Reaction rate constants were calculated from the slope of ln ($A_\infty - A_t$) vs. time; the error in k_{obs} is ≤1–3% for all the compounds examined. The energies of activation were calculated from the linear regression of ln k vs. $1/T$ by the least-square method and the entropies of activation were calculated by the standard formula derived from the absolute theory of reaction rates.

Registry No. **1a**, 6574-15-8; **1b**, 1204-85-9; **1c**, 10342-85-5; **1d**, 106947-61-9; **1e**, 101038-65-7; **1f**, 10552-10-0; **1g**, 22090-24-0; **2a**, 40832-54-0; **2b**, 106947-62-0; **2c**, 106947-63-1; **2d**, 106947-64-2; **2e**, 106947-65-3; **2f**, 106947-66-4; **2g**, 106947-67-5; **2h**, 19555-50-1; **3a**, 78039-75-5; **3b**, 106947-68-6; **3c**, 106947-69-7; **3d**, 106947-70-0; **3e**, 106947-71-1; **3f**, 106947-72-2.

Binding of NH_4^+ to Azoles in the Gas Phase. A Theoretical Study of the N...H⁺...N Ionic Hydrogen Bond

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Ab initio calculations have been carried out for 20 B–NH_4^+ complexes, where B represents methylpyrazoles and methylimidazoles. The corresponding ionic hydrogen bonds are not linear. Deviations from linearity are small but reveal strong repulsive interactions between methyl substituents and the ammonium ion. In the equilibrium conformation of these complexes, the proton of the NH_4^+ system has been partially transferred to the azolic system. The distance between this proton and the basic center of the azole decreases as its proton affinity increases. The hydrogen-bond energies for these complexes increase with the proton affinity of the azole, but they are smaller than the corresponding proton affinities. This attenuation effect is slightly greater for pyrazoles than for imidazoles. Moreover, the dissociation energies of the corresponding ionic hydrogen bonds are linearly correlated to the 1s binding energy of the basic center of the azole. These linear relationships are different for α- and β-substituted compounds. Both pyrazoles and imidazoles behave as reasonably hard bases. Their absolute hardness decreases upon methyl substitution and varies like the ionization potential. The multivariate linear correlations, gas-phase basicities vs. 1s binding energies, and HOMO energies yield information on changes in hardness of the bases.

In the past two decades, great effort has been made in the field of gas-phase ion chemistry to investigate the intrinsic basicities and acidities of organic and inorganic species.[1] As a consequence, a large scale of gas-phase proton affinities is now available. In this context, one of the concepts that attracted attention was the existence of a regular alkyl-substituent effect. It seems now clear, for instance, that the presence of alkyl groups at the basic site of amines stabilizes the charge at the site. However, some results[2] questioned the systematic effect of alkyl substituents on the acidic or basic properties of some compounds. Moreover, the usual rules which establish, for instance, that substituting a hydrogen by an alkyl group increases the base strength, are not fulfilled when the reference acid is other than the proton[3] (for instance, Li^+) because of specific characteristics of the acid–base interactions.

It seemed then interesting to study the behavior of known bases with regard to acids other than proton and to carry out a systematic analysis of possible substituent effects. To this respect, the theoretical calculations turned out to be a very useful tool and a quite convenient complement to the experimental work. In some cases, because the systems were not amenable to experiment or for other reasons, the only information regarding intrinsic basicities of a given set of compounds came from SCF calculations. In the past few years we have devoted some effort to this kind of research. In a previous article[4] we have discussed, by means of STO-3G SCF calculations, the systematic effect of methyl groups on the intrinsic basicity of pyrazoles and imidazoles, for which there was, at that time, an almost complete lack of experimental information regarding this particular effect.

In this paper, our aim is to analyze the same substituent effects when the reference acid is the ammonium ion. We consider it of interest to know the behavior of these azoles, whose chemistry is interesting per se, when they interact with an acid much softer than the proton. In particular, it seems appealing to know whether the substituent effects already investigated for the protonated species[4] are still present when the reference acid is more complex. On the other hand, most of the attention regarding this particular problem has been directed to the study of alkali ion (Li^+[3,5], K^+[6], etc.) or other metal ion (C_pNi^+)[5] affinities, but very little has been done by using organic cations or ammonium ions. There are, however, some illustrative examples such as the work of Wood et al.[7] on the methylation and ethylation of aniline, phenol, and thiophenol. Moreover, this study presents some additional interest because an analysis

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(6) Džidič, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466. Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6133.

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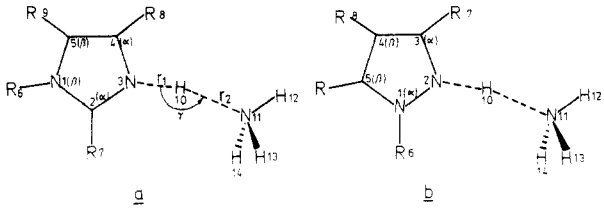


Figure 1. Numbering of the atoms for the complexes between NH_4^+ cations and (a) methylimidazoles and (b) methylpyrazoles.

of gas-phase ammonium affinities is equivalent to an investigation of positive-ion hydrogen bonds. Although lately we have witnessed a growing interest in proton-bound dimers, mainly from an experimental point of view,[8-11] very little has been done on theoretical grounds. To our knowledge, only small molecules have been considered, but the paper of Desmeules and Allen, devoted to the study of complexes involving NH_3, OH_2, FH, PH_3, SH_2, and ClH, deserves to be noticed.[12] Very recently, Del Bene et al.[13] reinvestigated a subset of these complexes but at a higher level of accuracy, including polarization, electron correlation effects, and correction for zero-point vibrational energies, and Cao et al.[14] have also carried out a theoretical analysis of proton transfer in several symmetric and asymmetric systems.

