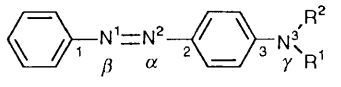
A Theoretical Study of Protonation and Tautomerization of N-Substituted Aminoazobenzenes

Adam Liwo, Anna Tempczyk, Teresa Widernik, Teresa Klentak and Jurand Czermiński
Department of Chemistry, University of Gdańsk, ul. Sobieskiego 18, 80-952 Gdańsk, Poland

Semiempirical AM1 and *ab initio* SCF STO-3G calculations with full geometry optimization were performed on aminoazobenzene (AAB) and its *N*-methyl (MAAB), *N,N*-dimethyl (DMAAB), and *N*-phenyl (PhAAB) derivatives, as well as their azonium and ammonium conjugated acids. AM1 calculations were also performed on hydrated cationic acids, in order to estimate the effect of amphiprotic solvents on tautomerization. In all the cases studied but DMAAB the AM1 and STO-3G proton affinity of the azo nitrogen was definitely higher than that of the amino nitrogen. For the amino nitrogen the calculated proton affinity was found to increase in the series AAB < MAAB < PhAAB < DMAAB. The calculated proton affinity of the azo nitrogen increased in the same order with the exception of the STO-3G results of PhAAB. The tautomerization energy/enthalpy (*i.e.* difference of the gas-phase proton affinity of the azo and the amino nitrogen) was found to increase in the series DMAAB < MAAB < AAB, the position of PhAAB in the series depending on whether the AM1 or STO-3G method was used. These results contradict the experimental data regarding aminoazobenzene protonation and tautomerization constants determined in various solvents, which indicates a strong effect of solvation on the protonation and tautomerization equilibria of aminoazobenzenes. AM1 calculations on hydrated cationic acids showed that solvation effects can be satisfactorily accounted for by enthalpy contributions in the case of tautomerization, because the order of tautomerization constants determined in methanol and dioxane–water mixture generally conforms with the order of tautomerization enthalpies with hydration included. However, the estimated proton affinities in water are still ranked in the same order as *in vacuo* which may indicate that entropy contributions play a much greater role in the case of protonation than in the case of tautomerization phenomena.

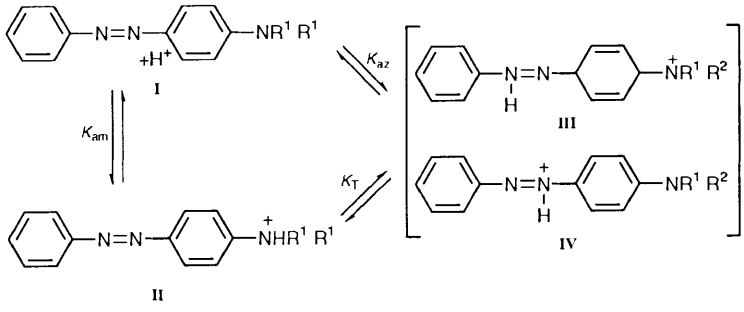
Aminoazobenzenes have three potential centres of protonation: the amino (N^{γ}), and two azo (N^{α} and N^{β}) nitrogen atoms (Scheme 1). In our previous papers[1,2] we investigated, by means of UV-spectroscopy, the proton-exchange phenomena of N-substituted aminoazobenzenes in various solvents, in order to evaluate the relative proton affinity of the possible protonation centres.



The azonium centres cannot be distinguished unambiguously by means of UV-spectroscopy, due to the similarity of the spectra of both protonated forms. However, the combined ^{13}C and ^{15}N NMR and theoretical MINDO studies by Kuroda *et al.*[3], as well as theoretical CNDO/2 studies by Raykhshtat *et al.*[4] have shown the preference of N^{β} protonation.

