J. Phys. Chem. A **2001,** *105,* 869−874

Ab Initio Study of Possible and Preferred Basic Site(s) in Polyfunctional N^1,N^1-Dimethyl-N^2-cyanoformamidine

Mariusz Makowski,[†] **Ewa D. Raczyńska,***[,‡] **and Lech Chmurzyński**[†]

Faculty of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland, and Department of Chemistry, Agricultural University (SGGW), 02-528 Warszawa, Poland

Received: July 7, 2000; In Final Form: November 8, 2000

Energies of protonation and of hydrogen-bond complex formation of neutral and protonated forms with one water molecule were studied by means of ab initio calculations for polyfunctional nitrogen “push−pull” base, $Me_2N-CH=N-C\equiv N$. Two potential basic sites, the *N*-imino and *N*-cyano were considered. Calculations with the 6-31G* basis set showed that the *N*-cyano site is more basic than the *N*-imino one for both reactions, proton-transfer and hydrogen-bonding in the gas-phase, whereas in water solution, the PCM model indicated the *N*-imino as the preferred basic site.

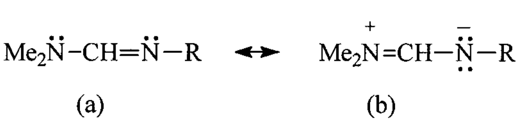
Introduction

Basicities of monofunctional N^1,N^1-dimethylformamidines ($Me_2N-CH=NR$, FDM*R) have systematically been studied under different conditions during the last 25 years.[1−10] Investigations have been carried out for the proton-transfer reaction (eq 1) in the gas phase and in polar solvents (water and water−ethanol solutions), as well as for the hydrogen-bonding reaction (eq 2) with alcohols and phenols (ZOH) in apolar solvent (CCl_4).

$$B + H^+ \rightleftarrows BH^+ \tag{1}$$

$$B + HOZ \rightleftarrows B\cdots HOZ \tag{2}$$

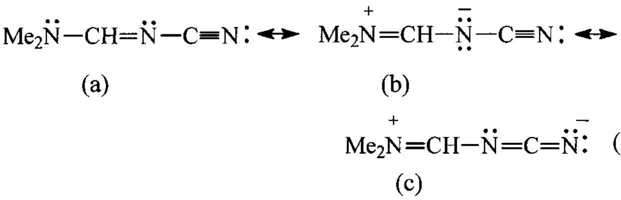
In each case the imino nitrogen atom (*N*-imino) has been found to be the preferred basic site, and high basicity has been observed. These facts have been explained by a strong conjugation of the lone pair of electrons of the amino nitrogen atom with the π electrons of the imino group (eq 3).[11]



$$\underset{(a)}{Me_2\ddot{N}-CH=\ddot{N}-R} \longleftrightarrow \underset{(b)}{Me_2\overset{+}{N}=CH-\overset{-}{\underset{..}{\ddot{N}}}-R} \tag{3}$$

Exceptional cases are so-called “push−pull” molecules in which a strong electron-accepting substituent (e.g., R=COPh, CN, SO_2Ph, 4-pyridyl) is directly linked to the *N*-imino atom.[4,5,10,12−19] In such type of molecules, the *n*-π conjugation effect in the amidine group (eq 3) can be transmitted through resonance to the heteroatom in substituent R decreasing the basicity of the *N*-imino and increasing the basicity of the respective heteroatom in R. For this reason, it is exceptionally difficult to indicate the preferred basic site in “push−pull” derivatives from simple basicity measurements. To solve this problem, theoretical calculations can be performed in parallel to basicity measurements.[16−23]

A particular case of the “push−pull” molecules is the cyano derivative (FDM*CN). It is well-known that for the isolated monofunctional systems RCN and FDM*R (where R is a simple alkyl or aryl group), the cyano (*N*-cyano) is less basic than the amidino group (*N*-imino) in the proton-transfer[6−8,16,22,24] as well as in the hydrogen-bonding reaction.[4,5,25] However, direct link of the amidino and cyano groups (completely opposite in electronic effects) in FDM*CN (eq 4) strongly changes their basicities. Due to “push−pull” effect, the basicity of the *N*-imino decreases and that of the *N*-cyano increases in comparison to the corresponding methyl derivatives (R=Me).[10]



$$\underset{(a)}{Me_2\ddot{N}-CH=\ddot{N}-C\equiv N:} \longleftrightarrow \underset{(b)}{Me_2\overset{+}{N}=CH-\overset{-}{\underset{..}{\ddot{N}}}-C\equiv N:} \longleftrightarrow \underset{(c)}{Me_2\overset{+}{N}=CH-\ddot{N}=C=\overset{-}{\ddot{N}}:} \tag{4}$$

On the basis of gas-phase and hydrogen-bonding basicity measurements, it has been postulated[26] that the *N*-cyano atom was the preferred basic site in FDM*CN. On the other hand, AM1 calculations showed that the “push−pull” effect in the cyano derivative led to the equalization of the gas-phase basicities of both sites, and it was impossible to indicate the preferred basic site.[16] Moreover, the value of the gas-phase basicity (GB−the negative value of the Gibbs free energy change of protonation reaction 1) measured for FDM*CN fit very well to the Taft and Topsom equation found for FDM*R (R = alkyl and heteroalkyl group),[8] indicating that the experimental GB value may correspond to the *N*-imino atom.

