Cooperative Intramolecular Hydrogen Bonding Effect and Basicity – An Ab Initio and DFT Study of the Superbasic Properties of *N*-[(Dimethylamino)alkyl]-2,3-diaminocycloprop-2-ene-1-imines

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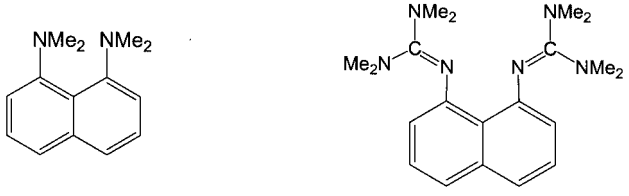
The MP2(fc)/6-311+G**//HF/6-31G* and B3LYP/6-311+G**//HF/6-31G* calculations show that *N*-[3-(dimethylamino)propyl] and *N*-[4-(dimethylamino)butyl] derivatives of 2,3-diamino-cycloprop-2-ene-1-imine (CPI) possess high gas phase proton affinities (PA) and pronounced basicities in acetonitrile (MeCN). Tris[*N*-dimethylaminopropyl(-butyl)]-CPI derivatives achieve superbasic PA and pK_a values. The reason behind these remarkable features is the stability of the resulting conjugate acids. They are stabilized by aromatization of the three-membered ring accompanied by the cationic resonance between the cyclopropyl ring and amino nitrogen atoms of the side chains, and, last but not least, by the cooperative multiple intramolecular hydrogen bonding effect. The latter is particularly enhanced in tris-substituted CPIs. It was found that the *N*-[4-(dimethylamino)butyl] side chains contribute more to the stability of the conjugate acids than those of the corresponding compound with a propyl chain, because they undergo a somewhat larger relaxation upon protonation. The studied compounds might be helpful in building up a dense ladder of strong bases and superbases, which could contribute to the development of the chemistry of superacids and superbases.

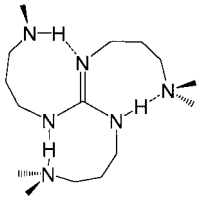
Introduction

In spite of its very small size, the proton plays important roles in a large number of chemical phenomena that are pivotal in acid-base chemistry and biochemistry.[1–3] Recently, there has been a lot of interest in designing strong organic bases in the gas phase. They include cyclic and acyclic guanidines,[4–8] phosphazenes,[9–10] quinolylboranes,[12] and some new unorthodox systems such as the zwitterion[13] $(CH_3)_3N^+–C_6H–COO^-$. It was found that aromatization of the conjugate acid is a very important factor in controlling the basicity of imines.[14–16] The aromatic domino effect seems to be particularly efficient in this respect as exemplified by extended 2,5-dihydropyrrolimines.[17] Another important motif is given by the intramolecular hydrogen bonding (IMHB) as in the archetypal DMAN(1,8-bis(dimethylamino)naphthalene)[18] (Scheme 1), its numerous off-spring,[19–22] and in the related but much more basic TMGN [1,8-bis(tetramethylguanidino)naphthalene] compound[23,24] (Scheme 1) and some related systems.[25]



Scheme 1.

Most of this work is covered by several review articles.[26–32] Recently, the cooperative multiple H-bond effect was found useful in tailoring strong superbases.[33] As an illustrative example *N*,*N*′,*N*′′-tris(3-aminopropyl)guanidine (**1**) is depicted in Scheme 2.



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Scheme 2.

The salient structural feature of **1** is a triple IMHB effect, which stabilizes the initial base. The strength of the hydro-

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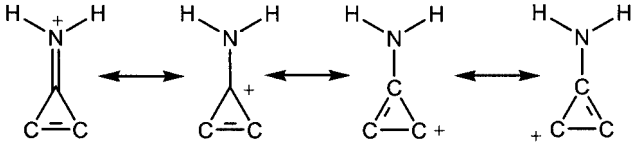
gen bonds is enhanced upon protonation, thus amplifying the basicity of **1**, which achieves a proton affinity (PA) of 268.4 kcal/mol.[33] Two important observations deserve attention: (1) the hydrogen bond strength is assisted by resonance and (2) the proton directly attached to one bridghead nitrogen atom also partially protonates the other nitrogen atom of the H-bridge.[24] We can build on that concept by selecting a central subunit, which provides a better molecular backbone than guanidine. An obvious candidate is cyclopropeneimine (CPI) **2**, since it exhibits high basicity due to the aromatization of the three-membered ring triggered by protonation,[15] as illustrated by Scheme 3. The aromatic effect is particularly pronounced in the protonated 2,3-diamino-CPI, because three amino groups participate in very strong cationic resonance at the same time.[15] We have systematically added *N*-[3-(dimethylamino)propyl] and *N*-[4-(dimethylamino)butyl] substituents to the imine N atoms in 2,3-diamino-CPI, in order to examine a step-wise increase in their basicity.



