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Design of Brønsted Neutral Organic Bases and Superbases by Computational DFT Methods: Cyclic and Polycyclic Quinones and [3]Carbonylradialenes

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The gas-phase proton affinities and basicities of a large number of extended polycyclic π systems possessing a carbonyl oxygen head serving as a basic proton scavenger are explored by using DFT at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory. Some of these neutral organic superbases exhibit proton affinities in the range of 264–284 kcal mol^{-1}. In constructing these systems it turned out that a =C(NMe$_2$)$_2$ fragment attached to a quinoid six-membered ring enhanced the basicity to a considerable extent. There is abundant and convincing evidence that protonation triggers strong aromatization of the quinoid rings. Moreover, sequential quinoid rings undergo the aromatic domino effect upon protonation if linearly aligned. Triadic analysis has revealed that highly pronounced basicity in some studied systems is a result of the synergistic action of Koopmans' frozen neutral base ionization energy contribution and subsequent relaxation of the radical cation.

Introduction

Notwithstanding its size, the proton plays a gargantuan role in many chemical phenomena being in particular of paramount importance in acid–base chemistry and biochemistry.[1–3] It is pivotal in the very definition of Brønsted acids and bases, which in turn are fundamental concepts in chemistry. In this paper we shall focus on neutral organic (super)bases which are very useful auxiliaries in chemical synthesis[4] as they have some distinct advantages over their inorganic ionic counterparts. The latter exhibit some unfavourable features, such as poor solubility in most organic solvents and pronounced sensitivity to moisture and CO$_2$. On the other hand, neutral organic (super)bases permit the use of mild reaction conditions.[5] They show very good stability at low temperatures[6] and exhibit an enhanced reactivity towards naked anions forming poorly associated ion pairs upon deprotonation.[7] Finally, it should be stressed that they are efficient catalysts particularly if immobilized on appropriate surfaces[8–11] being recyclable and consequently desirable and acceptable in green chemistry. Last but not least, neutral organic (super)bases have found useful applications in both catalytic and stoichiometric asymmetric syntheses.[12] In recent years, the work on proton affinities and proton transfer reactions has been reviewed in several review articles.[13–18]

It is, therefore, not unexpected that a lot of effort has been devoted over several decades to the design of new neutral organic bases with pronounced basicities both in the gas phase and in organic solvents. Examples include amides and imidates,[19] cyclic and acyclic guanidines,[20–23] phosphazenes,[24–26] quinoimines and related systems,[27] quinolylboranes,[28] extended 2,5-dihydropyrrolimines[29] and C$_2$ diamines.[30] The extensive theoretical and experimental work carried out by Koppel, Leito and co-workers should be singled out as it includes both the theoretical design and the synthesis of organic bases and superbases as well as measurements of their pK_a values in various solvents.[31–35] The intramolecular hydrogen bonding (IMHB) motif proved very useful for this purpose too,[36,37] being particularly effective if utilized in a cooperative way by including multiple hydrogen bonds.[38–40] A lot of attention has been focused on neutral organic bases known as "proton sponges" possessing chelating proton-acceptor functionalities. The archetypal proton sponge is Alder's DMAN [1,8-bis(dimethylamino)naphthalene] synthesized some 35 years ago.[41] The design of proton sponges more basic than DMAN has received unabated interest ever since.[42–52] Alder's seminal idea materialized in DMAN was advantageously extended recently through the preparation of TMGN [1,8-bis(tetramethylguanidino)naphthalene][53,54] and HMPN [1,8-bis(hexamethyltriaminophosphazenyl)-naphthalene][55] in which the NMe$_2$ groups in DMAN were replaced by the guanidino and phosphazeno functionalities, respectively.

Although all of these compounds offer a wide variety of superbases, there is a need for new alternative systems exhibiting different physical and chemical properties occu-

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pying different positions on the basicity scale. It is of the utmost importance to construct a dense ladder of strong organic superbases possessing as many rungs as possible because of 1) their use in various preparative laboratory investigations of academic interest, 2) their employment in the experimental determination of the basicity of new bases by the bracketing technique, 3) their applications in the chemical industry as convenient catalysts and 4) as the interactions of powerful mineral acids and superacids with (super)bases should lead to low barrier hydrogen bonds which are considered the first stage of spontaneous proton transfer reactions,[56–59] some novel materials exhibiting interesting properties might be expected due to the formation of (strongly) bound ion pairs. With these ideas in mind we started an extensive study of a large number of carbonyl compounds which should provide counterparts of the imine systems studied earlier.[23,27,60] This paper is a development of our earlier work on carbonyl polyenes.[61] Note that a computational study on some pyrone-like molecules has been performed by Suárez et al.[62] In this paper we report on results obtained by considering quinones and some related compounds in gas phase. In subsequent papers we shall discuss their basicities in some important organic solvents.

Theoretical Methods and Computational Procedures

This paper reports on the proton affinities (PAs) of mono- and polycyclic quinones with the carbonyl group as the most basic site. The theoretical framework for calculating the proton affinity (PA) as a negative value of the enthalpy change of protonation [reaction (1)] in the gas phase is given by Equations (2), (3) and (4).

$$\mathbf{B} + \mathrm{H}^+ \rightarrow \mathbf{B_\alpha H^+} \qquad (1)$$

$$\mathrm{PA}(\mathbf{B}_\alpha) = (\Delta E_{\mathrm{el}})_\alpha + (\Delta E_{\mathrm{vib}})_\alpha + (^5/_2)RT \qquad (2)$$

$$(\Delta E_{\mathrm{el}})_\alpha = E(\mathbf{B}) - E(\mathbf{B}_\alpha\mathbf{H})^+ \qquad (3)$$

$$(\Delta E_{\mathrm{vib}})_\alpha = E_{\mathrm{vib}}(\mathbf{B}) - E_{\mathrm{vib}}(\mathbf{B}_\alpha\mathbf{H})^+ \qquad (4)$$

The base in question and its conjugate acid are denoted by **B** and $\mathbf{B_\alpha H^+}$, respectively, where α denotes the site of proton attack. $(\Delta E_{\mathrm{el}})_\alpha$ is the electronic contribution to the proton affinity, E_{vib} includes the zero-point vibrational energy and temperature corrections to the room-temperature enthalpy and $(^5/_2)RT$ accounts for the translational energy of the proton as well as the $\Delta(pV)$ term. The gas-phase basicity is defined as the Gibbs free energy change of reaction (1). Basicity values will be given later in order to make easier comparison with future experiments. However, in what follows we shall focus only on the proton affinities and their interpretation as they offer a good description of the basicities, being simpler for analysis at the same time.

As a convenient computational model, we shall employ the density functional theory (DFT) in its B3LYP representation.[63,64] The molecular structures were calculated using the efficient, but flexible enough, 6-31+G(d) basis set, whereas the final molecular energies were obtained using the more intricate 6-311+G(d,p) basis set in the single-point calculations giving rise to the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) scheme. The true minima on the Born–Oppenheimer (BO) potential energy hypersurface were verified by vibrational frequency analysis at the B3LYP/6-31+G(d) level of theory, which were subsequently used in the zero-point vibrational energy (ZPVE) and thermal correction calculations. The latter values were employed without a scaling factor.

