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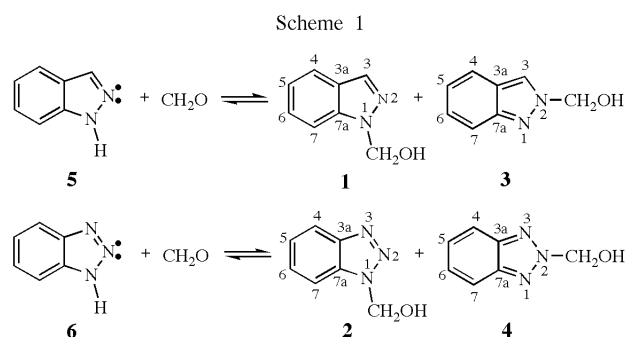
1-Hydroxymethylindazole and 1-hydroxymethylbenzotriazole have been studied in solution by ^1H , ^{13}C and ^{15}N NMR spectroscopy and the X-ray structure of the second compound determined. DFT and GIAO calculations have been used to discuss geometries, energies (comparatively with 2-substituted isomers) and NMR chemical shifts.

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The title compounds, 1-hydroxymethylindazole (**1**) and 1-hydroxymethylbenzotriazole (**2**), belong to the class of aminals, *i.e.* products of addition of amines to carbonyl compounds. Due to the aromaticity and good leaving group character of azoles, these *N,N*-disubstituted hemiaminals [**1**] are only stable when the carbonyl compound is very reactive, as in the cases of formaldehyde [**2**] and hexafluoroacetone [**3,4**]. We would like to report in the present work the structure of the compounds derived from the reaction of indazole and benzotriazole with formaldehyde.

Results and Discussion.

Both are known compounds and both are 1-substituted derivatives **1** and **2** (Scheme 1) [5-8].



The structure of **1** and **2** bears no automatic relationship with the tautomerism of indazole and benzotriazole (both *1H*-tautomers) because the reaction takes place through the lone pair of the $\text{N}(2)$ atom and, besides, the reaction is under thermodynamic control. That is, **1** and **2** are more stable than the 2-substituted derivatives, **3** and **4**, as in the parent NH compounds **5** and **6** [9].

Compounds **1** and **2** have had a very different history. While **1** has been the subject of very few studies [10], the benzotriazole derivative **2**, thanks to Katritzky's chemical interest, has been reported many times (for a few examples, see [11-13]). Nevertheless, both have been neglected as far as structural studies are concerned.

Crystal Structure of Compound **2**.

Crystal data and structure refinement details for compound **2** are reported in Table 4 (see Experimental Part). A molecular diagram of the crystal structure is presented in Figure 1. The benzotriazole ring structure is flat, as could be expected from the aromaticity of the fused benzene ring and the presence of an $\text{N}=\text{N}$ double bond in the pentagonal heterocycle, with the OH of the $-\text{CH}_2\text{OH}$ moiety roughly

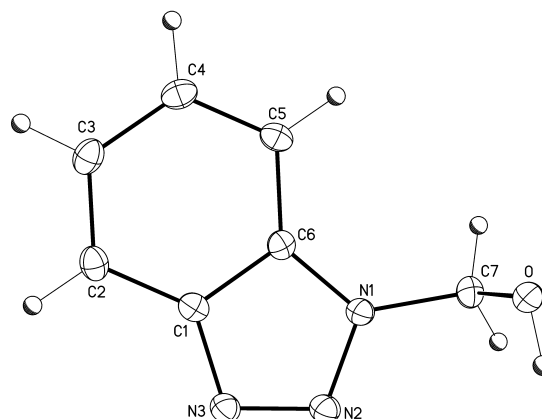


Figure 1. Molecular diagram of **2** with 30% probability ellipsoids except on hydrogen atoms which are depicted as spheres of arbitrary radii. Selected bond distances (Å), bond angles ($^\circ$), and torsion angles ($^\circ$): $\text{N}(1)-\text{N}(2)$ 1.3537(19), $\text{N}(2)-\text{N}(3)$ 1.307(2), $\text{N}(1)-\text{C}(7)$ 1.462(2); $\text{N}(2)-\text{N}(1)-\text{C}(7)$ 120.22(13), $\text{N}(2)-\text{N}(1)-\text{C}(6)$ 110.12(13), $\text{C}(6)-\text{N}(1)-\text{C}(7)$ 129.24(14); $\text{O}-\text{C}(7)-\text{N}(1)-\text{N}(2)$ $-85.63(17)$, $\text{O}-\text{C}(7)-\text{N}(1)-\text{C}(6)$ $86.28(19)$.

