

Synthesis and characterization of new (N→B) phenyl substituted[N-benzyliminodiacetate-O,O',N]boranes

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Dedicated to Professor Eusebio Juaristi on the occasion of his 55th birthday

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Abstract

The synthesis of nine (N→B) phenyl substituted[N-benzyliminodiacetate-O,O',N]boranes **3a-3i** is reported herein. These compounds were characterized by ¹H, ¹³C, ¹¹B, HETCOR, NOESY, infrared spectroscopy, mass spectrometry and in the case of compounds **3d** and **3g** also by ¹⁹F NMR. All compounds exhibit a bicyclic structure due to the presence of an intramolecular N→B coordination bond. The structure of 4-chlorophenyl[N-benzyliminodiacetate-O,O',N]borane **3e** was further established by a single crystal x-ray diffraction study. The correlation between $\delta(^{11}\text{B})$ of compounds **3a**, **3d-3i** and σ_{Hammett} values shows that the strength of the N→B bond depends on the electronic factors of the substituent on the B-phenyl group.

Keywords: Boranes, iminodiacetic acid, NMR, arylboranes and σ_{Hammett} .

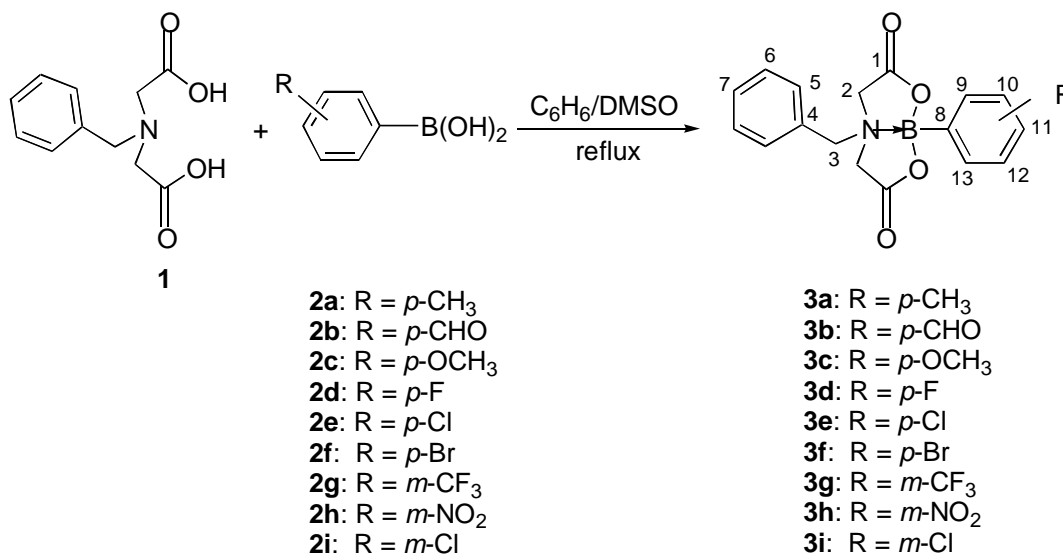
Introduction

There is considerable interest in boron heterocycles derived from aminoacids due to their potential use for biological studies. Cyclic boron compounds, mainly phenyl derivatives exhibit cytotoxic activity¹⁻⁵ and have application in boron neutron capture therapy (BNCT) for the treatment of brain tumors^{6,7} and melanomas.⁸ We have been interested in the synthesis, characterization, structural analysis and reactivity of boron heterocycles derived from iminodiacetic acid and N-substituted imino- and aminodiacetic acids.⁹⁻¹⁴ Herein, we describe the synthesis of nine new (N→B) phenyl substituted[N-benzyliminodiacetate-O,O',N]boranes, **3a-3i**, where the phenyl group is substituted at the *meta* and *para* positions. Compounds **3a-3i** were prepared by the reaction of N-benzyliminodiacetic acid **1** and phenyl substituted boronic acids **2a-2i** in a 1:1 molar ratio (Scheme 1). All Compounds were characterized by ¹H, ¹³C, ¹¹B NMR,

HETCOR, NOESY, infrared spectroscopy and mass spectroscopy, in addition, for compounds **3d** and **3g** the ^{19}F NMR spectra were also obtained.

