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Empirical Energy−Density Relationships Applied to the Analysis of the Basicity of Strong Organic Superbases

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Site selectivity and reactivity in some strong organic super bases $RN{=}C(NR_2)R$, containing several possible sites for protonation, have been analyzed qualitatively in terms of global and local chemical reactivity descriptors defined in the context of conceptual density functional theory. On the basis of the condensed-to-site Fukui function values, the protonation site is predicted to be located at the imino nitrogen. Linear relationships between global energy-dependent quantities and the variation of the Fukui function (or the local softness) at the protonation site have been also found. These linear relationships can be interpreted within a local HSAB rule framework, as observed for instance for the gas-phase basicity of alkylamines and gas-phase acidity of alcohols and thioalcohols. This work extends the range of applicability of reactivity models developed for the treatment of substituent effects based on empirical energy−density Hammett-like relationships (*J. Am. Chem. Soc*. **2000**, 122, 4756).

Introduction

Strong neutral organic superbases play an outstanding role in chemistry because of their primary impact in medicinal,[1] pharmaceutical,[2,3] and organic synthesis applications.[4−6] They require milder reaction conditions than their inorganic ionic counterparts, also being stable at low temperatures. Hence, the understanding and design of enhanced basicities,[7−10] both in the gas and solution phases, have been a primary goal from experimental[5,11−14] and theoretical[4,15−18] studies. These compounds play, for instance, an important role in the experimental determination of the basicity of new bases through the bracketing technique and also in the description of stabilizing special molecular interactions such as hydrogen bonds with superacids.[19]

Proton affinities, as a measure of the intrinsic basicities in the gas-phase, are found to be in the range of 250−300 kcal/mol for superbases.[4,15,20,21] Protonation equilibrium in the gas phase is governed by the proton affinity (PA), defined as the negative of the enthalpy for protonation reaction:

$$B + H^+ \rightarrow BH^+, \quad PA = -\Delta H° \qquad (1)$$

This quantity is generally obtained as a single number (i.e., as a global property of the Brönsted base B), both in experimental and in theoretical calculations performed within the supermolecule approach. In particular, it has been shown by Maksic et al.[15.22−24] that the presence of the imino fragment, $(R)_2N{-}C(R){=}N{-}R$, in conjunction with suitable effects of substituent (i.e.. inductive, resonance, conjugation, etc.) and structural changes (i.e., yielding hydrogen bonds stabilizing interactions) provide a route to find higher PA values for these type of compounds.

It is well-known that, from a theoretical point of view, the calculation of PA values involve accurate calculations of neutral base B and their conjugated acid BH^+. Moreover, the assignment of the reactive site (i.e., the most basic site) is achieved after the comparison of experimental values with those determined theoretically from different protonated BH^+ species. This procedure indeed should involve the inclusion of zero point energy, as well as the thermal corrections to the electronic energies due to translational, rotational, and vibrational contributions, to reach the desired chemical accuracy. However, it has been emphasized that for identification of active sites and characterization of the molecular structure effects on acid−base behavior in polyfunctional compounds, qualitative schemes may also be developed within the framework of conceptual density functional theory (DFT).[25] In this context, chemical reactivity indices have been introduced and interpreted as global or local responses of a system against perturbations in the external potential $v(\mathbf{r})$ and/or the number of electrons N.[26−30] Qualitative approximations to model chemical reactivity are based upon global hierarchies of descriptors such as the chemical potential, μ[31] (i.e., the negative of the electronegativity, χ), the chemical hardness, η, and softness, S,[32]

$$\mu = \left[\frac{\partial E}{\partial N}\right]_{v(\mathbf{r})} = -\chi, \quad \eta = \left[\frac{\partial^2 E}{\partial N^2}\right]_{v(\mathbf{r})}, \quad \text{and } S = \frac{1}{\eta} \qquad (2)$$

Additionally local descriptors, such as the electron density, $\rho(\mathbf{r})$, Fukui function, ×a6($\mathbf{r}$),[33,34] and local softness, $s(\mathbf{r})$,[35,36] are also used

$$\rho(\mathbf{r}) = \left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_N, \quad f(\mathbf{r}) = \left[\frac{\delta \mu}{\delta v(\mathbf{r})}\right]_N = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_{v(\mathbf{r})}, \quad \text{and } s(\mathbf{r}) = Sf(\mathbf{r}) \qquad (3)$$

Following our interest in the development and exploration of theoretical models for treatment and analysis of chemical reactivity[37,38−41] rooted within the conceptual DFT, our goal is

