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Versatile Behavior of 2-Guanidinobenzimidazole Nitrogen Atoms toward Protonation, Coordination and Methylation

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ABSTRACT

The structure, dynamic behavior, protonation, methylation, and coordination sites of 2-guanidinobenzimidazole **1a** *were investigated. Structures of compounds [2-guanidinium-1,3,10-trihydrobenzimidazole]sulfate* **1b**, *[2-guanidinium-1,3-dihydro-benzimidazole]sulfate* **1c–1d**, *[2-guanidinium-1,3-dihydro-benzimidazole]tetrafluoroborate* **1e**, *[2-guanidinium-1,3-dihydro-benzimidazole]chloride* **1f**, *[2-guanidinium-1,3-dihydro-benzimidazole] perchlorate* **1g**, *2-guanidino-1-methyl-benzimidazole* **2a**, *[2-guanidinium-1,3-dimethyl-benzimidazole]iodide* **2b**, *[2-guanidinium-1-methyl-3-hydro-benzimidazole]chloride* **2c**, *[2-guanidinium-1,10-dihydro-benzimidazole]acetate* **3**, *2-guanidino-1-hydro-3-borane-benzimidazole* **4a**, *2-guanidino-1-methyl-3-borane-benzimidazole* **4b**, *(2-guanidino-benzimidazole)dimethyltin* **5**, *[bis(2-guanidino-10-hydro-benzimidazole)nickel(II)]* **6**, *and [bis(2-guanidino-1,10-dihydro-benzimidazole)zinc (II)]nitrate* **7** *were determined based on* ^{1}H, ^{13}C, *and* ^{15}N *NMR spectroscopy. The X-ray diffraction structures of* **2a, 2b, 3, 6**, *and* **7** *were obtained. The results show that* **1a** *has an open structure without an intramolecular hydrogen bond in DMSO or DMF. The imidazolic N-3 is the preferred basic site in solution for protonation, methylation, and coordination and not N-10 as was suggested from semiempirical calculations. Under strong acidic conditions, diprotonation occurs at N-3 and N-10. In the solid state,* **3** *and* **6** *were protonated preferently at N10 rather than at N-1.*
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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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INTRODUCTION

2-Guanidinobenzimidazole **1a** is a polyfunctional planar molecule with a delocalized π electronic system, with five nitrogen atoms that may act as basic centers and with five labile N–H bonds. The molecule may present several tautomers and conformers. Its structure and dynamical behavior have been studied in solution by ^{1}H [2], ^{13}C [2,3], and ^{15}N [4] NMR spectroscopy, and the equivalent conformers **I** and **II** were suggested as the principal contributors to the molecular structure of **1a** in solution. These are in equilibrium and stabilized by intramolecular hydrogen bondings [2]. In the solid state, the X-ray diffraction structure [5] shows intramolecular hydrogen bonding giving rise to a six-membered ring (Figure 1).

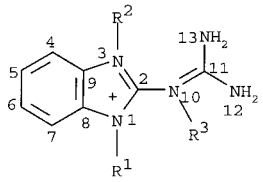
Due to the interest on the coordinating behavior [6] and biological activity [7] of compound **1a,** we decided to investigate the protonation, coordination, and methylation sites of the molecule using NMR spectroscopy and X-ray diffraction studies. Reactions of **1a** with Lewis acids such as borane-THF, methyl iodide, and metallic ions were performed. Substitution of the imidazolic proton and the blockage of the N-3 lone pair add information about the tautomeric equilibrium of **1a** and the preferred sites for coordination or alkylation. Therefore, we have prepared some of its N-protonated, N-methylated, and N-borane adducts and tin, nickel, and zinc heterocyclic compounds **1–7** that are depicted in Figures 2 and 3.

RESULTS AND DISCUSSION

*Structure, Hydrogen Bonding, and Dynamic Behavior of 2-Guanidinobenzimidazole (***1a***)*

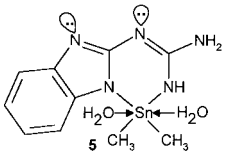
The N–H tautomerism in imidazoles and benzimidazoles cannot be described as an intramolecular exchange; the proton transfer in these systems has been explained to occur via highly ordered transition states that involve dimeric or polymeric structures with intermolecular hydrogen bondings [8]. In compound **1a,** due to the pendant guanidinic chain, intramolecular hydrogen bondings could be possible. Thus, we were interested in obtaining information about the tautomerization mechanism, the dynamic nature of the N–H bonds in solution, and the presence of intramolecular hydrogen bonding. The ^{13}C and ^{15}N NMR data show that the heterocyclic nitrogen atoms N1 and N3 are equivalent at 27°C, and the ^{1}H NMR (270 MHz) spectrum of compound **1a** in solution of DMSO-d6 at 27°C shows a slightly asymmetric coupling pattern for aromatic protons. This indicates a slow annular proton exchange as observed for similar molecules [9].

In order to check if the rate of this exchange depends on intermolecular or intramolecular hydrogen bondings, we determined the activation energy for the proton imidazole exchange between N-1 and N-3 in compound **1a.** This energy, calculated from



1a	R^1= H,	R^2= R^3= lone pair		
1b	R^1= R^2= H,	R^3= H	SO_4^{2-}, 12.1 M	
1c	R^1= R^2= H,	R^3= lone pair	HSO_4^-, 2.5 M	
1d	R^1= R^2= H,	R^3= lone pair,	HSO_4^-, 1.2 M	
1e	R^1= R^2= H	R^3= lone pair	BF_4^-	
1f	R^1= R^2= H,	R^3= lone pair	Cl^-	
1g	R^1= R^2= H,	R^3= lone pair	ClO_4^-	
2a	R^1= Me	R^2= lone pair	R^3= lone pair	
2b	R^1= R^2= Me	R^3= lone pair	I^-	
2c	R^1=Me R^2=H	R^3= lone pair	Cl^-	
3	R^1= H	R^2= lone pair	R^3= H	$^-OOCCH_3$
4a	R^1= H	R^2= BH_3	R^3= lone pair	
4b	R^1= Me	R^2= BH_3	R^3= lone pair	

FIGURE 2 Studied compounds.



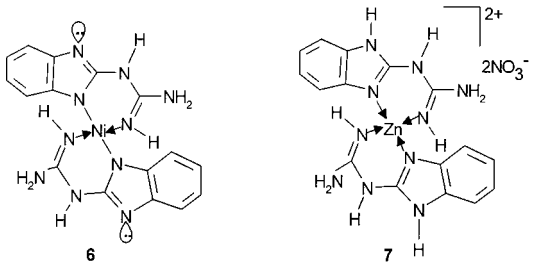


FIGURE 3 Studied compounds.

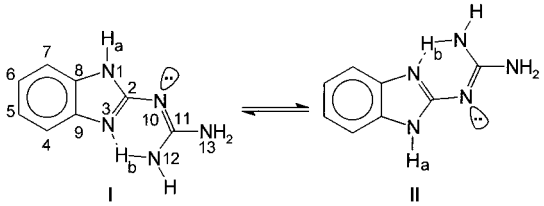


FIGURE 1 Preferred tautomers in solution of **1a.**

the line shape analysis in the ^{13}C NMR spectrum, was found to be $\Delta G^* = 13.3$ Kcal/mol in DMF. This value is very similar to that of 2-aminobenzimidazole **8** ($\Delta G^* = 13.1$ Kcal/mol in DMF, calculated from the *p*Ka data[10]) and of 2-thiomethylbenzimidazole **9** ($\Delta G^* = 13.3$ Kcal/mol in DMF[11b]). In neither of the latter two molecules is intramolecular hydrogen bonding possible. When hydrogen bonding in a quasi-five-membered ring is possible, data from the literature show that the activation energy values are higher; for example, in 2-acetylbenzimidazole, **10,** $\Delta G^* = 18.2$ Kcal/mol in DMSO[9], and in 2-(2-pyridine)-benzimidazole, **11,** $\Delta G^* = 15.4$ Kcal/mol in DMSO[12]. These structures are shown in Figure 4. Thus, the activation energy values for the proton imidazole tautomerism confirmed that the breaking of the intramolecular hydrogen bonding in compound **1a** in DMSO or DMF is not the rate-determining step in the tautomeric exchange, indicating that the pendant guanidine chain in **1a** is not giving assistance to this exchange in an intramolecular mechanism.