Results and Discussion

The reaction of N-benzyliminodiacetic acid **1** with substituted phenylboronic acids **2a-2i** in a 1:1 ratio, led to (N \rightarrow B) phenyl substituted[N-benzyliminodiacetate-O,O',N]boranes **3a-3i** (Scheme 1). Compounds **3a-3i** were obtained as white solids.



Scheme 1

NMR spectroscopy

The ^1H NMR spectra in DMSO- d_6 of compounds **3a-3i** clearly show the AB coupling pattern for the diastereotopic H-2 protons, which evidences the presence of the intramolecular N \rightarrow B coordination bond as has been observed for analogous compounds.⁹⁻²¹ The H-3 benzylic protons exhibit a single signal between 3.75 and 3.87 ppm (Table 1). The ^1H NMR spectrum of compound **3d** shows a doublet of doublets for H-9 and a triplet signal for H-10 due to coupling with ^{19}F . The (^1H - ^1H) NOESY spectra show correlation between H-2_A and H-9_{arom} with H-3, which indicates that the H-2_A protons are exo and H-9 is close to the H-3 benzylic protons.

The δ (^{11}B) values (Table 1) confirm the tetrahedral environment of the B nucleus, since they lie in the range reported previously for analogous boron heterocycles.⁹⁻²¹ Comparison of the δ (^{11}B) values for compounds **3a-3i** with the unsubstituted (N \rightarrow B) phenyl[N-benzyliminodiacetate-O,O',N]borane [12.5 ppm],¹¹ shows that: a) electron donating substituent at *para* position (**3a**) decrease the N \rightarrow B coordination bond, while electron-withdrawing groups (**3b**, **3d-3f**) strengthens this bond; b) electron-withdrawing groups at the *meta* position (**3g-3i**)

increase the N→B coordination bond. This shows that δ (^{11}B) is sensitive to inductive and resonance factors and there should exist a correlation with σ_{Hammett} values.²²

Table 1. ^1H and ^{11}B NMR data of **3a-3i**: δ_{H} and δ_{B} [ppm] and coupling constants J [Hz]

Compound	H-2	H-3	C_6H_5	B- $\text{C}_6\text{H}_4\text{R}$	$\delta(^{11}\text{B})$
3a	H _A 4.40 16.9 ^a	3.75	H-5 7.57-7-60	H-9,13 7.48 7.7 ^b	+12.9
	H _B 3.91 16.9 ^a		H-6,7 7.40-7.44	H-10,12 7.23 7.7 ^b H-14 2.33	
3b	H _A 4.47 16.8 ^a	3.82	H-5 7.58-7-60	H-9,13 7.95 8.0 ^b	+12.4
	H _B 3.96 16.8 ^a		H-6,7 7.40-7.42	H-10,12 7.84 8.0 ^b H-14 10.07	
3c	H _A 4.35 16.8 ^a	3.75	H-5 7.55-7-57	H-9,13 7.50 8.4 ^b	+12.0
	H _B 3.86 16.8 ^a		H-6,7 7.40-7.42	H-10,12 6.97 8.4 ^b H-14 3.75	
3d	H _A 4.41 16.9 ^a	3.79	H-5 7.55-7-60	H-9,13 7.63 9.0 ^b 6.4 ^c	+12.2
	H _B 3.91 16.9 ^a		H-6,7 7.40-7.47	H-10,12 7.24 9.0 ^b	
3e	H _A 4.40 16.8 ^a	3.79	H-5 7.56-7-58	H-9,13 7.59 8.4 ^b	+12.2
	H _B 3.90 16.8 ^a		H-6,7 7.39-7.43	H-10,12 7.47 8.4 ^b	
3f	H _A 4.40 16.8 ^a	3.79	H-5 7.56-7-58	H-9,13 7.61 8.0 ^b	+12.1
	H _B 3.90 16.8 ^a		H-6,7 7.39-7.43	H-10,12 7.53 8.0 ^b H-9 7.92	
3g	H _A 4.47 16.8 ^a	3.85	H-5 7.55-7-57	H-11 7.76 7.7 ^b	+12.0
	H _B 3.86 16.8 ^a		H-6,7 7.40-7.42	H-12 7.65 7.7 ^b H-13 7.88 7.7 ^b H-9 8.43	
3h	H _A 4.49 16.9 ^a	3.87	H-5 7.57-7-60	H-11 8.03 7.5 ^b	+11.4
	H _B 3.96 16.9 ^a		H-6,7 7.40-7.47	H-12 7.73 7.5 ^b H-13 8.27 7.5 ^b	
3i	H _A 4.44 16.9 ^a	3.84	H-5 7.55-7-57	H-9,13 7.58-7.61	+12.1
	H _B 3.92 16.9 ^a		H-6,7 7.40-7.42	H-11,12 7.42-7.48	

^a 2J . ^b 3J . ^c $J_{\text{H-F}}$.