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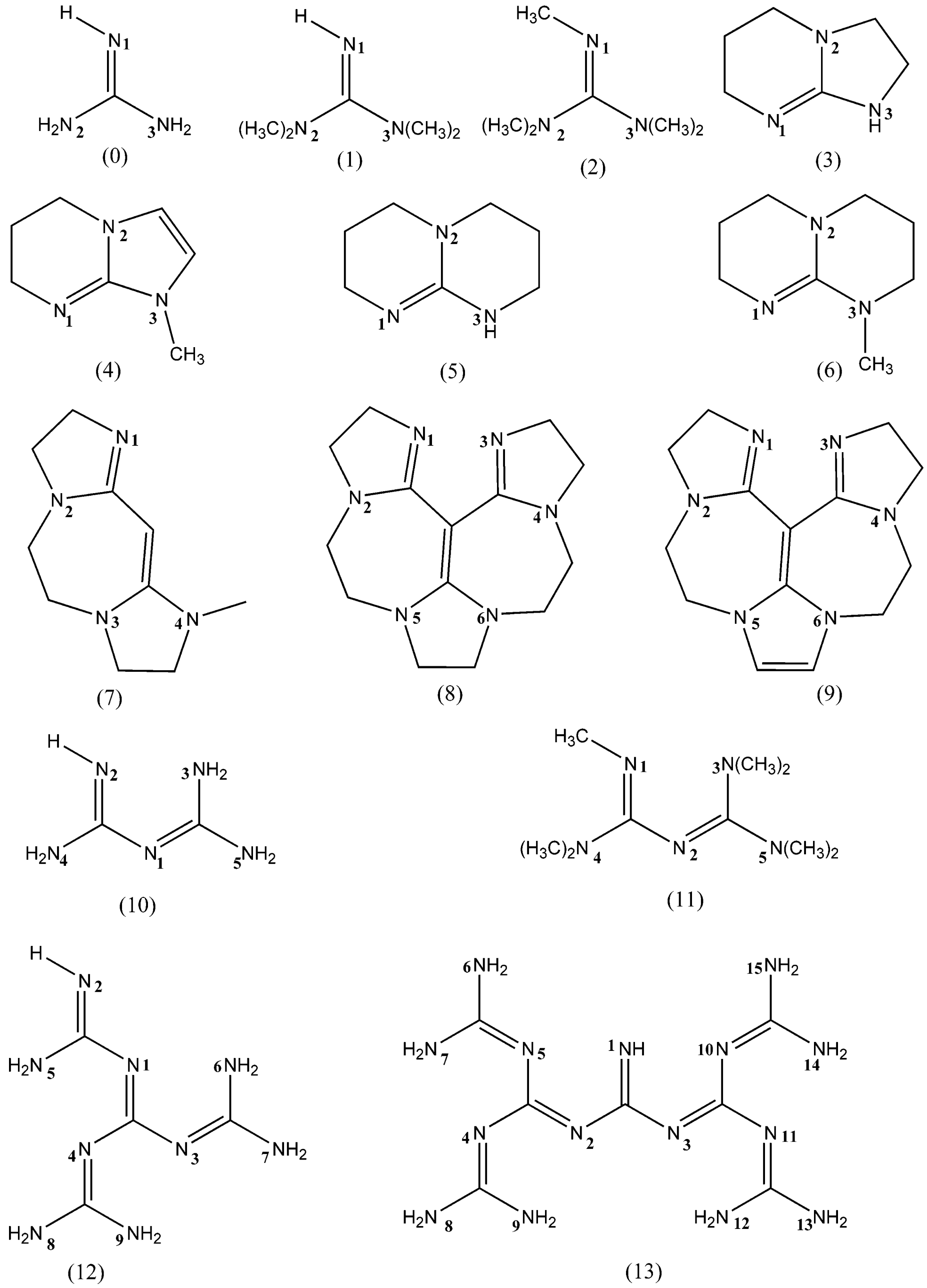
SCHEME 1: Series of Molecules Included in the Present Study and Atom Numbering



here to explore the models for more insights concerning the applicability of such a type of index in the description of the high PA values of the above-mentioned neutral organic superbases.

Theoretical Models

In the context of characterization of chemical reactivity and rationalization of electronic substituent effects, we have presented recently[38] a Hammett-like linear relationship between global energy-dependent quantities (i.e., μ) and local electronic descriptors (i.e., Fukui or softness functions), namely,

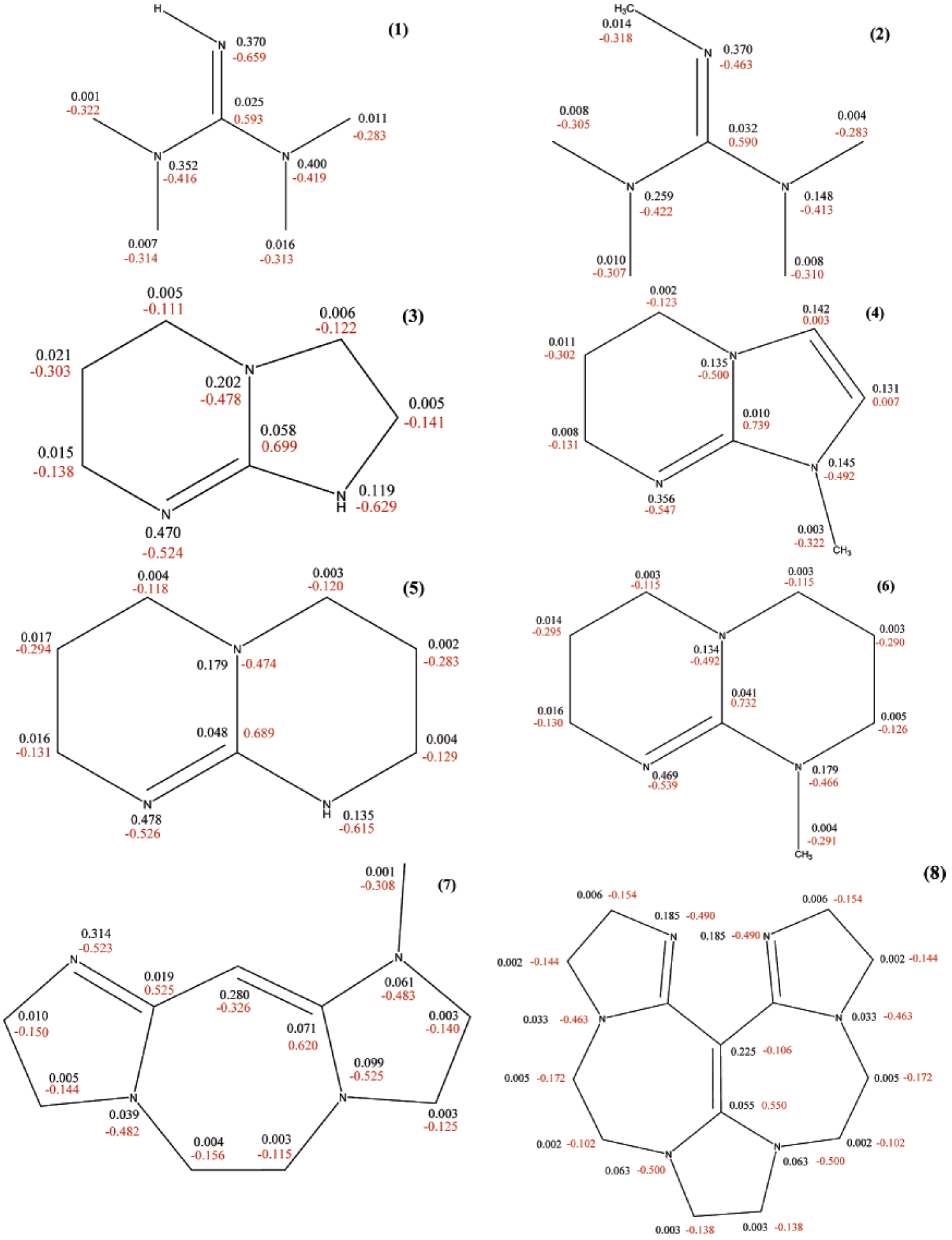
$$\ln\left[\frac{\mu(N+\Delta N)}{\mu^0(N)}\right] = \gamma f(\Delta N) \tag{4}$$

