In search of neutral organic superbases—iminopolyenes and their amino derivatives

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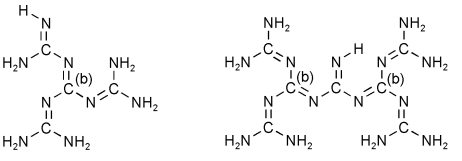
The intrinsic proton affinities of iminopolyenes and their amino derivatives are considered. It is shown that substitution of amino groups at strategic positions increases proton affinity (PA) to superbasic values particularly in branched polyenes. It follows that the number of double bonds, selection of the conformations and a judicious choice of substituents offer a closely spaced ladder of highly basic compounds spanning the range of values of PAs between 206.5 and 271.9 kcal mol^{-1}, which might be of some importance in acid–base chemistry. This conclusion is strengthened by the fact that several of the studied amino derivatives of iminopolyenes exhibit very high pK_a values between 30.0–33.5 in acetonitrile. Hence, they qualify as candidates for powerful neutral organic superbases.

Introduction

Experimental and theoretical design of strong neutral organic superbases and proton sponges has been a very active field of research for the last two decades.[1–7] This is not surprising for two reasons: (1) acid–base chemistry is one of the main avenues of investigation in chemical science and (2) neutral bases have some advantages over their ionic counterparts. For example, they require milder reaction conditions and possess better solubility.[8] These and other properties have led to their wide use in organic syntheses as important auxiliary bases.[9] Particular emphasis in experimental and theoretical studies was put on imine compounds like amidines, guanidines, vinamidines and phosphazenes.[10–13] We have shown that polyguanides exhibit very high proton affinities in the gas phase[14] and highly pronounced basicity in acetonitrile.[15] The origin of the large proton affinities and basicities was identified as a very strong cationic resonance effect triggered by protonation. It was also found that the terminal imine group in linear zig-zag polyenes was always the place most susceptible to the proton attack. Since the proton affinity of linear aminoimines approached rather quickly the asymptotic value of 255 kcal mol^{-1}, an important concept of bifurcation has been introduced in order to circumvent the saturation effect.[14] This has two favourable features: (i) the two (or more) branches are equally distant from the protonated imino center, which is always beneficial, and more importantly (ii) the intramolecular hydrogen bonding (IMHB) is more efficient in a branched polyene. As an illustration we give here tetraguanidine TG and heptaguanidine HG, depicted in Scheme 1. They possess one and two bifurcated carbon atoms, respectively, denoted by C(b). It came as no surprise that TG and HG exhibited proton affinities as high as 261.8 and 285.3 kcal mol^{-1}, respectively.[14] We have also argued that permethylation of branched aminoimines like TG and HG would be advantageous since it would further enhance their basicities at least in the gas phase. In addition, it would prevent proton migration from an amine nitrogen to the most basic imine nitrogen, which would lead to autosaturation of the latter with a concomitant decrease in basicity. It is the aim of this work to examine the basicity of linear and branched polyenes possessing only one imine nitrogen, to analyse the reasons behind their respectably high proton affinities in the light of a new triadic formula[13] and to estimate their pK_a values in acetonitrile.



Scheme 1

Theoretical framework and computational procedure

The absolute proton affinities (APAs) in the gas phase are computed in a standard way:

$$\mathrm{APA}(\mathrm{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha + (\Delta \mathrm{ZPVE})_\alpha \quad (1)$$

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

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

B and BH$^+$ denote the base and its conjugate acid, respectively, whereas α stands for the site of proton attack. Eqns. (2) and (3) give the electronic (E_{el}) and zero point vibrational energy (ZPVE) contributions to the proton affinity, respectively. The search of the Born–Oppenheimer energy hypersurfaces was performed with the Hartree–Fock model using the 6-31G* basis set. The minima on the hypersurfaces that correspond to equilibrium geometric structures were verified by vibrational analyses at the same level. The computed vibrational frequencies were used in deriving the ZPV energies by using a common scale factor, 0.89, as customary. The final single point calculations take into account the fact that a

