Gas-Phase Basicity of Polyfunctional Amidinazines: Experimental Evidence of Preferred Site(s) of Protonation

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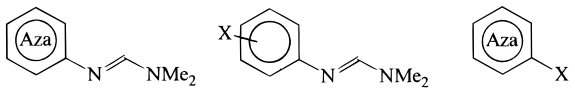
Gas-phase basicities of four polyfunctional N^1,N^1-dimethyl-N^2-azinylformamidines (**1**−**4**) are obtained from proton-transfer equilibrium constant determinations, using Fourier transform ion-cyclotron resonance mass spectrometry. Comparison with model amidines and azines (GB revised according to the recent compilation of Hunter and Lias) indicates the aza group as the favored site of protonation. The strong basicity of ortho derivatives is explained in term of intramolecular stabilization (the so-called "internal solvation").

Introduction

Investigations on proton-transfer reactions in the gas phase for polyfunctional compounds are usually more complicated than for monofunctional ones.[1] An intramolecular hydrogen bonding called "internal solvation" of proton[2] can take place in monoprotonated cations or monodeprotonated anions. This extra energetic stabilization contributes to the measured gas-phase acid/base parameters.[1−3] In the case of bidentate ligands (e.g., diamines, diethers, diketones, amino alcohols, amino ethers) a strong enhancement of basicity (5−20 kcal·mol^{-1}) has been observed.[2−4] For this reason, the site of protonation is difficult to assign without additional experiments for the corresponding model compounds and/or theoretical calculations carried out on the different forms of the polyfunctional derivative. For our studies on the preferred site(s) of protonation in polyfunctional nitrogen bases in the gas phase, a series of amidinazines (N^1,N^1-dimethyl-N^2-azinylformamidines, FDM*Aza: compounds **1**−**4** shown in Scheme 1) was chosen. As model compounds we used a series of amidines (N^1,N^1-dimethyl-N^2-phenylformamidines, FDMP*X) and a series of azines (pyridines, AZA*X) studied previously.[4−7] The gas-phase basicities (GBs, Gibbs free energies associated with the deprotonation process of a protonated base in the gas phase) of model FDMP*X reported in the literature[6] were revised in the light of reevaluated GB values for reference bases given in the recent compilation of Hunter and Lias.[4] For the experimental determination of GBs, FT-ICR mass spectrometry was used, and for the analysis of the gas-phase substituent effects in the model and polyfunctional compounds, the Taft and Topsom equation[8] was considered. Our experimental results were also compared with previously reported theoretical calculations[9] and hydrogen-bond formation in an apolar solvent (CCl_4).[10]

Scheme 1



FDM*Aza FDMP*X AZA*X

1 4-azinyl

2 3-azinyl

3 2-azinyl

4 1,3-diazin-2-yl

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Chart 1

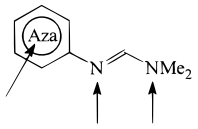


Table 1. Experimental GB Values Obtained from Proton-Transfer Equilibria between Amidinazine (B) and Reference Base (Ref) in kcal·mol^{-1}

compd	ref	GB(ref)[a]	ΔG	GB(B)	GB(B)[b]
1	*n*-Bu_3N	231.3	+1.2	232.5	
	$Me_2NCH{=}NMe$	232.0[c]	+0.6	232.6	
	$Me_2N(CH_2)_3NH_2$	233.1	−0.1	233.0	
	$Me_2N(CH_2)_3NMe_2$	235.5	<−2.1	<233.4	232.7
2	Et_3N	227.0	+0.6	227.6	
	n-Pr_3N	229.5	−1.1	228.4	228.0
3	*n*-Pr_3N	229.5	>+1.9	>231.4	
	n-Bu_3N	231.3	+1.8	233.1	
	$Me_2NCH{=}NMe$	232.0[c]	+0.6	232.6	
	$Me_2N(CH_2)_3NMe_2$	235.5	−2.4	233.1	232.9
4	*n*-Bu_3N	231.3	+1.8	233.1	
	$Me_2NCH{=}NMe$	232.0[c]	+0.5	232.5	
	$Me_2N(CH_2)_3NH_2$	233.1	+0.2	233.3	
	$Me_2N(CH_2)_3NMe_2$	235.5	−2.5	233.0	233.0