The spectra of ammonium and azonium cations are sufficiently different to enable the UV-spectroscopic investigation of the corresponding proton-exchange equilibria to be carried out (the absorption bands are centred around 320 and 510 nm, these positions being largely independent of solvent).[1,2] In our previous studies[1,2] it was found that the fractions of the ammonium and azonium forms depend on both the amino-nitrogen substituent and the solvent used: the ammonium form is generally more abundant for the unsubstituted compound than for its *N*-alkyl derivatives. Introducing the *N*-phenyl substituent makes the ammonium form disappear. It was also found that the fraction of azonium cations increases in solvents of gradually decreasing hydrogen-bonding propensity.[1,2]

The present study was aimed at theoretical evaluation of the protonation energies and relative energies/enthalpies of the azonium and ammonium conjugated acids (tautomerization energies/enthalpies) of selected model aminoazobenzenes: 4-aminoazobenzene (AAB), 4-(*N*-methylamino)- (MAAB), 4-(*N,N*-dimethylamino)- (DMAAB), and 4-(*N*-phenylamino)-



Scheme 1 Protonation of aminoazobenzene derivatives

azobenzene (PhAAB) by means of both *ab initio* and semi-empirical methods. In order to estimate the influence of solvent on the relative energy/enthalpy of both tautomeric forms we also performed semiempirical calculations on hydrated species in a supermolecular approach.

Methods

Semiempirical AM1[5,6] calculations were carried out with the use of the MOPAC package[7] for both free and hydrated aminoazobenzenes and their conjugated acids. *Ab initio* calculations were carried out for free species only with the use of the HONDO8 program included in the MOTECC package.[8] Because of the size of the systems studied, *ab initio* calculations were limited to the SCF calculations in the minimal (STO-3G) basis set. They are hereafter referred to as STO-3G calculations. The choice of AM1 out of the three advanced semi-empirical methods included in MOPAC (MNDO, AM1 and PM3) was motivated by the results of a recent extensive study by Ozment *et al.*[9] on the protonation of model nitrogen and oxygen bases. These workers have shown that generally AM1 gives protonation enthalpies much more similar to the experimental gas-phase values than those given by MNDO or PM3.

For each aminoazobenzene and its protonated forms AM1 calculations on free species were performed first. Initial structures were constructed using standard bond lengths and angles and the diazobenzene moiety was assumed to be in a planar conformation. Full (unconstrained) geometry optimization was performed, using a standard BFGS minimizer (included in MOPAC) with the 'precise' option turned on, and then optimization was completed with the EF minimizer. The final norm of energy gradient was less than 0.01 kcal mol^{-1} $Å^{-1}$* in each case. The AM1-optimized structures were taken as starting points for STO-3G calculations. In this case energy minimization was carried out with the use of the BFGS minimizer until the largest component of energy gradient had decreased below 5×10^{-3} E_h a_0^{-1} (*ca.* 1 kcal mol^{-1} $Å^{-1}$).

AM1 gas-phase proton affinities of azo and amino protonation sites of the compounds studied ($E_{PA(az)}$ and $E_{PA(am)}$, respectively), were calculated from the respective heats of formation according to eqn. (1). They are, therefore, estimates for the respective gas-phase enthalpies of protonation; where

$$E_{PA(q)}{}^{AM1} = \Delta H(BH_q^+) - \Delta H(B) - \Delta H(H^+) \quad (1)$$

q = am or az denotes the ammonium or azonium form of the cationic acid, respectively, $\Delta H(B)$ and $\Delta H(BH_q^+)$ are the AM1 heats of formation of free bases and their ammonium or azonium-protonated forms, respectively, while $\Delta H(H^+)$ = 367.2 kcal mol^{-1} is the experimental heat of formation of H^+.[10]

Because *ab initio* calculations give only total energies of species without contributions from the partition function, the STO-3G proton affinities obtained in this study are not gas-phase enthalpies of protonation, but energies of protonation. Because of the size of the molecules under study we did not evaluate partition-function contribution in the case of STO-3G calculations. However, from the study of Ozment *et al.*[9] it follows that the partition-function contribution to proton affinity is almost constant and amounts to *ca.* 10 kcal mol^{-1}. Therefore the relative *ab initio* proton affinities of the ammonium and azonium form should not be affected by not taking into consideration the partition function contribution. Thus, the STO-3G proton affinities were calculated from eqn. (2); where $E_{tot}(B)$ and $E_{tot}(BH_q^+)$, are the STO-3G total energies of free bases and their protonated forms. Obviously, the STO-3G total energy of the proton is equal to zero.

