Toward Organic Superbases: The Electronic Structure and the Absolute Proton Affinity of Quinodiimines and Some Related Compounds

Z. B. Maksić*,[†,‡] and B. Kovačević[†]

Quantum Organic Chemistry Group, Rudjer Bošković Institute, P.O. Box 1016, 10000 Zagreb, Croatia, and Faculty of Science and Mathematics, The University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

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Several molecular systems that may well serve as potent organic superbases are examined by using ab initio and semiempirical theoretical models. It is found that the imino group attached to the semiquinoid fragment or to a backbone of several quinoid six-membered rings exhibits a very high proton affinity (PA). It is found that the reason behind their amplified basicity is appreciable aromatization of the quinoid building blocks upon protonation. The underlying mechanism in extended systems is that of the aromaticity spin-off effect, triggered by the proton attack at the imino N atom and spread along the quinoid ribbon in a typical domino fashion. It yields an increase in the PA as high as roughly 20 kcal/mol per the quinoid ring. Susceptibility toward the proton attack is further amplified by the alkyl substitution at the imino nitrogen atom and by additional substitution of the amino groups at specific positions within the framework of the quinoid building block(s). It is stressed that synthesis of the studied systems might provide very potent organic superbases.

1. Introduction

Strong organic (super)bases and particulary the so-called molecular proton sponges (PS) are subject matter of continuous interest. A paradigmatic 1,8-diaminonaphthalene (DMAN) system was discovered by Alder et al.[1] 30 years ago. Since then tremendous progress has been made in the field centered mainly around the use of PSs in acid−base reactions.[2] Recently, it was pointed out that proton sponges belonging to a class of poly(ethyleneimines) might play a key role in a new gene therapy.[3,4] It is not suprizing that numerous experimental[5−10] and theoretical[9−13] studies have been performed in the past in order to elucidate properties of these strong bases that might shed more light on their reactivities. Most of the systems considered so far were diamines. Recently, the research interest has been shifted to some simple imines,[14] polyfunctional formamidines[15] and cyclic and acyclic guanidines[16] with a tendency to extend the existing basicity scale[17] toward the superbasic values. Continuing our interest in the proton affinity of aromatic compounds,[18] we felt it worthwhile to examine PAs of some quinodiimines, which could provide very potent bases. For this purpose we employ a relatively simple MP2(fc)/6-311+G**//HF/6-31G*+ZPVE(HF/6-31G*) theoretical model as a research tool, since it proved useful in reproducing PAs of aminoalkanes, aniline, and pyridine.[19] In fact, it will appear that the model above can be further simplified and reduced to the HF/6-31G* calculations only, if a proper scaling procedure is used, in line with our earlier work on the proton affinity of large aromatic molecules.[20] The scaled Hartree−Fock model will be then utilized in predicting PAs of poly(quinodiimines) together with an analogous AM1 procedure. Anticipating forthcoming results, one can say that this family of compounds represents a class of strong superbases.

2. Methodology

2.1. Choice of the Theoretical Model. We found that the MP2(fc)/6-311+G**//HF(6-31G*) + ZPVE(HF/6-31G*) model described the proton affinity of nitrogen atoms in a satisfactory way.[18] It includes optimization of the structural parameters and calculation of the harmonic vibrational frequencies at the HF/6-31G* level. This approach ensures that optimized structures correspond to the equilibrium geometries being practical enough at the same time. The harmonic frequencies enable estimates of the zero-point vibrational energies (ZPVE), which are subsequently scaled by the common empirical factor 0.89.[21] Perturbational Møller−Plesset single point calculation recovers the main portion of the correlation energy employing for this purpose the HF/6-31G*-optimized structural parameters. Proton affinities are calculated employing the general equation

$$\mathrm{PA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha - (\Delta\mathrm{ZPVE})_\alpha \qquad (1)$$

