Basicity of *N*-H- and *N*-Methyl-1,2,3-triazoles in the Gas Phase, in Solution, and in the Solid State − An Experimental and Theoretical Study

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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The gas-phase and aqueous basicities of six 1,2,3-triazoles have been determined, the former by FT-ICR and the latter by spectrophotometry and ^{1}H NMR. The gas-phase experiments agree very well with the Gibbs free energies calculated at the B3LYP/6-31G* level. In contrast, only semiquantitative ascertainments are possible when basicities in the gas phase and in solution are compared. It is possible, with the aid of calculations, to obtain a complete picture of the complex equilibria involved in *C*-substituted *N*-H-1,2,3-triazoles. The crystal structures of 4(5)-phenyl-1,2,3-triazole (**4**) and 4(5)-nitro-1,2,3-triazole (**15**) have been determined. In the gas phase, 2*H* tautomers **b** always predominate, while in aqueous solution, both 1*H* and 2*H* tautomers – **a** and **b** – are present. Finally, in the solid state, **1** exists as a 1:1 mixture of **1a** and **1b**, while **4** is in the **4b** tautomeric form and **15** is a 1*H* tautomer **15a**. These conclusions – **a** in the gas phase, **a** + **b** in solution, and equal probabilities of finding either **a** or **b** in the crystal – are probably general for all 1,2,3-triazoles.

Introduction

In the neutral and protonated forms of azoles, the related properties of acid-base equilibrium and tautomerism determine many of their biological, chemical, and physicochemical properties.[1−7] It is important to have quantitative data on basicity and tautomerism both in the gas phase and in solution. In this context, let us consider the parent azoles as one example. A summary of the situations involved (Table 1)[8−15] shows that the 1,2,3-triazole system is one of the most complicated. Moreover, the equilibria involved are still more complex in the case of *C*-substituted azoles, particularly triazoles and tetrazoles.[16]

Table 1. Relative stabilities (tautomerism) of neutral and protonated species in parent azoles

Azole	Neutral molecules		Cations
	Gas phase	Solution	Solution
Pyrazole	Only one tautomer		Only one cation
Imidazole	Only one tautomer		Only one cation
1,2,4-Triazole	1*H* >> 4*H*	1*H* >> 4*H*	1,4-diH^+
1,2,3-Triazole	2*H* > 1*H*	1*H* ≈ 2*H*	1,3-diH^+
Tetrazole	2*H* > 1*H*	1*H* > 2*H*	1,4-diH^+ ≈ 1,3-diH^+

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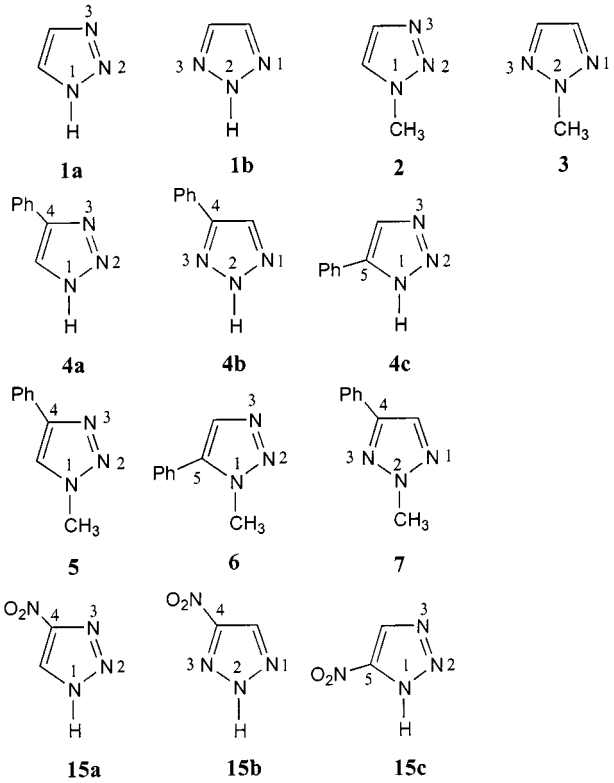

Scheme 1. Structure of 1,2,3-triazoles discussed in this study

The protolytic equilibria of 1,2,3-triazoles have many specific features that make them different from diazoles and 1,2,4-triazoles on one hand, and tetrazoles on the other.

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Whereas the thermodynamic stabilities of the 1*H* and 2*H* neutral tautomers of the parent heterocycle are quite close, the energy of the 1,3-di*H*-1,2,3-triazolium cation is significantly lower than that of its 1,2-diH^+ counterpart.[17−20]

We have already published some experimental[21−31] and theoretical work on *v*-triazoles,[3,32−36] but the problem of the equilibria involving all the neutral and protonated forms requires a specific study. To this end, the parent *v*-triazole **1** and its *C*-phenyl derivative **4** were selected. The approach taken involves the determination of gas-phase basicities (by FT-ICR), the measurement of pK_a values (by UV and ^{1}H NMR spectroscopy), together with comparison with theoretical computations (at the B3LYP/6-31G* level).

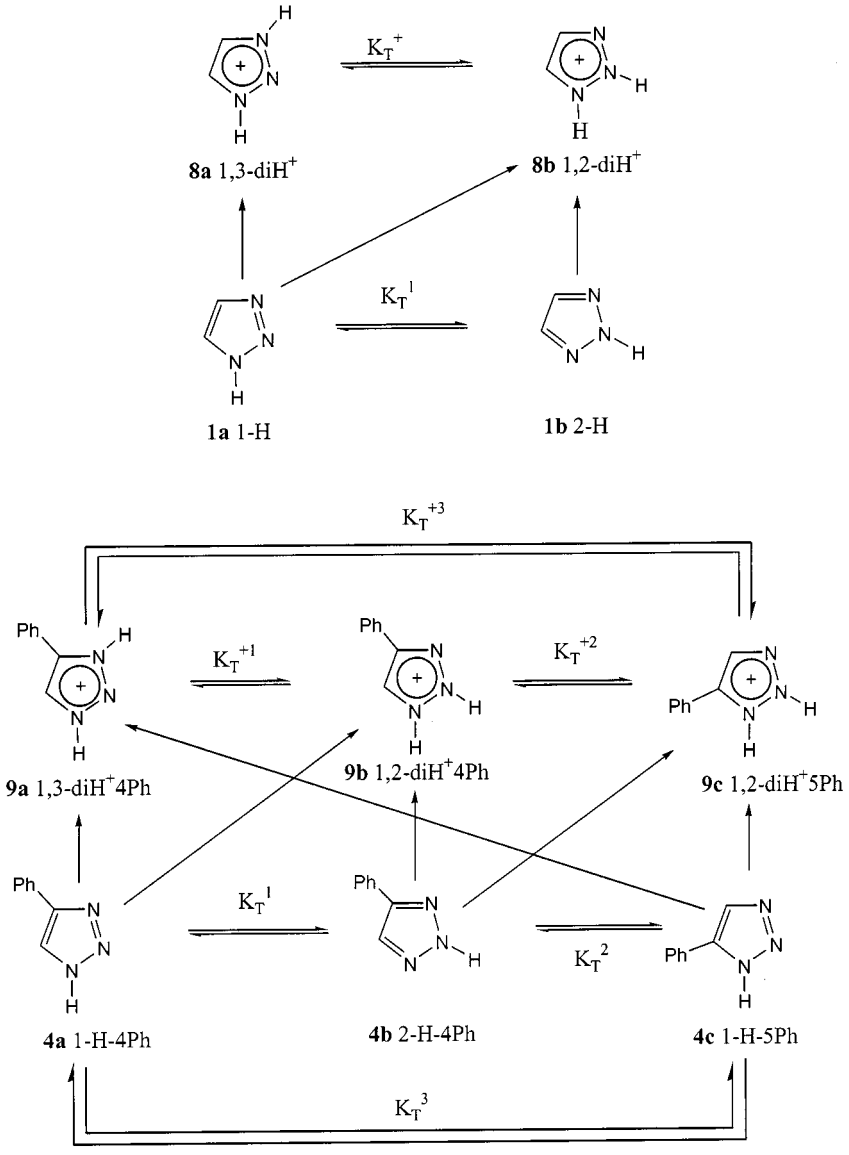
As in all other studies of this kind, it is necessary to use model compounds ("fixed derivatives")[5] **2**, **3**, **5**, **6**, and **7**, in which methyl groups replace the tautomeric hydrogen atom of the neutral molecules (Scheme 1).

