A theoretical study of the parent N*H*-benzazoles (benzimidazoles, indazoles and benzotriazoles): geometries, energies, acidity and basicity, NMR properties and molecular electrostatic potentials

Ibon Alkorta,[a]* Goar Sánchez-Sanz,[a] Cristina Trujillo,[a] José Elguero,[a]
and Rosa M. Claramunt[b]

[a] *Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain*
[b] *Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, UNED,*
Senda del Rey 9, E-28040 Madrid, Spain
E-mail: *ibon@iqm.csic.es*

Dedicated to Prof. Anthony J. Arduengo on the occasion of his 60th anniversary

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Abstract

The three parent N*H*-benzazoles, benzimidazole, indazole and benzotriazole, have been studied theoretically at the B3LYP/6-311++G(d,p) level. Optimized geometries have been compared with those obtained by X-ray crystallography, energies with studies about tautomerism, acid-base properties with pK_as, and chemical shifts with those reported in the literature. As aromaticity probe, Schleyer's Nuclear Independent Chemical Shifts (NICS) were used and represented in two 3D isosurfaces of the electron density.

Keywords: Benzimidazole, indazole, benzotriazole, tautomerism, acid-base equilibria, NMR, Nuclear Independent Chemical Shifts, carbenes

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Introduction

Although biological properties will not be reported, it is useful to note that the three heterocycles are very different in this respect. Limiting discussion to the NH-derivatives, benzimidazoles are the most natural and relevant in biology (for instance, 5,6-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin B_{12}),[1] indazoles in medicinal chemistry,[2] while benzotriazoles are less important.[3] On the other hand, concerning their use as materials, benzimidazole appears to be the most used,[4] but there are also interesting applications for indazoles[5] and benzotriazoles.[6]

Benzazoles bearing no substituents on the N atoms have been the subject of a large number of theoretical papers covering a wide range of levels for benzimidazoles,[7] indazoles[8] and benzotriazoles,[9] the more recent articles using higher levels. None of these publications covers the three heterocycles although some of them include substituted derivatives. In the past, to report literature values (including several from ourselves) and to compare them to those calculated in this study was common usage. Today this is a useless exercise because the methodological approaches are well established. Therefore, we will cite and discuss only the references that deserve our attention. There is also much experimental information about benzazoles that will be reported when comparing calculations and experiments.

The present work consists in the study of the sixteen compounds reported in Figures 1 (benzimidazoles), 2 (indazoles) and 3 (benzotriazoles).

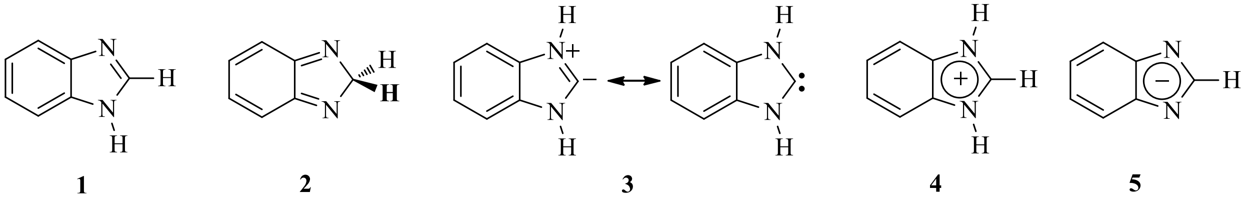


Figure 1. Benzimidazoles: 1*H* (**1**), 2*H* (**2**), carbene (**3**), benzimidazolium cation (**4**) and benzimidazolate anion (**5**).

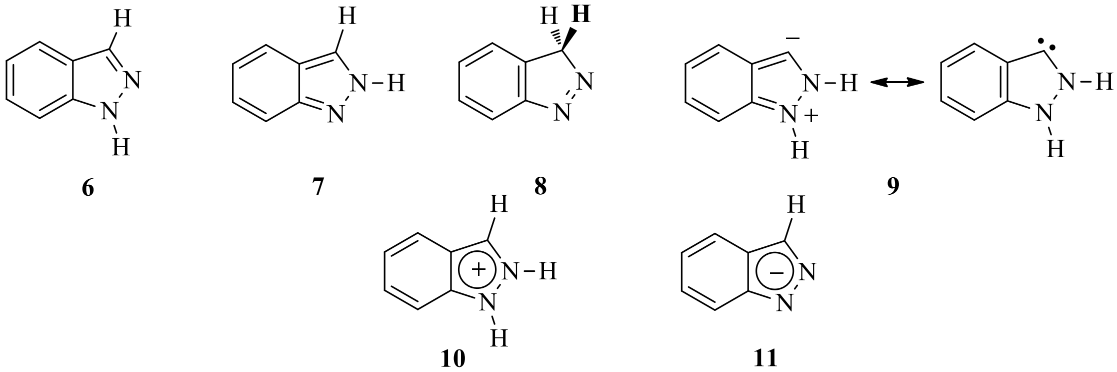


Figure 2. Indazoles: 1*H* (**6**), 2*H* (**7**), 3*H* (**8**), carbene (**9**), indazolium cation (**10**) and indazolate anion (**11**).

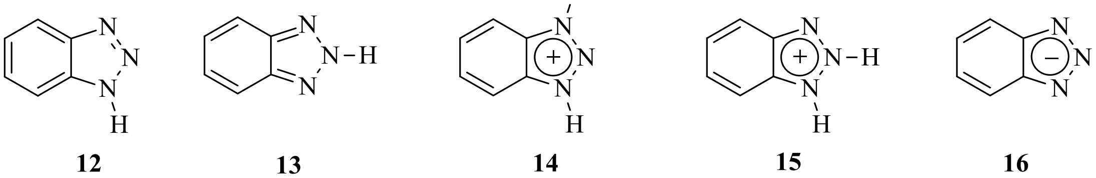


Figure 3. Benzotriazoles: 1*H* (**12**), 2*H* (**13**), 1,3-di*H* benzotriazolium cation (**14**), 1,2-di*H* benzotriazolium cation (**15**) and benzotriazolate anion (**16**).

The originality of the present work is to include amongst the neutral molecules the non-aromatic tautomers **2** and **8**, as well as Arduengo's heterocyclic carbenes[10] **3** (benzimidazol-2-ylidene) and **9** (indazol-3-ylidene). Cations and anions were studied to allow access to basicity and acidity properties.

