kinetic control. The syn products result in these reactions because the syn/anti isomerization of the radicals formed by oxidation of the free anions (or by oxidation of the anions in the ion pairs and subsequent loss of the metal cation to the oxidant) is slow compared to the rate of the coupling reaction.

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Supplementary Material Available: Structures (**Z** matrix) and vibrational frequencies (and transition vectors) of **2**–**10** (11 pages). Ordering information is given on any current masthead page.

Tautomerism and Aromaticity in 1,2,3-Triazoles: The Case of Benzotriazole

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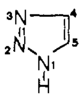
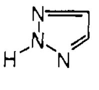
Abstract: This paper provides an explanation for the extraordinary difference in stability between 1,2,3-triazole and benzotriazole tautomers. In the gas phase, the 2*H* tautomer of 1,2,3-triazole represents more than 99.9% of the equilibrium mixture, whereas in benzotriazole the reverse is true (more than 99.99% of 1*H* tautomer at equilibrium). To understand the origin of this different behavior, an ab initio study at the 6-31G level was carried out on both tautomers of benzotriazole, on benzotriazolate anion, and on both tautomers of benzotriazolium cation (the 1,2- and the 1,3-*H*,*H*$^+$ ions). Theoretical results (the proton affinity of 1*H*-benzotriazole is 10.2 kcal mol^{-1} larger than that of 2*H*-benzotriazole) was checked against ICR measurements with excellent agreement (1-methylbenzotriazole is 10.4 kcal mol^{-1} more basic than 2-methylbenzotriazole). Thermodynamic measurements (enthalpies of solution, vaporization, sublimation, and solvation) in three solvents (water, methanol, and dimethyl sulfoxide) confirm the predominance of the 1*H* tautomer in solution. Taking into account lone pair/lone pair repulsions and aromaticity, it is possible to explain the different behavior of 1,2,3-triazole and benzotriazole in the case of neutral molecules and their similarity in the case of protonated species.

In a preceding paper[1] the tautomerism of 1,2,3-triazole was approached both experimentally and theoretically. The main conclusions of that study were (i) theoretical calculations at the 6-31G level satisfactorily account for acid and basic properties of 1,2,3-triazole, (ii) in the gas phase, tautomer 2*H*-**2a** is more stable than tautomer 1*H*-**1a** by about 4.5 kcal mol^{-1}, (iii) in solution, tautomer **1a** becomes the most stable species because the large difference in dipole moments favors the more polar tautomer, **1a**, and (iv) triazolium ion **4a** is predicted to be more stable than **5a** by about 13.5 kcal mol^{-1}, which complicates the discussion of basicity data (**4a** cannot be obtained directly from **2a**).

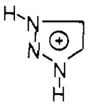


1a

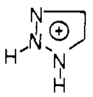


2a

3a



4a

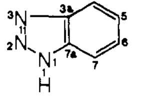


5a

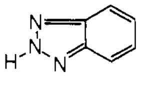
The origin of the lower stabilities of **1a** compared with **2a** and of **5a** compared with **4a** correspond to what we have termed "electrostatic proximity effects".[2] For neutral species, the effect correspondcs to the lone pair/lone pair repulsion of adjacent pyridine-like nitrogen atoms (N_2 and N_3 in **1a**) and for cations, to the repulsion between adjacent $^+$NH/$^+$NH pairs (N_1H and N_2H in **5a**). We have estimated[2] both these effects to 6.5 kcal mol^{-1}.

Two very recent works confirm these findings. Begtrup et al.[3] studied the structure of 1,2,3-triazole by microwave spectroscopy, by gas-phase electron diffraction, and by ab initio calculations. Their experimental results (Table I) perfectly agree with our 6-31G*//6-31G calculations, and their ab initio calculations (basis set of double-ζ quality) give values close to those we obtained at the 6-31G//6-31G level. Anders et al.[4] found a difference in energy at the 6-31G*//6-31G* level that compares quite well with our 6-31G*//6-31G result (Table I).

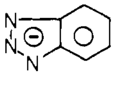
In the present work, 6-31G//6-31G calculations on the corresponding benzotriazoles **1b**–**5b** will be reported together with experimental thermodynamic data involving these molecules, both in the gas phase and in aqueous solution.



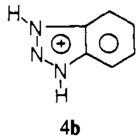
1b



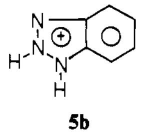
2b



3b



4b



5b

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Experimental Section

Materials. Pyrrole was obtained from Aldrich. Imidazole, pyrazole, and benzotriazole were kindly supplied as pure samples by Dr. Turriõn. The samples were identical with those described in ref 5.