For these reasons, we decided to perform ab initio calculations for each potential basic site (*N*-imino and *N*-cyano) in FDM*CN in the proton-transfer and hydrogen-bonding reactions. In the calculations, both isomers (E and Z) of FDM*CN were considered. We calculated the energies of protonation (E_{prot}) for isolated molecules, and energies of hydrogen-bond complex formation of neutral ($E_{HB-neut}$) and protonated forms ($E_{HB-prot}$) with one water molecule using the 6-31G* (and/or 6−31+G* basis set for comparison). We used the RHF, MP2, and DFT/B3LYP models in the gas phase and the PCM model with water as the solvent. For the hydrogen-bonding reaction, the BSSE error was estimated.

Computational Details

For ab initio quantum chemical calculations, the 6-31 G* basis set (split valence basis with polarization functions on the heavy

---

* Corresponding author. Ewa D. Raczyńska, Prof SGGW, Department of Chemistry, Agricultural University, Rakowiecka 26/30, PL-02-528 Warszawa, Poland. Tel/fax: + 48 22 8491393. E-mail: raczynskae@delta.sggw.waw.pl.

[†] University of Gdańsk.

[‡] Agricultural University (SGGW).

10.1021/jp002458t CCC: $20.00

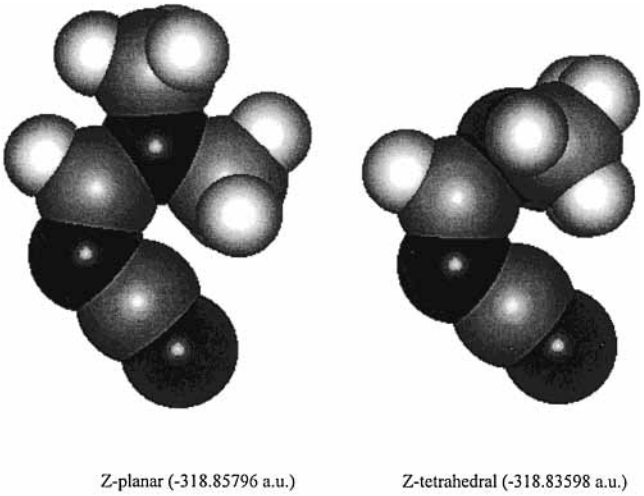


Figure 1. Planar and NMe_2 tetrahedral structures found for the Z isomer of FDM*CN.

atoms)[27] was chosen and applied to the E and Z isomers of FDM*CN. This basis set was found recently to be suitable for prediction of the protonation energies.[28] Calculations were realized using the GAMESS 98 program[29] for the planar and NMe_2 tetrahedral structures of the neutral, *N*-imino and *N*-cyano protonated forms, and their monohydrates. The *N*-amino protonated and hydrated forms were not considered due to strong n-π conjugation effect in FDM*CN. In all cases (except the neutral Z isomer), only planar structures were stable. For the neutral Z isomer two stable structures, planar and NMe_2 tetrahedral were found (Figure 1). However, the tetrahedral structure has a larger energy than the planar one by 14 kcal mol^{-1}, and thus it has not been taken for our analysis.

The geometries of all species were fully optimized without symmetry constraint and the stationary point on the potential energy surface found. The calculated harmonic vibrational frequencies indicated that the optimized structures correspond to the energy minima. The most stable planar conformations obtained for all investigated species are given in Figures 2 and 3. Their energies calculated at the HF/6-31 G* level are summarized in Table 1.

Geometries optimized at the HF/6-31 G* level were used for computations of the thermodynamic parameters of reactions 1 and 2. For these calculations, three methods were applied: the RHF (restricted Hartree−Fock),[28] MP2 (second-order Möller Plesset perturbation),[30,31] and DFT (density functional theory)[32] with the B3LYP functional (the combination of the Becke three-parameter hybrid exchange functional with nonlocal correlation functional of Lee, Yang, and Parr).[33,34] For each approximation the 6-31 G* basis set was taken (in some cases the 6-31+G* basis set was also applied). RHF and MP2 calculations were realized with the GAMESS 98 program,[29] and DFT/B3LYP calculations with the GAUSSIAN 94 program.[35]

Energies of protonation (E_{prot}) for each potential basic site of isolated FDM*CN were calculated according to eq 5. In these calculations, the energy of isolated proton was taken as equal to zero. The effect of solute−solvent interactions in an aqueous solution was studied using the PCM model (polarizable continuum method, which partially includes specific solvation),[36−41] and the geometries optimized at the HF/6-31 G* level. E_{prot} in water was estimated from eq 6. In this model, the energy of a proton was calculated as the difference between the energy of H_3O^+ (−76.4232408728 au) and water (−76.0209107822 au). Energies of hydrogen-bond complex formation with one water molecule for the neutral ($E_{HB-neut}$) and protonated forms of FDM*CN ($E_{HB-prot}$) were obtained from eqs 7 and 8, respectively. The energies of water in RHF, MP2, and DFT/B3LYP models were equal to −76.0107465158, −76.1959590517, and −76.4190876970 au, respectively.