where γ is a constant and $f(\Delta N)$ represents any well-behaved function of the change in the number of electrons introduced by chemical substitution.[38]

TABLE 1: Global and Local Responses for Superbases 1−13 and the Reference (0) System, Including Predicted Proton Affinities, PA, Chemical Potential, μ, Softness, S, Condensed-to-Site Mulliken Charges, q_{N1}, Fukui Function, f_{N1}^-, and Softness Function, s_{N1}^-

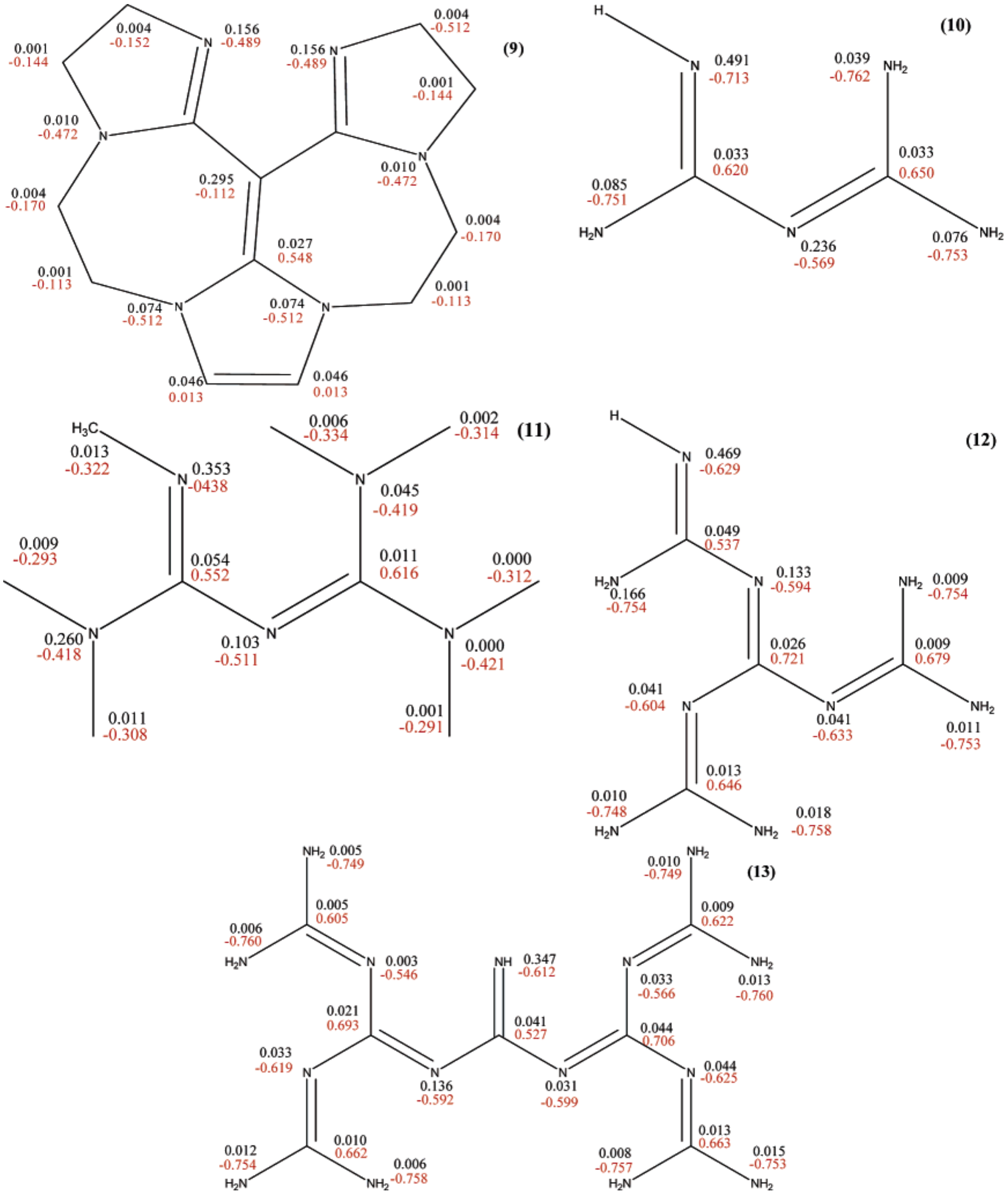
system	PA, kcal/mol	μ, au	S, au	q_{N1}	f_{N1}^-	s_{N1}^-
0	248.9	−0.0860	3.52	−0.6250	0.543	1.912
1	259.3	−0.1656	6.04	−0.6592	0.400	2.417
2	263.4	−0.2472	4.05	−0.4631	0.370	1.496
3	260.5	−0.2662	3.76	−0.5243	0.470	1.76
4	263.3	−0.2003	4.99	−0.5470	0.356	1.775
5	265.1	−0.2508	3.99	−0.5261	0.478	1.907
6	266.1	−0.2494	4.01	−0.5387	0.469	1.880
7	278.0	−0.1869	5.35	−0.5231	0.314	1.682
8	289.5	−0.1766	5.66	−0.4900	0.185	1.047
9	293.8	−0.1682	5.95	−0.4890	0.156	0.930
10	256.5	−0.2296	4.36	−0.7134	0.492	2.143
11	279.2	−0.2336	4.28	−0.4382	0.353	1.512
12	284.1	−0.1693	5.91	−0.5943	0.469	2.770
13	302.9	−0.1695	5.90	−0.6125	0.347	2.049