Finally, the results presented here on ammonium affinities, together with those reported previously[4] for proton affinities, would allow us to discuss the nature of these organic bases (pyrazoles and imidazoles) in the light of the hard–soft acid–base theory.[15]

Computational Details

We have carried out ab initio calculations on 20 complexes between methylpyrazoles or methylimidazoles and ammonium ion including the parent compounds, all monomethyl derivatives, all α,α'- and β,β'-dimethyl-substituted compounds, 2,5-, 4,5-, and 2,4,5-methyl-substituted imidazoles, and 1,4-, 3,4-, and 1,3,4-methyl-substituted pyrazoles (see Figure 1 for numbering) in order to better analyze possible cumulative effects of the substituents on the stability of the corresponding proton-bound complexes.

The corresponding ammonium affinities were obtained from

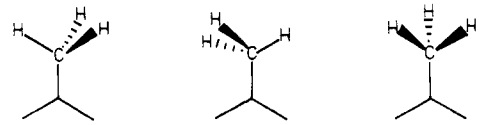
$$AA = E(\text{complex}) - [E(B) + E(NH_4^+)] \qquad (1)$$

where B symbolizes the base under study (methylpyrazoles or methylimidazoles).

As we have indicated previously,[16] the use of optimized structures can be crucial for this kind of study. On the other hand, since we aim to compare our calculated ammonium affinities (AA) for methylpyrazoles and methylimidazoles with previously[4] calculated proton affinities, we have adopted in both cases identical geometrical models in order to guarantee the consistency of both sets of calculations. That model is based on fully optimized INDO geometries, where the N–H and C–H bond lengths have been adequately scaled to account for the fact that this semiempirical method usually overestimates all C–H, N–H, and OH bond lengths.

It should be indicated, however, that, in the present case, scaling of all N–H bonds affects the distance between the two nitrogens involved in the hydrogen bond (N3 and N11 or N2 and N11, in Figure 1), which can become too short after scaling. Therefore, to correct this possible drawback of our geometrical model, this distance was reoptimized once, at the STO-3G ab initio level, for the 20 complexes included in this study.

In all cases, we have kept the ammonium ion in the conformation shown in Figure 1. However, since as we shall discuss later, both the interactions between the substituents and between the substituents and the attacking ammonium ion are not negligible, for each system the particular conformation of each methyl group was allowed to vary between the three extreme conformations shown below:



In conformations a and b one of the methyl hydrogens lies on the molecular plane, while in conformation c none of them lie on that plane. No other geometrical restrictions were imposed, and the remaining geometrical parameters were fully optimized by using the procedure of Rinaldi et al.[17]

It is then obvious that the number of possible conformers increases notably with the degree of substitution. From now on, all results presented and discussed throughout this paper will always refer to the most stable conformer.[18]

Quite often the proton-transfer potential energy surfaces present a double-well behavior, as it has been illustrated for several systems.[14] Although we have not exhaustively investigated the shape of the potential energy surface for azole–NH_4^+ complexes because that study is out of the scope of this paper, we have checked that the structure found for the complex corresponds to a local minimum of this surface. Moreover, we have also found that when the relative position of the proton within the N(azole)–H–N(NH_4^+) fragment is allowed to vary, keeping constant the N(azole)–N(NH_4^+) distance, the structure of the complex always evolves toward an azole H^+–NH_3 configuration (see supplementary material).

Although we have previously shown[16,19,20] that the geometrical model proposed yields reasonably good relative protonation energies, it seems convenient to check its reliability to evaluate ammonium affinities. Thus, we have carried out some additional STO-3G calculations on B–NH_4^+ complexes, where B is NH_3, OH_2, FH, HCN, and $H_2C{=}NH$. These calculations were performed at both STO-3G and (scaled) INDO fully optimized geometries,

(8) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504.
(9) Meot-Ner (Mautner), M.; Hamlet, R.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1980**, *102*, 6393.
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(11) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1983**, *105*, 2956. Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1983**, *105*, 4906. Ibid. **1984**, *106*, 278. Ibid. **1984**, *106*, 1257.
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(18) Optimized geometries of the most stable conformers in the complex can be obtained from any of the authors.
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Table I. Calculated Values for Methylpyrazoles and Methylimidazoles[a]

substituent	ΔAA or $\Delta D(B-NH_4^+)$	$\Delta D(BH^+-NH_3)$	ΔPA	ΔE_{1s}	ΔE_{HOMO}	γ, deg	r_1, Å
			Pyrazole and Methylpyrazoles				
H	0.0	0.0	0.0	0.0	0.0	178.5	1.105
1-Me	2.4	−2.7	5.1	6.3	3.4	178.6	1.102
3-Me	3.7	−2.9	6.6	8.4	6.8	177.5	1.098
4-Me	1.7	−2.0	3.7	2.2	5.5	178.0	1.104
5-Me	3.8	−2.2	6.0	3.7	9.9	175.8	1.099
1,3-Me	5.7	−5.6	11.3	14.0	10.9		1.094
1,4-Me	4.3	−3.9	8.2	8.4	8.3		1.100
3,4-Me	5.4	−3.8	9.2	9.7	9.8		1.097
4,5-Me	6.6	−3.2	9.8	5.5	16.4		1.098
1,3,4-Me	7.8	−6.1	13.9	15.3	13.1		1.094
			Imidazole and Methylimidazoles				
H[b]	0.0 (13.0)	0.0 (−5.6)	0.0 (18.6)	0.0 (31.9)	0.0 (7.4)	170.8	1.096
1-Me	2.9	−1.0	4.0	1.2	1.7	174.0	1.095
2-Me	4.7	−2.0	6.7	10.8	9.5	178.0	1.087
4-Me	3.0	−1.0	4.1	7.1	7.0	174.6	1.092
5-Me	2.7	−1.2	3.9	2.1	9.3	171.7	1.093
1,5-Me	5.7	−1.6	7.3	3.3	11.8		1.092
2,4-Me	7.4	−3.8	11.2	17.6	15.5		1.083
2,5-Me	7.3	−3.6	10.8	12.8	18.2		1.084
4,5-Me	5.2	−2.6	7.8	8.9	15.8		1.089
2,4,5-Me	9.8	−4.9	14.6	19.1	23.7		1.080

[a] Ammoniation energies (or dissociation energies of $B-H^+-NH_3$, complexes yielding $B + NH_4^+$) (ΔAA); dissociation energies of $B-H^+-NH_3$ complexes yielding $BH^+ + NH_3$ ($\Delta D(BH^+-NH_3)$); protonation energies (ΔPA); N1s orbital energies (ΔE_{1s}); HOMO energies (ΔE_{HOMO}). All values in kcal/mol and refer to those of the corresponding parent compound. See Figure 1 for definition of γ and r_1 geometrical parameters. [b] We give, within parentheses, those values for imidazole relative to pyrazole.

which will be indicated by the notation STO-3G//STO-3G and STO-3G//INDO, respectively.