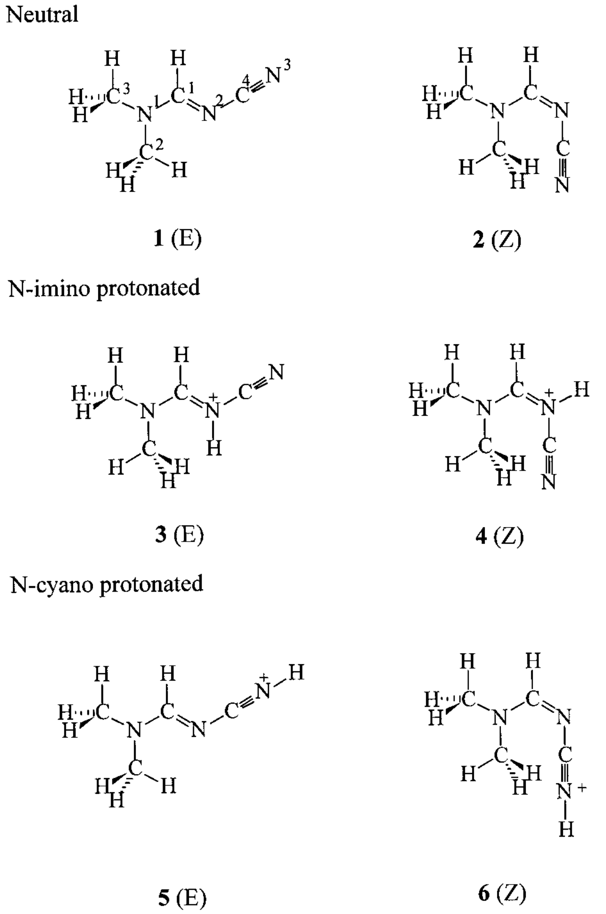


Figure 2. The most stable planar structures found at the HF/6-31G* level for the neutral and protonated FDM*CN.

$$E_{prot}(gas) = E_{BH^+}(gas) - E_B(gas) \qquad (5)$$

$$E_{prot}(aq) = E_{BH^+}(aq) - E_B(aq) - E_{H^+}(aq) \qquad (6)$$

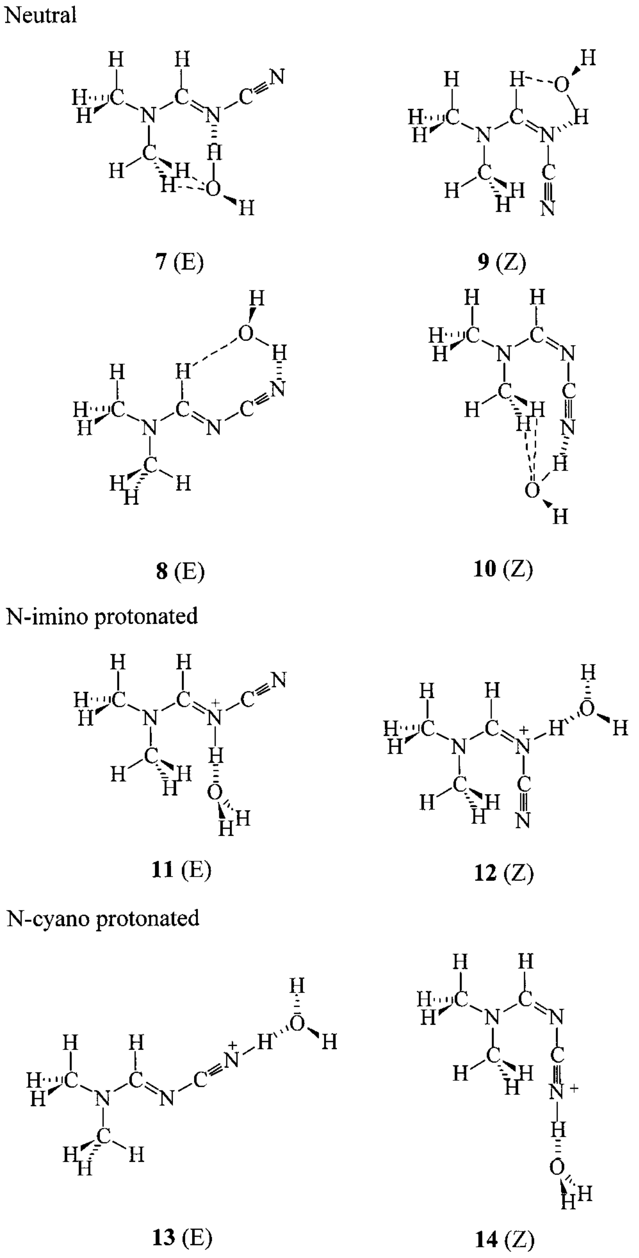
$$E_{HB-neut} = E_{B\cdots H_2O} - E_B - E_{H_2O} \qquad (7)$$

$$E_{HB-prot} = E_{BH^+\cdots H_2O} - E_{BH^+} - E_{H_2O} \qquad (8)$$

In the RHF calculations, the thermal corrections to the enthalpy and entropy were evaluated and included to the Gibbs free energies (G_{prot} and G_{HB}) according to procedures described previously.[28] In these calculations, the ideal gas equation-of-state, temperature of 298 K, and pressure of 1 atm were assumed.

To estimate the BSSE (basis set superposition error) for the energies of hydrogen-bond complex formation with one water molecule at HF/6-31 G* level, counterpoise calculations were performed using the method of Boys and Bernardi.[42−44] BSSE energies of the neutral ($E_{HB-neut,BSSE}$) and protonated monohydrates ($E_{HB-prot,BSSE}$) were obtained from eqs 9 and 10, respectively. In the BSSE free energies, the thermal corrections were included.

$$E_{HB-neut,BSSE} = E_{HB-neut} - E_{BSSE,B} - E_{BSSE,H_2O} \qquad (9)$$



7 (E) **9** (Z) **8** (E) **10** (Z) **11** (E) **12** (Z) **13** (E) **14** (Z)

Figure 3. The most stable planar structures found at the HF/6-31G* level for the neutral and protonated monohydrates of FDM*CN.

$$E_{HB-prot,BSSE} = E_{HB-prot} - E_{BSSE,BH^+} - E_{BSSE,H_2O} \quad (10)$$

Results and Discussion

Geometries. Due to geometrical isomerism around the C=N bond,[11,45] two structures E (**1**) and Z (**2**) are possible for the neutral molecule of FDM*CN (Figure 2). Each of these structures may be protonated on the *N*-imino and *N*-cyano, and thus four additional structures **(3−6)** are considered. Similarly, hydrogen-bonding complexes with one water molecule may take place on the *N*-imino and *N*-cyano (Figure 3). Therefore, four complex structures are possible for the neutral FDM*CN: two E (**7** and **8**) and two Z structures (**9** and **10**). There are also four hydrogen-bonding complex structures with one water molecule for the protonated forms **(11−14)**.