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. Here, B and BH^+ denote the base in question and its conjugate acid, respectively, and α stands for the site of the proton attack. Although the MP2(fc)/6-311+G**//HF/6-31G*+ZPVE(HF/6-31G*) model (in a shorthand notation MP2) is conceptually and computationally relatively simple, it is still too costly if large aromatics are to be studied. It is gratifying, however, that vibrational analyses and the final single-point MP2(fc)/6-311+G** calculations can be omitted without significant loss in accuracy.[20] In a nutshell, the corresponding simplified model is based on an observation that a change in the ZPVE upon protonation is fairly constant. Concomitantly, it can be safely absorbed in the least-squares fitting parameters relating the proton affinity calculated at the MP2 level with a difference in the electronic energy $\Delta E_{\mathrm{el}}(\mathrm{HF/6\text{-}31G^*})_{\mathrm{N}}$. The

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* Corresponding author. Fax: +385-1-4680084. E-mail: zmaksic@spider.irb.hr.

[†] Rudjer Bošković Institute.

[‡] The University of Zagreb.

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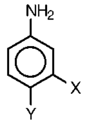
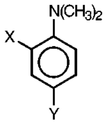
TABLE 1: Proton Affinity of Some Substituted Anilines As Obtained by Theoretical MP2 and HF$_{sc}$ Models Accompanied by the Corresponding Changes in the ZPVEs (in kcal)

X	Y	ΔE_{el} (HF/6-31G*)	ΔE_{el} (MP2)	ΔZPVE	PA(MP2)	PA(HF$_{sc}$)	δ
							
CN	H	212.68	207.40	8.6	198.8	200.2	−1.4
H	CN	210.44	207.08	8.6	198.5	198.2	0.3
CH_3	H	225.52	220.25	8.8	211.4	211.7	−0.2
H	CH_3	226.42	220.43	8.8	211.6	212.5	−0.8
F	H	218.07	213.53	8.7	204.8	205.0	−0.2
H	F	221.00	215.04	8.8	206.2	207.6	−1.4
OH	H	223.26	219.14	8.7	210.4	209.6	0.8
H	OH	226.89	220.19	9.0	211.2	212.9	−1.7
NH_2	H	226.13	222.04	8.5	213.5	212.2	1.3
H	NH_2	231.30	224.05	9.7	214.3	216.8	−2.5
NO_2	H	211.32	206.39	8.7	197.7	199.0	−1.3
H	NO_2	207.35	206.09	8.6	197.5	195.5	2.0
CHO	H	219.30	212.90	8.8	204.1	206.1	−2.0
H	CHO	215.13	210.88	8.6	202.3	202.4	−0.1
OCH_3	H	225.12	221.12	8.6	212.5	211.3	1.2
H	OCH_3	228.45	222.16	8.8	213.4	214.3	−0.9
							
H	H	239.15	234.59	9.0	225.6	223.8	1.8
H	NH_2	244.07	240.17	9.0	231.2	228.2	2.9
NH_2	H	244.11	238.41	8.7	229.7	228.3	1.5

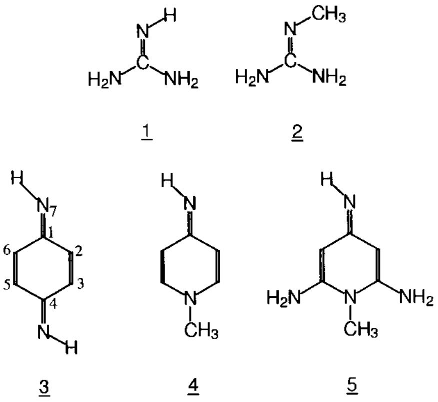


Figure 1. Schematic representation of guanidine **1**, methylguanidine **2**, monocyclic quinodiimine **3**, and semiquinodiimines **4** and **5**.

