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Composition of Tautomeric Mixtures Studied by Nitrogen Chemical Shifts and *Ab Initio* Molecular Orbital Calculations

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Some nitrogen and carbon chemical shifts and *ab initio* Gauge Invariant Atomic Orbitals – Coupled-Perturbed Hartree-Fock (GIAO-CPHF) calculations are reported for benzotriazole **1**, 5-nitrobenzimidazole **2**, 5-nitrobenzotriazole **3**, 4-nitrobenzotriazole **4**, and N-methyl derivatives of compounds **1–3**. A good correlation is found between the calculated and observed ^{13}C and ^{15}N chemical shifts. Two methods were employed for calculation of equilibrium constants. The prototropic equilibria exhibited by the system studied are found to be controlled by enthalpy rather than entropy.

Key words: prototropic equilibrium, NMR, *ab initio* calculations

Benzimidazole (BIM), benzotriazole (BTA), and their derivatives are very important compounds used in organic synthesis [1–3] and medicine [4–6]. They may exist in two benzenoid forms, with a proton attached to the N1 or N3 atom. In addition, a quinonoid structure with a proton attached to the N2 atom is possible for the benzotriazoles only (Figure 1) [7]. The equilibria have been studied by several experimental and theoretical approaches in gaseous, liquid, and solid states [8–25], and recently was reviewed [7]. In general, a prototropic exchange existing for BIM and BTA is fast in the liquid and gaseous states, while is very slow in the solid state. Although the [1*H*] BTA is more stable in solutions and solids, the presence of the [2*H*] tautomer has been confirmed by nuclear magnetic resonance (NMR) spectroscopy [8] as well as by other experimental techniques [9–14]. Earlier theoretical investigations, performed usually for gaseous molecules, have substantiated these results [9–16].

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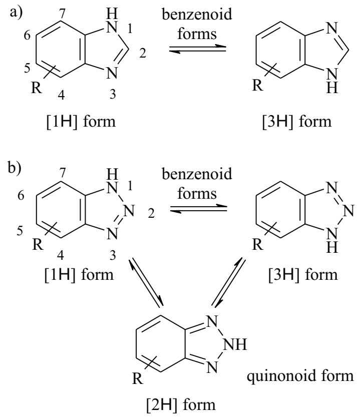

Figure 1. Prototropic equilibrium for substituted benzimidazoles (a) and benzotriazoles (b).

Rapid prototropic exchange in DMSO solution exists also for nitro derivatives of BIM and BTA causing an effort in collecting ^{15}N NMR data [20,21]. In NMR spectra of such a system, a fast proton exchange yielded an average of NMR resonances and only one set of data was observed with some peaks vanishing at so called coalescent point [20,21]. In the present paper, we want to compare both theoretical [26] and experimental [8,27] methods for the determination of the composition of tautomeric mixtures of nitro derivatives of BIM and BTA. For the calculations, we use Gauge Invariant Atomic Orbitals – Coupled-Perturbed Hartree-Fock (GIAO-CPHF) procedure [28,29], while the ^{13}C and ^{15}N NMR spectra provide the experimental data [20,21]. Earlier, these methods were proved skillful while exploiting a hydroxyquinoline derivative [26] and some tautomeric azole systems, including unsubstituted BIM and BTA [8,27]. Specifically we have studied the prototropic equilibrium of the unsubstituted benzotriazole **1**, which we utilized as a reference compound, 5-nitrobenzimidazole **2**, 5-nitrobenzotriazole **3**, and 4-nitrobenzotriazole **4**. In addition, we have used all possible N-methyl derivatives of compounds **1–3** as

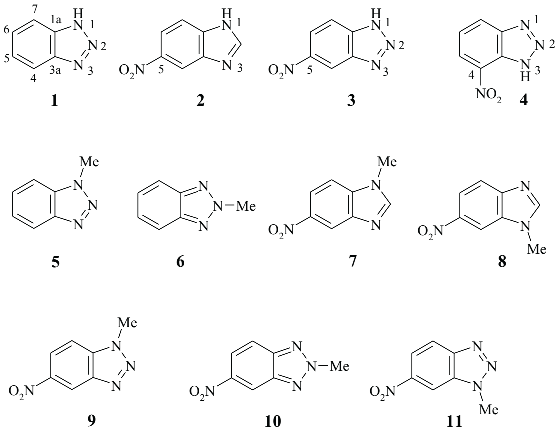

Figure 2. Compounds studied in present investigation.

models of the nonexchanging forms: [1*H*], [2*H*] or [3*H*] (Figure 2). Since compound **4** exists in only one [3*H*] form in solution [20], the use of N-methyl derivatives is not required for our study of this compound.

