contribution to these shifts, the chemical shifts of other hydrogens that are bound to carbons formally in conjugation with the rings would demonstrate the effects as well. The H6′ protons are just such a set, and they display only 0.05–0.07 ppm ranges over the three different substitutions. The limits of these ranges are defined not by the spirocyclopropanes and spirocyclobutanes but rather by the fluorenes and spirocyclopentanes. Thus, an explanation on the basis of π-conjugation is not warranted.

Cyclopropane clearly induces an upfield chemical shift on protons located over the face of the ring. The constant 0.5 ppm upfield shift relative to its expected position is consistent with earlier observations.[6,25] Cyclobutane does not display a "special" magnetic anisotropy that can be undeniably separated from this chemical shift data. The average 0.08 ppm downfield shift is six times smaller than the average cyclopropane induced shift, and inspection of Figure 2 makes it difficult to exclude the cyclobutane shifts from the swath cut by the spirocyclopentane and fluorene data. If the correlation lines were exact, approximately half of the difference between the fluorene and the spirocyclobutane series would be ascribed to an increase in the van der Waals' interaction energy. It is intriguing that all of the deviations for the cyclobutanes are downfield, but the small size makes assigning their origin difficult.

The magnetic anisotropy of the cyclopropane ring is unique in the realm of saturated hydrocarbons, giving rise to a component that is not predictable from the properties of other, simpler systems. The evidence for a magnetic anisotropy component in cyclobutane that produces unexpected downfield shifts is not convincing. The effect is at best small and difficult to extract from the relatively poor precision of the analytical method. The case for the antiaromaticity of cyclobutane structures will not be made on the basis of these data.

Acknowledgment. I would like to thank Dr. Jose Font and Dr. Dora Schnurr of Mosanto for assistance with the MM2 calculations. The original suggestion that the downfield shift of cyclobutane was caused by a van der Waals' interaction was made by Professor Charles Wilcox, Cornell University. Finally, the help and encouragement of my friends at Serena Software is gratefully acknowledged.

Supplementary Material Available: The shift–J matrices, a table of the ^{13}C chemical shifts, a table of the individual van der Waals' energy contributions for compounds 1–12, and the ^{1}H and ^{13}C NMR spectra for compounds 8, 9, 11, and 12 (27 pages). Ordering information is given on any current masthead page.

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Gas-Phase Basicity of N^1,N^1-Dimethyl-N^2-alkylformamidines: Substituent Polarizability Effects

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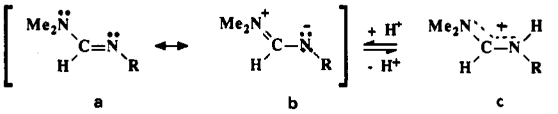
Gas-phase basicities (GBs) for a series of 14 N^1,N^1-dimethyl-N^2-alkylformamidines are obtained from proton-transfer equilibria, using Fourier transform ion cyclotron resonance mass spectrometry. The imino nitrogen atom appears to be the preferred protonation site. Relative GBs are linearly correlated to the alkyl substituent polarizability. Compared to other nitrogen bases (amines and nitriles), the sensitivity to this effect is strongly reduced by charge delocalization. Larger than expected GBs for long-chain alkyl derivatives are attributed to a coiling effect. An electron-withdrawing effect of the cyclopropyl linked to the electron-rich imino nitrogen atom is proposed as an explanation of the relatively weak GB measured for the corresponding compound.

Introduction

Amidines are known as important medicinal and biochemical agents.[1] They show antiviral, antibacterial, antibiotic, antifungal, and antihypertensive activities. They have also been tested as potential cancer therapeutic agents. The biological activity of amidines depends on their structure and on their basicity. N^1,N^1-Dimethylalkylformamidines contain the basic and electron-donating $Me_2NCH{=}N$ group. The strong basicity of this group is explained by the conjugation between the amino (N^1) and the imino (N^2) nitrogen atoms (structures a and b, Scheme I). For monobasic compounds the N^2 atom is the site of protonation in solution and yields the very stable amidinium cation (structure c).[2,3] Hydrogen bonding occurs also on the N^2 atom.[4,5] The influence of the substituent R on

Scheme I



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the Brønsted basicity in solution,[3,6,7] and on hydrogen-bonding basicity,[4,5] such as the formation constants of amidines with phenols in CCl_4 solution, have already been studied.