SCHEME 2: Nucleophilic Condensed-to-Site Fukui Functions Values (First Entry) and the Net Charges from the Mülliken Population Analysis (Second Entry) for the Most Important Atoms in Each System for Compounds 1−8



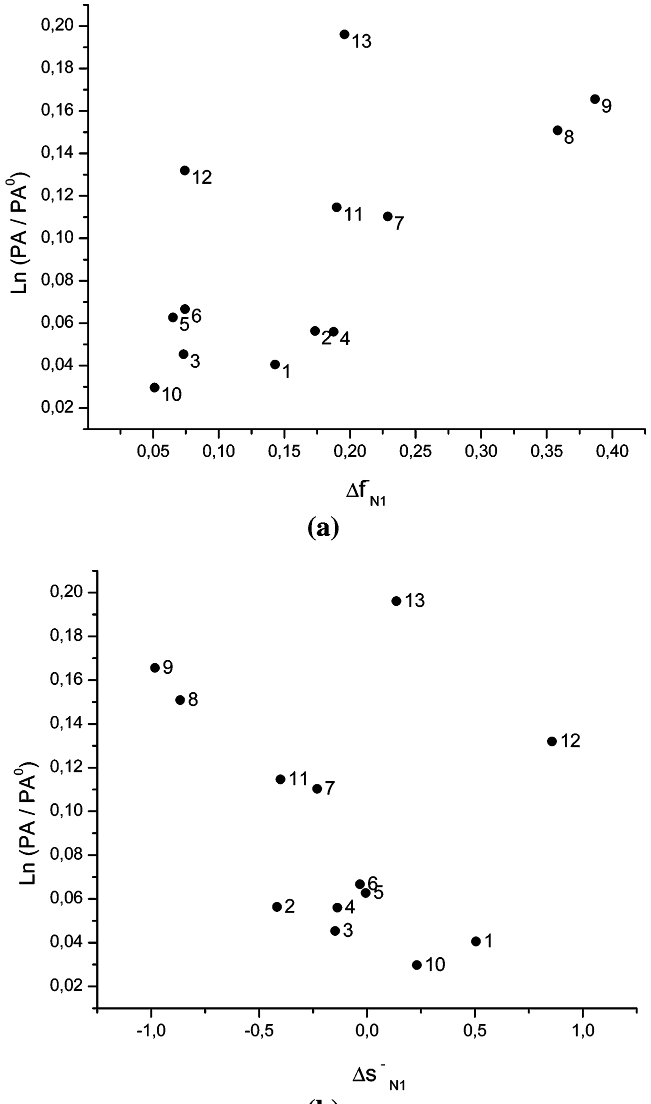
In such an approach, chemical substitution is thought to be a global perturbation that changes the number of electrons from N to $N + \Delta N$, being the local responses associated with *the variations of electron density to this change in N or even to changes in* μ through the Fukui function or local softness given in eq 3. Hereafter, it is assumed[42] that the chemical potential displays an exponentially decreasing with the number of electrons, being γ the falloff parameter. This is just the behavior first shown by Bartolotti and Parr for atoms,[42] $\mu(N + \Delta N) = \mu^0(N) \exp[\gamma(\Delta N)]$, and we have assumed that it holds for atoms embedded in molecules. It is clear that within such an approaching scheme, eq 4 represents an energy−density relationship. That is, it contains on the left-hand side the electronic chemical potential of eq 2, i.e., *the first variation of the electronic energy under a variation in the number of electrons induced by substitution*, whereas the right-hand side may be associated with the variations of a density dependent property of the system with respect to the number of electrons. As a first *ansatz*, such a function for the change in the number of electrons $f(\Delta N)$ could be represented by the variations of Fukui function or local softness because they are associated with these changes (see eq 3). Within such an *approximate* model, it is clear that the local effects become incorporated indirectly through the local responses at the active site.[38] Of course, such a model constitutes