RESULTS AND DISCUSSION

The nitrogen and carbon chemical shifts of compounds **1**, **2**, and **4–8** are given in the literature [8,20,21], whereas those for compounds **3** and **9–11**, are reported in this work. All experimental results are collected in Table 1. Note that the experimental data for compounds **1–3** were recorded at condition offering an exchanged nitrogen spectrum (25°C in DMSO solution and 60°C in DMF solution), while data for compound **4**, showing a very slow prototropic exchange, represent the [3*H*] form stabilized by hydrogen bond [20]. The assignment of the signals of **3** was completed according to previously reported methods [20,21]. The position of the N-methyl group in compounds **9–11** has been determined by ^{1}H-^{1}H NOE experiments, while the assignment of the nitrogen chemical shifts has been explicated using ^{15}N-^{1}H INEPT experiments. The carbon and hydrogen NMR signals of the aromatic nuclei were assigned according to procedures described previously [20,21].

Results of GIAO calculations performed for all possible prototropic forms of compounds **1–4** are gathered in Tables 2 and 3. Absolute shielding constants (σ_{abs}) along with corresponding chemical shifts (δ_{calc}, see explanation below) and atomic net charges (*q*) are collected in Table 2, while bond properties (lengths, orders, and angles) are in Table 3. First we note that the molecular properties (σ_{abs}, *q*, bond properties, and total self-consistent field (SCF) energies) are calculated for compounds studied in the absence of the potential electron correlation effects. Second, the σ_{abs} cannot be measured directly, but, they can be converted to a chemical shift scale using a reference: $\delta_{calc} = \sigma_{ref} - \sigma_{abs}$ [30]. Yet, it is well known that the *ab initio* shielding calculations may not give satisfactory results for nuclei with a lone electron pair and/or in a multiple bond system due to the absence of the electron correlation functions [29–33]. Therefore, the σ_{abs} values calculated for each tautomer of **1–4** are compared with the experimental chemical shifts (δ_{exp}) of a corresponding N-methyl derivative or of an appropriate stable form (compound **4** only). Note that these relations (see Figure 3) are linear with correlation coefficients of 0.9968 and 0.9510 for the nitrogen and carbon data, respectively. The intercepts of –130.8 ppm for ^{15}N and of 189.2 ppm for ^{13}C are close to absolute shielding constants of –135.0 ppm for ^{15}N and of 185.0 ppm for ^{13}C calculated for CH_3NO_2 and tetramethylsilane (TMS), respectively [30], which are accepted as references. Since the tz2p basis set, which seems to be sufficient for the first row elements [29], was used for calculations in this work, the difference from 1 of the line slopes arises more likely from exclusion of electron correlation contributions, rather than incompleteness of the chosen basis set [29–33]. Hence the least-squares transforms are used to compute the chemical shifts (δ_{calc}) given in Table 2 along with σ_{abs} and *q* values. The relevant equations are given by $\delta_{calc} = -0.714 \cdot \sigma_{abs} -$

Table 1. Nitrogen[a] and carbon[a] chemical shifts for compounds **1–11**[b].