An important task of the theoretical work is the interpretation of the experimentally measured or theoretically deduced data on molecular properties. Consequently, the interpretation of the calculated PAs is strongly emphasised. Earlier, we found that a triadic (trichotomy) formula given by Equation (5) is well suited to this purpose,[65]

$$(\mathrm{PA})_\alpha = -(\mathrm{IE})^{\mathrm{Koop}}_{\alpha,n} + E(\mathrm{ei})^{(n)}_{\alpha,\mathrm{rex}} + (\mathrm{BAE})^{\cdot+}_\alpha + 313.6\ \mathrm{kcal\,mol^{-1}} \qquad (5)$$

where $(\mathrm{IE})^{\mathrm{Koop}}_n$ refers to the nth Hartree–Fock-occupied orbital energy ε_n of the molecule **B**, which corresponds to the nth ionization energy computed in the clamped nuclei and frozen electron density (Koopmans') approximation.[66] This is the first step in the protonation process and corresponds to a jump of an electron to the incoming proton. Note that the highest occupied molecular orbital (HOMO) will be denoted by a subscript $n = 1$ and the lower MOs as $n > 1$. The bond association energy $(\mathrm{BAE})^{\cdot+}_\alpha$ term is a measure of the release of exothermic energy upon formation of a new covalent bond between atom α of the radical cation and the hydrogen atom. The electron affinity of the proton is 313.6 kcal mol^{-1}. Note that Koopmans' ionization corresponds to the sudden electron ejection event. This is not so crude an approximation as might be concluded at first glance. There is abundant evidence now that the one-electron picture is very useful in rationalizing the molecular photoelectron spectra.[67–70] There is also growing evidence that the concept of the molecular orbital has a touch of reality,[71–73] which means that frozen MOs reflect genuine properties of the initial state rather well. However, having said that, we should always bear in mind that true ionization occurs in real time and it is generally accepted that relaxation of the radical cation is completed at the end of the ionization process. Hence, the relaxation of the electrons and nuclei represents the second step in a protonation event. The corresponding energy is given by Equation (6),

$$E(\mathrm{ei})^{(n)}_{\alpha,\mathrm{rex}} = (\mathrm{IE})^{\mathrm{Koop}}_{\alpha,n} - (\mathrm{IE})^{\mathrm{ad}}_1 \qquad (6)$$

which should be explicitly taken into account in the quantitative prediction of the PAs, as indicated in Equation (5). In Equation (6) the first adiabatic ionization energy is represented by $(\mathrm{IE})^{\mathrm{ad}}_1$. Note that the creation of a new bond at an atom α also includes a certain relaxation of the nuclei, but this part of the stabilization energy is included in the $(\mathrm{BAE})^{\cdot+}_\alpha$ term. It should be strongly distinguished from the $E(\mathrm{ei})^{(n)}_{\alpha,\mathrm{rex}}$ relaxation term in Equation (6).

To epitomize, the initial state effect of the neutral base in question is mirrored in Koopmans' picture of ionization, implying that the energy required for electron ejection from the initial base is calculated in the approximation of the fixed geometry and frozen electron density. The final state effect of the protonated molecule is given by the bond association $(\mathrm{BAE})^{\cdot+}_\alpha$ term. The relaxation energy is an interplay between the initial and final state effects representing an intermediate step on its own. The advantages of the use of the triadic approach to interpretation were discussed at length by Deakyne.[74] We note in passing that this approach has proved useful in interpreting substituent effects too, as was convincingly shown recently.[75–77] As a final remark, it should be mentioned that Koopmans' $(\mathrm{IE})^{\mathrm{Koop}}_n$ orbital energies were computed using the HF/6-

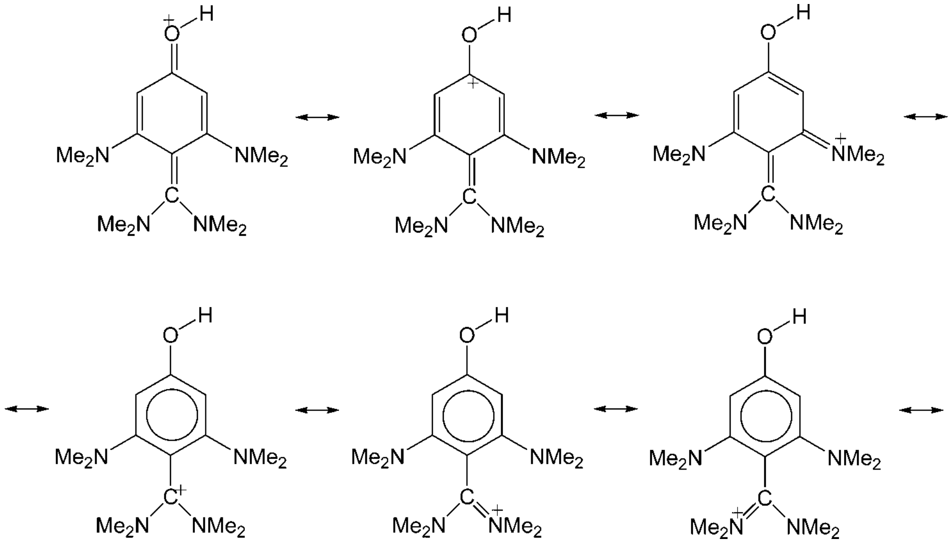
311+G(d,p)//B3LYP/6-31+G(d) model. All the calculations were carried out using the GAUSSIAN03 program.[78]

Results and Discussion

General Considerations

The compounds studied in this work are depicted in Figure 1. Note that it is useful to distinguish between the head of the molecule, the quinone or [3]radialene oxygen atom undergoing protonation, and the tail, a pending fragment at the other end of the system. In some cases molecules ending with the N–Me group are tailless, the nitrogen atom being a part of the six-membered ring. As a rule, the most basic site is the quinone/[3]radialene carbonyl oxygen atom, with two exceptions: the imino nitrogen atoms in ambident compounds **2** and **6** are more basic. The compounds studied encompass monoquinoid compounds **1**–**10**, dressed by NMe_2 groups in **7**–**10** in order to increase their basicity. In the systems **11** and **12** the methylene tail fragment present in **1** is replaced by the tailless >N–Me moiety. Inspection of the proton affinities presented in Figure 1 and Table 1 shows that compounds **1**–**12** exhibit moderate basicities. There are two exceptions, **5** and **7**, however, which possess superbasic PA values of 256.9 and 264.5 kcal mol^{-1}, respectively. These two molecules possess the $=C(NMe_2)_2$ group which is a very efficient tail thus leading to considerable enhancement of proton affinity and basicity. Note, in this connection a threshold for superbasicity is given by PA = 245.3 kcal mol^{-1}, the PA of DMAN.[79] The superbasicity of **7** is a consequence of the considerable stabilization triggered by protonation, termed the cationic resonance effect. It is illustrated by Pauling's resonance structures in Scheme 1.

Cationic resonance stabilization is a result of a combined effect of induction and π-electron conjugation. Protonation of the carbonyl oxygen atom increases its electronegativity. Concomitantly, the oxygen atom pulls the electron density from the nearest neighbour carbon atom through the σ channel forming a σ "hole". The latter is subsequently filled by the π electron placed at the same carbon atom thus creating a π "hole" which is delocalized over the π-electron network including the NMe_2 groups placed at judiciously chosen strategic positions, as shown in Scheme 1. Efficient dispersion of the positive charge in conjugate acid **7H$^+$** considerably contributes to its stability and consequently to the basicity of the initial base **7**. The same holds for compound **5**, but to a lesser extent, because two of the NMe_2 groups are missing. Clearly the π-electron-releasing NMe_2 groups play a very important role in cationic resonance, simultaneously stimulating the aromatization of the quinoid six-membered ring provided the amino groups are placed at the tail of the molecule. This directly follows from inspection of the resonance structures in Scheme 1. Note that the cationic resonance is related to an n–π resonance effect taking place in the so-called push–pull molecules. It would be useful to obtain some (semi)-quantitative information about the aromaticity of particular rings in polycyclic systems. There are two methods suitable for this purpose. The first is the geometric HOMA criterion,[80–83] the second is the magnetic nucleus independent chemical shift [NICS(1)] index.[84–86] The latter was employed in this work. The NICS(1) data were computed by the HF/6-31G(d)//B3LYP/6-31+G(d) model utilizing gauge-invariant atomic orbitals at a point 1 Å above the electron density critical point within the ring. The latter is found by the electron distribution analysis performed within Bader's atoms-in-molecule theory.[87] They are given in Figure 1 next to the respective rings with values for the conjugate acids given in square brackets, unless the ring in question is non-planar (like in **10**). Note that the



Scheme 1.