1-Methylpyrrole, 1-methylimidazole, 1-methylpyrazole, 1-methylbenzotriazole, and 2-methylbenzotriazole were prepared and purified according to literature procedures.[6] Their purity was determined by GP or HPLC chromatographies for liquid samples and by differential scanning calorimetry (Perkin-Elmer, DSC-2) for solid samples. In all cases, the purity was higher than 99.8%. DMSO and methanol of the highest purity available (Merck) were stored over 4-Å molecular sieves. Reagent grade, CO_2-free water produced by a Milli-Q filtration system was used.

Calorimetric Dissolution Measurements. The enthalpies of solution in water of benzotriazole and 1-methylbenzotriazole were determined by using a new calorimetric technique recently developed to study the heat of solution of sparingly soluble solids.[7] Calibrations were performed by dissolution of acetanilide. The enthalpy of solution, in water, of 2-methylbenzotriazole was obtained by the use of a vessel fitting the thermal activity monitor from Thermometrics.[8] A spiralized thin-walled gold tube was suspended in the water-filled sample cup of an insertion vessel of the type described in ref 9. The sample was injected into the gold spiral through which water was pumped at a rate of 11 $mm^3\ s^{-1}$. Calibrations were performed electrically and by dissolution of 1-propanol in water at 298.15 K. The enthalpies of solution of benzotriazole and 1-methylbenzotriazole in DMSO and methanol and those of imidazole and pyrazole in methanol were determined by using an isoperibol calorimeter similar to the one previously described.[10] The enthalpies of solution of pyrrole, 1-methylpyrrole, 1-methylimidazole, and 1-methylpyrazole in methanol were determined by using an LKB batch microcalorimeter equipped with a titration unit.[11] The instrument was calibrated electrically. The experiments were carried out by addition of 5.20 μL of sample to a reaction vessel that contained 6 mL of methanol.

Calorimetric Sublimation Experiments. The enthalpy of sublimation of 1-methylbenzotriazole was determined on a Morawetz calorimeter.[12]

ICR Measurements. The instrument used in this work is a modified Bruker CMS47 FT ICR mass spectrometer.[13] The main modification is the insertion of a Balzers BVB 063H butterfly valve between the high-vacuum turbomolecular pump and the section containing the ion-trapping cell and the head of the Bayard-Alpert ionization gauge. This allows the efficient reduction of the gas flow, thus minimizing the pressure gradient between the cell and the head of the ionization gauge. In every case, the readings provided by the Bayard-Alpert gauge were calibrated against an MKS Baratron capacitance manometer. The magnetic field strength provided by the superconducting magnet is 4.7 T.

Standard working conditions were as follows: ionization energy, 16 eV; pressure range, 10^{-7}–10^{-6} Torr; cell temperature, 333 K; reaction times, 10–15 s with samplings every 0.5 or 1 s.

The equilibrium constants, K_p, for reaction 1 in the gas phase have been determined:

$$BH^+ + R \rightleftharpoons RH^+ + B \qquad (1)$$

in which B is one of the N-methylated benzotriazoles, **1c** or **2c**, and R is a *reference* base. This leads to the standard free energy changes for reaction 2 in the gas phase (Table II).

$$B + NH_4^+ \xrightarrow{\Delta H_{298}^\circ} BH^+ + NH_3 \qquad (2)$$

The standard entropy changes for this reaction have been determined by means of symmetry numbers.[14] The standard enthalpy changes, ΔH_{298}°, have been obtained from these values and have been corrected for the temperature difference (333 vs 298 K): for 1-methylbenzotriazole (**1c**) $\Delta H_{298}^\circ = -17.1 \pm 0.1$ kcal mol^{-1}, and for 2-methylbenzotriazole (**2c**) $\Delta H_{298}^\circ = -6.7 \pm 0.1$ kcal mol^{-1}.

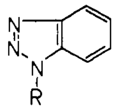
Each equilibrium constant is the average of some 20 runs at different total pressures. Also, the ratios of the pressures were varied as widely as possible. In every case, double-resonance experiments in both directions have always confirmed the existence of an equilibrium between the protonated species.

Theoretical Calculations

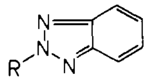
All computations were carried out by using a standard version of the GAUSSIAN 86 program.[16] The 6-31G basis set with complete optimization of the geometries (only the planarity of the molecules has been assumed) has been used (6-31G//6-31G).[16] The optimization was stopped when the internal coordinates changed less than 0.001 au.

Geometries. The geometrical characteristics of the five molecules studied are collected in Table III.

