625 (C–S); MS, m/e 258 (M^+), 201, 83, 73, 57, 41.

***trans*-2-*tert*-Butyl-5-(cyclohexylsulfinyl)-1,3-dioxane (*trans*-11).** The procedure was similar to that described in the preparation of *trans*-8, with 3.0 g (12 mmol) of *trans*-2-*tert*-butyl-5-(cyclohexylthio)-1,3-dioxane and 2.1 g (12.2 mmol) of *m*-chloroperoxybenzoic acid. The crude product was purified by flash chromatography (*n*-hexane/ethyl acetate, 85:15), to give 2.5 g (78.6% yield) of pure *trans*-11, mp 131–132 °C; ^{1}H NMR in Table II; ^{13}C NMR in Table III; IR (KBr) 2948 and 2850 (C–H), 1450 (c-C_6H_{11}), 1375 [$(CH_3)_3C$], 1142 and 1095 (C–O), 1040 cm^{-1} (S=O); MS, m/e 217 (M^+ – 57), 131, 83, 57, 41.

Anal. Calcd for $C_{14}H_{26}SO_3$: C, 61.28; H, 9.55. Found: C, 61.45; H, 9.35.

***cis*-2-*tert*-Butyl-5-(cyclohexylsulfinyl)-1,3-dioxane (*cis*-11).** The cis isomer was prepared from the chemical equilibration of *trans*-11, as described for *cis*-8 (see above). *trans*-2-*tert*-Butyl-5-[cyclohexylsulfinyl)-1,3-dioxane (1.4 g, 5.11 mmol) and boron trifluoride etherate (0.77 g, 5.11 mmol) gave a cis/trans mixture shown by ^{1}H NMR as 78:22, respectively. Separation by flash chromatography[17] (*n*-hexane/ethyl acetate, 70:30) afforded 1.0 g (71.4% yield) of the desired cis diastereomer, mp 146–147 °C; ^{1}H NMR in Table II; ^{13}C NMR in Table III; IR (KBr) 2930 and 2850 (C–H), 1440 (c-C_6H_{11}), 1375 [$(CH_3)_3C$], 1147 and 1050 (C–O), 1031 cm^{-1} (S=O); MS, m/e 274 (M^+), 217, 87, 83, 57, 41.

Anal. Calcd for $C_{14}H_{26}SO_3$: C, 61.28; H, 9.55. Found: C, 61.31; H, 9.57.

***trans*-2-*tert*-Butyl-5-(cyclohexylsulfonyl)-1,3-dioxane (*trans*-12).** This compound was prepared following the same procedure described for *trans*-9 (see above), with 0.31 g (1.2 mmol) of *trans*-2-*tert*-butyl-5-(cyclohexylthio)-1,3-dioxane (*trans*-10) and 1.2 mL of 30% H_2O_2. The crude product was recrystallized from *n*-hexane to give 0.29 g (82.9% yield) of the desired product, mp 175–176 °C; ^{1}H NMR in Table II; ^{13}C NMR in Table III; IR (KBr) 2946 and 2851 (C–H), 1440 (c-C_6H_{11}), 1375 [$(CH_3)_3C$], 1310 and 1140 (SO_2), 1130, 1100 and 1050 cm^{-1} (C-O); MS, m/e 233 (M^+ – 57), 151, 83, 57, 41.

Anal. Calcd for $C_{14}H_{26}SO_4$: C, 57.90; H, 9.02. Found: C, 57.87; H, 9.01.