Thus, a plot of $\delta(^{11}\text{B})$ for **3a**, **3d-3i** compounds versus σ_{Hammett} values (Fig. 2) gives the equation $\sigma_{\text{Hammett}} = -0.666[\delta(^{11}\text{B})] + 7.6224$, with a correlation coefficient $R^2 = 0.9036$. These data confirm that the strength of the N \rightarrow B coordination bond is governed by electronic factors. The ^{19}F NMR spectra of **3d** and **3g** compounds exhibit a triplet of triplets at -113.10 ppm ($J = 9.0, 6.4$ Hz) and a single signal at -61.23 ppm, respectively.

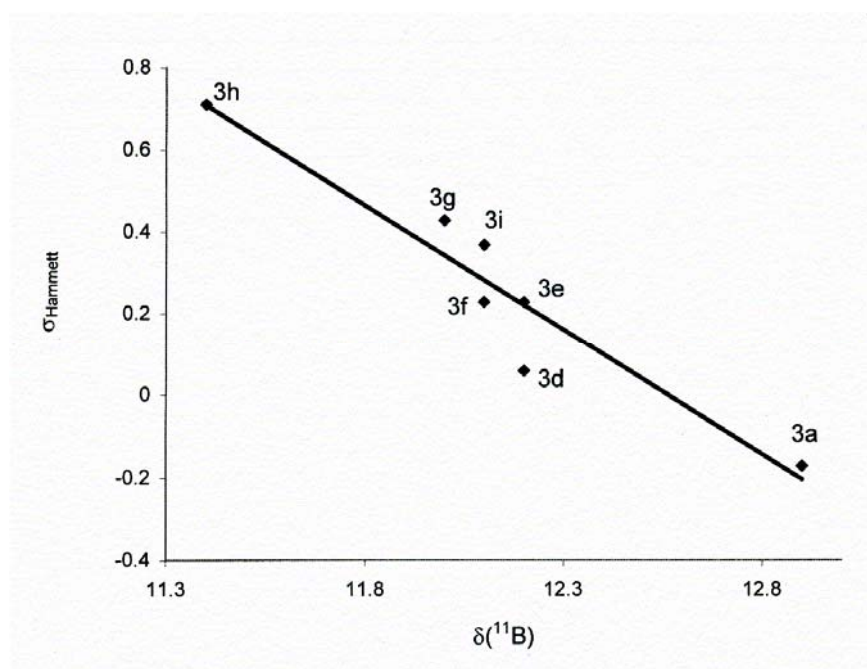


Figure 1. Plot of $\delta(^{11}\text{B})$ of compounds **3a**, **3d-3i** versus σ_{Hammett} values.

The ^{13}C NMR data for compounds **3a-3i** are summarized in Table 2. For all compounds the assignment of C-2 and C-3 are based on HETCOR experiments. Thus C-2 correlates with the signals showing an AB coupling, which appear in the range between 3.86 and 4.49 ppm and C-3 correlates with the single signal between 3.75 and 3.87 ppm. The C-8 signal is not observed in any of the compounds; C9 to C-13 in **3d** exhibit a doublet, while C9, C10, C11 and C14 in **3g** appear quartets due to coupling with F atoms.