perpendicular to the ring plane. In the pure crystal (the situation could be different in a solvate [14]), the hydroxyl group of one molecule acts as a donor in an intermolecular hydrogen bonding interaction with a neighboring nitrogen acceptor in the 3-position with a refined interatomic separation, $-OH\cdots N=N-N$, 2.815(2) Å. This is the expected situation because N(3) is the most basic nitrogen atom in 1*H*-benzotriazoles [15].

Since the pure compound crystallizes in a centrosymmetric space group, the crystal is racemic and both enantiomers are identically present in the solid state. The *R* and *S* enantiomers refer to the H-O-C7-N1 fragment.

^1H , ^{13}C and ^{15}N NMR spectroscopy of compounds **1** and **2**.

The results are reported in Table 1.

B3LYP/6-311++G** levels. The results are reported in Table 2. The conformations *gauche* (*g*), *gauche'* (*g'*) and *anti* correspond to the dihedral angle as defined below (the other dihedral angle, O-C-N-N is always positive and close to 90°). These conformations were used as starting geometries. In some cases a minimum was found close to them, in others the minimum is identical to that obtained from another starting point.

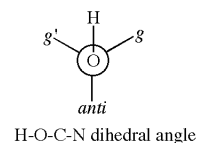


Table 1

Experimental NMR parameters of 1-Hydroxymethylindazole (**1**) and 1-Hydroxymethyl-benzotriazole (**2**) in CDCl_3 and $\text{DMSO}-d_6$

	Compound 1		Compound 2	
	CDCl_3	$\text{DMSO}-d_6$	CDCl_3	$\text{DMSO}-d_6$
H(3)	8.056	8.104	—	---
H(4)	7.774	7.783	8.107	8.056
H(5)	7.241	7.178	7.452	7.415
H(6)	7.484	7.421	7.586	7.566
H(7)	7.628	7.728	7.743	7.913
CH_2	5.897	5.736	6.158	6.051
OH	5.188	6.709	3.6 (vb)	3.9 (vb)
	(d, $J_{\text{CH}_2\text{OH}} = 7.8$)	(d, $J_{\text{CH}_2\text{OH}} = 7.4$)	(s)	(s)
$J_{\text{H}(3),\text{H}(7)}$	0.9	1.0	---	---
$J_{\text{H}(4),\text{H}(5)}$	8.1	8.1	8.4	8.4
$J_{\text{H}(4),\text{H}(6)}$	1.0	1.0	1.0	1.0
$J_{\text{H}(4),\text{H}(7)}$	1.0	1.0	1.0	1.0
$J_{\text{H}(5),\text{H}(6)}$	7.0	6.9	7.1	6.9
$J_{\text{H}(5),\text{H}(7)}$	0.9	0.9	1.0	1.0
$J_{\text{H}(6),\text{H}(7)}$	8.5	8.5	8.3	8.3
C(3)	134.49	134.17	—	—
C(3a)	124.35	125.03	c	146.38
C(4)	121.46 ^a	121.64 ^b	c	119.88
C(5)	121.20 ^a	121.67 ^b	c	124.95
C(6)	127.25	127.00	c	128.21
C(7)	109.40	110.96	c	111.74
C(7a)	139.35	139.82	c	133.14
CH_2	70.94	71.61	c	71.09
N(1)	c	-180.83 (-203.8) ^d	c	-139.78 (-161.5) ^d
N(2)	c	-60.47 (-57.6) ^d	c	-2.95 (-1.1) ^d
N(3)	—	—	c	-41.03 (-41.0) ^d
$J_{\text{N}(1),\text{H}(3)}$	c	7.9 (7.6) ^e	c	---
$J_{\text{N}(2),\text{H}(3)}$	c	13.0 (12.8) ^e	c	---
$J_{\text{N}(2),\text{CH}_2}$	c	2.7 (2.0) ^e	c	2.2

