Spatial and Electronic Structure of Highly Basic Organic Molecules: Cyclopropeneimines and Some Related Systems

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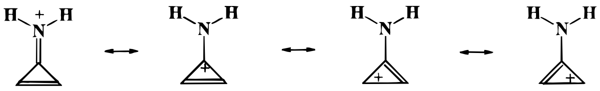
It is shown, by utilizing a reliable model at the MP2 level of theory, that the imino group attached to the cyclopropene moiety exhibits a high proton affinity (PA). The reason behind the appreciable PA is identified as significant aromatization of the three-membered ring spurred by the protonation. Further amplification of the PA can be achieved by NH_2 substitutions at the CC endo double bond, since amino groups stimulate aromatization of the cyclopropene fragment. Additionally, they release some of their lone pair electron density thus contributing to a uniform distribution of the positive charge over the entire molecular system. This effect is even more pronounced if the diaminoiminocyclopropene system is substituted by sizable alkyl groups. The aromatic stabilization in the protonated 2,3-diaminocyclopropeneimine, estimated by the corresponding homodesmic reaction, seems to be as high as 59.5 kcal/mol. Very potent organic bases can be obtained by designing polycyclic systems possessing two or more cyclopropene fragments, where the aromatization occurs by the conjugation interaction transmitted through the π-electron network in a typical domino fashion. The highest PA value is found, however, in a calicene-like structure embracing a quinoid six-membered ring and a cyclopropene moiety. Its proton affinity is well above the PA value of the Schwesinger's proton sponge, which is known as the stongest organic base so far. Importance of the iminocyclopropene motif in tayloring of the strong organic superbases is stressed. The role of the intramolecular hydrogen bonding in some specific systems is briefly discussed.

1. Introduction

A lot of efforts have been devoted lately in elucidating properties of strong organic bases and particularly in estimating their proton affinities (PAs).[1−17] This is not surprising because bases belong to protagonists in the acid−base chemistry. Furthermore, the proton affinity is a useful probe of the electronic structure of molecules, which gives valuable information about their hydrogen bond ability, distribution of the electron density, the electrophilic substitution susceptibility of aromatic compounds, a propensity to transmission of the substituent effects, etc. Most of the research interest was focused mainly on the PA of the so-called proton sponges as exemplified by their progenitor 1,8-bis(amino)naphthalene (DMAN)[18] and its numerous off−springs.[2−4] This type of restriction to DMAN-like systems only is not quite justified, because other organic molecules might well exhibit high basicities too, thus deserving much more attention. It is gratifying that some other families of organic molecules were studied more carefully recently, which provided good candidates for potent organic bases.[13−17] In this connection, it should be emphasized that the high basicity of some cyclic and acyclic guanidines has been explored[15] in an apparent attemp to extend the existing basicity scale toward the superbasic values.[20] Continuing our work on the proton affinity of organic compounds,[21] we consider here cyclopropeneimines and some related systems which might yield to very strong bases. Although the PA value is interesting per se as mentioned above, we would like to examine also how the protonation effect is transferred across several planar rings forming extended π electron networks. This could give some useful information about a mechanism, which might prove useful in designing composite systems and ultimatly new materials possessing desired properties. For this purpose a clear-cut interpretation of the underlying mechanism is necessary. It is obvious that the high PA value of the parent cyclopropeneimine can be qualitatively rationalized in terms of the resonance structures of its conjugate acid as depicted in Scheme 1.

SCHEME 1



Apparently, the protonation of the imino nitrogen atom leads to substantial aromatization of the three-membered ring and consequently to considerable lowering of the total electronic energy of the protonated form. It is important to mention in this connection that aromatization triggered by protonation is much more pronounced than conjugation present in the initial base (see later). The question arises whether one can amplify this effect thus leading to strong organic bases more powerful than any other known so far. This problem is addressed and some possible solutions are offerred in this paper.