SCHEME 3: Nucleophilic Condensed-to-Site Fukui Functions Values (First Entry) and the Net Charges from the Mülliken Population Analysis (Second Entry) for the Most Important Atoms in Each System for Compounds 9−13



an analogy with the Hammett-like free energy relationships, and its validity assumes an exponentially decay of the chemical potential for the valence states of atoms in molecules.[42] It has also been noted previously that proton affinity (PA) variations are proportional to changes in the electronic chemical potential for proton transfer (PT) reactions. For instance, PA differences appear as the driving force determining the PT energy barriers in an isoelectronic series of neutral and positively and negatively charged hydrogen-bonded systems.[43] Hence, PA, the Fukui function, and the local softness seem to be suitable for use as global and local quantities appearing in eq 4, respectively. These relationships have been shown to correctly assess the substituent electronic effects on both gas-phase basicity of alkylamines and acidity of alcohols and thioalcohols.[41,44,45] Additionally, an interpretation framed on the local hard and soft acids and bases (HSAB) principle has been given in agreement to previous results reported by Li and Evans.[46]

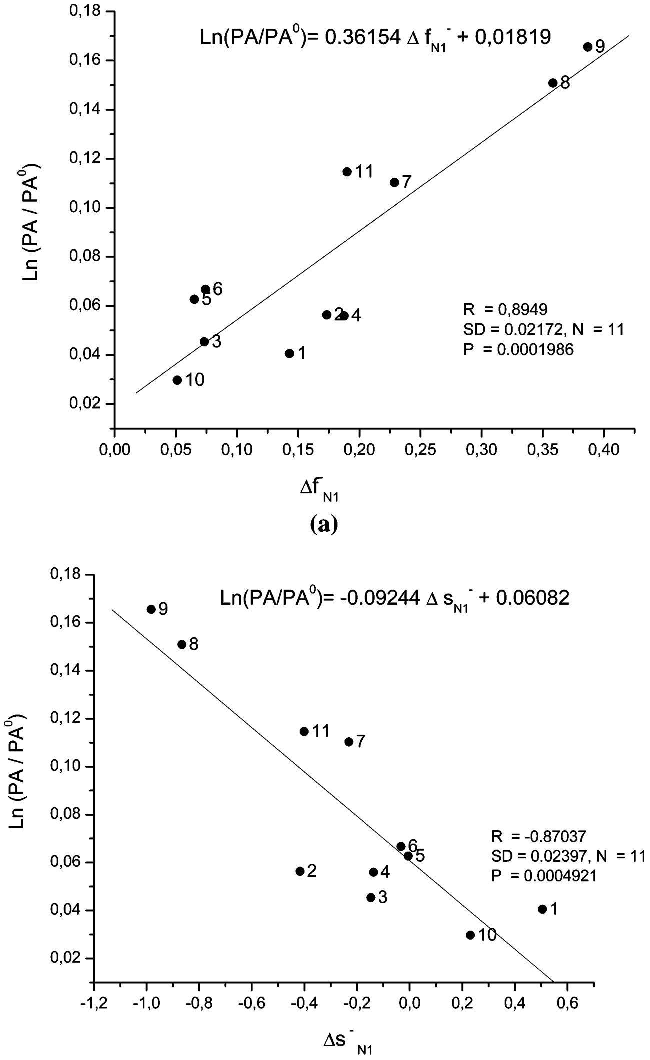
It seems that the site corresponding to the minimum condensed-to-site Fukui function will have predisposition to develop a hard−hard-interactions, whereas that soft−soft interactions are expected to occur when the condensed-to-site Fukui function display its maximum values. As it was already noted, this reactivity model has a potential advantage over models based on group properties using the electronegativity equalization principle (EEP), since the transferability of group properties is not required. It should be also mentioned in this respect that Chattaraj[47] has recently emphasized that the Li−Evans argument holds for the protonation process in systems with a single protonation site, but it could fail in polyfunctional systems possessing more than one protonation site. It is well-known that within a perturbative approximation of chemical reactivity, in the case of hard−hard interactions, the preferred site will be associated with the maximum net charge instead the minimum Fukui function. For instance, Toro-Labbé et al.[48] have recently



(a)

(b)

Figure 1. Correlation between ln(PA/PA°) and (a) local Fukui function differences and (b) local softness differences at the imino N1 site for the whole series studied here. See text for details.



(a)

(b)

Figure 2. Correlation between ln(PA/PA°) and (a) local Fukui function differences and (b) local softness differences at the imino N1 site, excluding systems **12** and **13**. *R* is the regression coefficient, SD is the standard deviation, *N* is the number of points, and *P* is the probability that the observed correlation is randomly obtained. See text for details.

reported a discussion concerning the nature of the internal proton-transfer interactions in the interconversion from hydroxyethylene (the enol form), to ethanal (the keto form). From the examination of the change of several types of atomic charges and the condensed Fukui function along the IRC reaction pathway for this process, it was found that hard−hard interactions are better mapped with natural population analysis charges than those from Fukui functions.

In this work we focus on the applicability and extension of Hammett-like approach[38] to describe the intrinsic basicities of strong superbases with higher PAs values ranged from 250 to 300 kcal/mol.