Computational details

The geometry of the systems has been optimized at the B3LYP[11,12]/6-311++G(d,p)[13] computational level. Frequencies calculations have been carried out to confirm that the structures obtained correspond to energetic minima. All the calculations have been performed with the Gaussian-09 program.[14]

The theoretical absolute shieldings (σ, ppm) and NICS values (ppm)[15] were calculated using the GIAO method[16,17] on the B3LYP/6-311++G(d,p) geometries. To study the spatial distribution of the NICS, their values have been calculated on a 3D cubic grid of 12 Å sides following the procedure described by Stanger.[18] The points in the grid are located at 0.2 Å one from other in the three spatial directions. The result is a cube with 226981 NICS values, which, in the next step, have been represented within the electron density isosurfaces of 0.05 and 0.001 au using the WFA program.[19] All the calculations have been carried out with the Gaussian 09 facilities.

Results and Discussion

Geometries

First we will compare the calculated geometries (Table 1) with those reported in the Cambridge Structural Data base (CSD). The structures and the corresponding Refcodes are reported in Figure 4.[20]

We limit the discussion to the five-membered ring (the azole moiety) and only to non-hydrogen atoms (C and N) since the distances involving H atoms are underestimated in X-ray crystallography.[21] For compounds **4**, **14** and **16**, with C_{2v} symmetry, the experimental values have been averaged.

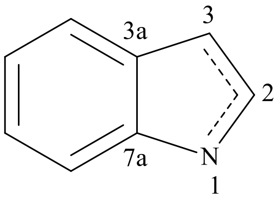
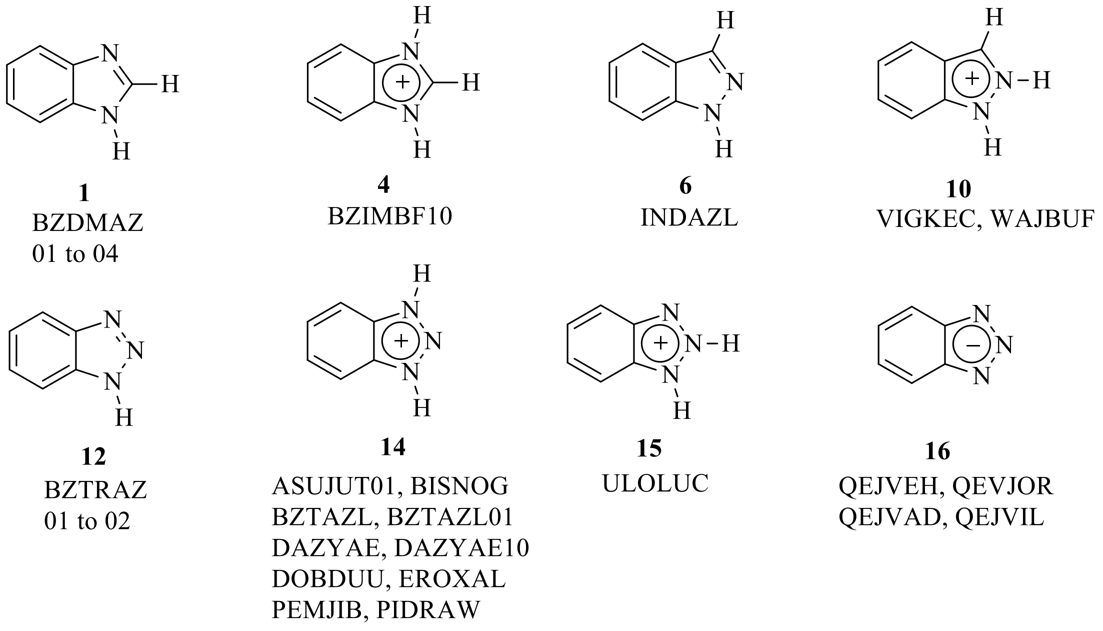


Table 1. Comparison between calculated (above) and average experimental X-ray geometries (below). Distances in Ångstroms (Å), angles in degrees (º)

	bond lengths					bond angles				
Compd**.**	**1-2**	**2-3**	**3-3a**	**3a-7a**	**7a-1**	**123**	**233a**	**33a7a**	**3a7a1**	**7a12**
Benzimidazoles										
(**1**) calc.	1.377	1.304	1.389	1.414	1.385	113.5	105.0	110.3	104.5	106.8
(**1**) exp.	1.345	1.315	1.395	1.396	1.378	114.1	104.1	109.6	105.5	106.0
(**4**) calc.	1.333	1.333	1.398	1.404	1.398	109.0	109.6	105.9	105.9	109.6
(**4**) exp.	1.327	1.327	1.382	1.398	1.382	109.0	109.4	106.0	106.0	109.4
Indazoles										
(**6**) calc.	1.358	1.318	1.429	1.416	1.367	106.1	111.5	104.3	105.6	112.5
(**6**) exp.[a]	1.375	1.304	1.414	1.404	1.355	106.0	112.4	103.6	107.4	110.8
(**10**) calc.	1.358	1.334	1.403	1.426	1.364	110.6	107.9	106.0	107.1	108.5
(**10**) exp.	1.342	1.321	1.408	1.414	1.356	111.8	107.2	105.4	108.0	107.6
Benzotriazoles										
(**12**) calc.	1.362	1.287	1.380	1.408	1.364	108.8	108.7	108.6	103.0	110.8
(**12**) exp.	1.343	1.309	1.370	1.386	1.355	108.5	108.2	108.5	104.2	110.7
(**14**) calc.	1.309	1.309	1.376	1.408	1.376	105.1	113.4	104.1	104.1	113.4
(**14**) exp.	1.312	1.312	1.362	1.391	1.362	105.3	112.6	104.8	104.8	112.6
(**15**) calc.	1.351	1.291	1.353	1.426	1.359	113.7	105.6	109.4	104.3	106.9
(**15**) exp.	1.317	1.311	1.387	1.378	1.364	106.8	110.4	105.9	104.9	112.0
(**16**) calc.	1.338	1.338	1.361	1.422	1.361	113.1	106.1	107.3	107.3	106.1
(**16**) exp.	1.330	1.330	1.360	1.389	1.360	111.8	106.7	107.4	107.4	106.7

[a] Including a recent determination of the structure of indazole still not part of the CSD.[8j]



1 BZDMAZ 01 to 04

4 BZIMBF10

6 INDAZL

10 VIGKEC, WAJBUF

12 BZTRAZ 01 to 02

14 ASUJUT01, BISNOG BZTAZL, BZTAZL01 DAZYAE, DAZYAE10 DOBDUU, EROXAL PEMJIB, PIDRAW

15 ULOLUC

16 QEJVEH, QEVJOR QEJVAD, QEJVIL

Figure 4. Structures determined by X-ray crystallography.

