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Experimental and Theoretical Studies of the Possible and Preferred Site of Protonation in Polyfunctional N^1,N^1-Dimethyl-N^2-benzoylformamidine in the Gas Phase

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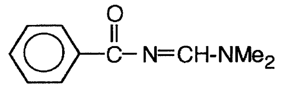
Proton-transfer reactions for N^1,N^1-dimethyl-N^2-benzoylformamidine containing three basic sites, the carbonyl-O, imino-N, and amino-N atoms, have been studied by experimental (FT-ICR) and theoretical (ab initio) methods. The ICR study gave a GB of 225.5 kcal mol^{-1} for this compound. The empirical structure-basicity relationships predicted GB values of 224.8 and 212.8 kcal mol^{-1} for protonation at the imino-N and carbonyl-O atoms, respectively. The observed GB values is close to the value for the imino-N atom. Theoretical calculations (B3LYP/6-311+G(2d,p)//HF/6-31G(d)) also showed that protonation at the imino-N atom is preferred by 7 kcal mol^{-1} compared to protonation at the carbonyl-O atom.

The gas-phase basicities (GB) of compounds containing the benzoyl[1)] and the N^1,N^1-dimethylaminomethylenamino ($Me_2N–CH=N–$)[2)] groups have been systematically investigated during the last 10 years. For benzaldehydes, acetophenones, methylbenzoates, and *N*,*N*-dimethylbenzamides, the carbonyl group is the favored site of protonation. An exception is observed for methyl 4-*N*,*N*-dimethylaminobenzoate, in which protonation occurs at the substituent.[1)] For N^1,N^1-dimethylformamidines, the imino nitrogen atom is the preferred site of protonation. Exceptions are found for N^1,N^1-dimethyl-N^2-pyridylformamidine, N^1,N^1-dimethyl-N^2-pyrimidinylformamidine, and N^1,N^1-dimethyl-N^2-(1,3,5-triazin-2-yl)formamidine, where the nitrogen atom in heterocycle seems to be slightly more basic than the imino nitrogen atom in the amidine moiety.[2f,2g)] Interesting cases are the so-called "push-pull" molecules in which the strongly electron-donating N^1,N^1-dimethylaminomethylenamino group is directly linked to a strongly electron-accepting group,[2e,3,4)] e.g., COR, CN, NO_2, SO_2R. Berthelot et al.[5)] postulated that the cyano, "super" basic, group is protonated in the gas phase. On the other hand, AM1 calculations show that the basicities of both groups, the N^1,N^1-dimethylaminomethylenamino and cyano groups, are almost of the same order of magnitude.[2e)] The difference between the calculated PA values of the N^1,N^1-dimethylaminomethylenamino and cyano group (3.6 kcal mol^{-1}), however, is smaller than the average unsigned error of the AM1 method found for the nitrogen bases (5.8 kcal mol^{-1}). Thus, it is not easy to determine the preferred site of protonation for these push-pull molecules. In this work, N^1,N^1-dimethyl-N^2-benzoylformamidine (FDM*Bz) (Chart 1) containing the benzoyl group directly linked to the imino nitrogen atom in the N^1,N^1-dimethylaminomethylenamino moiety has been chosen and the proton-transfer reactions in the gas phase were investigated by both experimental (FT-ICR) and theoretical (ab initio) methods.



FDM*Bz

Chart 1.

Results and Discussion

Experimental Gas-Phase Basicity (GB). The gas-phase basicity of N^1,N^1-dimethyl-N^2-benzoylformamidine (FDM*Bz) has been determined by measuring the equilibrium constant for the proton-transfer reaction between the formamidine and reference bases. The obtained $\Delta G°$ for the respective proton-transfer equilibria are summarized in Table 1. The GB value of FDM*Bz is obtained by

$$\mathrm{GB(B)} = \mathrm{GB(B_o)} - \Delta G°, \qquad (1)$$

where $\mathrm{GB(B_o)}$ is the basicity of the reference compound.[6)] The averaged GB value is 225.5 kcal mol^{-1}. There are three