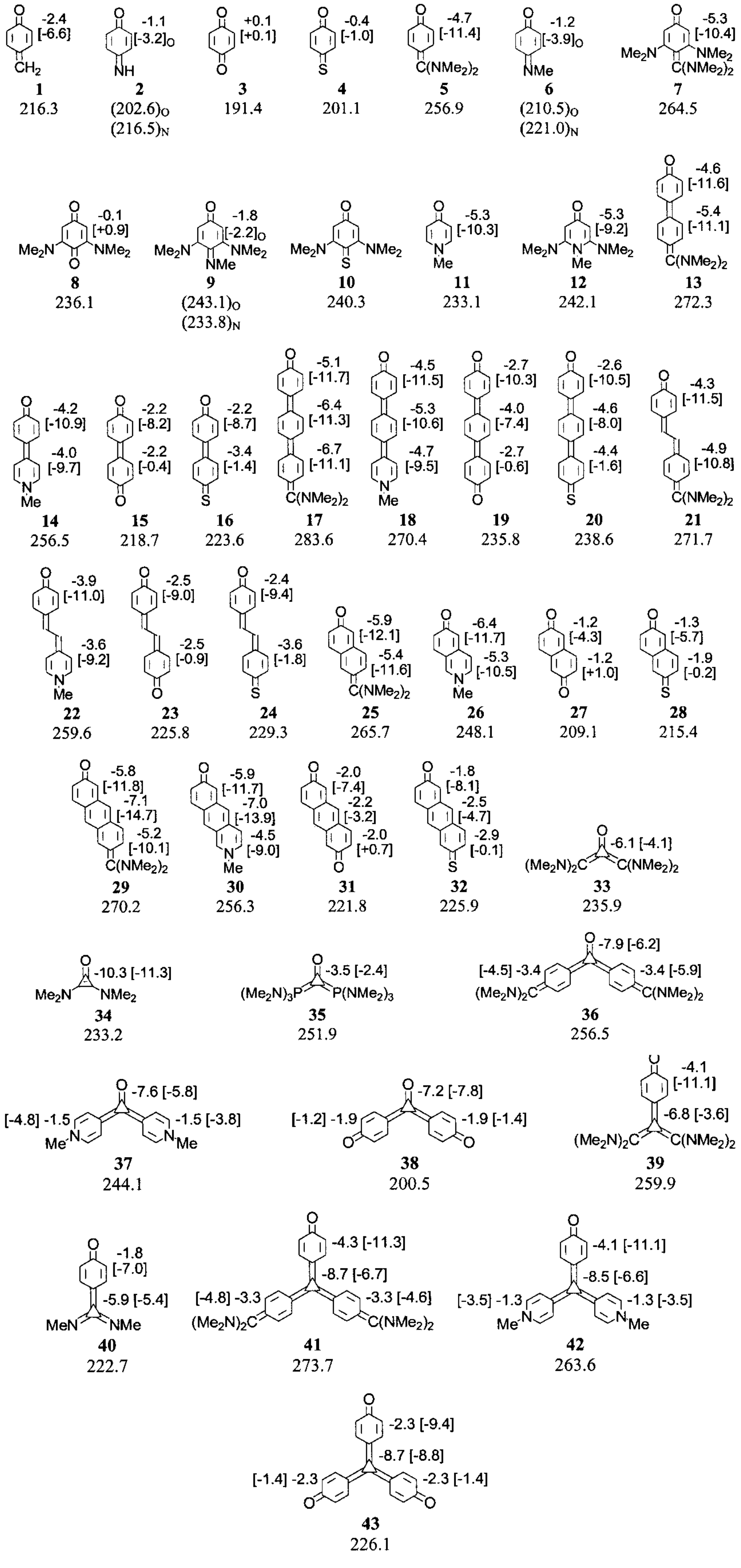


Figure 1. Schematic representation of the studied molecules. Schleyer's NICS(1) values are given for the neutral (without parentheses) and protonated (in square brackets) species. The values given below the structures refer to the absolute proton affinities (in kcal mol^{-1}).

Table 1. Triadic decomposition of the absolute proton affinities and their differences relative to the PA of quinone **3**. In addition, the first adiabatic ionization energies and basicities are given. All energies are in kcal mol^{-1}.[a]