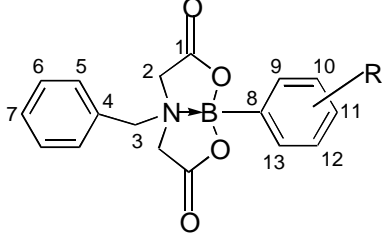
Mass spectrometry

The 70 eV EI mass spectra of compounds **3b** and **3d-3i** do not exhibit the molecular ion, while the spectra of **3a** and **3c** show the molecular ion. The following important fragment ions are observed, in the spectra of **3a**, **3b**, as well as **3d-3i**; the base peak is at $m/z = 91$ and corresponds to tropylium ion; **3c** exhibits the corresponding base peak at $m/z = 198$ $[\text{C}_6\text{H}_5\text{CH}_2\text{-C}_6\text{H}_4\text{OCH}_3]^+$. All compounds exhibit the fragment ion $[\text{C}_6\text{H}_5\text{CH}_2\text{-C}_6\text{H}_4\text{R}]^+$ and the fragment ion at $m/z = 42$ $[\text{CH}_2\text{NCH}_2]^+$. Compounds **3e**, **3i** and **3f** exhibit fragment ions containing ^{35}Cl , ^{37}Cl and ^{79}Br , ^{81}Br , respectively. Scheme 2 shows some fragment ions and a possible fragmentation pattern.

Infrared spectroscopy

The IR spectra exhibit the $\nu_{(C=O)}$ carbonyl oxygen band in the range between 1758 and 1772 cm^{-1} , and a band due to B-O between 1292 and 1304 cm^{-1} . Also the band due to N→B is in the range between 1026 and 1034 cm^{-1} .

Table 2. ^{13}C NMR data of **3a-3i**: δ_{C} [ppm]

			14 3a: R = <i>p</i> -CH ₃		14 3d: R = <i>p</i> -F		14 3g: R = <i>m</i> -CF ₃		
			14 3b: R = <i>p</i> -CHO		14 3e: R = <i>p</i> -Cl		14 3h: R = <i>m</i> -NO ₂		
			14 3c: R = <i>p</i> -OCH ₃		14 3f: R = <i>p</i> -Br		14 3i: R = <i>m</i> -Cl		
	3a^a	3b^b	3c^c	3d	3e	3f	3g^d	3h	3i
C-1	169.21	168.96	169.22	169.10	169.02	169.03	169.52	169.47	169.08
C-2	57.88	58.12	57.88	57.97	57.99	58.00	58.70	58.74	58.12
C-3	60.83	60.86	60.88	60.79	60.80	60.83	61.30	61.37	60.84
C-4	130.72	130.49	130.75	130.69	130.60	130.63	131.07	131.07	130.65
C-5	131.64	131.58	131.63	131.64	131.61	131.63	132.11	132.09	131.68
C-6	128.92	128.88	128.93	128.93	128.89	128.92	129.38	129.38	128.96
C-7	129.60	129.62	129.62	129.63	129.60	129.62	130.13	130.13	129.79
C-9	132.82	133.59	134.33	135.19 7.8 ^g	134.81	135.14	129.76 3.8 ^g	127.96	132.63
C-10	128.43	128.52	113.40	114.61 19.8 ^e	127.70	130.63	128.68 31.0 ^e	147.99	132.95
C-11	138.25	136.59	160.13	163.13 244.90 ^f	134.12	123.06	126.25 3.8 ^g	124.48	129.01
C-12	128.43	128.52	113.40	114.61	127.70	130.63	129.03	129.72	129.78
C-13	132.82	133.59	134.33	135.19 7.8 ^g	134.81	135.14	137.60	140.21	131.55