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2. Methodology

Proton affinities are computed by using the standard equation:

$$\mathrm{PA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha - (\Delta \mathrm{ZPVE})_\alpha$$

where $(\Delta E_{\mathrm{el}})_\alpha = E(\mathrm{B}) - \mathrm{E}(\mathrm{BH}^+{}_\alpha)$ and $(\Delta \mathrm{ZPVE})_\alpha = \mathrm{ZPVE}(\mathrm{B}) - \mathrm{ZPVE}(\mathrm{BH}^+{}_\alpha)$ are the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. Further, B and BH^+ denote the base in question and its conjugate acid, respectively, whereas α stands for the site of the proton attack. In the present case, it represents the imino nitrogen, since the proton affinities in the studied systems satisfy inequalities $\mathrm{PA(N)_{im}} > \mathrm{PA(N)_{am}} > P(\mathrm{C})$ and only the largest PAs are discussed in what follows. Here, the subscripts "im" and "am" denote the imino and amino nitrogen atom, respectively. Nowadays the PAs of small molecules can be calculated with high accuracy by using very sophisticated ab initio methods. For instance, G2 approach is so reliable that the resulting PAs are of substantial help in establishing the experimental absolute proton affinity scale.[22,23] Quite recently, Peterson et al.[24] calculated a very precise value for the proton affinity of ammonia $\mathrm{PA(NH_3)} = 204.1 \pm 0.3$ kcal/mol by using CCSD(T) approach with the correlation consistent augmented quadrupole ζ basis set. The total molecular energies are so accurate that the error margin appears only due to approximate ZPVEs estimates. However, both G2 and the coupled cluster methods are not applicable to large systems of chemical interest. Hence, one should sacrifice some accuracy in order to increase the range of feasibility of the theoretical models. One way of doing it is to apply DFT hybrid approach with the appropriate basis set. It seems that the B3LYP/6-311+G(d,p) serves the purpose rather well.[16,17,25] We preferred to use the MP2(fc)/6-311+G**//HF/6-31G* + ZPVE(HF/6-31G*) model, which proved very useful in estimating the proton affinity of nitrogen atoms in amines and imines[26−28] yielding quite reliable estimates of the proton affinity of all 20 α amino acids as well.[29] A convenient feature of our approach is that the optimization of molecular structures and vibrational analyses are performed at the HF/6-31G* level. The vibrational frequencies are then multiplied by 0.89 weighting factor[30] in deriving the ZPVE values. However, the final MP2 single-point calculations mentioned above become impractical if the PAs of very large molecules are desired. This is the reason we developed simplified formulas based on the HF/6-31G* and AM1 calculations only. It appears, namely, that a change in the ZPVE upon protonation is fairly constant implying that the vibrational analyses can be safely ommitted in most cases. Second, there is a very good correlation between the ΔE_{el} (HF/6-31G*) values calculated at the HF level and the proton affinity of nitrogen bases derived by the MP2 model[31] yielding:

$$\mathrm{PA(BN)} = 0.8924\Delta E_{\mathrm{el}}(\mathrm{HF/6\text{-}31G^*})_{\mathrm{N}} + 10.4\ (\mathrm{kcal/mol})$$

if the protonation at the N atom is considered. The difference ΔE_{el}(HF/6-31G*) refers to a change in the total molecular energy upon protonation taken with the opposite sign according to convention. An analogous formula at the semiempirical AM1 level reads as

$$\mathrm{PA(B_N)} = 1.0948\Delta\Delta \mathrm{H_f(AM1)_N} + 381\ (\mathrm{kcal/mol})$$

Here, $\Delta\Delta H_f$ is the difference in the enthalpies of formation of the conjugate acid and the initial base. These two approximate schemes will be referred to as the scaled HFsc and AM1sc models, respectively. All calculations are performed by using GAUSSIAN 94 and GAMESS programs.[32,33]

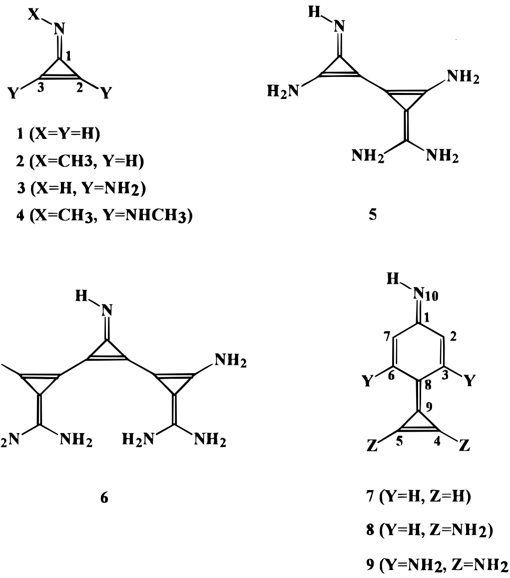


Figure 1. Schematic representation of studied organic bases and numbering of atoms.