Scheme 3.

This approach will provide several rungs on the basicity ladder of neutral organic (super)bases.

Although the gas-phase intrinsic basicity allows for a deconvolution of the energetics of the protonation process into structurally understandable and intuitively appealing factors,[11,34] the "real" chemistry takes place in solution. For that reason we shall also consider the basicity of multiply substituted diaminocyclopropeneimines in acetonitrile.

Computational Methods

Absolute proton affinities (APAs) in the gas phase are computed in the standard way, see Equation (1).

$$APA(B_\alpha) = (\Delta E_{el})_\alpha + \Delta ZPVE + (5/2)RT \quad (1)$$

where B and BH^+ denote the base in question and its conjugated acid, respectively, and α signifies the site of proton attachment. The additive temperature dependent term (5/2) RT includes the translational energy of the proton and $\Delta(pV)$ contribution of the pressure-volume work term. Equations (2) and (3) give the electronic and zero-point vibrational energy (ZPVE) contribution to the proton affinity, respectively. The search over the Born–Oppenheimer energy (hyper)surface (PES) was carried out with the efficient Hartree–Fock (HF) model employing the 6-31G* basis set. The minima on the PES corresponding to optimal geometric structures were verified by vibrational analyses at the same level. The calculated vibrational frequencies were used in obtaining the ZPV energies by using a customary common scale factor of 0.89. The final single-point calculations were performed by the Møller–Plesset perturbation theory of the second order (MP2) employing a flexible 6-311+G** basis set capable of providing a satisfactory description of the nitrogen atoms and their lone pairs. This gives rise to the **MP2(fc)/6-311+G**//HF/6-31G* +ZPVE(HF/6-31G*)** model, which will be abbreviated here as MP2. Extensive numerical experiments have shown that the MP2 model represents a good balance between accuracy, feasibility, and practicality.[35]

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

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

All calculations were performed by using the Gaussian 98 suite of programs.[36]

Results and Discussion

The Gas Phase Proton Affinities

The calculated molecular energies and ZPVEs of bases and their conjugate acids are given in Table 1. Let us focus on the single-substituted *N*-dimethylaminopropyl CPIs (Figure 1). It is important to notice that the IMHB corona can be localized on a single nitrogen atom attached to the three-membered ring as in $\mathbf{1aH^+}$, or extended to the next amino nitrogen atom as with $\mathbf{1bH^+}$. Hence, the intramolecular hydrogen-bonding corona can form pseudo-six-membered or nine-membered rings, respectively. In each case two bonds of the pseudo-cycle belong to the formed hydrogen bridge. The strength of the IMHB can be estimated by unfolding the *N*-dimethylaminopropyl chain, exemplified by **1(ocn)** and $\mathbf{1(ocn)H^+}$ (Figure 1), where **ocn** stands for open chain. The difference in the total energies between **1(ocn)** and **1** is 5 kcal/mol, implying that the IMHB is weak. It appears that the protonated form $\mathbf{1aH^+}$ is more stable and more basic than $\mathbf{1bH^+}$ by 1.5 kcal/mol. It is useful to observe that the unfolded *N*-dimethylaminopropyl form $\mathbf{1(ocn)H^+}$ is same for both isomers $\mathbf{1aH^+}$ and $\mathbf{1bH^+}$, yielding the IMHB values of 9.1 and 7.6 kcal/mol, respectively. However, in both cases, the IMHB strength is increased relative to the neutral initial base **1** as expected, because the HB should be stronger in cationic systems due to the Coulombic character of the hydrogen bonding. The proton affinities of **1** corresponding to conjugate acid isomers $\mathbf{1aH^+}$ and $\mathbf{1bH^+}$ are 261.8 and 260.4 kcal/mol, respectively. It is interesting to notice that the proton affinity of the same base at the same site could be different due to a difference in the IMH bonding in various conformers of the final conjugate acid. It is noteworthy that the proton affinity is considerably higher than in the archetypal proton sponge DMAN (245 kcal/mol).[37] This is a consequence of the aromatization of the cyclopropyl cation assisted by the resonance effect with the directly bonded amino groups in the conjugate acids. The IMHB itself contributes additionally, either ca 2.5 or 4 kcal/mol, to the increase in proton affinity in $\mathbf{1bH^+}$ and $\mathbf{1aH^+}$, respectively.

