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The proton affinity of some extended π-systems involving guanidine and cyclopropenimine subunits

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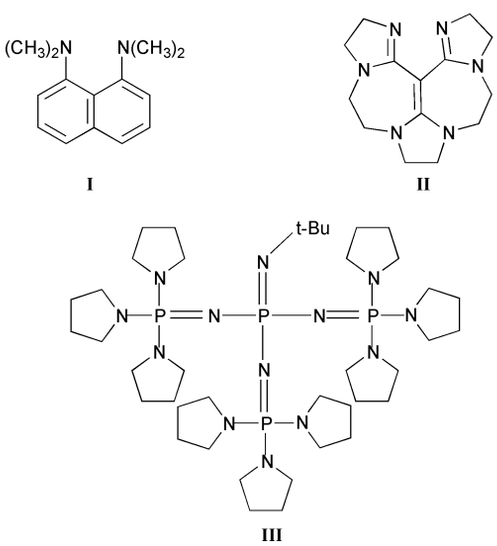
The proton affinity (PA) of some extended π-electron systems with guanidine and cyclopropenimine structural motifs is explored by theoretical MP2 and HF_{SC} models. It is shown that some of the studied molecules should exhibit higher gas-phase basicity than the Schwesinger proton sponge **II**, which is considered to be one of the most powerful organic superbases. The origin of the increased basicity is traced to a dramatic resonance effect triggered by the protonation. It is interesting to note that the examined compounds possess higher PAs than their polyguanide counterparts. The reason behind this is the well-established fact that three-membered rings undergo aromatization in the conjugate acids form. The important role of substituents in determining high inherent basicities is underscored.

Introduction

Notwithstanding its size, the proton plays a fundamental role in many biochemical processes, not to mention its participation in acid–base chemistry.[1–4] It is also a useful probe in studying the essential features of aromatic electrophilic substitution reactions[5–7] and a diagnostic tool in determining some important properties like hydrogen-bond strength[8] and ionization energy.[9] It is therefore not surprising that considerable effort has been invested in measuring[10–12] and computing[13–17] proton affinity (PA). Significantly, PA is intimately related to the intrinsic basicity of compounds in the gas phase, which is central to the understanding of the reactivity of bases. Particular attention has been focused on strong neutral organic bases and proton sponges. Compared to ionic bases, these have some distinct advantages, since they require milder reaction conditions while possessing better solubility.[18] Proton sponges have found a wide range of applications in organic synthesis in base-mediated transformations.[19] A paradigmatic 1,8-bis(dimethylamino)naphthalene (DMAN) system **I** was discovered by Alder some thirty years ago[20] and since that time considerable progress has been made in this field.[21] The most powerful organic bases so far are the Schwesinger proton sponges **II**[22] and **III**.[23] Our theoretical calculations of the PA values of **I**, **II** and **III** are 245.5, 269.5 and 301.0 kcal mol^{-1}, respectively[24] (in our treatment the *t*-Bu group of the latter compound was replaced, however, by a CH_3 in order to simplify computations).

Apparently, the imino group is a stronger proton attractor than the amino group, if the former is a part of a conjugated system. Our work in engineering new strong (super)bases has resulted in a simple and efficient strategy consisting of several stages: (a) identification of an intrinsically strong basic functional group (imino moiety); (b) selection of suitable molecular fragments serving as imino group carriers (cyclopropenimine, 2,5-dihydropyrrolimine, quinonimine and guanidine subunits); (c) exploitation of the substituent effect by placing suitable substituents (NH_2, OCH_3) in suitable positions and (d) use of special effects, like intramolecular hydrogen-bonding stabilization of the conjugate acid. The cyclic carrier subunits mentioned above undergo aromatization upon protonation, leading subsequently to stabilized conjugate acids and to increased basicity of the initial compound. Particularly enhanced basicities are obtained by aromatic tandem (two subunits) and domino (several subunits) effects.[25,26] Similarly, protonation triggers a very strong resonance effect in the conjugate acids of polyguanides, in particular if they are bifurcated near the protonation site.[27] Even the constitutive building block, guanidine, exhibits resonance stabilization in its protonated form,[27] which is as high as 24–27 kcal mol^{-1}. This is comparable to the aromatic stabilization of the archetypal benzene.[27] It is important to realize that the structural and bonding patterns embodied in motifs (a)–(d) are additive in nature. Consequently, we can use them in the tailoring of organic (super)bases as if they were Lego bricks, in order to obtain basicities within a certain desired range. In the present work we examine combinations of guanidine and cyclopropenimine moieties forming extended π-systems possessing high intrinsic basicities.