Molecule	$(IE)_n^{Koop}$	$(IE)_1^{ad}$	$E(ei)(n)_{rex}$	$(BAE)^{\cdot +}$	PA	$\Delta(PA)_3$	GB
1	$(263.8)_{\mathrm{HOMO-2}}$	206.2	57.6	108.9	216.3	24.9	209.2
2_O	$(275.8)_{\mathrm{HOMO-2}}$	218.9	56.9	107.9	202.6	11.2	195.1
2_N	$(290.8)_{\mathrm{HOMO-3}}$	218.9	71.9	121.8	216.5	25.1	209.3
3	$(281.1)_{\mathrm{HOMO-2}}$	226.5	54.6	104.3	191.4	0.0	184.9
4	$(283.9)_{\mathrm{HOMO-3}}$	205.3	78.6	92.8	201.1	9.7	194.0
5	$(233.1)_{\mathrm{HOMO-2}}$	151.2	81.9	94.5	256.9	65.5	249.2
6_O	$(266.4)_{\mathrm{HOMO-2}}$	210.6	55.8	107.5	210.5	19.1	202.7
6_N	$(266.4)_{\mathrm{HOMO-2}}$	210.6	55.8	118.0	221.0	29.6	213.6
7	$(218.3)_{\mathrm{HOMO-2}}$	155.6	62.7	106.5	264.5	73.1	256.7
8	$(266.0)_{\mathrm{HOMO-2}}$	167.4	98.6	89.9	236.1	44.7	228.9
9_O	$(254.1)_{\mathrm{HOMO-3}}$	161.9	92.2	91.4	243.1	51.7	235.3
9_N	$(247.9)_{\mathrm{HOMO-2}}$	161.9	86.0	82.1	233.8	42.4	225.9
10	$(272.7)_{\mathrm{HOMO-4}}$	162.9	109.8	89.6	240.3	48.9	233.2
11	$(247.6)_{\mathrm{HOMO-2}}$	186.9	60.7	106.4	233.1	41.7	226.5
12	$(239.7)_{\mathrm{HOMO-2}}$	165.1	74.6	93.6	242.1	50.7	235.3
13	$(223.9)_{\mathrm{HOMO-3}}$	129.9	94.0	88.6	272.3	80.9	264.1
14	$(234.9)_{\mathrm{HOMO-2}}$	150.1	84.8	93.0	256.5	65.1	249.0
15	$(273.1)_{\mathrm{HOMO-3}}$	193.7	79.4	98.8	218.7	27.3	211.2
16	$(275.9)_{\mathrm{HOMO-5}}$	181.5	94.4	91.5	223.6	32.2	216.2
17	$(210.7)_{\mathrm{HOMO-3}}$	115.9	94.8	85.9	283.6	92.2	275.1
18	$(225.6)_{\mathrm{HOMO-3}}$	131.4	94.2	88.2	270.4	79.0	261.5
19	$(267.9)_{\mathrm{HOMO-5}}$	168.3	99.6	90.5	235.8	44.4	228.0
20	$(270.9)_{\mathrm{HOMO-7}}$	165.8	105.1	90.8	238.6	47.2	230.9
21	$(228.4)_{\mathrm{HOMO-3}}$	127.1	101.3	85.2	271.7	80.3	264.4
22	$(237.7)_{\mathrm{HOMO-3}}$	144.1	93.6	90.1	259.6	68.2	251.9
23	$(271.1)_{\mathrm{HOMO-4}}$	182.8	88.3	95.0	225.8	34.4	218.5
24	$(272.6)_{\mathrm{HOMO-5}}$	174.8	97.8	90.5	229.3	37.9	221.9
25	$(229.0)_{\mathrm{HOMO-2}}$	138.4	90.6	90.5	265.7	74.3	257.9
26	$(239.8)_{\mathrm{HOMO-2}}$	162.9	76.9	97.4	248.1	56.7	240.1
27	$(278.4)_{\mathrm{HOMO-2}}$	211.0	67.4	106.5	209.1	17.7	201.6
28	$(279.7)_{\mathrm{HOMO-4}}$	190.5	89.2	92.3	215.4	24.0	208.0
29	$(227.6)_{\mathrm{HOMO-3}}$	128.8	98.8	85.4	270.2	78.8	262.6
30	$(237.1)_{\mathrm{HOMO-3}}$	147.5	89.6	90.2	256.3	64.9	248.0
31	$(273.6)_{\mathrm{HOMO-3}}$	190.4	83.2	98.6	221.8	30.4	214.3
32	$(275.2)_{\mathrm{HOMO-5}}$	178.9	96.3	91.2	225.9	34.5	218.5
33	$(217.2)_{\mathrm{HOMO-1}}$	126.4	90.8	48.7	235.9	44.5	230.1
34	$(231.4)_{\mathrm{HOMO-1}}$	158.5	72.9	78.1	233.2	41.8	228.9
35	$(195.3)_{\mathrm{HOMO-1}}$	103.8	91.5	42.1	251.9	60.5	246.9
36	$(212.0)_{\mathrm{HOMO-2}}$	101.2	110.8	44.1	256.5	65.1	246.8
37	$(221.4)_{\mathrm{HOMO-2}}$	119.9	101.5	50.4	244.1	52.7	237.0
38	$(270.5)_{\mathrm{HOMO-4}}$	190.3	80.2	77.2	200.5	9.1	193.0
39	$(236.0)_{\mathrm{HOMO-5}}$	132.0	104.0	78.3	259.9	68.5	251.9
40	$(269.9)_{\mathrm{HOMO-4}}$	132.6	137.3	41.7	222.7	31.3	215.7
41	$(224.2)_{\mathrm{HOMO-6}}$	108.0	116.2	68.1	273.7	82.3	266.0
42	$(232.6)_{\mathrm{HOMO-4}}$	126.5	106.1	76.5	263.6	72.2	257.0
43	$(276.4)_{\mathrm{HOMO-6}}$	181.1	95.3	93.6	226.1	34.7	218.1

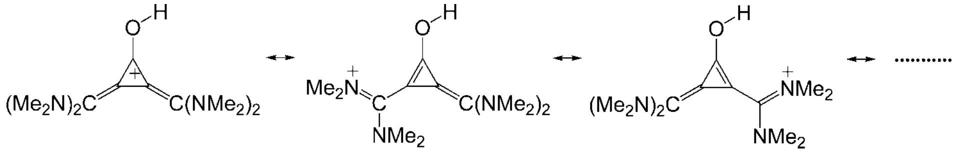
[a] The protonated atom is the carbonyl oxygen atom unless indicated otherwise.

NICS(1) value for free benzene is –12.8 units, which serves as a gauge of aromaticity. Comparison of the NICS(1) values for **5** and **1** reveals that double substitution of the methylene tail by the NMe_2 group in the latter compound yields some aromatic character even in the initial neutral base **5**, which is substantially enhanced upon protonation [–11.4]. The parent compound **1** undergoes a similar change, but to a much lesser extent. Double substitution at the lateral position in **7** actually diminishes the aromatic character of **7H$^+$** relative to that of **5H$^+$**, in accord with the resonance structures given in Scheme 1. In spite of this the basicity of **7** is higher than that of **5**, as evidenced by the increase in the PA of 7.6 kcal mol^{-1}, which rather nicely illustrates the importance of cationic resonance with or without the aromatic stabilization. This interesting finding is supported by a comparison of the proton affinities of other systems, including the following closely related pairs of molecules: **3** (191.4) versus **8** (236.1), **4** (201.1) versus **10** (240.3), **6** (210.5) versus **9** (243.1) and **11** (233.1) versus **12** (242.1). Clearly, attachment of two NMe_2 groups at carefully selected positions in the molecular backbone increases the proton affinity by more than 40 kcal mol^{-1}, which is remarkable indeed. On the other hand, molecules **2**–**4** and **6** are not aromatized by protonation and do not exhibit significant cationic resonance. Consequently their PA values are very low. Again, the systems **8** and **10** are typically non-aromatic, as evidenced in the former molecule by NICS(1) values close to zero even in the corresponding conjugate acids and yet their basicity is increased relative to **3** and **4** by 44.7 and 39.2 kcal mol^{-1}, respectively. Clearly, this is a consequence of strong cationic resonance involving two NMe_2 groups. The same almost holds for **9**, which possesses a PA higher by 32.6 kcal mol^{-1} than its counterpart **6**. Compounds **11** and **12** undergo aromatization and combined aromatic stabilization and cationic resonance, respectively, thus being more basic, attaining PA values of 233.1 and 242.1 kcal mol^{-1}, respectively. It appears that the N–Me ending is less efficient than the $=C(NMe_2)_2$ tail and that NMe_2 double substitution increases the PA by only 9 kcal mol^{-1}, based on a comparison of **11** and **12**. It turns out that stabilization of the conjugate acid by the cationic resonance mechanism is an important motif in the design of neutral superbases provided strong π-electron-releasing substituents like NMe_2 (or OMe) are placed at appropriate sites which in turn enable extended cationic resonance. This conjecture is further strengthened by analysis of the next two families of compounds, molecules **13**–**16** and **17**–**20**. The former should exhibit the so-called tandem aromaticity effect as both six-membered rings are expected to be aromatized upon protonation. A survey of the NICS(1) values shows that this is only partly true because the tandem aromaticity effect takes place only in **13** and **14**. In contrast, only the first ring, being in the immediate neighbourhood of the protonated oxygen atom, is aromatized in **15** and **16**. Moreover, in the latter two systems the six-membered ring furthest away from the protonation centre is even less aromatic in the conjugate acid than in the initial base. Concomitantly, **13** and **14** are superbases, as evidenced by PAs of 272.3 and 256.5 kcal mol^{-1}, respectively. Comparison with the corresponding smaller systems **5** and **11** reveals that proton affinities are increased by the tandem aromaticity effect by as much as 15.4 and 23.4 kcal mol^{-1}, respectively. The remote six-membered rings in **15** and **16** indirectly enable aromatization of the first ring carrying the basic oxygen centre, whereas they remain non-aromatic particularly in the protonated forms (Figure 1). Thus, the basicity of these two compounds is enhanced by 27.3 and 22.5 kcal mol^{-1} compared with **3** and **4**, respectively. In spite of this, **15** and **16** are only moderately basic compounds. Clearly, =O and =S as tails are poor acceptors of positive π charge and consequently do not support aromatization of the quinoid ring. The structural patterns found in molecules **17**–**20** and their conjugate acids show mutatis mutandis a similar trend. This conclusion is corroborated by all the matching pairs studied here (**3** versus **4**, **8** versus **10**, **15** versus **16**, **19** versus **20**, **23** versus **24**, **27** versus **28**, **31** versus **32**), as evidenced by both the NICS(1) values and the proton affinities. It appears that the NICS(1) index for thioketone derivatives exhibits more negative values for the corresponding six-membered rings while at the same time possessing larger proton affinities. All three six-membered rings are aromatized in **17H$^+$** and **18H$^+$**, thus indicating the aromatic domino effect[27] triggered by protonation. It is also fair to say that **19** and **20** only undergo the tandem aromatic effect for two of the aromatized rings upon protonation as the remote six-membered rings persistently remain non-aromatic due to the unfavourable =O and =S tails. It follows that compounds **17** and **18** have superbasic PA values of 283.6 and 270.4 kcal mol^{-1}, whereas **19** and **20** are below the superbasicity threshold on the basicity ladder.