TABLE 1: Energies of Neutral and Protonated Forms of FDM*CN and Their Monohydrates Calculated at the HF/6-31G* Level (in Hartree)

no. struct.	isomer	isolated molecule[a]	no. struct.	isomer	hydrogen-bonded complex
		Neutral Forms			
1	E	−318.86994	7[b]	E	−394.88923
			8[c]		−394.89381
2	Z	−318.85796	9[b]	Z	−394.88211
			10[c]		−394.88322
		N-Imino Protonated Forms			
3	E	−319.21896	11	E	−395.25893
4	Z	−319.21603	12	Z	−395.25669
		N-Cyano Protonated Forms			
5	E	−319.23047	13	E	−395.26937
6	Z	−319.23047	14	Z	−395.25860

[a] Planar structure. [b] Water molecule hydrogen-bonded to the *N*-imino. [c] Water molecule hydrogen-bonded to the *N*-cyano.

Generally, the E isomer is most stable for the neutral, protonated, and complexed form. This configuration (E) has also been found as the preferred one for other neutral formamidines (FDM*R, R = alkyl, aryl, arylalkyl, heteroalkyl, heteroaryl) by different experimental methods (X-ray, ^{1}H and ^{13}C NMR, dipole moment measurements).[3,11,13−15,46−51]

Some selected geometrical parameters for structures **1−14** are summarized in Table 2. For each type of planar structures (see values of the $N^1-C^1=N^2-CN$ angle) of the neutral, protonated, and complexed forms, the C−N, C=N, and C≡N bond lengths in the E isomer are slightly different from those in the Z isomer. The differences are not larger than 0.01 Å. This indicates that the configuration around the C=N double bond does not influence the geometrical parameters of the respective planar forms.

Comparison of the C−N and C=N bond lengths in planar FDM*CN with the standard single (C−N) and double (C=N) bond lengths (1.465 Å in CH_3-NH_2 and 1.269 Å in $CH_2=NH$,[52] respectively) confirms strong *n*-*π* conjugation in FDM*CN. The C−N bonds in the neutral forms (1.328 and 1.335 Å in E isomer, and 1.335 and 1.333 Å in Z isomer) shorten and the C=N bond (1.282 and 1.278 Å in E and Z isomers) lengthens in comparison to the respective standard C−N and C=N bond lengths. The same behavior has been observed for benzoyl derivative (FDM*COPh) in the gas phase by ab initio calculations.[19] The C−N bonds (1.330 and 1.388 Å in E isomer) shorten and the C=N bond (1.283 Å) lengthens. For $FDM*SO_2Ph$, an equalization of the C−N (1.315 Å) and C=N (1.307 Å) bond lengths has been observed in the neutral crystal E structure by X-ray measurements.[13] This confirms that the SO_2Ph group has a stronger electron-accepting effect than the COPh and CN group, and thus stronger *n*-*π* conjugation effect has been found. The C≡N bond length calculated for the planar neutral E and Z isomers of FDM*CN (1.141 Å) is close to that found by X-ray measurements for $(FDM)_2C=N-C≡N$ (1.147 Å).[14] To our knowledge, there are no crystallographic data for FDM*CN, and no other comparison can be performed.

Protonation on the *N*-imino or *N*-cyano atoms strongly changes the C−N and C=N bond lengths, but has only a slight influence on the C≡N bond length. The C^1-N^1 bond shortens to the length of the double bond (1.28−1.29 Å), and the $C^1=N^2$ bond lengthens to the length of the single bond (1.33−1.34 Å) independently of the site of protonation. The C^4-N^2 bond shortens to the length of the double bond (1.26 Å) only in the case of the *N*-cyano protonated forms. For the *N*-imino protonated forms, the C^4-N^2 bond slightly lengthens (1.35−1.36 Å) in comparison to the neutral molecule. This confirms that the *n*-*π* conjugation in the amidine group (structures a and b in eq 4) is stronger in the protonated than the neutral forms.

Hydrogen bonding on the *N*-imino or *N*-cyano has a similar effect to protonation, but the C−N, C=N, and C≡N bond

TABLE 2: Selected Geometrical Parameters of Neutral and Protonated Forms of FDM*CN and Their Monohydrates (at the 6-31G* level)[a]