[a] Data from ref 4. [b] Mean value. [c] GB value revised according to the measured ΔG given in ref 24 and the new GB for reference bases.[4]

Results and Discussion

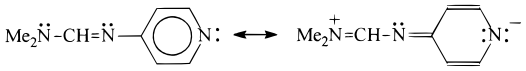
Possible Site(s) of Protonation. Amidinazines **1**−**4** can be considered as polyfunctional nitrogen bases. They contain two nitrogen atoms (amino and imino) in the amidine function and additionally one (in **1**−**3)** or two (in **4**) aza nitrogen(s) in the aryl ring. Each of these nitrogen atoms is prone to attach a proton in the gas phase (Chart 1).

Experimental and theoretical studies carried out for model series of FDMP*X have shown that the imino nitrogen atom in the amidine moiety is more basic than the amino nitrogen atom by ca. 25 kcal·mol^{-1} and that it is certainly the favored site of protonation in the gas phase.[5,6] This conclusion is in good agreement with the n−π conjugation effect in the amidine group (1) observed in solution.[11]

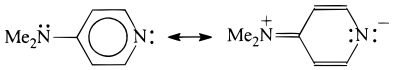
$$Me_2\ddot{N}-CH=\ddot{N}-R \leftrightarrow Me_2\overset{+}{N}=CH-\overset{-}{\underset{\cdot\cdot}{N}}-R \qquad (1)$$

Comparison of the gas-phase basicities of FDM*Aza (Table 1) and of model compounds FDMP*X (Table 2) and AZA*X[4] shows that for unsubstituted systems, the GB value attributed to the imino group in FDMP*H (229.4 kcal·mol^{-1}) is larger by 14.7 kcal·mol^{-1} than that of the aza group in pyridine (214.7 kcal·mol^{-1}). However, the electron-donating Me_2N group increases the GB of pyridine (the parent aza model) by 10.3, 10.7, and 17.4 kcal·mol^{-1} for 2-, 3-, and 4-position, respectively. Substituent effects of the electron-accepting aza nitrogen in FDM*Aza may be compared with those of the CF_3, CN, or NO_2 groups. In series of FDMP*X, the CF_3, CN, or NO_2 groups diminish the GB of FDMP*H (the parent formamidino model) by 5.7, 7.9, and 8.7 kcal·mol^{-1}, respectively.

All these observations indicate that the basicity contributions of the electron- donating amidine group (imino nitrogen atom) and the electron-accepting aza group(s) in amidinazines **1**−**4** can be of the same order of absolute magnitude. The n−π conjugation effect of the amidine group (1) may be transmitted to the aza atom(s). As a consequence of this effect the basicity of the aza atom(s) would increase and the basicity of the amidine group would decrease. The strongest effect is predicted for derivative 1 with the aza group in 4-position (2), similarly as it has been observed for pyridinamines (3).[7] The same type of conjugation effects and of basicity changes are possible for the ortho derivatives (**3** and **4**).



(2)



(3)

Preferred Site of Protonation. Theoretical semiempirical (AM1) calculations[9] performed for **1**−**4** indicate that the *N*-amino is the least basic site. The difference between the proton affinities (PA) calculated for protonation at the imino and amino nitrogen atoms is of the same order of magnitude as that found for series of model compounds FDMP*X *(*ca. 20−30 kcal·mol^{-1}).[6] This confirms that the n-π conjugation in the amidine group is also present in amidinazines **1**−**4**. The absolute difference between the calculated PA values for the imino and aza nitrogen atoms in **1**−**4** is considerably smaller (<7 kcal·mol^{-1}). Taking into account the different average errors for PA calculations found for the model series of FDMP*X (−1.3 kcal·mol^{-1})[6] and AZA*X (−5.2 kcal·mol^{-1})[12] it has been concluded without any doubt that only in compound **1** the aza nitrogen atom is the preferred site of protonation. For the other *5* compounds the indication of the most basic site, the imino or aza nitrogen is not possible from theoretical calculations at the AM1 level.