Table 1. Experimental $\Delta G°$ and GB Values (in kcal mol^{-1}) Determined from the Proton-Transfer Equilibria between $PhCON{=}CHNMe_2$ (FDM*Bz) and Reference Base (B_0)

Reference base (B_o)	GB (B_o)[a)]	$-\Delta G°$	GB (B)
Et_3N	227.0	−1.1	225.9
i-Pr_2NH	224.3	0.9	225.2
$PhCH_2NMe_2$	224.0	1.5	225.5
2,6-Me_2pyridine	222.5	2.8	225.3
			av. 225.5±0.3

a) Taken from Ref. 6.

possibilities for the protonation site in FDM*Bz, i.e., the carbonyl-O, imino-N, and amino-N atoms. The observed GB of FDM*Bz is significantly higher than that of $HNMe_2$ (214.3 kcal mol^{-1}).[6)] If protonation occurs at the amino-N atom in FDM*Bz, its basicity should be lower than $HNMe_2$, because the –CH=NCOPh group in FDM*Bz must behave as a strong electron-withdrawing group in a similar manner as the –CH=NPh group ($\sigma^\circ = 0.42$).[7)] This precludes the possibility of protonation at the amino-N atom. We now compare the GB value of FDM*Bz with those of MeN=CH–NMe_2 (231.8 kcal mol^{-1}) and $PhCONMe_2$ (215.5 kcal mol^{-1}). For the former compound, protonation occurs at the imino-N atom[2d)] and protonation occurs at the carbonyl-O atom for the latter.[1e)] The observed GB of FDM*Bz is intermediate between two typical compounds, giving no decisive information about the preferred site of protonation.

A correlation analysis of substituent effects often has practical use for predicting the site of protonation. If protonation occurs at the imino-N atom in FDM*Bz, we may estimate its basicity from the effect of the PhCO group on the substituent effect of the basicities of a series of RN=CH–NMe_2 derivatives. On the other hand, if protonation occurs at the carbonyl-O atom, we may predict it from the effect of the –N=CH–NMe_2 group on the substituent effect of a series of PhCOR derivatives. The substituent effects on GB of two models are excellently correlated in terms of the Taft's equation.[8)] For RN=CH–NMe_2 we can use Eq. 2 found for alkyl and heteroalkyl derivatives.[2c)] For PhCOR we can use Eq. 3 obtained on the basis of data for R = H, Me, OMe, NMe_2:[1e,1f)]

$$\text{RN=CH–NMe}_2: \quad \mathrm{GB} = 227.5 - 11.6\sigma_\alpha - 40.9\sigma_\mathrm{F} \qquad (2)$$

$$\text{PhCOR}: \quad \mathrm{GB} = 191.7 - 6.2\sigma_\alpha - 53.8\sigma_\mathrm{F} - 38.1\sigma_{\mathrm{R}^+} \qquad (3)$$

Applying the substituent constants, σ_α (−0.75) and σ_F (0.28), of the COPh group[9)] to Eq. 2, we obtain a GB of 224.8 kcal mol^{-1}, which corresponds to the basicity of the imino-N atom in FDM*Bz. This GB value is only 0.7 kcal mol^{-1} smaller than the observed value. In the same way, the GB for protonation at the carbonyl-O atom in FDM*Bz would be predicted. Unfortunately, the σ_{R^+} of the –N=CH–NMe_2 group is not available, while the σ_α and σ_F values are known, $\sigma_\alpha = -0.40$ and $\sigma_\mathrm{F} = 0.05$.[10)] To evaluate the σ_{R^+} value, the relation given by Taft[8)] for GB's of acetophenones (4-$MeCOC_6H_4R$) can be used:

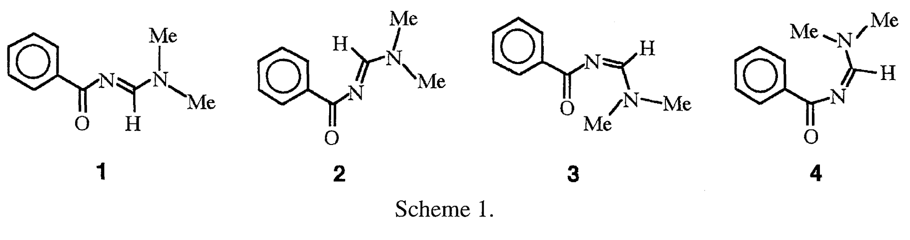
$$\mathrm{GB} = 198.1 - 4.4\sigma_\alpha - 16.1\sigma_\mathrm{F} - 27.4\sigma_{\mathrm{R}^+}. \qquad (4)$$