		Bond Length in Å					Angle in Degree
no. struct.	isomer	C^1—N^1	C^1═N^2	C^4—N^2	C^4≡N^3	N···H···O	∠N^1—C^1═N^2—CN
Isolated Molecules							
Neutral Forms							
1	E	1.328	1.282	1.335	1.141		178.53
2	Z	1.335	1.278	1.333	1.141		−0.46
N-Imino Protonated Forms							
3	E	1.279	1.337	1.355	1.133		−179.99
4	Z	1.278	1.341	1.353	1.133		−2.47
N-Cyano Protonated Forms							
5	E	1.285	1.327	1.260	1.141		179.63
6	Z	1.285	1.326	1.260	1.141		179.97
Hydrogen-Bonded Complexes							
Neutral Forms							
7[b]	E	1.320	1.288	1.337	1.140	3.130	−177.61
8[c]		1.325	1.288	1.330	1.143	3.193	−179.86
9[b]	Z	1.329	1.286	1.333	1.141	2.991	−3.28
10[c]		1.328	1.284	1.326	1.142	3.055	4.17
N-Imino Protonated Forms							
11	E	1.282	1.332	1.353	1.134	2.813	179.94
12	Z	1.282	1.334	1.351	1.134	2.785	−0.73
N-Cyano Protonated Forms							
13	E	1.289	1.320	1.271	1.139	2.709	179.94
14	Z	1.297	1.312	1.264	1.140	2.710	0.34

[a] Planar structure. [b] Water molecule hydrogen-bonded to the *N*-imino. [c] Water molecule hydrogen-bonded to the *N*-cyano.

lengths change even less. The N···H−O bridge length depends on the configuration around the C═N bond and on the type of the basic site. It is slightly longer for the E than Z isomers for both the neutral and protonated forms. It is also longer for the *N*-imino than *N*-cyano protonated forms. The later geometrical feature suggests that the *N*-cyano atom is more basic than *N*-imino one. It is interesting to mention that in **7**−**10** three (or four) centered hydrogen bonds are possible with one water molecule. Two types of hydrogen bonds can be formed, one between the *N*-imino or *N*-cyano and HOH (N···H−OH), and the other between the CH-formamidine (methine or methyl) and OH$_2$ (C−H···OH$_2$). In these cases, the hydrogen-bonding bridges are not linear.

Theoretical Infrared Spectra and Dipole Moments. Theoretical infrared ν(C═N) and ν(C≡N) frequency shifts, and the C═N and C≡N bond orders calculated according to the procedure from ref 53 (Table 3) give additional information on geometrical behavior in the neutral, protonated, and complexed forms of FDM*CN. Protonation on the *N*-imino (structures **3** and **4**) strongly decreases the frequency of the ν(C═N) band in comparison to the neutral molecules (**1** and **2**), whereas the frequency of the ν(C≡N) band increases. This confirms the "push−pull" effect in FDM*CN (eq 4). During protonation of the *N*-imino, the C═N bond lengthens, and behaves almost as a single bond, whereas the C≡N bond shortens slightly (see structure b in eq 4). Protonation of the *N*-cyano (structures **5** and **6**) changes the frequency of the ν(C═N) and ν(C≡N) bands to a considerably smaller degree than that of the *N*-imino. The same behavior is observed for the hydrogen-bonding complexes of protonated forms with one water molecule (structures **11**−**14**).

TABLE 3: Infrared ν(C═N) and ν(C≡N) Frequency Shifts (in cm^{-1}),[a] Bond Orders of the C═N and C−N and Dipole Moments (in Debyes) Calculated for Structures 1−14 at the 6-31G* Level

no.		Frequency Shift		Bond Order		Dipole Moment
struct.	isomer	ν(C═N)	ν(C≡N)	C═N	C≡N	μ
Isolated Molecules						
Neutral Forms						
1[b]	E	1841	2576	1.6	2.8	8.09
2	Z	1850	2564	1.7	2.8	7.61
N-Imino Protonated Forms						
3	E	1440	2646	1.2	2.8	6.93
4	Z	1433	2645	1.2	2.8	6.63
N-Cyano Protonated Forms						
5	E	1872	2551	1.3	2.1	2.61
6	Z	1872	2551	1.3	2.1	2.61
Hydrogen-Bonded Complexes						
Neutral Forms						
7[c]	E	1831	2576	1.6	2.8	6.74
8[d]		1830	2550	1.6	2.8	6.55
9[c]	Z	1830	2567	1.6	2.8	6.34
10[d]		1834	2551	1.6	2.7	5.87
N-Imino Protonated Forms						
11	E	1454	2644	1.2	2.8	6.27
12	Z	1456	2644	1.2	2.8	6.64
N-Cyano Protonated Forms						
13	E	1860	2535	1.3	2.3	2.62
14	Z	1827	2530	1.4	2.3	2.08

[a] For an HF/6-31G* theoretical frequency scaling factor see in ref 56. [b] Experimental[12] ν(C═N) = 1638 and ν(C≡N) = 2201 cm^{-1} in CCl$_4$ solution; use a scaling factor[56] of 0.8929 gives ν(C═N) = 1644 and ν(C≡N) = 2300 cm^{-1} at the HF/6-31 G* level. [c] Water molecule hydrogen-bonded to the *N*-imino. [d] Water molecule hydrogen-bonded to the *N*-cyano.

Changes of the infrared ν(C═N) and ν(C≡N) frequency shifts for the hydrogen-bonding complexes of neutral FDM*CN with one water molecule (structures **7**−**10**) in comparison to the neutral forms (structures **1** and **2**) would be exceptionally interesting if the ab initio results could be compared with those found by experiment for the hydrogen-bonding complexes of FDM*CN with 4-fluorophenol. It has been shown by infrared measurements[4,5,12,54] that the hydrogen-bond formation increases both the ν(C═N) and ν(C≡N) bands. However, the ab initio results

TABLE 4: Energies of Protonation (E_{prot}, in kcal mol^{-1}) in the Gas Phase (RHF, MP2, and DFT/B3LYP) and Aqueous Solution (PCM), and Energies of Hydrogen-Bond Formation ($E_{HB-neut}$ and $E_{HB-prot}$ in kcal mol^{-1}) in the Gas Phase (RHF, MP2, and DFT/B3LYP) Calculated According to Equations 5−8 for the *N*-Imino and *N*-Cyano Sites in FDM*CN with the 6-31G* (or 6-31+G*) Basis Set

