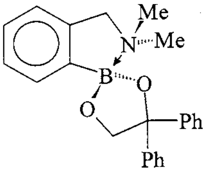
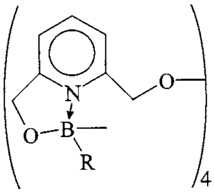
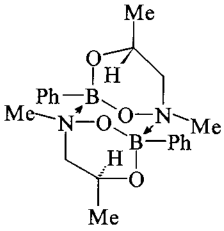
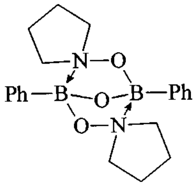
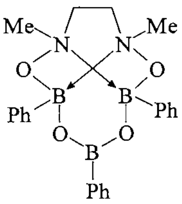
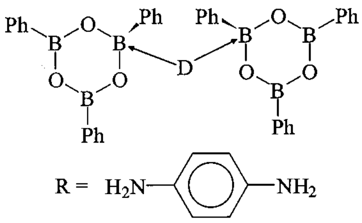
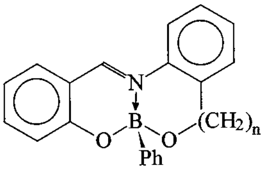
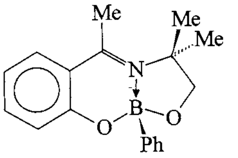
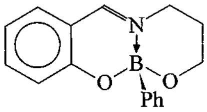
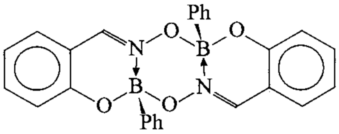
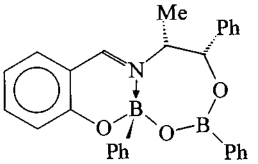
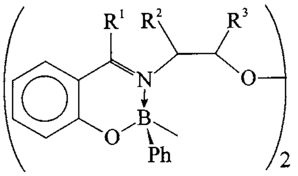
Compound	Structure	$d(N \rightarrow B)^a$ (Å)	$THC_{DA}{}^a$ (%)
103 [22]		1.754 (4)	58.3
			
104 [39]	R = Ph	1.667 (9)	72.8
105 [113]	R = $3\text{-}C_6H_4NO_2$	1.650 (9)	75.6
106 [103]		1.695 (2)	83.4
107 [114]		1.703 (3)	56.1
108 [115]		1.656 (6)	77.4
109 [116]		1.663 (8)	72.2

Table 4 (*Continued*)

Compound	Structure			$d(N\rightarrow B)^a$ (Å)	$THC_{DA}{}^a$ (%)
					
110 [117]	$n=0$			1.613 (5)	75.1
111 [117]	$n=1$			1.615 (7)	80.4
112 [117]	$n=2$			1.635 (4)	84.3
113 [40]				1.601 (4)	75.4
114 [40]				1.601 (9)	82.2
115 [118]				1.586 (2)	83.5
116 [40]				1.629 (5)	80.0
					
	R^1	R^2	R^3		
117 [39]	H	H	H	1.624 (3)	89.4
118 [40]	Me	H	H	1.634 (7)	86.1
119 [40]	H	Me	Ph	1.626 (5)	89.4
120 [40]	H	H	Me	1.632 (6)	87.1
				Mean value: ø 1.689[d]	ø 69.4[d]

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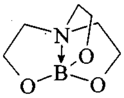
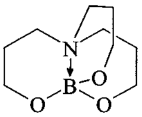
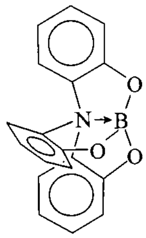
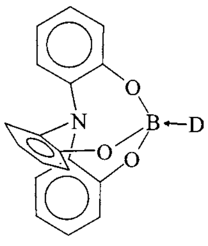
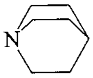
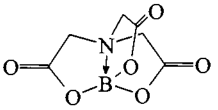
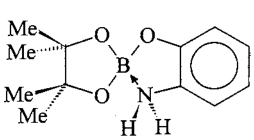
[a] Mean value from X-ray crystallographic data. A correction of 0.023 and 0.060 Å has been applied to $N_{sp2}\rightarrow B$ and $N_{sp}\rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value. Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

[b] Interaction N···B.