The results obtained (see supplementary material) show that ammonium affinities, calculated at both levels of accuracy, are in fairly good agreement, but, more importantly, *relative* STO-3G//INDO values present quite small deviations from STO-3G//STO-3G results. Therefore, taking into account that in our study we are interested in *relative* ammonium affinities within a homologous series of compounds, it is not adventurous to assume that these deviations would be even smaller than those obtained for the complexes indicated above.

In order to analyze the hardness of the bases under study, we have applied the quantitative model proposed by Parr and Pearson.[21] This requires the evaluation of the electron affinity of the different bases as the energy difference between the corresponding radical anion (azole$^{\bullet-}$) and the neutral molecule. Since it is a well-known fact[22] that the minimal basis set is not an adequate tool to study anionic forms, the electron affinities were calculated at the 4-31G level by using fully optimized STO-3G structures in order to guarantee the reliability of the results obtained.[23] These calculations were extended exclusively to the parent compound and all monomethyl derivatives. The energies of the radical anions were obtained by solving the UHF equations of Pople and Nesbet.[24]

Geometries

The structure of the azolic system in the complex changes mainly as a consequence of the extracoordination of the basic center. These structural changes are qualitatively similar to those observed in the corresponding protonated species, but quantitatively less important. These geometrical distortions, namely, the opening of the C2N3C4 (or N1N2C3) endocyclic angle in imidazoles (or pyrazoles), the lengthening of the C2N3 and N3C4 bond lengths in imidazoles and N3C4 in pyrazoles, etc., can be easily explained[14] in terms of valence-shell electron repulsion interactions and changes in the π-electronic density distribution of the HOMO and will not be discussed here in more detail.

However, there are other geometrical characteristics of these complexes that deserve more attention. For instance, our results show that the hydrogen bonds are not linear. Analogously to what is usual in normal (neutral) hydrogen bonds, deviations from linearity are small. In this respect, it may be also illustrative to indicate that the barrier to linearity of the corresponding hydrogen bond is approximately 0.2 kcal/mol. In Table I we have summarized the value of the angle (γ) subtended by the N...H...N molecular fragment (see Figure 1).

The most striking fact is that the deviations from linearity are neither constant nor regular. Our results show that for imidazole and 5-methylimidazole the N...H...N bond is nonlinear by about 10°, whereas this deviation is of only 2° for the 2-methyl derivative.

This last result can be explained by taking the parent compound as a reference. In the 2-methyl-substituted compound the interaction between the methyl group and the NH_3 group of the attacking ion is quite strong, and the angle N...H...N opens about 8° with respect to the situation in the parent compound. As we shall discuss in the next section, this repulsive interaction will also be reflected in the dissociation energy of the corresponding complex.

For the particular case of pyrazoles the situation is quite different and the deviations from linearity are always very small. This is due to the appearance of an extra repulsive interaction, absent in imidazoles, which takes place be-

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(22) Macias, A.; Riera, A. *Gazz. Chim. Ital.* **1978**, *108*, 329.
(23) In order to study anionic forms adequately, a diffuse basis set, as the one proposed by Chandrasekhar et al. (Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1981**, *103*, 5609) (4-31+G basis) should be used. This would imply a considerable increase in the cost of our computations, especially for methylazoles. Since we are not interested in absolute electron affinities but in their variations upon methyl substitution, we may assume that a 4-31G basis is flexible enough for this purpose. To confirm this assumption we have evaluated the electron affinities of the parent compounds and the *N*-methyl derivatives at the 4-31+G level. We have found that, though absolute electron affinities change (imidazole 3.9 eV (4-31G), 1.4 eV (4-31+G), pyrazole 3.4 eV (4-31G), 1.3 eV (4-31+G), *N*-methylimidazole 3.9 eV (4-31G), 1.4 eV (4-31+G) *N*-methylpyrazole 3.4 eV (4-31G), 1.3 eV (4-31+G) when the basis is supplemented by a diffuse sp shell, the relative values remain practically unchanged.
(24) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

tween the second ring nitrogen (α to the basic center in pyrazoles) and the nitrogen of the ammonium ion (see Figure 1).

Also the r_1 and r_2 distances (see Figure 1) are characteristic geometrical parameters of the nature of the hydrogen bond. In all cases, for both pyrazoles and imidazoles, r_2 is greater than r_1, the ratio r_2/r_1 being about 1.3. This indicates that in the equilibrium conformation the proton of the NH_4^+ cation has almost been transferred to the azolic system, revealing that these azoles are stronger bases than ammonia. In other words, the equilibrium conformation of the complex can be visualized as the protonated azole solvated by one NH_3 molecule.

In all cases, the value obtained for r_1 (see Table I) is only slightly longer than the normal NH bond length in the corresponding protonated form. This finding explains why the distortions of the azolic ring in the complex are qualitatively similar, although quantitatively weaker than those observed in the normal protonated form, as it corresponds to a less tightly bound proton in the former.

It is also interesting to note that r_1 becomes increasingly shorter as the basicity of the azolic system increases. These results are in agreement with the correlation reported by Desmeules and Allen[12] between ΔPA and partial proton transfer in the hydride dimers involving NH_3, OH_2, FH, PH_3, SH_2, and ClH. Similar findings, on experimental grounds, have been reported by Meot-Ner[11] for organic dimers.