Results and Discussion

Equilibria Involved and Theoretical Considerations

The equilibria (double arrows) corresponding to compounds **1** and **4**, as well as the elementary protonation steps (single arrows) are represented in Scheme 2. Note that some equilibria do not correspond to single steps; that between **1b** and **8a**, for instance, implies a tautomeric proton transfer between **1b** and **1a** or between **8b** and **8a**.

The energetic results of the calculations, together with the dipole moments, are reported in Table 2 (other properties, such as geometries, are not discussed). In terms of tautomerism between neutral species, **1b** is 17.5 kJ mol^{-1} more stable than **1a**. Other theoretical calculations have arrived at the same conclusion: 20.5 (HF/6-31G*),[33] 14.7 (HF/DZ),[37] 19.7 (HF/6-31G**//HF/6-31G*),[34] 14.8 (MP2/6-



Scheme 2. Tautomeric and acid-base equilibria of 1,2,3-triazoles **1** and **4**

Table 2. Energies (absolute values in Hartrees, relative values in kJ mol^{-1}) and dipole moments (in D) calculated at the B3LYP/6-31G* level

	Et	ZPE	G_{298}	ΔG_{rel}	GB	μ
1-H **1a**	−242.22233	155.18	−242.18940	17.5	–	4.40
2-H **1b**	−242.22976	157.23	−242.19604	0.0	–	0.06
1,3-diH$^+$ **8a**	−242.57978	192.97	−242.53252	0.0	857.2	–
1,2-diH$^+$ **8b**	−242.55920	190.00	−242.51319	50.8	806.4	–
1-Me **2**	−281.53831	228.70	−281.48005	–	–	4.57
1-Me-2H$^+$ **10a**	−281.88530	263.76	−281.81394	50.1	850.4	–
1-Me-3H$^+$ **10b**	−281.90498	265.56	−281.83304	0.0	900.5	–
2-Me **3**	−281.54673	230.33	−281.48813	–	–	0.48
2-Me-1H$^+$ **11**	−281.88760	263.68	−281.81624	–	835.2	–
1-H-4-Ph **4a**	−473.28416	368.61	−473.17787	16.5	–	3.99
2-H-4-Ph **4b**	−473.29098	370.54	−473.18414	0.0	–	0.34
1-H-5-Ph **4c**	−473.28304	368.78	−473.17650	20.1	–	5.04
1,3-diH$^+$-4Ph **9a**	−473.65333	405.93	−473.53266	0.0	888.8	–
1,2-diH$^+$-4Ph **9b**	−473.63065	402.33	−473.51202	54.2	834.6	–
1,2-diH$^+$-5Ph **9c**	−473.63623	401.83	−473.51752	39.8	849.0	–
1-Me-4Ph **5**	−512.60042	441.79	−512.46884	–	–	4.18
1-Me-2H$^+$-4Ph **12a**	−512.95522	475.68	−512.80966	57.1	868.6	–
1-Me-3H$^+$-4Ph **12b**	−512.97704	478.44	−512.83142	0.0	925.7	–
1-Me-5Ph **6**	−512.59672	442.88	−512.46373	–	–	5.06
1-Me-2H$^+$-5Ph **13a**	−512.95722	477.03	−512.81134	41.2	886.4	–
1-Me-3H$^+$-5Ph **13b**	−512.97388	479.39	−512.82702	0.0	927.6	–
2-Me-4-Ph **7**	−512.60817	443.14	−512.47709	–	–	0.56
2-Me-1H$^+$-4Ph **14a**	−512.95710	475.89	−512.81402	9.2	858.4	–
2-Me-3H$^+$-4Ph **14b**	−512.96217	476.18	−512.81752	0.0	867.6	–

31G**//HF/3−21G + ZPE),[38] 20.9 kJ mol^{-1} (MP2/6-31G*).[39,40]

The case of phenyl-*v*-triazole **4** had not been studied previously. Here, the 2*H* tautomer **4b** is also the most stable, the next one (**4a**) is 16.5 kJ mol^{-1} higher in energy and the least stable is **4c** (by 20.1 kJ mol^{-1}). The difference between the 1*H*-4-Ph and 1*H*-5-Ph tautomers is 3.6 kJ mol^{-1}, a value similar to that found between 4-phenylimidazole (the more stable) and 5-phenylimidazole (ref.[2], p. 178).

As regards the tautomerism of the protonated forms, **8a** is more stable than **8b** by 50.8 kJ mol^{-1}, again in agreement with previous calculations: 56.9 kJ mol^{-1} (6-31G**//6-31G).[33] A similar result (54.2 kJ mol^{-1}), moreover, is obtained in the case of cations (**9a** and **9b**) of the 4(5)-phenyl derivative **4**.