Excluding the experimental structure **15** (ULOLUC) for the reasons explained below, the following relationships are found between experimental and calculated values of Table 1:

$$\text{Exp. (Å)} = (0.22\pm0.06) + (0.83\pm0.04)\ \text{calc. (Å)},\ n = 35,\ R^2 = 0.91 \qquad \textbf{(1)}$$

$$\text{Exp. (}^{\text{o}}\text{)} = (11.5\pm4.5) + (0.89\pm0.04)\ \text{calc. (}^{\text{o}}\text{)},\ n = 35,\ R^2 = 0.93 \qquad \textbf{(2)}$$

The worst points according to eq. 1 are the 1-2 distances in benzimidazole (**1**) (–0.022 Å) and in indazole (**6**) (+0.024 Å) and those corresponding to eq. 2 are the 2-3-3a angle of benzimidazole (**1**) (–1.2 º) and the 3a-7a-1 angle of indazole (**6**) (+1.6 º).

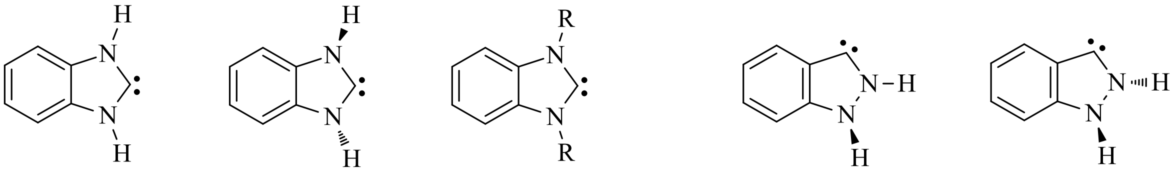
Regarding the structure of **15**, we must note that it was the only exception to the general observation that protonation of benzotriazole (**12**) leads to the 1,3-diH cation **14**. A simple examination of Table 1 data reveals that the published structure was wrong and that the cation should have the structure **14**. According to equations 1 and 2 the 1,2-di*H* cation **15** should have the following geometry: 1.345 (1-2), 1.296 (2-3), 1.347 (3-3a), 1.408 (3a-7a), 1.352 Å (7a-1), 113.1 (123), 105.8 (233a), 109.2 (33a7a), 104.7 (3a7a1), 107.0º (7a12), very different from the reported[22] figures. The structure of ULOLUC contains seven benzotriazolium cations, which is a strange number, two molecules of ethanol and five molecules of water; besides, the anions are very big, $Mo_{12}O_{40}P^{3-}$ and $Mo_{12}O_{40}P^{4-}$, all of this can explain the error in locating the proton.

Two of the compounds show polymorphism: benzimidazole (**1**) and benzotriazole (**12**).[23,24] In the same year (2005), Krawczyk and Gdaniek described the structure of second polymorphs of benzimidazole [25] and benzotriazole.[26] The previous structures of these compounds were determined in the 1973-1974 period.[27,28] The old benzimidazole polymorph (α) is stable while the new polymorph (β) is metastable at room temperature. In both polymorphs, benzimidazole molecules are connected into polymeric chains via N–H···N hydrogen bonds (HBs). However, the mode of aromatic ring interactions differs significantly in the two crystalline forms. In the α form, the molecules show edge-to-face interactions, whereas in the new β form, a sandwich–herringbone arrangement of the aromatic molecules is observed.

The α polymorph of **12** consists of 1*H*-tautomers. Three out of the four symmetry-independent molecules are connected into polymeric chains via N–H···N HBs, whereas the fourth molecule is attached to the chain via N–H···N and C–H···N interactions. In the β polymorph all molecules correspond to the 1*H*-tautomer **12**. A cyclic decamer (a centrosymmetric 10-membered ring) is formed via N–H···N HBs but the HBs in eight molecules use the N(3) lone pair, and in two the N(2) lone pair.

The structure of indazole (**6**) deserves further comment. The Escande and Lapasset structure shows that the H of the NH group is out-of-plane of the remaining atoms, therefore having diastereogenic center on the N-1 atom (at least, in the crystal where no N inversion occurs).[29] This point was verified recently,[8j] because it could be the reason why **6** crystallizes in a non-centrosymmetric group ($P2_1$); note that **6** shows spontaneous resolution (conglomerate).

Concerning the geometries without experimental counterparts, the most interesting are those of the carbenes (Figure 5). θ is defined as the dihedral H–N···N–H angle for **3** and H–N–N–H angle for **9**.



3, singlet q = 0.0º

3, triplet q = 136.4º

3' q = 5.3º

9, singlet q = 53.4º

9, triplet q = 109.7º

Figure 5. Structures of the carbenes. Those of **3′** were determined by X-ray crystallography and θ = 5.3º correspond to the average.

The following structures of type **3′** are found in the CSD (some of them having several independent benzimidazol-2-ylidene molecules, in all, ten different geometries):[20] LOGVUY, POYKOE, RENYEP, RENYIT, RENZEQ, SIRJIN and YUXJUX. The average value of θ is 5.3º with one of the structures being planar (θ = 0.0º). These geometries clearly belong to singlet carbenes. No data are available for the indazol-3-ylidenes related to **9**.

Energies

We report in Table 2 the energies corresponding to compounds **1** to **16**. These energies will be discussed in relation to tautomerism and to acid-base properties.

Table 2. Energies (absolute in hartree, relative in kJ mol$^{–1}$) and dipole moments (D) of the minima. The Proton Affinity, PA, and acidity are also indicated

Compound	$E_{electronic}$	$E_{electronic}$ + ZPE	Dipole	E_{rel}	E_{rel}+ZPE
Benzimidazoles					
1	–379.96728	–379.84964	3.54	0.0	0.0
2	–379.91699	–379.80081	2.19	132.0	128.2
3 singlet	–379.92849	–379.81028	2.46	101.8	103.3
3 triplet	–379.80386	–379.68895	0.88	429.1	421.9
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4	–380.34313	–380.21144	4.89		PA (kJ mol$^{–1}$) = – 949.9
5	–379.41226	–379.30831	3.34		ΔHº (acidity) = 1421.2
Indazoles					
6	–379.94402	–379.82632	1.84	0.0	0.0
7	–379.93619	–379.81831	2.55	20.5	21.0
8	–379.91226	–379.79611	3.86	83.4	79.3
9 singlet	–379.87267	–379.75568	3.88	187.3	185.5
9 triplet	–379.79570	–379.68033	1.19	389.4	383.3
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10	–380.30077	–380.17048	5.05		PA (kJ mol$^{–1}$) = –903.6
11	–379.37684	–379.27401	5.59		ΔHº(acidity) =1450.1
Benzotriazoles					
12	–395.97098	–395.86564	4.20	0.8	0.0
13	–395.97129	–395.86472	0.28	0.0	2.4
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14	–396.33225	–396.21243	1.19	0.0	PA (kJ mol$^{–1}$) = –910.5
15	–396.31146	–396.19314	4.67	50.7	PA (kJ mol$^{–1}$) = –859.8
16	–395.42371	–395.33214	6.45		ΔHº(acidity) =1400.7