Table 1. Total molecular energies (au), scaled ZPVEs (kcal/mol) and proton affinities (PA) obtained by the MP2 model (kcal/mol).

Compd.	MP2	ZPVE	PA(MP2)	Compd.	MP2	ZPVE	PA(MP2)
1	–610.32475	180.9	–	**4**	–649.52150	198.3	–
1aH$^+$	–610.75475	188.9	263.3	**4aH$^+$**	–649.95225	206.3	264.1
1bH$^+$	–610.75249	189.0	261.9	**4bH$^+$**	–649.95498	206.3	265.5
1(ocn)	–610.31621	180.6	–	**4(ocn)**	649.51323	197.6	–
1(ocn)H$^+$	–610.73923	188.3	259.2	**4(ocn)H$^+$**	–649.93825	205.5	260.3
2a	–822.31854	260.0	–	**5a**	–900.70794	294.2	–
2b	–822.32181	260.3	–	**5b**	–900.71549	294.7	–
2aH$^+$	–822.76047	268.6	268.5	**5aH$^+$**	–901.15657	303.1	269.9
2bH$^+$	–822.75766	268.1	267.2	**5bH$^+$**	–901.15328	302.7	268.2
2cH$^+$	–822.75532	268.1	265.7	**5cH$^+$**	–901.15507	302.8	269.2
2 (ocn)	–822.30507	259.2	–	**5(ocn)**	–900.69567	293.1	–
2 (ocn)H$^+$	–822.72676	266.7	258.6	**5(ocn)H$^+$**	–901.12038	300.9	260.2
3a	–1034.31122	338.8	–	**6a**	–1151.89732	390.2	–
3b	–1034.30520	338.5	–	**6b**	–1151.89307	389.9	–
3c	–1034.30721	338.8	–	**6c**	–1151.89053	390.1	–
3aH$^+$	–1034.76372	347.8	276.5	**6aH$^+$**	–1152.35842	399.7	281.4
3bH$^+$	–1034.75938	347.3	274.2	**6bH$^+$**	–1152.35341	398.9	279.0
3(ocn)	–1034.28620	337.5	–	**6(ocn)**	–1151.87825	388.7	–
3(ocn)H$^+$	–1034.71657	345.4	263.6	**6(ocn)H$^+$**	–1152.30525	396.5	261.6