^{a,b} These two values may be reversed; ^c The compound is not enough soluble in CDCl_3 ; ^d The values between parentheses belong to the corresponding *N*-methyl derivatives [16]; ^e These values are from reference [17].

DFT and GIAO Calculations of Compounds **1-4**.

The structure of compounds **1-4** was fully optimized (no imaginary frequencies) at the B3LYP/6-31G* and

The first conclusion that can be drawn from Table 2 values is that, using the larger basis set without ZPE correction, in the case of indazole isomers, **1** is more stable than

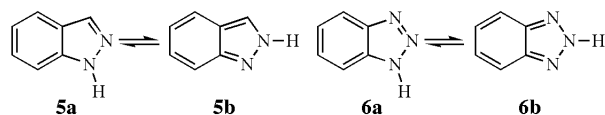
Table 2
Absolute Values (hartree), Relative Values and Zero-point Energy (ZPE) in kcal mol⁻¹ and Dipole Moments (in D) for Different Conformations of Compounds **1-4**

Compd.	Conf.	6-31G*	Erel	ZPE	6-311++G**	Erel	μ
1	<i>g'</i>	-494.37006	0.00	95.26	-494.51099	0.00	0.87
	<i>g</i>	-494.36665	2.14	95.11	-494.50770	2.07	
	<i>anti</i>	-494.36389	3.87	94.79	-494.51099	0.00	
3	<i>g'</i>	-494.36218	0.00	95.25	-494.50332	0.00	1.34
	<i>g</i>	-494.35798	2.64	95.07	-494.49922	2.57	
	<i>anti</i>	-494.36218	0.00	95.25	-494.50332	0.00	
2	<i>g'</i>	-510.39000	2.41	87.37	-510.53463	2.25	2.64
	<i>g</i>	-510.39382	0.00	87.55	-510.53822	0.00	
	<i>anti</i>	-510.38787	3.74	87.12	-510.53314	3.19	
4	<i>g'</i>	-510.39395	0.00	87.91	-510.53857	0.00	1.53
	<i>anti</i>	-510.39395	0.00	87.91	-510.53857	0.00	

3 by 4.81 kcal mol⁻¹, but in the case of benzotriazole **2** is less stable than **4**, although only by 0.22 kcal mol⁻¹.

These compounds, like azolides [9] and Mannich base derivatives (*N*-CH₂-NRR) [11] exist in equilibrium in solution but with transformation rates slow enough to observe both isomers when they exist. Thus, the experimental finding that only **1** and **2** are present in solution (and also in the solid state for **2** and almost certainly for **1**) must be related to their intrinsic stability and to phase effects. In the case of the equilibrium **1/3** the difference of near 5 kcal mol⁻¹ amply justify the presence of **1**. In the case of benzotriazoles **2/4** the calculations predict that both isomers should have the same stability, in contradiction with the experimental result.

It is interesting to remind the results concerning the tautomerism of indazole **5** and benzotriazole **6**.



1*H*-Indazole (**5a**) is experimentally and theoretically more stable than 2*H*-indazole (**5b**) [9,18]; at the B3LYP/6-311++G** level and without ZPE correction (this work), **5a** -379.94402 and **5b** -379.93619 hartree, that is the 1*H*-tautomer is the most stable by 4.91 kcal mol⁻¹. The much more controversial case of benzotriazole tautomerism is well summarized in the literature [18] (references till 1998): in the gas phase at 0 K the most stable tautomer is the 2*H*, **6b**, but in the solid state and in solution, the only observed tautomer is the 1*H*, **6a**

