PAPER www.rsc.org/njc | New Journal of Chemistry

The absolute proton affinity and the second order hyperpolarizability of some catacondensed linear polyacenes and pericondensed zethrenes

Andrea Knežević[a] and Zvonimir B. Maksić*[ab]

Received (in Montpellier, France) 14th October 2005, Accepted 25th November 2005
First published as an Advance Article on the web 14th December 2005
DOI: 10.1039/b514624k

Simple relationships between the absolute proton affinities APAs and second order hyperpolarizabilities γ is found for a class of condensed aromatic molecules with the conjugated π-electron network. Results are presented for "open" acenes and zethrenes in comparison with "closed" systems (coronene and kekulene). They indicate a strong dependence of the APA–γ relation on the molecular shape. Since γ is intimately related to a nonlinear response of the system, it follows that APA could serve as a useful probe for testing the nonlinear polarizability at the molecular level, thus selecting possible candidates for materials with nonlinear optical (NLO) properties. It also appears that zethrenes represent very useful building blocks for NLO materials. An interesting byproduct of this study is that zethrenes could be strongly basic compounds, if appended by a judicious selection of the electron releasing substituents placed at the strategic positions on the molecular perimeter.

Introduction

The proton affinity (PA) is of great importance in proton transfer reactions in chemical and biological systems, in defining Brønsted basicity and acidity of molecules, in catalysis, solvation and in determining susceptibility towards the electrophilic substitution reactivity of aromatics.[1–8] On the other hand, the proton affinity is a quantity interesting *per se*, since the proton provides a very useful probe of the electronic structure of molecules. Gas-phase experimental or single molecule theoretical proton affinities are most appropriate for that purpose, because they reflect intrinsic molecular features free of the solvent effect "contamination". Unlike experimental data,[9] theoretical affinities do not depend on a predetermined gauge value of an anchor base. Since they refer to the absolute proton affinities, they will be abbreviated as APA.

There has been a lot of research interest in this field focused particularly on the strong organic bases.[10–14] Continuing our work on the proton affinity,[15] we felt it worthwhile to explore APAs of linear aromatic catacondensed polyacenes and pericondensed zethrenes, the latter exhibiting the z-like shape. They form a subset of a large family of polycyclic aromatic compounds (PAHs), which have been at the focus of research interest for a long time in view of their role as ubiquitous air pollutants, carcinogens and as systems occuring in many celestial objects like planetary nebulae, reflection nebulae and active galaxies.[16] It is plausible to assume that they will possess high basicity in view of the appreciable resonance effect incited by protonation. More importantly, we would like to examine the second order hyperpolarizability mean value $\langle\gamma\rangle$ of these systems, which in our perception should provide good candidates for constituents of new materials exhibiting favourable nonlinear optical properties.[17–21] This is of considerable interest since the nonlinear effects are important in optical processing and information transfer technology.[22,23] To be more specific, tetracene and pentacene have been used as the active layer of high-performance organic field-effect transistors.[24,25] Acenes proved useful in organic light-emitting diodes (OLEDs), where their high fluorescence efficiency makes them optimal emitters. For instance, it has been shown that antracene yielded blue OLEDs,[26] whereas substituted pentacene derivatives acted as a guest dye in Alq_3-based devices to give red electroluminescence.[27] Consequently, a relation between APAs and $\langle\gamma\rangle$ will be studied, since it is intuitively clear that these two entities should be closely related. It is, namely, a common knowledge that the π-electron excitations are an important determinant of the NLO response. On the other hand, the APAs are larger if HOMO energies are higher. Thus it is not surprising that $\langle\gamma\rangle$s and APAs are in fact linearly related on a logarithmic scale. Hence, if APAs of the extended conjugated systems are determined to a good accuracy, then $\langle\gamma\rangle$s could be easily deduced by using our relationship. The present work complements an earlier study of the APAs of "long" polyacenes by Notario and Abboud.[16]

Methodology

The most accurate APAs are obtained by the G2 method or its G2(MP2) simplified form.[28] These theoretical schemes, however, are not feasible in large molecules. We found that a much simpler model denoted as MP2(fc)/6-31G**//HF/6-31G* + ZPVE(HF/6-31G*) reproduces rather well APAs of a large number of substituted benzenes and naphthalenes.[15] Unfortunately, all these models are still impractical, if the properties

---

[a] *Theoretical Physics Division, Ruđer Bošković Institute, Faculty of Science, University of Zagreb, Bijenička 54, Zagreb, Croatia. E-mail: aknezevic@irb.hr*
[b] *Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Faculty of Science, University of Zagreb, Bijenička 54, Zagreb, Croatia. E-mail: zmaksic@spider.irb.hr*

and APAs of the highly extended aromatic compounds are desired. It is gratifying that there is a fairly good correlation between the MP2 absolute proton affinities and differences in enthalpies of formation of bases and their conjugate acids $\Delta\Delta H_f^0$(AM1)[29a] calculated by the semiempirical AM1 scheme:[29b]

$$\mathrm{APA}(\mathrm{B}_\alpha) = 1.2055\,[\Delta H_f^0(\mathrm{B}) - \Delta H_f^0(\mathrm{B}_\alpha\mathrm{H}^+)] + 404.3\ \mathrm{kcal\ mol^{-1}} \qquad (1)$$

where B and BH^+ denote the base and its conjugate acid, respectively, and α stands for the site of proton attack on the aromatic ring. In deriving eqn (1) the experimental $\Delta H_f^0(\mathrm{H}^+)$ value for the proton of 367.2 kcal mol^{-1} was employed.[30] The correlation (1) puts the AM1 results in line with the MP2 absolute proton affinities of linear polyacenes with a relatively small loss in accuracy (4–5 kcal mol^{-1}).[29a] The correlation coefficient $R^2 = 0.96$ and the average absolute deviation (AAD) is 2.4 kcal mol^{-1}. It is percentage-wise a very small error compared to large APA values. This is the price to be paid for the economical AM1 semi-empirical scheme, which is feasible in very large systems being practical in calculating the $\langle\gamma\rangle$ values too (see below). However, if the error is systematic, then we would have a useful vehicle for examining very large condensed hydrocarbons and their derivatives. This seems to be the case as we shall see later. The heart of the scaled $\mathrm{AM1_{sc}}$ approximate approach is an observation that a change in ZPVEs upon protonation of the carbon atom belonging to the aromatic ring is fairly constant, being 6.4 kcal mol^{-1} on average with an absolute average deviation of only 0.3 kcal mol^{-1}.[29a] Hence, it is absorbed in the additive constant in approximate eqn (1). Another important feature is that the difference in two very large numbers yielding APAs is rather well reproduced by the highly parametrized semiempirical method like AM1.