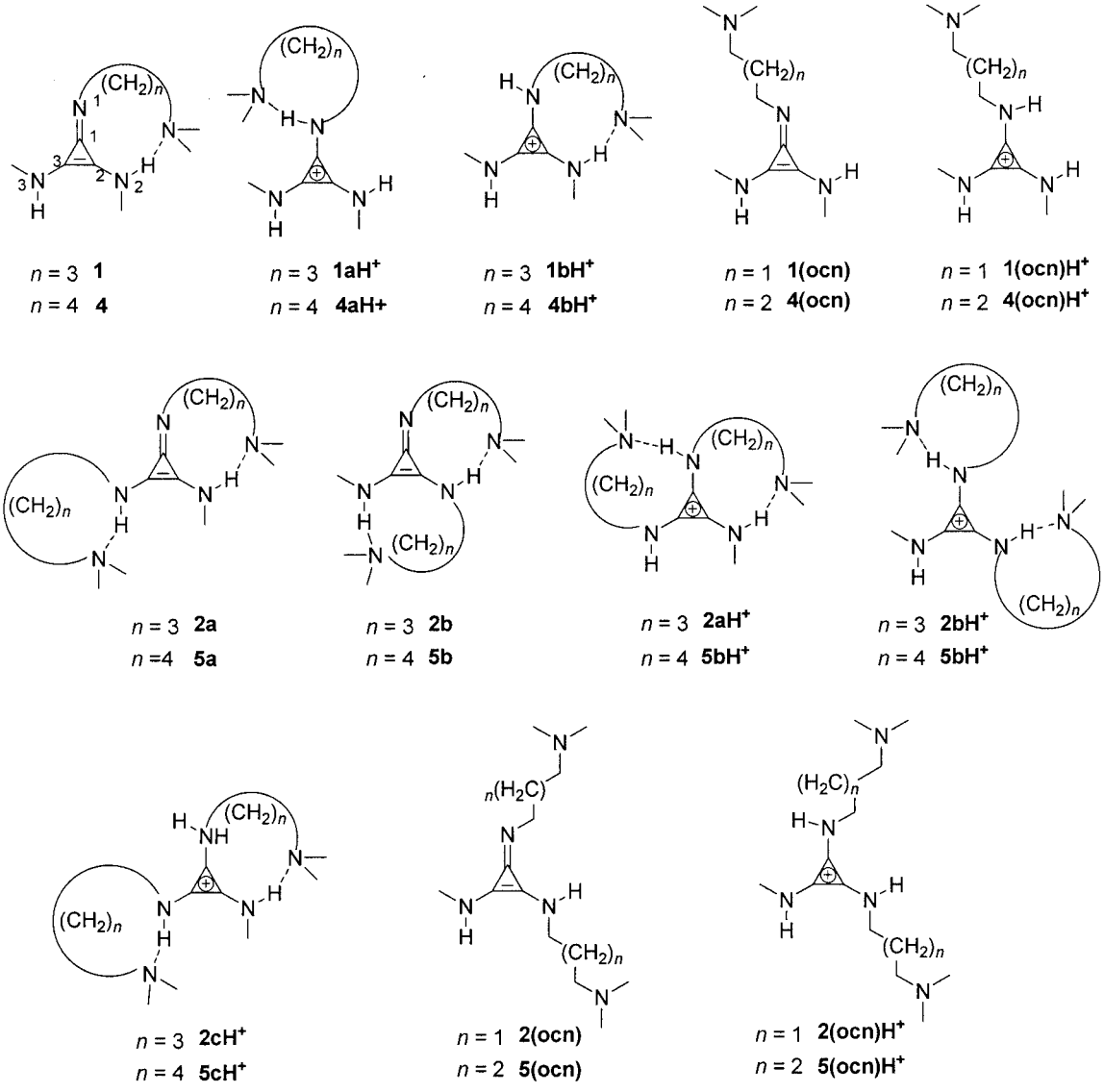


Figure 1. Schematic representation of the mono- and di-substituted *N*-[dimethylaminopropyl(-butyl)]-2,3-diamino-cyclopropeneimines and their protonated forms.

The cooperative IMHB effect takes place in systems containing two or three *N*-dimethylaminopropyl groups. It should be mentioned that by the cooperative effect we imply a total stabilization of the system by all IMHBs in a particular compound. The global cooperative effect should not be confused with the synergistic effect between the hydrogen bonds, which might or might not be present in a system under consideration. In the former, for derivatives of diamino-CPI, one can distinguish isomers **2a** and **2b** possessing local and extended IMHBs (Figure 1), respectively. Interestingly, **2b** is more stable by 2 kcal/mol. Similarly, the conjugate acid **2aH**$^+$, possessing two extended coronas, is more stable than **2bH**$^+$ and **2cH**$^+$ by 1.3 and 3 kcal/mol, respectively. The strength of the IMHB in **2b** is 9.4 kcal/mol. This number is increased in **2bH**$^+$ and **2cH**$^+$ to 18 and 16.5 kcal/mol, respectively. Since the IMHB strengths of **2a**