I II III

Methodology

Proton affinities are computed in a standard way [eqn. (1)]:

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$$PA(B_\alpha) = (\Delta E_{el})_\alpha + (\Delta ZPVE)_\alpha \quad (1)$$

$$(\Delta E_{el})_\alpha = E(B) - E(B_\alpha H^+) \quad (2)$$

$$(\Delta ZPVE)_\alpha = ZPVE(B) - ZPVE(B_\alpha H^+) \quad (3)$$

Eqns. (2) and (3) give the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively. Here B and $B_\alpha H^+$ denote the base in question and its conjugate acid, respectively, while α stands for the site of proton attack. The search of the Born–Oppenheimer energy hypersurfaces was performed at the economical Hartree–Fock level employing the 6-31G* basis set. The minima on the hypersurface corresponding to optimal geometries are verified by vibrational analyses at the same level. The corresponding frequencies are used in deriving the ZPV energies by applying a common scale factor, 0.89, as usual. The final single point calculations take into account the correlation energy effect at the Møller–Plesset (MP) perturbation level of theory, where the series is terminated after the second order correction. This gives rise to the MP2(fc)/6-311+G**//HF/6-31G* + ZPVE(HF/6-31G*) model. A very important detail of the approach is the use of the 6-311+G** basis set in the final calculation to ensure a proper description of the nitrogen lone pair. Although the MP2 formalism is applicable in quite large systems, the corresponding computations sometimes exhibit convergency problems. It is gratifying that a much simpler scaled Hartree–Fock (HF_{SC}) model[25] performs almost equally well with only a small sacrifice in accuracy [eqn. (4)] where it is tacitly assumed that

$$PA(B)_N = 0.8924\Delta E_{el}(HF/6\text{-}31G^*)_N + 10.4 \quad (kcal\ mol^{-1}) \quad (4)$$

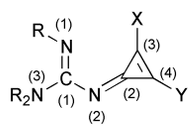
the proton attacks a nitrogen atom. The difference ΔE_{el}(HF/6-31G*) refers to the difference in the total molecular energy between a base and its conjugate acid. The high quality of the correlation [eqn. (4)] against the MP2 proton affinities is reflected in the high coefficient $R = 0.997$ and the low average absolute error 1.3 kcal mol^{-1}.[25] All calculations are performed by using GAUSSIAN 94 and GAMESS programs.[28,29]

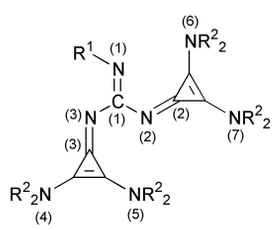
Results and discussion

The studied molecules **1**–**7** are depicted in Fig. 1. They encompass systems involving the central guanidine unit substituted by one or two cyclopropenimine fragments. The amino groups increase the conjugation effect, whereas the alkyl groups enhance the relaxation of the electron cloud upon protonation, serving as reservoirs of electron density (*vide infra*). Representative structural parameters for molecules **1**–**3** are given in Table 1. Changes in the bond distances induced by protonation in **1** and **3** are paradigmatic; they will be discussed in some detail. Protonation at N1 stretches and contracts the bond lengths in both systems in an alternating fashion as predicted by Pauling's resonance structures with one notable exception: the three-membered ring, which tends to achieve equal bond distances. For instance, the C1–N1 bond is elongated, whereas C1–N2 is considerably shortened in line with the resonance effect propagating along the N1–C1–N2–C2 backbone in systems **1H$^+$(N1)** and **3H$^+$(N1)**. The uniformity of the bond lengths in the three-membered ring in **3H$^+$(N1)** is in full agreement with its complete aromatization. Another notable feature is the fact that all C(sp^2)–N(sp^3) bond distances are substantially reduced due to a strong resonance interaction between the nitrogen lone pair and the π-network. This is corroborated by the simultaneous planarization of NH_2 groups in **3H$^+$(N1)**. The degree of pyramidalization (DP) of nitrogen atoms can be defined by eqn. (5),[30] where the summation is extended over all bond angles α_i (in degrees) of the apical nitrogen. The DP