Ammonium Affinities vs. Proton Affinities

We present in Table I the calculated ammonium affinities defined by eq 1 and relative to the corresponding parent compound. We have included in the same table, for better comparison, the calculated proton affinities, N_{1s} orbital energies, and HOMO energies, taken from ref 4.

Several facts should be singled out for comment:

Imidazole is predicted to be 18.6 kcal/mol more basic than pyrazole when the reference acid is a proton. This difference reduces to 13.0 kcal/mol when the reference acid is an ammonium ion.

This indicates that, similarly to what has been found[3,5] for other acids such as Li^+, there are some specific interactions characteristic of the particular acid–base system under investigation. Although it seems evident that the interactions between the azolic system and an ammonium ion are more complex than those between the azole and a proton, we shall illustrate that the main difference originates from ion–permanent dipole interactions. To do so, we shall use a very simple electrostatic model[25] which considers explicitly only charge–dipole and charge-induced dipole interactions

$$V(R) = -\frac{\alpha q^2}{2R^4} - \frac{q\mu \cos \theta}{R^2} \qquad (2)$$

where α is the molecular polarizability (assumed to be isotropic), μ is the dipole moment of the neutral molecule, q is the charge of the ion, R is the ion–neutral separation distance, and θ is the angle between the dipole orientation and the line joining the charge and the center of the dipole. Even though this simple model neglects the short-range repulsive forces, it yields, as it has been shown elsewhere,[26]

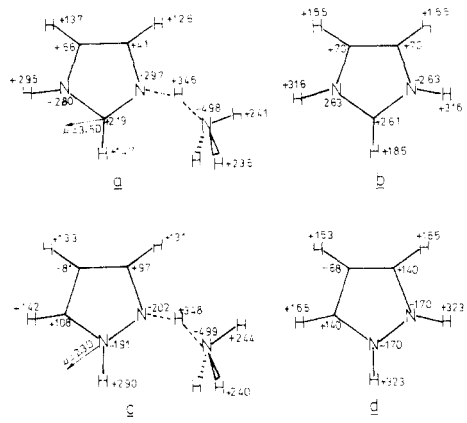

Figure 2. Charge distribution (in methyl for (a) complex imidazole–NH_4^+, (b) protonated imidazole, (c) complex pyrazole–NH_4^+, and (d) protonated pyrazole. In a and c we have indicated the magnitude and direction of the dipole moment of imidazole and pyrazole, respectively.

good first-order approximations of *relative* interaction energies.

In our case we are interested in comparing these interaction energies for complexes where the neutrals are imidazole and pyrazole, respectively. We can therefore write

$$\Delta V = V_{im}(R) - V_{py}(R) = \frac{q^2(\alpha_{im} - \alpha_{py})}{2R^4} - \frac{q(\mu_{im} \cos \theta_{im} - \mu_{py} \cos \theta_{py})}{R^2} \qquad (3)$$

where subscripts im and py stand for imidazole and pyrazole, respectively, and where we are assuming implicitly that the ion–neutral separation distance is the same whatever neutral we are considering. In our case, this is a good approximation (see r_1 values in Table I).

Our SCF results show that ΔV for im-H^+/py-H^+ systems is 5.6 kcal/mol greater than ΔV for im-NH_4^+/py-NH_4^+ complexes. Since, on the other hand, we can reasonably assume that $\alpha_{im} \simeq \alpha_{py}$, eq 3 strongly suggest that this difference arises from ion–permanent dipole interactions. This qualitative conclusion can be verified by using the second term on the right side of eq 3 to estimate the value of ΔV for both kinds of complexes. This term, though valid for H^+ complexes, must be generalized for the case of a polyatomic ion (i.e., NH_4^+) with a distribution of fractional charges, q_i. Thus

$$\Delta V = -\sum_i \frac{q_i(\mu_{im} \cos (\theta_{im})_i - \mu_{py} \cos (\theta_{py})_i)}{R_i^2} = -\sum_i \frac{q_i \Delta\mu_i}{R_i^2} \qquad (4)$$

where the summation runs over all the atoms in the ion

$$\Delta\mu_i = \mu_{im} \cos (\theta_{im})_i - \mu_{py} \cos (\theta_{py})_i \qquad (5)$$

and $(\theta_{im})_i$ and $(\theta_{py})_i$ have the same meaning as in eq 2.

By use of the numbering in Figure 1, eq 4 will take the form[27]

$$\Delta V = -\frac{q_{H10}\Delta\mu_{10}}{R_{10}^2} - \frac{q_{N11}\Delta\mu_{11}}{R_{11}^2} - \frac{3q_{H12}\Delta\mu_{12}}{R_{12}^2} \qquad (6)$$

where q_{H10}, q_{N11}, etc. represent the net charges at the corresponding atoms; R_{10}, R_{11}, etc. are the distances between these atoms and the center of the dipole, and $\Delta\mu_{10}$, $\Delta\mu_{11}$, etc. are given by eq 5.

It is now evident that for im-H^+/py-H^+ systems only the first term on the right side of eq 6 appears. Moreover, the

(25) Su, T.; Bower, M. T. *Int. J. Mass Spectrom., Ion Phys.* **1973**, *12*, 347.

(26) Grabowski, J. J.; De Puy, C. H., Bierbaum, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2565. Squires, R. R.; Bierbaum, U. M.; Grabowski, J. J.; De Puy, C. C. *J. Am. Chem. Soc.* **1983**, *105*, 5187. Lias, S. G. *J. Phys. Chem.* **1984**, *88*, 4401. Speller, C. V.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1985**, *89*, 5217.

(27) We are implicitly assuming, in eq 6, that $q_{H12} \simeq q_{H13} \simeq q_{H14}$ and $R_{12} \sim R_{13} \sim R_{14}$.