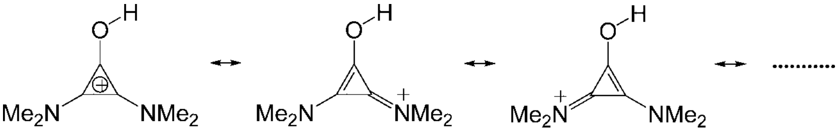
The C(sp^2)–C(sp^2) central bond serves as a relay between the two quinoid fragments rather well as the six-membered rings are strongly aromatized in the protonated forms of **21** and **22**. Their basicities are lower though than **17** and **18**, as measured by the differences in the proton affinities: PA(**21**) – PA(**17**) = –11.9 and PA(**22**) – PA(**18**) = –10.8 kcal mol^{-1}. The reason is simple: the systems **21H$^+$** and **22H$^+$** have one aromatized benzene-like ring less. The C=O and C=S tails are notoriously inefficient in promoting the cationic resonance effect, which proves true for compounds **23** and **24** too. The remote quinoid substructures remain non-aromatic in the conjugate acids, as evidenced by the NICS(1) values (Figure 1). Their proton affinities are as much as 10 kcal mol^{-1} lower than their counterparts in **19** and **20**. Condensed systems **25** and **26** undergo aromatization of both fused six-membered rings upon protonation forming naphthalene-like moieties, thus attaining PAs of 265.7 and 248.1 kcal mol^{-1}, respectively. The latter is just slightly greater than the superbasic threshold of DMAN. The conjugate acids **27H$^+$** and **28H$^+$** are not aromatized and consequently their neutral bases are of a low basicity. It is interesting that all three six-membered rings are aromatized in **29** and **30**, spurred on by protonation forming anthracene-like moieties. The central ring in their conjugate acids should be even more aromatic than free benzene itself according to the NICS(1) values. Note, in this connection, there is no direct proportionality between the NICS(1) index of aromaticity and the energetic stabilization of the ring in question. The NICS(1) parameter is able to provide only qualitative information on the aromatic stabilization. Molecule **29** is a strong superbase, as reflected in its PA = 270.2 kcal mol^{-1}. Compounds **31** and **32** are moderately basic, as expected, because of their unfavourable tails.

We have so far discussed the quinoid moiety as a proton-accepting head in tailoring superbases. The question arises as to whether there are moieties that perform even better than the quinoid head fragment. With this in mind, we examined the basic properties of [3]carbonylradialene **33**. To do this, it was useful to have qualitative information on the stability of the conjugate acid **33H$^+$**; this information is shown in the resonance structures depicted in Scheme 2.

It is clear that the basal C–C bond of the three-membered ring does not participate in the cationic resonance, implying that circulation of the double bond on the rim is hindered. This is reflected in a less negative NICS(1) value of –4.1 for **33H$^+$** compared with the value of –6.1 for the initial neutral base of **33** (viz. Figure 1). Despite a decrease in π-electron delocalization within the ring, the proton affinity is not as small as might be expected (235.9 kcal mol^{-1}). However, it is 7 kcal mol^{-1} less than its quinoid counterpart **9**. It appears that strong cationic resonance is stimulated by the NMe_2 substituents, which in turn is propagated along the lateral CC bonds of the ring directly to the amino groups, as illustrated in Scheme 2. A different



Scheme 2.



Scheme 3.

situation arises in the conjugate acid of cyclopropenone **34H⁺** (Scheme 3). In this case, both aromatization of the three-membered ring and resonance with electron-releasing NMe_2 groups contribute to the stability of the conjugate acid.

The delocalized nature of the **34H⁺** system is evidenced by the NICS(1) value of –11.3, which is close to that of benzene (–12.8). However, one should take into account a characteristic of the three-membered rings, that all have low NICS(1) values due to σ-surface aromaticity, as discussed by Cremer and Kraka.[88,89] Generally, the NICS(1) values for rings of different sizes are not directly comparable. All we can say is that the NICS(1) value slightly increases in **33** and **35** upon protonation, whereas it decreases by 1 ppm in **34H⁺**. The proton affinity of 233.2 kcal mol^{-1} is comparable to that of **19**. It is also comparable to the proton affinity of system **33** in which almost identical basicity is obtained with twice as many NMe_2 groups at the tail of the system. Finally, we would like to test the new type of substituent given by the $=P(NMe_2)_3$ fragment, a phosphorus atom with three directly attached dimethylamino groups. It turns out that two such groups placed at two ends of the [3]carbonylradialene backbone very efficaciously amplify the basicity of **35** yielding PA = 251.9 kcal mol^{-1}. It provides conclusive evidence that the $=P(NMe_2)_3$ group is a very proficient tail. The proton affinity of molecule **35** is 16 kcal mol^{-1} higher than that of **33**, which possesses remote $=C(NMe_2)_2$ fragments. The latter substituent is less capable of accommodating the positive charge formed upon protonation, which is apparent by inspection of the NICS(1) values of conjugate acids. In molecule **33H⁺** the NICS(1) value for the three-membered ring is –4.1, whereas in **35H⁺** it is –2.4 (Figure 1). Molecules **33** and **35** illustrate the importance of the number of NMe_2 substituents in amplifying and fine-tuning the basicity.

The extended π systems **36**–**38**, in which the [3]carbonylradialene fragment is used as the head of the neutral (super) bases, do not have high proton affinities and related basicities. The largest PA of 256.5 kcal mol^{-1} is found in **36**. Very modest aromaticity, as indicated by NICS(1) values of around –6, is found in all the rings upon protonation. The aromatic stabilization in **37H⁺** is even less pronounced leading to PA = 244.1 kcal mol^{-1}, whereas the carbonyl groups in **38** proved once again to be very ineffective as the terminal functionality in promoting either aromatization or cationic resonance. We have to conclude that the [3]carbonylradialene cannot serve as a basic head if superbases are desired and that at best it is able to produce only moderately superbasic compounds that are placed on the lowest rung of the superbasicity ladder.