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proper description of the nitrogen lone pairs requires the use of the flexible 6-311+G** basis set, and that reliable estimates of the proton affinity require an explicit account of the correlation energy at the level of Møller–Plesset (MP) perturbation theory of the second order. This gives rise to the MP2(fc)/6-311+G**//HF/6-31G* + ZPVE(HF/6-31G*) model,[16] which will be referred to henceforth as MP2. A more efficient, but somewhat less accurate model is given by the scaled Hartree–Fock scheme (HF_{SC}). It is founded on a very good correlation between the MP2 proton affinities and the difference in HF energies of a neutral base and its conjugate acid.[17] The corresponding formula for protonated nitrogen has the form:

$$\mathrm{APA}(\mathrm{B_N}) = 0.8924\Delta E_{\mathrm{el}}(\mathrm{HF/6\text{-}31G^*})_{\mathrm{N}} + 10.4 \text{ kcal mol}^{-1} \quad (4)$$

Formula (4) is very efficient and is very useful for pilot calculations. There is one point which should be clarified at this place. Strictly speaking, the proton affinity is defined as an enthalpy difference at 298 K between the interacting particles (a base and the proton) and the resulting protonated species. This includes an additional term $(5/2)RT$ in eqn. (1) appearing from the translation energy of the proton and the $p\Delta V$ contribution, if we tacitly assume that protonation does not change the heat capacity significantly. This correction is not necessary, however, since our MP2 model is selected in such a way that it reproduces the experimental data at room temperature with reasonable accuracy.[12] Hence, all terms are implicitly included in the MP2 model calculation.

An important task of theory is to provide rationalization of the computed and measured molecular properties. Recently, we developed a triadic formula:[13]

$$(\mathrm{APA})_{\alpha} = -(\mathrm{IP})_n^{\mathrm{Koop}} + E(\mathrm{ei})_{\mathrm{rex}}^{(n)} + (\mathrm{BAE})_{\alpha}{}^{+} + 313.6 \text{ kcal mol}^{-1} \quad (5)$$

enabling separation of the initial and final state effects in determining the proton affinities. The initial state is represented by the Koopmans' ionization potential $-(\mathrm{IP})_n^{\mathrm{Koop}}$, where the index refers to the nth orbital energy, the final state effect is given by the homolytic bond association energy $(\mathrm{BAE})_{\alpha}{}^{+}$ between the hydrogen atom and a radical cation. The central quantity $E(\mathrm{ei})_{\mathrm{rex}}^{(n)}$ describes the interplay between the initial and final state effects. It is defined as

$$E(\mathrm{ei})_{\mathrm{rex}}^{(n)} = (\mathrm{IP})_n^{\mathrm{Koop}} - (\mathrm{IP})_1^{\mathrm{ad}} \quad (6)$$

where $(\mathrm{IP})_1^{\mathrm{ad}}$ is the first adiabatic ionization potential. It is noteworthy that $(\mathrm{IP})_n^{\mathrm{Koop}}$ ionization potentials are obtained by the HF/6-311+G**//B3LYP/6-31G* model, since geometries are calculated by the density functional B3LYP procedure in the triadic analysis. Also, the first adiabatic potential $(\mathrm{IP})_1^{\mathrm{ad}}$ and the homolytic bond association energy between radicals $(\mathrm{BAE})^{+\bullet}$ are computed by the restricted open shell ROMP2(fc)/6-311+G**//B3LYP/6-31G* method. Formula (6) offers the relaxation energy upon electron ejection. Both eqns. (5) and (6) will be used for interpretative purposes.