3. Results and Discussion

3.1. Structural Features and Distribution of Charge. Characteristic molecular systems studied here are shown in Figure 1. All organic bases explored in this paper exhibited the highest PA for the imino nitrogen yielding to a planar $[\mathrm{NH_2}]^+$ group in all cases if not stated otherwise. Some selected structural parameters of systems **1**, **3**, and **7**, and their conjugate acids, denoted by ***n*p** ($n = 1$, 3, and 7), are presented in Table 1. The most striking feature of the protonated cyclopropeneimine **1p** is a clear tendency of equalizing the CC bond distances within a ring in accordance with the π-electron delocalization illustrated by Scheme 1. The same holds for **3p**, where a full uniformity in the CC bond distances is dictated by symmetry being indicative of a very strong aromatic stabilization of the three-membered ring. In **7p** a considerable aromatization of the six-membered quinoid structure is expected according to our previous results on the related systems.[27,31] This is indeed the case as evidenced by changes in the corresponding bond distances (Table 1). However, some quinoid character remains preserved as reflected in the C(2)−C(3) bond length of 1.36 Å. Aromatization of the three-membered ring in **7p** is slightly less pronounced than in **1p** showing that this effect attenuates as a distance from the protonated site increases. Another outstanding feature is rehybridization at the protonation NH center. The protonated $[\mathrm{NH_2}^+]$ group is planar assuming $[\mathrm{H{-}N{-}H}]^+$ angles of 117°−118° in all conjugate acids with one notable exception (vide infra). This is corroborated by the local bond orbital analysis of the hybrid s-characters.[34] The N−H s-character is increased from ~23% in the initial base to ~31% upon protonation, thus corresponding to a transition from the classical (Pauling's) $\mathrm{sp^3}$ to $\mathrm{sp^2}$ canonical states. It is a common wisdom that hybridization parameters represent one of the most important indices of the covalent bonding[35] influencing a large variety of local bond properties. In particular, the proton affinity increases if the s-content of a lone pair decreases.[26,36] A fact that imino group has higher PA value than an amino group should be therefore ascribed to a more pronounced conjugation taking place in immonium relative to ammonium ions. Distribu-

TABLE 1: Selected Bond Distances (angstroms), Bond Angles (degrees), Löwdin π-Bond Orders and Löwdin Electron Populations of some Characteristic Bases and their Conjugate Acids Studied in this Paper as Calculated by the HF/6-31G* Model

molecule	bond	distance/ angle	π-bo	atom	Q	Q^{π}
1/1p	C(1)−C(2)	1.414	0.36	C(1)	5.91	0.81
		1.374	0.50		5.82	0.71
	C(2)−C(3)	1.315	0.85	C(2)	6.11	0.84
		1.327	0.76		6.00	0.76
	C(1)−N	1.255	0.82	C(3)	6.14	0.87
		1.294	0.62		6.00	0.76
	C−H	1.070		N	7.50	1.36
					7.39	1.66
	N−H	1.005		H(N)	0.74	
		0.999			0.65	
				H(C)	0.80	
					0.75	
3/3p	C(1)−C(2)	1.411	0.40	C(1)	5.92	0.83
		1.361	0.53		5.87	0.84
	C(2)−C(3)	1.325	0.70	C(2)	5.96	0.90
		1.361	0.53		5.87	0.84
	C(1)−N	1.267	0.74	N(C1)	7.55	1.44
		1.322	0.50		7.46	1.75
	C(2)−N	1.364	0.38	N(C2)	7.52	1.74
		1.322	0.50		7.46	1.75
	C(3)−N	1.370	0.36	N(C3)	7.52	1.74
		1.322	0.50		7.46	1.75
	N(C1)−H	1.004		H(N(C1))	0.74	
		0.995			0.67	
	N(C3)−H	0.998		H(N(C3))	0.70	
		0.995			0.67	
7/7p	C(1)−C(2)	1.472	0.31	C(1)	5.91	0.82
		1.419	0.51		5.81	0.74
	C(2)−C(3)	1.331	0.88	C(2)	6.20	1.03
		1.358	0.75		6.23	1.10
	C(3)−C(8)	1.457	0.34	C(3)	6.13	0.95
		1.415	0.50		6.06	0.85
	C(8)−C(9)	1.341	0.74	C(8)	6.12	1.15
		1.394	0.53		6.13	1.17
	C(9)−C(4)	1.415	0.36	C(9)	5.96	0.86
		1.380	0.50		5.86	0.72
	C(4)−C(5)	1.306	0.85	C(4)	6.10	0.85
		1.323	0.76		6.01	0.76
	C(1)−N(10)	1.268	0.85	N	7.46	1.25
		1.332	0.54		7.46	1.72
	C(1)−C(7)	1.474	0.32	H(N)	0.75	
		1.419	0.51		0.68	
	N−H	1.006		H(C2)	0.83	
		0.995			0.81	
	C(2)−H	1.074		H(C4)	0.79	
		1.074			0.76	
	C(4)−H	1.068				
		1.069				