Table 1 Selected bond distances (Å) and dihedral angles (°) of compounds **1**–**3** and their protonated forms as obtained by the HF/6-31G* model

	1	**1H$^+$(N1)**	**1H$^+$(N2)**
d(C1–N1)	1.268	1.330	1.246
d(C1–N3)	1.376	1.317	1.363
d(C1–N2)	1.396	1.339	1.432
d(C2–N2)	1.268	1.292	1.305
d(C2–C3)	1.398	1.389	1.365
d(C2–C4)	1.399	1.380	1.369
d(C3–C4)	1.321	1.328	1.332
N1–C1–N2–C2	4.5	20.1	7.8
	2	**2H$^+$(N1)**	**2H$^+$(N2)**
d(C1–N1)	1.270	1.333	1.247
d(C1–N3)	1.381	1.322	1.367
d(C1–N2)	1.389	1.329	1.422
d(C2–N2)	1.278	1.307	1.320
d(C2–C3)	1.380	1.363	1.341
d(C2–C4)	1.403	1.391	1.382
d(C3–C4)	1.336	1.352	1.355
d(C4–N)	1.331	1.307	1.307
N1–C1–N2–C2	2.7	10.4	6.0
	3	**3H$^+$(N1)**	**3H$^+$(N2)**
d(C1–N1)	1.280	1.353	1.255
d(C1–N3)	1.378	1.326	1.364
d(C1–N2)	1.377	1.310	1.408
d(C2–N2)	1.292	1.327	1.340
d(C2–C3)	1.383	1.366	1.352
d(C2–C4)	1.380	1.366	1.354
d(C3–C4)	1.341	1.363	1.372
d(C3–N)	1.345	1.334	1.311
d(C4–N)	1.360	1.320	1.322
N1–C1–N2–C2	5.9	15.5	1.5





1 (X = H, Y = H, R = H)
2 (X = H, Y = NH_2, R = H)
3 (X = NH_2, Y = NH_2, R = H)
4 (X = $N(CH_3)_2$, Y = $N(CH_3)_2$, R = CH_3)

5 (R^1 = H, R^2 = H)
6 (R^1 = C_2H_5, R^2 = H)
7 (R^1 = CH_3, R^2 = CH_3)

Fig. 1 Model compounds for strong organic bases involving guanidine and cyclopropenimine fragments.

$$DP(\%) = \left[360 - \sum_{i=1}^{3}\alpha_i\right]/0.9 \quad (5)$$

values of the nitrogens in **3** attached to the carbon atoms C1, C3 and C4 are 32.5, 32.2 and 32.8%, respectively. The corresponding values in **3H$^+$(N1)** are 0.4, 0.1 and 6.6%, respectively, thus reflecting a striking planarization. If the proton is linked to the N2 nitrogen, then the degrees of pyramidalization are 13.1, 0.0 and 0.5%, respectively. This agrees with earlier findings that the resonance effect is transmitted more easily over a double bond (like C2–N2), than a single bond (as C1–N2).[25] This is also evident in a longer C1–N2 bond in **3H$^+$(N2)** compared to that in **3H$^+$(N1)**. It is important to notice that the guanidine and cyclopropenimine fragments are planar within the computational accuracy, and that the dihedral angles between them are not very large. In fact, the dihedral angles are small in the neutral bases **1**–**3**, and become more pronounced in the N1 protonated forms (Table 1). Specifically, the dihedral angle, θ, assumes values 20.0, 10.4 and 15.5° in ***n*H$^+$(N1)**, respectively,

Table 2 Löwdin population analysis,[31] total bond orders and π-bond orders in systems **1** and **3** and their protonated forms as given by the HF/6-31G* model. The total bond orders correspond to Mayer's analysis.[32] The hybridization s-characters are obtained by the NBO prescription.[33] Formal atomic charges q[31] are given in a.u.