First, we estimated a GB value of 214.1 kcal mol^{-1} as the basicity of the carbonyl oxygen atom of $MeCOC_6H_4N$=CH–NMe_2 by applying the $\Delta\nu(\mathrm{OH}) = 129$ cm^{-1} observed for the carbonyl group in 4-$MeCOC_6H_4N$=CH–NMe_2[11)] to the GB/$\Delta\nu$(OH) relation, $\mathrm{GB} = 158.2 + 0.433\Delta\nu(\mathrm{OH})$, $r = 0.9999$ for 4-$MeCOC_6H_4R$ (R = H, Me, OMe, and NMe_2), where $\Delta\nu$(OH) is the frequency shift of methanol hydrogen bonded to the carbonyl group of acetophenones.[12)] Then, substituent constants σ_α (−0.40) and σ_F (0.05) for the –N=CH–NMe_2 group[10)] and a GB value of 214.1 kcal mol^{-1} were applied to Eq. 4, giving a σ_{R^+} of −0.56 for the –N=CH–NMe_2 group. This value is smaller (in negative scale) than that of the NMe_2 group (−0.64).[9)] Finally, the GB value for the carbonyl-O atom in the FDM*Bz was calculated according to Eq. 3, giving 212.8 kcal mol^{-1}. This GB value is remarkably smaller than the observed one by 12.7 kcal mol^{-1}. Thus, the predicted GB values for the carbonyl-O and imino-N atoms strongly suggest that the imino-N atom is the preferred site of protonation in FDM*Bz.

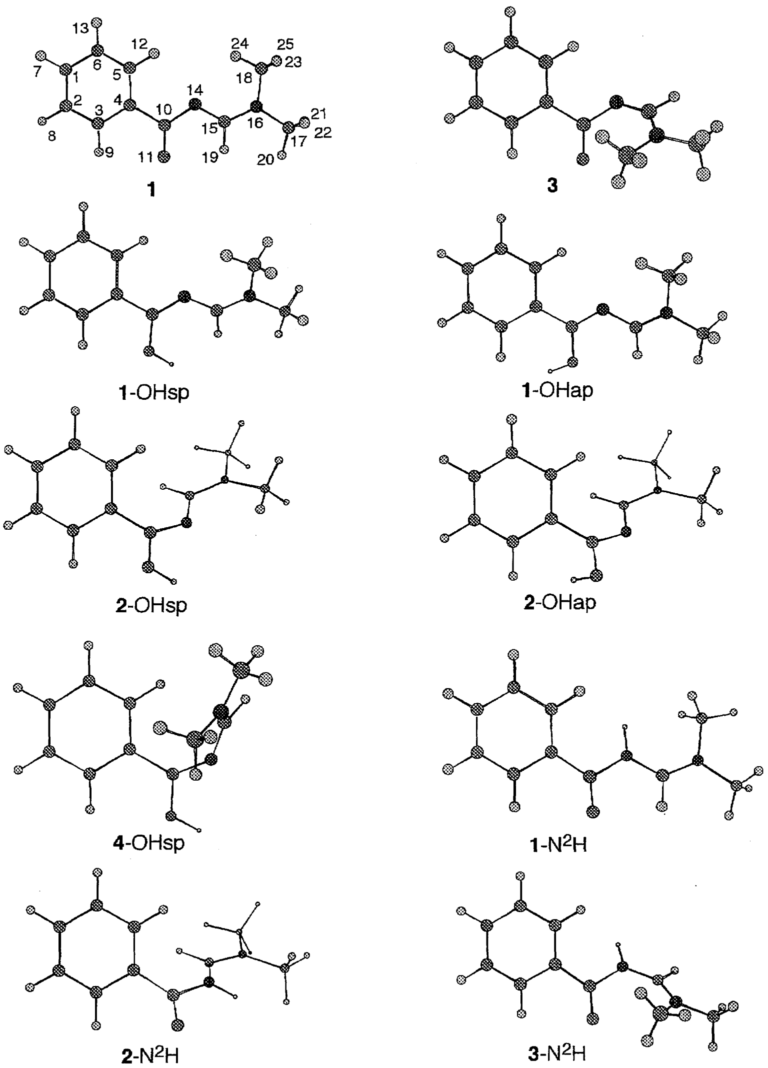
Stable Structures Found by Ab Initio Calculations. Prior to performing calculations, it is necessary to consider all possible stereochemical structures of the FDM*Bz, because there is no experimental data on the structure. Considering the geometrical and rotational isomerism around the C=N and C(carbonyl)–N bonds in the FDM*Bz, there are four structures: two *E* structures (**1** and **2**) and two *Z* structures (**3** and **4**) with the carbonyl-O *syn*- and *anti*-periplanar to the imino-C, respectively (Scheme 1). In the carbonyl-O protonated forms, two additional conformations are considered for each structure **1**—**4**, one with a hydrogen atom at the oxygen atom *syn*-periplanar (OHsp) and the other with one *anti*-periplanar (OHap) to the imino nitrogen atom. In the amino-N protonated forms, there are also two conformations for each structure, one with a hydrogen atom at the amino nitrogen atom *syn*-periplanar (N^1Hsp) and the other with one *anti*-periplanar (N^1Hap) to the imino nitrogen atom.