To compare the 6-31G geometries to experimental data, we have selected some molecules. For 1*H*-benzotriazole (**1b**), the X-ray structure of this compound has been determined,[17,18] but since four independent molecules are found in the unit cell, we have averaged the four values. Another possible model for this tautomer is 1-benzotriazoleacetic acid (**1d**).[19] Since the geometries of **1b** and **1d** are very similar (differences in bond lengths ≤0.005 Å, angles ≤0.5°), we propose to use 2-benzotriazoleacetic acid (**2d**) as a model of 2*H* tautomer (**2b**). The X-ray data of **2d**[20] have been averaged to preserve the C_{2v} symmetry. The structure of the tetramethylammonium salt of benzotriazole anion (**3b**) has been determined.[21] Here again we have averaged the experimental values to get a C_{2v} structure. There is no model available for the cation **5b**. For the 1,3-diprotonated benzotriazolium ion (**4b**) the structures of the hydrogensulfate[22] and the hydrogenphosphate[23] have been determined; after "symmetrization", both have been incorporated in the table of experimental geometries. This table is to be found in the supplementary material (see the paragraph at the end of the paper).



1c, R = CH_3
1d, R = CH_2CO_2H



2c, R = CH_3
2d, R = CH_2CO_2H

Concerning non-hydrogen atoms, the theoretical geometries and the experimental ones (two in the cases of **1b** and **4b**) are identical within the following values ±0.01 Å and ±0.8°. The most important deviations correspond to the N_2–N_3 bond in **1b** (exptl 1.311; calcd 1.269), and N_1N_2 and N_2N_3 bonds in **4b** (exptl 1.313, calcd 1.291), and the C_5C_6 bonds in **2b** (exptl 1.413, calcd 1.439)

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Table I. Triazole Experimental and Calculated Properties (Energies in kcal mol^{-1})

	exptl		6-31G*//6-31G 1		6-31G//6-31G 1		double-ζ 3		6-31G*//6-31G* 4
	$\Delta E_{1H\rightarrow 2H}$	$\mu(D)$	$\Delta E_{1H\rightarrow 2H}$	$\mu(D)$	$\Delta E_{1H\rightarrow 2H}$	$\mu(D)$	$\Delta E_{1H\rightarrow 2H}$	$\mu(D)$	$\Delta E_{1H\rightarrow 2H}$
1*H*-1,2,3-triazole (**1a**)	−4.5	4.38	−4.7	4.61	−3.9	5.11	−3.5	4.95	−4.9
2*H*-1,2,3-triazole (**2a**)		0.22		0.33		0.55		0.52	

Table II. Standard Free Energy Changes, $\Delta G_{298}°$, Used in the Determination of the PAs of Methylbenzotriazoles (the Reaction Is $B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+$)

base		$\Delta G_{298}°$, kcal mol^{-1}
B_1	B_2	
pyridine	NH_3	17.6[a]
cyclohexylamine	NH_3	18.1[b]
dimethylformamide	NH_3	8.0[a]
pyrazole	NH_3	9.1[a]
1-methylbenzotriazole (**1c**)	pyridine	−0.3[b]
1-methylbenzotriazole (**1c**)	cyclohexylamine	0.2[b]
2-methylbenzotriazole (**2c**)	dimethlformamide	−0.1[b]
2-methylbenzotriazole (**2c**)	pyrazole	−1.2[b]

[a] From ref 15. [b] This work.

and **3b** (exptl 1.395, calcd 1.418 Å).

Concerning the hydrogen atoms, the calculated bond lengths are longer (about 0.1 Å) than those determined by X-ray diffraction owing to the fact that this method systematically underestimates X–H distances.[24] Since the planar angles involving hydrogen atoms are determined with large errors, comparison with the coherent picture obtained from theoretical calculations has little sense.

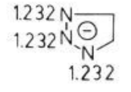
All the reported comparisons based on the experimental geometries of triazoles and benzotriazoles[20,25] can also be made using the values from Table III. For instance, the intranuclear angle $N_1N_2N_3$ (α_2)[25] decreases in the order **2b** (116.4°) > **3b** (112.7°) > **5b** (112.5°) > **1b** (109.1°) > **4b** (106.7°). Concerning the most important differences, it seems that the 6-31G basis set underestimates the lone pair/lone pair repulsion in 1*H*-benzotriazole (**1b**) and, as a consequence, the N_2–N_3 experimental bond is larger (1.311 Å) than calculated (1.269 Å). Another anomaly of calculated geometries corresponds to an excessive localization of the C_5–C_6 bond in compounds **2b** (1.439 Å) and **3b** (1.418 Å), which appear more "single bond" than in the experimental geometries (1.413 and 1.395 Å, respectively).

Charges. Mulliken population analysis has been employed to obtain the total and π-electronic densities gathered in Table IV (the corresponding charges for 1,2,3-triazoles can be found in the supplementary material, Table B).

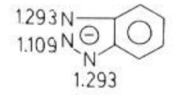
Formally, a benzotriazole can be dissected into a benzene ring and the three nitrogen atoms. The transfer of π-charge between these fragments is very similar for both tautomers (1*H*, +0.09 e; 2*H*, +0.07 e; a positive sign means electron transfer from the NNN part to benzene), different for both cations (1,3-*H*,*H*⁺, −0.06 e; 1,2-*H*,*H*⁺, −0.18 e), and larger for the anion (+0.3 e). The π-excessive nature of azoles[6] explains why the total amount of transferred charge is more important for the anion than for the cations. The heterocyclic part of the less stable 1,2-cation **5b** pulls more charge from the benzene than its tautomer **4b**.