[a] Total atomic and π-electron populations are denoted by Q and Q^{π}, respectively. [b] Items related to the conjugate acids are given always in the second row.

TABLE 2: Total Molecular Energies (au), Zero-Point Vibrational Energies (in kcal/mol), and Proton Affinity (in kcal/mol) for Systems 1−8 and their Conjugate Acids[a]

molecule	HF/6-31G*	MP2	ZPVE	PA(MP2)	PA(HFsc)
1	−169.679 86	−170.297 16	30.4		
1p	−170.079 88	−170.676 39	38.5	229.9	234.4
2	−208.708 07	−209.482 71	47.0		
2p	−209.115 40	−209.869 59	56.3	234.5	238.5
3	−279.752 99	−280.774 98	51.6		
3p	−280.183 97	−281.184 64	58.5	250.2	251.7
4	−396.937 41	−398.329 04	101.9		
4p	−397.278 97	−398.750 42	109.7	256.6	257.6
5	−542.334 16	−544.328 25	98.3		
5p	−542.772 19	−544.748 30	105.3	256.6	255.7
6	−804.912 47				
6p	−805.358 55				260.1
7	−399.197 07	−400.671 86	78.9		
7p	−399.643 68	−401.096 96	86.5	259.1	260.5
8	−509.272 71	−511.154 81	99.8		
8p	−509.747 33	−511.609 21	107.0	277.9	276.2
9	−619.339 76				
9p	−619.818 13				278.2

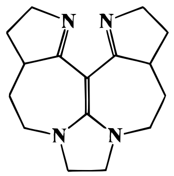
[a] The proton affinity PA(MP2) is calculated by employing the MP2(fc)/6-31G**//HF/6-31G* + ZPVE(HF/6-31G*) model.

tion of atomic and π-bond electron densities in bases and their redistribution in conjugate acids is therefore of considerable interest. It is worth mentioning that NH_2 groups attached initially to the CC endo double bond become planar upon protonation too, thus underlining a very important role of the nitrogen π-conjugation occurring in conjugate acids, which is discussed in more detail below. For that purpose we shall make use of the Löwdin symmetric partitioning technique of the mixed electron density.[37] It appears that a quite appreciable delocalization is present already in the three-membered ring in **1** as substantiated by the π-bond order of 0.36 found in the C(1)−C(2) bond. This value is increased to 0.50 after the proton attack. Concomitantly, the π-bond orders of the "localized" C(2)−C(3) and C(1)−N double bonds are significantly decreased in the protonated form. This effect is amplified in **3p**, where all three NH_2 groups become planar taking part in the π-delocalization, which leads to the highly pronounced stabilization of the resulting cation (vide infra). The same holds for the conjugate acid **4p** and the protonated form **7p**, where both rings undergo the aromatic stabilization. It follows that NH_2 groups underpin aromatization of the quinoid six-membered ring and/or of the cyclopropene moiety by releasing some electron density of their lone pairs, which in turn become more delocalized at the same time. Hence, in addition to aromatization effect, the final conjugate acids possess evenly distributed positive charge over entire molecules, which also contributes to the overall energetic stabilization.