Gas-Phase Basicity Measurements (FT-ICR)

The gas-phase basicity, GB, of a base B is formally defined as the standard Gibbs free energy change for the reaction in Equation (1), the corresponding proton affinity, PA, being the standard enthalpy change for the same reaction.

$$BH^+ (g) \rightarrow B (g) + H^+ (g)$$
$$\Delta G^0 = GB; \Delta H^0 = PA \quad (1)$$

The FT-ICR experiments provide the standard Gibbs free energy changes, ΔGB, pertaining to the proton exchange reaction [Equation (2)] between B and a reference base, B_{ref}, for the equilibrium according to Equation (3).

$$B (g) + B_{ref}H^+ (g) \rightarrow BH^+ (g) + B_{ref} (g)$$
$$\Delta G^0 = \Delta GB \quad (2)$$

$$\Delta GB = GB (B_{ref}) - GB (B) = -RT \ln K_p \quad (3)$$

The FT-ICR experiments do not directly provide proton affinities. The determination of PA (PA = GB + $T\Delta S^0$) thus requires an independent estimation of the entropy change pertaining to Equation (1). The results from the current measurements, together with some literature results, are reported in Table 3.

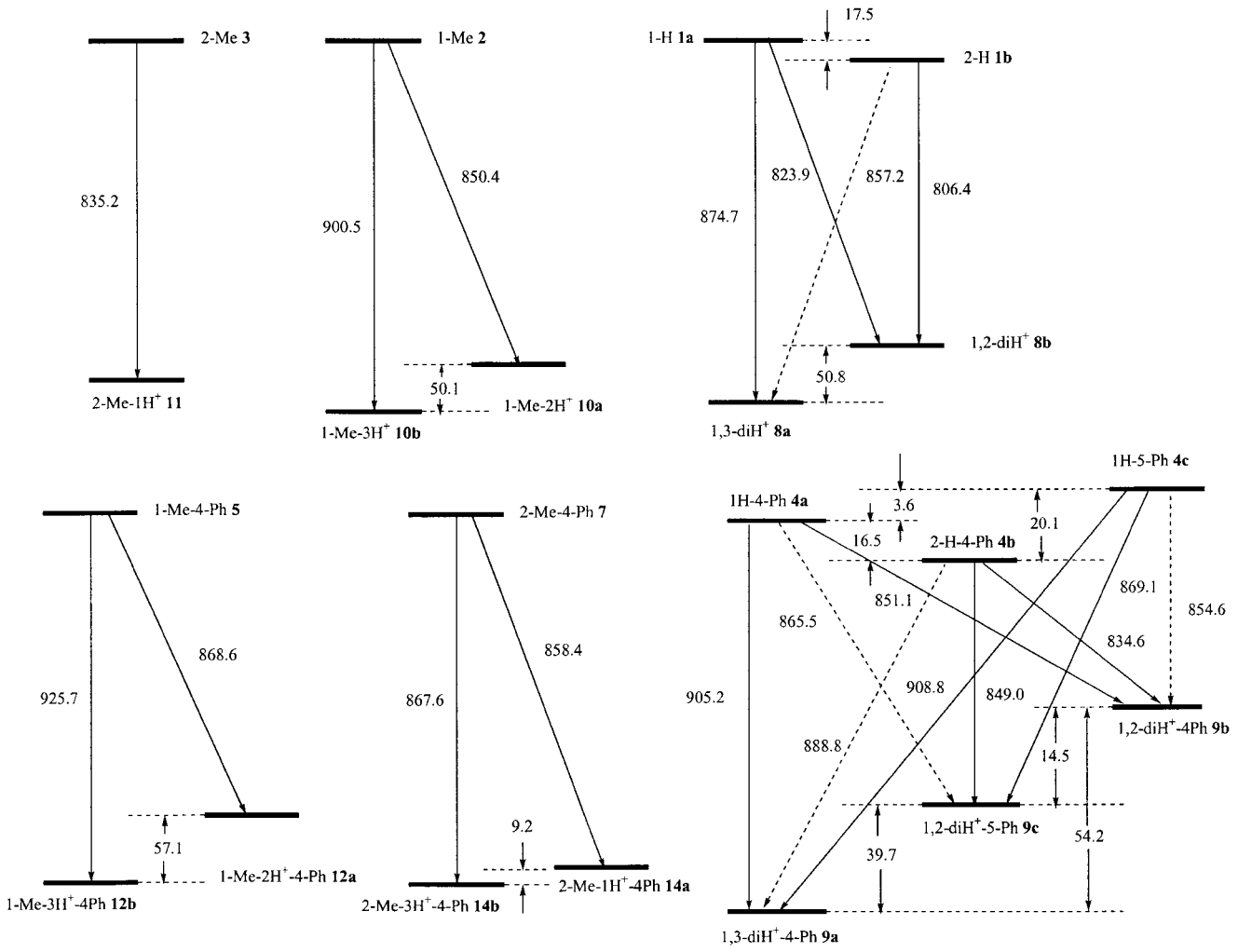
Table 3. Experimental and calculated (from Table 2) values of the gas-phase basicities (GB) of *v*-triazoles (in kJ mol^{-1})

	GB_{exp}	GB_{calc}[a]	PA_{exp}	PA_{calc}[a]	Ref.
1	847.4	857.2	879.9	883.2	[41][b]
2	881.6±1.4	900.5	915.2	925.8	this work
3	824.6±0.3	835.2	857.4	861.6	this work
4	872.7±1.7	888.8	904.8	916.0	this work
5	903.9±1.9	925.7	936.4	952.2	this work
6	not measured[c]	927.6	–[c]	953.7	(see Table 2)
7	853.6±1.5	867.6	884.2	890.9	this work

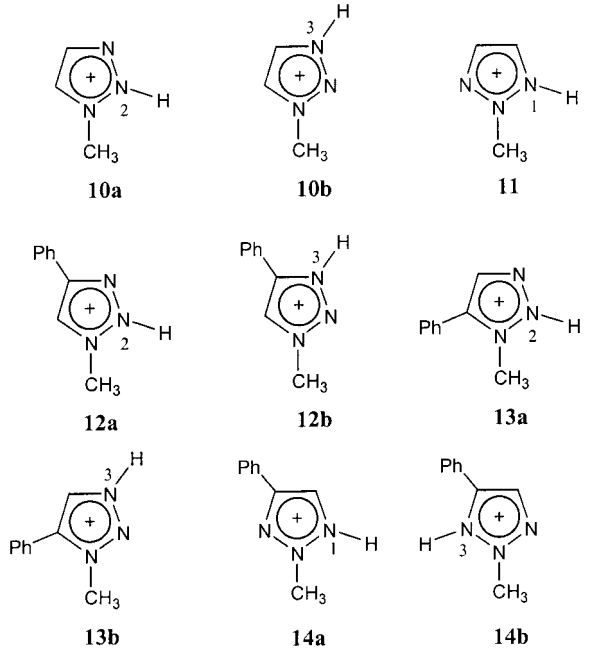
[a] Calculated using the most stable neutral and protonated forms. – [b] The basicity of **1** was determined experimentally[25] and then recalculated.[41] – [c] This compound was not prepared.