Concerning total charges, in the case of neutral benzotriazoles it can be observed that the transfer of electrons is opposite in direction to that of the π-charges (1*H*, −0.67 e; 2*H*, −0.45 e). With regard to the corresponding triazoles, the NNNH fragment receives 0.13 e in the 1*H* tautomer (**1a**/**1b** pair) and 0.05 e in the 2*H* tautomer (**2a**/**2b** pair). It seems that the difference in stability between tautomers in triazoles and benzotriazoles is not related to charge movements.

By comparison of charges in anions **3a**/**3b** it is possible to go further in this discussion. The sum of q_π for the three nitrogens in the same (3.695 e) for both compounds; however, the distribution is not the same:



3a



3b

The annellation localizes the π-charge on the two nitrogen atoms, N_1 and N_3, adjacent to the benzene ring. A similar behavior is observed for the total charge (N_1, N_3, 7.427 → 7.476; N_2, 7.201 → 7.114). This is the first indication that the protonation of both anions would lead to opposite tautomers.

As a consequence of the different charge distribution, the calculated dipole moments for both benzotriazoles are very different:

1b: $\mu = 4.64$ D ($\mu_x = 4.17$, $\mu_y = 2.05$, $\mu_z = 0$)

2b: $\mu = 0.78$ D ($\mu_x = 0.78$, $\mu_y = 0$, $\mu_z = 0$)

experimental values (benzene solution) being[26]

1b: $\mu = 4.15 \pm 0.02$ D

1c: $\mu = 3.95 \pm 0.02$ D

2c: $\mu = 0.49 \pm 0.1$ D

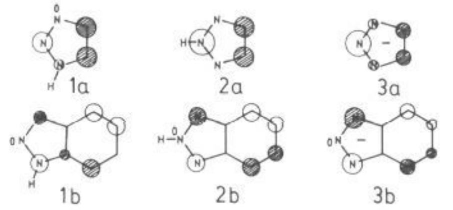


Figure 1. Coefficients of the HOMO (neutral molecules and anion).

Molecular Orbitals. The coefficients of the HOMO are represented schematically in Figure 1 with the usual convention.

As is immediately apparent, the distribution of the most labile electrons of the π-system, those of the HOMO, is very different in triazoles and benzotriazoles. There is always a node on N_2 (even for the C_s tautomer **1b**) in benzotriazoles, whereas in triazoles this atom has the largest coefficient. Thus, an important redistribution of the electronic structure takes place due to annellation, which corresponds to an increase of electron population of N_1 and N_3 at the expense of N_2.

Eigenvalues ϵ_i in au and orbital symmetry (Table C) and rotational constants of triazoles and benzotriazoles can be found in the supplementary material, Table D.

Thermodynamic Studies

In a recent paper[27] we described the existence of linear relationships (depending on the solvent) between $\delta\Delta H^{g\rightarrow sol}$ defined in eq 3 and the charge of the hydrogen atom bonded to the pyrrole type nitrogen.

$$\delta\Delta H^{g\rightarrow sol} = \Delta H_t^{g\rightarrow sol}(N\text{-methylazole}) - \Delta H_t^{g\rightarrow sol}(\text{azole}) \qquad (3)$$

We found that these relationships hold for three azoles (pyrrole, imidazole, and pyrazole) in two solvents (water and dimethyl sulfoxide).

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Table III. 6-31G Geometries of Benzotriazoles