Finally, the second order molecular hyperpolarizability γ_{ijkl} is defind as the third term of the induced dipole moment developed in a series:

$$\mu_i - \mu_i^0 = \alpha_{ij}\boldsymbol{E}_j + (1/2)\alpha_{ijk}\boldsymbol{E}_j\boldsymbol{E}_k + (1/6)\gamma_{ijkl}\boldsymbol{E}_j\boldsymbol{E}_k\boldsymbol{E}_l + \ldots \qquad (2)$$

where μ_i^0 is the ith component of the permanent dipole moment, whereas α_{ij}, α_{ijk} and γ_{ijkl} are tensor elements of the linear polarizability, first and second order hyperpolarizability, respectively, describing a response to the external perturbation produced by the electric field $\boldsymbol{E}$.[31,32] Summation upon repeated indices is assumed. It should be recalled that γ is the first nonvanishing nonlinear coefficient in systems possessing central symmetry. The quantity of experimental interest is the mean value:

$$\langle\gamma\rangle = (1/5)\{\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2[\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz}]\} \qquad (3)$$

Its theoretical treatment within the AM1 method is described by Stewart *et al.*[33] This semiempirical procedure employs the finite field algorithm, where a field strength of 0.001 a.u. was adopted in order to avoid numerical instabilities and reduce final errors. This is the second reason why the semiempirical AM1 method was selected as the method of choice being highly efficient and practical in calculating $\langle\gamma\rangle$. The high level *ab initio* calculation of the $\langle\gamma\rangle$ would be too demanding. All computations were executed by using the MOPAC program package.[34]

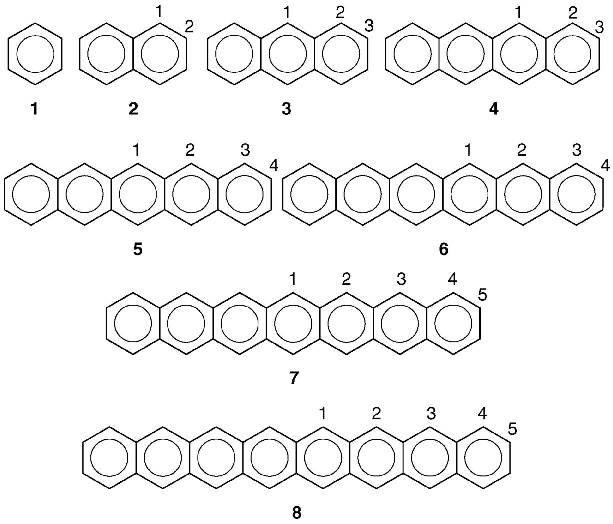


Fig. 1 Schematic representation and atom numbering in acenes.

Results and discussion

The absolute proton affinity

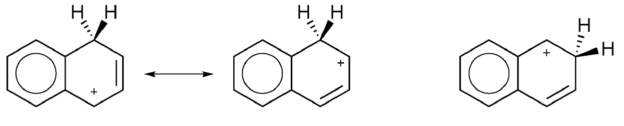
Polyacenes. We shall begin the discussion with polyacenes **1**–**8** (Fig. 1). It should be pointed out that numbering of the carbon atoms does not correspond to the standard numbering used in describing substituted derivatives of these species. It is well known that their reactivity increases along the series. Thus heptacene **7** was prepared as a derivative possessing some stabilizing substituents, but all reported syntheses escaped verification.[35] On the other hand octacene, nonacene and other higher polyacenes successfully avoided their syntheses so far. In fact, Clar claimed that they were incapable of existence.[36] It is well known that anthracene undergoes Diels–Alder reactions and addition of bromine,[37] while tetracene and pentacene are susceptible to 1,4-cycloadditions.[38,39] In order to prevent 1,4-cycloadditions at the central rings Anthony *et al.* developed synthetic routes to block central positions with large alkyne substituents in pentacene, hexacene and heptacene.[40,41] It is intuitively clear that larger systems should possess higher APAs because they can accommodate more efficiently the positive charge created by the protonation. This is also compatible with the increased number of the resonance structures in the protonated forms (*vide infra*). Perusal of data presented in Table 1 supports this contention. The APA values do increase with the number of benzene rings, although this increase is not linear, but attenuates instead. Hence, the differences $\Delta(\mathrm{APA}(n+1) - \mathrm{APA}(n))$ are 13.7, 7.1, 8.6, 9.1, 5.4 and 3.9 (in kcal mol^{-1}) for n running from 1 to 7, respectively, reflecting an apparent lessened increase, but not in a regular manner. The striking feature is that highly reactive heptacene **7** and elusive octacene **8** exhibit strong basicity as evidenced by APA values of *ca.* 242 and 246 kcal mol^{-1}, respectively.