This conjecture is supported by perusal of the atomic charges, which reveals that nitrogen atoms are slightly less negative after the proton attack. Nevertheless, they are still negatively charged possessing about 5.4−5.5 valence electrons. This finding deserves attention. The nitrogen atoms are namely tetravalent at the same time as evidenced by persistently high π-bond orders along the C−N bonds lying within a narrow range of 0.50−0.60. It follows that a common $N^+ H_2$ notation found in many textbooks is misleading, and that it should be replaced by the $[{=}NH_2]^+$ symbol, which indicates a more uniform distribution of the positive charge within this particular group and eventually over the whole molecule. The latter is indicative of the substantial final state relaxation effect already encountered in the inner-shell electron ejection processes monitored by ESCA.[38] Similar arguments were put forward by Greenberg et al., in discussing the electron density of nitrogen atom in NH_3 and NH_4^+.[39] It should be kept in mind that $[{=}NH_2]^+$ notation does not imply that exactly one positive charge is (semi)localized within the protonated imino grouping. Rather, it merely indicates that its H and N atoms have somewhat higher positive charges than in the initial neutral base (Table 1).

3.2. The Proton Affinities. Total molecular energies of bases and their conjugate acids are summarized in Table 2. Taking into account ZPVEs and MP2 results, one obtains pretty accurate estimates of the proton affinities. It is worth mentioning that the simple HF_{sc} model performs rather well too. Survey of the PA values shows that they increase along the series **1**−**9**. It appears that the basicity of iminocyclopropene is comparable to that of guanidine.[31] Methylation of the imino nitrogen yields

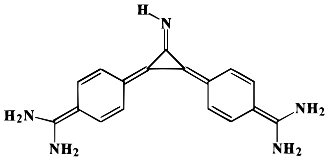
CHART 1



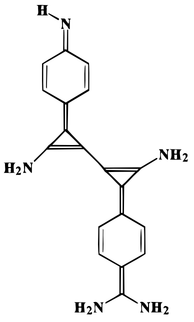
to an increase in the PA by 4.5 kcal/mol apparently due to enhancement of the electron density reorganization effect in the final state. It is credible to assume that substitution of a more bulky alkyl group would lead to further amplification of the basicity. Additional attachment of two methyl−amino groups at positions 2 and 3 increases the PA in **4** to 256.6 kcal/mol obviously due to a full aromatization of the three-membered ring as evidenced by equal bond distances in the protonated form (Table 1) and a uniform distribution of the π-bond orders. A pronounced relaxation effect also contributes to a high basicity. The conjugation involving NH$_2$ lone pairs plays apparently a pivotal role in this respect as mentioned earlier. It is interesting to note that even 2,3-diaminoiminocyclopropene **3** has a proton affinity by some 10 kcal/mol higher than that established for the archetypal proton sponge 1,8-bis(dimethylamino)naphthalene.[40] Triple methylation yielding to the derivative **4** provides additional increase in the PA by cca 6 kcal/mol. Is it possible to do better than that? Obviously, further enhancement of the basicity is expected in polycyclic systems such as **5** and **6**, which possess two or more cyclopropene moieties. Indeed, **5** has the PA value of 256.6 kcal/mol, which can be again easily increased to values above 260 kcal/mol by alkylation. Extended system **6** involving two methylenecyclopropene fragments has the PA value close to 260 kcal/mol, which can be amplified further by substitution of the bulky alkyl groups. This is remarkable because the most basic organic proton sponge−Schwesinger compound possessing vinamidine pattern within a pentacyclic system[41] (Chart 1) has the proton affinity about 270 kcal/mol.[42]

Recently, we have shown that quinodiimines exhibit high gas-phase basicity since protonation triggers aromatization of the six-membered quinoid ring.[31] It is of interest to examine the proton affinity of such a quinoid structure linked in a row to cyclopropene by an exocyclic double bond. One can expect that the proton attack at the imino nitrogen atom will spur aromatization of both rings in **7**−**9** in a domino fashion. This is indeed the case as evidenced by analysis of the relevant CC bond distances (vide supra) and very high PAs. They are 259 and 278 kcal/mol for **7** and **8**, respectively. Again, alkylation of system **8** will beyond doubt lead to very potent superbasic compounds. On the other hand, diamination leading to compound **9** does not exhibit higher PA as evidenced by the HF$_{sc}$ result of 278.3 kcal/mol. The reason behind it is a considerable crowding of NH$_2$ groups substituted at positions 3−6. Needless to say, construction of a branched chain by linking methylenecyclopropene moieties at positions C(4) and C(5) will inevitably provide even stronger organic superbases. It should be mentioned that in the protonated systems **7p**−**9p** there is a slight pyramidalization of the protonated imino group since the H−N−C(1)−C(2) dihedral angle is 7°. Within the context of the present study we examined the proton affinity of two additional composite systems **10** and **11** shown in Chart 2. Their proton affinities are estimated by utilizing AM1 semiempirial scheme via eq 3 in view of their size. The corresponding PA values are 265.8 and 287.0 kcal/mol for **10** and **11**, respectively. In both cases protonation occurs again at the imino nitrogen. It appears that the biscalicene motif in **11** yields to a highly basic system indeed. This is not surprising because compound **11** has an additional cyclopropene moiety compared to the extended system **10**. The difference in PA between **11** and **10** of 21 kcal/mol does illustrate very nicely the domino effect in the aromatization process taking place in the protonated forms.