[c] THC calculated by Eq. (1).

[d] Mean value from X-ray crystallographic data. A correction of 0.023 and 0.060 Å has been applied to $N_{sp2}\rightarrow B$ and $N_{sp}\rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value.

Table 5
Borate adducts

Compound	Structure	$d(N\rightarrow B)$[a] (Å)	THC_{DA}[a] (%)
121 [119]		1.677 (6)	58.6
122 [120]		1.67 (2)	90
123 [121]		1.681 (5)	65.0
			
124 [121]	D = pyridine	1.631 (4) 2.816 (4)[b]	64.0 –
125 [122]	D = 	1.643 (5) 2.845 (5)[b]	66.3 –
126 [123]		1.620 (3)	72.7
127 [124]		1.654 (6)	74.0
		Mean value: ø 1.657[c]	ø 70.1[c]

[a] Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

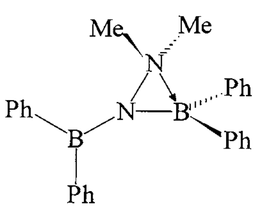
[b] Interaction N···B.

[c] Mean value from X-ray crystallographic data. A correction of 0.023 and 0.060 Å has been applied to $N_{sp2}\rightarrow B$ and $N_{sp}\rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value.

known, the boronate adducts **94**–**101** and the 1,3,5,7-tetraaza-2,4,6,8-tetraborocane derivatives **137**–**140**. Some gas phase structures like $HCN\rightarrow BF_3$ (**6**), $MeCN\rightarrow BF_3$ (**7**), $NCCN\rightarrow BF_3$ (**8**) and $N_2\rightarrow BF_3$ (**9**) complete the data known so far.

The curve in Fig. 4 demonstrates that molecules with a steric repulsion between the substituents around the N → B bond or a ring strain are placed to its upper side owing to an elongated N → B bond length and/or an alternation of the tetrahedral character at the boron atom.

Considering only X-ray crystallographic data the shortest mean N → B bond length and highest THC_{DA} mean value is obtained for amine boranes **1**–**36** (1.638 Å/82.9%) and aminoborane adducts **128**–**136** (1.627 Å/82.9%). This is surprising in the case of the aminoborane adducts, where a p_π–p_π interaction between the boron and the covalently bound nitrogen atom could be expected as it is the case for the 1,3,5,7-tetraaza-2,4,6,8-tetraborocane derivatives **137**–**140**. As a consequence, in the latter structures the N–B distance is extremely long (2.972 Å/0.6%). The mean N → B bond lengths for the borinate adducts **37**–**85**, boronate adducts **86**–**120** and borate adducts **121**–**127** are 1.665, 1.689 and 1.657 Å, respectively, with corresponding THC_{DA} values of 74.8, 69.4 and 70.1%, if N → B bond lengths over 2.0 Å are not considered. Fig. 5 shows that there exists a nearly linear correlation between these mean THC_{DA} values and mean N → B bond lengths of the different boron complex classes examined in Tables 2–8. The correlation indicates that the N → B bond in borinate, boronate and borate adducts is generally weaker than the one in borane amines and aminoborane adducts. This may be explained by a destabilizing thermodynamic contribution of ring strain effects considering that most of the borinates, boronates and borates studied so far by X-ray crystallography are chelate complexes. The higher hydrolytic stability of boron chelates [5] should therefore be attributed principally to the chelate effect, a kinetic parameter. That ring strain in boron complexes is destabilizing could recently be shown by a structural comparison between the monomer **113** and the dimers **117**–**120**, that are formed preferentially [39,40]. The macrocyclic structures **104** and **105** are other examples in this context.