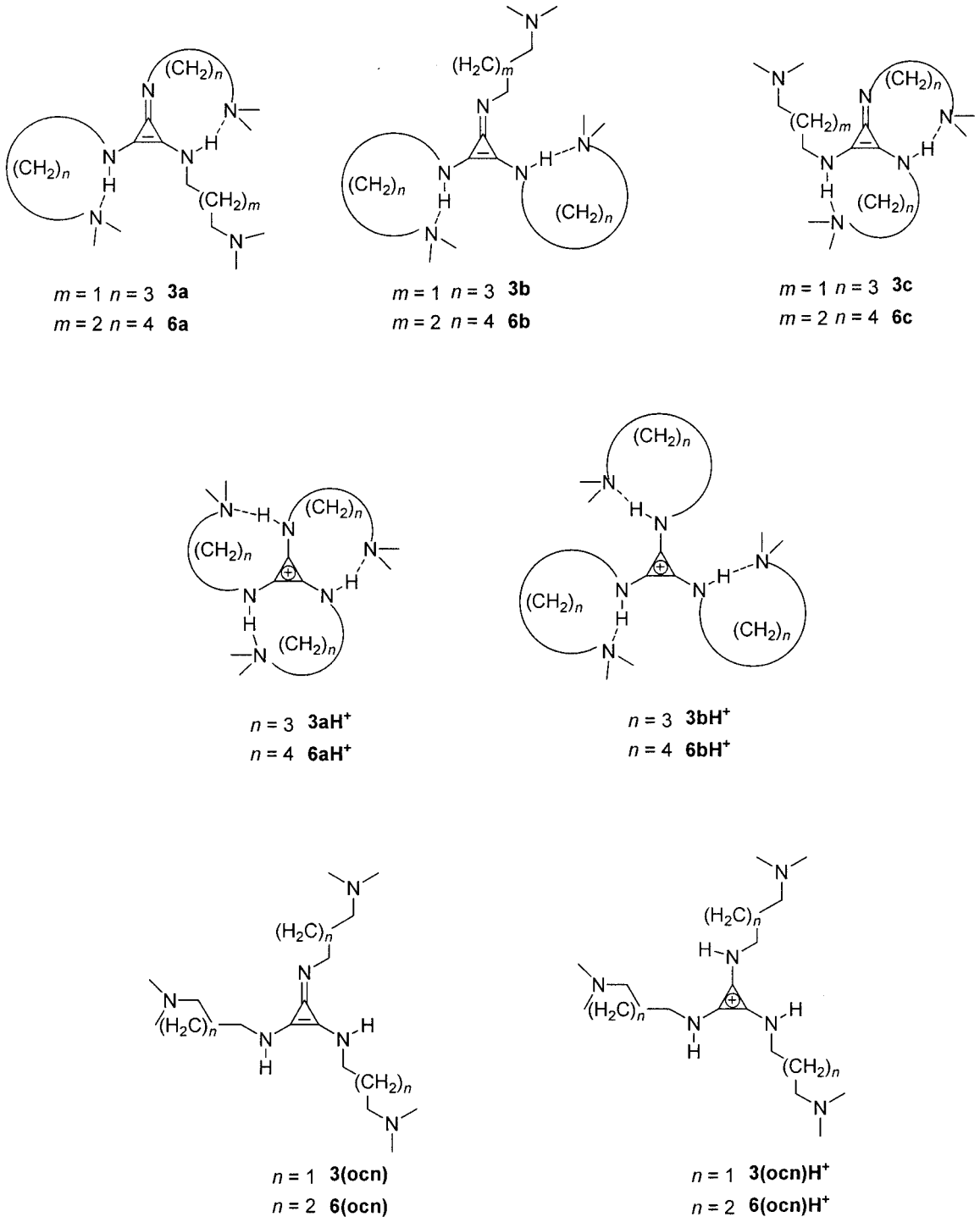


Figure 2. Schematic representation of the tris-substituted *N*-[dimethylaminopropyl(-butyl)]-2,3-diamino-cyclopropeneimines and their protonated forms.

and **2b** should be very close, it follows that the corona effects contribute to proton affinities between 7–9 kcal/mol. In other words, the intramolecular hydrogen-bonding contributions to the proton affinity are slightly more than doubled in **2a** and **2b** relative to **1**. The proton affinities of **2a** and **2b** are extended between 265.7–268.5 kcal/mol depending on the final state of the conjugate acid isomers **2aH**$^+$, **2b**H$^+$, and **2cH**$^+$ (Table 1). There is an obvious trend in the increased basicities upon double *N*-dimethylaminopropyl substitution, which culminates by triple substitution discussed below.

Despite the fact that systems **3a**, **3b**, and **3c** are tris-substituted derivatives of diamino-CPI, only two corona pseudo-rings can be formed in the neutral state (Figure 2). The most stable isomer is **3a**, which has a lower total energy than its **3b** and **3c** partners by 3.5, and 2.5 kcal/mol, respectively. Two different protonated forms, **3aH**$^+$ and **3bH**$^+$, are obtained upon protonation, which possess either three extended or localized coronas, correspondingly (Figure 2). The former conformer is more stable by 2.2 kcal/mol as expected, since the extended IMHB bridges are slightly more stable in the cationic conjugate acids. The IMHB strengths in neutral bases **3a**, **3b**, and **3c** are 14.4, 10.9 and 11.9 kcal/mol, respectively. One can anticipate a much more pronounced hydrogen-bonding effect in the conjugate acids **3aH**$^+$ and **3bH**$^+$ relative to the initial neutral bases in view of the three corona quasi-rings. This is indeed the case, since the estimated IMHB strengths in **3aH**$^+$ and **3bH**$^+$ are 20 and 17.8 kcal/mol, respectively. Hence, the cooperative IMHB effect in the protonated tris[3-(dimethylamino)propyl] derivatives of diamino-CPI exerts a strong influnce on their stabilization. The corresponding proton affinity is amplified, assuming large values within the range of 274–276 kcal/mol.