Tautomerism

For neutral molecules the stability decreases in the order **1** > **2** > **3** (singlet) > **3** (triplet) (benzimidazole); **6** > **7** > **8** > **9** (singlet) > **9** (triplet) (indazole); **12** ≈ **13** (benzotriazole). For benzotriazolium cations, the order is **14** > **15**.

Although triplet carbenes are known,[30] in all reported heterocyclic derivatives triplet carbenes are appreciably less stable than singlet carbenes.[31-33]

Experimental results concern only the N*H*-tautomers and they confirm that **6** > **7**, **12** ≈ **13**. The case of the indazole **6**/**7** pair is well known of old.[34a] The case of the benzotriazole 1*H*/2*H* (**12**/**13**) pair, although discussed in Minkin's review,[34] has been revisited many times, with the conclusion that both tautomers have similar stabilities and that the actual situation depends on the environment.[9]

The benzotriazolium cations **14**/**15** are a less studied case. Catalán *et al*. favored the 1,3-di*H* tautomer **14** based on thermodynamic considerations.[9a] Others authors have drawn the cation with the 1,3-di*H* structure **14** or with the 1,2-di*H* structure **15**, but without any proof.[35,36] In the solid state (see "Geometries" section) only cations **14** have been reported.

The tautomerism of indazoles and benzotriazoles is related to their aromaticity and to lone pair/lone pair repulsion on adjacent N atoms (for instance in **12**).[8b,9a,b,37,38]

Acid-base equilibria

From two sources we have found data relevant to this part of our paper. In the National Institute of Standards and Technology (NIST) database the following values are reported:[39] proton affinity, PA, (benzimidazole) = –953.8; PA (indazole) = –900.8; acidity ΔH° (indazole) = 1457; ΔH° (benzotriazole) = 1415 kJ mol^{-1}. In our review[40] of acid-base properties of azoles the following pK_as are reported: basicity: benzimidazole 5.56, indazole 1.04, benzotriazole 1.6; acidity: benzimidazole 12.86, indazole 13.86, benzotriazole 8.38. Comparing these values with the calculated ones reported in Table 2, equations 3 - 5 are obtained.

$$\text{PA}_{\text{exp}} = (3.8\pm2.6) + (1.005\pm0.002)\ \text{PA}_{\text{calc}},\ n = 4,\ R^2 = 0.999991 \qquad \textbf{(3)}$$

$$\text{p}K_{\text{a}}\ (\text{basic}) = -(139.1\pm72.7) + (0.099\pm0.002)\ \text{PA}_{\text{calc}},\ n = 3,\ R^2 = 0.9994 \qquad \textbf{(4)}$$

$$\text{p}K_{\text{a}}\ (\text{acid}) = -(88.1\pm2.2) - (0.106\pm0.002)\ \text{PA}_{\text{calc}},\ n = 3,\ R^2 = 0.811 \qquad \textbf{(5)}$$

Equations 3 and 4 are excellent; however, equation 5 is far from acceptable. The values of the pK_as determined in water that correspond to deprotonation (from neutral to anion) are probably contaminated by solvent and counterion effects. The fact that the pK_as of azoles and benzazoles can be calculated theoretically with accuracy is well established.[9k,41]

Chemical shifts

All the calculated absolute shieldings as well as all the known chemical shifts are reported in Table 3. Due to fast prototropic exchange between the N atoms, some values of compounds **1**, **12** and **15** in solution have been averaged.

Table 3a.[a] Calculated absolute shieldings (σ, ppm) and experimental chemical shifts (δ, ppm)

Comp'd	Atom	σ	Average σ	Exp. δ solution (300 K)	Exp. δ solid (300 K)	Exp. δ CH_3OH (178 K)
Benzimidazoles						
1	N-1	100.50	36.23	-185[42]		
	N-3	-28.04			--	-153.5
	C-2	40.90		141.5[43]	142.6[44,45]	143.0
	C-3a	32.46	38.54	137.9	143.0	143.0
	C-7a	44.62			136.1	134.4
	C-4	56.06	63.04	115.4	119.9	119.7
	C-7	70.03			112.2	113.7
	C-5	56.06	55.46	122.9	122.1	123.9
	C-6	54.87			123.0	124.7
4	N-1/3	85.54				
	C-2	45.11		137.0[46]		
	C3a/7a	48.29		128.4		
	C-4/7	64.10		113.3		
	C-5/6	44.00		126.3		
Indazoles						
6	N-1	62.04		–200.6[47]	–196.6[44]	
	N-2	–90.90		–65.1	–77.5	
	C-3	43.71		133.4[48]	134.4[44,45]	
	C-3a	53.02		122.8	123.3	
	C-4	57.27		120.4	121.8	
	C-5	57.58		120.1	121.8	
	C-6	51.89		125.8	126.6	
	C-7	70.92		110.0	111.6	
	C-7a	37.49		139.9	140.9	
10	N-1	87.53				
	N-2	65.29				
	C-3	45.18		129.8[46,48]		
	C-3a	57.50		118.4		
	C-4	52.37		121.4		
	C-5	46.51		124.7		
	C-6	34.49		140.2		
	C-7	68.97		109.9		
	C-7a	37.30		138.1		

Benzotriazoles					
12	N-1	25.34	–52.62	–96.7[42]	–157.6[44,49]
	N-3	–130.58			–56.4
	N-2	–157.44		–7.5	–24.5
	C-3a	31.73	38.51	139.8[49]	142.5[45]
	C-7a	45.29			132.7
	C-4	56.53	63.98	115.4	115.5
	C-7	71.42			110.7
	C-5	56.33	53.50	125.9	123.4
	C-6	50.66			123.4
14	N-1/3	20.11		–158.0[49]	
	N-2	–129.32		–29.4	
	C-3a/7a	44.00		133.8[49]	135.0[35]
	C-4/7	65.43		113.2	115.1
	C-5/6	42.20		131.9	131.8
15	N-1	50.30		–34.80	
	N-3	–119.91			
	N-2	21.91			
	C-3a	34.63		40.10	
	C-7a	45.57			
	C-4	1.81		60.54	
	C-7	69.26			
	C-5	42.64		37.45	
	C-6	32.26			

[a] Here we list only the compounds for which experimental data are available.