***cis*-2-*tert*-Butyl-5-(cyclohexylsulfonyl)-1,3-dioxane (*cis*-12).** The oxidation of 0.15 g (0.55 mmol) of *cis*-2-*tert*-butyl-5-(cyclohexylsulfinyl)-1,3-dioxane (*cis*-11) was achieved with 0.10 g (0.57 mmol) of *m*-chloroperoxybenzoic acid, according to the procedure described in the preparation of *cis*-9. The crude product obtained was purified by preparative TLC (*n*-hexane/ethyl acetate, 55:45) to give 0.12 (75.5% yield) of crystalline, pure *cis*-12, mp 138–139 °C; ^{1}H NMR in Table II; ^{13}C NMR in Table III; IR (KBr) 2994 and 2860 (C–H), 1460 (c-C_6H_{11}), 1380 [$(CH_3)_3C$], 1305 and 1167 (SO_2), 1138 and 1033 cm^{-1} (C–O); MS, m/e 233 (M^+ – 57), 151, 83, 57, 41.

Equilibrations and Analysis. Equilibrium was approached from both sides; boron trifluoride etherate was the catalyst: ca. 30 mg of the dioxane was placed in a 20-mL ampule and dissolved in 10 mL of chloroform before the addition of two to three drops of the catalyst. The ampule was sealed and submerged in a constant-temperature bath (Precision Circulating System, GCA Corp.) until equilibrium was reached. Quenching was effected by pouring the equilibrating solution into aqueous sodium bicarbonate. The dioxanes were then extracted with chloroform, dried, and evaporated, and the progress of the equilibration was conveniently monitored by ^{1}H NMR spectroscopy. Quantitative product analysis was carried out by vapor-phase chromatography (on a 7 ft × $^1/_8$ in. 20% FFAP column on Chromosorb W 60–80 mesh, at 175 °C) except in the case of the (nonvolatile) sulfoxides and sulfones where a less accurate analysis was obtained by integration of appropriate peaks in the ^{1}H NMR spectrum (e.g., H_5). In the case of the sulfoxides 8 and 11, the analysis was effected in the presence of $Eu(fod)_3$ to ensure adequate separation of the *tert*-butyl peaks used in the analysis.

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Gas-Phase Basicity of N^1,N^1-Dimethyl-N^2-phenylformamidines

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Gas-phase basicities (GB) for a series of N^1,N^1-dimethyl-N^2-phenylformamidines (FDMP) are determined in proton-transfer equilibria measured in ion cyclotron resonance experiments. The effects of substituents on the GB values are studied. The measured GB values are compared with Brønsted basicities in H_2O and the hydrogen-bonding basicities in CCl_4. These comparisons explain the various substituent effects on the protonation (deprotonation) and the formation of hydrogen bonding complexes in FDMP.

Introduction

Investigations on the effects of substituents on the gas-phase basicities of amidines are not reported in the literature, and to our knowledge, this is the first paper that addresses this question. A series of para-substituted N^1,N^1-dimethyl-N^2-phenylformamidines (FDMP), compounds 1–6 have been synthesized, and their GB values determined in proton-transfer equilibrium reactions carried out in an ICR spectrometer. All the compounds have the same *E* stereochemical structure.[1,2]

$Me_2N—CH=NC_6H_4X$ (FDMP)

1, X = 4-NO_2; 2, X = 4-CN; 3, X = 4-COMe

4, X = 4-Br; 5, X = H; 6, X = 4-Me

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Table I. Experimental GB Values Determined in the Proton Equilibrium Reaction $MH^+ + B \rightleftharpoons M + BH^+$ (M = Formamide FDMP-X and B = Reference Base)

X	B	GB(B)[a]	ΔG_r[b]	GB(M)[c]
(1) 4-NO_2	2-picoline	215.9	0.5	216.4
	pyrrolidine	216.1	0.2	
(2) 4-CN	2-picoline	215.9	0.8	216.9
	MeNHiPr	216.8	0.1	
	Et_2NH	216.9	−0.1	
	piperidine	217.3	−0.2	
	3,5-dimethylpyridine	217.7	−1.0	
(3) 4-COMe	$MeNHCH_2CH_2NHMe$	222.6	0.2	222.6[d]
	Et_3N	223.4	−0.9	
(4) 4-Br	Et_3N	223.4	0.1	223.6[d]
	Et_2NnPr	224.2	−0.4	
(5) H	Et_2NnPr	224.2	0.0	224.2
	n-Pr_3N	225.6	−1.3	
(6) 4-Me	Et_2NnPr	224.2	0.7	225.5[d]
	n-Pr_3N	225.6	0.3	

[a] Values in kcal/mol, taken from ref 8. [b] ΔG_r is the free energy change for the equilibrium proton transfer carried out at 313 K. [c] ±0.3 kcal/mol unless otherwise indicated. [d] ±0.5 kcal/mol.