An additional confirmation of the absence of this intramolecular hydrogen bond was afforded by an experiment involving ^1H NMR (DMSO) spectroscopy, in which the variation of the N–H chemical shift against temperature was measured, giving a value of $\Delta\delta/\Delta T = -2.1 \times 10^{-3}$ ppm/K for NH-1[13]. This value could conceivably suggest strong intramolecular hydrogen bondings between the NH1 and N-12 (in the imine tautomeric forms **a** and **b**) of the guanidine group [13b] (Figure 5). This was ruled out when the determination of the same parameters in 2-aminobenzimidazole **8** gave values of the same magnitude (-2.8×10^{-3} ppm/K), indicating that the NH-1 in **1a** and in **8** have similar intermolecular bondings.

In DMSO-d6 solution at 270 MHz, the imidazolic NH of **1a** and **8** are observed as a broad signal at $\delta = 11.1$ and 10.6, respectively. The similar chemical shifts indicate that the imidazolic protons have the same environment in the two compounds, confirming the absence of an intramolecular hydrogen bond in **1a.** From these results, it is proposed that compound **1a** in DMSO or DMF solutions presents an open structure, where all NH moieties form hydrogen bonds with the solvent (Figure 5c).

Unequivocal Assignment of C-2 and C-11 Chemical Shifts of Compounds **1a** *and* **1b**

A problem to be solved, before studying the coordination sites and the molecular electronic delocalization, was the correct assignment of the signals of carbon atoms 2 and 11 that have similar chemical-shift values due to their almost identical structure. The unequivocal assignment of **1a** was performed by an experiment of long-distance heteronuclear correlation ($^1H/^{13}C$)[14]. In compound **1a,** the signal at δ 158.90 interacts with the AA′BB′ aromatic system and was assigned to C-2, whereas the signal at δ 158.73 has a correlation with the guanidinic NH_2 (C-11). For compound **1b,** an experiment (gated without decoupling C-H)[14] to detect long-distance coupling in the carbon atoms afforded the observation that the signal at δ 139.2 of C-2 was a doublet of doublets and showed coupling constants ^2J(C-H) of 4.3 Hz, whereas that at C-11 at δ 154.03 was a sharp signal attributed to a system with very small coupling constants.

Protonation of 2-Guanidinobenzimidazole

It has been reported that protonation of benzimidazole derivatives shifted the resonances of carbon atoms 2, 4, 8, and 9 to lower frequencies, whereas the signals for carbon atoms 5 and 6 and protons 4–7 were shifted to higher frequencies. The δ of C-7 is dependent on the substituents at C-2 [15,16]. However, in the protonated compounds **1b–1g,** the C-4 signal suffered an opposite trend going to higher fre-

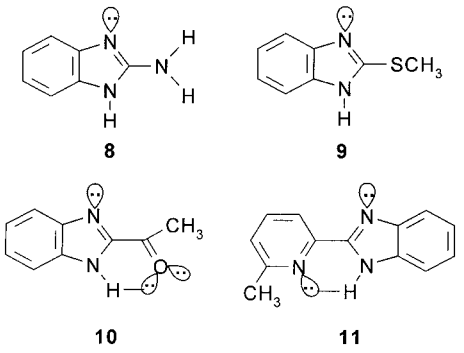


FIGURE 4 Benzimidazole derivatives.

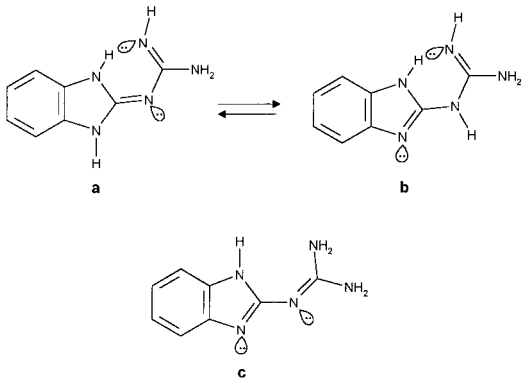


FIGURE 5 Tautomers of **1a.**

quencies (Tables 1 and 2). The ^{15}N NMR spectra in DMSO of compounds **1b–1d** presented a triplet in the ranges -295 to -292 ppm for the NH_2 groups (Table 3). These facts and the observation that C-4(C-7) and C-8(C-9) present averaged sharp signals indicate that the first protonation site of **1a** occurs at N-3 at any acidic concentrations (Figure 6). This conclusion was reached in spite of the fact that semiempirical calculations suggested that the first protonation site in water was at N-10[2].

Under stronger acidic conditions [**1b** in 12.1 M solution of sulfuric acid (98%)], the equilibration of the imidazolic N–H protons with the medium is very slow[17], N-1 and N-3 give a double signal [δ ^{15}N = -242.7 ppm, $^1J(^{15}N–^1H)$ = 102 Hz]. The ^{13}C NMR spectrum of **1b** shows a stronger shielding effect (20 ppm) at C-2, which has been explained by the electronic effect of positively charged substituents on an aromatic ring [18], indicating protonation at N-10. This is also denoted by δ ^1H = 10 of the guanidinic NH-10 (Figure 6). Thus, this is the only case where protonation occurs at N-10 in solution.

The chemical exchange processes of the N–H protons with the acidic solution were demonstrated by a magnetization transference experiment performed on the salt **1b** in which irradiation of the signal of the sulfuric acid protons allowed one to observe an exchange with the N-protons, the measurement of the spin-lattice relaxation time (T1), for ^1H and ^{13}C nuclei (inversion recovery method [19]), also changing with the acid concentration. In **1b,** the chemical exchange of the imidazolic NH-1 and NH-3 with the medium is very slow (longer T_1), whereas for **1d** (shorter T_1), there is a fast exchange with the solvent (Tables 4 and 5). Protonation of 2-guanidino-1-methylbenzimidazole with HCl afforded compound **2c,** which is another example of the favored protonation at N-3 in solution.

TABLE 1 ^1H NMR δ of **1a–7** in DMSO-d6 with TMS as an External Reference

Comp.	*NH-1,3*	*4-H*	*5-H*	*6-H*	*7-H*	*NH_2-12,13*
1a	11.12	7.20	6.92	6.92	7.20	6.89
1b[a]	12.72	8.54	8.42	8.42	8.54	8.32
1c	12.48	7.65	7.42	7.42	7.65	8.55
1d	8.10	7.39	7.17	7.17	7.39	7.65
1e	11.58	7.48	7.31	7.31	7.48	7.82
1f	10.45	7.44	7.21	7.21	7.44	8.21
1g	10.44	7.40	7.22	7.22	7.40	7.63
2a[b]	—	7.27	6.97	6.99	7.27	7.00
2b[c]	—	7.59	7.35	7.35	7.59	7.06
2c[d]	10.20	7.50	7.25	7.25	7.45	7.95
3	6.94	7.17	6.92	6.92	7.17	6.94
4a	10.77	7.25	6.78	6.92	7.08	7.00
5[e]	—	7.30	7.05	7.05	7.17	6.57
7[f]	10.20	7.46	7.16	7.16	7.16	6.65

[a]DMSO-d6 as external reference 10.02 (NH-10).
[b]3.53 (N-CH_3).
[c]3.54 (N-CH_3).
[d]3.64 (N-CH_3).
[e]0.82 (Sn–CH_3).
[f]7.16 (NH-10, $NH_2$14).

Protonation Site in the Solid State

The reaction of compound **1a** with manganese(III) acetate afforded the acetate **3** that crystallizes from water; its X-ray diffraction structure is shown in Figure 7, with data provided in Tables 6 and 7. The important feature in the solid-state structure of this molecule is that, contrary to the results in solution, N-10 instead of N-3 was protonated. The oxygen atoms of the acetate group and a water molecule were linked to the N-1, N-10, and N-13 protons of the 2-guanidinobenzimidazolium ion through hydrogen bondings in a planar conformation. An intramolecular hydrogen bonding was found between a proton of N-12 of the guanidine group and N-3. The bond lengths of the hydrogen bondings are N3-H21 1.841; O17-H1 1.856; O16-H10 1.725; O18-H132, 2.132; O16-H181, 1.719 Å. The driving force for protonation of N-10 in the solid state was the stabilization in the packing structure through hydrogen bonding.