CHART 2

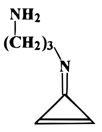


10

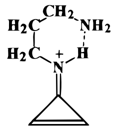


11

CHART 3



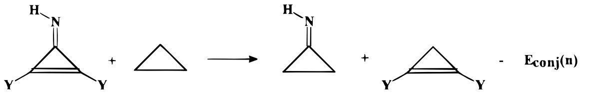
12



12p

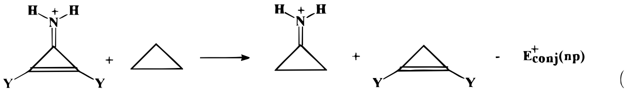
Although the aromatic stabilization represents the most important contribution to the proton affinity of the systems examined here, there are some other effects leading to the increased basicity. One of very interesting patterns of bonding so important in biological compounds is given by the intramolecular hydrogen bond formed upon protonation. For that purpose the proton affinity of **12** (Chart 3) is calculated at the HFsc level of theory. It appears that the PA of **12** is 248.6 kcal/mol thus being higher than that of the reference system **2** by 10 kcal/mol, implying that similar H-bonded chain could be useful in amplifying basicity of extended systems **5**−**11**. For example, the intramolecular crown generated by protonation, such as, e.g., that in **12p**, would yield to the PA of the modified system **11** close to a remarkable limit of 300 kcal/mol. It is of some interest to estimate the H-bond strength in **12p**. For that purpose we calculated the PA value of **12** in the zig-zag conformation of the side chain. The corresponding PA is 240.0 kcal/mol meaning that the hydrogen bond in **12p** is quite strong being 8.6 kcal/mol.

3.3. Protonation, Resonance, Aromaticity, and Rotation Barriers. Aromatization is apparently a very important mechanism which leads to potent organic bases provided by some planar cyclic π-electron networks. Therefore, it is in place to examine more closely its energetic consequences. For that purpose we shall focus attention to iminocyclopropene as a characteristic system and employ the corresponding homodesmic reactions.[43,44] Let's consider the initial conjugative interaction E_{conj} in the parent compound **1** and its derivative **3**. Appropriate homodesmic reactions read as follows:



(4)

where **n** stands for **1** and **3**, which correspond to Y=H and Y=NH$_2$, respectively. Notice that the conjugation energy is defined as a positive entity. The MP2(fc)/6-311+G**//HF/6-31G* model gives E_{conj} (**1**) = 15.7 kcal/mol and E_{conj} (**3**) = 25.8 kcal/mol implying that there is an appreciable conjugative stabilization in the parent system (**1**), which is further increased by the double amination at the CC endo-double bond in **3**. Analogously, the homodesmic reactions related to the imino protonated species take a form:



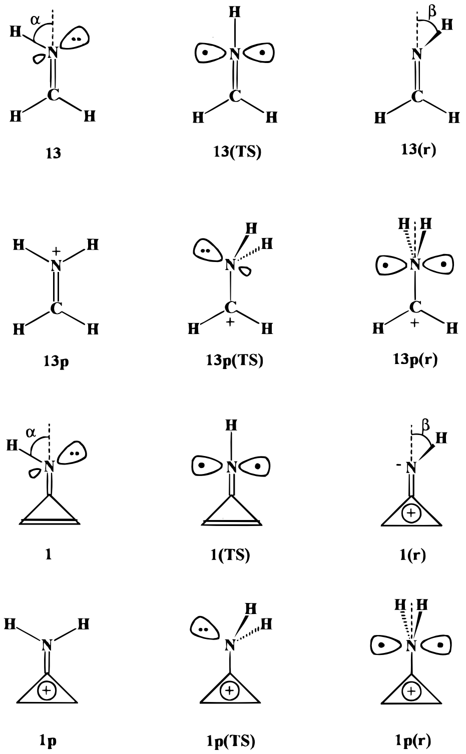
(5)