$$E_{PA(q)}{}^{STO} = E_{tot}(BH_q^+) - E_{tot}(B) \quad (2)$$

In order to estimate the influence of hydration on the relative energies of the ammonium and azonium-protonated forms, AM1 calculations were also performed on protonated species surrounded by eight water molecules. Taking this particular number of water molecules was motivated by the fact that four water molecules only can be accommodated in the neighbourhood of the azo (azonium) or amino (ammonium) site. In the initial configurations four water molecules were distributed symmetrically around the azo (azonium) and amino (ammonium) sites. However, as a result of energy minimization water molecules tended to move towards the protonated site. As for the free species, each optimization was finished using the EF minimizer. The final gradient norm of the energy gradient was less than 0.1 kcal mol^{-1}. For each final hydrated structure, eigenvalues of the energy Hessian were calculated, in order to check whether the structures were true minima. In order to test whether the calculated structures of the water complexes were not poor local minima of relatively higher energy, for the cationic acids of AAB we carried out additional minimizations starting from the previously obtained structures with randomly perturbed water-molecule positions (by about 2 Å on average). The final energies of these structures were either similar to or higher than those of the unperturbed structures. Therefore our structures of water complexes are probably minima with reasonably low energy. However, since we were unable to carry out more extensive searches for global energy minima at this level of calculations, and, moreover, one should average over a large number of structures, in order to obtain reliable estimates of solvation energies, the results of this part of our work can only be treated as qualitative estimates of the differences in solvation energies.

In all of the cases considered energy minimization was carried out using Cartesian coordinates as variables.

The accuracy of the AM1 estimates of solvation energies has been a subject of numerous studies which have been recently reviewed by Dannenberg and Eveleth.[11] It appears that the AM1 energies of interaction of amino bases and their conjugated acids with water are in quite good agreement with the available experimental data, the error being *ca.* 1 kcal mol^{-1}.[11] Moreover because for species of the same type (in our case the cationic acids conjugated to nitrogen bases) AM1 tends to underestimate the energies of interaction with water to approximately the same extent,[11] the error in the difference of solvation energies of the ammonium and the azonium forms of protonated aminoazobenzenes caused by the inaccuracy of AM1 can even be smaller.

An argument that is often put forward against using AM1 for the calculations of hydrogen-bonded complexes is that it tends to predict bifurcated hydrogen bonds,[6,7] even in the case of the water dimer which apparently contains a linear hydrogen bond.[12] However, extensive *ab initio* calculations[13,14] have shown that structures of the water dimer close to that obtained by AM1 have energies only tenths of a kcal mol^{-1} higher than that of the global-minimum structure with linear hydrogen bonds. Moreover, the hydrogen bonds involving nitrogen and oxygen atoms are often bifurcated,[15] as obtained in AM1 calculations.[6,7,11]

Figs. 1(*a*) and (*b*) show the energy-minimized structures of the complexes of the protonated forms of AAB with eight water molecules. As shown, though many of the hydrogen bonds are bifurcated, there are also linear ones, and the whole arrangement of solvent molecules seems to resemble that found around protonated nitrogens in the crystal state.[15]

* 1 cal = 4.184 J. 1 E_h = 4.360×10^{-18} J. 1 $a_0 \approx 5.291 \times 10^{-11}$ m.

Table 1 Average[a] values of bond lengths (Å) and angles (°) of the diazo moiety of the species studied obtained in AM1 and STO-3G calculations compared to available experimental data

	B			BH^+_{az}		BH^+_{am}	
Atoms	AM1	STO	Exp.	AM1	STO	AM1	STO
C(1)–N(1)	1.44	1.48	1.445,[b] 1.41[c]	1.44	1.46	1.43	1.47
C(2)–N(2)	1.43	1.47	1.439,[b] 1.46[c]	1.37	1.38	1.44	1.48
N(1)–N(2)	1.23	1.28	1.237,[b] 1.26[c]	1.26	1.31	1.23	1.28
C(1)–N(1)–N(2)	119.5	111.7	113.2,[b] 115.3[c]	123.0	122.0	120.8	112.9
C(2)–N(2)–N(1)	119.9	111.3	112.0,[b] 115.7[c]	124.1	120.7	119.0	110.9

[a] Arithmetic averages over the three compounds studied; the maximum difference between the values corresponding to individual compounds was 0.01 Å for bond lengths and 0.1° for bond angles. [b] Crystal data of 4-(*N*-acetyl-2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl)aminoazobenzene (ref. 17). [c] Crystal data of 2',3-dimethyl-4-aminoazobenzene (ref. 18).