*Mono- and Dimethylated-2-Guanidinobenzimidazole (***2a–2b***)*

The reaction of compound **1a** with metallic sodium in dry THF, followed by the addition of methyl iodide, afforded an orange product, the N-methylated derivative. It was extracted by the methylene chloride from its presence in a mixture of CH_2Cl_2-H_2O (30:70). The product was recrystallized from the same solvent mixture, and brown crystals suitable for X-ray diffraction analysis were obtained after five months (Figure 8, Tables 6 and 8).

The x-ray diffraction analysis of **2a** shows a dimeric array stabilized by intermolecular hydrogen bondings between H261-N10 (2.03 Å) and H121-N24 (2.02 Å) and intramolecular hydrogen bondings (H132-N3 and H271-N17) with a bond length of 2.0 Å. The asymmetry of the aromatic ring produced by the imidazole N-1 methylation is observed in the ^{13}C NMR spectrum (Table 2). In the ^1H and ^{15}N NMR spectra, only one signal was observed for the NH_2 groups (Tables 1 and 3), which indicates that there is a fast exchange between the two NH_2 groups.

A second reaction of compound **1a** with metallic

TABLE 2 ^{13}C-NMR δ of **1–7** in DMSO-d6 with TMS as an External Reference

Comp.	*C-2*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-11*
1a	158.90	111.69	119.36	119.36	111.69	135.70	135.70	158.73
1a[a]	160.00	115.40	119.90	119.90	109.40	133.00	143.10	159.50
1b	139.20	113.50	127.05	127.05	113.50	128.17	128.17	154.03
1c	143.84	113.65	125.00	125.00	113.65	130.77	130.77	155.71
1d	146.50	113.74	124.37	124.37	113.74	132.31	132.31	156.96
1e	148.11	112.64	123.62	123.62	112.64	131.66	131.66	157.76
1f	148.17	112.69	122.33	122.33	112.69	133.22	133.22	157.57
1g	149.58	112.08	122.71	122.71	112.08	131.98	131.98	158.45
2a[b]	157.99	114.95	118.89	120.04	107.47	133.47	141.34	158.72
2b[c]	151.02	110.31	123.28	123.28	110.31	130.49	130.49	158.18
2c[d]	148.95	112.84	122.27	122.64	109.70	131.52	132.25	158.91
3	158.56	111.78	119.33	119.33	111.78	137.00	137.00	158.56
4a	153.42	116.35	120.81	121.05	111.06	132.00	140.61	157.88
4b[e]	151.50	115.60	122.40	122.30	116.30	137.80	136.90	158.96
5[f]	155.97	112.06	121.09	121.20	109.69	131.19	136.71	162.27
7	149.08	114.80	122.64	122.64	112.33	131.97	138.00	157.07

[a]At −60°C, 28.69 MHz in DMF-d7.
[b]27.76 (N-CH_3).
[c]29.83 (N-CH_3).
[d]28.91 (N-CH_3).
[e]THF-d8.
[f](Sn-(CH_3) 6.96 ppm.

TABLE 3. ^{15}N NMR Data and $^{1}J(^{15}N–^{1}H)$ in Hz, DMSO-d6

	1a	***1b***	***1c***	***1d***	***1e***	***2a***	***2b***	***2c***	***4a***	***7***
NH_2-12	−301.4	−295.0	−293.9	−291.8	−291.9	−302.1	−297.3	−296.9		−300.4
J(N-H)	88.5	94.0	b	74.0	58.0			84.0		89.4
NH-1		−242.7							−247.7	−237.5
J(N-H)		102							102	
N-H10										−271.6
J(N-H)										72.3
N-CH_3							−253.7	−256.8		

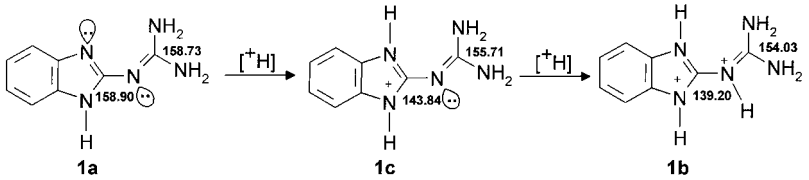


FIGURE 6 Schematic representation of protonation of **1a** showing the ^{13}C NMR data.

sodium, two equivalents of methyl iodide, and THF containing traces of water afforded compound **2b.** After evaporation of the THF, the compound was extracted using a mixture of CH_2Cl_2-H_2O (30:70). Compound **2b** dissolved in the aqueous phase. It was recrystallized from the same mixture giving colorless crystals, which were suitable for X-ray diffraction studies (Figure 9, Tables 6 and 9). The most interesting feature is that the guanidino group is out of the ring plane by 67°, owing to steric hindrance with the methyl groups. The structure has hydrogen bondings between three of the NH_2 protons and the iodide atoms, one being formed with H132 (2.79Å) and the other two with H131 (2.98 Å) and H122 (2.93 Å). Each 2-guanidinobenzimidazolium ion is bonded to two iodide ions and each iodide ion to two guanidinobenzimidazolium ions in a polymeric array as depicted in Figure 9. In both methylation re-

TABLE 4 T_1 (s) Measurements in ^{1}H NMR, (DMSO-d6)

	1a	*1b*[a,b]	*1c*	*1d*	*1e*	*1f*	*1g*[b]	*2a*[c]	*2b*[d]	*4a*
H-4	0.91	0.61	0.70	0.28	0.85	1.23	1.22	1.00	1.17	3.08
H-5	0.80	0.31	0.71	0.43	0.93	0.87	0.99	0.89	1.17	1.26
H-6	0.80	0.31	0.71	0.43	0.93	0.87	0.99	0.89	1.17	2.21
H-7	0.91	0.61	0.70	0.28	0.85	1.23	1.22	0.83	1.17	1.57
NH_2	0.35	0.30	0.34	0.07	0.26	0.25	0.17	[e]	0.23	[e]
N-H	0.56	0.35	0.33	0.08	0.25	0.23	0.26			0.46

[a]DMSO-d6 utilized as external reference.
[b]T_1 of NH_2 was obtained from the slope of T_1 and multiplied by 1.4.
[c]T_1 of N-CH_3 was 1.53 s.
[d]T_1 of N-CH_3 was 0.65 s.
[e]T_1 could not be obtained.

TABLE 5 T_1 (s) Measurements in ^{13}C NMR, (DMSO-d6)

	1a	*1b*	*1c*	*1d*	*1e*	*1f*	*1g*	*2a*[b]	*2b*[c]	*4a*
C-2	2.32	0.81	0.43	0.17	2.22	2.27	a	3.87	3.06	4.70
C-4	0.39	0.19	0.13	0.14	0.25	0.24	0.28	0.55	0.51	0.33
C-5	0.31	0.16	0.13	0.14	0.21	0.22	0.24	0.37	0.40	0.27
C-6	0.31	0.16	0.13	0.14	0.21	0.22	0.24	0.47	0.40	0.28
C-7	0.39	0.19	0.13	0.14	0.25	0.24	0.28	0.55	0.51	0.34
C-8	[a]	1.15	0.60	0.20	2.04	2.05	3.77	1.02	9.69	4.22
C-9	[a]	1.15	0.60	0.20	2.04	2.05	3.77	6.96	9.69	9.70
C-11	2.10	0.98	0.43	0.13	1.60	1.56	2.35	6.57	3.47	2.24

[a]T_1 could not be obtained.
[b]T_1 of N-CH_3 = 0.77 s.
[c]T_1 of NCH_3 = 1.55 s.