		E_{prot}				$E_{HB-neut}$			$E_{HB-prot}$		
isomer	basic site	RHF	MP2	DFT/B3LYP	PCM	RHF	MP2	DFT/B3LYP	RHF	MP2	DFT/B3LYP
E	*N*-imino	−219.1	−214.1	−215.8	−17.9	−5.4	−7.7	0.3	−18.3 (−15.1)	−21.7 (−20.1)	−14.3
	N-cyano	−226.3	−222.3	−229.0	−11.5	−8.2	−10.3	−3.1	−17.7	−20.7	−13.5
Z	*N*-imino	−224.8	−220.0	−215.2	−23.3	−8.4	−10.9	2.8	−18.8 (−16.2)	−21.7 (−20.1)	−14.7
	N-cyano	−233.8	−220.6	−230.0	−11.8	−9.1	−11.6	1.8	−10.9	−23.1	−7.3

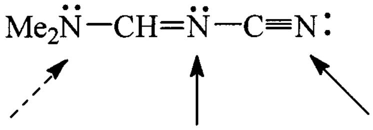


Figure 4. N sites in FDM*CN.

for the most stable E isomer indicate that the hydrogenbonding with one water molecule decreases the ν(C=N) and $\nu(C\equiv N)$ bands. This observation suggests that experimental IR results for hydrogen-bonding complexes are not well described by theoretical ones at the HF/6-31G* level. Similar behavior has been found for some other molecules.[55,56]

Theoretical dipole moments are exceptionally high, except the *N*-cyano protonated forms as isolated as hydrogen bonding with one water molecule (structures **5**, **6**, **13,** and **14**). This indicates that the electronic effect of the cyano group is very strong. The μ value (8.08 D) calculated for the E isomer of FDM*CN (**1**) is close to that measured for the E isomer of 4-nitrophenyl derivative (FDM*4-$NO_2C_6H_4$) in benzene solution (7.69 D).[48]

Possible and Preferred Basic Sites. FDM*CN may be considered to be a polyfunctional nitrogen base with three nitrogen sites, the *N*-amino, *N*-imino, and *N*-cyano (Figure 4). The *n*-π conjugation effect (see structure c in eq 4), strongly decreases the basicity of the *N*-amino and increases the basicity of the *N*-cyano. Indeed, the AM1 calculations[16] showed that the *N*-amino is the less basic site in FDM*CN (its basicity in the gas phase is smaller than those of the *N*-imino and *N*-cyano by more than 20 kcal mol^{-1}), and thus it has not been considered in our ab initio calculations for the proton-transfer (eq 1) as well as for the hydrogen-bonding reaction (eq 2).

Calculations were carried out only for the *N*-imino and *N*-cyano sites in the proton-transfer and hydrogen-bonding reactions in the gas phase with use of the RHF, MP2, and DFT/B3LYP models. The hydrogen-bond complexes with one water molecule were studied for the neutral and protonated forms. In these complexes, water displays the same dual character as in solution, hydrogen-bond donor for neutrals (B) and hydrogen-bond acceptor for cations (BH^+). This approach permits one to study the proton-transfer reaction for solvated species with only one water molecule. The proton-transfer reactions were also studied in water using the PCM model. Energies of protonation and hydrogen-bond complex formation calculated according to eqs 5−8 are summarized in Table 4.

The results indicate that independently of the method of calculation (RHF, MP2, or DFT/B3LYP) the *N*-cyano site is more basic than the *N*-imino for both isomers (E and Z) in the proton-transfer and hydrogen-bonding reactions in the gas phase. The *N*-cyano atom as a more basic site is conjugated with a weaker acidic site, and thus the weaker hydrogen bond with water is formed on the *N*-cyano (smaller absolute $\Delta E_{HB-prot}$) than *N*-imino protonated forms.

TABLE 5: Gibbs Free Energies of Protonation and Hydrogen-Bond Formation (G_{prot}, $G_{HB/neut}$, and $G_{HB/prot}$ in kcal mol^{-1}) Calculated in the Gas Phase for the *N*-Imino and *N*-Cyano Sites in E-FDM*CN[a]

		HF/6-31G*			HF/6-31G* BSSE	
isomer	basic site	G_{prot}	$G_{HB-neut}$	$G_{HB-prot}$	$G_{HB-neut}$	$G_{HB-prot}$
E	*N*-imino	-201.2	7.6	-4.5	4.8	-7.2
	N-cyano	-211.5	4.9	-4.7	2.8	-6.5

[a] Thermodynamic corrections included.

In water solution, it is well-known that monofunctional nitriles are very weak bases (p$K_a \approx -10$),[57] while N^1,N^1-dimethylformamidines (FDMs) exhibit exceptionally high basicities (pK_a > 4)[1,9,58] in comparison to other imines.[57] Strong electron-accepting groups decrease the basicity of FDMs below pK_a = 4, but are not smaller than those of nitriles.[10,11,58] Calculations for FDM*CN with the PCM model for an aqueous solution confirm that the *N*-imino is the preferred site of protonation for both the E and Z isomers.