An investigation of the gas-phase basicities of amidines has recently been reported for a series of para-substituted N^1,N^1-dimethyl-N^2-alkylformamidines (FDM*R:R = 4-C_6H_4X, X = NO_2, CN, COMe, Br, H, Me).[8] The GB value obtained for the parent compound (R = Ph) is greater than those obtained for the other bases containing sp^2- or sp^3-hybridized nitrogens, such as pyridine, aniline, and *N,N*-dimethylaniline. Analysis of different substituent effects shows that for all the derivatives studied, the N^2 atom is the favored site of protonation in the gas phase.

In the present work, we extend these preliminary results to N^1,N^1-dimethyl-N^2-alkylformamidines 1–14. The GB

$Me_2NCH{=}NR$ (FDM*R)

1: R = Me
2: R = Et
3: R = *n*-Pr
4: R = i-Pr
5: R = c-C_3H_5
6: R = *n*-Bu
7: R = i-Bu
8: R = s-Bu
9: R = t-Bu
10: R = *n*-C_5H_{11}
11: R = t-C_5H_{11}
12: R = *n*-C_6H_{13}
13: R = c-C_6H_{11}
14: R = 1-Adam

values have been determined from proton transfer equilibrium constants using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The influence of alkyl substituents on the measured GB values has been investigated and compared with that found for the corresponding primary amines (RNH_2), *N,N*-dimethylamines ($RNMe_2$), and nitriles (RCN).

Experimental Section

Chemicals. Reagents for synthesis and reference bases for GB measurements were commercial compounds (Aldrich or Fluka). FDM*R were synthesized by heating equimolecular amounts of dimethylformamide dimethyl acetal and primary amines as described in ref 6.

Purification of formamidines (1–12) was performed by preparative gas chromatography (Carlo Erba Fractovap 2400 V, 2-m preparative column 20% SE 30 or 5% Carbowax 20 M) and 13–14 by sublimation under reduced pressure. Structures of FDM*R were confirmed by their IR spectra (Beckman, Model 4210) recorded for liquid films between KBr windows and by 70-eV mass spectra recorded before GB measurements using FT-ICR mass spectrometry. Mass spectra were recorded at sufficiently low pressure to avoid ion/molecule reactions. Zero filling (up to 64 K) of the 16 K data points spectra was used in order to obtain accurate intensities.[6b]

GB Measurements. Gas-phase basicities (as GBs) were determined using the FT-ICR mass spectrometer constructed at the University of Nice–Sophia Antipolis.[9] The equilibrium constants for proton transfer between FDM*R(B) and the reference base (Ref), as given in eq 2

$$\mathrm{Ref} + \mathrm{BH}^+ \rightleftharpoons \mathrm{RefH}^+ + \mathrm{B} \qquad (2)$$

were calculated according to eq 3, where $I(\mathrm{RefH}^+)$ and $I(\mathrm{BH}^+)$ are the intensities of signals for ions RefH^+ and BH^+, respectively; $P_{\mathrm{BA}}(\mathrm{B})$ and $P_{\mathrm{BA}}(\mathrm{Ref})$ are the pressures measured with a Bayard-Alpert (BA) ionization gauge (Alcatel BN 111); $S_r(\mathrm{Ref})$ and $S_r(\mathrm{B})$ are the sensitivities (relative to N_2) of the BA gauge estimated according to Bartmess and Georgiadis (BG).[10] The BA gauge sensitivities of compounds 4 and 12 were measured using a spinning rotor gauge (Leybold, Viscovac VM 210)[11] and were found to be 5.89 ± 0.14 and 8.73 ± 0.23, respectively.

Table I. Experimental GB Values Obtained from Proton Transfer Equilibria between FDM*R (B) and a Reference Base (Ref) (kcal • mol^{-1})