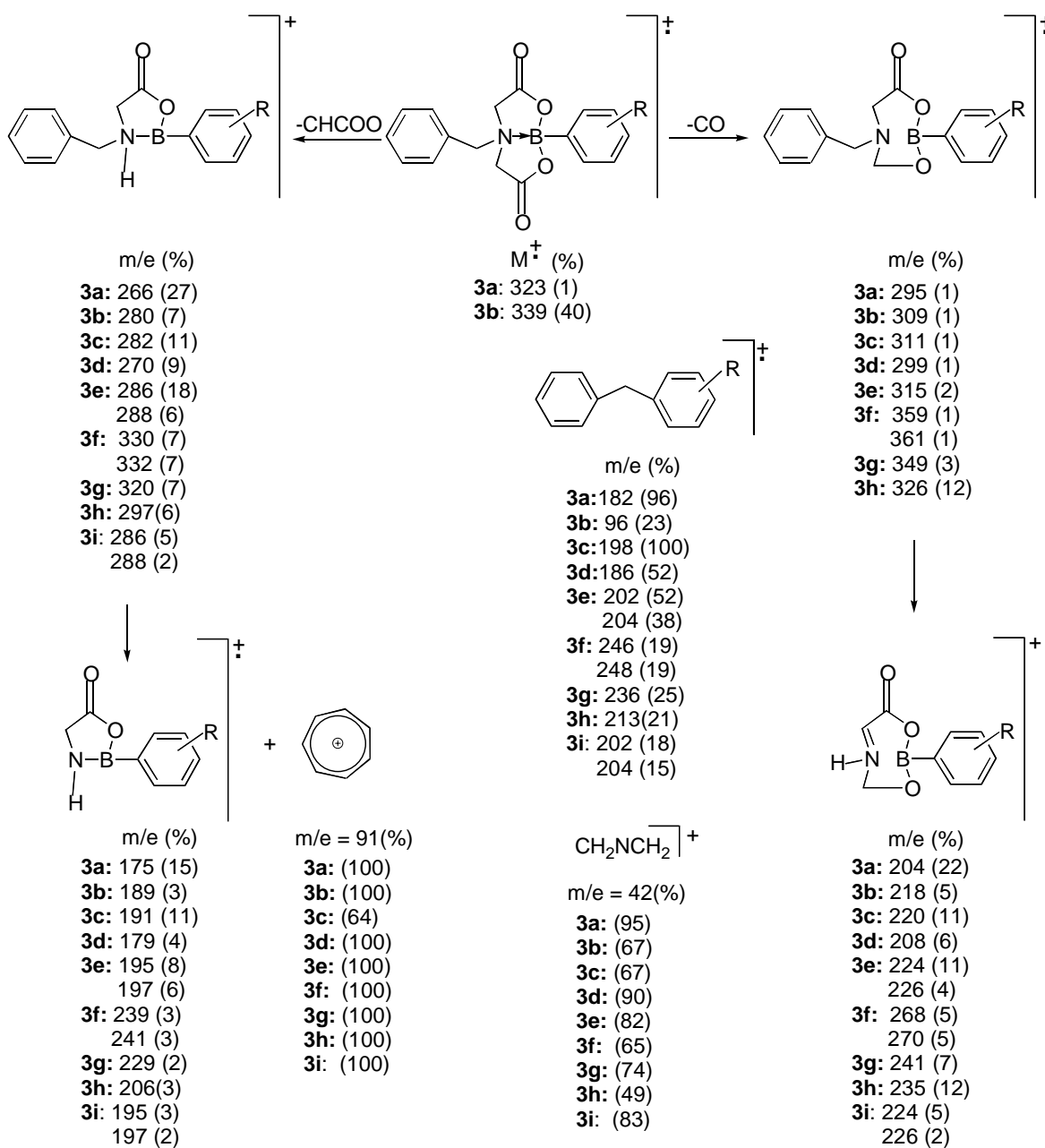
^a CH₃ δ = 21.08. ^b COH δ = 193.42. ^c OCH₃ δ = 54.92. ^d CF₃ δ = 129.56, J_{CF} = 273.30. ^e J_{CF} .

^f J_{CF} . ^g J_{CF} .

X-Ray diffraction

Suitable crystals of **3e** for X-ray analysis were obtained from methylene chloride; the molecular structure and crystallographic numbering is showing in figure 2. In general the bond distances are within the values characteristic of analogous compounds.^{13,18} Select bond lengths are: B₁-O₁₀ 1.466(3), B₁-O₁₃ 1.472(3), C₉-O₁₀ 1.320(3), C₁₂-O₁₃ 1.320(3), C₈-C₉ 1.502(3), C₁₁-C₁₂ 1.504(3), C₈-N₁ 1.495(2), C₁₁-N₁ 1.489(2). The conformations of the two five-membered rings are different

and they are not planar as indicated by the torsion angles (Table 3). The aryl-B and N-Bn groups are bent away from N-B, as indicated by the angle values C₇-N₁-B₁ 112.48°(13) and C₁₄-B₁-N₁ 114.78°(14). The molecular structure establishes the bicyclic structure showing a N→B bond length of 1.683(2) Å, the value being comparable to the N→B bond length in analogous compounds.^{13,18} This molecule shows a bicyclooctane structure with torsion angle of the junction, 17.25° (20).