Compound	**1**[b]	**5**[b]	**6**[b]	**2**[b]	**7**[b,c]	**8**[b,c]	**3**[b]	**9**[b,c]	**10**[b,c]	**11**[b,c]	**4**[b]
Solvent	DMSO[d]	DMSO[d]	DMSO[d]	DMSO[d]	DMSO[d]	DMSO[d]	DMF[e]	CDCl$_3$	CDCl$_3$	CDCl$_3$	DMF[e]
Temperature	25°C	25°C	25°C	25°C	25°C	25°C	60°C	25°C	25°C	25°C	–55°C
N1	–102.0	–161.5	–62.6	–185	–223.4	–134.7	–117.0	–163.1	–62.5	–41.6	–37.8
N2/C2	–10.3	–1.1	–116.8	146.7	148.7	149.8	4.4	8.6	–110.4	11.0	2.6
N3	–102.0	–41.0	–62.8	–170	–132.9	–229.4	–68.4	–36.2	–56.5	–160.5	–154.7
C4	139.8			112.7	115.5	107.6	114.2	117.1	115.9	106.5	133.8
C5	115.4			142.5	142.7	142.7	141.1	144.9	143.0	146.8	124.6
C6	125.9			117.5	117.9	117.0	121.2	122.4	120.5	118.8	124.3
C7	125.9			114.8	110.9	119.5	115.1	109.8	119.0	120.8	127.9
C1a	115.4			141.7	139.0	147.7	140.3	136.0	146.5	147.9	148.0
C3a	139.8			138.6	142.4	133.9	145.7	144.6	146.3	132.7	127.4
$\underline{\mathrm{N}}\mathrm{O}_2$				–8.4	–8.8	–8.2	–11.0	–13.9	–13.0	–14.1	–14.4

[a] Nitrogen chemical shifts are reported with respect to external neat nitromethane, while carbon are given with respect to TMS.
[b] NMR data are taken from: **1** [8,20], **2** [21], **4** [20], **5** [8], **6** [8], **7** [21], **8** [21], while for compounds **3**, **9–11** were obtained in this work.
[c] Carbon chemical shifts of N-methyl groups are: **7** 31.2, **8** 31.2, **9** 34.6, **10** 43.9, **11** 34.8. [d] Dimethylsulfoxide-d$_6$. [e] N,N-dimethylformamide-d$_7$.

Table 2. Results of GIAO-CPHF calculations of absolute nuclear shieldings (σ_{abs})[a], least squares calculated relative nitrogen and carbon chemical shifts (δ_{calc})[a,b], and atomic charges (*q*)[c], for compounds **1–4**.

	1		**2**		**3**			**4**		
	[1*H*]	[2*H*]	[1*H*]	[3*H*]	[1*H*]	[2*H*]	[3*H*]	[1*H*]	[2*H*]	[3*H*]
σ_{abs}										
N1	51.7	–88.9	125.9	–4.1	50.9	–86.8	–128.3	49.4	–92.6	–131.3
N2/C2	–176.5	–8.5	44.7	41.4	–182.4	–17.9	–194.7	–186.6	–15.4	–183.2
N3	–133.2	–88.9	–12.0	125.6	–140.2	–103.2	47.5	–131.2	–93.2	45.3
C4	62.8	66.2	62.9	77.5	61.1	62.0	79.2	49.0	50.8	59.4
C5	66.7	60.6	46.9	45.6	47.6	43.3	41.3	63.8	55.1	56.5
C6	56.6	60.6	63.0	66.1	58.3	64.2	68.2	61.0	66.1	70.9
C7	81.3	66.2	81.8	67.3	83.8	68.0	65.5	71.7	55.2	52.6
C1a	52.2	44.2	48.0	37.2	48.0	42.0	40.8	52.3	44.3	44.0
C3a	44.4	44.2	46.5	57.4	47.3	47.6	55.5	50.2	50.6	55.7
<u>N</u>O_2			–173.2	–173.3	–171.0	–171.3	–170.6	–167.5	–169.0	–173.3
δ_{calc}										
N1	–167.7	–67.3	–220.7	–127.9	–167.1	–68.8	–39.2	–166.1	–64.7	–37.1
N2/C2	–4.8	–124.7	142.5	145.9	–0.6	–118.0	8.2	2.4	–119.8	0.0
N3	–35.7	–67.3	–122.2	–220.5	–30.7	–57.1	–164.7	–37.1	–64.3	–163.1
C4	123.6	120.0	123.5	108.2	125.4	124.4	106.4	138.0	136.1	127.1
C5	119.5	125.9	140.2	141.5	139.5	144.0	146.0	122.5	131.6	130.2
C6	130.1	125.9	123.4	120.1	128.3	122.1	117.9	125.5	120.1	115.1
C7	104.2	120.0	103.7	118.9	101.6	118.1	120.8	114.3	131.5	134.2
C1a	134.7	143.0	139.0	150.3	139.0	145.3	146.6	134.5	142.9	143.2
C3a	142.8	143.0	140.6	129.2	139.8	139.5	131.2	136.7	136.3	131.0
<u>N</u>O_2			–7.1	–7.0	–8.7	–8.5	–9.0	–11.2	–10.1	–7.1
q										
N1	0.02	–0.29	–0.09	–0.37	0.03	–0.28	–0.19	0.04	–0.27	–0.19