Table 1 The absolute PA values of linear acenes as obtained by the AM1$_{sc}$ model defined by eqn (1); the experimental data (in parentheses) are taken from the NIST database[48]

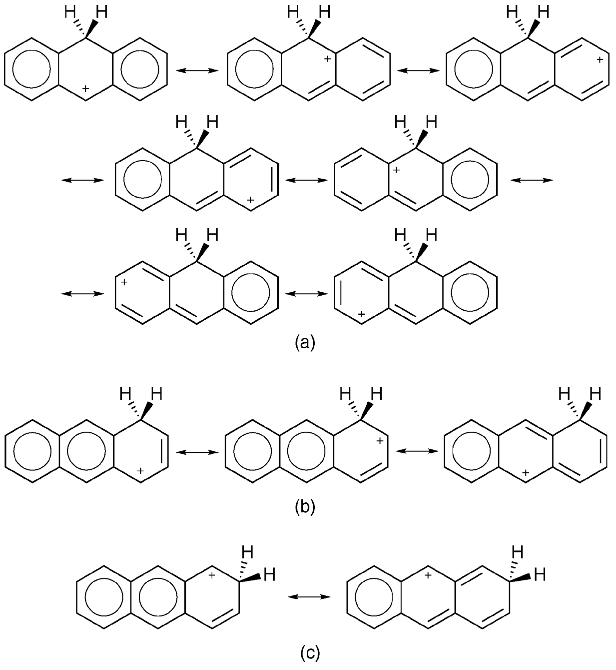
Linearly condensed benzenes	Proton affinity/kcal mol^{-1}					HOMO/eV
	1	2	3	4	5	
1	182.6 (179.9)					−9.65
2	196.3 (191.9)	192.0				−8.71
3	213.4 (208.0)	203.4	198.3			−8.12
4	222.0 (216.5)	207.9	202.9			−7.75
5	231.1 (225.7)^a	227.0	210.9	206.4		−7.50
6	236.5	230.3	213.1	209.0		−7.30
7	241.9	239.9	232.6	214.6	211.0	−7.20
8	245.8	242.7	234.7	216.3	212.0	−7.10

^{a} Ref. 16.

It should be recalled that acenes are alternate systems implying that the π-electron density is uniformly distributed over all carbon atoms. In spite of that, different carbon atoms do exhibit different affinities toward protons, which calls for a simple interpretation. According to Clar's rule[36] the linear acenes cannot have an aromatic sextet in all rings at the same time. In spite of that we shall use notation based on the aromatic sextet circles in the nearest rings when necessary, since it gives the simplest and most compact way of counting and book keeping of the resonance structures. In fact, only one (initial) ring can realize aromatic coupling, which can then "travel" along the 1D chain of the benzene rings resulting in some additional resonance stabilization. The latter is not given by a sum of aromaticities of free benzene rings. Instead, according to some theoretical considerations, the aromatic stabilization per electron slightly decreases in condensed benzenoid systems.[42,43] Wiberg has shown that the aromatic stabilization of benzene (**1**), naphthalene (**2**), anthracene (**3**), naphthacene (**4**) and pentacene (**5**) increases as 36, 60, 80, 99 and 117 (in kcal mol^{-1}), respectively, implying that the stabilization energy per π-electron slowly decreases like 6.0, 6.0, 5.7, 5.5 and 5.3 kcal mol^{-1} in the same order.[44] In any case, it appears naphthalene is less stabilized than two free benzenes *etc*. This helps in rationalizing the variation of proton affinities within the same molecule or within the series of acenes. Let us consider two characteristic examples. The most basic site in naphthalene **2** is position 1, which is easily understood by the number of resonance structures (Scheme 1).



Scheme 1



Scheme 2

Protonation of position 2 retains only one resonance structure, which contains the aromatic sextet within a six-membered ring, as opposed to two such resonance structures occurring upon protonation at position 1. Analogously, the difference in APAs in anthracene **3** is consistent with the number of resonance structures involving the aromatic fragments (Scheme 2). The control site C1 is most susceptible to the proton attack, since the corresponding resonance structures include 8 benzene moieties (Scheme 2(a)). Protonation at C2 position is described by the two resonance structures involving naphthalene fragments and one possessing benzene 6π-electron sextet as evident from Scheme 2(b). Since the aromatic stabilization of naphthalene is somewhat smaller than aromaticities of two free benzenes, it appears that the total stabilization of the protonated form $\mathbf{3}(\mathrm{C2})^+$ is $\leq 5E_{\mathrm{Ar}}(\mathbf{1})$, where $E_{\mathrm{Ar}}(\mathbf{1})$ denotes the aromatic stabilization of benzene. This is smaller than $8E_{\mathrm{Ar}}(\mathbf{1})$, which is an approximate, but good estimate of the stability of the form protonated at C1. Finally, protonation at C(3) position induces the resonance effect described by two important resonance structures involving one naphthalene and one benzene moiety, respectively (Scheme 2(c)). The resulting stabilization is $\leq 3E_{\mathrm{Ar}}(\mathbf{1})$ yielding the lowest APA value in **3**. It is safe to conclude that the variation in APAs within the same acene is determined by the extent of the cationic resonance effect and that it is a consequence of the properties of the final state (*i.e.* of the conjugate acids). The difference in APAs between various acenes depends also on the properties of initial bases. For example, it is well known that HOMO increases as stability of aromatics is enhanced. In the present case, the HOMO orbital energies increase along the acene series **1**–**8** (Table 1) implying that the price to be paid in forming a new bond upon protonation decreases thus amplifying basicity. It appears that both initial and final state effects contribute to the increase in basicity in larger acenes compared to smaller ones, but the latter effect prevails. Let us consider equivalent positions in **2** and **3**. The increase in APA for positions C1 and C2 are $\Delta(\mathrm{C1}) = \mathrm{APA}(\mathbf{3})_{\mathrm{C1}} - \mathrm{APA}(\mathbf{2})_{\mathrm{C1}} = 17.1$ kcal mol^{-1} and $\Delta(\mathrm{C2}) = \mathrm{APA}(\mathbf{3})_{\mathrm{C2}} - \mathrm{APA}(\mathbf{2})_{\mathrm{C2}} = 11.4$ kcal mol^{-1}. These values are