We now have available a series of experimental and theoretical values that we must compare while making one reasonable assumption: The phenomenon is a thermodynamic one and involves the most stable neutral tautomer or isomer and the most stable cation, even if these are not directly linked (marked with dashes in Scheme 3). The necessary prototropic transfers between cations are certainly not intramolecular (forbidden),[42,43] but involve collisions with other molecules or with the walls of the instrument.

The acid-base equilibrium between **3** and **11** is unique (Scheme 4). In the case of **2**, the most stable cation **10b**



Scheme 3. Calculated profiles (in kJ mol^{-1}) of the 1,2,3-triazoles discussed in this work



Scheme 4. Structure of the *N*-methyl-1,2,3-triazolium salts

should be formed. In the case of **1**, the measurement corresponds to the transformation between **1b** and **8a**: **1b** yields **8b** and a rapid tautomerism yields **8a**. Compounds **5** and **7** would yield the most stable cations **12b** and **14a**, respectively. To explain the basicity of 4(5)-phenyl-1,2,3-triazole (**4**), we propose that the most stable tautomer **4b** yields the most stable cation, **9a**, via **9c**.

With these data, Equation (4) is obtained by regression (in kJ mol^{-1}).

$$GB_{exp.} = (107\pm18) + (0.86\pm0.02)\,GB_{calc} \quad (4)$$
$$n = 6,\ r^2 = 0.998$$

Assuming that the model is valid, the protonation of 1-methyl-5-phenyl-1,2,3-triazole **6** should yield the most stable cation **13b**. For this equilibrium, Equation (4) yields an estimated GB of 953 kJ mol^{-1}.

Aqueous Basicity Measurements (pK_{BH+})

Let us consider the basicity of 1,2,3-triazoles **1**−**7** in solution. The basicity constants of some of these compounds − compounds **1**, **2**, and **4** − have already been determined quantitatively,[3,26,27] but those of compounds **3**, **5**, and **7** have been measured here for the first time.

The basicity of phenyltriazoles **5** and **7** was determined spectrophotometrically, while in the case of 2-methyl-1,2,3-triazole (**3**) we used a ^{1}H NMR spectroscopic titration method, due to the low electronic absorption of this compound. The spectral characteristics of the neutral triazoles **3**, **5**, and **7** and their cations are as follows: compound **3** (CH_3): δ_B = 4.05 (in 10 wt-% of H_2SO_4), δ_{BH+} = 4.40 (in 73 wt-% of H_2SO_4); compound **5**: λ_B^{max} = 244 nm (ε_B^{max} = 14500 L mol^{-1} cm^{-1}) in buffer solution (pH = 2.16), λ_{BH+}^{max} = 247 nm (ε_{BH+}^{max} = 11300 L mol^{-1} cm^{-1}) in 25.7 wt-% of H_2SO_4 (H_0 = −1.50); compound **7**: λ_B^{max} = 252 nm (ε_B^{max} = 14500 L mol^{-1} cm^{-1}) in aqueous H_2SO_4 (pH = 1), λ_{BH+}^{max} = 273 nm (ε_{BH+}^{max} = 10500 L mol^{-1} cm^{-1}) in 67.3 wt-% of H_2SO_4 (H_0 = −5.52). Protonation results in a red shift of the main absorption bands in the UV spectra for heterocycles **5** and **7** (see Figure 1 and Figure 2). In the case of 2-methyl derivative **7**, the shift is larger than in the case of 1-methyltriazole **5**. Isosbestic points are observed in both cases; in the case of 1-methyltriazole **5**, however, it is less marked. In all aspects, the UV spectra of both the neutral and the protonated forms of *N*-H-triazoles **4**[27] and 1-methyl-4-phenyltriazole (**5**) are quite similar. However, the spectrum of protonated 2-methyl-4-phenyl-1,2,3-triazole (**7**) differs markedly from those observed for compounds **4** and **5**. It is likely that this effect may be governed by the dissimilar structures of the cations obtained through the protonation of compounds **4** and **5** on the one hand and compound **7** on the other. Basicity constants were calculated for these compounds from the relationship between the spectral parameters and acidity, using pH and H_0 scales according to the procedures described in the Exp. Sect. (Table 4). Low solvent coefficient values *m* [see Equation (8)] are observed in the cases of protonation of 2-substituted 1,2,3-triazoles **3** and **7**. It is interesting to note that the pK_{BH+} value of compound **3**, experimentally determined in this work, is practically coincident with the one previously calculated for this compound by extrapolation from other heterocycles.[3]

According to previously published work,[11,44] it is reasonable to compare the basicity constants in solution with the PA values in the gas phase. However, there is no simple relationship between the gas-phase basicities of Scheme 3 and the pK_a values of Table 4.

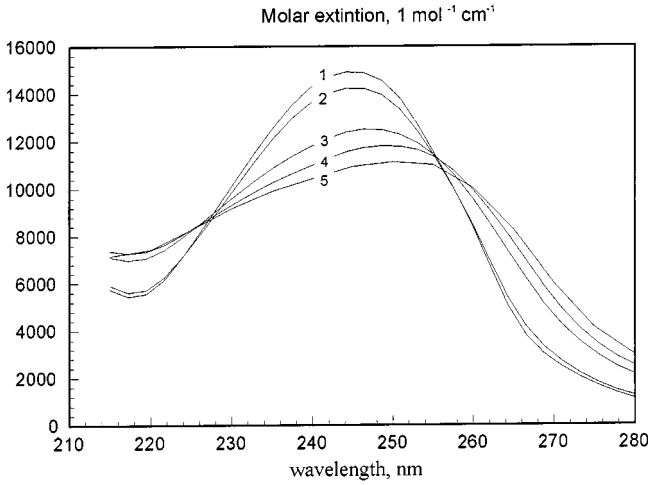


Figure 1. The UV spectra of 1-methyl-4-phenyl-1,2,3-triazole (**5**) in media of different acidities (aqueous buffer solutions and in aqueous solutions of sulfuric acid): 1: pH = 2.16; 2: pH = 1.00; 3: H_0 = −0.52; 4: H_0 = −0.30; 5: H_0 = −1.50

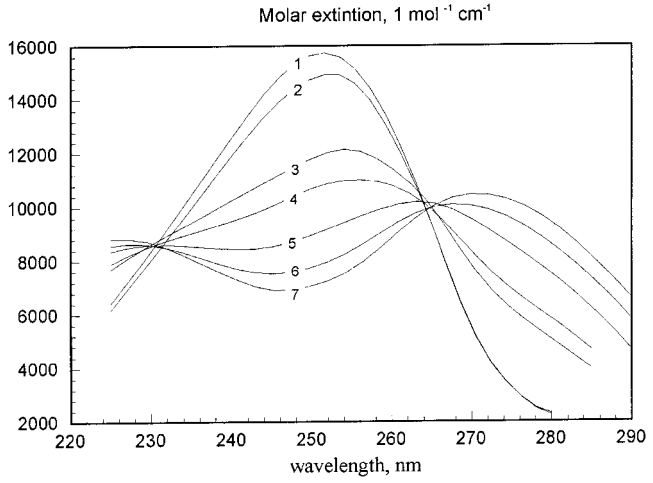


Figure 2. The UV spectra of 2-methyl-4-phenyl-1,2,3-triazole (**7**) in media of different acidities (aqueous solutions of sulfuric acid): 1: pH = 1.00; 2: H_0 = −1.50; 3: H_0 = −3.30; 4: H_0 = −3.52; 5: H_0 = −4.14; 6: H_0 = −4.75; 7: H_0 = −5.52