First comparison of the experimental gas-phase basicities obtained in this work for amidinazines **1**−**4** (Table 1) and revised data for model FDMP*X with X = H, CF_3, CN, and NO_2 (Table 2) and AZA*X[4] with X = H, NH_2, and NMe_2 indicates that the aza group is preferentially protonated in the gas phase in each case, and the substituent electronic effects of the amidine group are larger than those of the NH_2 and NMe_2 groups. For **3** and **4**, the GB values are almost the same as for **1**. Usually ortho substituent effects are smaller than para ones.[1,4,8] Moreover, the additional aza group in the phenyl ring in **4** should decrease the GB value. In the case of azines, the GB decrease for 3-aza group is equal to 10.2 kcal·mol^{-1} (found as difference between the GB of pyridine and pyrimidine).[4] The high GB values obtained for **3** and **4** suggest that an additional structural (internal) effect is present in ortho derivatives. This effect is higher by ca. 10 kcal·mol^{-1} for **4** than for **3**.

Theoretical calculations[9] (AM1) performed for **4** show that the PA value of the *N*-aza antiperiplanar to the functional carbon atom in the amidine group is more basic (by ca. 9 kcal·mol^{-1}) than the other one, synperiplanar. A similar effect is observed for **3**, for which two

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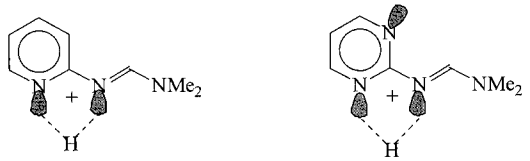
Table 2. Revised Experimental GB Values for Formamidines (FDMP*X) in kcal·mol^{-1}

X	ref	GB(ref)[a]	ΔG[b]	GB(B)	GB(B)[c]
4-NO_2	pyrrolidine	218.8	+1.8	220.6	
	Et_2NH	219.7	+0.6	220.3	
	$Me_2NCH{=}N$-(4-CF_3-C_6H_4)	223.7	−2.6	221.1	220.7
4-CN	$Me_2NCH{=}N$-(4-NO_2-C_6H_4)	220.7	+0.4	221.1	
	$Me_2NCH{=}N$-(4-CF_3-C_6H_4)	223.7	−1.8	221.9	221.5
4-CF_3	*n*-Pr_2NH	222.1	+2.2	224.3	
	N-Me-pyrrolidine	223.4	+0.3	223.7	
	$Me_2NCH{=}NCH_2$-CF_3	223.15[d]	−0.3	222.85	
	i-Pr_2NH	224.3	−0.5	223.8	223.7
4-Cl	$Me_2NCH{=}N$-(4-CF_3-C_6H_4)	223.7	+2.1	225.8	
	Et_3N	227.0	−0.5	226.5	
	$Me_2NCH{=}N$-(4-F-C_6H_4)	227.6	−0.4	227.2	
	$Me_2NCH{=}NPh$	229.4	−2.2	227.0	226.7
4-F	Et_3N	227.0	+0.3	227.3	
	c-$C_6H_{11}NMe_2$	227.7	+0.4	228.1	
	n-Pr_3N	229.5	−2.0	227.5	227.6
H	$Me_2NCH{=}N$(4-F-C_6H_4)	227.6	+1.1	228.7	
	n-Pr_3N	229.5	0.0	229.5	
	$Me_2NCH{=}N$(4-Me-C_6H_4)	231.6	- 1.6	230.0	229.4
4-Me	$Me_2NCH{=}N$(4-F-C_6H_4)	227.6	>+3.5	>231.1	
	n-Bu_3N	231.3	+0.4	231.7	
	$Me_2NCH{=}NMe$	232.0[d]	−0.4	231.6	231.6
4-OMe	$Me_2NCH{=}NPh$	229.4	+2.5	231.9	
	$Me_2NCH{=}N$(4-Me-C_6H_4)	231.6	+1.1	232.7	
	$Me_2NCH{=}N$(4-NMe_2-C_6H_4)	236.8	−2.7	234.1	232.9
4-NMe_2	$Me_2NCH{=}N$(4-Me-C_6H_4)	230.8	>+3.7	>234.5	
	$Me_2NCH{=}N$-*n*-C_5H_{11}	235.85[d]	+1.4	237.25	
	$Me_2N(CH_2)_3NMe_2$	235.5	+1.0	236.5	
	$Me_2N(CH_2)_4NMe_2$	237.3	−0.9	236.4	
	$(Me_2N)_2C{=}NH$	238.4	−1.2	237.2	236.8

[a] Data from ref 4. [b] Data from ref 9. [c] Mean value. [d] GB value revised according to the measured ΔG given in ref 24 and new GB for reference bases.[4]

Scheme 2



3 **4**

conformations, one with the *N*-aza synperiplanar and the other with one antiperiplanar to the functional carbon atom in the amidine group, are possible. The *N*-aza antiperiplanar is more basic (by ca. 5 kcal·mol^{-1}) than the other one. Its calculated PA value is almost of the same order of magnitude as the PA of the *N*-imino.