compd	R	Ref	GB (Ref)[a]	$\Delta G°(2)$	GB(B)[b]
1	Me	*n*-Bu_3N	228.3	+0.5	
		$Me_2N(CH_2)_3NH_2$	229.4	−0.3	228.7
		4-NMe_2-pyridine	228.8	−0.8	
2	Et	FDM*Me	228.7	+1.6	
		$Me_2N(CH_2)_3NH_2$	229.4	+0.7	229.9
		4-NMe_2-pyridine	228.8	+0.4	
3	*n*-Pr	FDM*Et	229.9	+0.5	
		FDM**n*-Bu	231.0	−0.1	230.6
4	i-Pr	$Me_2N(CH_2)_3NH_2$	229.4	+2.0	
		FDM*Et	229.9	+0.9	231.2
		$Me_2N(CH_2)_3NMe_2$	231.8	−0.4	
5	c-C_3H_5	FDM*Me	228.7	+0.8	
		FDM*Et	229.9	−0.5	229.4
6	*n*-Bu	FDM*Et	229.9	+1.2	
		FDM*i-Pr	231.2	−0.3	231.0
7	i-Bu	FDM*i-Pr	231.2	+0.1	
		FDM*CH_2CH_2OMe	232.4[c]	−0.9	231.4
8	s-Bu	FDM**n*-C_6H_{13}	232.0	+0.4	
		FDM*CH_2CH_2OMe	232.4[c]	−0.4	232.2
9	t-Bu	FDM*i-Pr	231.2	+1.9	
		$Me_2N(CH_2)_3NMe_2$	231.8	+0.8	
		$(Me_2N)_2C{=}NH$	234.8	−1.7	233.0
10	*n*-C_5H_{11}	FDM**n*-Bu	231.0	+1.2	232.3
		FDM**n*-C_6H_{13}	232.0	+0.4	
11	t-C_5H_{11}	FDM*t-Bu	233.0	+0.3	
		FDM*c-C_6H_{11}	232.7	+0.4	233.2
12	*n*-C_6H_{13}	*n*-Bu_3N	228.3	>+3.0	
		FDM*i-Pr	231.2	+0.9	
		$(Me_2N)_2C{=}NH$	234.8	−2.9	232.0
13	c-C_6H_{11}	FDM*t-Bu	233.0	−0.3	232.7
		$(Me_2N)_2C{=}NH$	234.8	−2.0	
14	1-Adam	FDM*t-C_5H_{11}	233.2	+2.3	
		$(Me_2N)_2C{=}NH$	234.8	+0.6	235.4

[a] Values of Taft et al. cited in refs 14 and 15. [b] ±0.3 kcal·mol^{-1}; standard state given in the Experimental Section. [c] To be published.

$$K = \frac{I(\mathrm{RefH}^+)}{I(\mathrm{BH}^+)}\,\frac{P_{\mathrm{BA}}(\mathrm{B})}{P_{\mathrm{BA}}(\mathrm{Ref})}\,\frac{S_r(\mathrm{Ref})}{S_r(\mathrm{B})} \qquad (3)$$

For comparison, the S_r values, estimated from the BG equation,[10] using the average molecular polarizability (α_{ahc} calculated according to Miller and Savchik),[12] are equal to 5.21 and 7.21, respectively, for 4 and 12. The BG equation underestimates the S_r values for these nitrogen compounds and for the amines used as reference bases by similar amounts.[11] It follows that no significant bias is introduced by the use of calculated (BG equation) S_r values.

Thus, GB(B) = GB(Ref) + $\Delta G°(2)$ was obtained from the equilibrium constant K and $\Delta G° = -RT \ln K$. All measurements were carried out at a FT-ICR cell temperature of 338K.[13] In fact the absolute reference data refer to 298 K, 0.1 MPa ideal gas standard state, but the temperature correction (338 to 298 K) is negligible for $\Delta G°(2)$.

Results and Discussion

Site of Protonation. N^1,N^1-Dimethylformamidines contain two nitrogen atoms: the imino (N^2) and the amino (N^1) atoms, each of which may be protonated in the gas phase. Because of the conjugation between the amino and the imino nitrogen atoms (Scheme I) the protonation at the N^1 atom is less probable.

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Table II. Polarizability Effects in Formamidines (FDM*R), Primary Amines (RNH_2), N,N-Dimethylamines ($RNMe_2$), and Nitriles (RCN)

