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X-ray crystallographic study of boroxazolidones obtained from L-ornithine, L-methionine, kainic acid and 2,6-pyridinedicarboxylic acid

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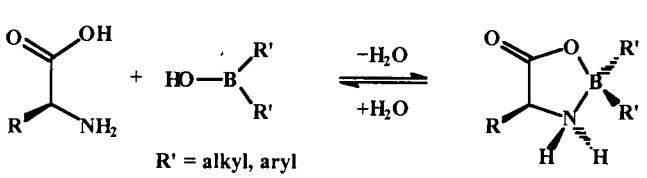
Abstract

In the present contribution, the boroxazolidones prepared from L-ornithine, L-methionine, kainic acid and 2,6-pyridinedicarboxylic acid have been studied by X-ray crystallography. A comparison of the structural data with corresponding boroxazolidines, bicyclic boronates and tricyclic borates has shown that in boron complexes with a boroxazolidone ring the B–O bond is longer in comparison to boron complexes with a boroxazolidine ring. At the same time the N→B bond length is shorter indicating that the hydrolytic stability of the complexes with boroxazolidone rings is enhanced.

Keywords: α-Amino acids; Kainic acid; Boron complexes; Boroxazolidones; Boroxazolidines; Hydrolytic stability

1. Introduction

For the past few years we have been interested in the synthesis and characterization of five- and six-membered borinates with a coordinative N→B bond [1–6], one important class being the five-membered boroxazolidones [7]. Such boroxazolidones are readily prepared by condensation of α-amino acids and dialkyl- or diarylborinic acids [7,8]:



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In these complexes with a coordinative N→B bond both functional groups of the α-amino acid are simultaneously bound to the boron atom. The hydrolytic stability is maintained in aqueous solution at pH 2–7 and the boroxazolidone ring does not decompose even in boiling water [9–12].

The simultaneous protection of the amino and carboxyl group in α-amino acids renders boroxazolidones into useful reagents for selective reactions on further functional groups in the side chain of the corresponding α-amino acids [12,13]. Furthermore, studies with [*N*,*N*-dimethylglycinato-*O*,*N*]borane have shown that the methylene hydrogen atoms between the coordinated amino and carboxyl groups are sufficiently acidic to undergo deprotonation and subsequent reaction with an electrophilic substrate [9], opening up the possibility of synthesizing substituted α-amino acids from *N*,*N*- dimethylglycine. The hydrolysis of boroxa-

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zolidones into the corresponding α-amino acids proceeds under relatively mild conditions (4 N HCl at 40°C) [12].

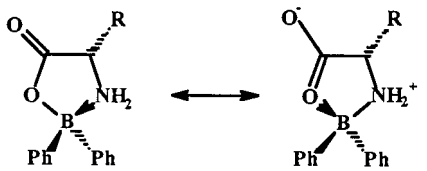
In boroxazolidones the polarity of the corresponding α-amino acid is reduced and its lipophilic character increases [11]. This property has been used to purify α-amino acids [14] and to enhance the transport rate through lipophilic solvents [15].

Enantiomers of α-amino acids have been successfully separated by crystallization-induced asymmetric transformation of the corresponding boroxazolidone diastereomers that are obtained, when the boron atom carries two different substituents [16]. Applications as intermediates in asymmetric hydroborations in order to enhance the enantiomeric purity of organoboron reagents are also known [17].

Owing to the importance of boroxazolidones, the X-ray crystallographic characterization of the 1,1-diphenylboroxazolidones with L-ornithine, L-methionine, kainic acid and 2,6-pyridinedicarboxylic acid was investigated and is presented in a comparative study with other five-membered borinates, boronates and borates. This comparison permits the evaluation of the hydrolytic stability of boroxazolidones which can be related to the N→B bond length [4]. Up to now, only a boroxazolidone with a secondary amino group, namely L-prolinatodiphenylboron, has been studied by X-ray crystallography [18]. The spectroscopic data of the boroxazolidones from L-ornithine, kainic acid and 2,6-pyridinedicarboxylic acid are published here for the first time.

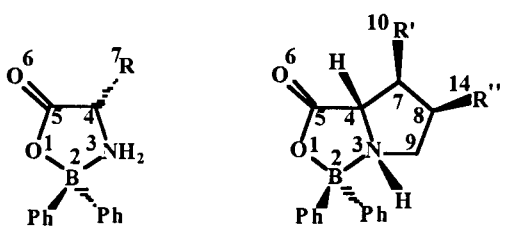
2. Results and discussion

One of the aims of the present study is to characterize boroxazolidones by X-ray crystallography in order to evaluate them on the basis of structural parameters such as the strength of the N→B bond compared to boroxazolidines that are obtained from 2-amino alcohols. Preliminary studies in solution have shown a higher hydrolytic stability for boroxazolidones [14] that may be explained by the following resonance structures [18]:



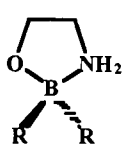
I II

In order to obtain information on this topic the following series of molecules with a coordinative N→B bond has been included in the present structural study (Scheme 1):