This basicity enhancement of both, the *N*-imino and *N*-aza antiperiplanar to the C-functional, can be explained by a relief of lone pair/lone pair repulsion in the neutral base upon protonation and/or by formation of an intramolecular hydrogen bond in the *N*-aza- or *N*-imino-protonated form (Scheme 2).[1,2,13] The smaller chelation effect in the protonated form of **3** than **4** can be explained by rotational isomerism of the aryl ring in **3** and absence of an additional aza atom in the ortho-position, which can interact with the imino nitrogen in the syn and anti conformation.

Analysis of Structural (Internal) Effects. For an analysis of structural effects on the gas-phase basicities, it is convenient to use the relative basicity, $\delta GB = GB(X) - GB(H)$, which represents the Gibbs free energy change for the proton-transfer reaction between the substituted and unsubstituted derivative (4). The experimental δGB values for model series of formamidines (FDMP*X), pyridines (AZA*X), and polyfunctional amidinazines considered as derivatives of pyridines with the N=CHNMe_2 group (AZA*N=CHNMe_2), together with polarizability, field/inductive, and resonance parameters[14−16] are listed in Table 3.

$$XBH^+ + B \rightleftarrows XB + BH^+ \qquad (4)$$

For a quantitative analysis of electronic substituent effects on the gas-phase basicity of formamidines and pyridines, the Taft and Topsom relation (5) can be applied,[6−8] where ρ_i and σ_i are the reaction constants and substituent parameters, respectively, for the polarizability, field/inductive, and resonance effects. In light of the GB values revised according to the data given in a recent compilation of Hunter and Lias,[4] the parameters of relation (5) were recalculated using the δGB values summarized in Table 3. In the calculations, the δGB values of all substituents listed in Table 3 (except the N=CHNMe_2 and aza groups) were considered. The regression parameters obtained are listed in Table 4.

$$\delta GB = \rho_\alpha \sigma_\alpha + \rho_F \sigma_F + \rho_R \sigma_R + \epsilon \qquad (5)$$

When the N=CHNMe_2 group is included in substituent sets of eqs 5c and 5e, good correlations ($r > 0.995$) are also obtained for azines (eqs 5d and 5f, respectively). This confirms that the aza nitrogen is the favored site of protonation in the amidinazines studied here. The total electronic substituent effects of the N=CHNMe_2 group in meta and para position in amidinazines (considered as azines) are higher than those of the NH_2 and NMe_2 in azines (Table 3). This indicates that amidinazines are the

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Table 3. Relative Gas-Phase Basicities of Model Formamidines[a] (FDMP*X) Pyridines[b] (AZA*X), and 1−3 Considered as Azines[c] (AZA*N=CHNMe$_2$) in kcal·mol^{-1}

				δGB			
X	σ_α[d]	σ_F[d]	σ_R^+[d]	FDMP*4-X	AZA*2-X	AZA*3-X	AZA*4-X
N=CHNMe$_2$	−0.4[e]	0.05[e]	−0.6[e]		18.2	13.3	18.0
NMe$_2$	−0.44	0.10	−0.64	7.4	10.3	10.7	17.4
NH$_2$	−0.16	0.14	−0.52		4.1	5.8	11.8
OMe	−0.17	0.25	−0.42	3.5	1.1	3.0	7.5
t-Bu	−0.75	0.00	−0.06		7.5		6.6
i-Pr	−0.62	0.00	−0.07		6.3		6.1
n-Pr	−0.54	0.00	−0.07		6.1		
Et	−0.49	0.00	−0.07		5.3	4.1	5.0
Me	−0.35	0.00	−0.08	2.2	4.5	3.2	4.1
H	0.00	0.00	0.00	0.0	0.0	0.0	0.0
F	0.13	0.44	−0.25	−1.8	−10.9	−6.7	−4.1
Cl	−0.43	0.45	−0.17	−2.7	−6.7	−6.4	−3.4
Br	−0.59	0.45	−0.15		−6.0	−4.8	−2.8
COH	−0.46	0.31	0.00				−6.1
COMe	−0.55	0.26	0.00			−3.3	−3.7
COOMe	−0.49	0.24	0.00		−1.1	−4.2	−0.9
CF$_3$	−0.25	0.44	0.00	−5.7	−10.3	−9.0	−8.7
CN	−0.46	0.60	0.00	−7.9	−13.7	−12.7	−11.8
NO$_2$	−0.26	0.65	0.00	−8.7			−13.3
Aza	*f*	*f*	*f*		−5.1	−10.2	−12.3