				δGB, kcal·mol^{-1}			
compd	R	$-\sigma_\alpha$[a]	α_d,[b] Å^3	FDM*R	RNH_2[c]	$RNMe_2$[d]	RCN[e]
1	Me	0.35	1.78	0.0	0.0	0.0	0.0
2	Et	0.49	2.51	1.2	2.8	2.3	4.2
3	n-Pr	0.54	2.84	1.9	4.3	3.0	5.3
4	i-Pr	0.62	3.28	2.5	5.6	4.7	5.9
5	c-C_3H_5	0.69 0.56[f]	3.03	0.7	1.4	–	7.0
6	n-Bu	0.57	2.94 3.24[g]	2.3	4.8	4.4	5.6
7	i-Bu	0.61	3.23	2.7	5.6	4.3	–
8	sec-Bu	0.68	3.64	3.5	6.9	5.9	–
9	t-Bu	0.75	4.07	4.3	8.0	6.5	7.4
10	n-C_5H_{11}	0.58	2.91 3.97[g]	3.6	5.4[h]	–	–
11	t-C_5H_{11}	0.82	4.44	4.5	9.4	7.9	–
12	n-C_6H_{13}	(0.58)[i]	2.80 4.58[g]	3.3	5.4[h]	–	–
13	c-C_6H_{11}	0.76	4.06 4.24[g]	4.0	7.7	7.3	8.3
14	1-Adam	0.95	5.42 5.89[g]	6.7	11.4	10.0	12.7

[a] Polarizability substituent parameter of Taft and co-workers: refs 20 and 21 and personal communication. [b] Effective polarizability of substituent according to Gasteiger and Hutchings, ref 22. [c] Values from the Taft's group: table 4 in ref 20, or cited in ref 14. [d] Values from the Taft's group: refs 16 and 17, or cited in ref 14. [e] Values of δPA from ref 19 ($T\Delta S°$ assumed to be constant). [f] Value from ref 19. [g] Value modified as in ref 19. [h] Selected value from ref 14. [i] Estimated.

The experimental GB values obtained in this work for FDM*R are reported in Table I. Comparison of the GB values for FDM*R with those for corresponding dimethylamines $RNMe_2$, taken from the literature,[14-17] shows that the N^1,N^1-dimethylformamidino group ($Me_2NCH{=}N$) is more basic by about 10 kcal·mol^{-1} than the dimethylamino group. Comparison with amines RNH_2[14,15] gives an even greater difference (about 20 kcal·mol^{-1}). The same trend is observed when we compare the solution Brønsted basicities of FDM*Rs and corresponding amines.[6,7] The formamidines studied, $Me_2NCH{=}NR$, can be considered as derivatives of imines with the two substituents: NMe_2 and R. Comparison of the GB values for $MeCH{=}NEt$,[14] and for $Me_2NCH{=}NEt$ (Table I) shows that the substitution of the Me group by the NMe_2 group increases the gas-phase basicity by about 15 kcal·mol^{-1}. A similar effect of the NMe_2 group, as compared with Me, is observed on the C≡N function: the basicity of dimethylcyanamide, which protonates preferentially on the cyano group[18] is about 16 kcal·mol^{-1} greater than that of acetonitrile.[19]

These observations allow us to conclude that, in the formamidines studied, the N^2 atom is the preferred site of protonation in the gas phase. Additional confirmation is given by the analysis of substituent effects.

Gas-Phase Substituent Effects. For a discussion of the substituent effects on the gas-phase basicities it is convenient to use the relative basicity, δGB = GB(FDM*R) − GB(FDM*Me), which represents the Gibbs energy for reaction 4. According to Taft and Topsom,[20] these δGB

$$\mathrm{Me_2\overline{N\text{-}CH\text{-}N}RH^+ + Me_2NCH{=}NMe \rightleftharpoons Me_2NCH{=}NR + Me_2\overline{N\text{-}CH\text{-}N}MeH^+} \quad (4)$$

values measured for nonconjugated alkyl derivatives will depend only on the polarizability of R, and should obey eq 5, where ρ_α is the reaction constant for polarizability effects and σ_α is the directional polarizability parameter of Taft and co-workers.[20,21] It was also shown that an

$$\delta GB = \rho_\alpha \sigma_\alpha + c \quad (5)$$

enhanced polarizability effect in the gas phase may be accounted for by the so-called effective polarizability,[22] α_d, of the substituent R linked to the basic group.[19] As α_d is easily calculated for a great number of substituents, it will be evaluated hereafter as a possible substitute for σ_α.