Scheme 2. Mass spectral data for compounds **3a-3i**.

The molecule in the crystal structure shows the following intramolecular contacts: $N_1 \cdots H_{7A}$ 2.0047(218), $N_1 \cdots H_{7B}$ 1.9786(198), $N_1 \cdots H_{8A}$ 2.0528(265), $N_1 \cdots H_{8B}$ 2.0181(307) Å, and $O_{13} \cdots H_{19}$, which are significantly shorter than the sum of the van der Waals radii for nitrogen and hydrogen atoms (2.75Å), as well as oxygen and hydrogen (2.70Å),²³ In addition, the following intermolecular contact is observed between $O_1 \cdots H_{11A}$ 2.3919(0.0249) Å.

Table 3. Selected torsion angles (°) for compound **3e**

$O_{10}-B_1-N_1-C_8$	14.19 (0.17)	$O_{13}-B_1-N_1-C_{11}$	17.93 (0.17)
$N_1-B_1-O_{10}-C_9$	17.11 (0.19)	$N_1-B_1-O_{13}-C_{12}$	11.91 (0.20)
$C_8-C_9-O_{10}-B_1$	13.38 (0.23)	$C_{11}-C_{12}-O_{13}-B_1$	1.0 (0.23)
$N_1-C_8-C_9-O_{10}$	2.30 (0.22)	$N_1-C_{11}-C_{12}-O_{13}$	12.19 (0.22)
$C_9-C_8-N_1-B_1$	7.70 (0.18)	$C_{12}-C_{11}-N_1-B_1$	18.02 (0.18)

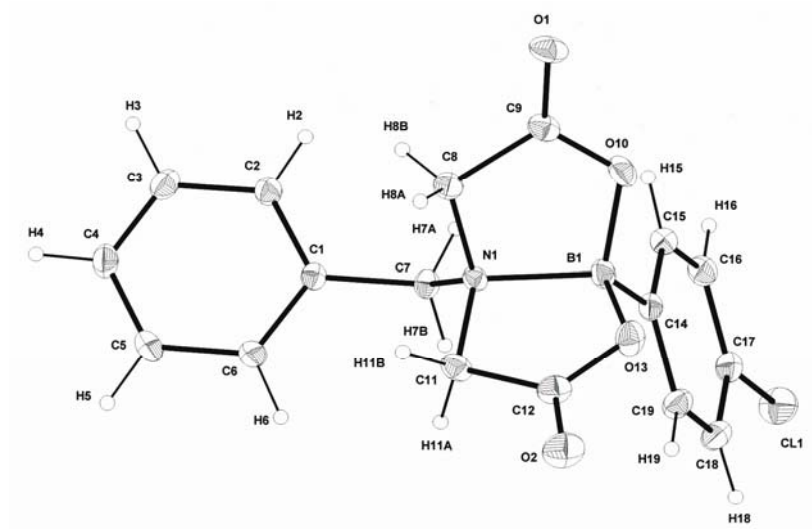


Figure 2. Molecular structure of compound **3e**.

Conclusions

The new (N→B) phenyl substituted[N-benzyliminodiacetate-O,O',N]boranes **3a-3i** were characterized by spectroscopic methods. These compounds exhibit a bicyclic structure due to the presence of an intramolecular N→B coordination bond and it is confirmed by a single crystal x-ray diffraction study of (N→B) 4-chlorophenyl[N-benzyliminodiacetate-O,O',N]borane **3e**. The correlation between δ (¹¹B) of compounds **3a**, **3d-3i** and σ_{Hammett} values shows that the strength of the N→B bond depends on the electronic factors of the substituent on the B-phenyl group.