[a] According to data given in Table 2. [b] According to data from ref 4. [c] According to data given in Table 1. [d] Substituent parameters of Taft and co-workers.[14] [e] Estimated substituent parameters.[15,16] [f] Not estimated.

Table 4. Correlations between the Relative Basicities of Formamidines and Azines in the Gas Phase[a] with σ Parameters (Eq 5)

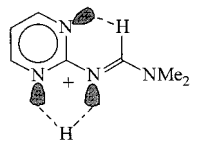
no.	series	$-\rho_\alpha$	$-\rho_F$	$-\rho_R$	ϵ	*n*	*r*	*s*
5a	FDMP*4-X	0.0 ± 1.1	13.7 ± 0.9	13.9 ± 1.0	0.5 ± 0.5	9	0.996	0.6
5b	AZA*2-X	9.1 ± 0.7	29.3 ± 0.8	13.9 ± 0.8	0.1 ± 0.4	15	0.998	0.6
5c	AZA*−3-X	4.6 ± 0.8	24.3 ± 0.9	17.2 ± 0.8	0.2 ± 0.4	13	0.997	0.6
5d		5.1 ± 1.0	24.8 ± 1.1	18.3 ± 1.0	0.1 ± 0.6	14[b]	0.996	0.8
5e	AZA*4-X	5.8 ± 0.9	23.8 ± 0.9	27.3 ± 1.1	0.2 ± 0.6	17	0.996	0.8
5f		5.8 ± 0.9	23.8 ± 0.9	27.5 ± 0.9	0.2 ± 0.5	18[b]	0.997	0.8

[a] Data from Table 3. [b] The Me$_2$NCH=N group included.

strongest bases in the family of azines. Lack of substituent parameters for the aza group makes impossible the estimation of the GB values of the amidine group in amidinazines. However, a comparison of the δGB found for azines indicates that the total electron withdrawing effect of the aza group in 3-position is comparable to that observed for the CF$_3$ and CN group, and in 4-position to that of CN and NO$_2$ group.

Parameters of eq 5b, the δGB value of pyrimidine,[4] and the δGB values of **3** and **4** (considered as derivatives of azines) can be used for the estimation of chelation effects of the proton by two nitrogens (the *N*-aza and *N*-imino shown in Scheme 2). The pure total substituent effects calculated from eq 5b for **3** and **4** are equal to 10.6 and 0.4 kcal·mol^{-1}, respectively. In calculations, it was assumed that the substituent effect of the second aza group in **4** (in meta position to the first *N*-aza—the site of protonation) is the same as in pyrimidine[4] (−10.2 kcal·mol^{-1}). Using the calculated pure substituent effects and the experimental δGB of **3** and **4**, the additional structural effects corresponding to the chelation effects of the proton are equal to 7.6 and 17.9 kcal·mol^{-1}, respectively. In both cases, calculations correspond to the N-aza as the preferred site of protonation. The chelation effect in **3** is comparable to that found for other bidentate ligands with flexible conformations containing the aza or amidine group.[13,17] The higher effect found for **4** is almost the same as for compounds with a rigid structure {e.g. 1,8-bis(dimethylamino)naphthalene, DMAN}.[18] This may result from two intramolecular hydrogen bonds which stabilize the planar structure of monoprotonated **4** (Chart 2). Planarity of structure increases the n-π conjugation of the amidine with aza groups, and thus it augments the basicity of aza groups and the respective intramolecular interactions (hydrogen bond formations). Theoretical calculations[9] confirm that both of the *N*-aza- and *N*-imino-protonated forms are planar in **4**. For **3**-*N*-aza- and *N*-imino-protonated forms, the pyridyl group is twisted out of the N−C=N plane by 16 and 48°. Similar twisting effects are observed for **1** and **2**.