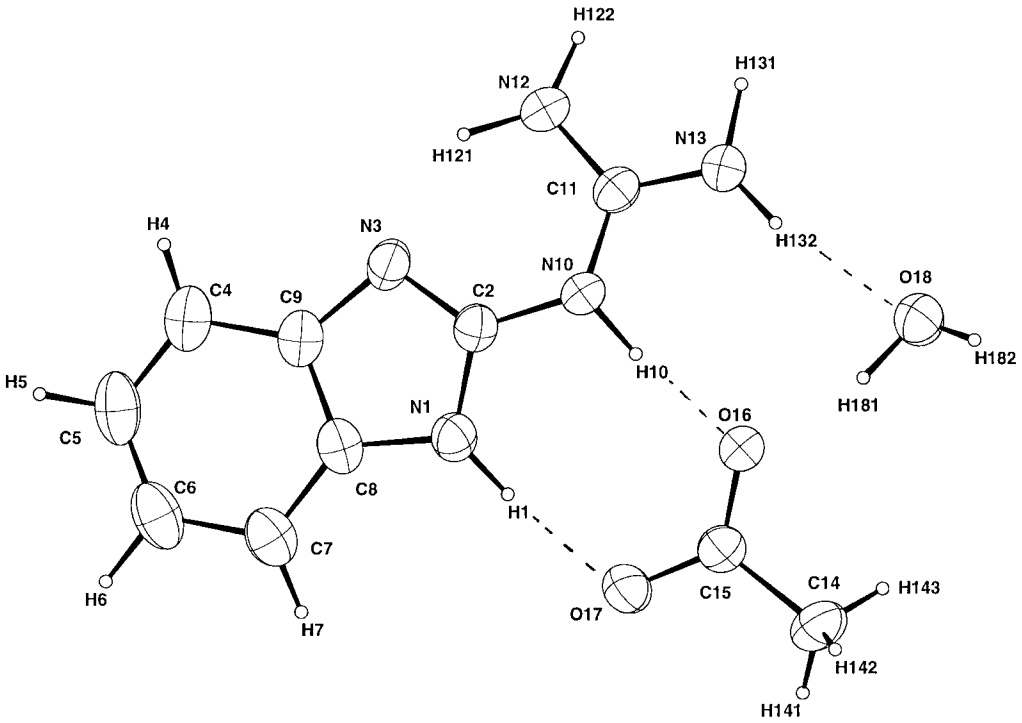


FIGURE 7 X-ray diffraction structure of compound **3.**

TABLE 6 Crystal Data of **2a, 2b** and **3**

	$C_9H_{11}N_5$ (**2a**)	$C_{10}H_{14}N_5I.H_2O$ (**2b**)	$C_{10}H_{15}N_5O_3$ (**3**)
fw	189.22	349.173	253.17
space group	*P b c a*	*P b c a*	*P b c a*
a (Å) =	9.499(1)	12.269(7)	4.987(4)
b (Å) =	14.739(1)	14.829(6)	14.928(3)
c (Å) =	28.023(4)	15.330(5)	33.958
a (°) =	90	90	90
b (°) =	90	90	90
g (°) =	90	90	90
V (Å^3)	3923.5(9)	2789.3(11)	2528.159(7)
Z	16	8	8
F(000)	1600	1376	1072
Crystal size	0.1 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.3
Diffractometer	CAD4-Enraf-Nonius	CAD4-Enraf-Nonius	CAD4-Enraf-Nonius
Radiation	Mo Kα (1 = .71069 Å)	Mo Kα (1 = .71069 Å)	Mo Kα (1 = .71069 Å)
Linear abs coeff cm^{-1}	0.79	22.66	0.94
r (calc) g/cm^{-3}	1.280	1.66	1.331
Scan type	$\varpi/2\theta$	$\varpi/2\theta$	$\varpi/2\theta$
Scan range (°)	0.33 + 0.53 tgθ	0.28 + 0.45 tgθ	0.39 + 0.55tgθ
θ limits (°)	1.98–25	1.95–25	2.03–25
Temperature of measurement	room temperature	room temperature	room temperature
Octants collected	−11, 0; 0, 17; 0, 33	−14, 0; −17, 0; −18, 0	0, 5; 0, 17; 0, 40
No. of data collected	3917	2783	2634
No of unique data collected	3445	2443	2205
No. unique data used	1255 ($Fo)^2 > 2s$ ($Fo)^2$	1909 ($Fo)^2 > 3s$ ($Fo)^2$	1235 ($Fo)^2 > 3s$ ($Fo)^2$
R(int)	1.57	0.00	0.08
Decay %	<1	<1	<1
$R = \Sigma\|\|Fo\| - \|Fc\|\|)/\Sigma\|Fo\|$	0.047	0.027	0.037
$R_w = [\Sigma w(\|Fo\| - \|Fc\|)2/\Sigma wFo]^{1/2}$	0.043 $W = 1.0$	0.029 $W = 1.0$	0.033 $W = 1.0$
Goodness of fit s	2.01	3.89	2.31
No. of variables	253	203	209
Δr min(e/Å^3)	−0.18	−0.23	−0.12
Δr max (e/Å^3)	0.22	0.81	0.13

TABLE 7 Selected Bond Lengths (Å) and Angles (°) for **3**

Bond Lengths		*Bond Lengths*	
N(1)–C(2)	1.354 (4)	N(12)-C(11)	1.320 (4)
N(3)-C(2)	1.317 (4)	N(13)-C(11)	1.330 (4)
N(10)-C(2)	1.379 (4)	N(1)-C(8)	1.393 (4)
N(10)–C(11)	1.344 (4)		
Bond Angles		*Bond Angles*	
N(1)-C(2)-N(3)	115.2 (3)	N(10)-C(11)-N(13)	118.7 (3)
N(1)-C(2)-N(10)	118.5 (3)	N(13)-C(11)-N(12)	120.1 (3)
N(1)-C(8)-C(7)	131.3 (3)	C(2)-(N1)-C(8)	105.3 (3)
N(1)-C(8)-C(9)	105.9 (3)	C(2)-N(3)-N(10)	126.3 (3)
N(3)-C(9)-C(4)	129.5 (3)	C(2)-N(3)-C(9)	103.4 (3)
N(3)-C(9)-C(8)	110.2 (3)	C(2)-N(10)-C(11)	124.7 (3)
N(10)-C(11)-N(12)	121.2 (3)		

actions depicted here, we have not found evidence of reaction at N-10.

*2-Guanidino-1-H-3-borane-benzimidazole (***4a***) and 2-Guanidino-3-borane—1-methyl-benzimidazole (***4b***)*

Reaction of compounds **1a** and **2a** with borane THF at low temperature gave the mono N-BH_3 adducts **4a** and **4b,** respectively, identified by the ^{11}B NMR spectra (quartets at $\delta = 20.5$ and -22, respectively, characteristic of imidazoleborane [11]). The borane coordination site (N-3) was deduced by the shift to higher frequencies of H-4, a similar effect having been observed for other N-BH_3 heterocycles [11a].