In the last part of this study we considered calixene-like compounds **39** and **40** and propeller-like systems **41**–**43**. In both sets of molecules only the quinoid ring closest to the protonation centre undergoes strong aromatization, whereas the expected aromatic stabilization of other rings is small at best. An exception is the central [3]radialene ring in **43**, for which a NICS(1) value of around –9 is found in the conjugate acid indicating significant conjugation. It appears that bifurcation of the quinoid fragments around the central [3]radialene moiety is not favourable for aromatization in the conjugate acids unless they are directly protonated as heads, as evidenced by compounds **41**–**43**. Finally, it should be mentioned that molecules **39**, **41** and **42** exhibit superbasic PAs of 259.9, 273.7 and 263.6 kcal mol^{-1}, respectively. The strongest base among them is compound **41**, a consequence of cationic resonance with the two $C=C(NMe_2)_2$ endings with four dimethylamino substituents.

In summary, it has been found that the strongest superbase is compound **17** with a PA of 283.6 kcal mol^{-1}, while several systems (**7**, **13**, **22**, **25**, **29**, **39**, **41** and **42**) possess PAs in the range of around 260–275 kcal mol^{-1}. These compounds are expected to serve as useful neutral organic superbases.

Triadic Analysis

The stability of the conjugate acids discussed in terms of cationic resonance, including the aromatic tandem and domino effects, provides a useful global, but qualitative description of the stability of conjugate acids, which in turn represents the final state of the protonation process. Its drawback lies in the fact that the properties of the initial state (neutral bases) are completely left out of such considerations not to mention the intermediate state. A more detailed and balanced picture is offered by triadic analysis, which treats the initial, intermediate and final state effects on an equal footing whilst at the same time providing quantitative information. It proved very useful in reproducing the trend in changes in proton affinities, as is now well documented.[65,77,90] For this purpose we employed a succinct description, yielding the changes in proton affinities relative to the predetermined gauge molecule, which in our case is the parent quinone **3** as a progenitor of all the quinoid systems. According to the triadic formula in Equation (5), the corresponding triad is given by Equation (7),

$$\Delta[\mathrm{PA}(\mathbf{B})_\alpha] = \mathrm{PA}(\mathbf{B})_\alpha - \mathrm{PA}(\mathbf{3}) = [-\Delta(\mathrm{IE})^{\mathrm{Koop}}_{\alpha,n};\ \Delta E(\mathrm{ei})^{(n)}_{\alpha,\mathrm{rex}};\ \Delta(\mathrm{BAE})^{\cdot+}_{\alpha}] \quad (7)$$

where the square brackets imply summation of the three terms within as usual, which in turn are given by Equations (8a–c).

$$\Delta(\mathrm{IE})^{\mathrm{Koop}}_{\alpha,n} = (\mathrm{IE})^{\mathrm{Koop}}_{\alpha,n}(\mathbf{B}_\alpha) - (\mathrm{IE})^{\mathrm{Koop}}_{\beta,m}(\mathbf{3}) \quad (8a)$$

$$\Delta E(\mathrm{ei})^{(n)}_{\alpha,\mathrm{rex}} = E(\mathrm{ei})^{(n)}_{\alpha,\mathrm{rex}}(\mathbf{B}_\alpha) - E(\mathrm{ei})^{(m)}_{\beta,\mathrm{rex}}(\mathbf{3}) \quad (8b)$$

$$\Delta(\mathrm{BAE})^{\cdot+}_{\alpha} = (\mathrm{BAE})^{\cdot+}_{\alpha}(\mathbf{B}_\alpha) - (\mathrm{BAE})^{\cdot+}_{\beta}(\mathbf{3}) \quad (8c)$$

$\mathbf{B}_\alpha$ denotes the base under consideration as earlier. Note that indices α and β as well as *n* and *m* are different in principle. The partitioning of PAs into triadic components is presented in Table 1. Before we start discussing the variation in the three key terms of the trichotomy description (8a)–(8c) within the large set of the very different molecules considered in this work, it is fitting to point out some outstanding features of the gauge molecule **3** itself. A survey of the data in Table 1 reveals that molecule **3** has the second highest Koopmans' ionization energy, the lowest relaxation energy and one of the highest bond association energies. Concomitantly, the variation in terms will be strongly pronounced. A very high Koopmans' term $-(\mathrm{IE})^{\mathrm{Koop}}_{\mathbf{O},3}$ means that the principal MO (HOMO–2) describing the oxygen (**O**) lone-pair to be protonated is very stable, implying that ionization from that orbital is very endothermic and that the corresponding basicity should be very low, which is useful to bear in mind. The relaxation energy of the radical cation acts in harmony with Koopmans' term. In other words, this contribution also contributes to the modest basicity of compound **3**. Finally, the last term (BAE) compensates for the unfavourable first two terms, but only to a small extent. We can safely conclude that molecule **3** is a very poor (super)base because its initial neutral form is not well prepared for protonation (a high energy is required to ionize the PRIMO). In addition, the radical cation created upon electron ejection exhibits a very small relaxation energy. In what follows, we shall discuss just a few important cases, mostly related to strongly basic compounds. Let us commence with the series **5**, **13**, **17**, **21**, **25**, **29**, **39** and **41**. Their differences (always in kcal mol^{-1}) relative to **3** are: Δ[PA(**5**)] = [48.0; 27.3; –9.8] = 65.5, Δ[PA(**13**)] = [57.2; 39.4; –15.7] = 80.9, Δ[PA(**17**)] = [70.4; 40.2; –18.2] = 80.9, Δ[PA(**21**)] = [52.7; 46.7; –19.1] = 80.3, Δ[PA(**25**)] = [52.1; 36.0; –13.8] = 74.3, Δ[PA(**29**)] = [53.5; 44.2; –18.9] = 78.8, Δ[PA(**39**)] = [45.1; 49.4; –26.0] = 68.5 and Δ[PA(**41**)] = [56.9; 61.6; –36.2] = 82.3. These molecules have a number of properties in common. They are superbases that exhibit very high proton affinities. Further, they have the same quinoid heads with =C(NMe$_2$)$_2$ tail(s). Finally, they undergo either tandem or domino aromatization after protonation, systems **39** and **41** being exceptions. It is therefore not surprising that their triadic components are similar. In the first place, Koopmans' term has an overwhelming influence, except in **39** and **41**, for which the relaxation energy is slightly larger. This implies that the initial state plays a decisive role in most cases because the principal MOs are strongly destabilized relative to **3**, meaning that it is easier to liberate (decouple) one electron from the oxygen lone-pair to form an H$^{\cdot}$ atom first and to create a new O–H bond at the end of the process. Further, the bond association energy is invariably lower than that in **3**, thus decreasing the basicity. However, a strong enhancement in basicity is obtained by relaxation. Large relaxation energies are in accord with the aromatization effect in conjugate acids, as discussed earlier. However, this analogy should not be pushed too far because the relaxation energy upon ionization and the stabilization energy of the conjugate acids by the cationic resonance effect (including aromatization of the six- and/or three-membered rings) are completely different quantities by their very definitions. Consequently, more than a very broad similarity could not be expected. To illustrate this conclusion we give the relaxation energies (within parentheses) of systems **13** (39.4), **17** (40.2) and **39** (49.2), in which two, three and one six-membered ring is aromatized upon protonation, respectively. Evidently, there is no proportionality between the extent of relaxation and the cationic resonance effect.