Our next task is to examine the length of the side chain(s). The question arises whether 4-(dimethylamino)butyl substituents offer more efficient corona effect(s). The corresponding systems are depicted in Figure 1 and Figure 2. Perusal of the results, summarized in Table 1, shows that the *N*-dimethylaminobutyl substituent(s) form slightly stronger IMHBs, thus leading to an increase in basicity (albeit moderate) relative to *N*-dimethylaminopropyl counterparts. This is not unexpected, since the increased number of atoms provides a larger domain for better accommodation of the positive charge, which in turn leads to a higher relaxation energy.

The largest cooperative IMHB effect is found in **6aH**$^+$ and **6bH**$^+$, which yields stabilization of 30.2 and 27.8 kcal/mol, respectively. It is, therefore, not surprising that **6aH**$^+$ and **6bH**$^+$ conjugate acids, derived by protonation of **6a**, yield PA values of 281.4 and 279.0 kcal/mol, respectively. It follows that *N*,*N*′,*N*′′-tris[4-(dimethylamino)butyl]-CPI represents a strong superbase indeed.

Structural Parameters

Some characteristic bond lengths for systems **1–3bH**$^+$ are presented in Table 2. Changes imposed by protonation are of importance, because they shed light on mechanisms leading to the stabilization of the conjugate acids. The latter is the main cause of the pronounced basicity of *N*-[3-(dimethylamino)propyl]-2,3-diamino-CPIs. The protonated C(1)=N(1) bond in **1** is elongated due to rehybridization and cationic resonance, which is spread over the whole **1aH**$^+$ species. Concomitantly, the C(1)–C(2) and C(1)–C(3) bonds are shortened, whereas the C(2)=C(3) bond is stretched. Since the nitrogen atoms N(2) and N(3) participate in the resonance effect by releasing a portion of its amino nitrogen lone pair density to the central ring subunit, the corresponding C(2)–N(2) and C(3)–N(3) bonds are significantly shortened. Consequently, the pyramidal character of the amino nitrogen atoms is considerably decreased (vide infra). It follows that the three-membered ring is largely aromatized, because all carbon–carbon distances within the ring are quite close. However, the aromatization effect is strongest in the protonated tris[3-(dimethylamino)propyl]-2,3-diamino-CPI **3a** species **3aH**$^+$ and **3bH**$^+$, where all carbon–carbon bonds are equal and are rather short. We can safely conclude that the high basicity of **3a** is a consequence of the aromatization of the central cyclopropyl cation ring in the protonated form, the strong resonance effect between the ring and the side chain, directly bonded amino nitrogens, and finally, the cooperative multiple intramolecular hydrogen bonding. The same features are behind tris(dimethylaminobutyl) derivatives of CPI **6aH**$^+$ and **6bH**$^+$.

Table 2. Characteristic bond lengths of *N*-[3-(dimethylamino)propyl] derivatives of 2,3-diaminocycloprop-2-ene-1-imine (Å) as computed by the HF/6-31G* model.

	C_1–C_2	C_2–C_3	C_3–C_1	C_1–N_1	C_2–N_2	C_3–N_3
1	1.410	1.330	1.404	1.266	1.359	1.361
1aH$^+$	1.367	1.359	1.367	1.316	1.327	1.326
1bH$^+$	1.362	1.366	1.363	1.322	1.327	1.319
2a	1.407	1.331	1.404	1.267	1.362	1.357
2b	1.407	1.332	1.407	1.267	1.354	1.368
2aH$^+$	1.364	1.363	1.363	1.326	1.324	1.318
2bH$^+$	1.363	1.370	1.362	1.330	1.319	1.318
2cH$^+$	1.368	1.359	1.366	1.319	1.323	1.325
3a	1.407	1.332	1.407	1.267	1.353	1.369
3b	1.403	1.331	1.411	1.266	1.359	1.363
3c	1.406	1.332	1.407	1.267	1.354	1.368
3aH$^+$	1.363	1.363	1.363	1.321	1.321	1.321
3bH$^+$	1.365	1.365	1.365	1.323	1.323	1.323

A strong resonance between the cationic ring and aminopropyl/butyl groups is reflected in planarization of the nitrogen upon protonation. A degree of pyramidalization (DP) is given (in percent) by Equation (4).

$$DP(\%) = (360 - \sum_{i=1}^{3} a_i)/0.9 \quad (4)$$

Here the summation is extended over the three sharp bond angles of the apical nitrogen atom in question (given in degrees).[38] The normalization constant 0.9 is introduced to yield 100% of pyramidalization in the case that all three NH bonds are equivalent, giving H–N–H angles of 90°. The degrees of pyramidalization are given in Table 3. Perusal of the data provides conclusive evidence that a significant

planarization of the amino nitrogen atoms takes place after protonation in order to enhance the resonance effect.