Table 2 (continuation)

N2/C2	–0.06	0.26	0.24	0.25	–0.05	0.28	–0.04	–0.05	0.27	–0.05
N3	–0.19	–0.29	–0.35	–0.09	–0.17	–0.26	0.03	–0.16	–0.24	0.05
C4	–0.03	–0.07	–0.01	–0.06	0.01	–0.01	–0.06	–0.02	–0.06	–0.07
C5	–0.06	–0.04	–0.04	–0.01	–0.04	–0.02	0.02	–0.02	0.02	0.02
C6	–0.01	–0.04	0.00	–0.03	0.02	–0.03	–0.04	–0.01	–0.06	–0.07
C7	–0.10	–0.07	–0.10	–0.06	–0.10	–0.06	–0.03	–0.06	–0.02	0.01
C1a	0.10	0.14	0.12	0.16	0.12	0.15	0.12	0.09	0.13	0.09
C3a	0.10	0.14	0.12	0.08	0.08	0.12	0.09	0.10	0.13	0.12
$\underline{N}O_2$			0.85	0.86	0.85	0.85	0.85	0.85	0.85	0.85

[a] In ppm. [b] δ_{calc} for ^{15}N and ^{13}C, computed from σ_{abs} using equations shown in Figure 3, are given with respect to external neat nitromethane and TMS, respectively.
[c] In atomic units.

Table 3. Bond lengths (in Angstroms), and bond orders (in atomic units) from SCF calculations for compounds **1–4**.

	1		**2**		**3**			**4**		
	[1*H*]	[2*H*]	[1*H*]	[3*H*]	[1*H*]	[2*H*]	[3*H*]	[1*H*]	[2*H*]	[3*H*]
lengths										
1-1a	1.354	1.322	1.366	1.374	1.348	1.321	1.371	1.352	1.322	1.373
1-2	1.329	1.293	1.365	1.282	1.334	1.295	1.249	1.322	1.287	1.246
2-3	1.247	1.293	1.277	1.356	1.244	1.286	1.323	1.249	1.293	1.330
3-3a	1.373	1.322	1.379	1.374	1.373	1.324	1.355	1.373	1.321	1.342
4-3a	1.398	1.424	1.387	1.382	1.392	1.417	1.393	1.406	1.429	1.398
4-5	1.369	1.351	1.376	1.377	1.369	1.350	1.368	1.365	1.350	1.371
5-6	1.413	1.440	1.400	1.398	1.410	1.436	1.407	1.409	1.432	1.403
6-7	1.370	1.351	1.373	1.374	1.366	1.349	1.368	1.367	1.351	1.375
7-1a	1.399	1.424	1.392	1.393	1.401	1.423	1.397	1.398	1.420	1.394
3a-1a	1.383	1.408	1.396	1.397	1.386	1.407	1.384	1.386	1.411	1.386

Table 3 (continuation)