(or 3*H*). In the gas phase, the population of the 1*H*-tautomer increases with temperature [19,20]. More recent work confirms these findings [21-24]. In the case of benzotriazole at the 6-311++G** level and without ZPE correction (this work), **6a** -395.97098 and **6b** -395.97129 hartree, that is the 2*H*-tautomer is the most stable by 0.20 kcal mol⁻¹. Thus, the differences in energy of the monomers in the gas phase are almost independent on the substituent (H or CH₂OH) on the nitrogen atom (compare 4.81/0.22 with 4.91/0.20). Therefore, we propose the same explanation for the stability of **2** and **6a** in the condensed phases. Besides, in the solid state, the OH...N(3) hydrogen bond is a possible source of stability of **2** because a OH...N(1) HB in isomer **4** should be much weaker due to the low basicity of 2-substituted benzotriazoles [15].

Although there are differences between both basis set results (88.4 vs. 92.3 kcal mol⁻¹) for compound **1**, selecting the larger basis set, in the case of indazoles **1** and **3**, the most stable conformation is the *g'*, the *anti* is not stable and reverts to the *g'*, and the *g* is a minimum but is less stable than the *g'*. For benzotriazole **2**, the three conformations are minima, the *g* being the most stable. Benzotriazole **4** has higher symmetry and, in this case only, the *g* conformation (identical to the *g'*) is stable. If we compare the X-ray structure of **2** with the two most stable conformations (the *g* and *g'*), the following HOCN and OCNN dihedral angles are obtained (not considering that all these compounds exist in two enantiomeric forms that correspond to a sign inversion of both angles): X-ray 81.0/-85.6°, *g* 68.3/-99.3°, *g'* -69.6/-90.8°. Therefore, the experimental structure presents a conformation close to the calculated minimum.

The results of GIAO calculations are reported in Table 3.

Table 3

NMR Absolute Shieldings (σ ppm) of Compounds **1** and **2**

Atom	Compd. 1	Compd. 2
H3	23.91	----
H4	24.02	23.64
H5	24.56	24.36
H6	24.40	24.27
H7	24.28	24.18
CH ₂	26.01/26.25	25.64/26.18
OH	30.31	30.27
C3	43.16	----
C3a	51.01	29.18
C4	57.18	56.69
C5	56.83	54.76
C6	51.60	50.50
C7	69.97	70.25
C7a	37.18	44.55
CH ₂	107.08	108.62
N1	30.99	-10.07
N2	-96.65	-162.51
N3	----	-130.18

The comparison of Tables 1 and 3 lead to the following equations:

$$\delta^1\text{H}(\mathbf{1+2}, \text{CDCl}_3) = (30.8 \pm 0.3) - (0.96 \pm 0.01)\sigma, n = 12, r^2 = 0.999 \quad (1)$$

$$\delta^1\text{H}(\mathbf{1+2}, \text{DMSO-}d_6) = (30.9 \pm 0.4) - (0.96 \pm 0.02)\sigma, n = 12, r^2 = 0.997 \quad (2)$$

$$\delta^{13}\text{C}(\mathbf{1}, \text{CDCl}_3) = (173.3 \pm 1.2) - (0.92 \pm 0.01)\sigma, n = 9, r^2 = 0.998 \quad (3)$$

$$\delta^{13}\text{C}(\mathbf{1+2}, \text{DMSO-}d_6) = (174.2 \pm 0.9) - (0.93 \pm 0.01)\sigma, n = 16, r^2 = 0.998 \quad (4)$$

$$\delta^{15}\text{N}(\mathbf{1+2}, \text{DMSO-}d_6) = -(151 \pm 3) - (0.90 \pm 0.03)\sigma, n = 5, r^2 = 0.997 \quad (5)$$

In the first four equations, the intercepts are relatively close to the GIAO/B3LYP/6-31G* values of TMS (¹H 32.18, ¹³C 189.69), but for ¹⁵N, the intercept is far from the calculated value for nitromethane (-117.8 ppm at the same level) but close to the experimental absolute value ($\sigma = -143$ ppm). We have already discussed this problem related to the difficulty to calculate nitro groups using basis of medium quality [25]. In any case, the excellent correlation coefficients prove the consistency of the assignments. Solvent effects are negligible [compare eqs. (1) and (2) and (3) and (4)].