			Bond order		Electron density	
Molecule	Bond	s-Character	Total	π	Atom	q
1	C1–N1	41.6–38.0	1.72	0.79	C1	0.21
	C1–N3	31.4–37.8	1.03	0.40	C2	0.15
	C1–N2	30.5–32.1	1.07	0.34	C3	−0.08
	C2–N2	38.8–41.7	1.64	0.72	C4	−0.10
	C2–C3	30.2–28.1	1.11	0.41	N1	−0.56
	C2–C4	27.8–28.7	1.17	0.43	N2	−0.33
	C3–C4	31.1–31.0	1.63	0.82	N3	−0.55
1H$^+$(N1)	C1–N1	38.5–33.1	1.16	0.51	C1	0.31
	C1–N3	32.4–39.0	1.23	0.54	C2	0.16
	C1–N2	34.3–34.5	1.29	0.46	C3	−0.07
	C2–N2	37.9–40.1	1.41	0.59	C4	−0.01
	C2–C3	31.0–28.2	1.19	0.45	N1	−0.47
	C2–C4	28.7–28.3	1.24	0.47	N2	−0.30
	C3–C4	29.6–30.4	1.55	0.71	N3	−0.43
1H$^+$(N2)	C1–N1	41.9–39.4	1.92	0.82	C1	0.22
	C1–N3	34.6–36.0	1.06	0.39	C2	0.19
	C1–N2	25.8–35.1	0.83	0.27	C3	0.03
	C2–N2	36.0–38.8	1.21	0.56	C4	0.00
	C2–C3	30.2–27.6	1.27	0.50	N1	−0.47
	C2–C4	30.7–27.8	1.30	0.52	N2	−0.23
	C3–C4	30.1–29.5	1.52	0.72	N3	−0.52
3	C1–N1	37.9–41.0	1.72	0.74	C1	0.24
	C1–N3	31.0–32.9	1.01	0.39	C2	0.14
	C1–N2	31.0–28.6	1.10	0.39	C3	0.07
	C2–N2	41.9–36.8	1.50	0.62	C4	0.06
	C2–C3	29.5–28.0	1.08	0.46	N1	−0.56
	C2–C4	28.2–30.1	1.19	0.49	N2	−0.38
	C3–C4	34.6–33.8	1.47	0.64	N3	−0.56
	C3–N	37.0–31.2	1.03	0.43	N(C3)	−0.52
	C4–N	35.8–32.1	0.99	0.38	N(C4)	−0.52
3H$^+$(N1)	C1–N1	32.7–37.1	1.10	0.32	C1	0.29
	C1–N3	31.9–39.0	1.18	0.43	C2	0.11
	C1–N2	35.4–36.9	1.44	0.54	C3	0.09
	C2–N2	39.5–34.9	1.24	0.47	C4	0.13
	C2–C3	31.2–31.1	1.23	0.54	N1	−0.51
	C2–C4	29.0–31.1	1.26	0.51	N2	−0.33
	C3–C4	30.9–30.3	1.28	0.51	N3	−0.46
	C3–N	37.7–36.8	1.10	0.45	N(C3)	−0.48
	C4–N	38.3–37.9	1.15	0.48	N(C4)	−0.46
3H$^+$(N2)	C1–N1	38.7–41.8	1.86	0.79	C1	0.23
	C1–N3	33.8–36.3	1.06	0.40	C2	0.12
	C1–N2	27.3–35.9	0.90	0.32	C3	0.15
	C2–N2	37.8–35.5	1.03	0.42	C4	0.13
	C2–C3	30.4–30.3	1.26	0.54	N1	−0.51
	C2–C4	31.6–31.3	1.34	0.57	N2	−0.27
	C3–C4	30.1–30.1	1.26	0.50	N3	−0.52
	C3–N	39.2–37.2	1.19	0.53	N(C3)	−0.44
	C4–N	38.3–37.8	1.14	0.50	N(C4)	−0.46

where $\boldsymbol{n} = \mathbf{1}$, **2** and **3**. Since the overlap between two π-atomic orbitals (AOs) depends on cos θ, it appears that the overlapping is diminished by only 6% at most. Hence, one can safely conclude that both conjugation and resonance are effective even in nonplanar systems, *e.g.*, **1H$^+$(N1)**.