We want to compare the GB values obtained here with previously studied Brønsted basicities,[3,4] measured as pK_a of amidinium ions in H_2O, and the hydrogen-bonding basicities,[5] measured as log K_{HB}, where K_{HB} is the formation constant of hydrogen-bonded complexes of amidines with 4-fluorophenol in CCl_4. This comparison should shed new light on the problem of the site of protonation (deprotonation) and on the substituent effects on the gas-phase basicity of FDMP.

Experimental Section

Materials. FDMP were synthesized according to procedure described in ref 6 from dimethylformamide dimethylacetal and corresponding primary anilines.

GB Measurements. Gas-phase basicities were determined in an ion cyclotron resonance (ICR) spectrometer under conditions similar to those previously described,[7] from the equilibrium constant for the proton-transfer reactions between the formamidines M and the reference bases B (eq 1).

$$MH^+ + B \rightleftharpoons M + BH^+ \quad (1)$$

$GB(M) = GB(B) + \Delta G^\circ_r$ is obtained from the measurement of the equilibrium constant for reaction 1, $K_{eq}(1)$, and from the relationship $\Delta G^\circ_r = -RT \ln K_{eq}(1)$, with $T = 313$ K. All GB values reported in Table I refer to GB (NH_3) = 196.4 kcal mol^{-1}.

Results and Discussion

Site of Protonation. N^1,N^1-Dimethyl-N^2-phenylformamidines have more than one basic site, i.e., the amino (N^1) or imino (N^2) nitrogen atom in the amidine group or the ring substituent X in compounds **1–3** may be protonated. Thus in the investigation of gas-phase substituent effects on the basicity of FDMP, all the possible resulting structures should be considered. The first observation from Table I is that the GB value obtained for the parent system

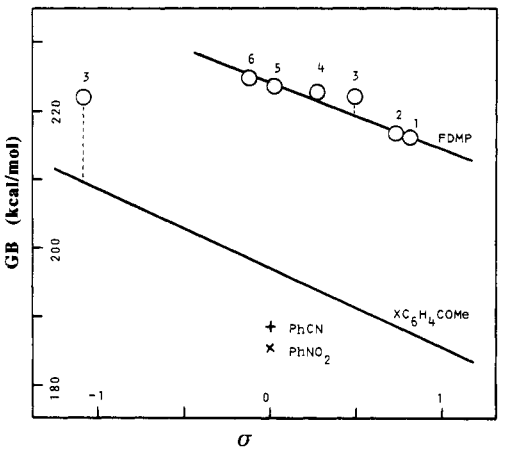
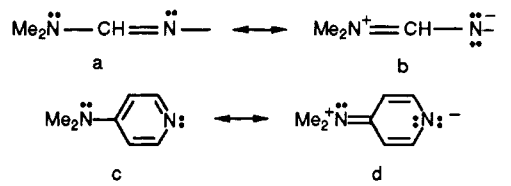


Figure 1. Correlation GB vs σ constants for FDMP. For comparison, line (- - -) for acetophenones and points (+) for benzonitrile and (×) for nitrobenzene are plotted.

(X = H) of FDMP is greater than those of the other bases containing sp^2 or sp^3 hybridized nitrogens as in pyridines, anilines, and N,N-dimethylanilines.[8] The same is observed for Brønsted basicities in solution when we compare the pK_a value in water[3] for **5** and for pyridine and/or anilines.[9]

Application of correlation analysis methods to the study of substituent effects on basicity of trisubstituted formamidines shows that in solution the imino nitrogen atom (N^2) is protonated.[10] The conjugation between the amino and imino nitrogen atoms, structures a and b, explains the



high basicity in amidines. Similarly, conjugation of the electron donating NMe_2 group in the para position and the nitrogen atom, structures c and d, explains the high basicity observed for 4-(dimethylamino)pyridine.