Chart 2



Comparison with Hydrogen-Bond Formation.[10] Both of the imino and aza nitrogen atoms can be possible sites of hydrogen bonding for **1** and **2**, but the aza nitrogen seems to be the preferred one. From the log K$_{HB}$ (K$_{HB}$ − formation constant with 4-fluorophenol) vs σ correlations the aza nitrogen (logK$_{HB}$: 2−2.5) is more basic than the imino nitrogen (logK$_{HB}$: 1−1.5).

From the Δν(OH) vs σ correlations found for FDMP*X: Δν(OH) = 318−48.3σ°, *r* = 0.992, *n* = 11, 4-

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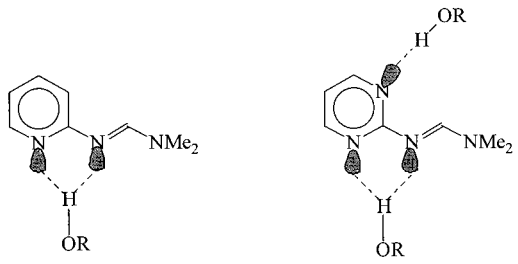
Scheme 3



3 **4**

and 3-substituted pyridines PY*4-X: $\Delta\nu$(OH) = 285−45.7σ_p^+, r = 0.988, n = 6 (X = H and donors), PY*3-X: $\Delta\nu$(OH) = 300−161.7σ, r = 0.972, n = 12, and the substituent constants σ_p^+($Me_2NCH{=}N$) = −1.1, σ_p°(aza) = 0.85, σ_m($Me_2NCH{=}N$) = −0.05, σ_m°(aza) = 0.53, the following $\Delta\nu$(OH) are predicted for the imino and aza nitrogen: 277 and 336 cm^{-1} for **1**, and 292 and 308 cm^{-1} for **2**. The experimental $\Delta\nu$(OH) values found for **1** (343 cm^{-1}) and **2** (317 cm^{-1}) indicate that the aza nitrogen atom is the favored site of hydrogen bonding. These effects are slightly smaller than those for the NH_2 and NMe_2-substituted pyridines. In the case of pyridines, the $\Delta\nu$(OH) is equal to 345 cm^{-1} for PY*4-NH_2, 366 cm^{-1} for PY*4-NMe_2, and 330 cm^{-1} for PY*3-NH_2. Comparison of the $\Delta\nu$(OH), $\log K_{HB}$ for **3** (340 cm^{-1} and 2−2.5), PY*H (286 cm^{-1} and 1.8), PY*2-NMe_2 (294 cm^{-1} and 1.6), and FDMP*H (316 cm^{-1} and 1.9) suggests that additional effects are present in 3, different from those possible in monofunctional derivatives. The high $\Delta\nu$(OH) and $\log K_{HB}$ values found for **3** can be explained by the formation of a three-centered complex (Scheme 3) between hydrogen-bond donor (ROH) and hydrogen-bond acceptor groups (imino and aza nitrogen). A kind of confirmation for the existence of a three-centered complex gives investigations of the ν(C═N) band. In the presence of ROH a stronger deplacement of the ν(C═N) band to higher frequency was observed for **3** in comparison to **1** and **2**.

Additional aza group in the 3-position of pyridine decreases the $\Delta\nu$(OH) value by 73 cm^{-1}. This effect should be similar in compound **4** when it is compared to **3**. Taking the $\Delta\nu$(OH) value obtained for **3** (340 cm^{-1}) and the effect of the second aza group in pyridines (73 cm^{-1}), we obtain $\Delta\nu$(OH) = 267 cm^{-1} for **4.** Comparison of this value with the experimental one [$\Delta\nu$(OH) = 261 cm^{-1}], and the deplacement of the ν(C═N) band to higher frequency in the presence of ROH, indicate that formation of a three-centered complex is possible also in **4** (Scheme 3). Larger ν(OH, hydrogen bonded) and nonsymmetrical bond observed for **4** than for **3** suggests that hydrogen bonding can take place also on the other aza group with $\Delta\nu$(OH)≈221 cm^{-1} predicted from the $\Delta\nu$(OH) value for PY*2-NMe_2 (294 cm^{-1}) and the effect of 3-aza group (73 cm^{-1}).