Ab initio calculations were conducted for all of these structures. Two optimized structures (**1** and **3**) were found for the neutral molecule. Five, three, and four stable conformations were obtained for the corresponding protonated forms: the carbonyl-O (**1**-OHsp, **2**-OHsp, **4**-OHsp, **1**-OHap, and **2**-OHap), imino-N (**1**-N^2H, **2**-N^2H, and **3**-N^2H), and amino-N protonated forms (**1**-N^1Hsp, **3**-N^1Hsp, **1**-N^1Hap, and **3**-N^1Hap), respectively. Some of their optimized structures are illustrated in Fig. 1. The total energies of the respective conformations are given in Table 2. The numbering of atoms is also shown in Fig. 1.

The optimized structure **1** is 7 kcal mol^{-1} more stable than **3**. This may allow us to believe that FDM*Bz has the *E* stereochemical structure in the gas phase. This is consistent with the theoretical estimations and measurements of the



Scheme 1.



1 **3** **1**-OHsp **1**-OHap **2**-OHsp **2**-OHap **4**-OHsp **1**-N²H **2**-N²H **3**-N²H

Fig. 1. Optimized structures of neutral and protonated molecules.

dipole moment (μ) of the neutral FDM*Bz in solution and X-ray data for model FDM.[4a,4b] A comparison between **1** and **3** shows that **1** has a perfectly planar conformation, while **3** has a highly twisted conformation, as shown in Fig. 1. In addition, it is found that the C(10)–N(14) and C(15)–N(16) bonds (1.388 and 1.330 Å, respectively) shorten and the C(15)–N(14) bond (1.283 Å) lengthens compared to the standard bond length values of the C–N single bond (e.g., 1.465 Å in CH_3–NH_2) and of the C=N double bond (e.g., 1.269 Å in CH_2=NH).[13] The C(10)–O(13) bond length (1.204 Å) is close to that of the C=O double bond (1.217 Å) in HCOOH monomer.[13] These geometrical features suggest that the imino group and the lone pair of electrons of the amino-N atom are conjugated and that the single-bond character in the dipolar ion structure of the carbonyl group is small, although the –N=CHNMe_2 group has a large electron-donor ability, as evaluated above.