Table III. Correlations between δGBs of FDM*R, RNH_2, $RNMe_2$, and RCN with σ_α from the Eight Substituents[a] Common to the Four Series

no.	series	slope (ρ_α)	intercept	correlation coefficient	standard deviation
5a	FDM*R	−11.12 ± 0.48	−4.13	0.9945	0.24
5b	RNH_2	−18.65 ± 0.65	−6.15	0.9964	0.32
5c	$RNMe_2$	−16.73 ± 0.70	−5.74	0.9948	0.35
5d	RCN	−19.03 ± 1.58	−5.79	0.9799	0.79

[a] Data from Table II: Me, Et, n-Pr, i-Pr, n-Bu, t-Bu, c-C_6H_{11}, 1-Adam.

Relative basicities for FDM*R and polarizability parameters are given in Table II. For comparison, δGB values for the corresponding amines (RNH_2 and $RNMe_2$) and for nitriles (RCN) are also given in this table. Table II shows that the amidine group is the least sensitive to the gas-phase alkyl substituent effect. A more quantitative comparison may be based on correlations of the δGB with σ_α of the eight substituents common to the four series (Table III). This minimal set of substituents covers the whole data range but excludes, in particular, the cyclopropyl group and linear chains of more than four carbon atoms. The first three linear relationships are of equally good fit. However, the standard deviation concerning the RCN regression is larger than the usual experimental uncertainties. It has been postulated that special resonance effects operate in this series, in particular a special C–H and C–C hyperconjugation for the alkyl groups.[23] Protonation of amines is strongly dependent on the polariz-

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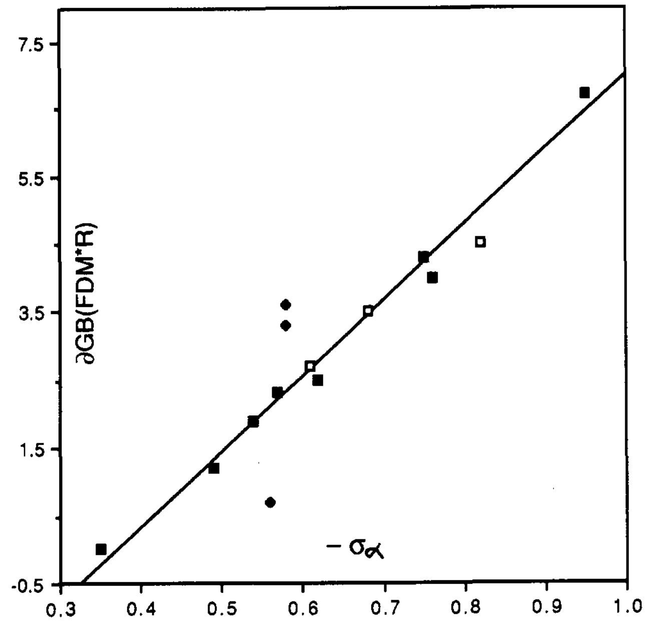

Figure 1. Relative gas-phase basicities of formamidines (kcal·mol^{-1}) vs the directional polarizability parameter. The least-squares line corresponds to eq 5a in Table III (eight data points); i-Bu, sec-Bu, and t-C_5H_{11} (□) fit; C_3H_5, n-C_5H_{11}, and n-C_6H_{13} (●) deviate strongly.

ability of the substituent R, the charge on the ammonium being localized on the nitrogen. The sensitivity to polarizability of the $RNMe_2$ series compared to RNH_2 is slightly decreased, probably by polarization of the methyl groups. The slope for the nitriles is not significantly different from those for the amines. Owing to the differences between these two series (nitrogen hybridization, nitrogen–substituent distance, charge delocalization on the cyano carbon) it is difficult to propose an explanation for this similarity using the present data.

As compared to RNH_2 (or $RNMe_2$) the FDM*R series exhibits a sensitivity lowered by a factor of about 1.7 (or 1.5). The FDM*R series gives charge delocalized conjugate acids (structure c in Scheme I) in which the positive charge is removed from the site of substitution, thus reducing the charge-induced dipole interaction.

The gas-phase basicities of the FDM*R series including a large variety of alkyl substituents were obtained in the same laboratory under the same experimental conditions. Thus, this data set allows us to address the question of the relevance of the description of the alkyl substituent effect exclusively in term of polarizability.