The Gibbs free energies of protonation and hydrogen-bond formation calculated for potential basic sites in the most stable E isomer of FDM*CN at the HF/6-31 G* level are summarized in Table 5. The BSSE-corrected HF/6-31G* energies for the neutral and protonated monohydrates are also given in this table. The results obtained for the proton-transfer reaction indicate that the *N*-cyano is more basic than the *N*-imino. Taking into account definition of the gas-phase basicity {GB = $-(G_{prot} - G_{H^+})$},[24] the calculated G_{prot} (Table 5) and the literature G_{H^+} which include mainly the translational contribution (−7.7 kcal mol^{-1}),[24,59] the following gas-phase basicities for the *N*-imino and *N*-cyano are calculated: 193.5 and 203.8 kcal mol^{-1}, respectively. Comparison of these values with the measured gas-phase basicity of FDM*CN (GB = 204.9 kcal mol^{-1})[24] indicates that the calculated GB of the preferred *N*-cyano site is slightly lower than the experimental one (by ca. 1 kcal mol^{-1}). Such kind of error confirms an earlier conclusion[28] that the 6-31 G* basis set is suitable for the E_{prot} (or G_{prot}) prediction in the gas phase.

Difference obtained for the *N*-imino and *N*-cyano sites between their calculated Gibbs free energies of the hydrogen-bond complex formation of the E-neutral FDM*CN with one water molecule ($G_{HB-neut}$) may be compared with that found on the basis of infrared measurements in an apolar solvent (CCl_4) for the hydrogen-bonding complexes of FDM*CN with 4-fluorophenol. Although 4-fluorophenol is a stronger hydrogen-bonding donor than water and larger formation constants with nitrogen bases should be observed, the relative hydrogen bonding basicities obtained for bases with 4-fluorophenol should be similar to those with water. For comparison of computational with experimental results, the measured formation constants for FDM*CN with 4-fluorophenol (log K_{HB}) were expressed as the free Gibbs energies changes of reaction 2: $-\Delta G_{HB}$(*N*-imino) = $RT \ln K_{HB}$(*N*-imino) $\leq$ 0.7 and $-\Delta G_{HB}$(*N*-cyano) = $RT \ln K_{HB}$(*N*-cyano) = 2.9 kcal mol^{-1}.[12,60] The difference between the calculated $G_{HB-neut}$ of the *N*-imino and *N*-cyano sites for complexes with one water molecule [$G_{\mathrm{HB-neut}}$(*N*-imino) − $G_{\mathrm{HB-neut}}$(*N*-cyano) = 2.7 kcal mol^{-1}] is of the same order of magnitude as experimentally obtained for 4-fluorophenol ($\geq$2.2 kcal mol^{-1}). Slightly smaller difference give the BSSE energies (2.0 kcal mol^{-1}). This comparison indicates that the HF/6-31G* method is also suitable for prediction of the preferred basic site in polyfunctional nitrogen bases in the hydrogen-bonding reaction.

Conclusions

Calculations performed by RHF, MP2, and DFT/B3LYP methods with the 6-31G* basis set for each potential basic site (*N*-imino and *N*-cyano) of $Me_2N{-}CH{=}N{-}C{\equiv}N$ (FDM*CN) in the proton-transfer and hydrogen-bonding reactions indicate that the *N*-cyano site is more basic than the *N*-imino one for both reactions in the gas phase. The experimental gas-phase basicity value (GB 204.9 kcal mol^{-1}) is close to that calculated for the *N*-cyano site in the E isomer (the most stable at the HF/6-31G* level) of FDM*CN (GB 203.8 kcal mol^{-1}) and larger by 11.4 kcal mol^{-1} than that of the *N*-imino site (GB 193.5 kcal mol^{-1}). Good agreement of the computational and experimental results indicates that the HF/6-31 G* method can be used for prediction of the preferred basic site in polyfunctional nitrogen bases in the gas phase. In an aqueous solution, calculations with the PCM model confirm that the *N*-imino atom is the preferred basic site in FDM*CN. In the E isomer of FDM*CN, its basicity is by 8 kcal mol^{-1} larger than the other one.

Acknowledgment. The authors thank Dr. A. Liwo for some useful discussion. Calculations were carried out with the use of the resources and software at the Interdisciplinary Center for Molecular Modeling (ICM—Warsaw) and the Informatics Center of the Metropolitan Academic Network (IC MAN—Gdańsk) at the Technical University of Gdańsk.

References and Notes

(1) Vaes, J.; Foubert, A. Z.; Zeegers-Huyskens, Th. *Can. J. Chem.* **1975**, *53*, 604.

(2) Foubert, A.; Huyskens, P. L. *Can. J. Chem.* **1976**, *54*, 610.

(3) Oszczapowicz, J.; Raczyńska, E. *Pol. J. Chem.* **1983**, *57*, 419.

(4) Raczyńska, E. D.; Laurence, C.; Nicolet, P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1491.

(5) Raczyńska, E. D.; Laurence, C.; Berthelot, M. *Can. J. Chem.* **1992**, *70*, 2203.

(6) Borgarello, M.; Houriet, R.; Raczyńska, E. D.; Drapala, T. *J. Org. Chem.* **1990**, *55*, 38.

(7) Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Raczyńska, E. D. *J. Org. Chem.* **1991**, *56*, 3669.

(8) Raczyńska, E. D.; Maria, P.-C.; Gal, J.-F.; Decouzon, M. *J. Org. Chem.* **1992**, *57*, 5730.

(9) Oszczapowicz, J. In *The Chemistry of Amidines and Imidates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Vol. 2, p 623, and references therein.

(10) Raczyńska, E. D. *Pol. J. Chem.* **1998**, *72*, 1215, and references therein.

(11) Häfelinger, G.; Kuske, F. K. H. In *The Chemistry ofAmidines and Imidates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Vol. 2, p 1, and references therein.