For hydrogen-bonding basicity, the values of log K_{HB} for FDMP are significantly greater than those observed for anilines and/or N,N-dimethylanilines, but they compare with those for pyridines, log K_{HB}(**5**) = 1.90[5] and log K_{HB}(Pyr) = 1.88.[11] For formamidines, as with pyridines, hydrogen bonding occurs at the imino nitrogen atom (N^2) in the amidine group and also in substituent X, when X = NO_2, CN, COMe.[5,12]

Comparison of the gas-phase basicities obtained here for the parent system **5** and those for monosubstituted benzenes (PhX)[8] shows that the GB value of **5** is significantly greater (20–40 kcal mol^{-1}) than those of PhX, and thus the protonation of the substituent X can probably be excluded. However, the dimethylformamidine group is a strong electron-donating group (like the NH_2 group) and for formamidines containing an electron-withdrawing substituent, as in **1–3**, the substituent X can conjugate with

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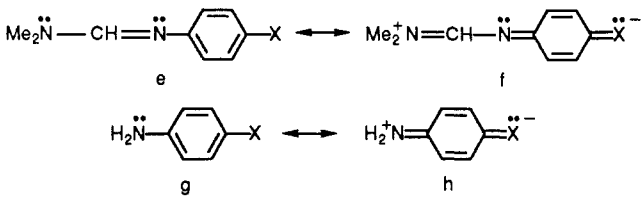
Table II. Relative Gas-Phase ($\Delta\delta G_g$) and Solution Brønsted Basicities ($\Delta\delta G^\circ_{aq}$) and Hydrogen-Bonding Basicities ($\Delta\delta G^\circ_{HB}$) of FDMP[a]

compd	$\Delta\delta G_g$	$\Delta\delta G^\circ_{aq}$	$\Delta\delta G^\circ_{HB}$
1	−7.8	−2.90	−0.85
2	−7.3	−2.33	−0.56
3	−1.6	−1.54	−0.08
4	−0.6	−1.02	−0.34
5	0	0	0
	(224.2)	(11.11)[b]	(2.59)[c]
6	1.3	0.41	0.23

[a] In kcal mol^{-1}; a negative sign denotes lower basicity. [b] Reference 3. [c] Reference 5.

the amidine system. Formation of charge and variation of electron configuration on the amino nitrogen atom and in substituent X can occur as shown in the conjugated structures e and f, similar to the case of anilines, structures



g and h, or *N*,*N*-dimethylanilines, but no change occurs at the imino nitrogen atom. This effect can augment the basicity of substituent X, and thus either the amidine group or the substituent X might be protonated. The correlation of the GB values obtained for compounds **1–6** against σ° constants[13] shows that **3** deviates slightly from the linear relationship (Figure 1). Compound **3** may be treated as a derivative of N^1,N^1-dimethyl-N^2-phenylformamidine with a MeCO group in the para position (σ°_p = 0.47) and with the amidine group being the site of protonation or as a derivative of acetophenone bearing a Me_2N–CH=N group in the para position ($\sigma^+_p \sim -1.1$[5]) with protonation occurring on the acetyl group. In Figure 1 the GB values of substituted acetophenones taken from the literature[14] have been plotted against corresponding σ^+ constants.[13] The comparison shows that the GB values of FDMP are greater (20 kcal mol^{-1}) than those of acetophenones containing the same substituents. The deviation of the experimental GB of **3** from the linear relationship for acetophenones is significantly greater than that found for FDMP. Considering **3** as a derivative of acetophenone, its relative gas-phase basicity ($\delta\Delta G_g \sim 25$ kcal mol^{-1}) is greater than that found for 4-aminoacetophenone ($\delta\Delta G_g$ = 11.4 kcal mol^{-1}) and even for 4-(dimethylamino)-acetophenone ($\delta\Delta G_g$ = 18.1 kcal mol^{-1}).[14] The σ^+_p of the Me_2NCH=N group is assumed to be comparable to that of the NH_2 group. These results suggest that in compound **3**, the protonation occurs at the amidine rather than on the carbonyl group.