Computational Details

Geometries for base B and the conjugate acid BH$^+$ of a selected series of molecules included in the present study (see Scheme 1) have been optimized at the B3LYP/6-31G(d) level of theory using the Gaussian 98 package of programs.[49] Because we deal only with general trends concerning *intrinsic* basicities, our calculated proton affinities do not include ZPE or thermal corrections. The calculation of the electronic chemical potential and the chemical hardness were obtained from the well-known approximation based on a finite difference scheme and Koopmans' theorem through the expressions: $\mu \approx \epsilon_H + \epsilon_L/2$ and $\eta \approx \epsilon_L - \epsilon_H$, given in terms of the one electron energies of the HOMO and LUMO frontier molecular orbitals, ϵ_H and ϵ_L, respectively. The global softness, *S*, was calculated as the inverse of the chemical hardness. The condensed-to-site Fukui function $f_k^i$was evaluated from single point calculations in terms of the *i*th-frontier molecular orbital coefficients, c_ν^i, and the overlap matrix, $S_\mu\nu$, taken over the atomic basis set, $\{\chi_\mu(\mathbf{r})\}$, using a procedure described elsewhere[50,51]

$$f_k^i \equiv \sum_{\mu \in k}\sum_{\nu} c_\mu^{\ i} c_\nu^{\ i} S_{\mu\nu},\ S_{\mu\nu} = \int \chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad (5)$$

The condensed-to-site softness has been evaluated correspondingly from $s(\mathbf{r})$ in eq 3 as follows: $s_k^i = Sf_k^i$.

Results and Discussion

We recall that, in the model defined by eq 4, the chemical substitution is treated as a global perturbation that changes the number of electrons in ΔN, while the local response of the system, including the associated change in the external potential, is mapped through Fukui or softness functions. Global quantities are associated with reactivity (i.e., thermodynamics), while the local ones are related to site selectivity. In particular, it has been shown that the Fukui function may be used as a natural local descriptor of reactivity within a generalized HSAB[46] context, both in some polyfunctional systems and within a family of related molecules with similar global reactivity.[38]

The superbases considered in the present study are depicted in Scheme 1. Selected global responses corresponding to proton affinities, the chemical potentialμ, and the chemical softness, *S*, are reported in Table 1. We have also included in Table 1 atomic Mülliken charges and the condensed-to-site Fukui and softness values at the imino nitrogen (N1) for superbases and the selected reference system (i.e., guanidine).

It may be seen that predicted PA values for the superbases are in the range 256.4−302.9 kcal/mol, excluding the reference system. These values are consistent with the experimental PA values reported by Maksic et al.[7−10] in the sense that these systems present larger values than traditional amines. On the other hand, it is clear that there is not a correlation between the theoretical PA values and the chemical potential and the global softness for the whole series presented. However, by considering subseries of systems **5**−**9** for our analysis, it may be seen that such correlation exists between the PA values, chemical potential and global softness of superbases. While PA values increase, the electronic chemical potential also increases. This result may be interpreted as an enhancement in the charge transfer when the proton affinity increases in this subseries, and therefore, a better interaction with the H^+ of the superbases is expected.

In Schemes 2 and 3, the nucleophilic Fukui function is given for the whole series (first entry). This constitutes the nucleophilic response of system against an electrophile species in the initial stage of the reaction. It may be observed that protonation sites are predicted to be those presenting the highest electrophilic Fukui function value in each superbase. The highest values correspond in all the cases to the N1 nitrogen center at the imino group (>C═N−). This result is in agreement with the expected electronic and resonance substituent effects in these series. It is interesting to note in this point that for system **1**, the HOMO and HOMO-1 energy levels are very close in energy by 0.0053 au (∼3.4 kcal/mol) and the electronic response, as measured from the condensed-to-site Fukui function becomes not a direct measure of the selectivity. In effect, the regional contribution from HOMO-1 is predicted to be 0.1142, 0.1615, and 0.4860 for the N1, N2, and N3 centers, respectively. Such an effect by orbital degeneracy is not present in the other systems, which cannot be explicitly treated with our model equations for reactivity indices via eqs 4 and 5. Note, however, that determination of the preferred protonation site in this polyfunctional system agrees with the expected resonance effects for such system. However, there is not a relation with a local HSAB rule.

Predicting the Gas-Phase Basicity of Superbases. Following the Li−Evans rule,[38,46] we can make use of the Fukui function or local softness to build up a Hammett-like relationship with proton affinity variations in a logarithmic scale as thoroughly discussed in the development of eq 4.[38,41,43,44] Hence, we can explicitly write that

$$\ln\left[\frac{\mathrm{PA}}{\mathrm{PA}^0}\right] = \gamma_f \Delta f_k^- \text{ or } \ln\left[\frac{\mathrm{PA}}{\mathrm{PA}^0}\right] = \gamma_s \Delta s_k^- \qquad (6)$$

The Fukui function Δf_k^- and local softness Δs_k^- differences correspond to the variation of the condensed-to-site Fukui and softness functions at the most basic nitrogen center N1 of the imino group of the reference system, and the corresponding values for the superbase B, i.e., $\Delta f_k^- = f_k^-(\mathbf{0}) - f_k^-(\mathrm{B})$ and $\Delta s_k^- = s_k^-(\mathbf{0}) - s_k^-(\mathrm{B})$, respectively. At present level of theory, these values are for the reference (**0**) system (i.e., guanidine) $f_{N1}^-(\mathbf{0}) = 0.5432$, and $s_{N1}^-(\mathbf{0}) = 1.9123$, as reported in Table 1.