	1*H*-benzotriazole (**1b**)	2*H*-benzotriazole (**2b**)	benzotriazolate anion (**3b**)	1,3-*H*,*H*$^+$-benzotriazolium cation (**4b**)	1,2-*H*,*H*$^+$-benzotriazolium cation (**5b**)
			Bond Lengths, Å		
N_1-N_2	1.359	1.321	1.327	1.291	1.348
N_2-N_3	1.269	1.321	1.327	1.291	1.282
N_3-C_{3a}	1.389	1.334	1.362	1.380	1.343
$C_{3a}-C_4$	1.395	1.420	1.404	1.396	1.413
C_4-C_5	1.374	1.356	1.372	1.372	1.359
C_5-C_6	1.413	1.439	1.418	1.417	1.430
C_6-C_7	1.375	1.356	1.372	1.372	1.368
C_7-C_{7a}	1.397	1.420	1.404	1.396	1.401
$C_{7a}-C_{3a}$	1.389	1.415	1.406	1.388	1.413
$C_{7a}-N_1$	1.362	1.334	1.362	1.380	1.349
C_4-H_4	1.071	1.070	1.074	1.070	1.070
C_5-H_5	1.072	1.072	1.075	1.071	1.070
C_6-H_6	1.073	1.072	1.075	1.071	1.071
C_7-H_7	1.071	1.070	1.074	1.070	1.070
N_1-H_1	0.987			0.996	0.995
N_2-H_2		0.989			0.996
N_3-H_3				0.996	
			Bond Angles, deg		
$N_1-N_2-N_3$	109.1	116.4	112.7	106.7	112.5
$N_2-N_3-C_{3a}$	109.0	103.6	106.5	112.3	106.9
$C_{3a}-C_4-C_5$	117.4	116.9	118.1	115.8	116.5
$C_4-C_5-C_6$	121.1	122.1	121.2	122.1	121.5
$C_5-C_6-C_7$	121.9	122.1	121.2	122.1	123.2
$C_6-C_7-C_{7a}$	116.6	116.9	118.1	115.8	115.6
$C_7-C_{7a}-C_{3a}$	121.8	121.0	120.7	122.1	121.8
$C_{3a}-C_{7a}-N_1$	103.8	108.1	107.2	104.3	104.9
$C_{7a}-N_1-N_2$	110.2	103.6	106.5	112.3	107.1
$C_{7a}-C_{3a}-C_4$	121.2	121.0	120.7	122.1	121.4
$C_{7a}-C_{3a}-N_3$	107.9	108.1	107.2	104.3	108.5
$H_1-N_1-N_2$	119.5			118.5	122.0
$H_2-N_2-N_3$		121.8			123.5
$H_3-N_3-N_2$				118.5	
$H_4-C_4-C_5$	121.8	122.5	121.1	122.0	122.6
$H_5-C_5-C_6$	119.9	118.2	118.9	118.7	118.4
$H_6-C_6-C_5$	119.0	118.2	118.9	118.7	118.1
$H_7-C_7-C_6$	121.7	122.5	121.1	122.0	122.2

Table IV. 6-31G//6-31G Total Atomic Electronic Densities (q_T) and Gross Orbital Populations (q_π) of Benzotriale Derivatives

	1-*H*-benzotriazole (**1b**)		2*H*-benzotriazole (**2b**)		benzotriazolate anion (**3b**)		1,3-*H*,*H*$^+$-benzotriazolium cation (**4b**)		1,2-*H*,*H*$^+$-benzotriazolium cation (**5b**)	
atom	q_T	q_π	q_T	q_π	q_T	q_π	q_T	q_π	q_T	q_π
N_1	7.834	1.685	7.281	1.195	7.476	1.293	7.725	1.543	7.700	1.651
N_2	6.913	1.090	7.351	1.541	7.114	1.109	6.711	0.975	7.209	1.545
N_3	7.336	1.132	7.281	1.195	7.476	1.293	7.725	1.543	7.133	0.980
C_{3a}	6.006	1.094	5.906	1.041	5.923	1.053	5.722	1.045	5.982	1.105
C_4	6.080	0.947	6.076	0.992	6.116	1.012	6.038	0.995	6.023	0.915
C_5	6.234	1.041	6.222	1.001	6.239	1.086	6.199	0.929	6.227	0.986
C_6	6.202	0.966	6.222	1.001	6.239	1.086	6.199	0.929	6.165	0.842
C_7	6.086	1.059	6.076	0.992	6.116	1.012	6.038	0.995	6.075	1.071
C_{7a}	5.607	0.985	5.906	1.041	5.923	1.053	5.722	1.045	5.582	0.904
H_4	0.756		0.762		0.826		0.713		0.699	
H_5	0.792		0.795		0.863		0.730		0.730	
H_6	0.791		0.795		0.863		0.730		0.728	
H_7	0.774		0.762		0.826		0.713		0.716	
H_1	0.587						0.517		0.528	
H_2			0.564						0.503	
H_3							0.517			

Through the thermodynamic studies reported in Tables V and VI, we have extended these relationships to a fourth azole, benzotriazole, and to a third solvent, methanol (Table VII and Figure 2).

Since the vertical separation of the lines (N-methylation effect) is proportional to the hydrogen-bond basicity of the solvent,[27] methanol ($\beta = 0.62$)[30] occupies in intermediate position between water ($\beta = 0.18$)[30] and DMSO ($\beta = 0.76$).[30]

A more relevant consequence of Figure 2 is that the points corresponding to benzotriazole have been calculated from 1-methylbenzotriazole **1c** [$\delta\Delta H_{solv}(H_2O) = -16.10 + 19.28 = 3.18$ (Table VI)] and 1*H*-benzotriazole [**1b**, $q_H = 0.587$ (Table IV), $1 - q_H = 0.413$]. Since the point corresponding to a hypothetical 2*H* tautomer **2b** [from 2-methylbenzotriazole (**2c**), $\delta\Delta H^\circ_{solv}(H_2O) = -12.36 + 19.28 = 6.92$ (Table VI) and **2b**, $q_H = 0.564$ (Table IV), $1 - q_H = 0.436$] clearly does not correspond to anything plausible, it is reasonable to assume that the 19.28 kcal mol^{-1} value belongs to the 1*H* tautomer **1b**, which is the tautomer present in the three studied solvents.