For the 14 substituents studied the fit obtained with σ_α is poor ($r = 0.85$) as compared with that obtained with eq 5a (Table III) for the eight substituents previously used. Among the six added data points, three fit eq 5a: i-Bu, sec-Bu, and t-C_5H_{11}, and three deviate strongly: c-C_3H_5, n-C_5H_{11}, and n-C_6H_{13}, see Figure 1. The calculated δGB for the cyclopropyl derivative is too large by 2.8 kcal·mol^{-1} ($\sigma_\alpha = -0.69$) or 1.4 kcal·mol^{-1} ($\sigma_\alpha = -0.56$). The same behavior is observed for the cyclopropylamine when using eq 5b.[24] If we assume that the cyclopropyl σ_α value is close to that for isopropyl, this observation indicates that the polarizability does not suffice to describe the cyclopropyl substituent effect. The particular bonding properties of cyclopropane are well documented.[25] Its unsaturated character allows conjugative interactions with neighboring π- or p-electron systems. The expected consequences are (1) an electron-donating effect stabilizing electron-deficient centers. This strong effect has been intensively studied.[25] (2) An electron-withdrawing effect on electron-rich centers. Although weaker, this effect has long been recognized.[26] In the same vein the cyclopropyl group is electron-withdrawing relatively to other alkyl groups on the σ_p^- scale.[27a] The increased s character of the exocyclic orbitals is expected to induce an electron withdrawal via field/inductive effect. Indeed, a small effect is experimentally evidenced when the cyclopropyl is compared to alkyl groups.[27b,28,29] We suggest that the deviations of cyclopropyl derivatives, when using eq 5a (FDM*R) and eq 5b (RNH_2), are due to an electron-withdrawing field/inductive effect, and possibly to a resonance effect in the same direction. In the gas phase, it appears that the polarizability alone is not sufficient to describe the effect of the cyclopropyl directly linked to an electron-rich center.

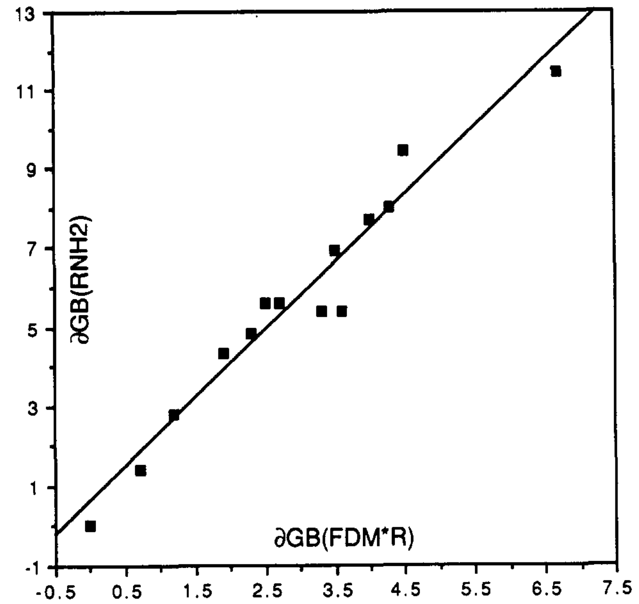

Figure 2. Relative gas-phase basicities (kcal·mol^{-1}) of primary amines vs formamidines. The least-squares line encompasses all the data points of Table II. For the significances of the deviations see text.

As mentioned above, deviations were also observed for formamidines bearing the n-pentyl and n-hexyl goups. Equation 5a underestimates their δGBs by 1.3 and 1.0 kcal·mol^{-1}, respectively. The long-chain amines do not show the basicity leveling expected from the attenuation of the polarizability effect with the distance between the positive charge of the protonated nitrogen and a progressively more remote group.[30] A similar observation was made for the acidity of long-chain alcohols.[31] It was suggested that linear alkyl chains may coil to bring the polarizable groups close to the positive or negative charge.

In the case of protonated formamidines, examination of molecular models shows that a coiling of the chain may bring the fifth carbon atom in close proximity to the positive charge delocalized on the amidine framework. We

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[24] For the RCN series in which the substituent is attached to an electron-deficient center the Taft's σ_α (−0.69) for the c-C_3H_5 satisfactorily explains the experimental δGB. The independently estimated σ_α (−0.56) underestimates δGB.

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tentatively suggest that the basicity enhancement of long-chain formamidines is due to this effect.