It appears that the conjugative stabilization is considerably increased as evidenced by E^{+}_{conj} (**1p**) and E^{+}_{conj} (**3p**), which assume values of 30.3 and 59.5 kcal/mol, respectively. Contributions of the resonance interactions to the proton affinity of **1** and **3** are thus 14.6 and 33.7 kcal/mol, respectively. It is noteworthy that virtually the same resonance stabilization energies are obtained by using a smaller basis set within the MP2(fc)/6-31G*//HF/6-31G* framework thus illustrating the well-known fact that the energy of homodesmic reactions are highly insensitive to details of the electron density distribution. More importantly, the resonance stabilization of (**3p**), which possesses a fully aromatic three-membered ring, is very close to the corresponding stabilization of the unsusbstituted cyclopropenyl cation estimated to be 59.1 kcal/mol by the G2 method.[45] Obviously, the electronic structure motif of iminocyclopropene should be very useful in tayloring potent organic superbases as illustrated here by the extended π-systems **5**−**11**. This is an important finding because 2,3-dialkyl and 2,3-diaryl derivatives of cyclopropeneimine have been synthesized already.[46]

The barriers of rotation of N−H bond in **1** and the [NH$_2$]$^+$ group in **1p** are of some interest since they are related to the energies of inversion and isomerization reactions, respectively, in some biologically important imines and their conjugate acids. Lehn et al.[43] have shown that the barriers of nitrogen inversion and rotation about the C=N bond in methyleneimine **13** (Chart 4) are 26−28 and 57 kcal/mol, respectively, as obtained by the double-ζ HF model.

Hence, the energy of inversion is lesser by factor 2 than the isomerization energy. We examined this problem at the MP2-(fc)/6-311+G** level of theory since isomerization and rotation energies of methyleneimine will serve as reference for cyclopropeneimine (**1**). The corresponding values were 30.7 and 47.1 kcal/mol, respectively. The former result reflects the rehybridization effect leading to a pure 2p$_{\mathrm{N}}$ AO occupied by the lone pair electrons, which is energetically unfavorable. It should be strongly pointed out that a qualitative discussion will be limited heretofore to dominating AOs only as if the calculations were performed by using a minimal basis set. The latter value is much higher being a consequence of a weakening of the C=N double bond, which is formed by poor overlapping between the hybrid AO of N and a 2p$_{\mathrm{c}}$ (π) AO of the carbon atom in the rotated perpendicular configuration **13(r)**. It should be mentioned that the N−H angle β in **13(r)** had to be fixed in order to prevent a collapse to the transition structure **13(TS)**. We put β to be 1/2 of the [H−N−H]$^+$ angle found in the fixed perpendicular configuration **13p(r)** of the protonated methyleneimine for comparative purposes.