TABLE 2: Proton Affinity of Some Imines and Diimines As Predicted by Theoretical MP2 and HF$_{sc}$ Models as Well as the Changes in the ZPVE Induced by Protonation (in kcal/mol)

molecule	ΔE_{el} (HF/6-31G*)	ΔE_{el} (MP2)	ΔZPVE	PA(MP2)	PA(HF$_{sc}$)	δ
1	252.00	240.42	6.7	233.7	235.3	−1.6
2	256.41	244.40	7.2	237.2	239.2	−2.0
3	239.91	229.63	7.7	221.9	224.4	−2.5
4	275.07	265.96	8.5	257.5	255.9	1.6
5	286.72	275.78	8.0	267.8	266.3	1.5

latter gives a difference in the total electronic energy between the initial base and its conjugate acid protonated at nitrogen. The final formula reads as

$$\mathrm{PA(B_N)} = A_1 \cdot \Delta E_{el}(\mathrm{HF/6\text{-}31G^*})_N + A_2 \qquad (2)$$

It appears that only HF/6-31G* calculations have to be executed. This procedure will be referred to as the HF$_{sc}$ model. An analogous scheme can be designed for the semiempirical AM1 approach (vide infra). Finally, all computations were performed by making use of GAUSSIAN[22] and GAMESS[23] programs.

2.2. The Proton Affinity of Substituted Anilines and Imines. It is well-established by now that aniline protonates at nitrogen.[19] Effects of various ring substituents on the PA of aniline are examined here, and the corresponding MP2 results are given in Table 1. The studied substituents cover a wide range of electron-releasing and -withdrawing groups. Their influence on the PA of aniline (209.5 kcal/mol) is relatively small, however. The strongest activating substituents are NH_2 and OCH_3, whereas the most powerful deactivators are NO_2 and CN as expected. Substitution of two CH_3 groups at nitrogen enhances susceptibility of aniline toward the proton attack, thus reflecting a well-known electron reorganization effect upon protonation and creation of a positive “hole”.[19] Additional substitution of an amino group in aniline at ortho or para positions increases the proton affinity to a respectable 230 kcal/mol. Since imines are objects of our primary interest in this work, we list also the proton affinities of guanidine, its methyl derivative, and two imines possessing quinoid-like structure (Figure 1). Perusal of data presented in Table 2 shows that systems **4** and **5** are potent bases, which is very interesting per se and deserves to be discussed later in some more detail. The MP2 results summarized in Tables 1 and 2 serve a purpose of providing reliable data necessary to obtain explicit HF correlation indicated by eq 2. The least-squares fit parameters are $A_1 = 0.8924$ and $A_2 = 10.4$ kcal/mol if ΔE_{el} and the resulting proton affinity PA(B$_N$) are given in kcal/mol. The quality of this correlation is very good as evidenced by the correlation coefficient $R = 0.997$ and low average absolute error $|\delta|_{av} = 1.3$ kcal/mol. It is important to note that ΔZPVE values are fairly constant, their average being $(\Delta\mathrm{ZPVE})_{av} = 8.5$ kcal/mol. The corresponding average absolute deviation is as low as 0.4 kcal/mol. It is worth mentioning that the gas-phase PA of guanidine was determined by FT-ICR mass spectrometry recently.[10] The observed value (233 kcal/mol) is in good agreement with our PA(MP2) and PA(HF$_{sc}$) estimates of 233.7 and 235.2 (in kcal/mol), respectively, thus lending additional credence to the simple HF$_{sc}$ model. The latter will be employed as a suitable vehicle in exploring PAs of large polycyclic systems. We estimate that the average error of the HF$_{sc}$ model is ±2 kcal/mol. We have tried also to find a correlation between the MP2 proton affinities and the enthalpies of formation offered by the semiempirical AM1 method, since this approach could be useful in calculating the PA of very large planar systems. For this purpose one makes use of ΔH_f (AM1) enthalpies of initial bases and their conjugate acids, which has led finally to a formula of the following form:

$$\mathrm{PA(B_N)} = 1.0948\,\Delta\Delta H_f(\mathrm{AM1})_N + 381.0\ \mathrm{(kcal/mol)} \qquad (3)$$