Table 3. Degrees of pyramidalization of nitrogen atoms (%) calculated by the HF/6-31G* model.

	N_1	N_2	N_3		N_1	N_2	N_3
1(ocn)	/	15.0	13.4	**4**	/	9.9	14.8
1	/	14.2	11.6	**4(ocn)**	/	13.7	15.0
1aH$^+$	1.6	1.9	1.7	**4(ocn)H$^+$**	1.6	1.6	1.5
1bH$^+$	0.3	1.6	2.1	**4aH$^+$**	0.0	1.7	1.7
1(ocn)H$^+$	1.4	1.2	1.3	**4bH$^+$**	0.6	0.1	2.0
2(ocn)	/	15.1	13.7	**5(ocn)**	/	15.5	13.7
2a	/	12.5	13.5	**5a**	/	5.5	13.4
2b	/	13.3	11.4	**5b**	/	13.8	13.8
2aH$^+$	1.3	0.0	3.8	**5aH$^+$**	0.1	3.3	1.4
2bH$^+$	2.4	1.8	3.0	**5bH$^+$**	1.8	0.1	3.8
2cH$^+$	1.8	2.1	0.7	**5cH$^+$**	1.5	4.1	1.4
2(ocn)H$^+$	0.8	1.6	1.3	**5(ocn)H$^+$**	1.7	1.8	1.5
3(ocn)	/	16.8	15.2	**6(ocn)**	/	15.5	13.9
3(ocn)H$^+$	1.6	1.6	1.6	**6a**	/	13.8	15.2
3bH$^+$	2.6	2.6	2.6	**6b**	/	13.4	14.3
3aH$^+$	0.1	0.1	0.1	**6c**	/	9.5	7.3
3a	/	15.8	12.8	**6aH$^+$**	0.0	0.0	0.0
3b	/	14.1	15.7	**6bH$^+$**	2.2	2.2	2.2
3c	/	13.3	11.7	**6(ocn)H$^+$**	1.5	1.5	1.5

Let us now focus on some characteristic properties related to the strength of the IMHBs. They are summarized in Table 4, where the structural parameters of the hydrogen bridges and some data offered by the atoms in molecules (AIM)[39] theory are given. It was suggested by Koch and Popelier,[40] and utilized by many other researchers,[41] that topological features, such as the electron density at the H···N bond critical point $\rho_{H\cdots N}$ and Laplacian of the density $\nabla^2\rho_{H\cdots N}$, might serve as good probes of the IMHB strength. It seems to be generally accepted that $\rho_{H\cdots A}$ lying within the range of 0.002–0.040 au and $\nabla^2\rho_{H\cdots A}$ extending from 0.024 to 0.139 au are indicators of an appreciable IMHB strength,[42] where A stands for any hydrogen-bond accepting (electronegative) atom. As to the structural characteristics, we shall consider N–H and H···N bond lengths and their N–H···N bond angle.

Perusal of the data presented in Table 4 offers some interesting conclusions. The N···H contact is dramatically shortened in the protonated forms. The N–H···N angle is appreciably increased, particularly in **6aH$^+$**, where the IMHB becomes almost linear. The bond critical point (bcp) density $\rho_{H\cdots N}$ increases, as well as its Laplacian value $\nabla^2\rho_{H\cdots N}$, upon protonation, implying a stronger hydrogen bond. In addition to the ρ(bcp) density along the IMHB contact H···N, we examine here also ρ_{N-H} and $\nabla^2\rho_{N-H}$ of the N–H bonds participating in hydrogen bridges. It is well known that $\nabla^2\rho$(bcp) at the bond critical point is negative and measures the extent of the covalent bonding.[39] It appears that ρ_{N-H} values are lowered by protonation, and their Laplacians $\nabla^2\rho_{N-H}$ are less negative (Table 4). This is indicative of H-bond stabilization, since a (small) portion of the electron density is shifted from the covalent N–H bond region into the H···N domain of the H-bond bridge. The topological analysis is helpful in rationalizing our finding that the cooperative hydrogen bond stabilization in protonated tris(dimethylaminobutyl)-2,3-diamino-CPI derivatives is larger than in the corresponding tris(dimethylaminopropyl)-2,3-diamino-CPIs. The former are more linear, possess higher $\rho(bcp)_{N\cdots H}$ densities and larger $\nabla^2\rho(bcp)_{H\cdots N}$ values. The physical reason behind these changes is the increased relaxation effect as mentioned above (vide supra).