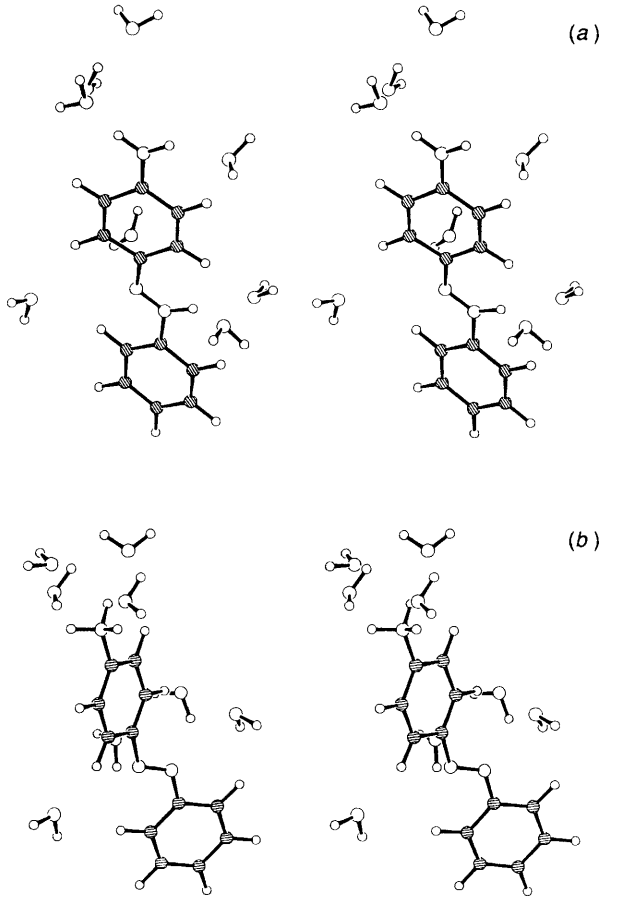


Fig. 1 Energy-minimized structures (AM1 method) of the complexes of the azonium (*a*) and the ammonium (*b*) of protonated aminoazobenzene. The carbon atoms are presented by hatched spheres, all other atoms by empty spheres.

Results and Discussion

Geometry of the Species Studied.—In both AM1 and STO-3G calculations the bond lengths and angles of the species studied turned out to be almost independent of substitution, but depended on protonation. The average values of the bond lengths and angles of the diazo moiety for neutral and protonated species obtained in AM1 and STO-3G calculations, together with accessible experimental data of related compounds, are summarized in Table 1. As shown, they compare quite well with experimental data, except for AM1 values of the N=N–C planar angles which are remarkably overestimated. It can also be noted that STO-3G calculations overestimate, though to a lesser extent, the length of all bonds.

Consistent with experimental data,[16–18] the diazo moiety turned out to be almost planar. The other interesting geometric parameters are the angles of torsion of the first [*i.e.* containing C(1)] and second [containing C(2)] benzene ring with respect to the C(1)–N(1)–N(2)–C(2) plane, the twist of the terminal amino group with respect to the benzene ring that it is attached to, as well as the pyramidicity of the terminal amino group which can be expressed as the 'improper' torsional angle between R^1–N(3)–C(3)···R^2. These dihedral angles can be considered as a measure for the conjugation between the two benzene rings of the aminoazobenzene moiety and the amino-azobenzene moiety and the amino group. The values of these angles obtained in AM1 and STO-3G calculations are listed in Table 2. As shown, the two methods give comparable values. The values obtained for AAB are close to those of the most related compound, 2',3-dimethyl-4-aminoazobenzene (Table 2).

Proton Affinities.—The AM1 proton affinities and tautomerization 'gas-phase' enthalpies (AM1) and energies (STO-3G), as well as AM1-estimated tautomerization enthalpies in water are summarized in Table 3, with the experimental protonation and tautomerization constants determined in nitromethane, acetonitrile, methanol, dimethylformamide, and dioxane–water mixture in Table 4. The constants given in Table 4 are expressed by eqns. (3*a*)–(3*c*).