Table 3b.[b] Calculated absolute shieldings (σ, ppm)

Compound	Atom	σ	Compound	Atom	σ
Benzimidazoles			Indazoles (cont)		
2	N-1/3	-168.54	**9** singlet	N-1	70.11
	C-2	83.84		N-2	49.01
	C3a/7a	13.06		C-3	–75.62
	C-4/7	45.76		C-3a	38.96
	C-5/6	43.78		C-4	42.07
3 singlet	N-1/3	68.59		C-5	56.23
	C-2	–55.68		C-6	46.55
	C3a/7a	43.69		C-7	69.94
	C-4/7	69.43		C-7a	36.11
	C-5/6	56.45	**9** triplet	N-1	121.33

3 triplet	N-1/3	144.55
	C-2	66.23
	C3a/7a	40.54
	C-4/7	65.47
	C-5/6	54.40
5	N-1/3	–11.10
	C-2	22.38
	C3a/7a	26.59
	C-4/7	63.32
	C-5/6	67.28
Indazoles		
7	N-1	–62.24
	N-2	26.88
	C-3	59.49
	C-3a	55.42
	C-4	57.95
	C-5	55.35
	C-6	52.20
	C-7	58.00
	C-7a	27.54
8	N-1	–279.24
	N-2	–282.41
	C-3	98.90
	C-3a	38.28
	C-4	56.72
	C-5	49.21
	C-6	49.90
	C-7	55.78
	C-7a	17.70
	N-2	113.72
	C-3	26.76
	C-3a	56.78
	C-4	67.36
	C-5	51.73
	C-6	58.71
	C-7	70.88
	C-7a	25.95
11	N-1	–98.53
	N-2	–154.82
	C-3	50.83
	C-3a	51.66
	C-4	62.82
	C-5	68.98
	C-6	66.10
	C-7	62.56
	C-7a	25.00
Benzotriazoles		
13	N-1/3	–90.75
	N-2	–17.10
	C-3a/7a	33.04
	C-4/7	58.30
	C-5/6	51.43
16	N-1/3	–112.96
	N-2	–212.55
	C-3a/7a	29.68
	C-4/7	63.32
	C-5/6	65.62
	C-3a/7a	29.68

[b] This table lists calculated values of σ for those compounds without experimental data.

The data of Table 3 when analyzed afford the following equations:

$$\delta^{15}\text{N (solid)} = -(145.7\pm3.8) - (0.740\pm0.036)\ \sigma^{15}\text{N},\ n = 5,\ R^2 = 0.993 \quad \textbf{(6)}$$

$$\delta^{15}\text{N (solution, average)} = -(145.8\pm1.8) - (0.891\pm0.020)\ \sigma^{15}\text{N},\ n = 7,\ R^2 = 0.997 \quad \textbf{(7)}$$

$$\delta^{13}\text{C (solid)} = (172.1\pm2.7) - (0.872\pm0.047)\ \sigma^{13}\text{C},\ n = 23,\ R^2 = 0.932 \quad \textbf{(8)}$$

$$\delta^{13}\text{C (solid)} = (170.4\pm2.4) - (0.854\pm0.046)\ \sigma^{13}\text{C} + (7.1\pm2.5)\ \text{C-2},\ n = 23,\ R^2 = 0.952 \quad \mathbf{(9)}$$

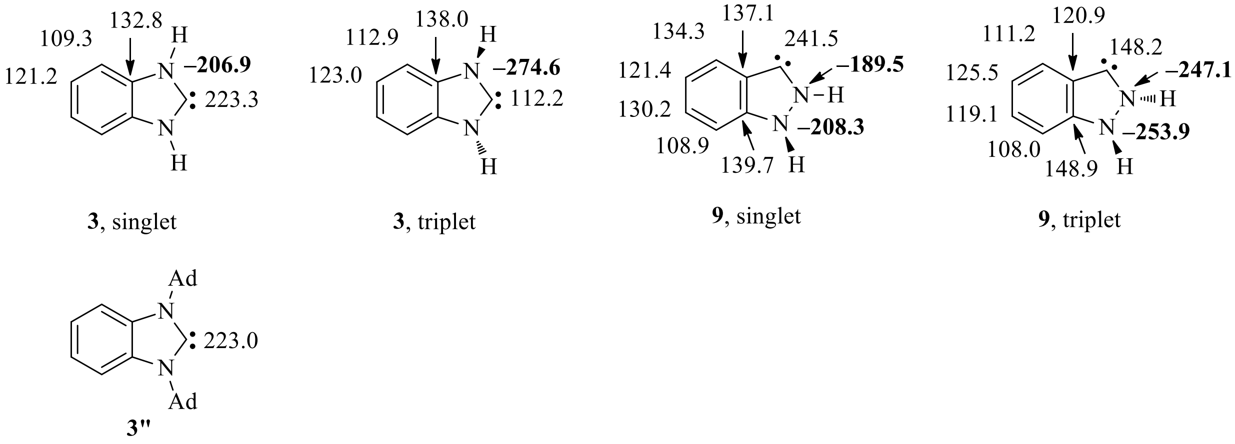
$$\delta^{13}\text{C (MeOH)} = (174.2\pm5.8) - (0.893\pm0.112)\ \sigma^{13}\text{C},\ n = 27,\ R^2 = 0.927 \quad \mathbf{(10)}$$

$$\delta^{13}\text{C (MeOH)} = (169.3\pm4.2) - (0.817\pm0.078)\ \sigma^{13}\text{C} + (7.1\pm2.6)\ \text{C-2},\ n = 7,\ R^2 = 0.975 \quad \mathbf{(11)}$$

$$\delta^{13}\text{C (solution, average)} = (172.6\pm2.5) - (0.911\pm0.049)\ \sigma^{13}\text{C},\ n = 28,\ R^2 = 0.930 \quad \mathbf{(12)}$$

$$\delta^{13}\text{C (solution, average)} = (170.4\pm2.1) - (0.877\pm0.039)\ \sigma^{13}\text{C} + (6.6\pm1.6)\ \text{C-2},\ n = 28,\ R^2 = 0.959 \quad \mathbf{(13)}$$

Equations 9, 11, and 13 were calculated to afford a value for the carbon C-2 of benzimidazole, that systematically deviated by about 7 ppm. It appears that the B3LYP/6-311++G(d,p) cannot reproduce satisfactorily this atom, may be because it is situated between an N(H) pyrrole-like and an N pyridine-like nitrogen atom. An attempt to improve the results using GIAO/MP2/6-111++G(d,p) calculations failed.