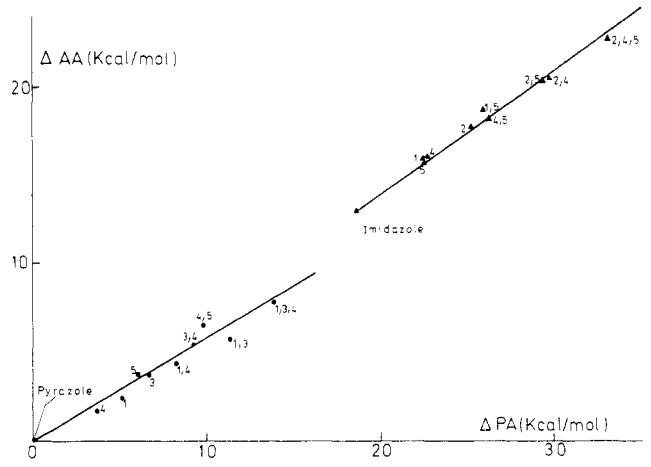

Figure 3. Ammonium affinities (ΔAA) vs. proton affinities (ΔPA) for methylpyrazoles (●) and methylimidazoles (▲). All values refer to pyrazole.

contribution of this term to ΔV is about the same for H^+ complexes or NH_4^+ complexes because in both cases both q_{H10} and R_{10} are practically equal (see Table I and Figure 2). Hence, for our purposes we need to consider only the last two terms on the right side of eq 6, whose contributions to ΔV are of opposite sign ($q_{N11} < 0$, $q_{H12} > 0$).

Taking into account that $\mu_{im} = 3.5$ D, $\mu_{py} = 2.3$ D, and the relative orientations of the dipoles (see Figure 2), one finds that

$$\frac{q_{N11}\Delta\mu_{11}}{R_{11}^2} \simeq -11 \text{ kcal/mol}$$

and

$$\frac{3q_{H12}\Delta\mu_{12}}{R_{12}^2} \simeq 4 \text{ kcal/mol}$$

Accordingly, ΔV for im-NH_4^+/py-NH_4^+ complexes must be about 7 kcal/mol smaller than ΔV for im-H^+/py-H^+ systems, in fairly good agreement with our SCF results, verifying that this difference originates from ion–permanent dipole interactions.

The results presented in Table I also show that hydrogen-bond energies for B–NH_4^+ complexes increase with increasing proton affinity differences: PA(B) – $PA(NH_3)$. Actually, there is a good linear correlation (see Figure 3) between the dissociation energies of the B–NH_4^+ complexes (relative to the parent compound) and the relative proton affinities: PA(B′) – PA(B), where B represents pyrazole (or imidazole) and B′ any other of the azoles studied. These linear correlations obey the equations

$$D(B'\text{–}NH_4^+) - D(B\text{–}NH_4^+) = 0.58\ (PA(B') - PA(B)) \quad (n = 10,\ r^2 = 0.954)\ (7)$$

for pyrazoles and

$$D(B'\text{–}NH_4^+) - D(B\text{–}NH_4^+) = 0.67\ (PA(B') - PA(B)) \quad (n = 10,\ r^2 = 0.992)\ (8)$$

for imidazoles.

These relationships are in very good agreement with the experimental findings of Larson et al.[10] These authors have found, for oxygen *n*-donor bases H_3O^+ complexes, a similar correlation to that represented by eq 7 and 8 but with slope 0.46. In summary, our results show that for both pyrazoles and imidazoles the stability of proton-bound complexes with NH_4^+ increases with increasing proton-affinity differences PA(B) – $PA(NH_3)$. On the contrary, the stability of azole H^+–NH_3 complexes decreases as the

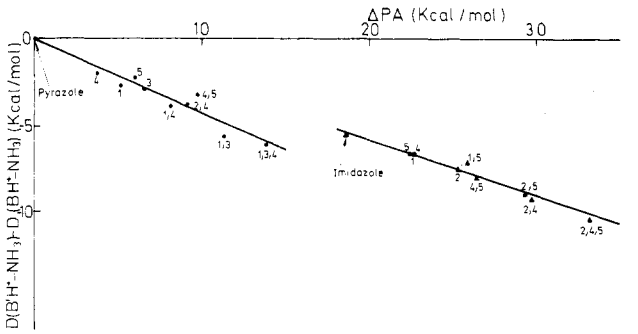

Figure 4. Dissociation energies B–H^+–NH_3 → BH^+ + NH_3 ($D(B'H^+\text{–}NH_3) - D(BH^+\text{–}NH_3)$) vs. relative proton affinities (ΔPA) for methylpyrazoles (●) ($D(B'H^+\text{–}NH_3) - D(BH^+\text{–}NH_3) = -0.42$ (PA(B′) – PA(B)), $r^2 = 0.919$) and methylimidazoles (▲) ($D(B'H^+\text{–}NH_3) - D(BH^+\text{–}NH_3) = -0.35$ (PA(B′) – PA(B)), $r^2 = 0.969$). All values refer to the parent compound.

difference PA(B) – $PA(NH_3)$ increases (see Figure 4) because both relative dissociation energies are related to the corresponding relative proton affinities through the equation

$$\Delta D(B\text{–}NH_4^+) - \Delta D(BH^+\text{–}NH_3) = \Delta PA$$

At this point of the discussion it should also be mentioned that both dissociation energies, $D(B\text{–}NH_4^+)$ and $D(BH^+\text{–}NH_3)$, correspond to the processes which take place when determining relative gas-phase PA's by Cook's method.[28] In this method the proton-bound dimer $B_1HB_2^+$ is formed and then the relative abundances of the ions produced in the competitive reactions

$$B_1HB_2^+ \rightarrow B_1H^+ + B_2$$
$$B_1HB_2^+ \rightarrow B_1 + B_2H^+$$

are determined. This experimental technique has been successfully used[29–31] to measure the gas-phase PA of a number of organic bases.

There is an alternative way to look at the problem. Equations 7 and 8 show that there is an attenuation of the gas-phase basicity of both pyrazoles and imidazoles when the reference acid is a NH_4^+ cation instead of a proton. Besides, this attenuation effect is greater for pyrazoles than for imidazoles. This result is not surprising since, for instance, Woodin and Beauchamp[3] have found that Li^+ binding energies for amines are smaller than the corresponding proton affinities by approximately a factor of 5.