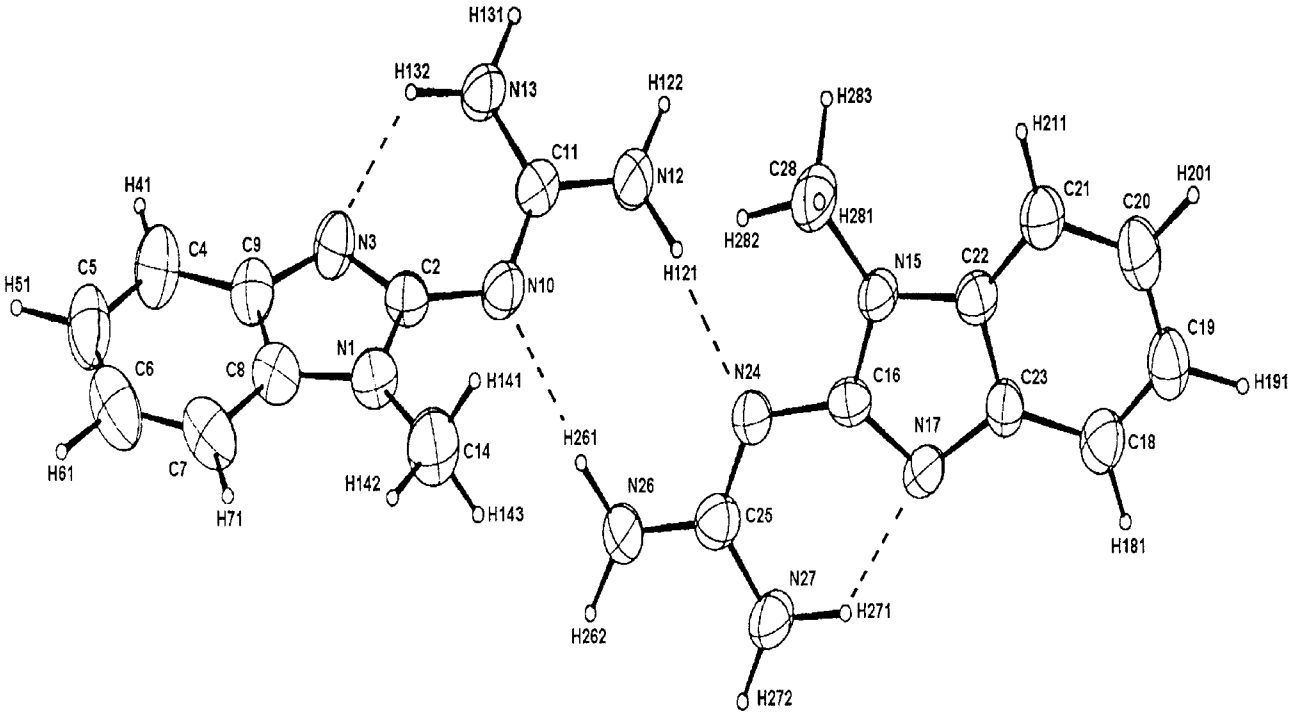


FIGURE 8 X-ray diffraction structure of compound **2a.**

TABLE 8 Selected Bond Lengths (Å) and Angles (°) for 2a

Bond Lengths		*Bond Lengths*	
N(1)-C(2)	1.382 (6)	N(13)-C(11)	1.344 (7)
N(3)-C(2)	1.329 (6)	N(1)-C(8)	1.377 (6)
N(10)-C(2)	1.364 (7)	N(3)-C(9)	1.397 (7)
N(10)-C(11)	1.319 (7)	N(1)-C(14)	1.444 (7)
N(12)-C(11)	1.335 (7)		
Bond Angles		*Bond Angles*	
N(1)-C(2)-N(3)	112.2 (5)	N(10)-C(11)-N(12)	117.1 (6)
N(1)-C(2)-N(10)	116.1 (5)	N(10)-C(11)-N(13)	124.4 (6)
N(1)-C(8)-C(7)	132.6 (6)	N(13)-C(11)-N(12)	118.4 (6)
N(1)-C(8)-C(9)	105.3 (5)	C(2)-N(1)-C(8)	107.3 (5)
N(1)-C(14)-C(8)	126.7 (5)	C(2)-N(3)-N(10)	131.7 (5)
N(3)-C(9)-C(4)	129.6 (6)	C(2)-N(3)-C(9)	104.7 (5)
N(3)-C(9)-C(8)	110.5 (5)	C(2)-N(10)-C(11)	121.1 (5)

There is no evidence of borane coordination to the imine exocyclic nitrogen atom N-10. The ^{13}C NMR spectrum of **4a** presents six signals for the aromatic ring (Table 2). The ^{1}H NMR spectrum presents a coupling pattern ABCD for the aromatic protons (Table 1). The N-borane coordination makes the imidazole N–H bond less labile and allows us to observe a doublet assigned to NH-1 in the ^{15}N NMR spectrum ($\delta = -247.7$, $^{1}J(^{15}N–^{1}H) = 117$ Hz). The value of the coupling constant shows that the NH-1 has less electronic density, owing to the electron-attracting effect of the N-3 coordination of borane. The NMR data indicate that the borane group is not in equilibrium with the other nitrogen atoms in the molecule. Even in an excess of borane, we have not found coordination of a second borane molecule; only N-3 reacted with BH_3. Compound **4b** could not be isolated because it is very reactive.

Coordination Behavior of 2-Guanidinobenzimidazole toward Metal Atoms (2-Guanidinobenzimidazole)dimethyltin 5, [Bis(2-guanidino-10-hydro-benzimidazole) nickel(II)] 6, [Bis(2-guanidino-1,10-dihydro-benzimidazole)zinc] (II) Nitrate **7**

The different coordination behavior of 2-guanidinobenzimidazole in three metallic compounds each bearing a six-membered ring allows us to obtain compounds in which the ligand has different degrees of protonation.

We have reacted one equivalent of compound **1a** with one equivalent of dimethyldichlorotin, in THF, in the presence of potassium carbonate, with refluxing of the solution for 4 hours. The reaction product presented in its ^{119}Sn NMR spectrum a single signal at δ-202.9, characteristic of a hexacoordinated tin atom. The mass spectrum showed that the structure of **5a** has a tin atom bonded to one ligand, two methyl groups, and two water molecules. The ^{13}C

TABLE 9 Selected Bond Lengths (Å) and Angles (°) for **2b**

Bond Lengths		*Bond Lengths*	
N(1)-C(2)	1.351 (6)	N(13)-C(11)	1.332 (6)
N(3)-C(2)	1.332 (6)	N(1)-C(8)	1.399 (5)
N(10)-C(2)	1.349 (5)	N(1)-C(14)	1.458 (6)
N(10)-C(11)	1.320 (6)	N(3)-C(15)	1.448 (8)
N(12)-C(11)	1.327 (6)	N(3)-C(9)	1.399 (6)
Bond Angles		*Bond Angles*	
N(1)-C(2)-N(3)	109.3 (4)	N(3)-C(9)-C(4)	130.6 (5)
N(1)-C(2)-N(10)	126.5 (4)	N(3)-C(9)-C(8)	107.1 (4)
N(1)-C(8)-C(7)	131.7 (4)	N(10)-C(11)-N(12)	118.9 (5)
N(1)-C(8)-C(9)	106.6 (4)	N(10)-C(11)-N(13)	124.1 (4)
N(1)-C(14)-C(8)	125.9 (4)	N(13)-C(11)-N(12)	116.9 (5)

and ^{1}H NMR data correspond to a pure compound; the chemical shifts of C-2 and C-11 (δ 156.9 and 162.3) in the ^{13}C NMR spectrum indicate that N-10 is not protonated. The presence of a strong base in the reaction mixture insured that the reaction product was not protonated at N-1 or N-10.

The nickel derivative **6** was prepared by the reaction of $NiCO_3 \cdot Ni(OH)_2 \cdot 4H_2O$ and two equivalents of **1a** in a mixture of methanol and water (60–40), reddish crystals being obtained after a week. The X-ray diffraction structure was obtained (Figure 10, Tables 10 and 11). It shows a complex formed with two ligand bonded atoms in a square planar to a nickel geometry. The molecule is not completely planar due to a steric interaction between the exocyclic amino group and the benzenic ring. N-10 is protonated instead of N-3. An explanation for the different preferred protonation site in compound **6** is related to the formation of a chelate ring that makes N-10 more suitable for protonation. It was not possible to obtain the NMR data of the nickel complex that is diamagnetic in the solid state, but, in DMSO solution, it becomes hexacoordinate and paramagnetic. The diprotonated N-1 and N-10 analog of compound **6** has already been reported by some of us [6a].

The reaction of compound **1a** with zinc nitrate in hot methanol afforded a crystalline compound that was analyzed by NMR spectroscopy and X-ray diffraction. Two 2-guanidinobenzimidazole ligands were coordinated through N-3 and N-12 atoms to the zinc(II) that presented a tetrahedral geometry (Figure 11 and Tables 10–12). Protonation was due to the acidic medium produced in the reaction. The reaction afforded an example of a 2-guanidinobenzimidazole protonated at N-1 and N-10. The diamagnetic zinc complex was observed in its ^{1}H and ^{13}C NMR spectra and allowed us to confirm that protonation at N-10 induces a shift to lower frequencies of C-2 with respect of the nonprotonated compounds, as in the tin heterocycle **5.**

CONCLUSION

Compound **1a** is a molecule with several basic sites and labile protons that permits complex equilibria to exist among several conformers and tautomers. The molecule may coordinate protons, methyl, or borane groups and metallic atoms. A careful NMR study allowed us to establish that the open structure without an intramolecular hydrogen bond is the more populated one in DMSO or DMF. The imidazolic N-3 is the preferred basic site in solution for protonation, methylation, and coordination and not N-10 as was suggested from semiempirical calculations [2]. Under strongly acidic conditions, diprotonation occurs at N-3 and N-10. In the solid state, we found two examples, **3** and **6,** where protonation of N-10 is preferred over that of N-1. It is also a very strong bidentate ligand for metallic ions.