145

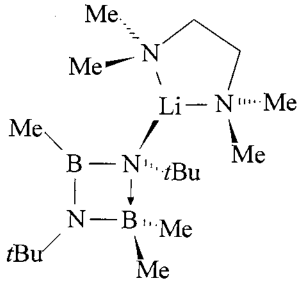


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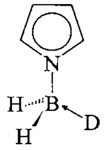
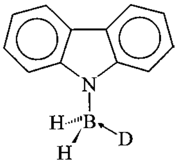
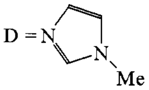
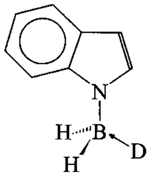
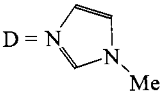
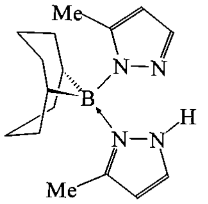
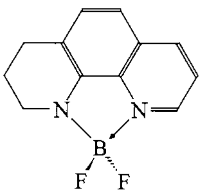
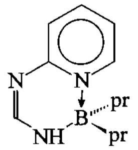
Table 6
Aminoborane adducts

Compound	Structure	$d(N \rightarrow B)^a$ (Å)	THC_{DA}^a (%)
			
128 [51]	D = pyridine	1.619 (5)	79.7
129 [51]	D = imidazol	1.575 (4)	87.4
			
130 [51]	D = pyridine	1.607 (6)	77.6
131 [51]		1.583 (6)	90.4
			
132 [51]		1.580 (7)	83.4
133 [125]		1.613 (3)	77.4
134 [126]	$Me_3N \rightarrow BCl_2N(CF_3S)_2$	1.63	92
135 [127]		1.629 (7)	71.8
136 [128]		1.621 (7)	86.1
		Mean value: ø 1.627^b	ø 82.9^b

[a] Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

[b] Mean value from X-ray crystallographic data. A correction of 0.023 and 0.060 Å has been applied to $N_{sp2} \rightarrow B$ and $N_{sp} \rightarrow B$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value.

Molecules with a highly strained three- or four membered ring structure formed by a coordinative N → B could not be included in the present study, because the bond angles at the boron atom are altered too much. Examples are compounds **145** [41] and **146** [42] with N–B–N bond angles of 54.9 (5) and 85.5 (1)°, respectively. The corresponding N → B bond lengths and THC_{DA} values are 1.65 (1) Å/ − 2% and 1.633 (1) Å/47%.

Similarly, boron complexes with delocalized ring systems like pyrazaboles $R_2B(\mu\text{-pz})_2BR_2$ (Hpz = pyrazole) were omitted, because in these cases the N–B bond is intermediate between a covalent and a coordinative bond.

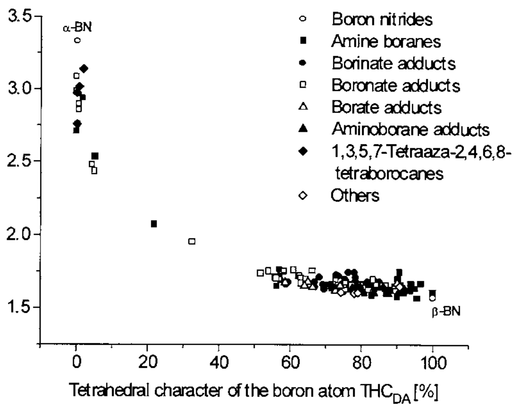


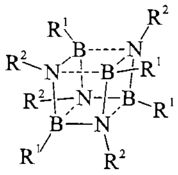
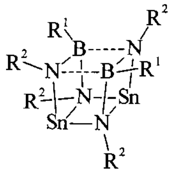
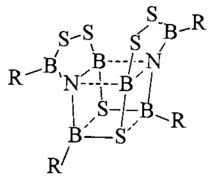
Fig. 4. Correlation between the tetrahedral character of the boron atom and the N → B bond length for compounds **1**–**144**. Molecules with an N_{sp2}–B and an N_{sp}–B bond have been corrected by + 0.023 and + 0.060 Å, respectively.