Finally, we shall estimate the basicity of some of the studied iminopolyenes in acetonitrile, which might prove useful for their experimental measurements. It was shown recently that the electrostatic model of Miertuš *et al.*[18] served very well the purpose of describing the solvent effect in moderately polar solvents such as acetonitrile.[15] In determining the cavities that surround solvated molecules, we utilized a suggestion of Wiberg *et al.*[19] who used isodensity shells that involve the electron density of 0.0004 e B^{-3}. This gave rise to the isodensity polarized continuum model (IPCM). Since the calculation of pK_a values in MeCN with $\varepsilon = 36.64$ requires several iterations, this is the expensive part of the computations, if large systems are studied. Hence, we employed a more economical B3LYP/6-311+G**//HF/6-31G* model, in which ZPVEs are taken from the gas phase calculations, estimated at the HF/6-31G* level. We found[15] an excellent least squares fit correlation between the absolute proton affinities APA(MeCN) calculated in acetonitrile and the experimental pK_a values:

$$pK_a(\mathrm{MeCN}) = 0.4953 \times \mathrm{APA}(\mathrm{MeCN}) - 119.7 \quad (7)$$

The large regression coefficient $R = 0.997$ and a relatively low average absolute error of 0.4 pK_a bear witness to the high correlativity of the theoretical results and experimental data. Formula (7) will be used here in a predictive manner in estimating the basicity of iminopolyenes and their derivatives.

All computations were performed by utilizing GAUSSIAN 94 and GAMESS programs.[20,21]

Results and discussion

The considered iminopolyenes and their amino derivatives are depicted in Fig. 1. Let us focus on iminopolyenes first and discuss the corresponding MP2 results. Methyleneimine is a weak base as evidenced by its PA = 206.5 kcal mol^{-1} (Table 1). Extension of the π-system by an additional double bond leads to rotamers **2** and **2a** exhibiting PAs of 218.1 and 216.1 kcal

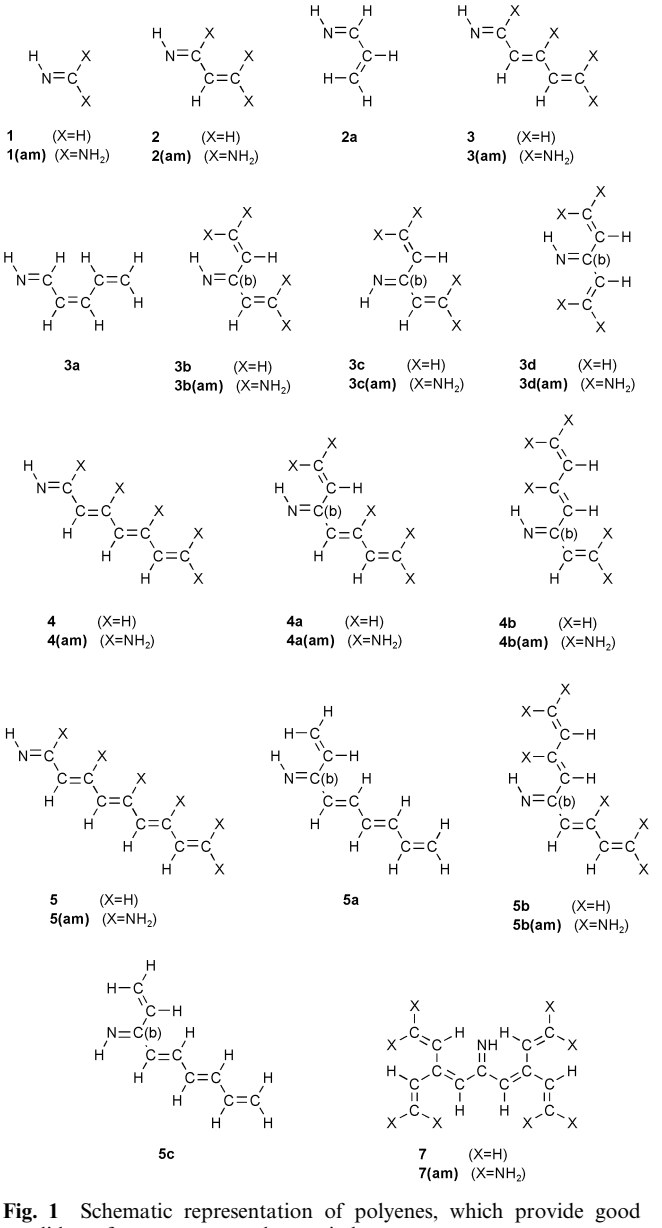


Fig. 1 Schematic representation of polyenes, which provide good candidates for strong neutral organic bases.