3, singlet **3**, triplet **9**, singlet **9**, triplet

3″

Figure 6. Predicted (top) and experimental (bottom) ^{13}C and ^{15}N (bold) chemical shifts of singlet and triplet carbenes. Ad stands for 1-adamantyl.

Using equations 7 and 13 the following values are predicted for the carbenes **3** (benzimidazol-2-ylidene) and **9** (indazol-3-ylidene) in their singlet and triplet states (Figure 6). The chemical shifts are very different, including some carbons of the benzene ring, particularly in the case of **9**. The ^{13}C chemical shift of carbon C-2 of **3″** has been reported (223.0 ppm), leaving no doubt about **3** being a singlet.[31-33] In the case of **9**, the dimethyl derivative **9″** has been characterized by mass spectrometry but it is too labile to record its ^{13}C NMR spectrum.[50-52]

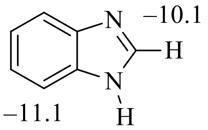
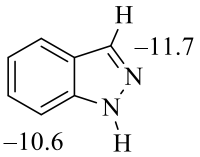
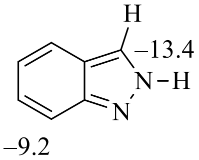
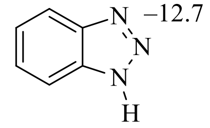
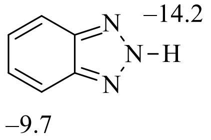
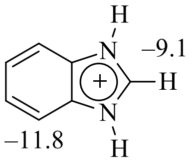
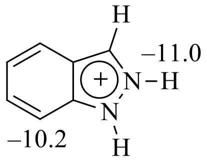
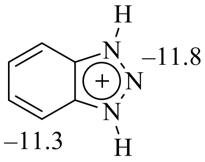
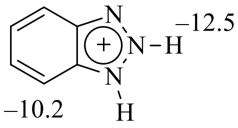
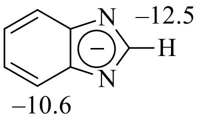
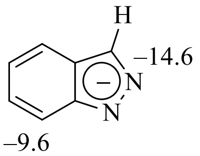
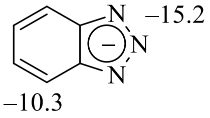
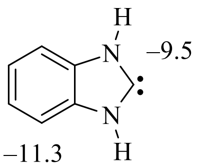
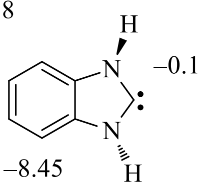
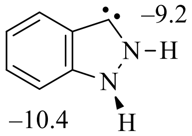
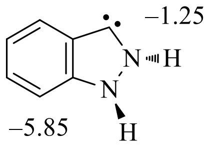
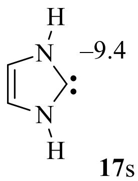
Aromaticity

We discuss the aromaticity of the compounds of the present work using Schleyer's NICS. We have calculated their values at 0, 1 and 2 Å (Table 4), but we will use the NICS(1) values as a good compromise between NICS(0), too close to the sigma frame, and NICS(2), less sensitive. For non-planar compounds, carbenes **3**t (triplet), **9**s (singlet) and **9**t (triplet), we have calculated the NICS above and below the ring plane. However, as the perturbation arises from H atoms, the values are very similar and in Figure 7 we have averaged their values. We also report the sum of the NICS of the 6- and the 5-membered rings (Σ, ppm).

Table 4. NICS values on both rings of benzazoles determined in the center of the ring at 0, 1 and 2 Å above the ring plane

	Six-membered ring			Five-membered ring		
	NICS(0)	NICS(1)	NICS(2)	NICS(0)	NICS(1)	NICS(2)
Neutrals						
1	–10.1	–11.1	–5.3	–11.4	–10.1	–4.3
6	–9.5	–10.6	–5.2	–12.9	–11.7	–4.7
7	–7.5	–9.2	–4.7	–15.6	–13.4	–5.3
12	–9.8	–11.0	–5.4	–13.0	–12.7	–5.1
13	–8.0	–9.7	–4.9	–15.4	–14.2	–5.5
Cations						
4	–10.9	–11.8	–5.3	–12.6	–9.1	–3.8
10	–8.5	–10.2	–5.0	–14.9	–11.0	–4.3
14	–10.2	–11.3	–5.4	–14.6	–11.8	–4.6
15	–8.4	–10.2	–5.1	–15.6	–12.5	–4.8
Anions						
5	–9.4	–10.6	–5.1	–11.2	–12.5	–5.3
11	–8.4	–9.6	–4.9	–13.3	–14.6	–5.9
16	–9.1	–10.3	–5.2	–13.1	–15.2	–6.0
Carbenes						
3s	–10.7	–11.3	–5.2	–10.6	–9.5	–3.9
3t (up)	–7.5	–8.4	–3.7	–3.1	–0.2	–0.4
3t (down)	–7.5	–8.5	–3.6	–3.1	0.0	0.0
9s (up)	–8.7	–10.5	–5.2	–9.3	–9.1	–3.9
9s (down)	–8.7	–10.3	–5.0	–9.3	–9.3	–3.9
9t (up)	–4.4	–6.0	–2.8	–4.7	–1.3	–0.3
9t (down)	–4.4	–5.7	–2.7	–4.7	–1.2	–0.3

Table 5. NICS(1) values (ppm) and sum of the NICS(1) values for both rings (Σ)

Benzimidazoles	Indazoles	Benzotriazoles
Neutral:  S = –21.2 **1**	 S = –22.3 **6**  S = –22.6 **7**	 S = –23.7 **12**  S = –23.9 **13**
Cations:  S = –20.9	 S = –21.2 **10**	 S = –23.1 **14**  S = –22.7 **15**
Anions:  S = –23.1 **5**	 S = –24.2 **11**	 S = –25.5 **16**
Carbenes:  S = –20.8 **3**s  S = –8.55 **3**t	 **9**s S = –19.6  **9**t S = –7.1	 **17**s