This attenuation effect reveals the existence of strong repulsive interactions upon ammoniation that are not present upon protonation. In fact, the proton is a single positive charge while the NH_4^+ system is a polyatomic cation. Therefore, in ammoniated complexes in addition to the polarization interactions already present upon protonation, there are repulsive interactions between the net atomic charges on the azolic system and those on the NH_4^+ cation. These repulsive interactions are more important in those particular cases where the methyl group is physically closer to the NH_4^+ cation, as, for instance, in 2-methylimidazole, which presents the greatest attenuation effect among all monomethyl-substituted imidazoles. Furthermore, this attenuation effect increases with the

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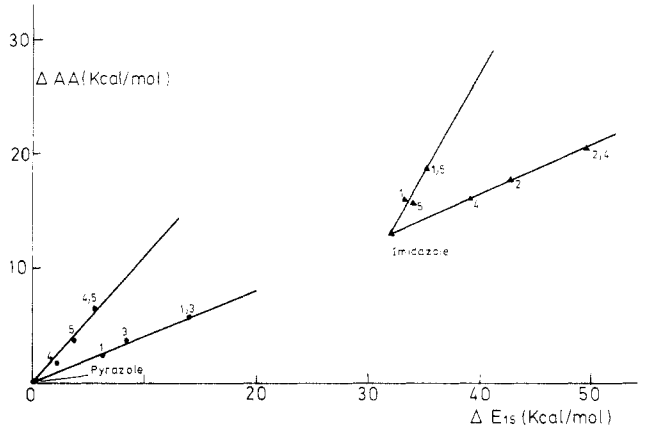

Figure 5. Ammonium affinities (ΔAA) vs. the N1s orbital energy of the basic center of the corresponding azole: (●) methylpyrazoles; (▲) methylimidazoles. All values refer to pyrazole.

proton affinity of the corresponding compound. This is also a consequence of a greater repulsive interaction between the azolic nitrogens and the nitrogen of the ammonium ion, because the net charge of the former is bigger the higher will be the PA of the corresponding compound (even though there is only a rough correlation between both magnitudes).[32,33] This would also explain why this attenuation effect is larger for pyrazoles: In pyrazoles–NH_4^+ complexes, both ring nitrogens are physically close to that of the NH_4^+ cation, while in imidazole–NH_4^+ complexes, the substituted ring nitrogen is further away.

For some particular cases there is a qualitative change when proton affinities and ammonium affinities are compared. 3-Methyl- and 5-methylpyrazoles constitute a suitable example. Their relative PA's measure the relative stability of both isomers because they yield a common cation upon protonation. Since 3-methylpyrazole is more stable than 5-methylpyrazole, the former is found to be more basic than the latter. On the contrary, the corresponding azole–NH_4^+ complexes are different, and due to a smaller repulsive interaction between the methyl substituent and the NH_4 fragment, the 5-methylpyrazole–NH_4^+ complex is more stable than the 3-methylpyrazole–NH_4^+ system. Obviously, this effect will tend to compensate or even invert the difference observed between the corresponding PA's. Accordingly, upon ammoniation 3-methylpyrazole must be less basic than 5-methylpyrazole, in agreement with our results.

Ion–Hydrogen Bond Dissociation Energies and 1s Orbital Energies

We have previously shown[33,34] that good linear correlations exist between experimental (or calculated) gas-phase proton affinities and the 1s orbital energy of the basic center within a homologous series of compounds.

These correlations were analyzed,[4] in particular, for methylpyrazoles and methylimidazoles. Since we have found that the hydrogen-bond energies of azole–NH_4^+ complexes are directly related to the corresponding relative proton affinities (eq 7 and 8), a similar linear relationship between relative ion–hydrogen bond dissociation energies [D(B′–NH_4^+) − D(B–NH_4^+)] and N_{1s} orbital energies should exist. Both magnitudes have been plotted in Figure 5 for α-, α′-, β-, and β′-monomethyl derivatives and α,α′- and β,β′-dimethyl-substituted compounds.

As we have previously found[4] when investigating gas-phase proton affinities, within each family of compounds there are two different kinds of linear correlations with quite different slopes. The straight line of smaller slope gives the variation of the dissociation energy produced when one or two substituents are introduced at the α-positions relative to the basic center, what we have named[4] the α-effect. Conversely, the line with greater slope gives the variation when the substituents are introduced at the β-positions relative to the basic center (β-effect). The origin of these two effects has been fully discussed elsewhere[4] and the discussion will not be repeated here. However, it should be noticed that due to the fact that the attenuation effect discussed in the previous section is slightly greater for α-substituted than for β-substituted compounds, the difference between the slope of both straight lines increases when hydrogen-bond dissociation energies are dealt with.

In summary, one may conclude that dissociation energies of ion–hydrogen bonds between a homologous series of bases and a common reference acid (as NH_4^+) vary linearly with the 1s binding energy of the corresponding basic center.

The above arguments do not apply to D(BH^+–NH_3) dissociation energies because, as indicated before, these energies actually measure the solvation energies of the protonated species by one NH_3 molecule.

Discussion on the Degree of Hardness

One question that deserves to be discussed in some detail concerns the degree of hardness of pyrazoles and imidazoles. The results presented in the previous section together with those reported in ref 4 offer some useful information to this respect, in the sense that we have evaluated the binding energies of both families of compounds to two acids (H^+ and NH_4^+) of different hardness.

Both pyrazoles and imidazoles behave as reasonably hard bases since the absolute value of the ammonium binding energies (evaluated according to eq 1) are much smaller than the corresponding proton affinities (calculated as the energy difference between the protonated and the unprotonated forms): 55.6 kcal/mol vs. 282.4 kcal/mol for imidazole and 42.6 kcal/mol vs. 263.8 kcal/mol for pyrazole. Whether imidazoles are harder or softer than pyrazoles is more difficult to establish.