Basicity in Acetonitrile

Acetonitrile is a moderately polar solvent useful in hosting strong neutral (super)bases. We have recently shown[43] that the solvent effect in acetonitrile can be satisfactorily treated by a simple electrostatic model of Miertuš, Scrocco and Tomasi.[44] The cavities that surround molecules immersed in a homogeneous solvent are determined by a boundary isodensity surface with ρ = 0.0004 eB^{-3}.[45] Since the calculations of the pK_a in MeCN require several expensive iterations, a more economical B3LYP/6-311+G**//HF/6-31G* model is used. The ZPVEs are taken from the gas phase calculations evaluated at the HF/6-31G* level. Employing the dielectric constant of MeCN ε = 36.64, an excellent least-squares fit between the calculated proton affinities PA(MeCN) and the experimental pK_a values was obtained for a large variety of organic bases containining imino nitrogen atoms.[43]

$$pK_a(MeCN) = 0.4953PA(MeCN) - 119.7 \quad (5)$$

Equation (5) is employed here to estimate the pK_a values of the most basic compounds studied in this paper. These are given as **3a** with its resulting conjugate acid **3aH$^+$** and **6a** with its **6aH$^+$** protonated form. The corresponding pK_a

Table 4. Relevant bond lengths (Å) and bond angles (degrees) necessary for description of H-bond bridges. densities at the bond critical points ρ(bcp) and their Laplacians (au) as computed by the HF/6-31G* model.

System	N–H	N···H	N–H····N	$\rho(bcp)_{H\cdots N}$	$\nabla^2\rho(bcp)_{H\cdots N}$	ρ_{N-H}	$\nabla^2\rho_{N-H}$
1	0.996	2.857	122.0	0.006	0.022	0.346	–1.796
1aH$^+$	1.005	2.068	136.6	0.027	0.079	0.331	–1.728
1bH+	1.003	2.362	162.2	0.015	0.045	0.335	–1.750
3aH$^+$	1.003	2.107	134.9	0.025	0.074	0.334	–1.743
3bH$^+$	0.998	2.493	139.9	0.011	0.037	0.340	–1.774
4	0.999	2.439	166.6	0.012	0.038	0.342	–1.777
4bH$^+$	1.007	2.164	178.2	0.021	0.059	0.330	–1,718
4aH$^+$	1.008	2.043	150.9	0.028	0.078	0.328	–1.705
6aH$^+$	1.008	2.105	176.1	0.024	0.066	0.329	–1.711
6bH$^+$	1.009	1.981	156.5	0.032	0.088	0.328	–1.700

values are 28.5 and 30.9, respectively, indicating that both compounds are very good candidates for strong organic superbases in acetonitrile and most likely in other moderately polar solvents. Hence, they should be useful in (super)acid–(super)base chemistry.

Concluding Remarks

It is conclusively shown that *N*,*N*′,*N*′′-tris[3-(dimethylamino)propyl] and *N*,*N*′,*N*′′-tris[4-(dimethylamino)butyl] derivatives of 2,3-diamino-cyclopropeneimine are very good candidates for powerful organic superbases, both in the gas phase and in acetonitrile. Less-substituted mono and bis-derivatives of CPI are less basic. Nevertheless, they provide useful rungs on the (super)basicity ladder of neutral organic compounds. The latter is a prerequisite for the development of a common scale of strongly acidic and basic compounds, which might lead to new superacid–superbase chemistry. Experimental work in the direction of Koppel, Leito and coworkers is very encouraging.[46] The origin of the pronounced basicity of poly-*N*-dimethylaminopropyl(-butyl)-2,3-diamino-cyclopropeneimines is identified as the aromatization of the three-membered ring. This is triggered by protonation, which is accompanied by the cationic resonance effect, between the cyclopropenyl cation moiety and amino groups at positions 2 and 3 of the CPI ring, and the cooperative IMHB effect, realized by corona structural motifs. The *N*-[4-(dimethylamino)butyl] side chains contribute more to the stability of the resulting conjugate acids, because they exhibit a somewhat larger relaxation effect. In other words, they accommodate the positive charge better than the *N*-[3-(dimethylamino)propyl] groups.

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