From the analysis of gas-phase substituent effects it appears that in compounds **1–6** the imino nitrogen atom of the amidine group is the favored site of protonation in the gas phase as well as in solution. The same conclusions have been derived from comparison of GB with the free energies of ionization of N^1,N^1-dimethyl-N^2-phenylformamidinium ions (ΔG°_{aq}) and with the free energies of complexation of FDMP with 4-fluorophenol (ΔG°_{HB}) in solution (vide supra).

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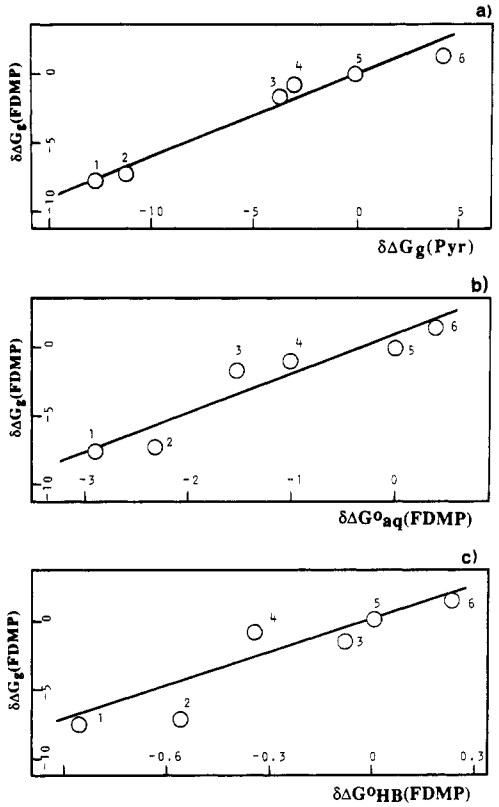
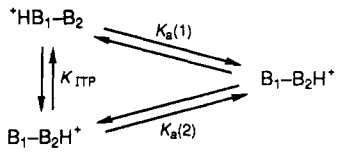


Figure 2. Plots of $\delta\Delta G_g$(FDMP) against (a) $\delta\Delta G_g$(pyr), (b) $\delta\Delta G^\circ_{aq}$(FDMP), (c) $\delta\Delta G^\circ_{HB}$(FDMP); see text.

Scheme I



Gas-Phase Substituent Effects on Basicity. Figure 1 shows that the GB values of FDMP can be correlated with σ° constants, eq 2.

$$\mathrm{GB(FDMP)} = 224.6 - 10.1\sigma^\circ \qquad r = 0.978 \qquad (2)$$

The value of parameter ρ (−10.1), compared with that found for the $\Delta G^\circ_{aq}/\sigma^\circ$ correlation in water at 25 °C (−3.5) and for the $\Delta G^\circ_{HB}/\sigma^\circ$ correlation in CCl_4 at 25 °C(1.2) shows that the GB values are the most sensitive ones to the effects of substituents (Table II). Similar effects have been observed for other nitrogen bases such as pyridines[15,16] and anilines.[15]

The relative gas-phase basicities obtained here are also correlated with those found for pyridines[15] in Figure 2a, displaying a linear relationship (r = 0.979). The slope is equal to 0.58, a little greater than that found for the $\delta\Delta G^\circ_{aq}$(FDMP)/$\delta\Delta G^\circ_{aq}$(pyr) correlation in water (slope = 0.51) and almost the same as that found for the $\delta\Delta G^\circ_{HB}$(FDMP)/$\delta\Delta G^\circ_{HB}$(pyr) correlation in CCl_4 (slope = 0.57). These results suggest that in both cases, gas phase and solution, the transmission of polar substituent effects to the reaction center is almost the same for FDMP and for pyridines (within the derivatives employed in this study). The sensitivity of FDMP to substitution at the