EXPERIMENTAL

Crystallographic Structural Determination (Table 4).

Compound **2** was crystallized by slow evaporation from a saturated solution in methanol solvent. A suitable crystal was selected, mounted with Paratone oil on a glass fiber and flash-cooled to the data collection temperature. Data was collected using a Bruker AXS SMART APEX diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell parameters were obtained from 60 data frames, $0.3^\circ \omega$, from three different sections of the Ewald sphere. Systematic absences in the diffraction data and unit cell parameters were uniquely consistent with the reported space group $P2_1/c$. The data-set was treated with SADABS absorption corrections based on redundant data [26]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxyl hydrogen atom, H(1), was located from the

Fourier electron difference map and refined with a riding model. All other hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library [26]. The CIF is available from the Cambridge Crystallographic Data Centre under the depository number CCDC 222190.

Table 4

Crystal data and structure refinement details for compound **2**

Formula	C ₇ H ₇ N ₃ O
Formula weight	149.16
<i>T</i> , K	150(2)
Space group	$P2_1/c$
<i>a</i> /Å	7.408(4)
<i>b</i> /Å	9.924(4)
<i>c</i> /Å	9.283(4)
β /°	94.56(4)
<i>V</i> /Å ³	680.2(5)
<i>Z</i> , <i>Z'</i>	4, 1
<i>D_c</i> /g cm ⁻³	1.456
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	1.04
<i>R</i> (<i>F</i>), % ^a	4.37
<i>R</i> (<i>wF</i> ²)/% ^a	11.58

$$[a] \text{ Quantity minimized} = R(wF^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^2\}^{1/2} : R(F) = \Sigma\Delta/\Sigma(F_o), \Delta = |F_o - F_c| : w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1} : P = [2F_c^2 + \text{Max}(F_o, 0)]/3$$

NMR

The NMR spectra were recorded on a BRUKER Avance 250 spectrometer working at 62.895 MHz for ¹³C and 25.355 MHz for ¹⁵N, with digital resolution of 0.09 Hz/pt and 0.12 Hz/pt respectively. Solutions contained about 100 mg of each compound in 2.5 ml of DMSO-*d*₆ for recording ¹³C and ¹⁵N spectra and they were diluted ten times for ¹H. ¹³C chemical shifts are expressed in ppm from TMS with $\delta_{\text{CDCl}_3} = 77.00$ ppm and ¹⁵N chemical shifts are measured in ppm from external NO₂Me.

Computations.

Geometries of the stationary structures **1** and **2** were fully optimized at the Becke 3LYP [27,28] theoretical level, with the 6-31G* [29] and the 6-311++G** basis set [30] as implemented in the Gaussian 98 program [31]. Harmonic frequency calculations [32] verified the nature of the stationary points as minima (all real frequencies). Absolute shielding have been calculated over the fully optimized geometry within the GIAO approximation [33] at the B3LYP/6-311++GG** level.

Synthesis.

1-Hydroxymethylindazole (**1**).

Indazole (5 g, 42 mmol) are dissolved in 30 mL of 30% hydrochloric acid, then 3.85 mL of a 30% aqueous solution of formaldehyde (42 mmol) was added. After 1 h, 30 mL of water were added and the mixture was kept at room temperature for 1 h. The precipitate is collected by filtration to give a white solid, mp 116 °C, lit. mp 115 °C [5], 113-114 °C [6].

Anal. Calcd. for C₈H₈N₂O: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.68; H, 5.41; N, 19.03.

1*H*-Benzotriazole-1-methanol (**2**).

Aldrich, 41,023-3, 98% mp 150-152 °C. Purified by crystallization in water.

Anal. Calcd. for C₇H₇N₃O: C, 56.37; H, 4.73; N 28.17. Found: C, 56.42; H, 4.81; N 28.10.

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