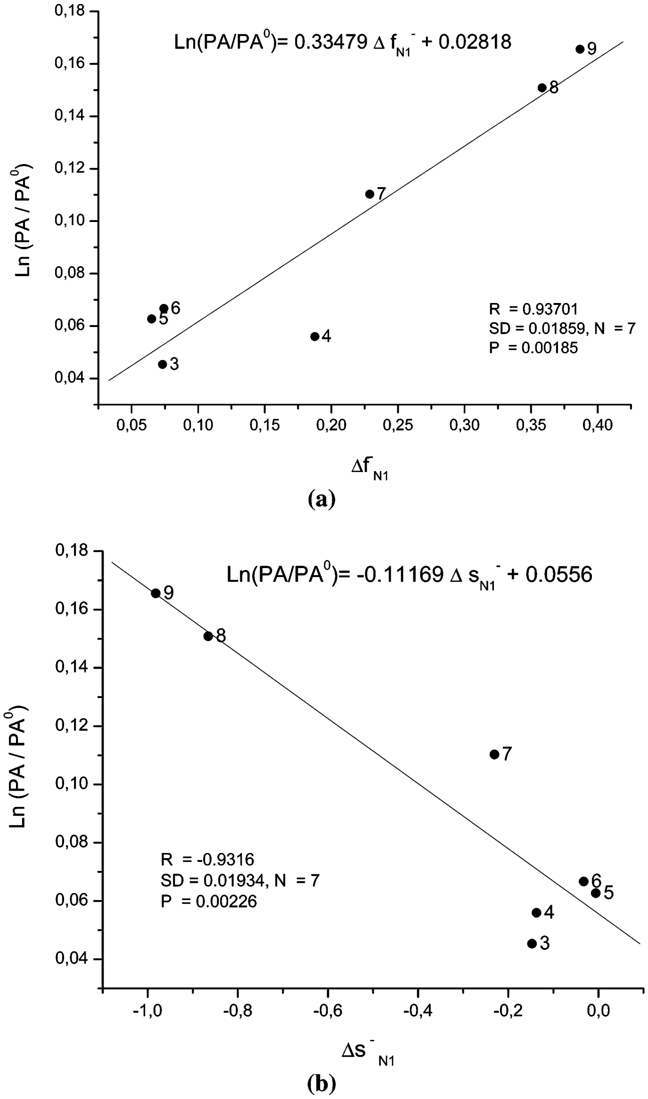


Figure 3. Correlation between Ln(PA/PA°) and (a) local Fukui function differences and (b) local softness differences at the imino N1 site, excluding systems **1**, **2**, **10**−**13**. *R* is the regression coefficient, SD is the standard deviation, *N* is the number of points, and *P* is the probability that the observed correlation is randomly obtained. See text for details.

It may be seen from Figure 1 that such type of correlation is not feasible for the entire set of selected superbases. Systems **1**, **2**, and **10**−**13**, belonging to a ramified type subseries of superbases, do not show apparent correlations between PA and Fukui function or softness differences. However, excluding compounds **12** and **13**, we have obtained a fairly good correlation, as depicted in Figure 2. An explanation to this behavior might be given considering that this subseries undergoes a great molecular framework reorganization (i.e., drastic changes in the external potential) under protonation, which is an effect not being considered by our treatment of substituent effects via the Hammett-like model of eqs 4 or 6.

It is clear that eq 6 can be applied only within a family of molecules structurally closely related. In fact, a good correlation could be expected for the whole subseries of systems **3**−**9**,