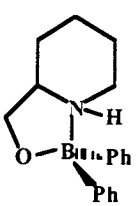


1a: R = $(CH_2)_3NH_3^+OAc^-$
1b: R = $(CH_2)_3N{=}C(CH_3)_2$
1c: R = $(CH_2)_2SCH_3$

2a: R' = H; R'' = H
2b: R' = CH_2COOH
R''= $C(CH_3){=}CH_2$



3a: R = C_6H_5
3b: R = p-FC_6H_4
3c: R = p-$CH_3C_6H_4$



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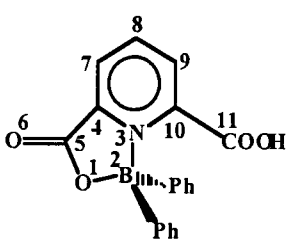

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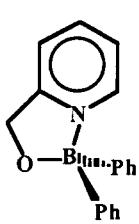

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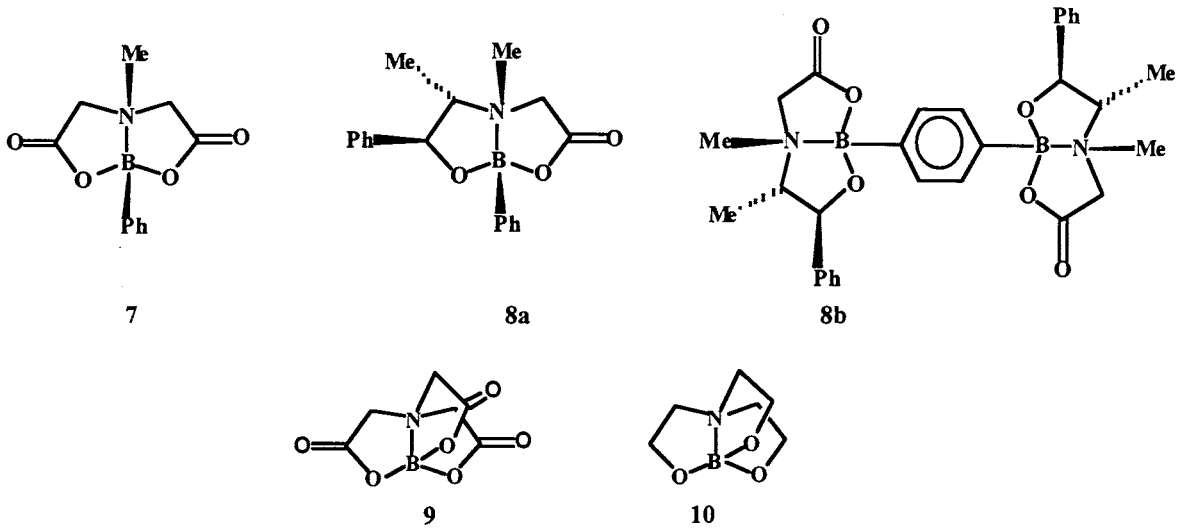
The previously unpublished crystallographic data of compounds **1a**–**1c**, **2b** and **5** are summarized in Table 1. Table 2 contains a summary of the most important structural data for compounds **1**–**10** and will be the basis for discussion. Selected torsion angles for compounds **1a**–**1c**, **2b** and **5** are listed in Table 3. Their molecular structures are depicted in Figs. 1–5.

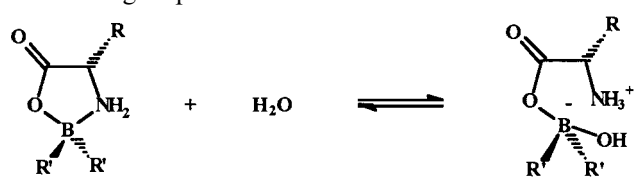


Scheme 1. Series of molecules with a coordinative N→B bond involved in the structural comparison.

2.1. Comparison of boroxazolidones *1–2* and boroxazolidines *3–4*

Compounds **1–4** are monocyclic borinate complexes. It may be expected that the geometry of the boroxazolidones **2a–2b** with a secondary amine coordinated to the diphenylboryl group would be significantly different from that of compounds **1a–1c** with a primary amine, but a comparison of the structural data in Table 2 indicates that this is not the case. Significant differences can only be observed in the torsion angles (Table 3) probably due to different substituents in the molecules and crystal packing effects (hydrogen bonds etc.). The conformations of compounds **1a** and **1b** are significantly different, although the boroxazolidone ring is identical. This may be explained by the intramolecular hydrogen bond between N(10) and N(3) (1.99 Å, 158°) in **1b** as can be seen from Fig. 2.

The average N→B bond length of the boroxazolidones **1–2** is 0.030 Å shorter than the one in the boroxazolidines **3–4**, while at the same time the average B–O bond length is 0.056 Å longer. This observation seems to confirm the contribution of resonance structure II in the chelate of the boroxazolidones **1–2**, but their C=O and C–O bond lengths are not significantly different from the ones in free carboxylic acids (1.214 and 1.308 Å, respectively) [19]. Considering that the sum of covalent radii for a B_{sp^3}–O_{sp^3} bond is 1.54 Å, it is probable that in the boroxazolidines **3–4** with an average bond length of 1.478(3) Å there exists a negative n_O–σ^*_B hyperconjugation [20] between the oxygen and the boron atom that is absent in the boroxazolidones **1–2** (1.534(5) Å) owing to the electron attractive effect of the carbonyl group. As a compensation the N→B bond decreases in compounds **1–2** and probably there is also some hyperconjugation along the B–C_{ar} bond, although the difference of 0.018 Å between **1**, **2** and **3**, **4** is just at the limit of being significant. The hydrolytic stability of boroxazolidones and boroxazolidines may be related to the length of the N→B bond, the weakest bond in these molecules. The N→B bond energy is about one third of the covalent N–B bond energy [21]. Therefore it is assumed that the first step in the hydrolysis of boroxazolidones and boroxazolidines is the N→B bond dissociation followed by the formation of a borate and protonation of the amino group:



R' = alkyl, aryl

Indeed, intermediates of this type have been isolated and characterized by different authors [6,22].