The quality of the correlation is somewhat lower ($R = 0.993$ and $|\delta|_{av} = 1.8$ kcal/mol), but it is obvious that the AM1 scheme should be quite reliable in estimating PAs of extended systems if employed with due care. In this connection it should be pointed out that molecules given in Tables 1 and 2 possessing methyl group(s) attached directly to amino or the imino protonated nitrogens have been excluded from correlation. Namely, the highly approximate AM1 scheme is unable to describe properly the alkyl effect on the PA. Furthermore, it appears that the PA value of the alkyl-substituted amino or imino nitrogen atom is diminished in disagreement with ab initio

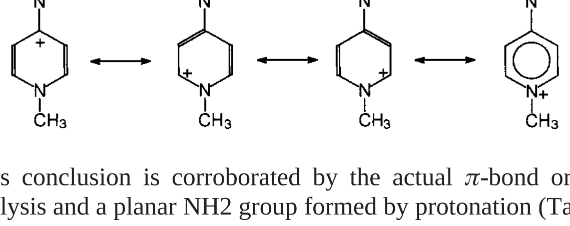
TABLE 3: Selected Structural Parameters of Bases 3 and 6 and Their Conjugate Acids, 3p and 6p, s-Characters of the NBO Local Hybrid Orbitals, Lövdin π-Bond Orders, and Charge Densities As Obtained by the HF/6-31G* Wave Functions[a]

					electron density		
molecule	bond or angle	distance	s-character	π-bond order	atom	total	π
3	C(1)−N(7)	1.260	38.4−43.6	0.88	C(1)	5.92	0.84
	C(1)−C(2)	1.478	31.4−31.1	0.28	C(2)	6.14	0.93
	C(2)−C(3)	1.325	38.1−38.4	0.90	C(3)	6.19	0.99
	C(3)−C(4)	1.479	31.5−34.0	0.28	C(4)	5.92	0.84
	N(7)−H	1.006	23.3	0.00	N(7)	7.38	1.16
					H(N7)	0.73	0.00
	H−N(7)−C(1)	111.8					
	C(2)−C(1)−C(6)	116.4					
3p	C(1)−N(7)	1.298	30.6−41.0	0.69	C(1)	5.76	0.65
	C(1)−C(2)	1.455	34.2−30.4	0.37	C(2)	6.20	1.05
	C(2)−C(3)	1.331	37.9−37.5	0.87	C(3)	6.06	0.82
	C(3)−C(4)	1.476	31.6−33.8	0.28	C(4)	5.96	0.91
	N(7)−H	1.000	29.4	0.00	N(7)	7.36	1.58
					H(N7)	0.66	0.00
					N(10)	7.24	0.98
	H−N(7)−H	116.4			H(N10)	0.70	0.00
	C(2)−C(1)−C(6)	120.6					
6	C(1)−N(13)	1.263	34.5−43.4	0.87	C(1)	5.92	0.83
	C(1)−C(2)	1.469	33.7−32.0	0.30	C(2)	6.19	0.99
	C(2)−C(3)	1.329	38.1−38.1	0.88	C(3)	6.14	0.95
	C(3)−C(10)	1.470	32.2−30.9	0.33	C(10)	6.00	0.95
	C(9)−C(10)	1.360	37.8−37.8	0.77	N(13)	7.40	1.18
	N(13)−H	1.006	23.0	0.00	H(N13)	0.74	0.00
	H−N(13)−C(1)	111.6					
	C(2)−C(1)−C(12)	115.1					
	C(1)−C(2)−C(3)	122.2					
6p	C(1)−N(13)	1.321	30.2−40.3	0.59	C(1)	5.79	0.71
	C(1)−C(2)	1.423	34.8−32.1	0.47	C(2)	6.23	1.09
	C(2)−C(3)	1.350	36.8−36.9	0.78	C(3)	6.06	0.83
	C(3)−C(10)	1.437	33.4−32.1	0.45	C(10)	6.09	1.09
	C(9)−C(10)	1.396	35.6−36.2	0.63	C(4)	6.18	1.01
	C(4)−C(9)	1.463	31.6−31.5	0.37	C(5)	6.10	0.87
	C(4)−C(5)	1.332	37.8−37.8	0.87	C(6)	5.95	0.89
	C(5)−C(6)	1.470	31.8−33.8	0.29	C(9)	5.84	0.71
	C(6)−N(14)	1.259	34.4−43.3	0.88	N(13)	7.43	1.68
	N(13)−H	0.996	29.8	0.00	N(14)	7.28	1.03
	N(14)−H	1.006	24.0	0.00	H(N13)	0.67	0.00
					H(N14)	0.71	0.00
	H−N(13)−H	116.8					
	C(2)−C(1)−C(12)	118.7					
	C(1)−C(2)−C(3)	120.2					