It should be emphasized that we distinguish between the conjugation and resonance effect in spite of their similarity. Their mechanisms are somewhat different in neutral and ionic systems, which makes their distinction advantageous. Conjugation describes a stabilization taking place in a neutral molecule due to π-electron delocalization. It may include mixing of the spin-coupling valence bond (VB) schemes, involving π-electron transfer from one atom to (an)other atom(s) in a molecule, like in C=C–C=N ↔ C$^+$–C=C–N$^-$, but not necessarily so. The resonance effect in protonated planar bases involves, in addition, a relaxation of the electron density triggered by the protonation, resulting in a distribution of the positive charge all over the molecule. Use of charge transfer resonance structures is imperative in this case. The positive charge is transmitted most easily *via* the π-network (*i.e.*, conjugation), but reorganization of the electron density through σ-bonds cannot be excluded either. In fact, the latter does take place in protonated saturated systems too. It has been shown that the relaxation effect is usually quite large,[25–27,34] which is also supported by the present evidence. Since the conjugation and the relaxation effects are not easily disentangled, they are considered together here as a single and common resonance effect taking place in protonated systems. The strong resonance effect in the protonated forms is reflected in the π-bond orders (Table 2). Their variation is compatible with the alternating changes in bond distances upon protonation mentioned above. The proton attack at N1 induces virtually the same π-bond orders within

Table 3 Total molecular electronic energies, scaled zero-point vibrational energies and the proton affinities of the molecular systems **1**–**7**[a]

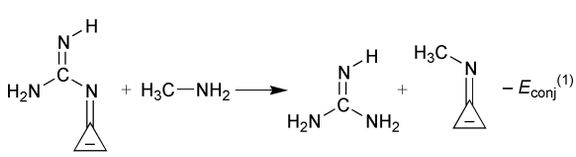
Molecule	$E(HF)_{tot}$	$E(MP2)_{tot}$	$ZPVE_{SC}$	$PA(HF_{SC})$	PA(MP2)
1	−317.62089	−318.75914	54.4	—	—
1H$^+$(N1)	−318.03607	−319.15367	61.9	242.9	240.1
1H$^+$(N2)	−318.01397	−319.13467	62.2	230.5	227.8
2	−372.66570	−374.00586	64.9	—	—
2H$^+$(N1)	−373.09536	−374.41457	72.5	251.0	248.9
2H$^+$(N2)	−373.07301	−374.39627	72.9	238.5	237.0
3	−427.70780	−429.25061	75.8	—	—
3H$^+$(N1)	−428.13765	−429.66127	82.9	251.1	250.6
3H$^+$(N2)	−428.12633	−429.65170	83.0	244.8	244.5
4	−700.88316	—	—	—	—
4H$^+$(N1)	−701.33386	—	—	262.8	—
5	−651.28554	−653.62392	105.9	—	—
5H$^+$(N1)	−651.74542	−654.06048	112.5	267.9	267.3
5H$^+$(N2)	−651.72869	−654.04561	112.3	258.6	258.2
5H$^+$(N3)	−651.71761	−654.03818	112.6	252.4	253.2
6	−729.34647	—	—	—	—
6H$^+$(N1)	−729.81071	—	—	270.4	—
6H$^+$(N2)	−729.79060	—	—	259.1	—
6H$^+$(N3)	−729.78062	—	—	253.5	—
7	−1002.52099	—	—	—	—
7H$^+$(N1)	−1003.00259	—	—	280.1	—

[a] Total energies in a.u., ZPVEs and PAs in kcal mol^{-1}. The scaled ZPVEs are obtained by a common empirical factor, 0.89.

the three-membered ring in **3H$^+$(N1)**, thus being in accord with its aromaticity. There is also an apparent increase in the π-bond order of the C–NH_2 bonds in conjugate acids, in agreement with the participation of the amino groups in the resonance interactions. Interestingly, protonation at the N2 nitrogen makes the guanidine subunit more isolated than in the initial base. This is evidenced by a decrease in the bond order along the C1–N2 bond and an increase in those of the C1–N1 and C1–N3 bonds. This is in agreement with the conjecture that the resonance effect does not spread over a single bond linked to the protonated nitrogen (*vide infra*). The rest of the data for **1H$^+$(N2)** and **3H$^+$(N2)** fit the overall picture discussed above (Table 2).