2.2. Comparison of boroxazolidone *5* and boroxazolidine *6*

Comparison of the N→B, B–O and B–C bond lengths of the boroxazolidone **5** and the boroxazolidine **6**, which may be considered as unsaturated derivatives of the complexes discussed above, confirm some of the aforementioned observations. Although in the boroxazolidone **5** and the boroxazolidine **6** the N→B bond lengths are not significantly different, in compound **5** the B–O bond is 0.056 Å longer and the B–C bond is 0.026 Å shorter. This indicates a stronger B–O bonding character in **6** that is missing in **5** in favor of a stronger B–C_{ar} interaction. In this case the N→B bond is not

Table 1
Crystallographic data for compounds **1a-1c**, **2b** and **5**

	1a[b]	**1b**[b]	**1c**[c]	**2b**[b]	**5**[b]
Crystal data					
Formula	$C_{19}H_{25}BN_2O_4$	$C_{20}H_{25}BN_2O_2$	$C_{17}H_{20}BNO_2S$	$C_{22}H_{24}BNO_4$	$C_{19}H_{14}BNO_4$, $2CH_3OH$
Crystal size (mm)	$0.3\times0.3\times0.4$	$0.3\times0.4\times0.5$	$0.3\times0.4\times0.4$	$0.2\times0.5\times0.6$	$0.4\times0.4\times0.6$
Molecular weight (g mol^{-1})	356.23	336.24	313.20	377.25	331.14
Space group	$P2_1$	$P1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
Cell parameters					
a (Å)	8.850(2)	5.906(2)	6.165(1)	5.8080(8)	8.596(1)
b (Å)	11.196(2)	9.059(4)	14.442(3)	15.517(2)	21.225(1)
c (Å)	9.589(2)	9.685(4)	18.353(4)	20.2526(9)	11.517(1)
α (°)	90	77.85(3)	90	90	90
β (°)	90.5 (2)	73.69(2)	90	90	90.48 (1)
γ (°)	90	78.74(3)	90	90	90
V (Å^3)	950.2(4)	481.1(3)	1634.1(6)	1942.8(3)	2101.2(4)
Z	2	1	4	4	4
μ (cm^{-1})	0.81	0.70	2.03	0.80	0.85
$D_{calc.}$ (g cm^{-3})	1.25	1.15	1.27	1.30	1.25
Data collection[a]					
θ limits (°)	$2<\theta<25$	$2<\theta<27$	$2<\theta<22$	$2<\theta<25$	$2<\theta<26$
hkl limits	-11, 11; 0, 14; 0, 12	-7, 0; -11, 11; -12, 12	0, 6; 0, 15; -19, 19	0, 6; -18, 18; -23, 23	0, 10; -26, 0; -14, 14
No. collected reflections	1885	2302	2403	6126	4537
No. of independent reflections (R_{int})	1768 (0.02)	2098 (0.02)	2002	1763 (0.02)	4123 (0.02)
No. of observed reflections[d]	1188	1691	1531[g]	1096	1639
Refinement					
R	0.038[e]	0.044[e]	0.044[e]	0.032[e]	0.055[e]
R_w	0.035[f]	0.037[f]	0.117[h]	0.032[f]	0.051[f]
w	$1/\sigma^2$	$1/\sigma^2$	x/y: 0.0673/0.9032[i]	$1/\sigma^2$	$1/\sigma^2$
No. of variables	236	303	199	254	264
Goodness-of-fit	1.85	3.61	1.03	0.78	3.89
Maximum Δ/σ	0.008	0.07	—	0.05	0.005
$\Delta\rho_{min}$ (e Å^{-3})	-0.17	-0.17	—	-0.16	-0.22
$\Delta\rho_{max}$ (e Å^{-3})	0.14	0.20	0.22	0.15	0.31

[a] T, 293 K; λ_{Mo-K_α}, 0.71069 Å; [b] Structure refined by CRYSTALS; [c] Structure refined by SHELXL-93; [d] $I>3\sigma(I)$.; [e] $R=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; [f] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$; [g] $F>4\sigma(F)$; [h] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^2]^{1/2}$; [i] $w^{-1}=\sigma^2F_o^2+(xP)^2+yP$ where $P=(F_o^2+2F_c^2)/3$.

shortened, a fact that may be explained by the lower Lewis basicity of the pyridine moiety in comparison to aliphatic amino groups.

2.3. Comparison of the bicyclic complexes *7* and *8*

Comparison of the structural parameters of the bicyclic boronate complexes **7** and **8a**–**8b** again confirm the above mentioned differences between boroxazolidones and boroxazolidines. The bicyclic structures **8a** and **8b** are each formed by one boroxazolidone and one boroxazolidine ring and permit a direct comparison of the B–O bond lengths, pointing out a significant difference of 0.082 Å. The N→B bond length of 1.715 (9) Å is long in comparison to compound **7** (1.668(3) Å), while the B–O bond length in **7** (1.476(3) Å) is just between the two values in **8a**–**8b** (1.424(8) and 1.506(8) Å). The 0.034 Å smaller B–C bond length in **7** should be also noticed.