Table 4. Experimental values of the pK_a and pK_{BH+} of *v*-triazoles **1**−**7** in aqueous solution

Compound	pK_a	pK_{BH+}	Ref.
1,2,3-Triazole (**1**)	9.26[a]	1.17[a]	[3]
1,2,3-Triazole (**1**)	–	−0.16[b]	[26]
1-Methyl-1,2,3-triazole (**2**)	–	1.25[a]	[3]
2-Methyl-1,2,3-triazole (**3**)	–	−3.5±0.1[b]	this work[c]
4(5)-Phenyl-1,2,3-triazole (**4**)	6.25[a]	0.40[d]	[27]
1-Methyl-4-phenyl-1,2,3-triazole (**5**)	–	0.05±0.01[d]	this work[c]
2-Methyl-4-phenyl-1,2,3-triazole (**7**)	–	−3.71±0.02[d]	this work[c]
4(5)-Nitro-1,2,3-triazole (**15**)	[e]	−6.80	[26]

[a] By potentiometric titration. − [b] By ^{1}H NMR titration. − [c] Solvent coefficients *m* [see Equation (8)] for compounds **3**, **5**, and **7** are 0.74, 1.20, and 0.79, respectively. The pK_{BH+} values of compounds **5** and **7** were calculated at λ = 250 and 245 nm, respectively. − [d] By spectrophotometric titration. − [e] The acidity of **15** at room temperature was estimated to be K_a = 1.6·10^{-5}, which corresponds to pK_a = 4.8.[54]

It is true that solvation would modify the stability of the different species in equilibrium. As is shown in Table 2, the 1*H* tautomers **1a** and **4a** have much larger dipole moments than their 2*H* counterparts **1b** and **4b**, which explains why both tautomers have similar stabilities in solution.[2,33]

If imidazoles are viewed as models of 1-methyl-1,2,3-triazoles **2** and **5** (protonation on N3) and pyrazoles as models of 2-methyl-1,2,3-triazoles **3** and **7** (protonation on N1), one would expect, in the first case, a pK_a shift of −1.0 units and in the second case, one of −0.4 pK_a units.[2,5] According to Table 4, the effects are −1.2 (**2** → **5**) and −0.2 (**3** → **7**). Actually, the value of −3.5 for **3** is only a rough extrapolation: A value of −3.2 would be more consistent with the effect of a *C*-phenyl substituent on basicity. In any case, the calculations and the FT-ICR measurements are in disagreement with the findings in solution since, in the gas phase, **5** is more basic than **2** (22 kJ mol^{-1}) and **7** more basic than **3** (29 kJ mol^{-1}). The case of the *N*-H compounds **1** and **4** is more complex, due to the large number of equilibria involved. In this case, the phenyl group increases the basicity both in solution (+0.56 pK_a units) and in the gas phase (25 kJ mol^{-1}).

The pK_{BH+} values of the *N*-methyl derivatives can be used to determine the tautomeric constants K_T corresponding to equilibria **1a** ⇄ **1b** and **4a** ⇄ **4b** ⇄ **4c**.[1,5] This methodology has been applied by Albert and Taylor to the first equilibrium.[45] These authors used Equation (5) to calculate K_T (obviously the very weak 2*H* tautomer does not play any role on the experimental K_{tot}). The factor *f* was introduced to take the effect of *N*-methylation into account;[5] Albert and Taylor used −log *f* = 0.68 for triazoles.[45]

$$\log (K_T + 1) = pK_{NMe} - pK_{tot} - \log 2 - \log f \quad (5)$$

Using their value of 1.17 for the basicity of **1**, Equation (5) provides K_T = 1.88; that is, 65% of **1b**.[44] Using the value recently determined by some of us (−0.16[26]), the result is K_T = 60.5, corresponding to 98.5% of **1b**.

The term "log 2" arises from the fact that cation **8a** has two equivalent ways to lose a proton; if it is assumed that cation **9a** only yields **4a**, then the "log 2" term should be eliminated. Under these conditions, Equation (6) applies.

$$\log (K_T + 1) = pK_{NMe} - pK_{tot} - \log f \quad (6)$$

From the values of Table 4, it follows that K_T = 1.14 and 53% of **4b**. Use of lower values for |log *f*| diminishes the percentages of **b** tautomers. We have established that the basicity and acidity of *N*-H-azoles are proportional, if pyrazoles are excluded[3] [Equation (7)].

$$pK_a(\text{acid}) = 6.78 + 0.956\, pK_a(\text{basic}),\quad n = 30,\ r^2 = 0.992 \quad (7)$$

Of the three pairs of values reported in Table 4 (**1**, **4**, and **15**), only **4** belongs to this equation, the two others deviate considerably, being predicted to be more basic or more acidic than measured. The semiquantitative value for the acidity of **15** should be revised.

We have performed calculations for the three tautomers of nitrotriazole **15** at the same level (B3LYP/6-31G*). The most stable is **15b**, followed by **15a** (15.4 kJ mol^{-1}) and, finally, **15c** (19.1 kJ mol^{-1}). In this last compound there is

Table 5. Selected geometrical parameters [Å, °]; "Cent" represents the centroid of the phenyl ring

		Compound **4**		Compound **15**
N1−N2		1.315(3)		1.345(2)
N2−N3		1.321(3)		1.300(2)
N3−C4		1.332(3)		1.341(2)
C4−C5		1.386(3)		1.363(2)
C5−N1		1.325(3)		1.323(2)
C4−C6/N6		1.472(3)		1.424(2)
C5−N1−N2		103.6(2)		111.9(1)
N1−N2−N3		115.5(2)		107.2(1)
N2−N3−C4		103.9(2)		107.3(1)
N3−C4−C5		107.9(2)		110.7(1)
C4−C5−N1		109.1(2)		102.9(1)
C6/N6−C4−N3		121.5(2)		121.6(1)
C6/N6−C4−C5		130.6(2)		127.7(1)
N3−C4−C6/N6−C7/O7		−22.7(3)		−0.7(2)
Hydrogen interactions:	D−H	H···A	D···A	D−H···A
Compound **4**				
N2−H2···N1 (1−*x*, −1/2 + *y*, −1/2−*z*)	0.89(3)	1.99(3)	2.877(3)	175(3)
C5−H5···N3 (*x*, 1 + *y*, *z*)	0.95(3)	2.65(3)	3.556(4)	159(2)
C8−H8···Cent (*x*, −1/2−*y*, 1/2 + *z*)	1.00(3)	2.80(3)	3.559(3)	133(2)
C11−H11···Cent (*x*, 1/2−*y*, −1/2 + *z*)	0.96(3)	2.84(3)	3.494(3)	126(2)
Compound **15**				
N1−H1···N2 (1−*x*, −*y*, 1−*z*)	0.83(2)	2.36(2)	2.944(2)	129(2)
N1−H1···N3 (*x*, 1/2−*y*, 1/2 + *z*)	0.83(2)	2.42(2)	3.025(2)	131(2)
C5−H5···O7 (*x*, 3/2−*y*, 1/2 + *z*)	0.92(2)	2.41(2)	3.170(2)	141(2)