orders										
1-1a	1.50	1.67	1.47	1.52	1.52	1.68	1.52	1.50	1.53	1.50
1-2	1.40	1.51	1.48	1.93	1.38	1.50	1.79	1.41	1.67	1.81
2-3	1.81	1.51	1.96	1.51	1.82	1.54	1.41	1.79	1.51	1.40
3-3a	1.51	1.67	1.50	1.44	1.50	1.65	1.49	1.52	1.69	1.53
4-3a	1.78	1.66	1.84	1.86	1.80	1.68	1.80	1.73	1.63	1.74
4-5	2.01	2.11	1.91	1.90	1.95	2.06	1.95	1.96	2.04	1.92
5-6	1.79	1.68	1.80	1.80	1.76	1.67	1.77	1.79	1.70	1.82
6-7	1.99	2.11	1.96	1.97	2.01	2.12	2.01	1.99	2.10	1.97
7-1a	1.77	1.66	1.81	1.80	1.76	1.66	1.77	1.78	1.67	1.80
3a-1a	1.79	1.70	1.77	1.77	1.78	1.70	1.79	1.78	1.69	1.77
angles										
1a-1-2	110.4	103.1	106.6	105.0	110.5	103.1	108.5	110.3	103.1	108.5
1-2-3	110.0	118.1	113.8	114.1	110.0	118.3	110.3	110.4	118.4	110.2
2-3-3a	108.6	103.1	104.9	106.4	108.6	103.0	110.2	108.4	103.1	110.2
3a-4-5	117.3	116.8	116.7	115.5	115.9	115.4	114.9	119.3	118.8	118.6
4-5-6	121.2	122.1	123.2	123.4	123.2	124.1	124.1	120.9	121.8	120.9
5-6-7	122.1	122.1	120.2	120.0	120.8	120.7	119.9	121.5	121.4	121.0
1a-7-6	116.1	116.8	117.1	118.2	116.4	117.2	117.4	116.5	117.4	117.8
1-1a-3a	102.9	107.8	104.6	110.1	102.9	107.6	107.9	103.0	107.8	107.5
3a-1a-7	122.3	121.1	122.5	120.1	122.3	121.0	121.1	123.6	122.3	121.5
1a-3a-3	108.0	107.8	110.1	104.5	108.1	108.0	103.0	107.8	107.7	103.4
1a-3a-4	121.0	121.1	120.3	122.8	121.4	121.6	122.6	118.2	118.3	120.2

130.8 for ^{15}N data (Figure 3a) and by $\delta_{calc} = -1.045 \cdot \sigma_{abs} + 189.2$ for the ^{13}C data (Figure 3b). Good agreement between the experimental and calculated data provides confirmation of the assignment of the nitrogen and carbon NMR signals for the compounds studied.

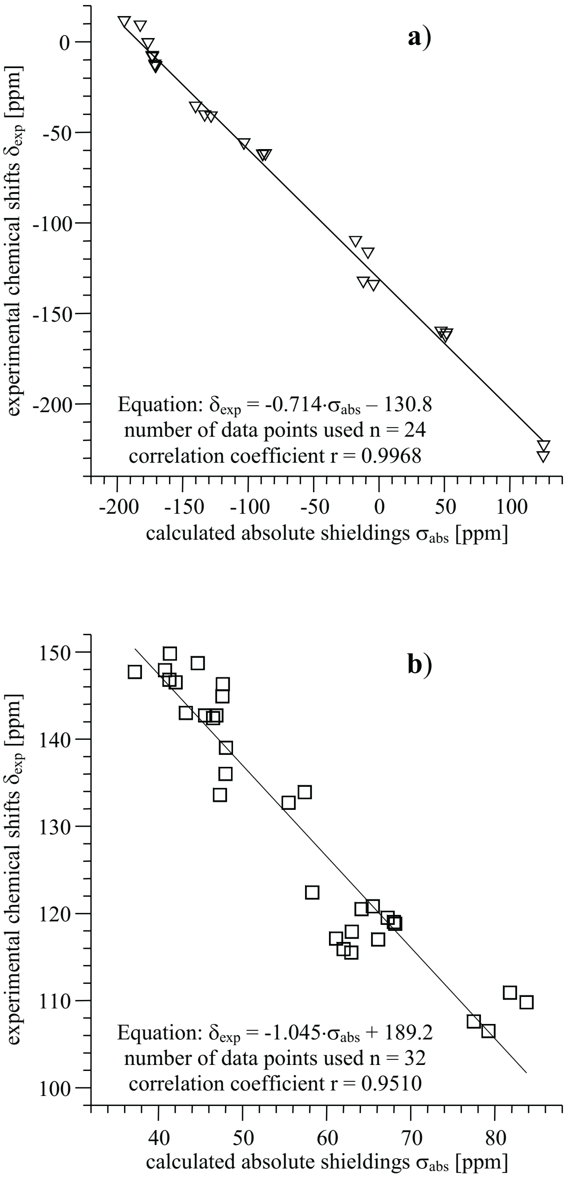

Figure 3. A plot of experimental chemical shifts (δ_{exp}) *vs*. calculated absolute shieldings (σ_{abs}) for nitrogen (a) and carbon (b) nuclei of compounds studied. Values of δ_{exp} measured for samples **5**, **6**, **7**, **8**, **9**, **10**, **11**, and **4** are compared with σ_{abs} calculated for [1*H*], [2*H*] tautomers of **1**, [1*H*], [3*H*] tautomers of **2**, [1*H*], [2*H*], [3*H*] tautomers of **3**, and [3*H*] tautomer of **4**, respectively. This gives 24 and 32 data points of nitrogen and carbon data, respectively, which are utilized to obtain the least-squared lines.