3. Conclusions

The present study has shown that there is a correlation between the N → B bond length and the $\mathrm{THC_{DA}}$ value including both complexes with weak, van der Waals type N → B bond interactions and complexes with covalent N–B bonds. The smooth transition between these different bond types allows the conclusion that the d(N → B)–$\mathrm{THC_{DA}}$ graphs can be used to represent the reaction path of the formation of a N → B coordination on the basis of experimental data, that may be considered as snapshots on this path.

For the future it would be interesting to study the relationship between the tetrahedral character and the coordinative bond length in other Lewis acid–base adducts and to develop similar parameters for the evaluation of intermediate geometries in metal complexes with coordination numbers 4–6.

Table 7
1,3,5,7-Tetraaza-2,4,6,8-tetraborocanes and analogues

Compound	Structure	$d(\mathrm{N \rightarrow B})^{a}$ (Å)	$\mathrm{THC_{DA}}^{a}$ (%)
			
137 [129]	$R^1 = \mathrm{Me}$ $R^2 = {}^{t}\mathrm{Bu}$	2.758^{b}	0.08^{c}
138 [130]	$R^1 = i\mathrm{pr}$ $R^2 = \mathrm{CH_2C_6H_5}$	2.974^{b}	0.0^{c}
			
139 [131]	$R^1 = \mathrm{Me}$ $R^2 = \mathrm{SiMe_3}$	3.140^{b}	1.8^{c}
			
140 [132]	$R = \mathrm{NEt_2}$	3.017^{b} Mean value: ø 2.972^{d}	0.7^{c} ø 0.6^{d}

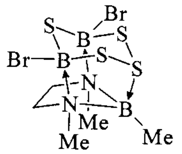
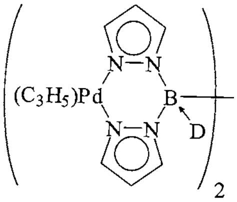
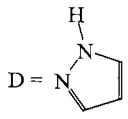
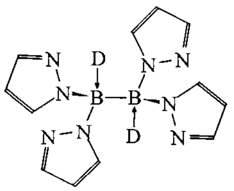
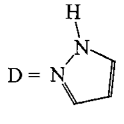
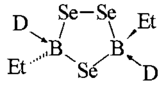
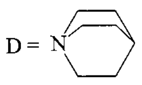
[a] Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

[b] Interaction N···B.

[c] THC calculated by Eq. (1).

[d] Mean value from X-ray crystallographic data only. A correction of 0.023 and 0.060 Å has been applied to $\mathrm{N_{sp2} \rightarrow B}$ and $\mathrm{N_{sp} \rightarrow B}$ bonds, respectively. Bond lengths over 2.0 Å have not been included in the calculation of the mean value.

Table 8
Others

Compound	Structure	$d(\mathrm{N \rightarrow B})^{a}$ (Å)	$\mathrm{THC_{DA}}^{a}$ (%)
141 [133]		1.603 (15)	78
			
142 [134]		1.584 (12)	79
			
143 [134]		1.586 (5)	74.2
144 [135]	 	1.649 (9)	90.7

[a] Average values have been calculated, if the molecular structure had two or more identical structural units or in the case of two independent molecules in the asymmetric unit of the crystal structure.

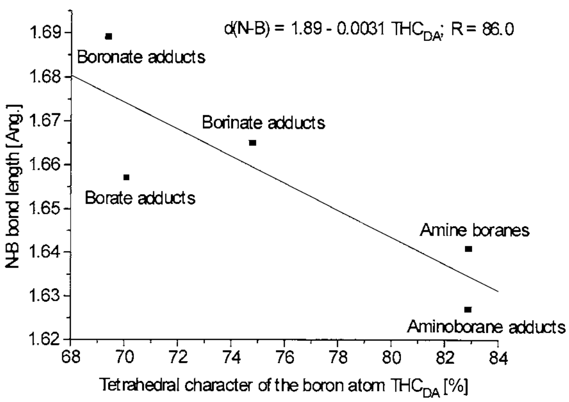


Fig. 5. Correlation between the mean THC$_{DA}$ value and mean N → B bond length of borane amines **1**–**36**, borinate adducts **37**–**85**, boronate adducts **86**–**120**, borate adducts **121**–**127** and aminoborane adducts **128**–**136**.

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