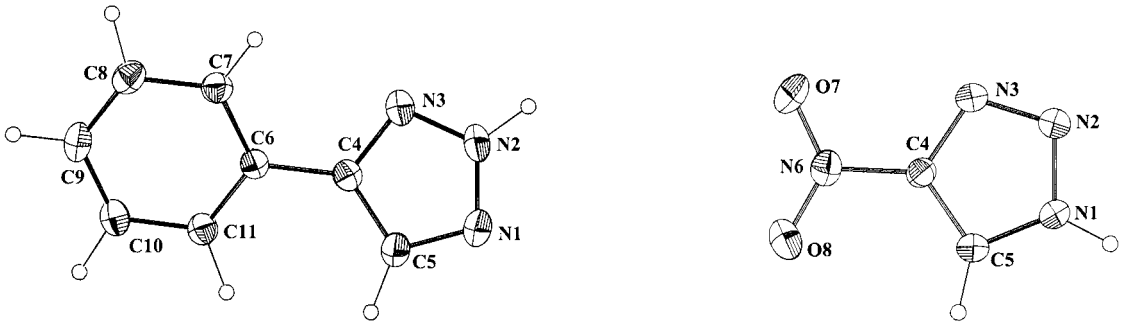


Figure 3. Molecular structure of compound **4** (a; left) and compound **15** (b; right), showing the numbering system; thermal ellipsoids are drawn at the 30% probability level

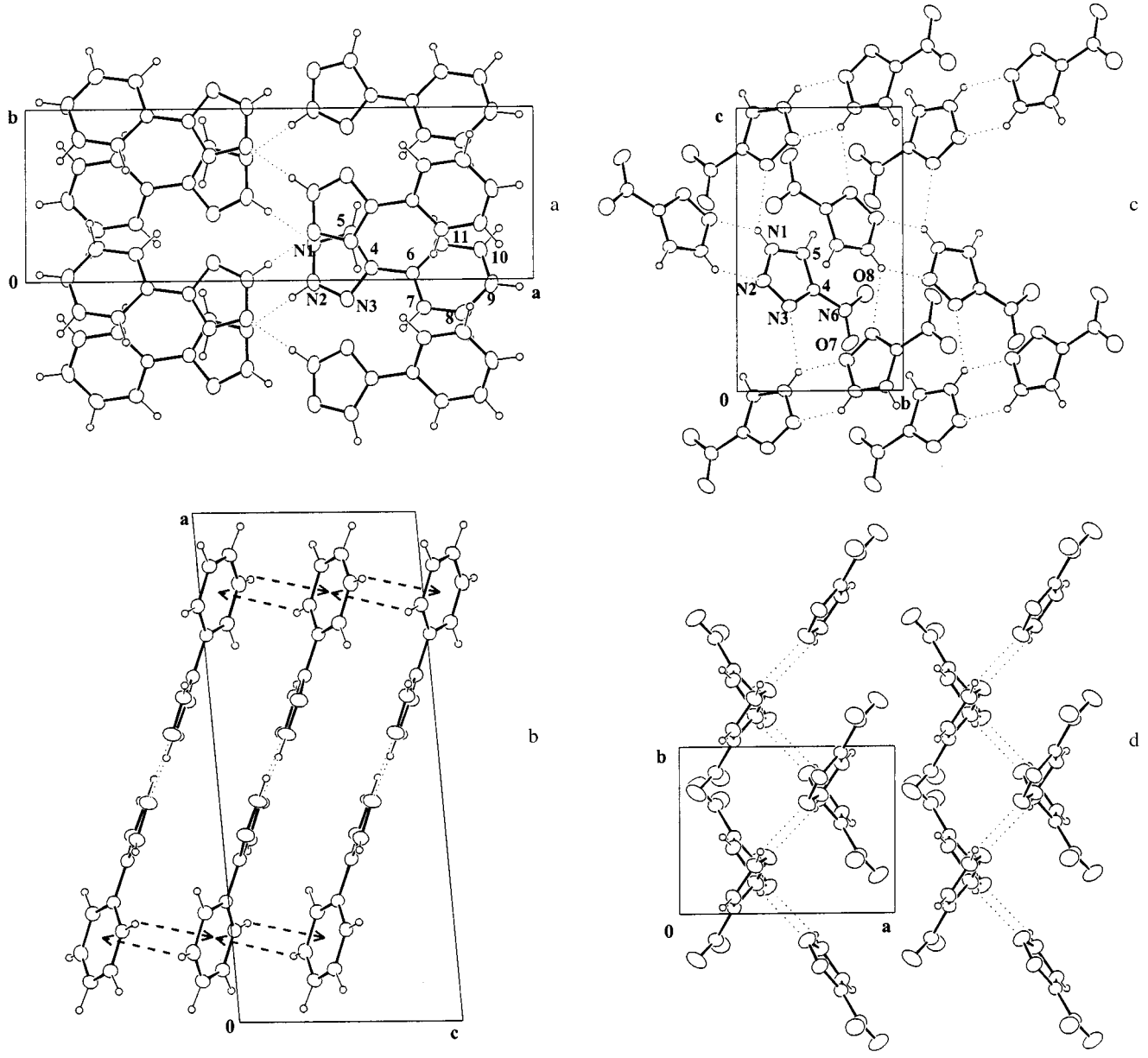


Figure 4. Crystal packing of compound **4**, showing the two centrosymmetric chains in the unit cell (a; left top) and the packing of the chains (b; left bottom); a projection of a layer in **15** (c; right top) and the packing of the layers (d; right bottom); dotted and dashed lines represent N−H···N hydrogen interactions and C−H···π contacts

no hydrogen bond between the NH and the nitro group. The high dipole moment of **15a** (6.25 D) should favour this tautomer over **15b** (4.05 D) and **15c** (0.88 D) in condensed phases.