2.4. Comparison of the tricyclic complexes *9* and *10*

Compounds **9** and **10** are tricyclic borate complexes. The N→B bond length changes significantly between the two structure types, but in this case the B–O bond does not vary. An explanation could be that the B–O bond length is also influenced by steric effects. This statement is confirmed by the observation that the B–O bond length is decreasing for both the boroxazolidones and boroxazolidines in the following direction: Boroxazolidones: **1**, **2** (1.534(5) Å)→**8** (1.506(8) Å)→**7** (1.476(3) Å)→**9** (1.446(6) Å). Boroxazolidines: **3**, **4** (1.478(3) Å)→**8** (1.424(8) Å)→**10** (1.439(10) Å).

3. Conclusions

The present X-ray crystallographic study has shown that the B–O bond is significantly longer in boroxa-

Table 2
Selected bond lengths (Å) and bond angles (°) for compounds **1**–**10**[a]

Compound	N–B	B–O	C–O	C–C	N–C	B–C	C=O	OBN	BNC	NCC	CCO	COB
1a	1.624(6)	1.528(6)	1.301(6)	1.516(6)	1.503(6)	1.600(7)	1.215(6)	98.1(4)	106.2(3)	102.7(4)	113.0(3)	113.0(4)
1b	1.606(5)	1.540(4)	1.307(4)	1.519(5)	1.488(4)	1.602(5)	1.207(4)	97.4(3)	104.7(3)	102.7(3)	111.7(3)	111.9(3)
1c	1.613(6)	1.535(5)	1.298(5)	1.519(5)	1.483(5)	1.597(7)	1.213(5)	97.7(3)	105.6(3)	102.8(3)	111.9(4)	113.0(3)
2a[b]	1.646(6)	1.545(6)	1.309(5)	1.532(7)	1.488(6)	1.586(7)	1.216(6)	95.9(3)	103.9(3)	102.7(4)	111.9(4)	111.3(4)
2b	1.626(3)	1.524(3)	1.297(3)	1.513(3)	1.503(3)	1.609(3)	1.216(3)	98.5(2)	103.4(2)	103.6(2)	112.4(2)	112.6(2)
ϕ **1**, **2**[c]	1.623(5)	1.534(5)	1.302(5)	1.520(5)	1.493(5)	1.599(6)	1.213(5)	97.5(3)	104.8(3)	102.9(3)	112.2(4)	112.4(3)
3a[d]	1.654(3)	1.480(3)	1.411(3)	1.506(4)	1.487(3)	1.612(2)	—	99.1(1)	105.8(2)	104.1(2)	105.6(2)	108.9(2)
3b[e]	1.652(4)	1.471(4)	1.418(4)	1.494(6)	1.491(4)	1.618(5)	—	99.9(2)	105.5(2)	105.0(3)	106.0(3)	108.2(2)
3c[f]	1.657(3)	1.478(3)	1.413(3)	1.501(4)	1.488(3)	1.616(3)	—	99.9(1)	105.3(2)	104.4(2)	105.3(2)	107.8(2)
4[g]	1.648(3)	1.481(3)	1.425(3)	1.531(3)	1.506(3)	1.622(3)	—	98.4(2)	99.7(2)	103.1(2)	107.8(2)	110.1(2)
ϕ **3**, **4**[h]	1.653(3)	1.478(3)	1.417(3)	1.508(4)	1.493(3)	1.617(3)	—	99.3(2)	104.1(2)	102.9(3)	106.2(2)	108.8(2)
5	1.658(6)	1.543(6)	1.308(6)	1.477(7)	1.344(5)	1.595(8)	1.210(6)	96.2(4)	109.0(4)	110.4(5)	109.6(5)	114.8(4)
6[c]	1.642(3)	1.487(3)	1.407(3)	1.504(3)	1.347(3)	1.621(3)	—	97.4(2)	108.4(2)	108.5(2)	105.6(2)	109.0(2)
7[j]	1.668(3)	1.476(3)	1.322(3)	1.506(3)	1.494(3)	1.565(3)	1.203(3)	100.9(2)	103.3(2)	106.6(2)	111.1(2)	114.5(2)
8a, **8b**[k, l]	1.715(9)	1.506(8)	1.320(8)	1.502(9)	1.504(8)	1.589(9)	1.215(7)	99.6(5)	104.7(5)	107.0(5)	112.8(5)	115.5(5)
8a, **8b**[k, m]	1.715(9)	1.424(8)	1.422(7)	1.536(8)	1.521(8)	1.589(9)	—	102.1(6)	101.5(5)	102.9(5)	103.8(5)	111.6(5)
9[n]	1.620(3)	1.446(6)	1.336(2)	1.510(11)	1.499(5)	—	1.198(5)	105.2(4)	103.8(2)	106.5(2)	111.6(2)	112.8(2)
10[n]	1.677(6)	1.439(10)	1.423(3)	1.519(6)	1.487(6)	—	—	103.0(6)	103.0(3)	103.7(2)	105.1(6)	108.2(2)