The hardness of an acid or a base is usually characterized by a great charge/atomic radius ratio of their active center and low polarizability; conversely, softness is usually related to low electronegativity and high polarizability. This seems to bear some relation with the model[35] in which the multivariate linear correlations[4,35] gas-phase PA's vs. 1s orbital energies and HOMO energies are based. This model assumes that the protonation process takes place in two steps: in the first one a positive charge is bound to a particular site of the molecule (the basic center) and in the second one there is an electronic charge transfer from the molecule to the bare proton. The energy change of step 1 can be characterized by the 1s binding energy of the basic center, and that associated to step 2 depends on the ability of the base to donate charge and can be quantitatively measured by its first ionization potential (or the negative of the HOMO energy).

Since the 1s orbital energy (E_{1s}) of a given center acts as a probe of the electrostatic potential near the nucleus,

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it reflects, in some way, its charge/radius ratio. Accordingly, one may expect this index to give some relative information on the hardness of the base. Similarly, the energy of the HOMO should yield information on the polarizability of the system, i.e., on its relative softness. This is consistent with the fact that, similarly to what has been found for 1s orbital energies, relative dissociation energies vary linearly with the HOMO energy (see supplementary material). As for 1s orbital energies, these linear relationships are different for α- and β-substituted compounds. But the situation is reversed, and now the line of greater slope corresponds to α-substituted compounds, while that of smaller slope corresponds to β-substituted compounds.

Therefore, we have considered it to be worthwhile to compare the multivariate linear correlations $D(B'-NH_4^+) - D(B-NH_4^+)$ vs. E_{1s} and E_{HOMO} to the correlations PA vs. E_{1s} and E_{HOMO}; i.e., the question to be answered is whether the relative contribution of E_{1s} and E_{HOMO} to these correlations changes with the hardness of the acid and whether these changes have some physical meaning. To achieve this it is necessary to use, in the corresponding least-squares fitting technique, standardized variables,[36] defined as those that have a mean equal to zero and a variance and standard deviation equal to one.

To carry out this analysis we have chosen the set of methylpyrazoles included in Figure 4. The correlations obtained obey the equations

$$PA = -0.566E_{1s} - 0.605E_{HOMO} \quad (R^2 = 0.994) \quad (9)$$

and

$$D(B'-NH_4^+) - D(B-NH_4^+) = -0.334E_{1s} - 0.798E_{HOMO} \quad (R^2 = 0.990) \quad (10)$$

which indicate that when the reference acid is softer (eq (10) there is a relative greater contribution of the E_{HOMO} term.

Once more this result is consistent with the quantitative model of hardness proposed by Parr and Pearson.[16] These authors have defined as absolute hardness the quantity

$$\eta_s = \tfrac{1}{2}(I_S - A_S) \quad (11)$$

where I_S and A_S represent the ionization potential and the electron affinity of a species S, respectively.

Since we are not aware of the existence of experimental values for the electron affinities of methylpyrazoles or methylimidazoles, we have employed in eq 11 the corresponding calculated values, obtained as the energy difference between the corresponding radical anionic (azole$^{\bullet-}$) and neutral forms. For the reasons indicated under Computational Details, these calculations were carried out at the 4-31G level and at STO-3G fully optimized structures.[23] The corresponding ionization potentials were evaluated as the energy difference between the corresponding radical cations (azole$^{\bullet+}$) and neutral forms at this level of accuracy. The results obtained for the monosubstituted derivatives have been summarized in Table II.

It can be seen that the variation of the absolute hardness parallels that of the ionization potentials of the bases because the variations obtained for the corresponding electron affinities are smaller by almost 1 order of magnitude, in agreement with the greater contribution of the E_{HOMO} term found in our multivariate linear correlations.

It should also be noticed that the absolute hardness, for both pyrazoles and imidazoles, decreases with methyl substitution, although the basicity of the reference acid as either a proton or an NH_4^+ cation increases.

Also, hardness variation is quite similar for both families of compounds, indicating that the methylation effect on the polarizability of the azolic system is almost independent of the relative position of the two ring nitrogens.

Going back to the multivariate linear correlations discussed above, we must keep in mind that their applicability is questionable at least in two cases.

a. When the Two Variables E_{1s} and E_{HOMO} Are Strongly Correlated. This is not the case for the set of compounds selected for our example (where $r_{12}^2 = 0.18$). Had we selected, for instance, the set of compounds formed by the α-substituted derivatives (1-methyl, 3-Me and 1,3-methylpyrazole) and those which present an additional substituent at a β position (1,4-dimethyl, 3,4-dimethyl, and 1,3,4-trimethylpyrazole), we would have obtained an apparent equally good multivariate linear correlation:

$$D(B'-NH_4^+) - D(B-NH_4^+) = -0.483E_{1s} - 0.524E_{HOMO} \quad (R^2 = 0.977) \quad (12)$$

In this case the two independent variables are strongly correlated ($r_{12}^2 = 0.85$), and therefore the meaning of their correlation coefficients in eq 12 is very doubtful.

b. When the Relative Basicities Are Not Linearly Related to the E_{HOMO}. Methyl-substituted imidazoles constitute a good example. Whereas a good linear correlation between relative basicities and the E_{HOMO} for α-methyl-substituted compounds exists, that is not the case for β-methyl-substituted derivatives. In fact, from Table I it follows that while the variations upon substitution in the intrinsic basicities of 1-methylimidazole and 5-methylimidazole are very similar (4.0 and 3.9 kcal/mol, respectively), the energy variation of the HOMO is very

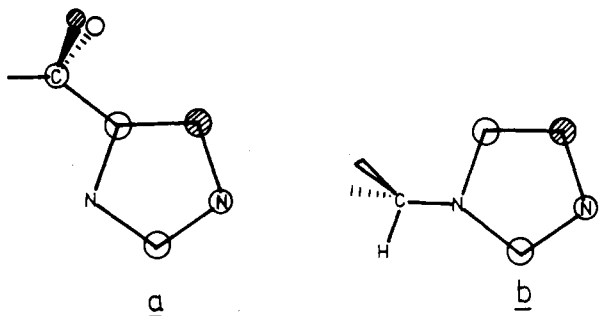

Figure 6. HOMO's for (a) 5-methylimidazole, showing the existence of a hyperconjugative effect, and (b) 1-methylimidazole, where the hyperconjugative effect is not possible.