The values reported in Table 5 deserve several comments:

i) If we consider Σ as a descriptor of the aromaticity of the benzazoles, Σ increases in absolute value (the compound becomes more aromatic) in the order benzimidazole < indazole < benzotriazole and in the order cation < neutral < anion. Thus, the less aromatic is the cation benzimidazolium (**4**) and the most aromatic is the benzotriazolate anion (**16**). Martin *et al*. reported that, according to NICS approach, indazole is more aromatic than benzimidazole.[53] Novak *et al*. reported that the NICS of the 6-membered ring is lower for **13** than for **12**.[54]

ii) The singlet carbenes, **3**s and **9**s, are aromatic compounds with Σ values about –20 ppm similar to the cations, **4** and **10**. Using other aromaticity criteria, imidazol-2-ylidenes appear slightly less aromatic than imidazolium cations.[55] For Arduengo's *N*-heterocyclic carbene **17** a NICS(1) value of –9.4 ppm (Scheme 7) has been recently reported.[56]

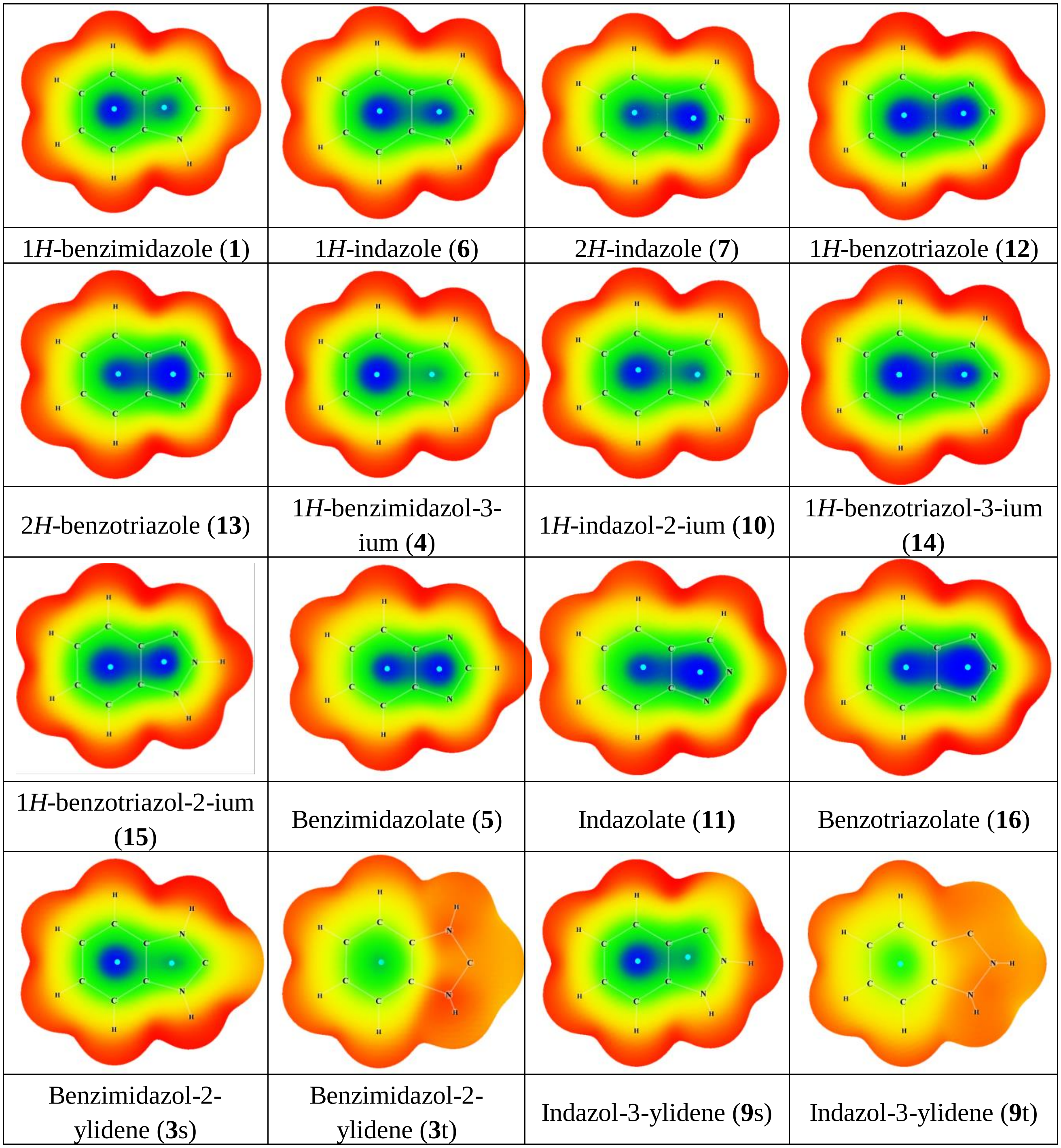
iii) The 6-membered ring is always aromatic but varies from –5.85 (**9**t) to –11.8 (**4**). Tautomerism affects the NICS of this ring, being greater in the more aromatic tautomer (benzenoid: **6**, **12**) than in the less aromatic tautomer (quinonoid: **7**, **13**). In singlet carbenes, NICS values of the 6-membered ring are similar to those of the corresponding cations. In triplet carbenes, the 6-membered ring suffers a great decrease in aromaticity, more in indazoles than in benzimidazoles probably related to the distance between the carbene and the benzene ring.

iv) Excluding triplet carbenes, the values of the NICS(1) of the 5-membered ring range from –9.1 (**4**) to –15.2 ppm (**16**), as reflected in the Σ values.

v) Triplet carbenes, **3**t and **9**t have non-aromatic 5-membered rings. This is a new and interesting result. It is known that between singlet and triplet states there is an inversion of aromaticity and antiaromaticity.[57] Here, we move from an aromatic singlet to a non-aromatic triplet.

We decided to use a technique we have recently developed to represent the NICS values on one van der Waals isosurface.[58] Figure 7 illustrates the NICS values on the electron density isosurface of 0.001 au (vdW). Blues areas correspond to regions with NICS values less than –5 ppm, while red ones belong to positive NICS values. For instance, similar distributions can be found in the 6-membered ring when comparing 1*H*-benzimidazole (**1**) and 1*H*-indazole (**6**), but some differences appear in the 5-membered ring. Thus, comparing **6** and **7**, the effect of the position of the NH proton, either on N-2 or on N-1, is observed. When the proton changes from N-2 to N-1, there is an enlargement of the negative area on the 5-membered ring concomitantly with a contraction of the area over the 6-membered ring. These effects are reflected in the minimum values on the vdW surface, which suffer an inversion from **6** (–6.2, –5.7 ppm, 6- and 5-membered rings, respectively) to **7** (–5.6, –6.4 ppm, 6- and 5-membered rings, respectively) (Table 6). The same features can be observed for the compounds **12** and **13**.