In general, a lone electron pair of nitrogen atoms produces a negative atomic charge around these atoms, whereas N atoms bonded to hydrogen have a positive charge. In the case of quinonoid forms, the distribution of the charge around N2 and N1/N3 is near 0.3 or –0.3 atomic units (a.u.), respectively, which is larger than that for the benzenoid forms. Therefore, both the N1 and N3 positions are very susceptible to protonation. Indeed, compounds **9** and **11** form stable N3 and N1 cations in TFA solution, respectively, whereas **10** shows a fast proton exchange between the N1 and N3 positions.

Table 3 contains a collection of bond data such as lengths (in Angstroms), orders (in a.u.), and angles (in degrees) from the SCF calculations for compounds **1–4**. These data agree within a few percent with previous calculation reports [10–12,14], and with the X-ray measurements for the unsubstituted BTA [22] and BIM [23,24], showing that compounds **1** and **2** exist entirely in the [1*H*]/[3*H*] form. In the present study, the calculated data reveal that bonds C4–C5, C6–C7 are the shortest C–C bonds in compounds studied, and yet their orders are the largest. Further analysis shows that the C2–N3 (N1–C2) bond for the [1*H*] ([3*H*]) form of compound **2** has a length of 1.277 Å (1.282 Å) and an order of 1.96 a.u. (1.93 a.u.) indicating a double bond character. When the N atom introduced in position 2 in compounds **1**, **3**, and **4**, this bond (in the [1*H*] or [3*H*] form) usually slightly longer than an N=N bond and its order is less than 1.82 a.u. From this probably, the C1a–C7, C3a–C4, and C5–C6 bonds gain a benefit of in a form of an increased bond order. The above suggests that the [1*H*] ([3*H*]) tautomer consists of a localized π-bond system, partially delocalized in five-membered ring when N atom is present in position 2, which may be an effect of interaction between two lone electron pairs form neighbor N atoms [11]. For the [2*H*] form of **1**, **3**, and **4**, all bonds except the C4–C5 and C6–C7 bonds are of a close order of a main value of 1.6 a.u., while the remaining two bonds have an order greater than 2 a.u. This indicates a delocalization of π electrons within the five-membered ring of the quinonoid form.

As mentioned before, in the NMR spectra of compounds **1–3** (without methyl groups) only one set of data is observed. Each of the NMR signals appears at an averaged value represented by the sum of the products of the molar ratio and the chemical shift of all possible tautomeric structures, as shown by equation (1) [34]:

$$\delta_{j\_avr.} = \sum_{a} x_a \cdot \delta_{aj} \tag{1}$$

where: $\delta_{\mathrm{j\_avr.}}$ – an averaged chemical shift of nucleus j, $\mathrm{x_a}$ – molar ratio of tautomer a, δ_{aj} – a chemical shift of nucleus j in tautomer a. Based on this equation and using nitrogen chemical shifts of corresponding N-methyl derivatives [8,27], we have calculated the molar ratios for each tautomer of compounds **1** to **3**. The choice of nitrogen chemical shifts for this investigation is due to the greater accuracy obtained from the nitrogen rather than the carbon or hydrogen NMR data [27].

It is known that the equilibrium constant for a given process depends on temperature and on the Gibbs energy of the process according to equation (2):

$$\Delta G = -RT \cdot \ln K \Rightarrow K = e^{-\frac{\Delta G}{RT}} \tag{2}$$

where: ΔG – Gibbs free energy change, K – an equilibrium constant, R – the gas constant, T – temperature. We assume that the difference in the total electron energy between the tautomers equals the Gibbs free energy change of the process. From this equation, using SCF energies, we have calculated molar ratios of each tautomer of compounds **1** to **4** at 25°C and 60°C, as shown in Table 4 along with the experimental values.