For the carbonyl-O protonated forms, the **1**-OHap and **2**-OHsp are 4 to 5 kcal mol^{-1} more stable and planar than the three others. Their high stabilities may be due to the higher planarity. For the imino-N protonated forms, the **1**-N^{2}H is the most stable and planar among three structures. In addition, the **1**-N^{2}H is more stable than **1**-OHap and **2**-OHsp by 6 to 7 kcal mol^{-1}. For the amino-N protonated forms, although three stable structures were found, their energies are distinguishably higher than those of the carbonyl-O or imino-N protonated forms, suggesting that there is no possibility of protonation at the amino-N atom. This is understandable because there is no intramolecular charge-delocalization mechanism in the amino-N protonated forms.

In order to compare the experimental basicity with theoretical values, the gas-phase basicities were calculated for the carbonyl-O and imino-N atoms (**2**-OHsp, **1**-OHap, and **1**-N^{2}H) of FDM*Bz using the energies obtained at B3LYP/6-311+G(2d,p)//HF/6-31G(d) level and thermal corrections calculated at HF/6-31G(d) level. The results are given in Table 3 together with the corresponding values predicted based on the empirical structure-basicity relationships. The theoretical basicities show that the imino-N atom is 7 kcal mol^{-1} more basic than the carbonyl-O atom. The calculated basicity value for the imino-N atom agrees with the observed value within 2 kcal mol^{-1}. The degree of agreement between the

Table 2. Calculated Energies of Neutral and Protonated N^1,N^1-Dimethyl-N^2-benzoylformamidines at the HF/6-31G(d) and MP2/6-31G(d)//HF/6-31G(d) Levels

Structure	Energies[a]			
	HF/6-31G*	ZPE[b]	TCF[b]	MP2/6-31G* //HF/6-31G*
A. Neutral structures				
1	−569.44168	0.22170	0.18116	−571.19813
3	−569.42528	0.22204	0.18285	−571.18737
B. Carbonyl-O protonated forms				
1-OHsp	−569.81005	0.23534	0.19578	−571.55993
2-OHsp	−569.81705	0.23615	0.19700	−571.56824
4-OHsp	−569.80654	0.23565	0.19529	−571.56000
1-OHap	−569.81852	0.23576	0.19610	−571.56706
2-OHap	−569.80937	0.23600	0.19680	−571.56187
C. Imino-N protonated forms				
1-N^{2}H	−569.82993	0.23657	0.19650	−571.57900
2-N^{2}H	−569.82012	0.23630	0.19707	−571.57257
3-N^{2}H	−569.81927	0.23687	0.19830	−571.57273
D. Amino-N protonated forms				
1-N^{1}Hsp	−569.78164	0.23641	0.19634	−571.53551
3-N^{1}Hsp	−569.78350	0.23654	0.19661	−571.53982
1-N^{1}Hap	−569.77880	0.23657	0.19650	−571.53310
3-N^{1}Hap	−569.76515	0.23621	0.19812	−571.52666

a) All values in hartree. b) Zero point energies and thermal corrections to Gibbs free energy at HF/6-31G* level. Scaled by the empirical factor 0.8929.

Table 3. Gas-phase Basicities[a] of the Imino Nitrogen and Carbonyl Oxygen Atoms for FDM*Bz Given by Theoretical and Empirical Methods

Method	GB (N^{2}H)	GB (OH)
Ab initio		
(B3LYP/6-311+G(2d,p)//	227.4 (**1**-N^{2}H)	220.6 (**1**-OHap)
HF/6-31G(d))[b]		220.1 (**2**-OHsp)
Empirically estimated[c]	224.8	212.8
Observed	225.5	

a) In kcal mol^{-1}. b) At 298.15 K. c) Empirically estimated values based on linear free energy relationships, see in the text.

experimental and theoretical values is comparable with that observed for the proton affinities calculated at the G2 level of theory for a wide variety of organic bases.[14] In conclusion, both theoretical and empirical predictions indicate that the imino-N atom is more basic than the carbonyl-O atom and that the observed GB value agrees with that for the imino-N protonation.