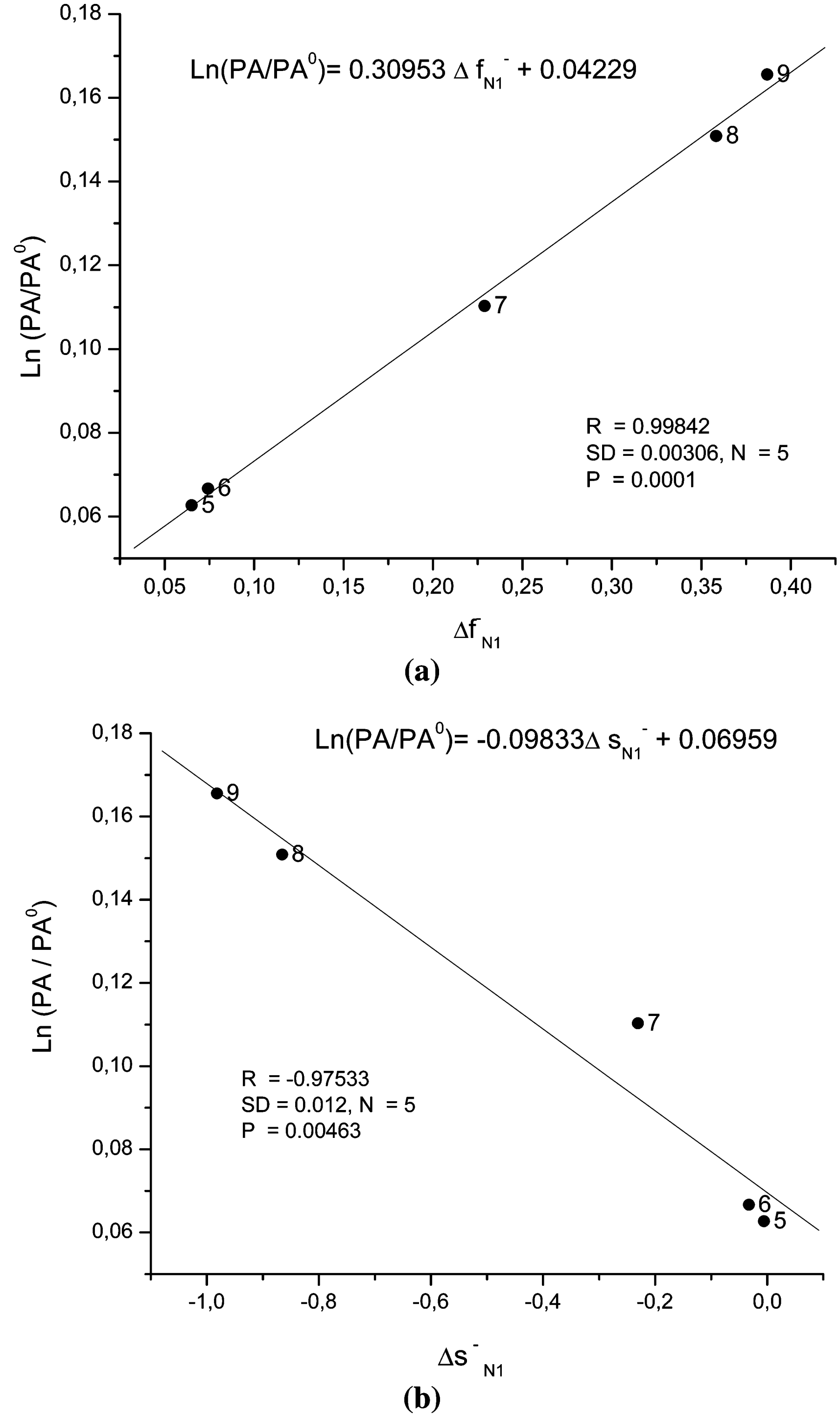


Figure 4. Correlation between Ln(PA/PA°) and (a) local Fukui function differences and (b) local softness differences at the imino N1 site for compounds **5**−**9**. *R* is the regression coefficient, SD is the standard deviation, *N* is the number of points, and *P* is the probability that the observed correlation is randomly obtained. See text for details.

where it is expected that the chemical substitution could be treated like a perturbation in the number of electrons. Linear relationships for the variations in the condensed-to-site Fukui and softness functions are shown in Figures 3 and 4. In all cases, the local softness differences provide slightly less satisfactory linear relationships. Note that for Li− Evans selectivity rule to be satisfied, an additional prerequisite should be fulfilled. This additional condition requires that the whole series of molecules have to be characterized by global reactivity patterns not differing too much from each other. In this case, the natural descriptor is the global softness appearing in eq 6, i.e., $s_k^i = Sf_k^i$. As noted from Table 1, this response presents a significant variation along the entire subseries. Thus, the great variations in *S* do not account for the complete effect of the substituent effect around the imino fragment. The condensed-to-site Fukui function is only slightly better than the condensed-to-site softness on the entire system. Note that a structural change in system **4**, i.e., inclusion of a double bond and the methyl group, does not excessively affect the site reactivity of the imino nitrogen if compared with system **3**. It may be seen that an even better correlation exists between relative proton affinities and the Fukui function differences for the subseries **5**−**9** (see

Figure 4) with a correlation coefficient $R = 0.998$ and a regression slope of 0.309. The positive slope for these correlations may be interpreted in terms of a higher electron population at the imino (N1) center promoted by chemical substitution with respect to the reference system. This is also clear from reported charges in Table 1 and Schemes 2 and 3 (see second entry).

It is clear from the Mulliken atomic charges reported that any correlation exists between the most probable protonation site and high PA values for these systems. However, for the subseries **5**−**9** and **3**−**9**, we have found fairly good correlations: $\ln[\mathrm{PA}/\mathrm{PA}^0] = -\,0.10788\Delta q_{N1} - 1.96522$ (coefficient $R = -0.94272$, standard deviation SD $= 0.01813$, test $p = 0.01631$) and $\ln[\mathrm{PA}/\mathrm{PA}^0] = -\,0.10947\Delta q_{N1} - 1.9347$ (coefficient $R = -0.89128$, standard deviation SD $= 0.02413$, test $p = 0.00705$), respectively. In our Hammett-like model of eq 6 we have used the atomic charges difference with respect to the guanidine system (**0**), $\Delta q_{N1} = q_{N1}(\mathbf{0}) - q_{N1}(\mathrm{B})$. Note that only in the sense of eq 4 could a charge increment at the imino nitrogen be associated with a higher PA value. For these families of superbases, the minimum value in the condensed-to-site Fukui function is directly related with a decreasing of the condensed-to-site softness, (i.e., an increase of the hardness in a local approximation)[38] and hence an accumulation of the electronic charge at the N1 center.

Of course, although the protonation process could be understood like a hard−hard interaction (i.e., a charge controlled process), the existence of a Hammett-like linear relationship which could also be interpreted on the basis of a local HSAB rule in the context of the Li−Evans generalized HSAB principle is remarkable. The enhanced basicity at the imino nitrogen N1 site shown by superbases along subseries **5**−**9** and **3**−**9** seems to be framed on a local HSAB principle in the sense that a low (high) value for the condensed-to-site Fukui (softness) functions is linearly related to a hard interaction global property. Such was the case for the gas-phase basicity of alkylamines and the gas-phase acidity of alcohols and thioalcohols.[38]

Concluding Remarks

Site selectivity and reactivity in strong organic superbases containing the imino group, $\mathrm{RN{=}C(NR_2)R}$, have been analyzed qualitatively in terms of global and local chemical reactivity descriptors within an empirical energy−density Hammett-like relationship framework.[38] The protonation site is predicted to be at the imino nitrogen in each superbase within an empirical simple model based on condensed-to-site Fukui functions. Linear relationships between global energy-dependent quantities (proton affinities) and the variation of the Fukui function (or softness) at the imino nitrogen have been discussed. It seems that these linear relationships could be *also* interpreted within a local HSAB rule framework.

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