CHART 4



In the protonated **13p** species the conformation possessing the rabbit ears NH$_2$ group is the transition structure **13p(TS)**. It is 73.6 kcal/mol above the most stable configuration **13p** since the double bond character is completely lost and a single conceivable stabilizing interaction is that of the hyperconjugation of NH$_2$ pseudo-π-orbital with the formal carbocationic center. The structure **13p(r)** exhibiting C_{2v} symmetry is even more unstable (81.0 kcal/mol) being a double saddle apparently because the lone pair electrons occupy a pure 2p$_{\mathrm{N}}$ AO. It is noteworthy that the destabilization energy of **13p(r)** is less than a double destabilization of the perpendicular configuration **13(r)**, which is persumably a consequence of a strong hyperconjugative interaction between NH$_2$ group and the formal C$^+$ center. The isomerization barrier of **1** is 26.1 kcal/mol, thus being lower than that of **13** by 4.6 kcal/mol. A plausible rationalization of a decrease in the isomerization hindrance can be found in the interaction between the lone pair and the empty Walsh orbital of appropriate symmetry of the cyclopropene ring in the transition structure **1(TS)**. The barrier for C=N−H rotation in **1** of 29.5 kcal/mol is significantly lower than in **13** because the lone pair of nitrogen in the perpendicular form donates some of its electron density to the carbocationic three-membered ring. This is reminiscent of an early interpretation of a low rotational barrier but high resonance energy in esters.[48] An analogous albeit much more pronounced effect is observed in the rotated protonated form **1p**, since the transition structure **1p(TS)** is only 28.3 kcal/mol higher in energy, whereas in the gauge system **13p(TS)** the barrier was as large as 73.6 kcal/mol. One is tempted to conlude that the hyperconjugative interaction between NH$_2$ antisymmetric combination of semilocal MOs and the cyclopropyl cation moiety is very strong indeed. The total energy of the perpendicular configuration **1p(r)** is higher than **1p(TS)** by 3.1 kcal/mol as expected in view of the thwarted rehybridization effect. It appears also that a difference in destabilization between **1p(r)** and **1(r)** is only 1.9 kcal/mol, which does not reflect a difference in the resonance energies between the parent system **1** and its conjugate acid **1p**. Rather, it is a result of a combined effect of a lower resonance energy in **1** and an effective lone pair pseudo-π back-bonding interaction between the lone pair and the cyclopropenyl ring cation. In contrast, the resonance energy in **1p** is large, but it is lost in the **1p(r)** configuration. The barrier is lowered, however, by hyperconjugation as mentioned above. An important role of the conjugation effect in **1p** in determining the C=N barrier for rotation is corroborated by the calculated energy of internal rotation of the $[NH_2]^+$ group in the protonated iminocyclopropane, where the aromatic stabilization is absent. For the perpendicular $[NH_2]^+$ configuration this energy is 64.8 kcal/mol thus being more than twice as large as that in **1p(r)**. It is noteworthy that the experimental barriers of rotation around C=N bonds in a variety of substituted cyclopropenylideneimonium salts, employing BF_4^- as a counterion, cluster around 25 kcal/mol.[49] This is in qualitative agreement with our estimate of the internal rotation barrier for **1p** of 31 kcal/mol.

4. Concluding Remarks

It is shown that iminocyclopropene exhibits a high gas phase basicity, which can be considerably enhanced by NH_2 groups attached to the C=C double bond and by subsequent substitution(s) by bulky alkyl group(s). The origin of the amplified susceptibility toward protonation was traced down to the aromatization of the three-membered ring coupled with the conjugation interactions with NH_2 groups. The latter release some of their lone pair electron density distribution thus enabling a uniform distribution of the positive charge over the whole molecule. Alkyl groups serve also as reservoirs of the electron density, which allow for the energetically very favorable reorganization of the electron density distribution triggered by protonation. The resonance stabilization in **1** and **3** after protonation is 30.3 and 59.5 kcal/mol, respectively. Since the corresponding stabilization energies in initial bases **1** and **3** are 15.7 and 25.8 kcal/mol, respectively, it appears that the corresponding resonance contributions to PAs are 14.6 and 33.7 kcal/mol. Consequently, the following important conjectures can be drawn: (1) the imino group is undoubtedly the most basic atomic grouping as far as the first row elements are concerned. (2) Its basicity is dramatically enhanced if it is attached to the cyclopropene moiety by the exocyclic double bond. (3) A substantial additional amplification of the basicity is obtained by strong electron releasing NH_2 group(s) substituted at proper positions. (4) Bulky alkyl groups provide not only protection of the π-electron system but they increase also the electron relaxation effect in the resulting conjugate acids at the same time. (5) Formation of a proper aminoalkane “crown” upon protonation attached to the imino group contributes about 10 kcal/mol to the proton affinity. It follows as a corollary that organic bases exhibiting predeterminated PA values could be designed utilizing an interplay of various judiciously selected substituents placed at specific molecular sites. Very potent organic superbases can be obtained by forming polycyclic π-systems involving cyclopropene moieties. The highest PA values in the present series of molecules were found, however, in calicene-like structures **7**−**11** possessing quinoid six-membered ring(s) and cyclopropene fragment(s). Particularly powerful organic superbases should be given by the system **11** possessing biscalicene structure and its subsequent derivatives. Finally, formation of the cyclic H-bonded diadem pattern generated by bending of an aminoalkane tale upon the imino nitrogen protonation as, for example, in **12** should additionaly contribute to high basicity of systems studied in this paper and of their off-springs.

Finally, it is shown that a strong resonance effect in **1p** dramatically diminishes the barrier of rotation around the $[C{=}NH_2]^+$ double bond.

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