General Discussion

The experimental difference in basicity between both isomers of benzotriazole is 10.4 kcal mol^{-1}, the 1-methyl isomer **1c** being

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Table V. Enthalpies of Solution, ΔH°_{sol}, and Enthalpies of Vaporization or Sublimation, $\Delta H^\circ_{v/sub}$, for Some Azoles at 298.15 K (kcal mol^{-1})

compound	$\Delta H^\circ_{sol}(H_2O)$	ΔH_{sol}(DMSO)	ΔH_{sol}(MeOH)	$\Delta H^\circ_{v/sub}$
pyrrole	0.65 ± 0.04[a]	−2.23 ± 0.06[a]	−0.27 ± 0.09	10.84 ± 0.02[a]
1-methylpyrrole	0.25 ± 0.03[a]	0.13 ± 0.04[a]	0.81 ± 0.01	9.73 ± 0.07[a]
imidazole	3.09 ± 0.01[a]	2.58 ± 0.02[a]	1.77 ± 0.02	19.86 ± 0.05[a]
1-methylimidazole	−2.33 ± 0.03[a]	−0.04 ± 0.03[a]	−1.64 ± 0.06	13.06 ± 0.11[a]
pyrazole	3.73 ± 0.04[a]	2.08 ± 0.02[a]	2.52 ± 0.06	17.68 ± 0.05[a]
1-methylpyrazole	−1.47 ± 0.06[a]	−0.16 ± 0.07[a]	0.42 ± 0.01	10.00 ± 0.04[a]
benzotriazole	5.02 ± 0.07	1.19 ± 0.04	2.81 ± 0.21	24.3[b]
1-methylbenzotriazole	5.36 ± 0.06	4.07 ± 0.15	4.96 ± 0.24	21.46 ± 0.10
2-methylbenzotriazole	1.34 ± 0.01			13.70 ± 0.12[c]

[a] From ref 27. [b] From ref 28 (uncertainties not given by the authors). [c] From the linear relationship existing between ΔH°_v and T_{bp} in tertiary amines and *N*-methylazoles; see ref 27.

Table VI. Enthalpies of Solvation, ΔH°_{solv}, of Some Azoles in Water, DMSO, and Methanol, at 298.15 K (kcal mol^{-1})

compound	$\Delta H^\circ_{solv}(H_2O)$	ΔH°_{solv}(DMSO)	ΔH°_{solv}(MeOH)
pyrrole	−10.19 ± 0.06	−13.07 ± 0.08	−11.11 ± 0.11
1-methylpyrrole	−9.48 ± 0.10	−9.60 ± 0.11	−8.92 ± 0.80
imidazole	−16.77 ± 0.06	−17.28 ± 0.07	−18.13 ± 0.07
1-methylimidazole	−15.39 ± 0.14	−13.10 ± 0.14	−14.69 ± 0.15
pyrazole	−13.95 ± 0.09	−15.60 ± 0.07	−15.18 ± 0.16
1-methylpyrazole	−11.47 ± 0.10	−10.16 ± 0.11	−10.42 ± 0.11
benzotriazole	−19.28	−23.11	−21.49
1-methylbenzotriazole	−16.10 ± 0.16	−17.39 ± 0.25	−16.50 ± 0.34
2-methylbenzotriazole	−12.36 ± 0.13		

Table VII. Hydrogen Net Positive Charge, $1 - q_H$, and Loss of Exothermicity in Water, DMSO, and Methanol Due to N-Methylation Effect, $\delta\Delta H^\circ_{solv}$

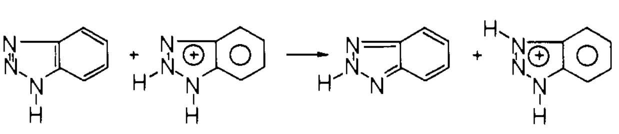
compound	$1 - q_H$	$\delta\Delta H^\circ_{solv}(H_2O)$	$\delta\Delta H^\circ_{solv}$(DMSO)	$\delta\Delta H^\circ_{solv}$(MeOH)
pyrrole	0.380[a]	0.71[b]	3.47[b]	2.19
imidazole	0.392[a]	1.38[b]	4.18[b]	3.44
pyrazole	0.405[a]	2.48[b]	5.44[b]	4.76
benzotriazole	0.413	3.18	5.72	4.90

[a] 6-31G//6-31G calculations, from ref 29. [b] From ref 27.