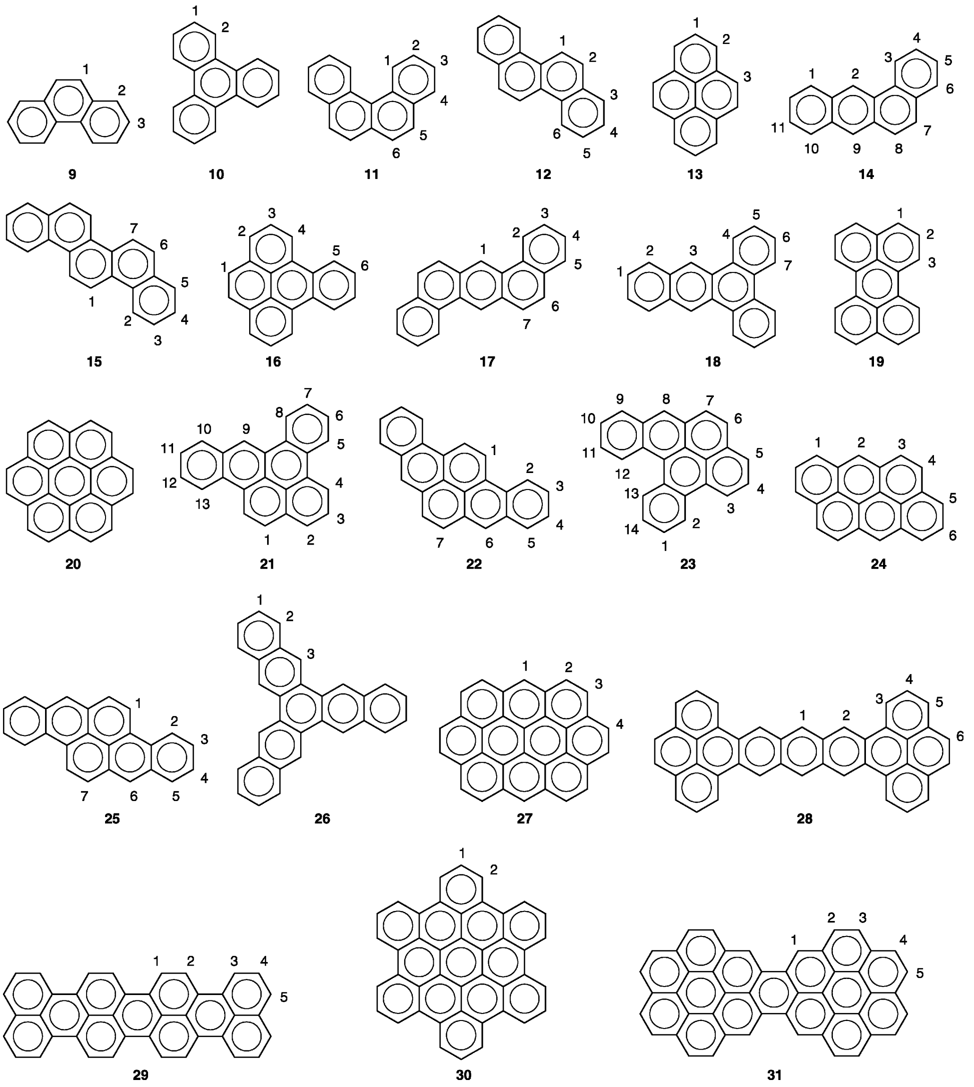


Fig. 2 Schematic representation and atom numbering in some bent or branched acenes and condensed polybenzenes.

compatible with HOMOs of **2** and **3** being −8.71 and −8.12 eV, respectively, and a large difference in the number of resonance structures in the protonated forms $\mathbf{3H}^+$ and $\mathbf{2H}^+$ (*viz*. Schemes 1 and 2). It is important to realize that the difference $\Delta(\text{C1}) - \Delta(\text{C2}) = 5.7$ kcal mol^{-1} is completely free of the influence of initial states being a consequence of a greater ease of larger acenes (here anthracene) to accommodate the excess positive change as intuitively expected and evidenced by the larger number of the resonance structures in more sizeable cations (*viz*. Schemes 1 and 2). The finding that APA is the highest for the central C1 atom in **3** and that it is lowered for more peripheral protonation positions holds in general in other acenes. The increase in APA along the series of acenes is evident by the data given in Table 1, but it exhibits a saturation effect.

Finally, a comparison with available experimental APA values is in place here. The latter are unfortunately scarce. Considering available data it turns out that the estimated APAs are 3–4 kcal mol^{-1} higher than the measured proton affinities (Table 1). Taking into account this offset value one can obtain fairly accurate estimates of the proton affinities in other related systems. It is interesting to compare the present results with those of Notario and Abboud.[16] Following our procedure expounded in ref. 29*a* they derived the scaled AM1_{sc} formula by utilizing the experimental APAs for linear polyacenes up to pentacene. The resulting formula reads: APA(exp.) = 1.15 APA(AM1) − 31.6 kcal mol^{-1} with AAD = 0.3 kcal mol^{-1}. Hence, it is more accurate than our formula (1). However, it should be strongly pointed out that our formula was developed for derivatives of benzene and naphthalene containing a wide variety of multiply substituted groups.[29a]

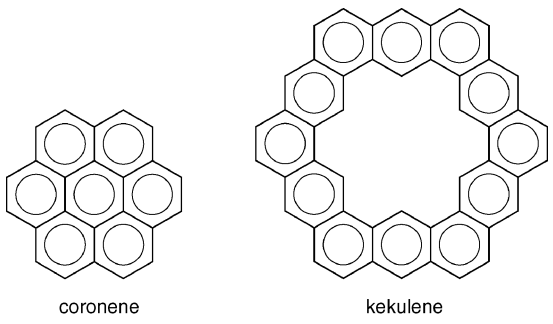
As a final remark, it is worth mentioning that LUMO energies decrease in parallel with the increase in the HOMO orbital energies, thus lowering the HOMO–LUMO gap. This is in accordance with the reduction of the ionization energy[45] and increased electron affinity.[46]

Nonlinear acenes and some condensed aromatics. Since the experimental data for APAs of polyaromatic hydrocarbons

Table 2 Absolute proton affinities for different PAHs calculated by the scaled AM1 method; the experimental data (in parentheses) are taken from ref. 49 and the highest APAs are given in bold