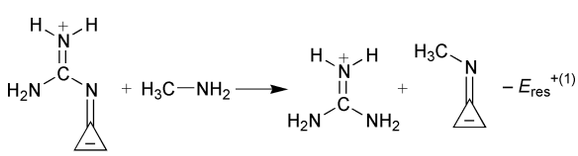
Perusal of the atomic charges (Table 2) reveals two important features: (a) the relaxation effect leaves the electron density of the protonated nitrogen practically unchanged compared to that in a neutral base, and (b) the positive charge is evenly distributed over the whole conjugate base. In this way the perturbation of the electron density distribution in the initial base is minimized and the increased effective nuclear charges of all but the protonated atom enable more favourable nucleus–electron attraction. These conclusions are drawn from analysis of the Löwdin atomic charges of systems **1** and **3** and their protonated forms obtained by the symmetric orthogonalization of AOs in the resulting wavefunctions (Table 2). They are representative of all the molecules examined in this study. A point of interest is that the electron density of the N2 atom is invariably lower than that of atoms N1 and N3. This can be rationalized by the fact that the hybrid orbital emanating from the ring describing the σ-part of the C2=N2 bond has high s-character, thus being more electronegative.

The central part of our study is that of the energetic properties of compounds **1**–**7**, which are displayed in Table 3. We observe, firstly, that the $ZPVE_{SC}$ values are practically the same for different protonated forms of a single base. Secondly, the increase in the $ZPVE_{SC}$ upon the protonation of all nitrogen bases varies within a narrow range (6.5–7.5 kcal mol^{-1}). This is an essential feature that has led to the scaled Hartree–Fock method.[35] Further, the HF_{SC} model offers PA values very close to the MP2 estimates. This is encouraging, since the former model is more practical and economical. Hence, it was exclusively applied here to predict the proton affinities of the rather large compounds **4**, **6** and **7**. The variation in the proton affinity is interesting. The PA(N1) increases along the series **1**–**7** with one exception: PA[**2H$^+$(N1)**] and PA[**3H$^+$(N1)**] are virtually the same. The amplification in basicity in the series can be rationalized by the resonance effect as follows. Let us use for this purpose the concept of homodesmic chemical reactions.[36] Two points should be kept in mind in this connection: (a) the initial bases are stabilized by the inherent conjugation effect and (b) molecules **1** and **3** are considered as extended guanidine moieties. Consequently, it is convenient to consider the resonance contribution to the proton affinities PA(**1**) and PA(**2**) relative to that occurring in the parent guanidine. The increase in the conjugation effect in **1** due to a fusion of the cyclopropenimine moiety to the guanidine subunit is given by eqn. (6).



(6)

Notice that the hybridization left and right is approximately conserved. Protonation yields eqn. (7).



(7)

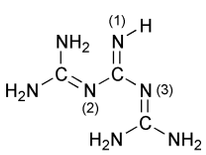
The difference between eqns. (6) and (7) gives the proton affinity of system **1** relative to that of guanidine, eqn. (8).

$$PA[\mathbf{1}(\mathbf{N1})] = PA(\text{guanidine}) + (E_{res}^{+(1)} - E_{conj}^{(1)}) \quad (8)$$

It follows that the amplification of the proton affinity of **1** over the parent guanidine is given by the dominance of the

resonance effect ($E_{res}^{+(1)}$) over the intrinsic conjugation in **1**. Since $E_{res}^{+(1)} - E_{conj}^{(1)}$ is 7.1 kcal mol^{-1}, the protonation of **1** at N1 should equal 233.7 + 7.1 = 240.8 kcal mol^{-1}, because PA(guanidine) = 233.7 kcal mol^{-1}, as obtained by both gas-phase measurement and *ab initio* calculations.[27] Directly, we obtained PA[**1**(**N1**)] = 240.1 kcal mol^{-1}. Since the resonance contribution to the PA of guanidine[27] was estimated to be within the range of 24–27 kcal mol^{-1}, depending on the choice of the homodesmic reaction, it can be concluded that the resonance stabilization of **1H$^+$(N1)** is 31–34 kcal mol^{-1}. Hence, it can be safely stated that the resonance triggered by the protonation is somewhat larger than the aromatic stabilization of the paradigmatic benzene. The resonance effect in **3H$^+$(N1)** can be estimated in an analogous way. It turns out that in this case $E_{res}^{+(3)} - E_{conj}^{(3)}$ = 17.3 kcal mol^{-1} leading to a value for PA[**3H$^+$(N1)**] = 251 kcal mol^{-1}. Again, by adding up the resonance stabilization of 24–27 kcal mol^{-1} in guanidine one obtains a total resonance contribution to the PA of **3** protonated at N1 between 41–44 kcal mol^{-1}, which is remarkable indeed. This simple analysis underscores the importance of the substituent (NH_2) effect in determining high basicities of strong bases, *e.g.*, in **3H$^+$**(N1).