[a] Data have been averaged in all cases with repeating structural units (also for independent molecules in the asymmetric unit of the red crystal); [b] Data from Ref. [18]; [c] Average value for compounds **1a**–**1c** and **2a**–**2b**; [d] Data from Refs. [24,25]; [e] Data from Ref. [26]; [f] Data from Ref. [25]; [g] Data from Ref. [6]; [h] Average value for compounds **3a**–**3c** and **4**; [i] Data from Ref. [3]; [j] Data from Ref. [27]; [k] Data from Ref. [28]; [l] Boroxazolidone ring; [m] Boroxazolidine ring; [n] Data from Ref. [29].

zolidone rings when compared to boroxazolidine rings owing to the electronic acceptor properties of the carbonyl group. As a consequence the N→B bond and/or the B–C_{ar} bonds are shortened, indicating in general a stronger coordinative bond, that could account for the higher hydrolytic stability of the boroxazolidone moiety.

4. Experimental

NMR studies were performed with the following spectrometers: Jeol FX 90 Q, Jeol GSX 270 and Jeol ECLIPSE + 400. Standards were TMS (^{1}H, ^{13}C) and BF_3OEt_2 (^{11}B). Chemical shifts are stated in ppm; they are positive, when the signal is shifted to higher frequencies than the standard.

Table 3
Selected torsion angles (°) for compounds **1a**–**1c** and **2a**–**2b**[a]

Compound	OBNC	BNCC	NCCO	CCOB	COBN
1a	−25.8	21.9	9.2	9.0	−21.3
1b	32.9	−29.5	−14.2	−8.7	25.6
1c	29.0	27.5	−15.3	4.8	−20.8
2a[b]	−28.3	24.0	−10.0	−10.3	24.0
2b	36.3	−29.7	−10.7	−11.3	31.5

[a] A positive rotation is counter-clockwise from atom 1, when viewed from atom 3 to atom 2; [b] Data from Ref. [18].

Infrared spectra have been recorded with a Perkin Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were obtained with an HP 5989 A equipment. Melting points were determined with a Gallenkamp MFB-595 apparatus and have not been corrected.

X-ray diffraction studies of single crystals were performed on an Enraf-Nonius CAD4 diffractometer (λ_{Mo-K_α}, 0.71069 Å; monochromator, graphite; T, 293 K; $\omega - 2\theta$ scan). Cell parameters were determined by least-squares refinement on diffractometer angles for 24 automatically centered reflections. Absorption correction was not necessary, corrections were made for Lorentz and polarization effects. Solution and refinement: direct methods (SHELXS-86) for structure solution and the CRYSTALS (version 9, 1994) or SHELXL-93 software package for refinement and data output. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were determined by difference Fourier maps (in the case of **1b** and **5**) or calculated (in the case of **1a**, **1c** and **2b**). In the first case their positions and one overall isotropic thermal parameter were refined, while in the second case only one overall isotropic thermal parameter was refined. In all cases a reflection-parameter ratio >5 has been considered sufficient for the type of structural studies performed in

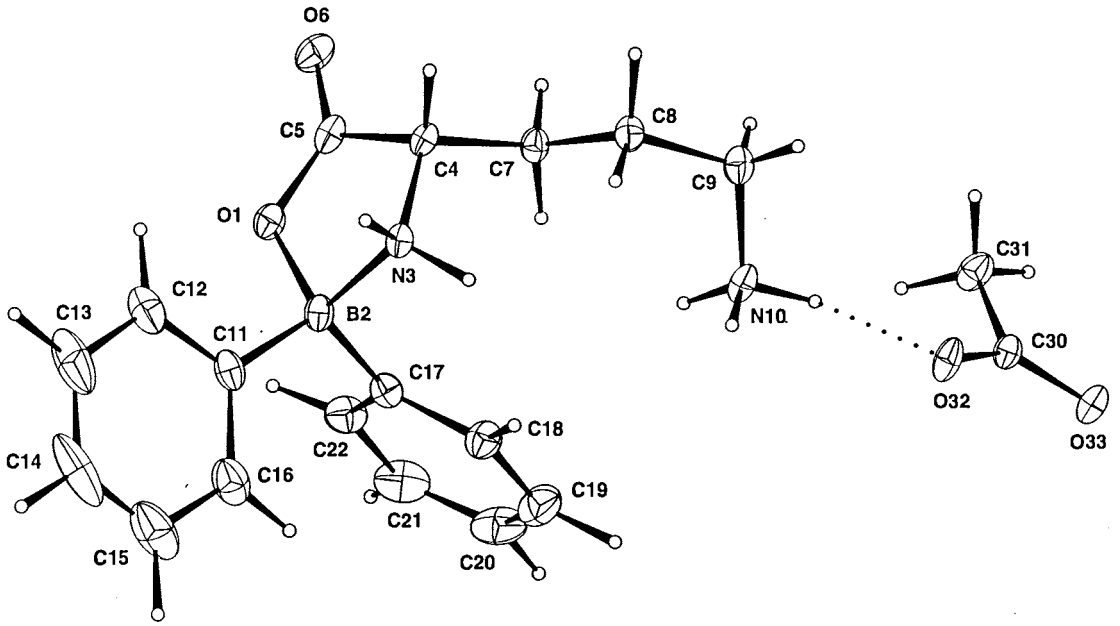


Fig. 1. Molecular structure of compound **1a**.