Table II. Variation upon Methyl Substitution of the Ionization Potentials (ΔP_I), Electron Affinities (ΔA_e), and Absolute Hardness ($\Delta\eta$)[a]

substituent	ΔP_I	ΔA_e	$2\Delta\eta$
	Pyrazole and Methylpyrazoles		
H[b]	0.0 (8.21)	0.0 (3.38)	0.0 (5.79)
1-Me	−0.58	−0.001	−0.58
3-Me	−0.38	0.07	−0.31
4-Me	−0.38	0.00	−0.38
5-Me	−0.21	0.06	−0.16
	Imidazole and Methylimidazoles		
H[b]	0.0 (7.85)	0.0 (3.92)	0.0 (5.88)
1-Me	−0.27	−0.03	−0.30
2-Me	−0.34	0.04	−0.30
4-Me	−0.40	0.02	−0.38
5-Me	−0.49	0.08	−0.41

[a] All values in eV. Values calculated at the 4-31G level. [b] We give, within parentheses, the corresponding absolute values for the parent compounds.

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different for both systems (only 1.7 kcal/mol for the former and 9.3 kcal/mol for the latter). These values reveal a particular characteristic of the HOMO of imidazoles. This is a π-type orbital (see Figure 6), and an inspection of its wave function indicates that the atomic orbitals centered on N1 do not participate in it, whereas the contribution from those atomic orbitals centered on C5 is noticeable. Consequently, in 5-methylimidazole there is a certain contribution to the HOMO wave function coming from the atomic orbitals centered on the methyl group (a typical hyperconjugative effect), a contribution which is forbidden if the methyl group is bound to N1. Accordingly, the energy of the HOMO of the 1-methyl derivative does not change appreciably upon methyl substitution.

This absence of hyperconjugation for *N*-methyl-substituted imidazole has another important consequence. Heteroaromatic compounds can be taken, in general, as aromatic derivatives where the heteroatom plays the role of a perturbation. Thus, azines, like pyridine, would be a benzene with a basic center (aza and lone-pair effects). However, this is no longer true for N-substituted azoles; i.e., there is nothing in aromatic chemistry comparable to the N–R bond of an azole. This fact has been recognized by experimentalists[37] but was never satisfactorily explained. Figure 6 and the preceding discussion on the characteristics of the HOMO provide a simple explanation.

Conclusions

From the results discussed throughout this paper we can conclude that the ionic hydrogen bonds between azoles (pyrazoles and imidazoles) and NH_4^+ are not linear. Although deviations from linearity are small, they are neither constant nor regular, revealing in some significant cases strong repulsive interactions between the NH_4^+ cation and the substituent groups of the azolic system. Deviations from linearity are very small for pyrazoles due to the repulsive interaction between the second ring nitrogen and the nitrogen belonging to the NH_4^+ system.

In the equilibrium conformation the proton of the NH_4^+ cation has almost been transferred to the azolic system. In all cases the distance from the proton to the basic center of the azolic compound decreases as its proton affinity increases.

The gap between the gas-phase basicities of imidazole and pyrazole when the reference acid is NH_4^+ is about 6 kcal/mol smaller than if the reference acid is a proton, due mainly to differences in charge–dipole interactions. This result agrees with previous findings reported in the literature[6,10] for other kinds of bases and acids.

The hydrogen-bond energies for B–NH_4^+ complexes where B is an azolic system, increase with the increasing proton affinity of the azole, but these dissociation energies are smaller than the corresponding relative proton affinities, showing that the gas-phase basicity of azoles when the reference acid is softer than the proton undergoes a certain attenuation. This attenuation effect is slightly greater for pyrazoles than for imidazoles.

Moreover, these hydrogen-bond dissociation energies are linearly correlated to the 1s orbital energy of the basic center of the azole, though these linear relationships are different for α- and β-substituted compounds.

Both pyrazoles and imidazoles behave as reasonably hard bases. Their absolute hardness decreases upon methyl substitution and varies like the ionization potential. Consequently, we have found that, in general, the multivariate linear correlations gas-phase basicities vs. E_{1s} and E_{HOMO} may yield some useful information on the changes undergone by the hardness of the base upon substitution.

Acknowledgment. This research has been partially supported by the CAICYT Project Number 913/82. All calculations have been performed at the UAM/IBM and CC/UAM Centers, Madrid.

Supplementary Material Available: Comparison between ammonium affinities obtained from STO-3G//INDO and STO-3G//STO-3G calculations for small bases, scaled INDO optimized geometries of azole–NH_4^+ complexes, including imidazole, pyrazole, and their monomethylated derivatives, and a graph of ammonium affinities (ΔAA) vs. the energy of the HOMO for methylpyrazoles referred to the parent compound (4 pages). Ordering information is given on any current masthead page.

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Thiol–Olefin Cooxidation (TOCO) Reaction. 7. A ^{1}H NMR Study of Thiol Solvation

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The examination of ^{1}H NMR spectra of *p*-chlorothiophenol in various solvents, including some olefins, indicates the presence of two types of interactions, namely, the formation of hydrogen-bonded and charge-transfer complexes. The association constants for some of these interactions are estimated. The chemical shifts of the sulfhydryl proton of various substituted thiophenols in the presence of indene supports the existence of charge-transfer complexes.

Introduction

In view of our work with thiols in the thiol–olefin cooxidation reaction,[1–6] and with solvent effects in the noncatalyzed oxidation of thiols by molecular oxygen,[7] it was also of interest to study the nature of thiol solvation by means of ^{1}H NMR. The elucidation of solute–solvent

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