$$K_1 = \frac{[BH^+_{(am)}]}{[H^+][B]} \quad (3a)$$

$$K_2 = \frac{[BH^+_{(az)}]}{[H^+][B]} \quad (3b)$$

$$K_T = \frac{[BH^+_{(az)}]}{[BH^+_{(am)}]} \quad (3c)$$

The proton affinities estimated by STO-3G calculations are remarkably higher (in absolute value) than their AM1 counterparts. Based on the results of the study by Ozment *et al.*,[9] it can be concluded that our STO-3G values are most probably too high. The main reason for this is that we employed only the minimal basis set, whereas the estimates of absolute proton affinities are highly basis-set dependent, although the relations between proton affinities are well reproduced even with a small basis.[9] The second cause of the divergence of our AM1 and STO-3G estimates of proton affinities is that the AM1 values correspond to enthalpies, while the STO-3G values correspond to differences in total energies (see Methods). However, despite these discrepancies, the relations between the proton affinities of the compounds studied

Table 2 Selected dihedral angles of the bases studied obtained in AM1 and STO-3G calculations

	AAB			MAAB		DMAAB		PhAAB	
Angle	AM1	STO	Exp.[a]	AM1	STO	AM1	STO	AM1	STO
ω_1[b]	13.4	6.0	12.7	9.0	8.1	7.0	6.9	1.9	4.2
ω_2[c]	3.2	2.6	2.0	1.5	0.8	0.5	0.4	0.8	0.5
ω_3[d]	23.1	31.4	13.9	19.3	19.5	7.3	4.0	38.6	28.3
τ[e]	137.3	120.9	162.5	141.4	129.6	139.7	132.7	153.1	137.4

[a] Crystal data of 2',3-dimethyl-4-aminoazobenzene (ref. 18). [b] The twist of the benzene ring attached to N(1) with respect to the plane of diazo moiety. [c] The twist of the benzene ring attached to N(2) with respect to the diazo moiety. [d] The twist of the amino group with respect to the plane of the benzene ring to which it is attached. [e] The pyramidicity of the amino group defined as the 'improper' torsion angle R^2–N(3)–C(3)···R^1.

Table 3 AM1 and STO-3G proton affinities and tautomerization enthalpies/energies (kcal mol^{-1}) of aminoazobenzene and its N-substituted derivatives

	$E_{PA(az)}$		$E_{PA(am)}$		$E_{PA(az)} - E_{PA(am)}$		
Compound[a]	AM1	STO-3G	AM1	STO	AM1	STO	AM1h[b]
AAB	−219.0	−279.7	−210.8	−267.9	−8.2	−11.8	22.5
MAAB	−220.0	−282.7	−212.5	−275.0	−7.5	−7.6	−6.0
DMAAB	−221.4	−281.2	−215.1	−281.5	−6.3	0.3	−9.2
PhAAB	−219.8	−284.4	−214.2	−277.5	−5.6	−6.9	−2.4

[a] See text for name abbreviations. [b] AM1 tautomerization enthalpy in a model with eight water molecules in the hydration sphere of the protonated species.

Table 4 Comparison of protonation and tautomerization constants determined in various solvents (values from ref. 1)[a]

	Solvent														
	Nitromethane			Acetonitrile			Methanol			Dimethyl-formamide			Dioxane–water (1:1)		
Compound	$K_1 \times 10^3$	K_2	K_T	$K_1 \times 10^2$	$K_2 \times 10^2$	K_T	$K_1 \times 10^{-3}$	$K_1 \times 10^{-3}$	K_T	K_1	K_2	K_T	$K_1 \times 10^{-1}$	$K_2 \times 10^{-1}$	K_T
AAB	6.50	0.25	6.23	1.30	2.03	1.25	4.50	1.21	0.27	11.2	1.71	0.154	5.73	1.17	0.204
MAAB	7.10	3.92	23.5	0.07	11.9	12.7	0.52	2.79	5.40	2.15	3.32	1.55	2.83	5.11	1.80
DMAAB	6.70	14.4	46.3	0.01	17.7	40.7	0.53	1.97	3.71	1.35	2.28	1.69	2.50	4.90	1.96
PhAAB	—	0.06	—	—	0.32	—	—	0.0535	—	—	—	—	—	—	—

[a] See eqns. (3*a*)–(3*c*) for the definition of equilibrium constants. K_1 and K_2 in dm^3 mol^{-1}.

estimated from STO-3G and AM1 calculations are similar (Table 3).