[a] Distances in Å, angles in deg.

results, available experimental data, and chemical intuition. However, even in this case one can use relation 3 and add an off-set value of ca. 5 kcal/mol per each CH_3 group, which will remedy the above-mentioned shortcoming.

2.3. Polycyclic Quinoimines and Quinodiimines—The Domino Effect. *2.3.1. Structural Features.* The high basicity of molecules **4** and **5** can be traced down to significant aromatization of the semiquinoid structure upon protonation. Concomitant thermodynamic stabilization may be qualitatively described by the resonance structures of **4**:



This conclusion is corroborated by the actual π-bond order analysis and a planar NH2 group formed by protonation (Table 3). For interpretative purposes we shall use natural bond hybrid's s-characters, Löwdin π-bond orders, and Löwdin electron densities.[24] Perusal of the presented data for characteristic systems **3** and **6** reveals some interesting features occurring upon protonation. There is a considerable electron density drift toward the protonated nitrogen, which in turn retains practically all of its electron population even after protonation. Such a strong relaxation effect is characteristic for ESCA chemical shifts taking place after ejection of an inner-shell electron.[25] This statement deserves a brief disgression. In classical (Lewis) bonding theory the tetracoordinated nitrogen atom is possible only if one electron of the lone pair is released yielding the N^+ cation capable of binding four ligands. Our calculations show that the classical picture is misleading, since the protonated N atom has practically the same electron density as the unprotonated one in the neutral base. In fact, the N(7) atom in **3p** has the π-bond order $\cong$ 0.7 along the C(1)=N(7) partial double bond, implying that it is a tetravalent atom indeed. It follows that the N^+ representation of the tetravalent nitrogen atom widely used in textbooks of organic chemistry should be taken *cum grano salis*.

An obvious rehybridization effect is found at the protonated N(7) atom (Table 3). The in-plane $sp^2(\sigma)$ lone pair disappears upon formation of a new N−H bond. It is interesting to note that the electron population of the π-AO_N in **3p** is increased by 0.42e assuming a partial π-lone pair character. This is obviously a consequence of the electron density shift toward the protonated

TABLE 4: Proton Affinity of Some Polyquinoid Imines and Diimines That Provide Good Candidates for Organic Superbases (in kcal/mol) As Predicted by the Scaled HF and AM1 Models

PA	6	7	8	9	10	11
HF_{sc}	242.0	293.9	299.6			
$AM1_{sc}$	242.6	294.2	298.1	295.3	315.3	335.3

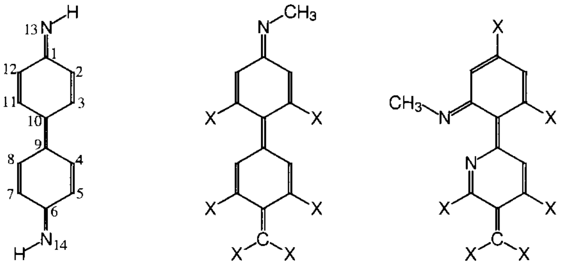
nitrogen. Changes in the bond π-electron distribution triggered by protonation are easily visualized by examining the relevant π-bond orders. One observes a highly localized character of the quinoid structures in the initial bases **3** and **6**. An increased π-electron delocalization can be clearly identified in the respective conjugate acids **3p** and **6p** (Table 3). It can be quantified by a simple localization index $L_m(d)$[26] in view of the intimate relationship between the π-bond orders and bond distances in delocalized systems:

$$L_m(d) = \sum_n |d_{cc}^{(n)} - \bar{d}_{cc}|/\text{Å} \tag{4}$$

Here $\bar{d}_{cc}$ denotes the average CC bond distance of the six-membered ring and summation is extended over the aromatic perimeter. Further, m stands for the molecule in question while n signifies a particular CC bond. Obviously, $L_m(d)$ is zero for a perfectly aromatic molecule. Its increase, on the other hand, reflects the partial π-electron localization and the concomitant aromaticity defect. The localization indices $L_{\mathbf{3}}(d)$ and $L_{\mathbf{3p}}(d)$ are 0.41 and 0.35, respectively, thus reflecting a decrease in the aromaticity defect in the protonated **3p** form. Aromatization of the latter system is reflected also in the C−C−C bond angles within the six-membered ring, which become very close to 120°. It is important to note that both the bond distances and the corresponding π-bond orders presented in Table 3 show that the delocalization in the region opposite to the protonated NH group in **3p** is relatively little influenced by protonation. This is a consequence of a fact that the ═NH group is not suitable for accommodation of the positive π-charge as it can be easily established by examining the relevant resonance structures. Protonation at one of the imino nitrogens in **6** leads to aromatization of the corresponding six-membered fragment and to a subsequent spin-off aromatic stabilization effect in the second planar quinoid ring. It is plausible that this domino effect will increase the PA (vide infra). The aromaticity spillover effect is faithfully reflected in the localization indices. In planar polycyclic systems the total π-bond fixation is obtained by summation over all rings

$$L_m^{t}(d) = \sum_r L_m^{r}(d) \tag{5}$$

where r denotes a particular ring within the extended system. In the initial base **6** both ring fragments are equivalent, contributing 0.38 each to the total localization index $L_{\mathbf{6}}^{t}(d)$. One observes that each ring in **6** is somewhat more delocalized than in the parent system **3**. Delocalization in the ring nearest to the protonated nitrogen in **6p** is very pronounced as evidenced by a low $L_{\mathbf{6p}}^{(1)}(d) = 0.21$ value, whereas the second ring exhibits delocalization virtually equal to that found in **3p** since $L_{\mathbf{6p}}^{(2)}(d) = 0.35$. One concludes that the aromatic stabilization effect in the remote quinoid ring is less pronounced than in the ring nearest to the protonation site. Finally, it is noteworthy that the atomic π - -populations in the protonated species **3p** and **6p** follow the π-electron distribution pattern as offered qualitatively by the leading resonance structures, which can be easily verified. The geometric and electronic features of bases **3** and **6** and their conjugate acids are typical also for more complex systems discussed in this paper.



6 7 8

Figure 2. Schematic representation of polycyclic quinoimines and quinodiimines that exhibit very high basiciy (X = NH_2).

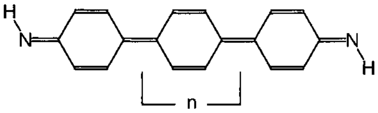


Figure 3. Schematic representation of the quinoid ribbon diimines, which make good candidates for organic superbases (molecules with n = 3, 4, and 5 are denoted by **9**, **10**, and **11**, respectively).

Proton Affinity. Analysis presented above shows that one can expect very high basicity of molecules **6** and **7**. This is indeed the case as revealed by the HF_{sc} and $AM1_{sc}$ results (Table 4). Compound **7** underlines importance of the NH_2 groups substituted at particular positions on the six-membered ring perimeter. They increase the conjugative propensity of the planar systems thus enhancing the relaxation effect as easily found out by examining the resonance structures in question. It appears that the amino group is capable of accommodating the positive charge, thus increasing the classical valence of the protonated nitrogen atom by one unit. This leads to an enlarged double-bond character in the $C{=}NH_2^+$ fragment. The estimated proton affinity of **7** (293.9 kcal/mol) comes close to a threshold of 300 kcal/mol, which we tenatively set up as a criterion of the superbasicity. An obvious way to increase the PA further would be to combine the principle of aromatization with the hydrogen bonding between the newly created N−H bond in the protonated form and the rest of the molecular system. This feature occurs, e.g., in compound **8**, where the hydrogen bond bridge between the imino group and the pyridine-like nitrogen is formed. The corresponding PA value is increased, being ≅300 kcal/mol (Table 3) as expected.