Cations **4** and **10**, present very similar NICS arrangement to those observed in the neutral parent molecules (**1** and **6**) with a main difference, the negative area on the 5-membered ring is considerably smaller that in the neutral ones. The protonation of **12** to afford **14** is accompanied by a slight decrease (in absolute value) of the minimum NICS value on the 5-membered ring (from –6.5 to –6.0 ppm), while that of the 6-membered ring remains almost constant. The same occurs in going from **13** to **15** that present slight differences, appreciable in both rings. In the comparison between **14** (1,3-diH) and **15** (1,2-diH), the effect of the position of the proton is again apparent, following the same pattern observed in the comparison between **6** and **7** (or between **12** and **13**).



1*H*-benzimidazole (**1**)
1*H*-indazole (**6**)
2*H*-indazole (**7**)
1*H*-benzotriazole (**12**)
2*H*-benzotriazole (**13**)
1*H*-benzimidazol-3-ium (**4**)
1*H*-indazol-2-ium (**10**)
1*H*-benzotriazol-3-ium (**14**)
1*H*-benzotriazol-2-ium (**15**)
Benzimidazolate (**5**)
Indazolate (**11**)
Benzotriazolate (**16**)
Benzimidazol-2-ylidene (**3**s)
Benzimidazol-2-ylidene (**3**t)
Indazol-3-ylidene (**9**s)
Indazol-3-ylidene (**9**t)

Figure 7. 3D representation of the NICS values (ppm) on the van der Waals surface (0.001 a.u.); NICS Color scheme: Blue < –5.0, Green > –5.0, Yellow > –2.5, Red > 0.0.

The comparison of the negative zones over the rings in the anions **5**, **11** and **16** shows the increasing negative NICS values on both rings in going from benzimidazolate to indazolate and to benzotriazolate, being this increase larger for the 5-membered ring than for the 6-membered ring.

The case of the singlet carbenes can be observed comparing the **3**s and **9**s compounds. The position of the carbene corresponds to the yellow region around the C atoms (C-2 and C-3), showing more negative values around it than in the vicinal C atoms. Finally, one interesting observation results from the comparison between singlet and triplet states. When the surfaces of **3**s and **3**t are examined, the increase of the NICS values is evident. The minimum located on the 6-membered ring becomes less deep (from –6.2 to –4.5 ppm, Table 6) and that over the 5-membered one completely disappears. Instead of the minima, a large positive NICS value area is present over the 5-membered ring. Similar, but enhanced features, are observed in the **9**s *vs*. **9**t comparison, where the variation of the 6-membered ring minimum is more pronounced (from –6.2 to –3.4 ppm). These are in agreement with the non-aromatic nature of the triplet carbenes discussed previously.

Table 6. Minimum NICS values on the van der Waals surfaces

Compound	Six-membered ring	Five-membered ring
1*H*-benzimidazole (**1**)	–6.3	–5.3
1*H*-indazole (**6**)	–6.2	–5.7
2*H*-indazole (**7**)	–5.6	–6.4
1*H*-benzotriazole (**12**)	–6.4	–6.5
2*H*-benzotriazole (**13**)	–5.8	–7.0
1*H*-benzimidazol-3-ium (**4**)	–6.6	–4.9
1*H*-indazol-2-ium (**10**)	–6.1	–5.3
1*H*-benzotriazol-3-ium (**14**)	–6.6	–6.0
1*H*-benzotriazol-2-ium (**15**)	–6.2	–6.3
Benzimidazolate (**5**)	–6.0	–6.3
Indazolate **(11)**	–5.7	–7.1
Benzotriazolate (**16**)	–6.1	–7.4
Benzimidazol-2-ylidene (**3**) singlet	–6.2	–4.8
Benzimidazol-2-ylidene (**3**) triplet [a]	–4.5(–4.4)	..
Indazol-3-ylidene (**9**) singlet [a]	–6.2(–6.0)	–4.8 (–4.8)
Indazol-3-ylidene (**9**) triplet [a]	–3.4(–3.3)	..

[a] Values correspond to up (down) positions over the ring.

Conclusions

Because here, for the first time, the most significant neutral (including Arduengo's carbenes), cationic and anionic structures of the three benzazoles have been compared, some interesting conclusions can be reached:

– Some errors in the literature concerning the position of N*H*-protons in one X-ray structure (ULOLUC) have been found.

– The triplets of benzimidazol-2-ylidene (**3**t) and indazol-3-ylidene (**9**t) are much higher in energy than the corresponding singlets, **3**s and **9**s. However, the gap is much larger in the benzimidazole series (318.6 kJ mol^{-1}) than in the indazole ones (197.8 kJ mol^{-1}); this results from the singlet being lower in energy (103.3 *vs*. 185.5 kJ mol^{-1}) and the triplet being higher in energy (421.9 *vs*. 383.3 kJ mol^{-1}), respectively.

– The calculated relative energies of the different tautomers agree with experimental results.

– The acid base properties of the three benzazoles are in excellent agreement with gas-phase measurements; for aqueous pK_as the calculations agree very well with the basicity but only poorly with the acidity.

– The correlations found between experimental chemical shifts and calculated absolute shieldings could be used to estimate the chemical shifts of the compounds where no data are available. For instance, the estimated values for the C-2 atoms in **3**s (223.3 ppm) and in **3**t (112.2 ppm) when compared with the experimental value of carbene **3″** (223.0 ppm) are further proofs that **3″** is a singlet carbene.

– The aromaticity of all the compounds were discussed based on Schleyer's NICS values. The most important conclusion is that the triplet carbenes are not aromatic while the singlets are aromatic.

– The representation of NICS values over the van der Waals surface is a useful approach to visualize the aromaticity of these systems.

Acknowledgements

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Graphical Abstract

A theoretical study of the parent N*H*-benzazoles (benzimidazoles, indazoles and benzotriazoles): geometries, energies, acidity and basicity, NMR properties and molecular electrostatic potentials

Ibon Alkorta, Goar Sánchez-Sanz, Cristina Trujillo, José Elguero and Rosa M. Claramunt