	Proton affinity/kcal mol^{-1}													
Molecule	1	2	3	4	5	6	7	8	9	10	11	12	13	14
9	**198.8** (201.1)	198.7	195.0	197.0	197.1									
10	197.7	**198.8** (199.7)												
11	198.8	198.9	198.6	201.3	**204.9**	200.3								
12	199.4	**205.4** (203.3)	201.1	197.0	198.7	200.3								
13	193.9	**210.3** (208.5)	200.9											
14	203.2	211.7	198.2	200.1	197.5	200.7	202.5	202.5	**213.0**	204.1	199.1	200.1		
15	205.5	200.8	200.1	198.1	202.1	**206.4** (205.8)	201.7							
16	201.4	**209.7**	195.9	209.6	198.8	198.4								
17	**211.6**	199.6	200.8	198.4	201.8	205.4	202.6							
18	200.1	203.6	**211.8**	199.5	199.6	199.5	200.1							
19	**214.9** (213.0)	193.7	212.3											
20	**206.0** (207.0)													
21	208.6	213.2	197.1	212.4	200.1	200.0	200.2	199.6	**218.5**	207.7	198.0	205.8	201.8	201.0
22	207.3	201.5	208.7	198.2	210.2	**222.0**	206.4							
23	200.7	212.4	199.4	211.9	204.7	205.6	**222.6**	210.3	199.9	207.7	201.0	201.7	200.1	
24	220.9	**223.7**	205.6	205.3	219.7	196.5								
25	204.1	209.9	199.3	212.2	**226.2**	214.2								
26	201.6	204.5	**212.2**											
27	**225.4**	213.1	205.8	210.5										
28	**225.4**	219.6	211.4	198.8	212.5	203.2								
29	221.5	213.4	227.7	196.7	**228.5**									
30	202.5	**212.4**												
31	**221.3**	212.6	207.6	207.5	212.7									

(PAHs) are not abundant, it is of some interest to provide the AM1 results for a large number of bent or branched acenes and some other condensed aromatics. The studied systems are depicted in Fig. 2. This is important because susceptibility towards the electrophilic attack is proportional to the APA values.[6,47] Therefore, a knowledge of the most basic sites of PAHs provides useful information about their electrophilic reactivity. The estimated APAs are presented in Table 2. Survey of the results indicates that PAHs are moderately basic compounds. If only the largest APAs are taken into account for each molecule, then the average absolute proton affinity is 213.2 kcal mol^{-1}. This is by 33 kcal mol^{-1} higher than APA of the elementary building block benzene. It appears that APAs of PAHs depend both on the size (*i.e.* the number of benzene fragments) and molecular topology (size). The linear acenes have the highest APAs, whereas the lowest are found in bulky cyclic molecules (coronene, kekulene depicted in Scheme 3). Theoretical APAs are in a reasonably good accordance with the sparse measured data (Table 2), which lends support to the computed numbers.



Scheme 3

Zethrenes. Zethrenes are a somewhat forgotten family of pericondensed compounds, which should receive due attention. The first two zethrenes **32** and **33** (Fig. 3) were synthesized a long time ago.[36] Let us discuss the proton affinities of **32** and **33** (Table 3). It is obvious that protonation at C2 and C5 positions of zethrene **32** will give the lowest APA values. The reason behind is that the positive charge has to be "fixed" at the carbon atoms C3 and C4, respectively, since only in this case the resonance structure including one benzene and one naphthalene moiety could take place. In contrast, the proton attack at C1 will provide two such resonance structures, which in addition describe the cationic resonance effect over the allyl cation fragment C_9–C_{10}–C_{11}. It is, therefore, not surprising that APA(C1)$_{\mathbf{32}}$ is 220.4 kcal mol^{-1} being larger than APA(C2)$_{\mathbf{32}}$ = 195.8 and APA(C5)$_{\mathbf{32}}$ = 195.6 kcal mol^{-1} by 24 kcal mol^{-1}. The most basic site is C4 with APA(C4)$_{\mathbf{32}}$ = 228.0 kcal mol^{-1} since the corresponding conjugate acid has four resonance structures involving one benzene and one naphthalene π-electron fragment, which describe the propagation of the unit positive charge along the C_5–C_6–C_{12}–C_7–C_8–C_{10}–C_9 carbon atoms. The second most basic site is given by C6 carbon atom, since the corresponding 3 resonance structures that encompass naphthalene and benzene substructures and the cationic resonance effect spread over the C_{12}–C_7–C_8–

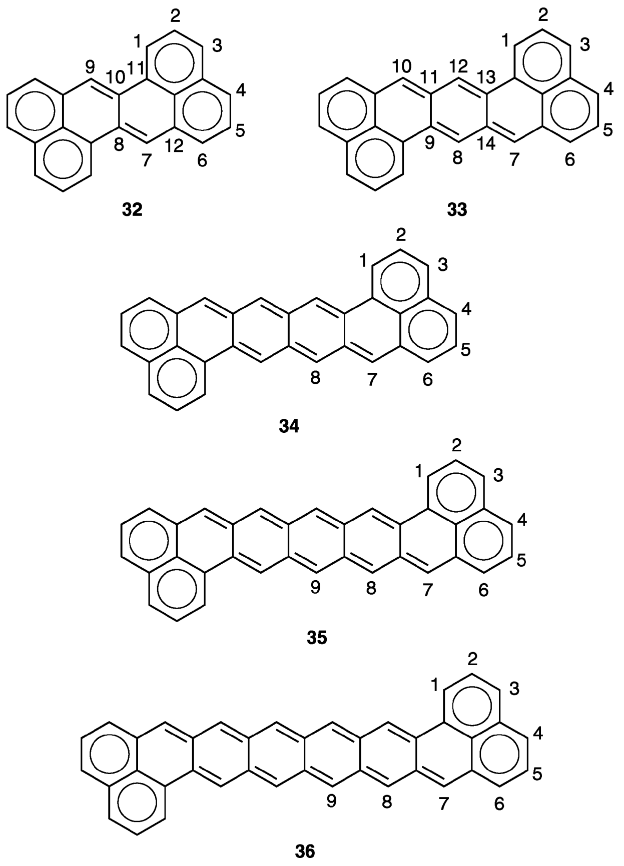


Fig. 3 Schematic representation and atom numbering in zethrenes.