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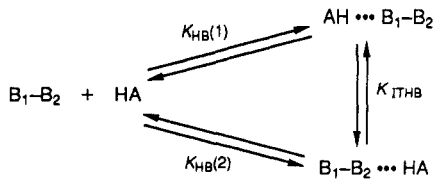
Scheme II



imino nitrogen atom is about 2 times smaller than that of pyridines. These observations lead us to conclude that gas-phase protonation in FDMP occurs on the imino nitrogen atom (N^2) of the amidine group, quite similarly to what occurs in solution.

Comparison of the Gas-Phase and Solution Basicities. In solution it is well-known that for bifunctional compounds B_1–B_2, which dissociate according to Scheme I, the measured dissociation constant $K_a(m)$ and the internal transfer of proton constant $K_{ITP} = ({}^+HB_1 - B_2)/(B_1 - B_2H^+)$ obey eq 3 and 4, respectively.

$$1/K_a(m) = 1/K_a(1) + 1/K_a(2) \quad (3)$$

$$K_{ITP} = K_a(2)/K_a(1) \quad (4)$$

If the dissociation constant of one of the sites is negligible with respect to the dissociation constant of the second one ($\Delta pK_a > 2$), the measured $K_a(m)$ is approximately equivalent to the K_a of the more basic site, and the protonation of this site is about 100%.

In the case of FDMP, compounds **1–3**, the difference of the pK_a values of each site, the amidine group and a basic group in substituent X (NO_2, CN, or MeCO), is greater than 10 pK_a units. This fact indicates clearly that in **1–6** only the amidine group is protonated in solution. For estimation of the pK_a values of NO_2, CN, and MeCO groups in **1–3**, the pK_a values of monosubstituted benzenes from literature[9,17,18] were used.

Further comparison of the gas-phase and solution properties appears in Figure 2b, where the relative gas-phase basicities of FDMP, $\delta\Delta G^\circ_g$, have been correlated with the relative free energies of ionization of formamidinium ions in water, $\delta\Delta G^\circ_{aq}$, yielding a fair linear relationship with a slope equal to 2.8. Note that a slope of 2.5 was found for para-substituted pyridines.[15] In the literature the small deviations from the $\delta\Delta G_g/\delta\Delta G^\circ_{aq}$ correlation are explained by specific aqueous solvent effects on substituent.

Comparison of the Gas-Phase and Hydrogen-Bonding Basicities. It has been shown earlier[5] that for FDMP hydrogen bonding takes place on the N^2 atom in the amidine group and also in substituent X in the case of bifunctional amidines. For bifunctional compounds B_1–B_2, two acid–base equilibria are observed (Scheme II). The measured formation constant of complexes of B_1–B_2 with *p*-fluorophenol in CCl_4 at 25 °C, $K_{HB}(m)$, is the sum of the microscopic formation constants $K_{HB}(1)$ and $K_{HB}(2)$ for the N^2 atom and substituent X, eq 5, and the internal transfer hydrogen-bonding constant $K_{ITHB} = (AH{\cdots}B_1 - B_2)/(B_1 - B_2{\cdots}HA)$ is the ratio of these microscopic constants, eq 6.

$$K_{HB}(m) = K_{HB}(1) + K_{HB}(2) \quad (5)$$

$$K_{ITHB} = K_{HB}(1)/K_{HB}(2) \quad (6)$$

For the nitro derivative **1**, the microscopic constant of the nitro group is very small and the experimental K_{HB} value