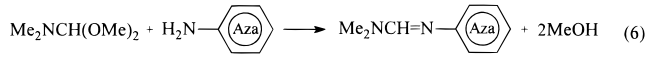
Conclusions

Comparison of experimentally obtained GB values for polyfunctional amidinazines (**1**−**4**) with those for model amidines (FDMP) and azines (AZA), considered as monofunctional derivatives, shows that the aza group is the preferred site of protonation in the gas phase. Amidinazines **1**−**4** are the strongest bases in the gas phase known in the family of monosubstituted pyridines. The total substituent electronic effect of the N═CH−NMe_2 group is larger than that of the NMe_2 group.

Structural (internal) effects observed for ortho derivatives (**3** and **4)** are exceptionally high. They are a sum of the total electronic substituent and 'internal solvation' effects. Although these contributing effects in **3** are completely different than in **4**, their sums are almost the same. The small total electronic effect in **4** is compensated by a large 'internal solvation' effect which is twice higher than in **3**.

Experimental Section

Chemicals. Reagents for synthesis and reference bases for GB measurements were commercial compounds (Aldrich or Fluka). Amidinazines **1**−**4** were synthesized according to reaction (6) by heating an equimolar mixture of *N*,*N*-dimethylformamide dimethylacetal and the appropiate aminazine at 60−70 °C without solvent.[19]



(6)

The reaction was controlled by TLC on silica gel plates using a mixture of chloroform and ethyl acetate as eluent and ultraviolet light for visualization. After evaporation of MeOH, compounds **1** and **4** were recrystallized from MeOH and then sublimated in a vacuum. Compounds **2** and **3** were purified by distillation under reduced pressure. Their structures were confirmed by IR, ^{1}H NMR, and mass spectra. FT-IR studies (Perkin-Elmer 2000, KBr cell of 0.627 mm) of the ν(C═N) frequency region for **1**−**4** in CCl_4 solution at room temperature showed signals at 1640.0, 1638.8, 1629.6, and 1629.2 cm^{-1}, respectively, similarly as for model compound FDMP*H (1640.3 cm^{-1}). For compound **4**, containing two aza groups at 1- and 3-positions in the ring, two signals for the methyl groups at the amino nitrogen atom in the amidine moiety [δ(NMe_2) 3.20 and 3.24 ppm] were observed in the ^{1}H NMR spectra (Bruker), recorded in $CDCl_3$ at room temperature. This indicates that electron-withdrawing effects of the two aza groups are very strong and thus the methyl groups are nonequivalent. The same was found for compound **3**, containing one aza group at 2-position in the ring. Two ^{1}H NMR signals for the methyl groups [δ(NMe_2) 2.80 and 2.95 ppm] were observed. For **1** and **2**, only one signal was observed [δ-(NMe_2) 2.88 and 2.95 ppm, respectively]. For comparison, one signal was found in $CDCl_3$ {δ(NMe_2) 2.90 ppm} for the model compound FDMP*H.[19] A comparison of the ^{1}H NMR chemical shifts found for the NMe_2 and CH groups in FDM*Aza and FDMP*X indicated additionally that compounds **1**−**4** have configuration (E) on the C═N double bond, similarly as model compound FDMP*H.[20] FT-ICR mass spectra were recorded at sufficiently low pressure to avoid ion/molecule reactions[21] and compared with literature data for model compounds FDMP*X.[22] The comparison confirmed the mass spectral fragmentation proposed by Grützmacher and Kuschel for FDMPs.[22]

GB Measurements. Gas-phase basicities were determined using the FT-ICR mass spectrometer constructed at the

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University of Nice-Sophia Antipolis.[23] The same procedure as described previously[24] was applied. The GB values were obtained from the equilibrium constants for the proton-transfer reaction (7) between the amidinazines (B) and reference bases (ref) using relation (8). All measurements were carried out at a FT-ICR cell temperature of 338 K.[25] The results obtained are summarized in Table 1. The GB values of model compounds FDMP*X, revised according to new data for reference bases recently compiled by Hunter and Lias,[4] are listed separately in Table 2.

$$BH^+ + Ref \rightleftarrows B + RefH^+ \quad (7)$$

$$GB(B) = GB(Ref) + \Delta G(2) \quad (8)$$

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