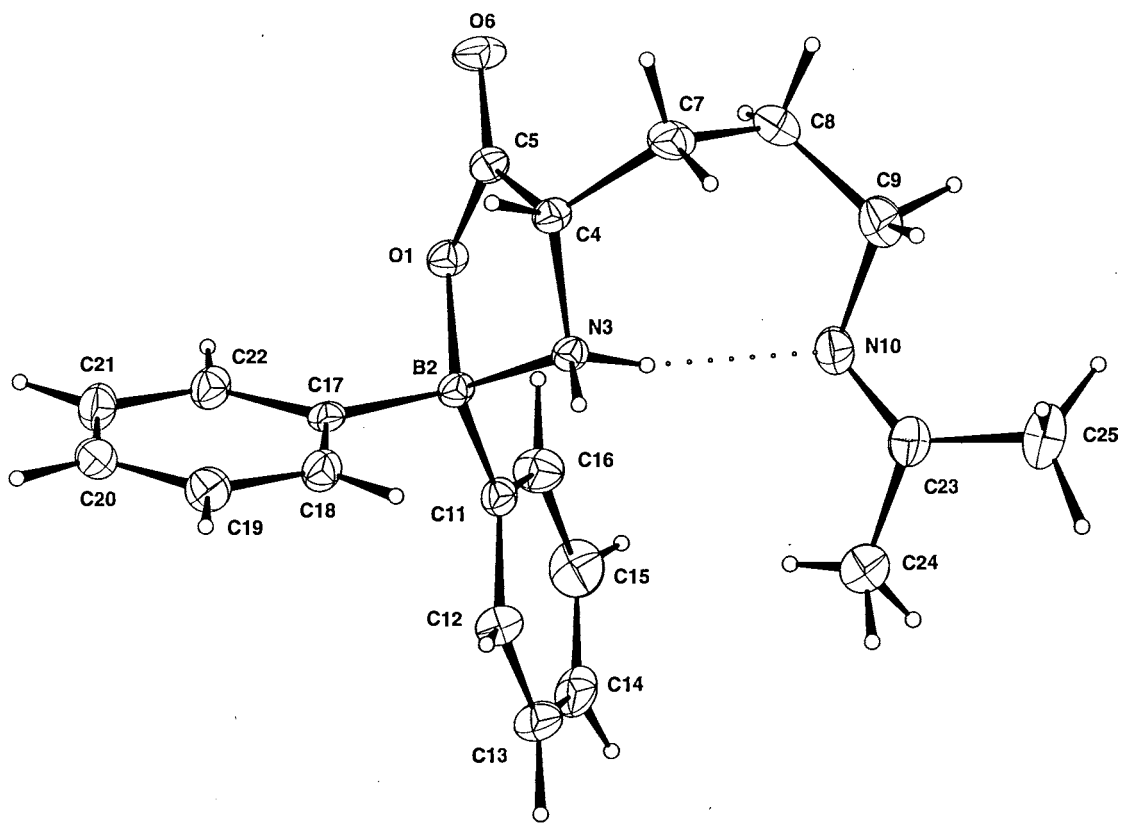


Fig. 2. Molecular structure of compound **1b**.

here. A list of the atomic parameters, bond lengths, bond angles and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre.

Solvents were used without further purification, but single crystals were grown from spectrophotometric grade solvents. All starting materials were commercial. Diphenylborinic acid was prepared from 2-aminoethyldiphenylborinate (5% of molar excess) as described in the literature [23].

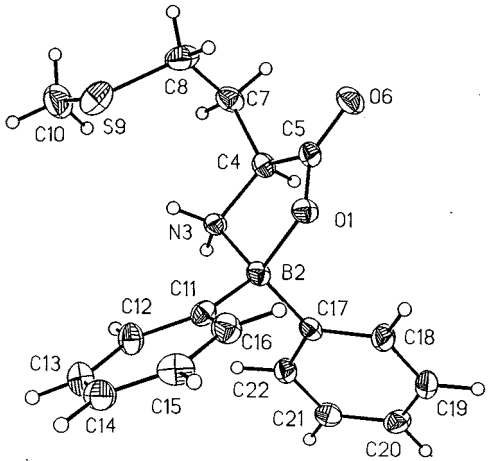


Fig. 3. Molecular structure of compound **1c**.

4.1. Synthesis of diphenyl[L-ornithinato-O,N]boron · CH_3COOH (1a)

A total of 1.00 g (6.75 mmol) of L-ornithine was dissolved in 100 ml of water/ethanol (1:1) and diphenylborinic acid prepared from 1.88 g (8.37 mmol) of 2-aminoethyldiphenylborinate in 20 ml of diethyl ether was added (15% excess). After refluxing for 2 h, a precipitate formed. The colorless product was filtered, washed with water and dried to obtain 1.38 g of **1a**. Crystals suitable for X-ray crystallography were obtained on recrystallization from ethanol/acetic acid. Yield 60%. M.p. 212–214°C.