EXPERIMENTAL

The syntheses of **2a,2b,** and **4a** were carried out under a dry nitrogen atmosphere. All solvents were freshly distilled and dried before use according to established procedures. 2-Guanidinobenzimidazole **1a** and 2-aminobenzimidazole **8** were commercial products and used as received. Melting points were measured on a Gallenkamp apparatus and are uncorrected. The IR spectra were taken in a KBr disc using a Perkin Elmer 16F PC IR spectrophotometer. The mass spectra (70 eV) were measured in an HP 5989 spectrometer. NMR spectra were determined in a Jeol GX 270 spectrometer. ^{1}H and ^{13}C NMR spectra (270.05, 67.80 MHz) were measured with TMS as an internal reference and ^{15}N using $\Xi^{15}N = 10.136767$ MHz as the reference. ^{15}N spectra were recorded at 27.25 MHz using a multinuclear 5 mm probe, and approximately 0.3 mmol of each compound was dissolved in 0.5 mL of DMSO-d6 (99% deuterated, Aldrich, used directly without any further purification). ^{11}B and ^{19}F spectra were obtained in Jeol GX 270 (86.84 MHz) and Jeol FX-90Q (89.25 MHz) spectrometers, respectively.

*2-Guanidinobenzimidazole (***1a***).* Yellow solid, mp 242.8–244.5°C. I.R. ν cm^{-1}: 3448, 3210 (N–H), 1648 (C=N), 1600, 1542 (C=C), 1392, 1274 (C–N). MS, m/z (%): 175.2 (99%).

*[2-Guanidiniumbenzimidazole]sulfate (***1b–1d***)*

These compounds were prepared directly in three resonance tubes of high resolution and 5 mm diameter as reported below.

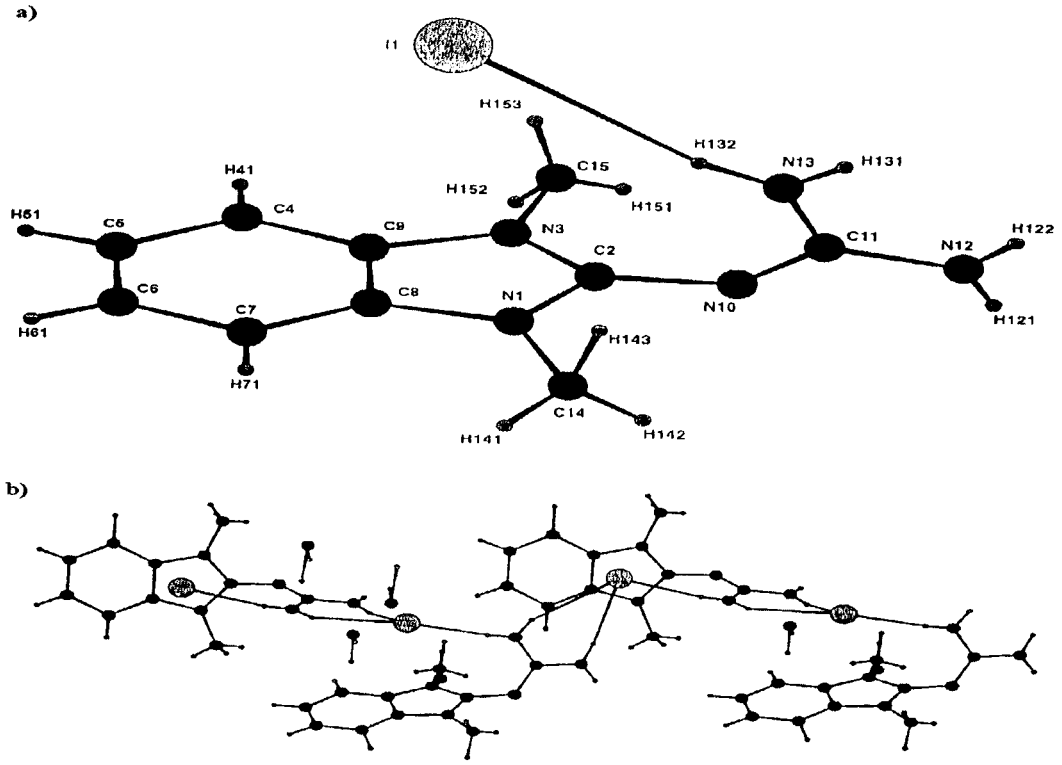


FIGURE 9 (a) X-ray diffraction structure of compound **2b.** (b) View of the polymeric array of **2b.**

*[2-Guanidinium-1,3,10-trihydro-benzimidazole]sulfate (***1b***).* A solution of 250 mg (1.43 mmol) of **1a** in 0.5 mL of H_2SO_4 (97%) was prepared.

*[2-Guanidinium-1,3-dihydro-benzimidazole]sulfate (***1c***).* A solution of 250 mg (1.43 mmol) of **1a** in 0.4 mL of DMSO-d6 and 0.1 mL of H_2SO_4 (97%) was prepared.

*[2-Guanidinium-1,3-dihydro-benzimidazole]sulfate (***1d***).* A solution of 250 mg (1.43 mmol) of **1a** in 0.45 mL of DMSO-d6 and 0.05 mL of H_2SO_4 (97%) was prepared.

*[2-Guanidiniumbenzimidazole (***1e–1h***)*

*[2-Guanidinium-1,3-dihydro-benzimidazole]tetrafluoroborate (***1e***).* To a solution of 210 mg (1.19 mmol) of **1a** in 20 mL of THF, 0.20 mL of HBF_4 (85%) was added, and the mixture was stirred for 30 minutes at 27°C. Then the solvent was removed in vacuo, and an orange unstable solid was obtained, 210 mg (95%), mp 270–273°C. IR ν (B–F) = 1088 cm^{-1}. ^{11}B NMR (DMSO-d6): $\delta = -1.40$ (q, J(B–F) = 1.2 Hz, $\underline{^{-}BF_4}$). ^{19}F NMR (DMSO-d6): $\delta = -146.00$ (s, $\underline{^{-}BF_4}$).

*[2-Guanidinium-1,3-dihydro-benzimidazole]chloride (***1f***).* To a solution of 250 mg (1.43 mmol) of **1a** dissolved in 20 mL of THF, 0.12 mL of HCl (37%) was added, and the mixture was stirred for 30 minutes at 27°C. The solvent was evaporated in vacuo. An orange solid was obtained, 250 mg (100%), mp 217–218°C. IR, ν cm^{-1}: 3330 (N–H), 2624 (NH^+), 1688 (C=N^+), 1628 (C=N), 1600, 1554 (C=C). MS, *m/z* (%): 176.3 (9%), 158 (100%). $C_8H_{10}N_5Cl.3/2H_2O$ (238.7): calcd. C, 40.66; N, 29.18; H, 5.55; found: C, 40.26; N, 29.34; H, 5.48.

*[2-Guanidinium-1,3-dihydro-benzimidazole]perchlorate (***1g***).* To a solution of 250 mg (1.43 mmol) of **1a** in 20 mL of THF, 0.12 mL of $HClO_4$ (72%) was added, and the mixture was stirred for 30 minutes at 27°C. The solvent was removed in vacuum. An orange solid, 245 mg (98%), was obtained, mp 186°C (dec.). IR ν cm^{-1}, 3362 (N–H), 2462 (NH^+), 1696 (C=N^+), 1634, 1608 (C=C), 1136 (ClO_4^-). MS, *m/z* (%): 175.3 (2%).