As shown in Table 3, in almost all of the cases considered the estimated proton affinity of the azo centre is greater than that of the amino centre (with the exception of the STO-3G proton affinities of DMAAB). This is consistent with most of the experimental data on aminoazobenzene–carboxylic acid complexes in such solvents as acetonitrile,[1] nitromethane,[1] hexane,[2] cyclohexane[2] and chlorobenzene,[19] as the free enthalpy of a proton-transfer complex for a fixed proton donor in these relatively poor and very poor solvents will depend, first of all, on the proton affinity of acceptor centres.

Unfortunately, no direct numerical data on proton-exchange phenomena are available in definitely apolar solvents, like hydrocarbons, as only proton-transfer complexes with a great excess of carboxylic acids can be investigated in such cases. Nevertheless, our earlier experimental studies indicate that the less the hydrogen-bonding propensity of a solvent, the greater the fraction the azonium associates.[1,2] On the other hand, the values in pure water cannot be measured either, due to a low solubility of aminoazobenzene derivatives in this solvent.

From both AM1 and STO-3G calculations it follows that the proton affinities of both amino and azo nitrogen increase in the series AAB < MAAB < PhAAB < DMAAB, except for the STO-3G estimates of the proton affinities of the azo nitrogen of DMAAB and PhAAB which are ranked in a reversed order. The change of the proton affinity of the amino nitrogen in the series of methyl-substituted aminoazobenzenes can be attributed to the induction effect of the substituents. Owing to the conjugation of the diazo moiety to the amino group through a benzene ring, this effect can also be transmitted to the β-azo nitrogen, which can account for the same ranking of proton affinities of the azo nitrogen as those of the amino nitrogen.

From the values of tautomerization constants [eqn. (3*c*)] summarized in Table 4 it can be concluded that the azonium form constitutes a greater fraction of the aminoazobenzene conjugated-acid mixture than the ammonium form in such solvents as nitromethane and acetonitrile, which is in agreement with the results of theoretical calculations (Table 3). In contrast to this, the ammonium form is more abundant in methanol, dimethylformamide, and dioxane–water systems. This can be attributed to the difference of the solvation properties of these two groups of solvents, as the solvents of the second group, being capable of effective hydrogen bond formation, will better solvate the ammonium form.

In order to estimate qualitatively the effect of amphiprotic solvents on tautomerization energy we performed AM1 calculations on both protonated forms of each of the compounds studied with the inclusion of explicit water molecules, as described in the Methods section. The resulting values of

tautomerization enthalpies are summarized in the last column of Table 3. As shown, in the case of AAB the ammonium form is now definitely favoured over the azonium one, which is in agreement with the data for the amphiprotic solvents (methanol and dioxane–water mixture) in Table 4. The azonium form is favoured over the ammonium one for MAAB and DMAAB, and the tautomerization enthalpy of DMAAB is more positive than that of MAAB, which agrees with the order of experimental tautomerization constants in methanol and dioxane–water mixture. Thus, for AAB and its *N*-methyl derivatives the enthalpy contribution to hydration seems to be sufficient to explain qualitatively the extent of the shift of tautomeric equilibria. However, in the case of PhAAB, although the estimated enthalpy of tautomerization of the ammonium form is still lower than zero after including hydration, its absolute value is less than the absolute value of the estimated enthalpy of tautomerization of the methyl derivatives, which is in contradiction with the fact that the ammonium form of PhAAB is never observed (Table 4). This can be attributed to the fact that in the present calculations we estimated only enthalpy, while free enthalpies of reactions should rather be compared with experimental equilibrium constants. Evaluating the entropy contribution to free enthalpy in the case of hydration cannot be accomplished without extensive Monte Carlo simulations.

It can also be noted that the order of amino nitrogen protonation constants of AAB and its derivatives is almost exactly opposite to the order of AM1 and STO-3G proton affinities (Tables 3 and 4). This difference must also be caused by the solvation effect, which is understandable, since the increasing bulkiness of substituent at the positively charged site both makes the radius of the first solvation sphere greater and causes an additional loss of entropy due to restricting the mobility of the solvent molecules of the first solvation sphere with respect to nonpolar substituents (solvophobic effect).[20] Our trial AM1 calculations using a model of neutral hydrated aminoazobenzenes and a model of the solvated hydronium cation showed that the order of protonation enthalpies does not reverse with respect to the estimated gas-phase proton affinities after hydration is included (data not shown). It can therefore be concluded that in this case the entropy contribution to free energy must play a definitely greater role than in the case of tautomerization.

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