C_{10}–C_9 fragment. Finally, protonation at C7 induces the cationic resonance along the C_8–C_{10}–C_9 allylic structural building block giving rise to two resonance structures possessing two naphthalene subunits. Thus, it leads to the third largest APA(C7) of 224.6 kcal mol^{-1}.

The most favourable sites of the proton attack of zethrene **33** can be rationalized along the same line. The most basic position is C7, since the propagation of the positive charge over the quinoid moiety C10···C14 yields one resonance structure containing two naphthalenes and one benzene π-electron network and three resonance structures possessing two naphthalene moieties. Hence, a high APA(C7)$_{33}$ = 240.4 kcal mol^{-1} is not surprising. For the same reason the most basic position in zethrenes **34**, **35** and **36** is C7, because the protonation induces *inter alia* aromatization of the quinoid substructure. Hence, the APAs of **34**, **35** and **36** are 250.7, 258.1 and 263.8 kcal mol^{-1}, respectively, implying that they represent neutral organic superbases.

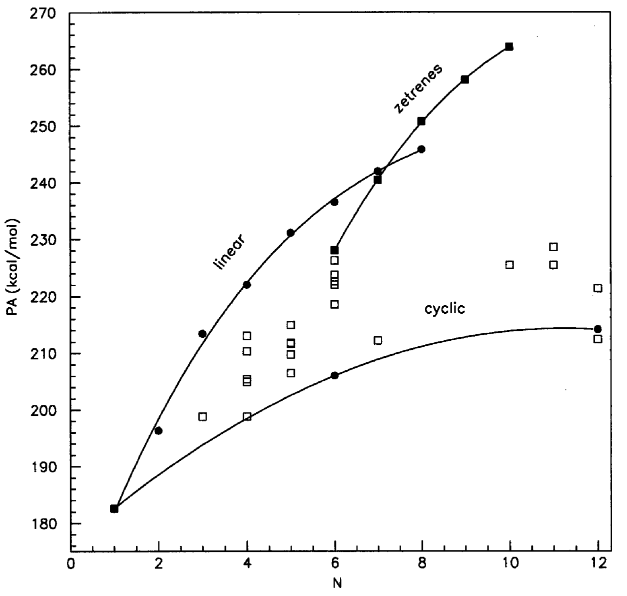


Fig. 4 Absolute proton affinities of PAHs against the number of the six-membered rings.

It is interesting to note that the APAs of linear acenes and zethrenes form the upper limit curves, whereas benzene, coronene and kekulene provide the lower limit curve (against the number of benzene rings) for all other absolute proton affinities of condensed polybenzenoids considered here (Fig. 4). The APA values for coronene is 206.0 kcal mol^{-1}, whereas for kekulene at the C1 and C2 protonation sites assume 207.8 and 214.1 kcal mol^{-1}, respectively. Here C2 atom is the central outward carbon of the anthracene fragment.

It is important to point out that judicious choice of substituents and their strategic distribution on the right position over the molecular perimeter could considerably enhance the basicity of zethrenes. For this purpose the electron donor groups like NH_2 or NMe_2 would be helpful. It is intuitively clear that their substitution at positions C(9) and C(10) in **32** and **33**, respectively, would substantially increase the cationic resonance effect. In **32** this would encompass C7–C8–C10–C9 butadiene moiety, whereas in **33** protonation would form an additional benzene fragment within C14–C8–C9–C11–C12–C13. Our pilot calculations show that substitution of NH_2 at these positions would lead to APA(C7)$_{32}$ = 243.1 and APA(C7)$_{33}$ = 260.1 kcal mol^{-1}. In other words, the proton affinity is increased by 15 kcal mol^{-1} and 20 kcal mol^{-1} relative to unsubstituted zethrenes, respectively. It follows that higher zethrenes are candidates for strong superbases, which

Table 3 The absolute proton affinities of zethrenes as obtained by the scaled AM1 semiempirical model (in kcal mol^{-1})

	Position of the proton attack										
System	1	2	3	4	5	6	7	8	9	10	11
32	220.4	195.8	222.4	**228.0**	195.6	226.4	224.6	—	—	—	—
33	227.0	197.3	228.3	237.7	197.2	236.8	**240.4**	225.6	—	—	—
34	232.7	198.7	233.3	245.1	198.6	244.6	**250.7**	241.7	227.6	—	—
35	237.4	199.7	237.6	251.0	199.7	250.6	**258.1**	251.7	242.9	228.6	—
36	241.5	200.4	241.4	255.9	200.5	255.6	**263.8**	258.8	252.6	243.6	229.3

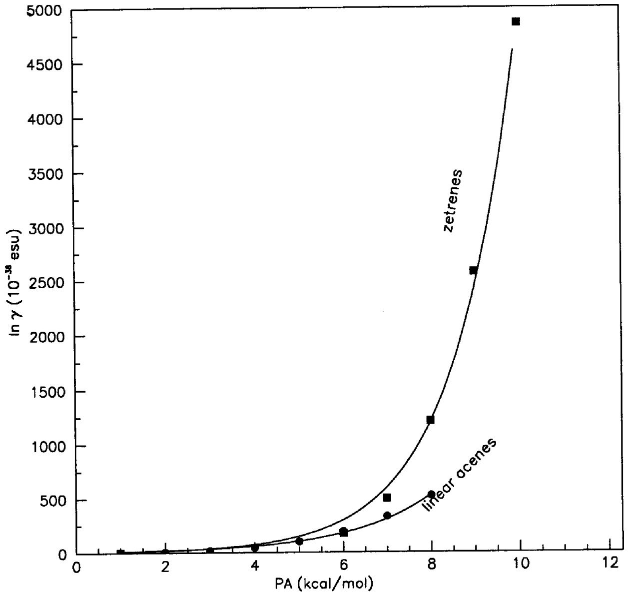


Fig. 5 Second order hyperpolarizabilities of linear acenes and zethrenes *vs.* the number of six-membered rings.