*2-Guanidino-1-methylbenzimidazole (***2a***) and [2(guanidinium)-1,3-dimethyl-benzimidazole]iodide (***2b***).* To a solution of 250 mg (1.43 mmol) of **1a** in 20 mL of dry THF, was added 33 mg of Na, and the reaction mixture was heated to the THF reflux temperature for 5 hours. Then an excess of 200 mg of

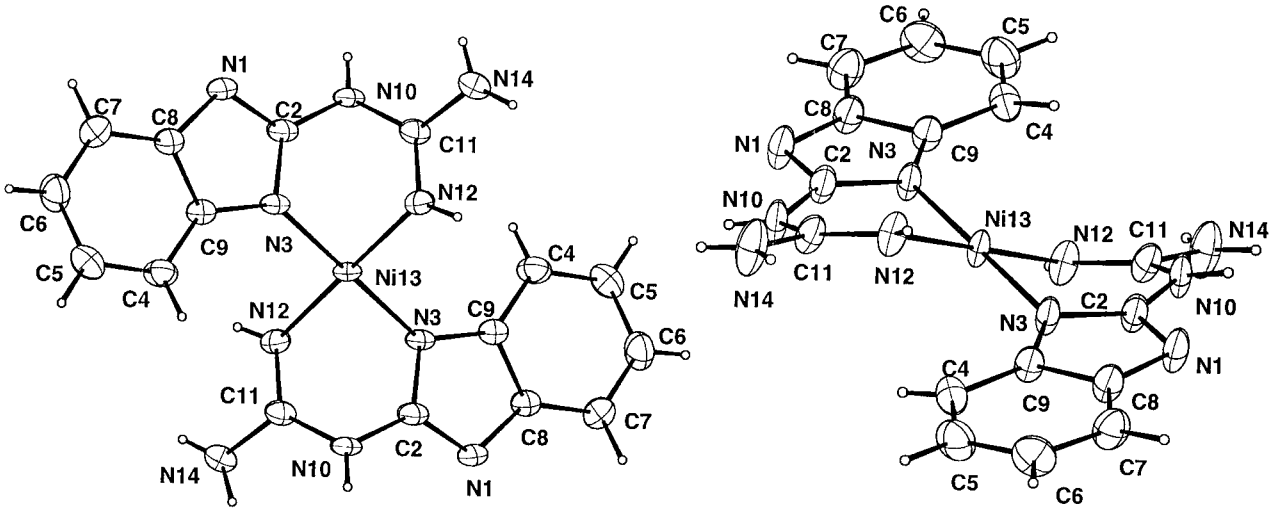


FIGURE 10 Two views of the X-ray diffraction structure of compound **6.**

TABLE 10 Crystal Data of **6** and **7**

	$C_{17}H_{20}ON_{10}Ni$ (**6**)	$C_{16}H_{18}O_6N_{12}Zn$ (**7**)
Fw (g/mol)	439.12	539.78
Space group	C 2/*c*	C 2/*c*
a (Å) =	21.049 (3)	22.753 (4)
b (Å) =	7.114 (1)	13.970 (3)
c (Å) =	14.032 (2)	14.622 (2)
α (°) =	90.0	90.0
β (°) =	118.42 (1)	105.74 (2)
γ (°) =	90.0 (1)	90.0 (1)
V (Å^3)	1848.04 (6)	4473.483 (1)
Z	8	8
Crystal dimensions	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.2
Diffractometer	CAD4-Enraf-Nonius	CAD4-Enraf-Nonius
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Linear abs coeff cm^{-1}	20.91	11.872
ρ (calc) g cm^{-3}	1.91	1.656
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan range (°)	0.95 + 0.56 tgθ	1.0 + 0.58 tgθ
θ limits (°)	2.45–25	2.49–25
Temperature of measurement	room temperature	room temperature
Octants collected	0, 24; 0, 8; − 16, 14	−26, 26; −16, 0; 0, 17
No. of data collected	3606	8524
No. of unique data collected	1621	3927
No. of unique data used	1297 $(Fo)^2 > 3\sigma(Fo)^2$	2102 $(Fo)^2 > 3\sigma(Fo)^2$
R (int)	1.57	2.9
Decay %	<1	<1
$R = \Sigma(\|\|Fo\| - \|Fc\|)/\Sigma\|Fo\|$	0.034	0.034
$Rw = [\Sigma w(\|Fo\| - \|Fc\|)^2/\Sigma wFo^2]^{1/2}$	0.037 $w = 1$	0.034 $w = 1$
Goodness of fit s	4.88	2.53
No. of variables	172	376
$\Delta\rho$ min (e/Å^3)	−0.38	−0.19
$\Delta\rho$ max (e/Å^3)	0.43	0.30

TABLE 11 Selected Bond Lengths (Å) and Angles (Å) for **6**

Bond Lengths		*Bond Lengths*	
N(1)-C(2)	1.332(4)	N(1)-C(8)	1.392(4)
N(3)-C(2)	1.343(4)	N(3)-C(9)	1.400(4)
N(10)-C(2)	1.380(4)	Ni(13)-N(3)	1.893(2)
N(10)-C(11)	1.346(5)	Ni(13)-N(12)	1.867(3)
N(12)-C(11)	1.292(4)	C(16)-O(15)	1.490(1)
N(14)-C(11)	1.359(5)		
Bond Angles		*Bond Angles*	
N(1)-C(2)-N(3)	117.0(3)	C(2)-N(1)-C(8)	103.3(2)
N(1)-C(2)-N(10)	120.5(3)	N(3)-C(2)-N(10)	122.5(3)
N(1)-C(8)-C(7)	129.7(3)	C(2)-N(3)-C(9)	103.0(3)
N(1)-C(8)-C(9)	109.1(3)	C(2)-N(10)-C(11)	122.9(3)
N(3)-C(9)-C(4)	132.1(3)	N(3)-Ni(13)-N(3′)	179.99
N(3)-C(9)-C(8)	107.5(3)	N(3)-Ni(13)-N(12)	91.9(1)
N(10)-C(11)-N(12)	121.4(3)	N(3)-Ni(13)-N(12′)	88.1(1)
N(10)-C(11)-N(14)	115.4(3)	Ni(13)-N(3)-C(2)	122.7(2)
N(12)-C(11)-N(14)	123.2(3)	Ni(13)-N(12)-C(11)	126.4(3)
N(12)-Ni(13)-N(12′)	179.99	Ni(13)-N(3)-C(9)	133.2(2)
C(16)-O(15)-C(16)	154.4(14)		

Na_2CO_3 and 0.63 mL of CH_3I were added, and the mixture was heated for 30 minutes. The solvent was evaporated in vacuo. The reaction product was a yellow solid that was purified by dissolving it in CH_2Cl_2 (20 mL) and extracting three times with H_2O (60 mL).

From the organic fraction, compound **2a** was obtained as a hygroscopic orange solid, 158 mg (63%). Brown crystals were obtained from a mixture of CH_2Cl_2–H_2O (30:70), mp 218–221°C. IR ν cm^{-1}:3422 (N–H), 2926 (C–H), 1698 (C=N), 1636, 1542 (C=C), 1386, 1282 (C–N). MS, *m/z* (%): 189.4 (100%). $C_9H_{11}N_5$ (189.4): calcd. C, 57.14; N, 37.03; H, 5.82; found: C, 57.03; N, 36.80; H, 5.84.

From the aqueous fraction, colorless crystals of **2b** were obtained, 92 mg (32%), mp 273–275°C. IR ν cm^{-1}: 3456 (N–H), 1636 (C=N^+), 1570, 1482 (C=C). MS, *m/z* (%):186.2 (100%). $C_{10}H_{14}N_5I$ (331.6): calcd. C, 36.27; N, 21.15; H, 4.26; found: C, 36.96; N, 21.81; H, 4.40.

*[2-Guanidinium-1-methyl-3-hydro-benzimidazole]chloride (***2c***).* To a solution of 142 mg (0.75 mmol) of **2a** dissolved in 10 mL of THF, 0.05 mL of HCl (37%) was added, and the mixture was stirred for 30 minutes at 27°C. The solvent was evaporated in vacuum. A beige solid was obtained, 168 mg (100%), mp 219–221°C. IR ν cm^{-1}: 3280 (N–H), 2595 (NH^+), 1684 (C=N). MS, *m/z* (%):M^+ 189.0 (100%).

*[2-Guanidinium-1,10-dihydro-benzimidazole]acetate (***3***).* To a hot solution of 175 mg (1 mmol) of **1a** in 15 mL of methanol was added a solution of 268 mg (1 mmol of $Mn(CH_3COO)_3(H_2O)_2$) in 15 mL of methanol. This mixture was warmed for 30 minutes, and a green solid was obtained. This solid was dissolved in 20 mL of water, and after two weeks, amber crystals were obtained. 30 mg (17%), mp 209–211°C. IR ν cm^{-1}: 3350 (N–H), 2600 (NH^+), 1700 (C=N^+), 1630 (C=N), 1550 (C=C), 1280 (C=N). MS, *m/z* (%): 176.2 (12%), 175.2 (100%). $C_{10}H_{10}N_5O_2.H_2O$ (250.2): calcd. C, 47.43; N, 27.65; H, 5.92; found: C, 47.50; N, 28.04; H, 5.97.