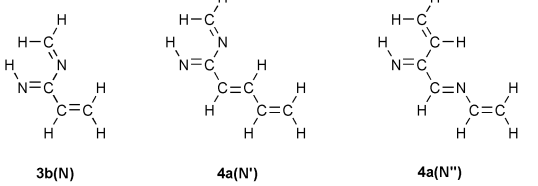
Table 1 Total molecular energies by the MP2 model of some imine polyenes and their amine derivatives (in atomic units). The PAs are given in kcal mol^{-1}

Molecule	MP2	PA(MP2)	PA(HF_{SC})	pK_a(MeCN)
1	−94.37929	206.5	209.0	—
1p	−94.72181	—	—	—
2	−171.56196	218.1	221.2	—
2p	−171.92261	—	—	—
2a	−171.55758	216.1	219.1	—
2ap	−171.91501	—	—	—
3	−248.74313	225.9	228.5	—
3p	−249.11626	—	—	—
3a	−248.73952	225.0	227.8	—
3ap	−249.11099	—	—	—
3b	−248.73797	225.4	227.6	—
3bp	−249.10857	—	—	—
3c	−248.73651	224.6	228.4	—
3cp	−249.10857	—	—	—
3d	−248.73531	224.6	227.3	—
3dp	−249.10593	—	—	—
4	−325.92492	231.5	233.0	—
4p	−326.30669	—	—	—
4a	−325.91950	230.7	233.1	—
4ap	−326.29988	—	—	—
4b	−325.91912	229.5	232.0	—
4bp	−326.29988	—	—	—
5	−403.10695	235.5	235.9	—
5p	−403.49502	—	—	—
5a	−403.10139	235.3	236.7	—
5ap	−403.48889	—	—	—
5b	−403.10081	234.6	236.6	—
5bp	−403.48727	—	—	—
5c	−403.10091	233.7	235.1	—
5cp	−403.48574	—	—	—
7	−557.44936	237.7	238.7	—
7p	−557.84071	—	—	—
1(am)	−204.87136	233.7	235.3	24.1
1(am)p	−205.25450	—	—	—
2(am)	−337.28191	247.8	248.9	27.4
2(am)p	−337.68719	—	—	—
3(am)	−469.69653	253.4	253.5	29.2
3(am)p	−470.11010	—	—	—
3b(am)	−469.68456	261.4	262.4	31.9
3b(am)p	−470.11138	—	—	—
3c(am)	−469.69388	255.6	256.9	28.7
3c(am)p	−470.11138	—	—	—
3d(am)	−469.69360	254.6	255.0	29.3
3d(am)p	−470.11011	—	—	—
4(am)	−602.11187	256.9	255.9	30.1
4(am)p	−602.53098	—	—	—
4a(am)	−602.10858	260.0	260.0	28.9
4a(am)p	−602.53312	—	—	—
4b(am)	−602.10950	259.5	260.0	30.0
4b(am)p	−602.53287	—	—	—
5(am)	−734.52745	259.4	257.4	29.9
5(am)p	−734.95043	—	—	—
5b(am)	−734.52339	262.2	262.0	30.0
5b(am)p	−734.95074	—	—	—
7(am)	−999.33837	271.9	268.7	33.5
7(am)p	−999.78170	—	—	—