If alkyl group effects operate similarly on FDM*R and RNH_2 series, we expect a precise relationship between the gas-phase basicities of the two series. Considering the heterogeneous origin of the RNH_2 data, we observe in fact a fairly good fit ($n = 14$, $r = 0.9751$, sd = 0.70 kcal·mol^{-1}) for δGB (RNH_2) vs δGB (FDM*R), as shown on Figure 2. It is noteworthy that the cyclopropyl derivatives fit well, confirming a similar behavior in the two series. Nevertheless, the *n*-pentyl and *n*-hexyl derivatives deviate by more than one standard deviation. Further measurements are warranted before any interpretation, since the data for *n*-pentyl- and *n*-hexylamine come from a separate source (footnote *h* to Table II).

The directional substituent polarizability parameter σ_α was initially obtained from electrostatic polarization potentials calculated at the 3-21 G level. A simpler approach was proposed by Gasteiger and Hutchings[22] to obtain the so-called effective polarizability of substituents, α_d. They used the atomic hybrid components calculated by Miller and Savchik,[12] τ_i, weighted by a damping factor d^{n-1} which takes into account the smallest number of bonds n between the reaction site and the polarizable atom

$$\alpha_d = 4[\sum_i d^{n-1}\tau_1]^2/N \qquad (6)$$

where N is the total number of electrons in the substituent. The value $d = 0.75$ was arrived at by investigation of several series of experimental gas-phase data. It has been shown previously that this model suffers from a deficiency for $n > 4$.[19] For example, in the sequence $(CH_2)_mCH_3$, α_d increases from $m = 0$ to $m = 3$, and then, decreases from $m > 3$ (see Table II). It has been suggested that not counting in N the electrons of atoms linked to the reaction site by more than 4 bonds may compensate for this deficiency. The modified α_d values are also given in Table II (superscript g).

In fact, we obtain a precise relationship of the form of eq 5, where α_d is substituted for σ_α:$r = 0.9941$, sd = 0.18 kcal·mol^{-1}, $n = 8$. Substituents with $n > 4$, for which α_d are anomalous, were a priori excluded. The cyclopropyl derivative was also excluded for the above mentioned reasons.

The predictive ability of the model was then tested. As expected, the calculated δGB for the cyclopropyl derivative is overestimated. The deviation from the experimental value (1.5 kcal·mol^{-1}) is to be compared with that obtained when using eq 5a (1.4 kcal·mol^{-1} for $\sigma_\alpha = 0.56$). Substituents for which $n \leq 5$, i.e. *n*-butyl, cyclohexyl, and 1-adamantyl, give reasonable fit for both the original and the modified α_d values. For $n > 5$ (*n*-pentyl and *n*-hexyl) the values of Gasteiger and Hutchings are too small and cannot reasonably be used. Unfortunately, the modification of the α_d values, proposed earlier,[19] produces a too sharp increase with *n*, and then leads to increasingly overestimation of calculated δGBs. Further studies on rigid alkyl substituents are needed to produce a better polarizability damping model, which in turn should permit a test of the hypothesis of long chain coiling.

Conclusion

In the gas-phase FDM*R with R = alkyl are among the strongest organic bases yet known, comparable to tetramethylguanidine and 4-(dimethylamino)pyridine. Formamidines are protonated on the imino nitrogen atom. The gas-phase basicity depends linearly on the polarizability of alkyl substituents linked to the imino nitrogen. Due to the charge delocalization on the protonated amidine framework the sensitivity to this effect is reduced by a factor of about 1.7 (or 1.5) as compared to RNH_2 (or $RNMe_2$). The electron-withdrawing effect of the cyclopropyl group, as compared to the isopropyl group, on electron-rich amino and amidino systems is clearly observed. The results for *n*-alkyls lend support to the hypothesis of long-chain coiling.

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Anodic Oxidation of Methylbenzenes. Synthetic Routes to Certain Cyclohexa-1,4-dienes

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The anodic methoxylation of a series of methylbenzenes (mesitylene, pseudocumene, hemimellitene, pentamethylbenzene, and hexamethylbenzene) afforded chain methoxylated products as well as nuclear-addition products. For nuclear-addition products both cis/trans isomers are possible. In the cyclohexa-1,4-dienes obtained from these substrates the cis/trans ratio found is different. A probable mechanism is provided.

In the last years we have developed a series of works on anodic oxidation of alkyl aromatics[1-7] and have found that nuclear-addition products are obtained from inactivated substrates that do not stabilize the electrogenerated cation radical, showing that this type of reaction is quite general and not only observed in anthracene derivatives.[8] Some

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