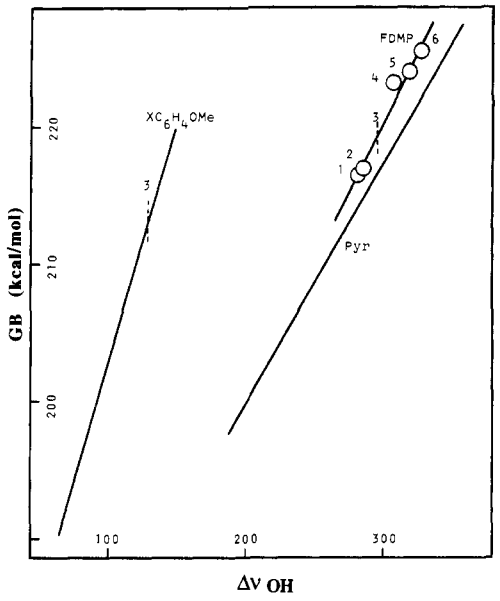


Figure 3. Plots of GB vs $\Delta\nu_{OH}$ for acetophenones (XC_6H_4COMe), FDMP, and pyridines (pyr).

is close to the microscopic constant of the amidine group.

For cyano and acyl derivatives **2** and **3**, the microscopic constants of each site are of the same order of magnitude, and thus the measured K_{HB} values are about twice the corresponding microscopic constants.

In Figure 2c the relative gas-phase basicities $\delta\Delta G_g$ have been plotted against the relative free energies of the formation of complexes of FDMP with 4-fluorophenol $\delta\Delta G^\circ_{HB}$. For compounds **1**, **5**, and **6**, which deviate the least from the correlation, both the gas-phase and the hydrogen-bonding basicities correspond to the reactive properties of the amidine group. The correlation shows that compound **2** deviates the most from the linear relationship. In this case, the GB of the cyano group is considerably smaller than that of the amidine group; therefore, protonation occurs at the latter group, whereas hydrogen bonding can take place on the N^2 atom in the amidine group and also on the cyano group, thus resulting in $\delta\Delta G^\circ_{HB}$ being relatively greater than $\delta\Delta G_g$. The acetyl derivative **3** deviates somewhat less than expected on the ground that it protonates on the amidine group whereas hydrogen bonding occurs on two sites, i.e., on the acetyl and amidine groups.

For estimation of the GB values for each site in compound **3** the GB values of FDMP and acetophenones[14] have been correlated with the frequency shift $\Delta\nu_{OH}$ of methanol hydrogen bonded to basic site in amidines and acetophones in CCl_4. For comparison, the GB/$\Delta\nu_{OH}$ correlation with pyridines has also been plotted. The $\Delta\nu_{OH}$ values of corresponding compounds have been taken from literature.[5,12,19] The GB/$\Delta\nu_{OH}$ correlations are particular valuable, because such relationships not only provide information on the reaction center and substituent effects but also have predictive uses for GB in the case of bifunctional compounds. For these compounds it is impossible to measure microscopic gas-phase basicities for both sites when their values are almost the same. The microscopic gas-phase basicities for compound **3** can be predicted from the GB/$\Delta\nu_{OH}$ correlations for acetophenones and FDMP and from the $\Delta\nu_{OH}$ values found[5] for the acetyl and the amidine group, $\Delta\nu_{OH}(MeCO) = 129\ cm^{-1}$

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Table III. Microscopic GB, pK_a and log K_{HB} Predicted for Each Group, MeCO and $Me_2NCH{=}N$, in Compound 3

group	GB	pK_a	log K_{HB}[a]
MeCO	213.5	<0[b]	1.67
$Me_2NCH{=}N$	219.5	7.02[c]	1.52

[a] Reference 5. [b] Reference 18. [c] Reference 20.

and $\Delta\nu_{OH}(N^2) = 295\ cm^{-1}$. The resulting GB values are given in Table III. For comparison, the solution Brønsted basicities (as pK_a) and the hydrogen-bonding basicities (as log K_{HB}) for each group are also summarized. These results confirm that the amidine group is the favored site of protonation in both gas phase and solution; however, hydrogen bonding is enhanced by the presence of the acetyl group. As a consequence, in aqueous solution, acetophenones as well as benzonitriles and nitrobenzenes are very weak bases.[9,17,19] The acetyl group forms strong hydrogen bonds with water or other hydrogen-bond-donor solvents, thereby reducing basicity in aqueous solution relative to the intrinsic gas-phase basicity.