Crystal Structures

The crystal structure of 1,2,3-triazole (**1**) has been determined by Goddard;[46] it crystallized as a 1:1 mixture of tautomers **1a** and **1b**. When **1** is allowed included in Toda's host, only the 1*H* tautomer **1a** is found.[24] For a more comprehensive study of the tautomerism of 1,2,3-triazoles in the solid state, we determined the crystal structures of two derivatives, 4(5)-phenyl-1,2,3-triazole **4** and 4(5)-nitro-1,2,3-triazole **15**.

The X-ray analyses revealed that compounds **4** and **15** exist in the crystal as the 2*H* and 1*H* tautomers, respectively. The hydrogen atoms were located unambiguously, the bond length and angle patterns (Table 5 and Figure 3) shown by the triazole rings are different and, the substituent aside, both patterns are consistent with the nondisordered structures reported for the corresponding tautomers (CSD[47] ref. codes for 1*H* tautomers: AEXTAZ,[48] ATZCBX;[49] 2*H* tautomers: COMLEV,[50] MSACTZ10,[51] and RUVQOO[46]). The bond angles in both compounds reflect the electronic properties of the phenyl and nitro substituents,[52] which close and open the endocyclic angle at C4 and break the C_{2v} symmetry of the ring. In **15**, the molecule as a whole is planar, while in **4** the phenyl ring is twisted by ca. 23°.

The crystal packing of **4** can be described as chains of molecules connected by N2−H···N1 bonds along the *b* axis, stabilized by C−H···N3 contacts. The chains are held together by two edge-to-face phenyl interactions (Table 5, Figure 4, a and b). The crystal of **15** consists of hydrogen-bonded dimers packed in layers through intermolecular bifurcated N1−H···N2/N3 bonds (Figure 4, c and d). Weak C−H···O contacts within the layer, in which only one oxygen atom is involved, are observed but no other specific intermolecular contacts between layers were found. In this network, the molecules are tighter than in the previous one as reflected by the values of the total packing coefficients of 0.687 and 0.713, respectively.

Conclusions

We have determined the positions of the tautomeric equilibria for some 1,2,3-triazoles in the gas phase, in aqueous solution and in the solid state. In the gas phase, 2*H* tautomers **b** always predominate. In aqueous solution, both 1*H* and 2*H* tautomers, **a** and **b**, are present. Finally, in the solid state, **1** exists as a 1:1 mixture of **1a** and **1b**,[46] while **4** is in the **4b** tautomeric form and **15** is a 1*H* tautomer **15a**. These conclusions are probably general for all 1,2,3-triazoles, **a** in the gas phase, **a** + **b** in solution, and equal probabilities of finding **a** or **b** in the crystal. This is a simple consequence of the opposing forces of "lone pair/lone pair repulsions",[3,25,33−35] disfavouring tautomer **a**, and of dipole moments which stabilize this tautomer in solution and in the solid state. A third factor operating in condensed phases is the hydrogen bonding, which is different in tautomers **a** and **b** (mixed networks involving both tautomers can also be formed).[46]

One aspect related to this discussion is the curious fact that **1** is the only parent azole capable of forming N−H···N hydrogen bonds that is liquid at room temperature (1*H*-pyrrole is also a liquid but it cannot form N−H···N hydrogen bonds). We have summarized the melting points of parent azoles and their *C*-phenyl and *C*-nitro derivatives in Table 6.

Table 6. Melting points of azoles [°C] from ref.[53] unless otherwise indicated

	Parent	*C*-phenyl		*C*-nitro	
		Symm	Asymm	Symm	Asymm
Imidazole	90	2: 148	4(5): 133	2: 284	4(5): 313
Pyrazole	70	4: 230	3(5): 78	4: 162	3(5): 175
1,2,4-Triazole	121	121		215	
1,2,3-Triazole	14[46]	144		158[54]	
Tetrazole	258	218		101[a]	

[a] In ref.[53], p. 350, the m.p. of 5-nitrotetrazole is missing but a reference (292) is given. The publications quoted in reference 292 relate to this compound, but its m.p. is not reported. The m.p. of 101 °C is from: G. I. Koldobskii, D. S. Soldatenko, E. S. Gerasimova, N. R. Khokhryakova, M. B. Shcherbinin, V. A. Ostrovskii, *Russ. J. Org. Chem*. **1997**, *33*, 1771−1783 (*Zh. Org. Khim*. **1997**, *33*, 1854−1866).

Even taking the strength of the N−H···N hydrogen bonds into account (X-ray structures of most compounds of Table 6 are known), the melting points are far too complex to be discussed on the simple basis above. Although the relatively low melting points of **1** (14 °C) and **15** (158 °C) suggest a special characteristic for 1,2,3-triazoles, compound **4** (144 °C) behaves differently. We do not believe that the melting point of **1** is a consequence of its being a mixture of **1a** and **1b**, because **15**, formed exclusively by **15a**, also has a relatively low melting point. Moreover, no polymorph of **1** comprising only one tautomer and with a higher melting point has ever been observed. Therefore, the mystery of liquid **1** remains.

Experimental Section

Compounds: In the case of 1,2,3-triazole (**1**), we used the commercially available compound. *N*-H- and *N*-methyl-1,2,3-triazoles **2**−**7** and **15** were obtained by previously described procedures.[55−59] Their physical and spectral properties agree with those reported.[55−62]

FT-ICR Experiments: The experimental measurement of the gas-phase basicities of the investigated compounds was carried out by FT-ICR mass spectrometry[63−68] with a modified Bruker CMS 47 mass spectrometer[69] used in previous studies.[70−72] A detailed description of the main features of this instrument is given in ref.[69,70]

The main modifications with respect to the standard instrument were given in ref.[70] The substantial field strength of its superconducting magnet, 4.7 T, allows the monitoring of ion-molecule reactions for relatively long periods of time, up to 120 s in some cases. A sufficiently long residence time of the ions in the cell is important whenever thermalizations of the ions is relevant, as in equilibrium studies.[68] The ions are thermalized through collisions with the neutral species and radiation exchange with the surroundings.[73] As in our previous studies,[70–72] the equilibrium constant, K_p, for reaction according to Equation (2) was determined as follows: Briefly, mixtures of B_{ref} (g) and the studied compound (g) of known partial pressures (total pressures in the range $5\cdot10^{-7}$ to $5\cdot10^{-6}$ mbar) were introduced into the high-vacuum section of the instrument, and were ionized by electron impact (nominal ionization energy of 12−14 eV). The corresponding protonated ions were generated by chemical ionization, the proton sources being the ionic fragments of B_{ref}. That a constant ratio of the ion intensities corresponds to the attainment of the equilibrium according to Equation (2) was proven by means of experiments of the double resonance type.[70] The pressure readings for the neutral reactants, as determined by the Bayard−Alpert gauge of the FT-ICR spectrometer, were corrected for each reactant with the aid of the gauge sensitivity. The gauge sensitivities relative to N_2 (S_r) were estimated according to Bartmess and Georgiadis,[74] using the average molecular polarizabilities, α(ahc), calculated according to Miller.[75] The results obtained here are reported in Table 7.