Experimental Section

General Procedures. *N*-benzyliminodiacetic acid **1** was prepared according to our methodology.²⁴ Reagents **2a-2i** were purchased from Aldrich Co. ¹H, ¹³C and ¹¹B NMR spectra were recorded on Jeol GLX-270, Jeol Eclipse-400 and Bruker Avance 300-DPX spectrometers, DMSO-*d*₆ was used as solvent. Infrared spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer. Melting points were measured in an open capillary tube on a Gallemkamp MFB-595 apparatus and are uncorrected. The single-crystal X-ray study was performed on an Enraf Nonius Kappa CCD diffractometer. Compound **3e**, C₁₇H₁₅BClO₄N (MW = 343.56), crystallized in the space group P 21 21 21, orthorhombic from methylene chloride as colorless flakes, size: 0.12 x 0.1 x 0.9 mm³ with a = 9.9928(2), b = 11.1546(3), c = 14.5858(3) Å, V = 1625.82(6) Å³, α = 90.00°, β = 90.00°, γ = 90.00°, ρ = 1.404 g/cm³, Z = 4, μ = 0.256 mm⁻¹, F(000) = 712. Data collection: a total of 3715 reflections were measured (2° < θ < 26°), 3619 were independent and of these 2951 were considered observed [*F*_o > 4.0σ(*F*_o)]. Solution and refinement: direct methods, all non hydrogen atoms were refined anisotropically, R = 0.0382, R_w = 0.0847, w = 1/σ², GOF = 1.019, largest residual electron density peak/hole in the final difference map: 0.137/-0.211 eÅ⁻³. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.²⁵ Data reduction were performed by Denzo.²⁶ All calculations were carried out using the SHELXL-97 (Sheldrick 1997)²⁷ and the molecular graphics by Diamond 2.1.²⁸

The procedure outline is general for the preparation of compounds **3a** to **3i**

(N→B) 4-Methylphenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3a**).** A suspension of 0.40 g (1.79 mmol) of *N*-benzyliminodiacetic acid **1**, 0.24 g (1.79 mmol) of 4-methylphenylboronic acid **2a** and 66 ml of a mixture of dimethylsulfoxide/benzene (1/10) was placed into a 100 ml flask equipped with a stirrer and a Dean Stark Trap. The mixture was kept under reflux for 12 h. After being cooled to room temperature, the solvent was evaporated under vacuum. The residue was dissolved in acetone and precipitated with hexane to yield 0.57 g (98%) of compound **3a** as a white solid, mp 223-225°C. IR: 3014, 2952, 2866, 1766, 1612, 1538, 1498, 1296, 1240, 1208, 1034 cm⁻¹ (KBr). MS: *m/z* (%), 323 (1), 295 (1), 266 (1), 204 (22), 182 (22), 175 (15), 91 (100), 42 (95). Anal. Calcd. for C₁₈H₁₈BNO₄ (323): C, 66.87; H, 5.57; N, 4.33. Found: C, 66.94; H, 5.78; N, 4.23.

(N→B) 4-Formylphenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3b**).** Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.27 g (1.79 mmol) of 4-formylphenylboronic acid **2b**, 0.58 g (95%) of compound **3b** were obtained as a white solid, mp 213-215°C. IR: 3008, 2936, 2858, 1768, 1696, 1640, 1562, 1540, 1506, 1298, 1224, 1038 cm⁻¹ (KBr). MS: *m/z* (%), 339 (40), 309 (1), 280 (7), 218 (5), 196 (23), 189 (3), 91 (100), 42 (67). Anal. Calcd. for C₁₈H₁₆BNO₅ (337): C, 66.87; H, 5.57; N, 4.33. Found: C, 63.87; H, 5.10; N, 4.10.

(N→B) 4-Methoxyphenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3c**).** Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.27 g (1.79 mmol) of 4-methoxyphenylboronic acid **2c**, 0.59 g (96%) of compound **3c** were obtained as a white solid, mp 251-253°C. IR: 3006, 2958, 2840,

1772, 1604, 1570, 1512, 1294, 1246, 1026 cm^{-1} (KBr). MS: m/z (%), 311 (1), 282 (11), 220 (11), 198 (100) 191 (11), 91 (64), 42 (67). Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{BNO}_5$ (339): C, 63.71; H, 5.30; N, 4.12. Found: C, 63.45; H, 5.25; N, 4.29.

(N→B) 4-Fluorophenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3d). Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.25 g (1.79 mmol) of 4-fluorophenylboronic acid **2d**, 0.57 g (97%) of compound **3d** were obtained as a white solid, mp 227-228°C. IR: 3066, 3010, 2954, 2868, 1772, 1638, 1600, 1508, 1292, 1218, 1036 cm^{-1} (KBr). MS: m/z (%), 299 (1), 270 (9), 208 (6), 186 (52), 179 (4), 91 (100), 42 (90). Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{BFNO}_4$ (327): C, 62.38; H, 4.58; N, 4.28. Found: C, 62.34; H, 4.72; N, 4.32.