*2-Guanidino-1-hydro-3-borane-benzimidazole (***4a***).* A solution of 150 mg (0.86 mmol) of **1a** in 30 mL of dry THF was reacted with 0.4 mL of BH_3-THF (2.4 M) for 30 minutes at 0°C. The solvent was evaporated in vacuum (0.05 mmHg). The product was a yellow unstable solid obtained in quantitative yield. Mp 297°C. IR ν cm^{-1}: 2358 (B–H). ^{11}B (DMSO-d6): $\delta = -20.50$. MS *m/z* (%): 185.4 (3%), 175.2 (9%), 17.9 (100%).

*2-Guanidino-1-methyl-3-borane-benzimidazole (***4b***).* A solution of 150 mg (0.79 mmol) of **2a** in 5 mL of dry THF was reacted with 0.7 mL of BH_3-THF (2.0 M) for 30 minutes at 0°C. The solvent was evaporated in vacuum (0.05 mmHg). The product was a yellow unstable solid obtained in quantitative yield. ^{11}B (DMSO-d6): $\delta = -21.9$

*(2-Guanidinobenzimidazole)dimethyltin (***5***).* A solution of 250 mg (1.43 mmol) of **1a** in 50 mL of dry THF was added to 314 mg of $Sn(CH_3)_2Cl_2$ dissolved in 10 mL of methanol and 380 mg of K_2CO_3. The mixture was refluxed for 5 hours and filtered. The THF solution was evaporated in vacuo, to give a white solid (94.8%), mp 238–240°C. IR ν cm^{-1}: 3244, 3182 (N–H), 1612, 1572 (C=C), 772 (Sn–O). ^{119}Sn NMR (DMSO-d6):$\delta = -202.95$. MS *m/z* (%): [MH^+–CH_3] 344.1 (1%), 296.9 (1%), 284.2 (1%), 283.2 (1%), 158.2 (100%).

[bis(2-Guanidino-10-hydro-benzimidazole)-nickel(II)] **6**. A solution of 1.835 g (5 mmol) of $NiCO_3$ $2Ni(OH)_2$ $4H_2O$ in 60 mL of hot water was added to a hot solution of 876.0 mg (5 mmol) of **1a** in 40 mL of methanol. The green solution was heated and stirred for 30 minutes. After this time, the solution became reddish, and it was set aside for a week. Reddish crystals were obtained. They were removed by filtration and dried in vacuo. IR ν cm^{-1}: 3330 (N–H), 1670 (C=N), 1620 (C=N), 1580 (C=N). $C_{17}H_{22}N_{10}ONi$ (441.12): calcd. C, 46.29; N, 31.75; H, 5.03; found: C, 46.47; N, 32.54; H, 4.80.

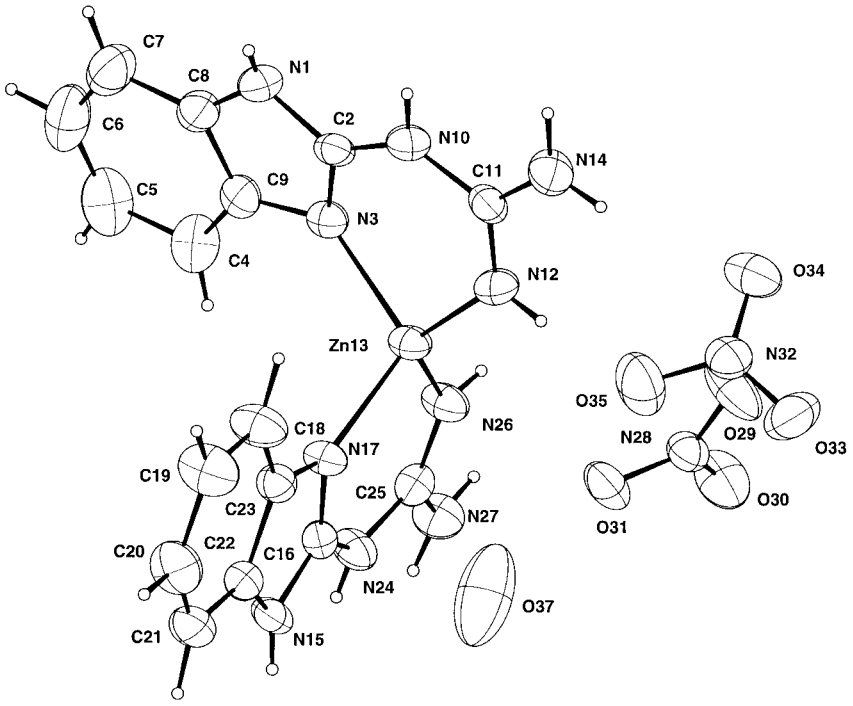


FIGURE 11 X-ray diffraction structure of compound **7.**

TABLE 12. Selected Bonds Lengths (Å) and Angles (Å) for **7**

Bond Lengths		*Bond Lengths*	
N(1)-C(2)	1.338(7)	N(17)-C(16)	1.313(5)
N(3)-C(2)	1.321(6)	N(17)-C(23)	1.384(7)
N(10)-C(2)	1.360(7)	N(24)-C(16)	1.374(8)
N(10)-C(11)	1.367(6)	N(24)-C(25)	1.368(6)
N(12)-C(11)	1.288(6)	N(26)-C(25)	1.283(6)
N(14)-C(11)	1.328(6)	N(27)-C(25)	1.339(6)
N(1)-C(8)	1.369(7)	Ni(13)-N(17)	1.987(4)
N(3)-C(9)	1.394(6)	Ni(13)-N(3)	1.996(4)
N(15)-C(16)	1.344(6)	Ni(13)-N(26)	1.953(4)
N(15)-C(22)	1.392(6)	Ni(13)-N(12)	1.942(4)
Bond Angles		*Bond Angles*	
N(1)-C(2)-N(3)	112.8(5)	N(12)-Zn(13)-N(26)	129.5(2)
N(1)-C(2)-N(10)	121.8(5)	N(24)-C(25)-N(27)	114.3(5)
N(1)-C(8)-C(7)	132.0(6)	N(3)-Zn(13)-N(17)	110.0(2)
N(1)-C(8)-C(9)	105.6(5)	N(3)-Zn(13)-N(12)	91.9(2)
N(3)-C(9)-C(4)	130.5(5)	N(3)-Zn(13)-N(26)	116.7(2)
N(3)-C(9)-C(8)	109.4(5)	N(26)-C(25)-N(27)	123.8(5)
N(10)-C(11)-N(12)	121.4(5)	C(16)-N(15)-C(22)	107.3(4)
N(10)-C(11)-N(14)	113.9(5)	C(16)-N(24)-C(25)	127.9(4)
N(12)-C(11)-N(14)	124.6(5)	C(16)-N(17)-C(23)	105.0(4)
C(2)-N(1)-C(8)	107.7(4)	N(3)-C(2)-N(10)	125.4(5)
C(2)-N(3)-C(9)	104.6(4)	N(15)-C(16)-N(24)	121.3(4)
C(2)-N(10)-C(11)	129.0(4)	N(15)-C(22)-C(21)	132.2(5)
N(17)-C(23)-C(22)	109.7(4)	N(15)-C(16)-N(17)	112.8(4)
N(17)-C(16)-N(240)	125.8(4)	N(15)-C(22)-C(23)	105.2(4)
N(17)-C(23)-C(18)	130.1(4)	N(24)-C(25)-N(26)	121.9(5)

[bis(2-Guanidino-1,10-dihydro-benzimidazole)zinc(II)] Nitrate **7**. A solution of 87.6 mg (1 mmol) of **1a** in 15 mL of hot methanol was added to a hot solution of 297 mg of $Zn(NO_3)_2$. H_2O in 15 mL of methanol. The solution was heated and stirred for 30 minutes, then set aside for a week. White crystals were obtained. They were removed by filtration and dried in vacuum. One crystal was used for the X-ray diffraction study. IR ν cm^{-1}: 3326, 3202 (N–H), 1670 (C=N^+), 1558, 1490 (C=C), 1380 (C–N). $C_{14}H_{18}N_{12}O_{6.}H_2O$: calcd. C, 34.45; N, 30.13; H, 3.61; found: C, 35.04; N, 29.39; H, 3.36.

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