Table VIII. 6-31G//6-31G Energies of Benzotriazoles (au)

compound	abs value, au	rel value, kcal mol^{-1}
1*H*-benzotriazole (**1b**)	−393.241 73	0
1*H*-benzotriazole (**2b**)	−393.234 01	+4.8
benzotriazolate anion (**3b**)	−392.669 95	
1,3-*H*,*H*⁺-benzotriazole cation (**4b**)	−393.613 32	0
1,2-*H*,*H*⁺-benzotriazole cation (**5b**)	−393.589 36	+15.0

the more basic (Table II). From the 6-31G//6-31G calculated energies (Table VIII) and eq 4, the difference in basicity (15.0 − 4.8 = 10.2 kcal mol^{-1}) between both tautomers can be calculated.



1b **5b** **2b** **4b**

(4)

The agreement between both values shows that although the effect of N-methylation on intrinsic properties is important,[27] it cancels in such equations.

The situation is now clear from both a theoretical point of view and from experimental evidence. Taking into account the good agreement between theory and experiment in the case of 1,2,3-triazole (Table I), we can safely assume that theoretical ΔE values are similar to experimental ΔG values, i.e., that the entropic term is small compared with the enthalpic contribution. Thus, in the gas phase, the theory predicts the *intrinsic* tautomeric constants to be about K_T = **2a**/**1a** = 2800, K_T = **2b**/**1b** = 3 × 10^{-4}, K_T = **5a**/**4a** = 1 × 10^{-10}, and K_T = **5b**/**4b** = 1 × 10^{-11} at 25 °C, corresponding to differences in energy of 4.7, −4.8, −13.6, and −15.0 kcal mol^{-1}, respectively. In solution, the much higher dipole moment of 1*H* tautomers **1a**[1,3] and **1b** (see above) will favor these structures and, as a consequence, mixtures of **1a** and **2a** will be observed in solution[1] whereas the higher stability of 1*H*-benzotriazole (**1b**) will be reinforced.

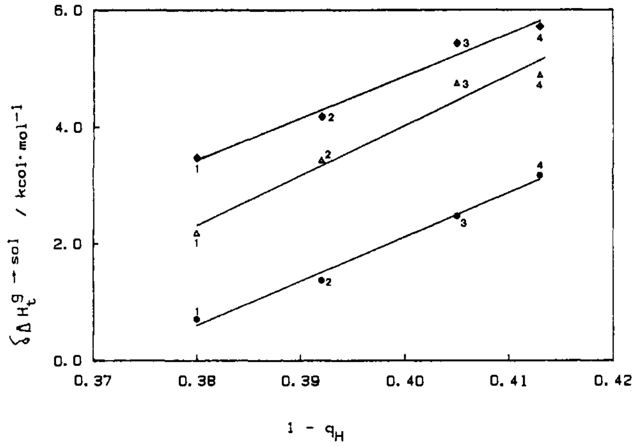


Figure 2. $\delta\Delta H^{g\to sol}$ in water (●), methanol (▵), and DMSO (◆) plotted against the net positive charge ($1 - q_H$). 1, pyrrole, 2, imidazole; 3, pyrazole; 4, benzotriazole.

All the available experimental evidence agrees with the above picture, the previous one,[31] and the more recent results: predominance of the 2*H*-1,2,3-triazole (**2a**) in the gas phase (microwave,[3] electron gas diffraction,[3] mass spectrometry[32]), mixture of both tautomers **1a** and **2a** in solution,[1,3] and predominance of the 1*H*-benzotriazole (**1b**) both in the gas phase and in solution (ICR, photoelectron spectroscopy,[33] mass spectrometry,[34] ^{15}N NMR[35,36]).

Strong evidence concerning the relative stability of the cations in the gas phase is absent (though attainable by mass spectroscopy) and is only circumstantial in solution.[1,37,38] In the solid state, benzotriazolium ion has the structure **4b** (see above). However, the theoretical differences in energy are so high that solvent modifications are not expected.

Finally, is it possible to plainly explain the results so far obtained? In the case of neutral molecules the *intrinsic* position of the tautomeric equilibrium is the result of two simple energetic terms: the electrostatic proximity effects[2] and the aromaticity.[39,40]

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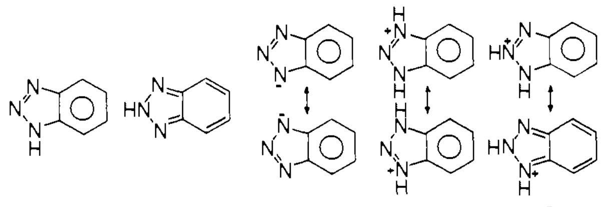

1b (1.028) **2b** (1.061) **3b** (1.034) **4b** (1.033) **5b** (1.049)

Figure 3. More representative canonical forms of benzotriazoles and ratio $2r_{56}/(r_{45} + r_{67})$.