Generalization of the aromatization principle is straightforward. It is obvious that very strong superbases can be obtained by the domino effect in systems involving three or more quinoid fragments (Figure 3). The proton affinity of the linear quinoid ribbon systems **9**, **10**, and **11** involving five, six, and seven quinoid building blocks, respectively, assumes values 295.3, 315.3, and 335.3 (in kcal/mol) as offered by the $AM1_{sc}$ scheme. One observes that there is an increase in the PA of about 20 kcal/mol per quinoid building block, which compares with a difference of 17 kcal/mol between PAs of systems **3** and **6**. Two comments are in place here. Since the most recent estimate of the aromatic stabilization of benzene estimated by homodesmic reactions is 21−22 kcal/mol,[2,2] one concludes that very substantial aromatic stabilization of the quinoid fragment takes place upon protonation. Second, it should be pointed out in this connection that the aromatization of the second six-membered ring in **6** is less pronounced because the positive charge cannot be placed at the unprotonated imino nitrogen as discussed earlier. However, it is safe to conclude that the contribution of the nonpheripheral quinoid structures to the resulting proton affinity is approximately 20 kcal/mol. Utilizing a common knowledge about the influence of various substituents on the PA, it follows as a corollary that the basicity of superbases **10** and **11** could be further amplified by the following: (a) alkyl substitution at the imino nitrogen. The larger alkyl groups will yield the larger proton affinity. (b) Attachment of NH_2 groups at six-membered rings on specific positions. (c) Last but not least, inclusion of additional quinoid building blocks. The question arises whether this family of molecules can be synthesized. The search through the literature has revealed that derivatives of compounds of the type **3** and **6** have been obtained already[29,31] and that their protonation easily occurred in acidic medium.[32] It is plausible to assume that systems **9**−**11** and higher homologues are prone to chemical synthesis, which should provide powerful organic superbases. More experimental work along these guidelines would be highly desirable.

3. Conclusion

We have shown that there is an excellent correlation between the proton affinity of nitrogen atom in chemical environments obtained by the MP2(fc)/6-311+G**//HF(6-31G*)+ZPVE(HF/6-31G**) model and by simple HF/6-31G* calculations. This finding has led to the efficient HF_{sc} computational procedure, which enabled theoretical estimates of PA values in large systems involving several quinoid rings and possessing several imino and amino substituents. A similar albeit somewhat less accurate scheme is found at the semiempirical AM1 level, thus increasing the range of feasibility of theoretical models. It appears that the approximate HF_{sc} scheme reproduces very well available experimental data including guanidine. The imino group in the latter compound exhibits a high PA value, which is subsequently reinforced in semiquinoid systems such as **4** and **5**. A dramatic amplification of the intrinsic basicity is found in polyquinoid imines or diimines **7**−**11**, which provide good candidates for organic superbases. The underlying mechanism behind their high PA is indentified as aromatic stabilization of the quinoid building block upon protonation of the imine nitrogen atom being as large as approximately 20 kcal/mol per ring. The resulting intrinsic basicity is extremely high as a consequence of the aromatic spin-off domino effect and additivity of the aromatic stabilization energies. Bulky alkyl substituent at the site of the proton attack (imino group), NH_2 attachment at specific positions in the quinoid fragments, and intramolecular hydrogen bonding in specific structural arrangements may well lead to even stronger superbases. To conclude, systems examined in the present theoretical work as well as related even more extended systems not explored as yet deserve attention. Their synthesis and experimental verification of their basicity would be highly desirable.

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