Measurements of pK_a: UV and ^{1}H NMR spectra of compounds **3**, **5**, and **7** in media of different acidities (aqueous buffer solutions and solutions of H_2SO_4) were recorded using Perkin−Elmer Lambda 40 and Bruker DPX 300 apparatuses. Tetramethylammonium bromide was used as an internal standard (δ = 3.33) in the latter case. The aqueous buffer solutions, with ionic strengths $\mu \leq 0.01$ and $\mu \leq 0.1$, were used for spectrophotometric and NMR studies, respectively.

The pK_{BH+} value of triazoles **3**, **5** and **7** were calculated by Equation (8), using a modification of the method of Yates and McClelland[76–79] where pK'_{BH+} and m are the free term and solvation coefficient of the linear relationship of lg I to H_0 (I is the ionization ratio).

$$\lg I = -mH_0 + pK'_{BH+} \quad pK_{BH+} = pK'_{BH+}/m \tag{8}$$

In the case of 2-methyl-1,2,3-triazole (**3**), the I values were calculated from the relationship of δ to medium acidity by Equation (9).

$$I = (\delta - \delta_B)/(\delta_{BH+} - \delta) \tag{9}$$

In the case of compounds **5** and **7**, the I values were calculated from the relationship between molar extinction coefficient and acidity function by Equation (10) (at the analytical wavelength, nm).

$$I = (\varepsilon - \varepsilon_B)/(\varepsilon_{BH+} - \varepsilon) \tag{10}$$

The δ_B, δ_{BH+}, ε_B, and ε_{BH+} values were found in the range $H_0 = \pm1.5$ from the bend points on the sigmoid curves.[77] The H_0 values of fixed H_2O/H_2SO_4 mixtures were taken from Cox and Yates.[80]

X-ray Crystallography: Crystal data and experimental details are given in Table 8. The structures were solved by direct methods (SIR97)[81] and the weighting schemes were established[82] in an empirical way such as to give no trends in $<\omega\Delta^2F>$ vs $<F_o>$ or $<\sin\theta/\lambda>$: $\omega = K/[(a + b\cdot F_o)\ 2][c + d\cdot\sin\theta/\lambda]$; the a, b, c and d parameters were adjusted to flatten the initial trends. The scattering factors were taken from the International Tables for X-ray Crystallography.[83] Most of the calculations were performed using the Xtal3.6 system[84] of programs and PARST.[85] The CIF files were deposited with the Cambridge Crystallographic Data Centre (**4**: CCDC-151609; **15**: CCDC-151610).

Theoretical Calculations: All calculations were performed using the Gaussian-98 program package.[86] Geometries of all structures were

Table 7. Experimental results pertaining to the determination of the gas-phase basicities of the studied compounds

	Reference	GB(B_{ref})[a][b]	ΔGB	GB(compound)[c]	GB(compound) average
2	*c*-$C_3H_5NH_2$	869.9	−11.6	881.5	
	3-Cl-pyridine	871.5	−8.7	880.2	881.6±1.4
	n-$C_3H_7NH_2$	883.9	+0.9	883.0	
3	$(n\text{-}C_4H_9)_2CO$	821.9	−2.9	824.8	
	camphor	827.3	+2.5	824.8	824.6±0.3
	$(i\text{-}C_3H_7)_2O$	828.1	+3.9	824.2	
4	*c*-$C_3H_5NH_2$	869.9	−1.1	871.0	
	2-Cl-pyridine	869.0	−3.9	872.9	872.7±1.7
	$CH_2{=}CHCH_2NH_2$	875.5	+1.2	874.3	
5	$(HC{\equiv}CCH_2)_3N$	894.4	−7.6	902.0	
	pyridine	898.1	−7.7	905.8	903.9±1.9
	t-$C_5H_{11}NH_2$	903.6	−0.3	903.9	
7	$(i\text{-}C_3H_7)_2S$	846.6	−6.9	853.5	
	$HC{\equiv}CCH_2NH_2$	853.5	+1.4	852.1	853.6±1.5
	$HCONMe_2$	856.6	+1.5	855.1	

[a] All values in kJ mol^{-1}. – [b] All values taken from ref.[41] – [c] Calculated as GB(compound) = GB(B_{ref}) − ΔGB according to Equation (3).

Table 8. Crystal analysis parameters at room temperature

	Compound **4**	Compound **15**
Crystal data:		
Empirical formula	$C_8H_7N_3$	$C_3H_2N_4O_2$
Crystal habit	Colourless plate	Colourless prism
Crystal size [mm]	0.75 × 0.13 × 0.05	0.33 × 0.17 × 0.10
Symmetry	monoclinic *P*21/*c*	monoclinic *P*21/*c*
Unit cell determination	least-squares fit from 45 reflections ($2 < \theta < 35°$)	Least-squares fit from 61 reflections ($5 < \theta < 45°$)
Unit cell dimensions [Å, °]	*a* = 17.0418(9) *b* = 5.7415(3) *c* = 7.4782(5) 90, 95.35(1), 90	*a* = 7.7164(4) *b* = 5.8568(2) *c* = 10.1259(5) 90, 101.399(4), 90
Packing: *V* [Å^3], *Z*	728.52(7), 4	448.60(4), 4
D_c [g/cm^3], *M*, *F*(000)	1.324, 145.16, 304	1.867, 1126.07, 256
μ [mm^{-1}]	6.82	14.01
Experimental data:		
Technique	Four-circle diffractometer, bisecting geometry, graphite monochromator, Cu-K_α, ω/2θ scans, θ_{max} = 65°	
	Seifert XRD3000-S	Philips PW1100
Number of reflections		
Independent	1126	762
Observed	907, 2σ(*I*) criterion	692, 2σ(*I*) criterion
Standard reflections	2 reflections every 90 min, no variation	
Solution and refinement:		
Solution	Direct methods: Sir97	
Refinement	Least-squares on *F*, full matrix	
Parameters		
Number of variables	129	81
Ratio of freedom	7.0	8.5
Final <shift/error>	0.008	0.004
H atoms	From difference synthesis	
Weighting scheme	Empirical as to give no trends in $<\omega\Delta^2F>$ vs $<F_o>$ and $<\sin\theta/\lambda>$	
Max. thermal value [Å^2]	U_{22}[C9] = 0.065(2)	U_{11}[O8] = 0.084(1)
Δ*F* peaks and holes [e/Å^3]	0.31, −0.28	0.15, −0.16
Final *R* and *Rw*	0.052, 0.059	0.033, 0.037

fully optimised using the B3LYP/6-31G* basis set.[87] All stationary points were proved to be minima by frequency calculations carried out at the same computational level. The free energy of the systems was calculated from the electronic energy, the ZPE, the thermal correction and the entropy.

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