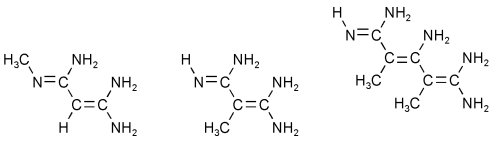
mol^{-1}, respectively. The number of conformers and branched isomers possessing three double bonds considered here is much larger. Linear all-*trans* polyene **3** is slightly more basic than *cis* conformer **3a**, which is generally the case in higher polyenes. Introduction of bifurcation in **3b**, **3c** and **3d** does not yield an increase in the PAs as in polyguanides.[14] This somewhat unexpected result is a consequence of the interplay of several factors, one of them being the cationic resonance stabilization, which in turn is larger in linear all-*trans* iminopolyene than in its branched counterparts. This assertion is easily proved. If we follow a procedure based on homodesmic reactions,[22] then the stabilization describing an increase in stability triggered by protonation is 11.0, 1.9, 2.8 and 1.5 kcal mol^{-1} for **3**, **3b**, **3c** and **3d**, respectively. The same applies to higher iminopolyenes. Apparently, the cationic resonance is diminished by considerable H···H nonbonded repulsion in branched isomers and induced nonplanarity (*vide infra*). The additional double bond in **4** amplifies the PA giving 231.5 kcal mol^{-1}. Once again branching does not result in more basic compounds. The same holds for **5** and its branched isomers, which leads finally to the following general conclusion: linear zig-zag imino polyenes exhibit basicity, which increases with the number of double bonds, but it seems that an attenuation effect takes place as evidenced by PA(**5**) = 235.5 kcal mol^{-1}. In other words, increments become smaller as n increases. Increased basicity is qualitatively in accordance with the increase in the additional cationic resonance stabilization, which assumes 3.2, 11.0, 16.4 and 20.4 kcal mol^{-1} in the series **2**, **3**, **4** and **5**, respectively. Branching does not yield an amplification of the basicity unlike in polyguanides due to the increasing number of H···H contacts and enhanced Coulomb repulsion.[14] The situation dramatically changes in amino substituted polyenes. The PAs are substantially increased quickly reaching superbasic values. For example, the difference PA(**2(am)**) − PA(**2**) = 29.7 kcal mol^{-1} is remarkable indeed. Here **am** within parentheses denotes NH_2 derivatives. Another point of interest is that branching does increase the basicity in amino substituted iminopolyenes as illustrated by compounds **3(am)**, **3b(am)**, **3c(am)** and **3d(am)** assuming PA values of 253.4, 261.4, 255.6 and 254.6 kcal mol^{-1}, respectively. The cationic resonance stabilization in the protonated species relative to the π-electron conjugation energy in **2(am)**–**4(am)** assumes values of 33.7, 38.9 and 42.3 kcal mol^{-1}, respectively. Hence, amino substitution considerably amplifies the resonance effect. The highest basicities were found in **5b(am)** and **7(am)**, where PAs as high as 262.2 and 271.9 kcal mol^{-1}, respectively, are estimated. The latter is, however, appreciably less basic than the polyguanide counterpart HG (285.3 kcal mol^{-1}). The reason behind this is a lack of unfavorable H···H repulsions in polyguanides, which make them stronger bases. In contrast, nonbonded repulsion between hydrogen atoms in the polyenes studied here leads to appreciable nonplanarities, which *inter alia* diminish π-conjugation and the cationic resonance. As to the linear all-*trans* amino substituted imines **2(am)**, **3(am)**, **4(am)** and **5(am)** their PA values are 247.8, 253.4, 256.9 and 259.4 kcal mol^{-1}, respectively, implying that the increments drop from 5.6 to 2.5 kcal mol^{-1}, or in other words, that the asymptotic PA value lies somewhat above 260 kcal mol^{-1}.

An interesting question arises: what happens if the =CH fragment is replaced by the imino moiety =N in some polyenes? Typical examples are shown in Scheme 2. The proton affinity of **3b(N)** is smaller by 1.8 kcal mol^{-1} than that of **3b** (Table 1). Similarly, the PAs of **4a(N′)** and **4a(N″)** compare with that of **4a** (230.7 kcal mol^{-1}).

Another point of interest is methylation of amino substituted polyenes as illustrated in Scheme 3. The methylation at



Scheme 2



Scheme 3

the imino center in **2(am)$_{Me'}$** slightly increases the PA apparently through a relaxation effect in the protonated species. In contrast, attachment of the CH_3 group on the carbon backbone as in **2(am)$_{Me''}$** hardly changes the proton affinity. Double methylation on the carbon skeleton in **3(am)$_{Me,Me}$** diminishes the PA by 2.7 kcal mol^{-1} again because of the increased repulsion between nonbonded methyl groups.