It is of interest to examine the effect of the double NMe$_2$ substitution at the lateral positions of the systems **8**, **9** **10** and **12** relative to unsubstituted compounds **3**, **6**, **4** and **11**, respectively. Let us consider for this purpose the differences in proton affinities in the triadic representation: PA(**8**) – PA(**3**) = [15.1; 44.0; –14.4] = 44.7, PA(**9**) – PA(**6**) = [21.9; 26.8; –16.1] = 32.7, PA(**10**) – PA(**4**) = [11.2; 31.2; –3.2] = 39.2 and PA(**12**) – PA(**11**) = [7.9; 13.9; –12.8] = 9.0 kcal mol^{-1}. The pattern is always the same: the first two terms are positive and large, whereas the bond association energy reduces the basicity. These examples prove that the real situation is more complex than is suggested by arguments based only on the cationic resonance in the conjugate base triggered by protonation and possibly amplified by the NMe$_2$ substituents. An important contribution is also provided by Koopmans' term, which is a pure initial state effect as well as the predominating relaxation energy.

It is well known that naphthalene has less than twice the aromatic stabilization of free benzene. It can, therefore, be intuitively expected for compounds in the series **25**–**28** to be less basic than the corresponding members of the series **21**–**24** if the final state effect is decisive. What kind of an answer is offered by the triadic formula? The corresponding triplets of terms are PA(**25**) – PA(**21**) = [–0.6; –10.7; 5.3] = –6.0, PA(**26**) – PA(**22**) = [–2.1; –16.7; 7.3] = –11.5, PA(**27**) – PA(**23**) = [–7.3; –20.9; 11.5] = –16.7 and PA(**28**) – PA(**24**) = [–7.1; –8.6; 1.8] = –13.9 kcal mol^{-1}. It follows that the condensed systems **25**–**28** are less basic than the linearly "unfolded" compounds **21**–**24** because of the smaller relaxation effect, an answer that is close to chemical intuition based on the aromaticity argument. Having said this, it should be mentioned that a genuine final state effect mirrored in the bond association energy actually opposes this trend.

Another point of considerable interest relates to the [3]-carbonylradialenes **33**–**35**. The changes in triadic terms Δ[PA(**33**)] = [63.9; 36.2; –55.6] = 44.5 kcal mol^{-1} show that the overriding effect is exerted by a large and positive Koopmans' term, which means the principal molecular orbital HOMO–1 is considerably destabilized (see Figure S1 of the Supporting Information). Similarly, in systems **34** and **35** the trend in changes is the same. The corresponding triads relative to molecule **3** are Δ[PA(**34**)] = [49.7; 18.3; –26.2] = 41.8 kcal mol^{-1} and Δ[PA(**35**)] = [85.8; 36.9; –54.9] = 60.5 kcal mol^{-1}. Note once again the efficiency of the =P(NMe$_2$)$_3$ group in enhancing the basicity of molecule **35**. It is 16 kcal mol^{-1} more basic than compound **33** with a =C(NMe$_2$)$_2$ ending. If we consider the difference in proton affinities between these two system, we obtain PA(**35**) – PA(**33**) = [21.9; 0.7; –6.6] = 16.0 kcal mol^{-1}, which shows that the price of releasing an electron from the lone pair of the carbonyl oxygen in **35** is considerably lower than in **33**. The other two contributions are negligible, once more underlining the important role of the initial state.

We are now in a position to comment on the differences in the protonation sites of bidentate molecules **6** and **9**. Molecule **6** is, after **2**, the only compound that has a nitrogen atom as the most basic centre. Let us consider the difference PA(**6**)$_N$ – PA(**6**)$_O$ = [0.0; 0.0; 10.5] = 10.5 kcal mol^{-1}. Interestingly, the lone pairs of the oxygen and nitrogen atoms belong to the HOMO–2 molecular orbital (the PRIMO is the same, see Figure S1 of the Supporting Information). Therefore, the initial state effect mirrored through Koopmans' ionization term and the intermediate effect reflected in the relaxation energy are exactly the same, although they belong to different conjugate acids (**6H^+_O** and **6H^+_N**). It appears that (BAE)$^{\cdot+}_N$ is larger than the (BAE)$^{\cdot+}_O$ bond energy by 10.5 kcal mol^{-1}, thus making the nitrogen atom more basic by this amount. An interesting case is provided by alternative protonation sites at the oxygen and imino nitrogen atoms in **9**. In this system the carbonyl oxygen atom provides the thermodynamically most favourable position to accept the proton. Examination of the first four occupied orbitals of this molecule reveals that the PRIMO for protonation on the nitrogen atom is HOMO–2, whereas the oxygen lone-pair corresponding to protonation on the oxygen centre is placed in the HOMO–3 molecular orbital (see Figure S1 of the electronic supporting information). The corresponding triad reads PA(**9**)$_O$ – PA(**9**)$_N$ = [–6.2; 6.2; 9.3] = 9.3 kcal mol^{-1}. Remarkably, it is easier to ionize the nitrogen lone-pair in molecule **9** (HOMO–2) than the oxygen lone-pair (HOMO–3) by 6.2 kcal mol^{-1}. Taking only this contribution into consideration, which mirrors the properties of the initial base, one could conclude that nitrogen protonation is more exothermic. However, the Koopmans' and relaxation terms exactly cancel out, as should be the case for different protonation sites within the same molecule. The decisive contribution is again the (BAE) term. It appears that the carbonyl oxygen is more basic than imino nitrogen atom in **9** because the O–H bond energy is 9.3 kcal mol^{-1} higher than the N–H bond energy in the respective conjugate acids **9H$^+$**. The reason for this is two-fold: the formation of the O–H bond additionally stimulates the resonance with the two NMe$_2$ groups at the *meta* positions. On the other hand, the NMe$_2$ groups are at unfavourable (*ortho*) positions with respect to the imino group implying that cationic resonance upon imino protonation cannot take place. Moreover, creation of a new H–NMe bond increases somewhat the steric crowding, which also diminishes the bond energy term.

The last, but not the least, relevant comment is related to principal molecular orbitals. The latter are defined as the MOs that are the most suitable for the chemical reaction under scrutiny and that are changed the most after the reaction. In this case, it is the MO that describes the lone pair to be protonated. The latter is the oxygen (or nitrogen) unshared pair located in the molecular plane. All PRIMOs are energetically much lower than the HOMO, sometimes having an energy as low as HOMO–6 or HOMO–7. It follows that the HOMO would be completely unsuitable for interpreting the protonation of cyclic and polycyclic quinones and [3]carbonylradialenes.

Structural Characteristics

It is beyond the scope of this paper to discuss the fine structural details of all the molecules, their radical cations and conjugate acids studied herein. Instead, we shall focus on some important geometric features in some of the systems if they bear particular relevance for the interpretation of proton affinities. We shall commence with a discussion of the cyclic compounds **5**–**8** presented in Figure 2 in which the structural data of the conjugate acids are provided in square brackets. The structural parameters of the initial bases are given without parentheses. Inspection of the results obtained for **5** and **6** reveals that the double bonds are shortened and the single bonds are lengthened upon protonation. The alternation of the bond lengths in the rings is decreased in accordance with aromatization. This effect is more pronounced in **5H$^+$** than in **6H$^+$**, in accordance with the NICS(1) values (Figure 1). The significant shortening of the C–NMe$_2$ bonds in **5H$^+$** should be emphasized because it reflects the cationic resonance of this important substituent group. Note that the heavy atoms of the NMe$_2$ group in **5** and **5H$^+$** are planar. Comparison of structures **7** and **8** is instructive. It shows that the aromatization in **7H$^+$** is somewhat less than that in **5H$^+$** (once again in accord with the NICS(1) index). On the other hand, the six-membered ring in **8H$^+$** is not aromatized, as evidenced by the lengthening of the two remote C–C bonds from 1.518 to 1.525 Å upon protonation, which is in good agreement with practically vanishing NICS(1) values (Figure 1).