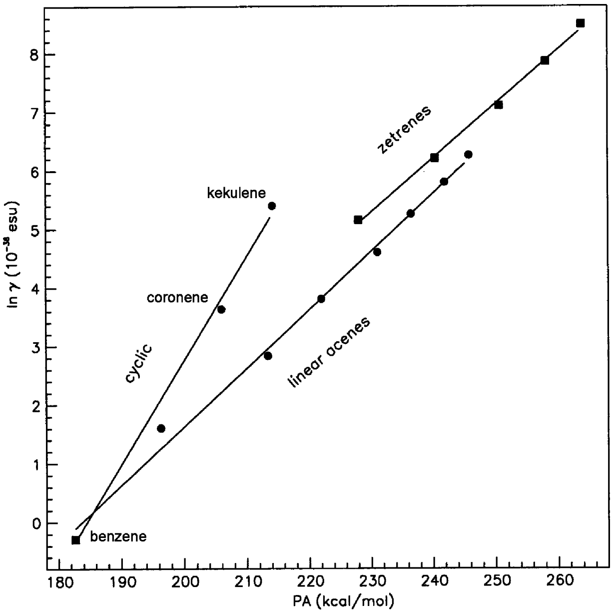


Fig. 6 Linear relationship between γ and PA for linear acenes, zethrenes and cyclic polyacenes.

should be better explored both experimentally and theoretically in the future by introducing stronger electron-releasing substituents like *e.g.* NMe_2.

Second order hyperpolarizabilities of acenes and zethrenes

Over the past two decades the study of nonlinear optical (NLO) processes in organic and polymer systems has enjoyed a wide interest and rapid growth.[17–19] This is not surprising, because organic nonlinear optical materials exhibit a number of favourable features including mechanical, chemical, thermal and optical stability. NLO response in organic materials originates primarily from π-electron excitation usually taking place in individual molecular units, which can be incorporated in thin films and/or fibers. Each unit is essentially an independent source of nonlinear optical response and the collective global effect is obtained by averaging individual contributions.[20] Computational methods can aid in pinpointing molecular systems, which could serve as building blocks of organic materials possessing NLO properties. Lee *et al.*[21] have shown by MNDO calculations that the mean value of the second order polarizability $\langle\gamma\rangle$ of linear polyacenes increases, whereas the HOMO–LUMO gap decreases along the series. This is in harmony with a common knowledge that the π-electron excitations are important in describing the NLO effects.

Since the APA values are larger if the HOMO energies are higher, it is plausible to assume that there is a relation between $\langle\gamma\rangle$ and proton affinities. The present AM1 calculations confirm that this conjecture is correct. It turns out that $\langle\gamma\rangle$ exponentially increases as the number of six-membered rings is larger both in linear polyacenes and zethrenes. The exponential dependence is particularly steep for the latter family of compounds (Fig. 5). The similar conclusion holds for the proton affinities ultimately leading to linear relationships on the logarithmic scale:

$$\ln(\langle\gamma\rangle) = -18.4 + 0.100 \cdot \text{APA linear polyacenes} \qquad (4)$$

and

$$\ln(\langle\gamma\rangle) = -16.0 + 0.093 \cdot \text{APA zethrenes} \qquad (5)$$

(γ is in 10^{-36} esu, APA in kcal mol^{-1}). The good quality of correlations is evidenced by R^2 coefficients, which assume 0.997 for linear acenes and 0.999 for zethrenes. The average absolute error is 0.1×10^{-36} esu in both cases. These relations are pictorially illustrated by Fig. 6. It appears that $\langle\gamma\rangle$ is really larger for higher APAs as a rule. However, it came as a surprize that kekulene exhibits much higher second order hyperpolarizability than **3** despite a similar APA value (214.1 *vs.* 213.4 kcal mol^{-1}, respectively (Fig. 6). The results lead to three important conclusions:

(1) The relatively inexpensive calculations of APAs enable fairly good estimates of the average second order hyperpolarizability.

(2) Zethrenes are very good candidates for NLO organic materials particularly if they are substituted by the electron releasing donors and electron withdrawing acceptors placed at the strategic positions.

(3) "Circular" compounds like coronene and kekulene seem to be better PAHs for NLO systems compared to small linear acenes **2**, **3**, **4** and **5** (Fig. 6).

Conclusions

Results of the present investigations can be summarized as follows:

(1) Absolute proton affinities of linear polyacenes are affected both by the initial state and final state effects related to

neutral bases and their conjugate acids, respectively. The initial state effect is reflected in the increase in HOMO energies along the series, which implies that the energy cost in activating the outer valence electron during formation of a new C–H bond is lower. This contributes to the amplified basicity. The overwhelming effect, however, is given by the appreciable cationic resonance interaction in the final conjugate acids, which is more pronounced in larger polyacenes. The lowest APAs are found in "circular" condensed PAHs. All other values are placed in between the boundary curves given by APAs of acenes (with zethrenes) and "circular" benzoaromatics benzene, coronene and kekulene plotted against the number of benzene fragments.

(2) Zethrenes are excellent candidates for neutral organic superbases possessing APAs between 228 and 264 kcal mol^{-1}. Their basicity can be additionally amplified by appropriate substituent groups exhibiting strong electron releasing properties such as *e.g.* NH_2 and NMe_2.

(3) Very good albeit separate linear relations are found between the average second order hyperpolarizabilities and APAs in polyacenes and zethrenes. Zethrenes offer very good spacers in designing new materials exhibiting nonlinear optical response properties, particularly if substituted with carefully selected donor–acceptor groups placed at the right positions.

Acknowledgements

We thank Dr B. Kovačević and Dr R. Vianello for useful discussions and comments.

References

1 R. P. Bell, *The proton in Chemistry*, Cornell University Press, Ithaca, NY, 1973.

2 Proton Transfer, in *Comprehensive Chemical Kinetics*, ed. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1977, vol. 8.

3 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, NY, 1976.

4 R. Stewart, *The proton: Applications to Organic Chemistry*, Academic Press, Orlando, FL, 1985.

5 R. Taylor, *Electrophylic Aromatic Substitution*, Wiley, Chichester, 1990.

6 (*a*) M. Eckert-Maksić, Z. B. Maksić and M. Klessinger, *Int. J. Quantum Chem.*, 1994, **49**, 383; (*b*) M. Eckert-Maksić, Z. B. Maksić and M. Klessinger, *J. Chem. Soc., Perkin Trans. 2*, 19942), 285.