^{1}H-NMR (270 MHz, DMSO-d_6) δ(ppm): 1.68 (2H, m, H-8), 1.78 (2H, m, CH_3), 2.73 (2H, m, H-7), 3.48 (1H, m, H-4), 3.53 (2H, t, H-9), 4.65–5.34 (br, NH), 7.12 (2H, m, *p*-BC_6H_5), 7.21 (4H, m, *m*-BC_6H_5), 7.42 (4H, m, *o*-BC_6H_5); ^{13}C-NMR (67.8 MHz, DMSO-d_6) δ (ppm): 23.9 (CH_3), 25.5, 26.8 (C-7, C-8), 38.7 (C-9), 54.6 (C-4), 125.8 (*p*-BC_6H_5), 125.9 (*p′*-BC_6H_5), 127.0 (*m*-BC_6H_5), 127.1 (*m′*-BC_6H_5), 131.0 (*o*-BC_6H_5), 131.1 (*o′*-BC_6H_5), 148.0 (br, *i*-BC_6H_5), 148.1 (br, *i′*-BC_6H_5), 174.3 (C-5, OAc^-); ^{11}B-NMR (86.6 MHz, DMSO-d_6) δ (ppm): 5.3. IR (KBr) ν (cm^{-1}): 3204 (m), 1716 (C=O), 1600 (m), 1424 (m), 1298 (m). MS (EI, 70 e V, DIP) *m*/*z*: 297 (1) [M–OAc^-], 219 (10), 182 (24), 165 (2), 115 (28), 78 (39), 69 (57), 45 (54), 43 (100).

4.2. Synthesis of the dimethylketimine of diphenyl-[L-ornithinato-O,N]boron 1b

A few crystals of compund **1b** were obtained on crystallization of compound **1a** in acetone.

4.3. Synthesis of diphenyl[L-methionato-O,N]boron 1c

Diphenyl[L-methionato-*O*,*N*]boron has been synthesized as described in the literature [7]. Crystals suitable

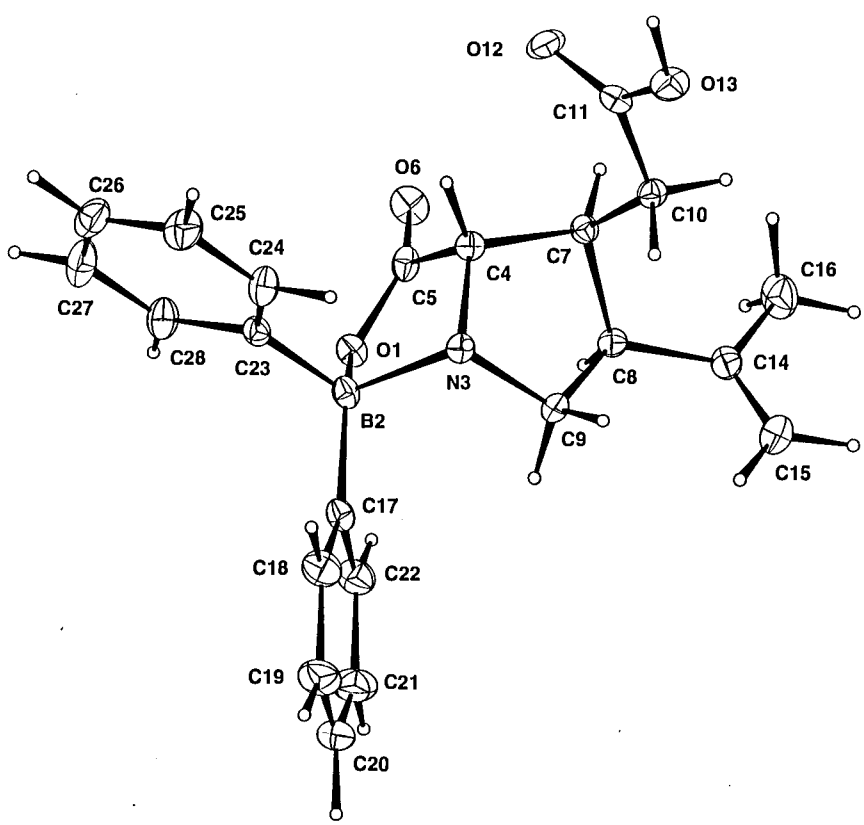


Fig. 4. Molecular structure of compound **2b**.

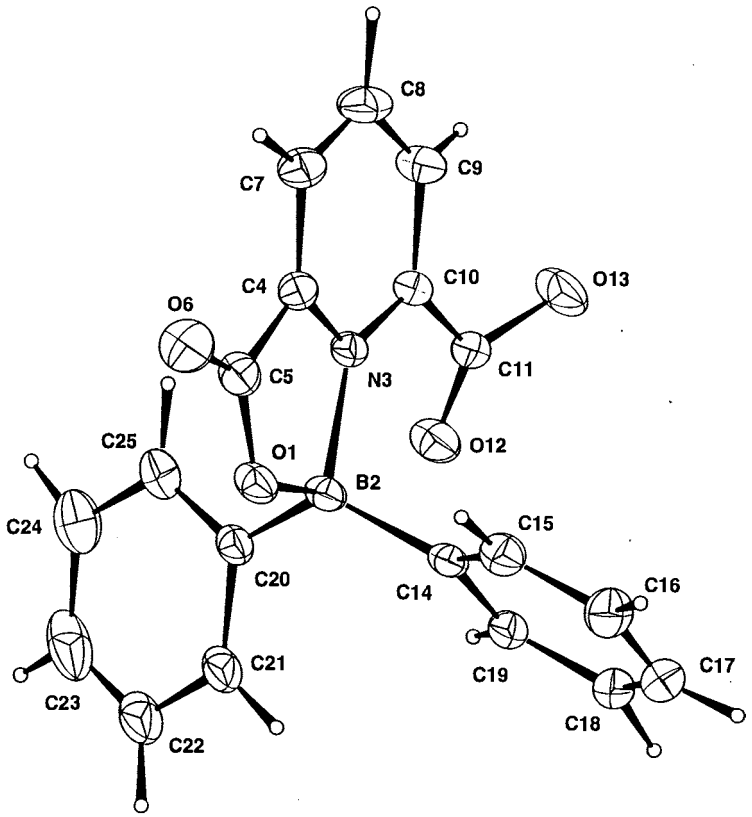


Fig. 5. Molecular structure of compound **5**.

for X-ray crystallography were obtained on recrystallization from acetone.