It follows that insertion of the imino moiety =N in the molecular backbone and methylation of unsubstituted carbon atoms introduce variation in the PAs by a few kcal mol^{-1}. Therefore, they can be applied for fine tuning of the basicity in amino derivatives of iminopolyenes.

Finally, it should be noticed that the scaled HF_{SC} model provides a good description of the APAs in aminoimine polyenes.

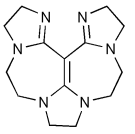
Triadic analysis *via* eqn. (5) offers some interesting conclusions (Table 2). Consider first the zig-zag linear polyenes **1**–**4**. Koopmans' ionization potential $(IP)_n^{Koop}$ is the price to be paid in the protonation process. It is practically constant varying between 271.6 and 269.0 kcal mol^{-1} despite the fact that it is the HOMO in **1** which is ionized, the HOMO − 1 in **2** etc. On the other hand, the relaxation energy $E(ei)_{rex}$ sharply increases with the number of double bonds assuming values of 40.9, 49.9, 70.0 and 86.6 kcal mol^{-1} for **1**, **2**, **3** and **4**, respectively. This is in agreement with the conclusion drawn on the basis of homodesmic reactions: the cationic resonance increases in extended π-systems albeit not linearly. The corresponding stabilization is diminished by a decrease in the bond association energy $(BAE)^{+\bullet}$, which has a negative gradient by changing from 120.6 to 98.6 kcal mol^{-1}, but the net effect is an increase in the proton affinity along the series. The role of amino groups is crucial in enhancing the basicity. In the first place, amination decreases $(IP)_n^{Koop}$ by some 10 kcal mol^{-1}. More importantly, the relaxation energy is increasing in the series **2(am)**, **3(am)** and **4(am)** by taking values 91.0, 103.6 and 111.7 kcal mol^{-1}, respectively. The extent of the stabilization of the conjugate acids relative to unsubstituted imino polyenes is dramatic. Examination of the structural features of **2(am)**, **3(am)** and **4(am)** after ionization shows that they exhibit characteristics typical for the relaxation effect: the double bonds are lengthened, whereas the single bonds are shortened. Moreover, amino groups are planarized in order to insure participation of the lone pairs in the conjugation. It appears that a relaxed radical cation is well prepared for the formation of a new bond with the incoming hydrogen atom. It is interesting to observe that branching does not increase the relaxation effect. On the contrary, it is diminished. This surprizing fact at first sight is easily understood if it is taken into account that the relaxation energy during ionization involves also increased repulsion between the nonbonded H-atoms. The number of the latter is larger in the branched polyenes compared to linear zig-zag ones. It is important to realize that the resulting proton affinity is always a result of a complex interplay between 3 terms appearing in formula (5). Consider for instance the effect of methylation at the imino center in **2(am)$_{Me'}$**. The Koopmans' ionization potential is decreased by 20 kcal mol^{-1}, but the relaxation energy $E(ei)_{rex}$ and $(BAE)^{+\bullet}$ are decreased together by 18 kcal mol^{-1}. The net effect is an increase in the proton affinity upon methyl substitution by 2 kcal mol^{-1}. On the other hand, methylation at the central carbon atom in **2(am)$_{Me}$** increases $E(ei)_{rex}$, but decreases $(BAE)^{+\bullet}$ by the same amount, thus leaving the APA practically unchanged (Table 2).

Table 2 Various contributions determining absolute proton affinities, APA(tri) of studied systems (in kcal mol^{-1})[a]