Table 4. Molar ratios for compound **1–4** calculated experimentally and theoretically.

		molar ratios [%]			ΔE [kJ·mol^{-1}]	
		exp.[a]	SCF		exp.[b]	SCF
			25°C	60°C		
1	[1*H*]	58[c]	58.5	57.6	0.0	0.00
	[3*H*]	42[c]	41.5	42.4	0.8	0.85
2	[1*H*]	95[c]	97.7	96.6	0.0	0.00
	[2*H*]	5[c]	2.3	3.4	7.3	9.30
3	[1*H*]	67[d]	88.5	85.8	0.0	0.00
	[2*H*]	4[d]	0.8	0.1	7.0	11.62
	[3*H*]	29[d]	10.7	12.9	1.3	5.24
4	[1*H*]	0[e]	0.0	0.0	–	36.82
	[2*H*]	0[e]	0.0	0.0	–	36.37
	[3*H*]	100[e]	100.0	100.0	0.0	0.00

[a]Calculated according to equation (1) using nitrogen chemical shifts of N-methyl derivatives.
[b]Calculated according to equation (2) using experimental molar ratios. [c]At 25°C. [d]At 60°C. [e]At 55°C.

Comparison of the molar ratios for compounds **1–4**, that are calculated from the *ab initio* SCF energies, with the experimental values shows satisfactory agreement. The experimental data do not include any corrections for solvents, temperatures or substituents, all of which can change a nitrogen chemical shift by about ±10 ppm [35]. Yet, the calculated data are obtained without introducing electron correlation functions and solvent effects [11,17]. Nevertheless, all of these effects may have an opposite influence on overall energy, and it seems that they average out. By assuming that ΔE calculated by the SCF procedure for the prototropic equilibrium approximates to the enthalpy change, the good agreement between the experimental and SCF calculated values for ΔE given in Table 4 may indicate that any contribution of entropy change to this equilibrium is rather small.

CONCLUSIONS

A very good correlation between the calculated absolute shieldings and experimental chemical shifts for the ^{13}C and ^{15}N nuclei of compounds **5–11** was found. Therefore, a simplified equations $\delta_{(N)} = -0.7 \cdot \sigma_{abs(N)} - 131$ and $\delta_{(C)} = -1.0 \cdot \sigma_{abs(C)} + 189$ may be used as a guidance for peak assignments.

The molar ratios of the prototropic forms of compounds **1** to **4** calculated using nitrogen chemical shifts are in good agreement with those calculated using the SCF energies. This suggests that the prototropic equilibrium for the systems studied is more probably controlled by enthalpy rather than entropy change. The differences observed may be a result of the chemical shift dependence on solvent, substitution, and temperature. Such effects were not included in the calculations of the tautomeric mixture.

EXPERIMENTAL

Preparation and NMR measurements. Compounds **9–11** were prepared by methylation of compound **3** using a 20% overabundance of MeI. The N-methyl derivatives obtained were separated by chromatography on silica gel. All NMR measurements of compounds **9–11** were taken on a BRUKER AM 500 spectrometer, operating at 500.18 MHz for ^{1}H, 125.76 MHz for ^{13}C, and 50.68 MHz for ^{15}N nuclei using standard conditions described previously [20,21].

Computational methodology. The *ab initio* GIAO-CPHF molecular orbital calculations were performed on a Silicon Graphics Onyx Workstation using the Turbomole program of Biosym/MSI™ [36]. The geometry of molecules was optimized with the double-ζ basis set with a polarization function (dzp) [37]. The triple-ζ basis set with two polarization functions (tz2p) [37] was used for the molecular property calculations *i.e.*: SCF electron energies [36], absolute nuclear shielding constants [28,29], and Roby-Davidson population analysis based on occupation numbers [38]. The last mentioned produced the atomic net charges and bond orders (shared electron numbers). The calculations were carried out on isolated molecules in the gas phase with no solvent effects included. Moreover electron correlation effects were not taken into account, and C_s symmetry was used for all of the molecules studied with the exception of structure [2*H*] of compound **1**, which has C_{2v} symmetry. Although Turbomole calculates all principal components of a shelding tensor (σ_{ii}, where i = 1, 2, or 3), only an isotropic value of chemical shift can be

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