4.4. Synthesis of diphenyl[kainato-O,N]boron **2b**

A solution of 0.12 g (0.52 mmol) 2-aminoethyldiphenylborinate in methanol was hydrolyzed as described in the literature [23]. The solution of diphenylborinic acid in diethylether was added in a 5% excess to a solution of kainic acid (0.10 g, 0.47 mmol) in 3 ml of water and 30 ml of methanol. The crystals formed were filtered and washed with hexane, chloroform and water. Yield 0.06 g (34%). M.p. 250°C (decrease).

^{1}H (400 MHz, DMSO-d_6) δ (ppm): 1.60 (3H, s, CH_3), 2.06 (1H, dd, $J = 17$, 4 Hz, H-10), 2.29 (1H, dd, $J = 17$, 10 Hz, H-10′), 2.52 (1H, t, H-8), 2.84 (1H, dd, $J = 9$ Hz, H-9), 2.99 (1H, quint, H-7), 3.20 (1H, m, $J = 11$, 9 Hz, H-9), 4.11 (1H, d, $J = 7$ Hz, H-4), 4.56 (1H, s, H-15), 4.87 (1H, s, H-15′), 7.17 (2H, m, p-BC_6H_5), 7.25 (4H, m, m-BC_6H_5), 7.45 (4H, m, o-BC_6H_5), 8.12 (1H, t, NH), 12.41 (1H, s, COOH); ^{13}C (100.5 MHz, DMSO-d_6) δ (ppm): 22.8 (CH_3), 30.8 (C-10), 39.6 (C-7), 45.7 (C-8), 48.9 (C-9), 67.2 (C-4), 112.4 (C-15), 126.4 (p-BC_6H_5), 126.5 (p'-BC_6H_5), 127.3 (m-BC_6H_5), 127.4 (m'-BC_6H_5), 130.9 (o-BC_6H_5), 131.5 (o'-BC_6H_5), 139.8 (C-14), 144.8 (br, i-BC_6H_5), 147.2 (br, i'-BC_6H_5), 173.0 (C-11), 173.3 (C-5); ^{11}B (128.3 MHz, DMSO-d_6) δ (ppm): 6.6 ($h_{1/2} = 1540$ Hz). IR (KBr) ν (cm^{-1}): 3250 (br, m), 3110 (s), 3072 (m), 3006 (m), 2936 (w), 2910 (w), 2862 (w), 2822 (w), 1728 (s), 1710 (s), 1688 (s), 1670 (w), 1654 (w), 1648 (w), 1430 (m), 1420 (m), 1406 (w), 1320 (m), 1286 (w), 1270 (w), 1214 (w), 1194 (m), 1164 (m). MS (EI, 70 eV, DIP) m/z: 377 (7) [M$^+$], 300 (100) [M$^+$-C_6H_5], 282 (30), 240 (27), 168 (19), 78 (11), 77 (10), 51 (8), 41 (9).

4.5. Synthesis of diphenyl[[2-(6-carboxypyridyl)]-carbonyloxy-O,N]boron (**5**)

Compound **5** was synthesized from 0.60 g (3.60 mmol) of 2,6-pyridinedicarboxylic acid and diphenylborinic acid prepared from 0.90 g (4.00 mmol) 2-aminoethyl diphenylborinate in methanol at −78°C. After evaporation of the solvent with N_2 a colorless product (1.03 g, 3.11 mmol) is obtained in crystalline form that was further purified with hexane. The crystals were suitable for X-ray crystallography. Yield 86%. M.p. 248–250°C (decrease).

^{1}H (270 MHz, DMSO-d_6) δ (ppm): 7.20 (2H, m, p-BC_6H_5), 7.42 (4H, dd, m-BC_6H_5), 7.70 (4H, d, o-BC_6H_5), 8.57 and 8.69 (2H, d, H-7, H-9), 8.81 (1H, t, H-8); ^{13}C (67.8 MHz, DMSO-d_6) δ (ppm): 130.0 (br, p-BC_6H_5), 131.3 (br, m-BC_6H_5), 134.5 (br, o-BC_6H_5),

143.2, 143.3 (br, *i*-BC_6H_5, *i'*-BC_6H_5), 143.7 (C-4, C-10), 145.3 (C-8), 146.4 (C-7, C-9), 161.2 (C-11), 162.6 (C-5); ^{11}B (86.6 MHz, DMSO-d_6) δ (ppm): 10 ($h_{1/2} = 1060$ Hz). MS (EI, 70 eV, DIP) m/z: 312 (1) [M^+-H_2O], 196 (1), 165 (1), 123 (24), 105 (23), 78 (23), 78 (100), 77 (46), 51 (51).

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