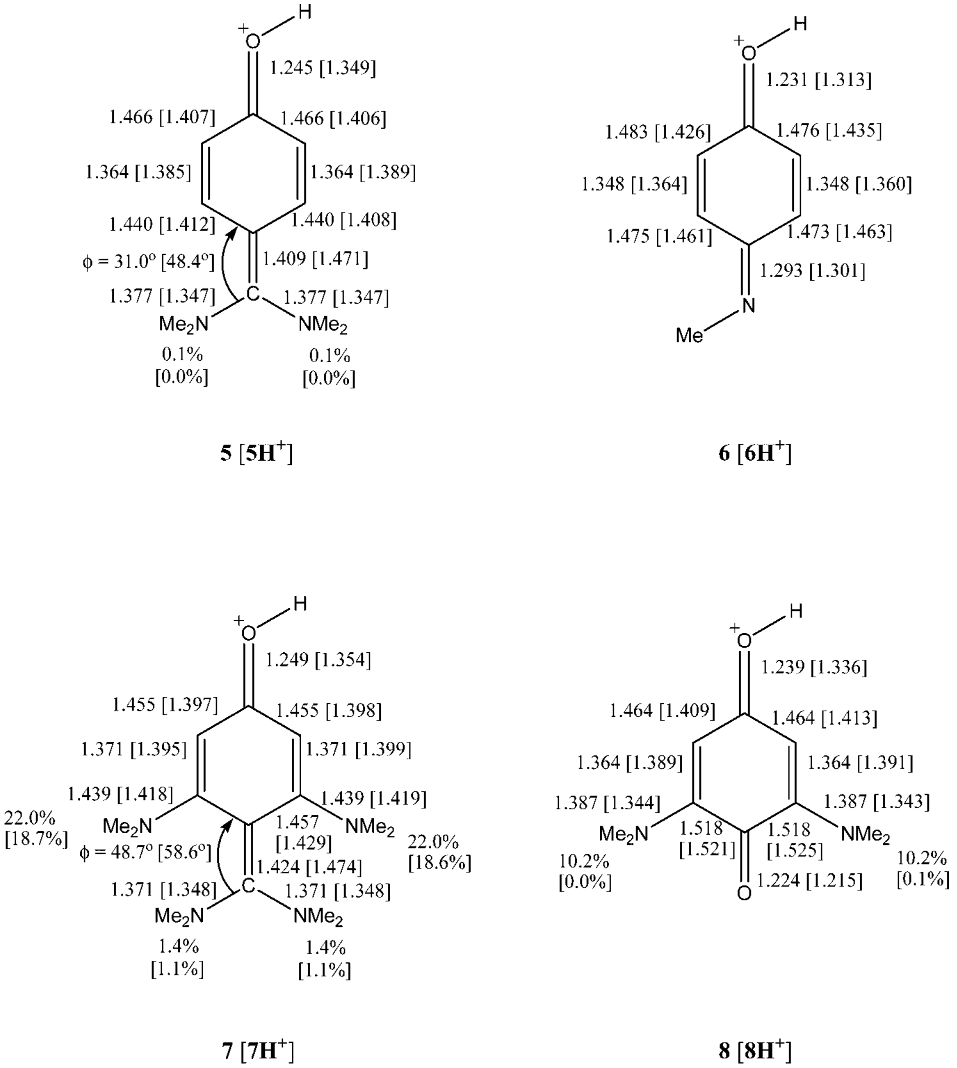


Figure 2. Bond lengths (in Å) and degrees of pyramidalization of the nitrogen atoms (in %) for systems **5**–**8** and their conjugate acids (given within square brackets) obtained at the B3LYP/6-31+G(d) level of theory. The torsional angle is given next to the curly arrows.

In contrast, the cationic resonance effect of the NMe_2 groups is amplified as the C–NMe_2 bond is as short as 1.343 Å. Note that the corresponding bond in **$7H^+$** is much longer (1.419 Å). An important indicator of (cationic) resonance is the pyramidalization of the nitrogen atoms. The degree of pyramidalization [DP(%)] is readily calculated by using a formula given elsewhere.[91] The DP values for the nitrogen atoms belonging to the NMe_2 tail groups are very low in **7** and **$7H^+$**, being 1.4 and 1.1 %, respectively. In contrast, the corresponding values for the lateral NMe_2 groups are high, being 22.0 and 18.7 %. Interestingly, the nitrogen atoms in **$8H^+$** are planar.

Next, molecules **13** and **15** are compared, as depicted in Figure S2 of the Supplementary Information. It is clear that both six-membered rings are significantly aromatized in **$13H^+$**. Moreover, their dihedral angle *φ* is increased to 32° in an apparent tendency to minimize the delocalization perturbation between the two aromatic π sextets. In addition, the dihedral angle between the Me_2N–C–NMe_2 plane and the second aromatic ring is increased to 48°. Consideration of the pyramidalization of the nitrogen atoms shows that in **13** and **$13H^+$** both nitrogen atoms are planar. In **$15H^+$** only the six-membered ring nearest to the molecular (spear)head is somewhat aromatized. The second ring is almost unchanged by protonation as expected from the NICS(1) evidence described earlier. The dihedral angle *φ* is moderately increased to 11°. Finally, a survey of the data given in Figure S3 reveals that three rings are aromatized in **$17H^+$** and only two in **$19H^+$**. The dihedral angles between the aromatic rings in **$17H^+$** are above 30°. The nitrogen atoms are persistently planar and the NMe_2 groups participate in the strong cationic resonance effect. It can safely be concluded that Pauling's intuitive (cationic) resonance picture, NICS(1) values and the changes in the structural parameters induced by protonation are in qualitative terms in full agreement with the interpretation of the proton affinity and basicity of the systems studied in this work.

Conclusions

We have shown that the quinone unit can serve as an efficient proton scavenging head in extended and highly basic polycyclic π systems in the gas phase. The building blocks of these large, essentially planar molecules were provided by quinoid and [3]radialene moieties. Particular emphasis is placed on the selection of the molecular ending. It was found that the >NMe terminal motif and the $=C(NMe_2)_2$ tail proved very effective in enhancing basicity. The role of the NMe_2 groups placed at strategic positions on the molecular backbone has been elucidated. It turns out that they considerably amplify basicity in the resulting conjugate acids through the cationic resonance effect. It has also been conclusively shown that quinoid substructures undergo aromatization upon protonation and exhibit an interesting tandem or domino effect if linearly aligned. Triadic analysis of the trend in changes in proton affinities gave interesting hints about the importance of the initial state. It turned out that a strong synergism between Koopmans' frozen ionization contribution and the relaxation effect in the molecular radical cation leads to some strong superbases, as in the polycyclic systems **13**, **17**, **21**, **29** and **41**. They should become useful rungs on the superbasicity ladder once prepared in the laboratory, which is strongly recommended. Another important issue, which will be addressed in a future publication(s) is the basicity of quinones in organic solvents. It is well known that the carbonyl group is strongly affected by solvation, which in turn diminishes its basicity. In spite of this, we feel that some of the superbases discussed herein exhibit strong basicity even in solvents. Additionally, whether the studied quinones undergo Michael addition[92] or not is a legitimate question which will be examined in the future.

Supporting Information (see also the footnote on the first page of this article): Schematic representation of some selected representative principal molecular orbitals (PRIMOs) as well as a graphical illustration of the geometrical parameters of systems **13**, **15**, **17** and **19** and their protonated forms.

Acknowledgments

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