(N→B) 4-Chlorophenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3e). Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.28 g (1.79 mmol) of 4-chlorophenylboronic acid **2e**, 0.58 g (94%) of compound **3e** were obtained as a white solid, mp 226-228°C. IR: 3010, 2960, 2866, 1764, 1636, 1590, 1560, 1490, 1294, 1224, 1034 cm^{-1} (KBr). MS: m/z (%), 315 (2), 288 (6), 286 (18), 226 (4), 224 (11), 204 (38), 202 (52), 197 (6), 195 (8), 91 (100), 42 (82). Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{BClNO}_4$ (343): C, 59.47; H, 4.37; N, 4.08. Found: C, 59.76; H, 4.76; N, 4.06.

(N→B) 4-Bromophenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3f). Prepared from 0.40g (1.79 mmol) of compound **1** and 0.36 g (1.79 mmol) of 4-bromophenylboronic acid **2f**, 0.64 g (92%) of compound **3f** were obtained as a white solid, mp 231-233°C. IR: 3010, 2934, 2860, 1764, 1638, 1584, 1558, 1490, 1294, 1240, 1224, 1034 cm^{-1} (KBr). MS: m/z (%), 361 (1), 359 (1), 332 (7), 330 (7), 270 (5), 268 (5), 248 (19), 246 (19), 241 (3), 239 (3), 91 (100), 42 (65). Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{BBrNO}_4$ (388): C, 52.57; H, 3.86; N, 3.60. Found: C, 52.24; H, 3.82; N, 3.86.

(N→B) 3-(Trifluoromethyl)phenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3g). Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.34 g (1.79 mmol) of 3-(trifluoromethyl)phenylboronic acid **2g**, 0.63 g (93%) of compound **3g** were obtained as a white solid, mp 275-277°C. IR: 3060, 2934, 2860, 1768, 1640, 1540, 1300, 1216, 1034 cm^{-1} (KBr). MS: m/z (%), 349 (3), 236 (25), 320 (7), 241 (7), 229 (2), 91 (100), 42 (74). Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{BF}_3\text{NO}_4$ (377): C, 57.29; H, 3.97; N, 3.71. Found: C, 57.30; H, 4.10; N, 3.80.

(N→B) 3-Nitrophenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3h). Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.30 g (1.79 mmol) of 3-nitrophenylboronic acid **2h**, it was obtained a white solid, which was washed with chloroform and dissolved with acetone. The mixture was filtered and the solvent was evaporated under vacuum to give 0.32g (50%) of compound **3h**, as a white solid product, mp 309-311°C. IR: 3060, 3012, 2938, 2862, 1766, 1612, 1570, 1524, 1304, 1220, 1032 cm^{-1} (KBr). MS: m/z (%), 326 (12), 297 (6), 213 (21), 206 (3), 91 (100), 42 (49). Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{BN}_2\text{O}_6$ (354): C, 57.62; H, 4.23; N, 7.90. Found: C, 58.02; H, 4.36; N, 7.57.

(N→B) 3-Chlorophenyl[*N*-benzyliminodiacetate-*O,O',N*]borane (3i). Prepared from 0.40 g (1.79 mmol) of compound **1** and 0.28 g (1.79 mmol) of 3-chlorophenylboronic acid **2i**, 0.59 g (95%) of compound **3i** were obtained as a white solid product, mp 263-265°C. IR: 3066, 3012, 2956, 2862, 1758, 1612, 1570, 1524, 1288, 1230, 1030 cm^{-1} (KBr). MS: m/z (%), 288 (2), 286

(5), 226 (2), 224 (5), 204 (15), 202 (18), 197 (2), 195 (3), 91 (100), 42 (83). Anal. Calcd. for $C_{17}H_{15}BClNO_4$ (343): C, 59.47; H, 4.37; N, 4.08. Found: C, 59.61; H, 4.76; N, 4.06.

Supplementary Material

Crystallographic data for **3e** has been deposited at the Cambridge Crystallographic Data Center, UK, CCDC as supplementary material No. 275644.

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