We can now assume that the most plausible structures of neutral FDM*Bz and the protonated one are **1** and **1**-N^{2}H, respectively. It is worth noting that the Mulliken charges in both molecules account for the high basicity of the imino-N atom compared to the carbonyl-O atom. Although a pull-push interaction (n–π conjugation effect) between the carbonyl group and the lone pair electrons of the amino nitrogen is possible in neutral FDM*Bz (**1**), the Mulliken charge on the carbonyl-O atom (−0.620) is smaller than that on the imino-N atom (−0.737). This is consistent with the geometrical features that the carbonyl group has a less single-bond character. The differences in the Mulliken charges on the respective positions between neutral and protonated molecules may be regarded as being a measure of the intramolecular distribution of the positive charge formed by protonation. Table 4 summarizes the differential Mulliken charge on the respective atoms and/or groups for **1**-OHap, **2**-OHsp, and **1**-N^{2}H. It is evident that in the **1**-N^{2}H the positive charge distributes to all atoms and/or groups, while the charge in the **1**-OHap and **2**-OHsp is highly localized at the carbonyl-O atom, although the delocalization of the charge into the phenyl group is higher than that in **1**-N^{2}H. The high delocalization of the positive charge in **1**-N^{2}H in addition to the high electron density on the imino-N atom of the neutral molecule **1** may determine the preferred site of protonation in FDM*Bz.

Table 4. Differential Mulliken Charge[a] on Respective Atoms and/or Groups for 1-OHap, 2-OHsp, and 1-N^{2}H

Position	1-OHap	2-OHsp	1-N^{2}H
Ph	0.223	0.228	0.165
C(10)	−0.008	−0.018	0.051
O(11)	0.429	0.485	0.086
N(14)	0.062	0.051	0.307
C(15)	0.062	0.023	0.181
N(16)	0.053	0.056	0.029
Me$_2$	0.178	0.176	0.181

a) Obtained at the structure optimized at RHF/6-31G* level. Differences of Mulliken charges between the neutral **1** and a given protonated structure. Atomic charges on each position with a hydrogen are summed into heavy atoms.

Experimental

Chemicals. N^1,N^1-Dimethyl-N^2-benzoylformamidine (FDM*Bz) was synthesized by the same procedure as previously studied model compounds from dimethylformamide dimethylacetal and benzamide.[2,3] The reaction was controlled by the IR method using a Perkin–Elmer 2000 Fourier-transform spectrometer and a 0.627 KBr cell at room temperature. Samples of the reaction mixture were dissolved in CCl$_4$. For FDM*Bz the following signals were found: ν(C=O) 1654 cm^{-1} and ν(C=N) 1597 cm^{-1}. They are consistent with those reported previously.[3a] The reference bases for the GB measurements of FDM*Bz were commercial.

ICR Measurements. Equilibrium-constant measurements of the proton-transfer reactions were performed on an Extrel FTMS 2001 spectrometer with a superconducting magnet at 3 T and a modified inlet system. The details concerning the experimental techniques used for measurements of the equilibrium constants (K) are described elsewhere:[15]

$$\mathrm{B} + \mathrm{B_oH^+} \rightleftharpoons \mathrm{BH^+} + \mathrm{B_o} \tag{5}$$

$$K = [\mathrm{B_o}/\mathrm{B}][\mathrm{BH^+}/\mathrm{B_oH^+}] \tag{6}$$

$$\Delta G^\circ = -RT.\ln K \tag{7}$$

The equilibrium constant is expressed by Eq. 5, where B refers to FDM*Bz and B$_\mathrm{o}$ is a reference base. The arithmetic means of the values of K were used to calculate ΔG° at 323 K, the average uncertainty being ±0.2 kcal mol^{-1}. The GB values for the reference compounds were taken from the literature.[6)]

Ab initio Calculations. All ab initio LCAO-MO calculations were performed using the Gaussian 94 program.[16)] The closed-shell restricted Hartree–Fock calculation with STO 6-31G(d) basis set was applied to find the stationary point on the potential energy surface. To improve the calculated energies electron-correlation contributions were estimated by the Møller–Plesset perturbation theory;[17)] single-point MP2 calculations were carried out at the 6-31G(d) basis set using the frozen-core approximation. Structures with high basicity were further subjected to a single-point calculations at the B3LYP/6-311+G(2d,p) level using the optimized geometries at HF/6-31G(d). Thermal corrections to Gibbs free energy were evaluated at HF/6-31G(d) level.

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