(12) Laurence, C.; Berthelot, M.; Raczyńska, E. D.; LeQuestel, J.-Y.; Duguay, G.; Hudhomme, P. *J. Chem. Res. (S)* **1990**, 250.

(13) Anulewicz, R.; Krygowski, T. M.; Raczyńska, E. D.; Laurence, C. *J. Phys. Org. Chem.* **1991**, *4*, 33.

(14) Krygowski, T. M.; Anulewicz, R.; Raczyńska, E. D.; Laurence, C. *J. Phys. Org. Chem.* **1991**, *4*, 689.

(15) Häfelinger, G.; Krygowski, T. M.; Kuske, F. K. H. *Z. Naturforsch* **1992**, *47B*, 1480.

(16) Gal, J.-F.; Leito, I.; Maria, P.-C.; Raczyńska, E. D.; Taft, R. W.; Anvia, F. *J. Chim. Phys.* **1995**, *92*, 22.

(17) Raczyńska, E. D.; Taft, R. W. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1297.

(18) Raczyńska, E. D.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Taft, R. W.; Anvia, F. *J. Org. Chem.* **2000**, *65*, 4635.

(19) Raczyńska, E. D.; Mishima, M.; Mustanir, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2175.

(20) Taft, R. W.; Raczyńska, E. D.; Maria, P.-C.; Leito, I.; Gal, J.-F.; Decouzon, M.; Drapala, T.; Anvia, F. *Pol. J. Chem.* **1995**, *69*, 41.

(21) Maria, P.-C.; Leito, I.; Gal, J.-F.; Exner, O.; Decouzon, M. *Bull. Soc. Chim. Fr.* **1995**, *132*, 394.

(22) Castano, O.; Notario, R.; Hori, K.; Abboud, J. L. M. *Struct. Chem.* **1996**, *7*, 321.

(23) Raczyńska, E. D.; Maria, P.-C.; Gal, J.-F. *Analyst* **1998**, *123*, 621.

(24) Hunter, E. P. I.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(25) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 521.

(26) Berthelot, M.; Helbert, M.; Laurence, C.; LeQuestel, J.-Y.; Anvia, F.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1993**, 625.

(27) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(28) Makowski, M.; Liwo, A.; Wróbel, R.; Chmurzyński, L. *J. Phys. Chem. A* **1999**, *103*, 11104.

(29) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(30) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(31) Pople, J. A.; Brinkley, J. S.; Seeger, R. *Int. Quantum. Chem. Symp.* **1976**, *10*, *1*.

(32) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(34) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(35) Frish, C. P. M.; Trucks, G.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Anders, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. GAUSSIAN 94, VERSION B.3; Gaussian Inc.: Pittsburgh, PA, 1995.

(36) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.

(37) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

(38) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

(39) Szafran, M.; Karelson, M. M.; Katritzky, A. R.; Koput, J.; Zerner, M. C. *J. Comput. Chem.* **1993**, *14*, 371.

(40) Cammi, R.; Tomasi, J. *J. Comput. Chem.* **1995**, *16*, 1449.

(41) Pomelli, C. S.; Tomasi, J. *J. Theor. Chem. Acc.* **1997**, *96*, 39.

(42) Boys, S. F.; Bemardi, F. *Mol. Phys.* **1970**, *19*, 553.

(43) Chałasiński, G.; Kendall, R. A.; Simons, J. *J. Chem. Phys.* **1987**, *87*, 2965.

(44) Hamza, A.; Vibók, A.; Halász, G. J.; Mayer, I. *J. Mol. Struct. (THEOCHEM)* **2000**, *501*−*502*, 427, and references therein.

(45) Perrin, C. L. In *The Chemistry of Amidines and Imidates*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Vol. 2, p 147, and references therein.

(46) Naulet, N.; Filleux, M. L.; Martin, G. J. *Org. Magn. Reson.* **1975**, *7*, 326.

(47) Oszczapowicz, J.; Krawczyk, W.; Osek, J.; Raczyńska, E. *J. Chem. Res. (S)* **1985**, 384.

(48) Oszczapowicz, J.; Raczyńska, E.; Osek, J. *Magn. Reson. Chem.* **1986**, *24*, 9.

(49) Exner, O.; Buděšínský, M.; Hnyk, D.; Všetečka, V.; Raczyńska, E. D. *J Mol. Struct.* **1988**, *178*, 147.

(50) Kosturkiewicz, Z.; Ciszak, E.; Tykarska, E. *Acta Crystallogr. Sect. B: Struct. Sci.* **1992**, *B48*, 471.

(51) Cellerin, C.; Abouelfida, A.; Pradere, J. P.; Proutiere, A.; Roze, J. C.; Bouzid, M.; Exner, O. *J. Mol. Struct.* **1992**, *265*, *215*.

(52) Krygowski, T. M. J. *Chem. Inf. Comput. Sci.* **1993**, *33*, 70, and references cited therein.

(53) Wiberg, K *Tetrahedron* **1978**, *24*, 1083.

(54) Berthelot, M.; Helbert, M.; Laurence, C.; LeQuestel, J.-Y. J. *Phys. Org. Chem.* **1993**, *6*, 302.

(55) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(56) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502, and references therein.

(57) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworth: London, 1965.

(58) Raczyńska, E. D. J. *Chem Res. (S)* **1991**, 90.

(59) *NIST Chemistry WebBook, NIST Standard Reference Database Number 69, February 2000*; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899 (http://webbook.nist.gov/chemistry/).

(60) Raczyńska, E. D. J. *Chem. Res. (S)* **1997**, 214.