7 M. Eckert-Maksić, W. M. F. Fabian, R. Janoschek and Z. B. Maksić, *J. Mol. Struct. (THEOCHEM)*, 1995, **1**, 338.

8 M. Eckert-Maksić, M. Klessinger, D. Kovaček and Z. B. Maksić, *J. Phys. Org. Chem.*, 1996, **9**, 269.

9 A. G. Harrison, *Chemical Ionization Mass Spectrometry*, CRC Press, Boca Raton, FL, 1989 .

10 R. W. Alder, *J. Am. Chem. Soc.*, 2005, **127**, 7924.

11 B. Kovačević and Z. B. Maksić, *Chem.–Eur. J.*, 2002, **8**, 1694.

12 M. Alcami, O. Mó and M. Yáñez, *Mass Spectrom. Rev.*, 2001, **20**, 195.

13 S. T. Howard, J. A. Platts and M. P. Coogan, *J. Chem. Soc., Perkin Trans. 2*, 2002, 899.

14 Z. B. Maksić and B. Kovačević, *J. Org. Chem.*, 2000, **65**, 3303.

15 Z. B. Maksić and M. Eckert-Maksić, Theoretical Organic Chemistry, in *Theoretical and Computational Chemistry*, ed. C. Parkany, Elsevier, Amsterdam, 1998, vol. 5, p. 203 and references therein.

16 R. Notario and J.-L. M. Abboud, *J. Phys. Chem. A*, 1998, **102**, 5290 and references therein.

17 Special issue of *Chem. Rev.*, 1994, **94**, (1) and references therein.

18 I. D. L. Albert, T. J. Marks and M. A. Ratner, *J. Phys. Chem.*, 1996, **100**, 9714.

19 H. A. Kurtz and D. S. Dudis, in *Review in Computational Chemistry*, ed. K. B. Lipkowitz and D. B. Boyd, Wiley-VCH, NY, 1998, vol. 12, p. 241.

20 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, NY, 1991.

21 S.-L. Lee, K.-C. Yang and J.-H. Shen, *Int. J. Quantum Chem.*, 1995, **Symp 29**, 509.

22 *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, vol. 1 and 2, 1987.

23 *Nonlinear Optical Properties of Organic and Polymeric Materials*, ed. D. Williams, American Chemical Society, Washington, 1983.

24 D. J. Gundlach, J. A. Nichols, L. Zhou and T. N. Jackson, *Appl. Phys. Lett.*, 2002, **80**, 2925.

25 F. Wűrthner, *Angew. Chem., Int. Ed.*, 2001, **40**, 1037.

26 D. Y. Kondakov, J. R. Sandifer, C. W. Tang and R. H. Young, *J. Appl. Phys.*, 2003, **93**, 1108.

27 L. C. Picciolo, H. Murata and Z. H. Kafafi, *Appl. Phys. Lett.*, 2001, **78**, 2378.

28 (*a*) B. J. Smith and L. J. Radom, *J. Am. Chem. Soc.*, 1993, **115**, 4885; (*b*) B. J. Smith and L. J. Radom, *Chem. Phys. Lett.*, 1994, **231**, 345.

29 (*a*) Z. B. Maksić, B. Kovačević and D. Kovaček, *J. Phys. Chem. A*, 1997, **101**, 7446; (*b*) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

30 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. McDonald and A. N. Syverud, JANAF Thermochemical Tables, 3rd edn, *J. Phys. Chem. Ref. Data*, 1985, **14**(suppl. 1), 1.

31 (*a*) M. Ratner, *Int. J. Quantum Chem.*, 1992, **43**, 5; (*b*) D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.

32 J. L. Bredas, C. Adant, P. Tackx and A. Persoons, *Chem. Rev.*, 1994, **94**, 243.

33 H. A. Kurtz, J. J. P. Stewart and K. M. Dieter, *J. Comput. Chem.*, 1990, **11**, 82.

34 J. J. P. Stewart, *QCPE Program*, No. 455, version 5.0, 1990.

35 M. Benedikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891.

36 E. Clar, *Polycyclic Hydrocarbons*, AP, London, 1964, vol. 1, p. 32.

37 W. C. Herndon, *J. Chem. Soc., Chem. Commun.*, 1977, 817.

38 U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Mathias, D. Philip and J. F. Stoddart, *Pure Appl. Chem.*, 1993, **65**, 199.

39 Y. Murata, N. Kato, K. Fujimara and K. Komatsu, *J. Org. Chem.*, 1999, **64**, 3483.

40 J. E. Anthony, D. L. Eaton and S. R. Parkin, *Org. Lett.*, 2004, **4**, 15.

41 M. M. Payne, S. R. Parkin and J. E. Anthony, *J. Am. Chem. Soc.*, 2005, **127**, 8028.

42 B. A. Hess Jr. and L. J. Schaad, *J. Org. Chem.*, 1971, **36**, 3418.

43 B. A. Hess Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, 1973, **95**, 3907.

44 K. B. Wiberg, in *Pauling's Legacy: Modern Modelling of the Chemical Bond*, ed. Z. B. Maksić and W. J. Orville-Thomas, Elsevier, Amsterdam, 1999, p. 519.

45 E. S. Chen, E. C. M. Chen, N. Sane, L. Tolley, N. Kozanecki and S. Shulze, *J. Chem. Phys.*, 1999, **110**, 9319.

46 J. C. Rienstra-Kiracofe, C. J. Borden, S. T. Brown and H. F. Schaefer III, *J. Phys. Chem. A*, 2001, **105**, 524.

47 M. Eckert-Maksić, M. Klessinger and Z. B. Maksić, *Chem.–Eur. J.*, 1996, **2**, 1251 and references therein.

48 S. G. Lias and J. F. Liebman, Ion Energetics Data, in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, ed. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg, MD, March 2003, 20899 (http://webbook.nist.gov).

49 M. Meot-Ner, *J. Phys. Chem.*, 1980, **84**, 2716.