Molecule	$(IP)_n^{Koop}$	$(IP)_1^{ad}$	$E(ei)_{rex}$	$(BAE)^{+\bullet}$	APA(tri)
1	$(271.6)_1$	230.7 [229.9]	40.9	120.6	203.5 [203.8]
2	$(271.0)_2$	221.1 [222.5]	49.9	122.5	215.0
2a	$(269.3)_2$	221.8	47.5	121.3	213.1
3	$(269.9)_2$	199.9	70.0	110.2	223.9
3a	$(269.8)_2$	200.6	68.2	110.8	222.8
3b	$(270.5)_3$	214.0	56.5	122.2	221.8
3c	$(269.8)_3$	212.8	57.0	122.3	223.1
3d	$(267.5)_3$	213.3	54.2	121.7	222.0
4	$(269.0)_3$	182.7	86.3	98.6	229.5
4a	$(268.6)_3$	207.7	60.9	122.5	228.4
4b	$(269.6)_3$	203.0	66.6	116.5	227.1
1(am)	$(267.7)_2$	198.1	69.5	116.4	232.0 [235.7]
2(am)	$(259.4)_3$	168.4	91.0	101.0	246.2
3(am)	$(258.1)_4$	154.5	103.6	92.3	251.4
3b(am)	$(248.6)_3$	173.3	75.3	117.4	257.7
3c(am)	$(248.1)_3$	169.4	78.7	108.5	252.7
3d(am)	$(245.7)_3$	162.6	83.1	100.9	251.9
4(am)	$(256.9)_5$	145.2	111.7	86.3	254.7
4a(am)	$(247.4)_4$	168.0	79.4	110.9	256.5
4b(am)	$(245.5)_4$	147.0	98.5	89.7	256.3
3b(N)	$(258.1)_2$	215.0	43.1	121.9	220.5
4a(N′)	$(253.8)_2$	200.2	53.6	113.1	226.5
4a(N″)	$(267.5)_3$	194.8	72.7	100.7	219.5
2(am)$_{Me'}$	$(239.7)_3$	161.4	78.3	95.9	248.1
2(am)$_{Me''}$	$(258.3)_3$	162.7	95.6	94.7	245.6
3(am)$_{Me,Me}$	$(258.8)_4$	155.9	102.9	90.4	248.1

[a] Available experimental data are placed within square brackets and are taken from ref. 23.

The problem of basicity of the studied polyenes in acetonitrile is an important one, since it will decide whether the explored systems will be useful in acid–base chemistry or not. The pK_a values estimated by formula (7) are presented in Table 1. It appears that more extended π-systems exhibit higher basicities. For example, in the series **2(am)**, **3(am)**, **4(am)** and **5(am)** pK_a assumes values of 27.4, 29.2, 30.1 and 29.9, respectively. The slight decrease in **5(am)** relative to **4(am)** illustrates the fact that basicity is determined by two factors.[15] The first is the intrinsic gas phase proton affinity of the compound in question. The second is size. The larger the molecule is, the smaller is the positive charge density on its surface in the conjugate acid. This implies a smaller polarization of the solvent continuum and a weaker solvent effect. Another point of considerable interest is that a small molecule such as **3b(am)** has a pK_a value of 31.9. The Schwesinger's proton sponge **SPSG** (Scheme 4), considered to be the strongest neutral organic base nowadays, has a pK_a value of 29.8.[15] Furthermore, the branched system **7(am)** has an extremely high pK_a value of 33.5 too, which makes it the most potent superbase



Scheme 4

studied in this work. It has exactly the same basicity as the corresponding bifurcated heptaguanide,[15] in spite of the fact that the latter has a higher gas phase proton affinity. Obviously, the larger number of CH groups, at the expense of the imino nitrogens in polyguanides, is beneficial for the basicity in acetonitrile. To conclude, a number of amino derivatives of iminopolyenes have higher basicity than Schwesinger's proton sponge **SPSG** implying that they are worthy of synthesis in a laboratory.

Concluding remarks

Amino derivatives of iminopolyenes possess high intrinsic proton affinities in the gas phase. The role of amino groups is important and their influence is twofold. They decrease Koopmans' ionization potential of the imino lone pair and increase the cationic relaxation effect in the resulting conjugate acids. A number of the studied polyenes exhibit high pK_a values in acetonitrile in the range 30.0–33.5 implying that they are more basic than the Schwesinger sponge **SPSG** which possesses the vinamidine pattern (Scheme 4). Consequently, the preparation of amino derivatives of iminopolyenes is strongly recommended, since they are very good candidates for powerful organic superbases.

Note added in proof: In the meantime Howard *et al.*[24] reported a related B3LYP/6-31+G**//HF/6-31G* study of proton affinities of iminoamines and achieved a maximum APA value of 289.0 kcal mol^{-1} in such systems.

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