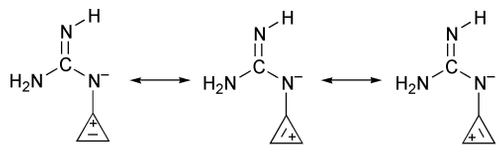
The relaxation effect is illustrated by a comparison of the PAs of **4** and **3**. It appears that complete methylation of **3** increases the proton affinity by 11.7 kcal mol^{-1}. The favourable influence of alkyl groups is a consequence of their inductive effect through σ- and pseudo-π-hyperconjugation channels. Similarly, comparison of the PAs of **6** and **7** with that of **5** shows that the PA(**6**) is higher by a modest 2.5 kcal mol^{-1}. On the other hand, the permethyl derivative, **7**, should be highly basic in the gas phase, as shown by its PA(**7**) value of 280.1 kcal mol^{-1} obtained by the HF_{SC} model. This is higher than the PA of the Schwesinger proton sponge **II** (269.5 kcal mol^{-1}), but falls short of the gas-phase basicity of compound **III** (301.0 kcal mol^{-1}). Nevertheless, it is obvious that the compounds **1**–**7** considered in this work cover a wide range of PAs, extending from the parent guanidine to the phosphazene *t*-Bu–P4 supersponge **III**. This is a desirable feature, because bases between these limits are badly needed. It is of some interest to compare the proton affinities of systems involving guanidine–cyclopropenimine subunits to the PA values of the corresponding polyguanides. It appears that **3** has a higher PA value than biguanide[27] by 10 kcal mol^{-1}. Similarly, **5** has increased proton affinity compared to the triguanide **8** by 16.5 kcal mol^{-1}, which



8

is indeed a substantial increase in basicity. This is not surprising, because the resonance interaction in the protonated guanidine–cyclopropenimines involves the aromatic stabilization of the three-membered ring(s), on top of the fact that they possess a larger number of C atoms, implying a higher relaxation effect at the same time.

Finally, a word on the most favourable site of protonation in the ambident bases explored here is required. It appears that the nitrogen atom N1 is the most basic in all cases, since it ensures the largest resonance stabilization. It is well established by now that a double bond involving an atom protonated in the σ-plane is an excellent "conductor" of the resonance interaction, which is in turn transmitted over alternating single and double bonds in a form of domino effect. In contrast, a single bond linked to the protonated nitrogen behaves as an "insulator", which does not permit an efficient spread of the resonance interaction *via* π-electrons.[27] This conclusion is illustrated by the conjugation interaction involving formation of an anion at the N2 atom in the **1** system (Scheme 1).



Scheme 1

It is easy to see that the conjugation effect with N1$^-$ as the anionic center is spread over the whole system (**1**), and thus can be larger, whereas the anionic center N2$^-$ implies the distribution of positive charge over the three-membered ring only (Scheme 1). The same holds *mutatis mutandis* for the corresponding protonated forms. It is, therefore, intuitively clear that protonation at the N2 and N3 positions in systems **1**–**7** should be less profitable, which is indeed the case (Table 3). These findings lend support to the resonance effect interpretation of the high PAs in the extended π-systems offered by our computations.

Concluding remarks

We have shown that a combination of guanidine and cyclopropenimine structural motifs in forming extended planar π-electron systems leads to very basic compounds. Some of them should exhibit gas-phase basicity higher than that of the Schwesinger proton sponge **II**. The origin of the increased basicity is identified as a strong resonance effect triggered by protonation, which is sometimes quite dramatic. The resonance effect also helps in interpreting the variation in the PA of ambident planar nitrogen bases as evidenced by earlier findings[27] and the present results. It is interesting to point out that guanidine–cyclopropenimine compounds possess higher intrinsic (gas-phase) basicity than their polyguanide counterparts. This is a consequence of the fact that the resonance in the conjugate acids of the former family of compounds involves formation of crypto-aromatic three-membered ring(s), which exhibit substantial stabilization. Finally, the present analysis underscores the role of substituents in increasing the proton affinity of approximately planar π-systems as illustrated by compounds **2**, **3**, **4**, **6** and **7**. More specifically, the amino group affects the basicity *via* the resonance effect, whereas the CH_3 group contributes to it by the inductive effect in the neutral base and by the relaxation effect in the conjugate acid.

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