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Registry No. 1, 74739-51-8; 1·H$^+$, 123834-37-7; 2, 119044-58-5; 2·H$^+$, 123834-38-8; 3, 119044-59-6; 3·H$^+$, 123834-39-9; 4, 119044-60-9; 4·H$^+$, 123834-40-2; 5, 56687-95-7; 5·H$^+$, 123834-41-3; 6, 56638-68-7; 6·H$^+$, 123834-42-4.

A Study of New Bis(macrocyclic polyamine) Ligands as Inorganic and Organic Anion Receptors

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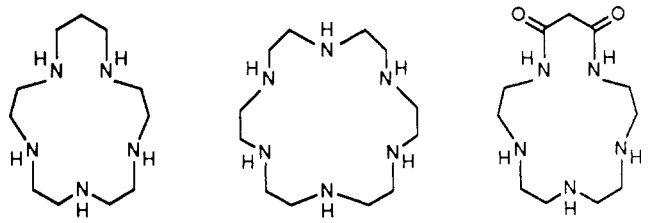
Propylene-bridged bisdioxo[16]aneN_5 (**4b**) and diether-bridged (**5a**) and propylene-bridged (**5b**) bis[16]aneN_5 ligands [bis(macrocyclic pentaamine)] were synthesized as host molecules for inorganic and organic anion guests. By the polarographic and potentiometric methods, **4b** (di- and tetraprotonated) and **5a** and **5b** (tetra- and hexaprotonated) were found to yield stable 1:1 complexes with citrate^{3-}, AMP^{2-}, ATP^{4-}, HPO_4^{2-}, $[Fe(CN)_6]^{4-}$, and $[Fe(CN)_6]^{3-}$ anions. Comparison of these association constants (K) with those of the parent monomeric polyamines reveals that the attachment of the second polyamine moiety always enhances anion encapsulating abilities, suggesting the formation of sandwich-type complexes. Diprotonated tetraoxo[24]aneN_8 **6**, $[\mathbf{6}\cdot(H^+)_2]^{2+}$, forms more stable 1:1 complexes with nucleotide anions than the diprotonated **4b**, $[\mathbf{4b}\cdot(H^+)_2]^{2+}$.

The interaction of organic anion receptors with biologically important anions has received much attention, both for its intrinsic interest and potential applications[1,2] as well as for the role it can play as a model for biological processes.[3,4] In earlier studies it was discovered that the macrocyclic pentaamines ([16]aneN_5, **1**) and hexaamines ([18]aneN_6, **2**) accommodate three protons within their macrocyclic cavities at neutral pH and that the resulting triprotonated species display selective complexing abilities toward polycarboxylate anions,[5-7] CO_3^{2-},[8] catechols,[9,10] and nucleotide anions (AMP^{2-}, ADP^{3-}, and ATP^{4-}).[11-13] An amide-containing polyamine derivative, dioxo[16]aneN_5 (**3**), in its singly and doubly protonated forms, also interacts with these anions to form 1:1 complexes.[11] Recently, studies with more expanded macromonocyclic polyamines (e.g., [21]aneN_7, [24]aneN_8, [27]aneN_9, [30]aneN_{10}, etc.) have been reported.[14] Macromonocyclic polyamines studied thus far are limited in their structural variations. Further structural modifications might provide us with more efficient and selective host molecules, as well as with new information on their anion coordination chemistry.

To this end, we have synthesized new anion receptor molecules, bisdioxo[16]aneN_5 (**4b**) and bis[16]aneN_5 (**5a** and **5b**), both of which are comprised of two identical



1 2 3

macrocyclic units linked with a polyether or a propylene chain (see Scheme I). The association constants of these

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