The aromaticity of both 1,2,3-triazole tautomers being probably similar, the lone pair/lone pair repulsion accounts for the lack of stability of tautomer **1a**. If we assume[2] that the lone pair/lone pair repulsion amounts of 6.5 kcal $\mathrm{mol^{-1}}$, then, in the absence of such an effect, tautomer **1a** would be 1.8 kcal $\mathrm{mol^{-1}}$ more stable than **2a**. In the case of benzotriazoles, the aromaticity of the benzenoid tautomer **1b** being obviously greater than that of the quinonoid tautomer **2b**, the situation is reversed. We can estimate the difference in aromaticity between both tautomers as 9.5 kcal $\mathrm{mol^{-1}}$.

In the case of cations, the annellation modifies the difference in energy by 1.4 kcal $\mathrm{mol^{-1}}$ only (−13.6 kcal $\mathrm{mol^{-1}}$ in favor of **4a**[1] to −15.0 kcal $\mathrm{mol^{-1}}$ in favor of **4b**). This small variation is due to the fact that the 1,2-cation is only slightly less aromatic than the 1,3-cation.

Cannonical forms of the five benzotriazole structures together with the $2r_{56}/(r_{45} + r_{67})$ (r being the bond lengths of Table III) are given in Figure 3, where the relationship between stability and localization of the π-system in the benzene ring becomes apparent. (The quinonoid character increasing in the order **1b** < **4b** $\simeq$ **3b** < **5b** < **2b**).

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Supplementary Material Available: Tables of experimental geometries of benzotriazoles, 6-31G//6-31G total atomic electronic densities (q_T) and gross orbital populations (q_π) of 1,2,3-triazole derivatives, eigenvalues ϵ_i in au and orbital symmetry, and rotational constants (in megahertz) (4 pages). Ordering information is given on any current masthead page.

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Comprehensive Theoretical Study of Vinylsilane Primary Dissociation Pathways

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Abstract: Primary dissociation pathways have been investigated for vinylsilane by ab initio molecular orbital methods. Reactant, transition-state structures, and products were fully optimized at the HF/3-21G and HF/6-31G* levels of theory. Relative energies have been calculated at the MP4SDTQ/6-31G* level of theory, while zero-point energies and vibrational frequencies are calculated at the HF/3-21G level. With these barrier heights and vibrational frequencies, a unimolecular dissociation rate constant $k(E)$ has been determined by using RRKM theory for the primary dissociation channels for vinylsilane. Together these data are used to assess available experimental kinetic data for vinylsilane. The barrier height of the 1,1-H_2 elimination channel is predicted to be 64.4 kcal/mol, while that for the 1,2-SiH_2 elimination channel is predicted to be 68.7 kcal/mol. These theoretical results agree very well with experimental barrier heights for these two lowest channels. However, a *new* primary dissociation pathway is predicted to be competitive with the 1,1-H_2 and 1,2-SiH_2 elimination channels. This finding is discussed in light of previous experimental results on vinylsilane.

The thermal decomposition of vinylsilane has been studied extensively by thermal shock tube studies.[1,2] Despite these thermal studies, the chemistry of the simplest alkenylsilane, $CH_2{=}CHSiH_3$, is not well characterized. Whether the primary dissociation reaction proceeds to generate stable species or reactive intermediates that induce long radical chain reactions is still open to question for these systems. However, vinylsilane holds particular interest not only because it is the simplest alkenylsilane but also because knowledge of its chemistry is essential in assisting experimental identification of reactive intermediates that are implicated in the deposition of amorphous silicon. To data, much of the chemistry of vinylsilane has been speculated on the basis of results from alkylsilanes such as methylsilane[3-6] and ethylsilane.[1,7-12] With vinylsilane there is a large number of primary products that can be produced from unimolecular decomposition as follows:

$$CH_2{=}CHSiH_3 \rightarrow CH_2CHSiH_2 + H \quad (1)$$

$$\rightarrow CH_2CSiH_3 + H \quad (2)$$

$$\rightarrow CHCHSiH_3 + H \quad (3)$$

$$\rightarrow CH_2 + CHSiH_3 \quad (4)$$

$$\rightarrow CHCH_2 + SiH_3 \quad (5)$$

$$\rightarrow C_2H_3SiH + H_2 \quad (6)$$

$$\rightarrow C_2H_4 + SiH_2 \quad (7)$$

$$\rightarrow HCCH_2(SiH_3) \quad (8)$$

$$\rightarrow HCCSiH_3 + H_2 \quad (9)$$

$$\rightarrow CCHSiH_3 + H_2 \quad (10)$$

$$\rightarrow C_2H_2 + SiH_4 \quad (11)$$

$$\rightarrow CH_2CSiH_2 + H_2 \quad (12)$$

$$\rightarrow CH_3SiH_3 \quad (13)$$

$$\rightarrow :C{=}CH_2 + SiH_4 \quad (14)$$

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