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Probing the Limits of Resonance Stabilization. The Case of Linear Polyacenes

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The gas-phase basicity and proton affinity of pentacene have been determined by means of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. AM1 semiempirical calculations for neutral and protonated linear polyacenes ranging from benzene to pentaicosacene were carried out. The influence of successive annellations (up to 25 rings) on structures, heats of formation, and proton affinities was investigated. Extrapolated values for an infinite linear polyacene have been derived. AM1-calculated electronic structures (HOMO and LUMO energies) for the studied linear polyacenes have been compared with the available experimental ionization potentials and electron affinities.

Introduction

The design and study of very strong organic acids¹ and bases^{2,3} has long attracted interest, for both fundamental and practical reasons. One of the main factors affecting the intrinsic basicity of a molecule is charge delocalization within the ions derived therefrom. Charge delocalization can be enhanced by intramolecular chelation or by conjugation. "Proton sponges",⁴ histamine,⁵ or N_α, N_α -dimethylhistamine^{3a} are strong bases characterized by strong chelation of the protonated species. Molecules with intrinsic gas-phase basicities higher than 1000 kJ mol⁻¹ (239 kcal mol⁻¹) are called "superbases".^{2c} The strong basicity of guanidines, possibly the strongest bases measured so far,^{2d} originates in the stabilization of the guanidinium cations induced by the so-called "cross-conjugation" or "Y-delocalization"⁶ of the six π electrons of the guanidinium system.^{2d}

In this work we want to explore the limits of charge delocalization by conjugation. To this end, linear polyacenes, a class of polycyclic aromatic hydrocarbons (PAHs), were chosen as probes. The chemistry and properties of PAHs have been of practical and theoretical importance for many years.^{7–15} They are of high current interest as key intermediates and products in carcinogen and soot formation processes and in coal conversion processes. PAHs are ubiquitous air pollutants arising from incomplete combustion of organic matter. They are often included in a larger class termed polycyclic organic matter (POM).^{15b} The presence of PAHs in many celestial objects such as planetary nebulae, reflection nebulae, and active galaxies is now generally accepted.^{16–18} Duley and Jones¹⁹ proposed that small linear polyacenes (from benzene to pentacene) were responsible for the IR emission in several nebulae and that these PAHs have only a transient existence in localized regions of the interstellar medium. They suggested¹⁹ that two-to-five-ring linear polyacenes could be important constituents in such objects as the Orion Bar.

Unsubstituted linear polyacenes up to heptacene have been described.^{7a} Following Clar's ideas,⁷ only one can exist aromatic sextet in linear polyacenes. It is obvious that, if in a higher polyacene one sextet is shared among several rings, this must necessarily lead to a gradual loss of benzenoid character. In fact,^{7b} the reactivity increases rapidly in the series. Naph-

thalene is more reactive than benzene. Likewise, anthracene is still more reactive than naphthalene. The photooxidation becomes such a danger to the preparation of the higher polyacenes that pentacene and hexacene must be handled under nitrogen. Heptacene is so unstable that it has never been obtained in a pure state.²⁰ It is obvious that with an infinite number of rings the system becomes a cyclic polyene in which one sextet is not enough to give some degree of stability.^{7b} The dilution of the sextet also increases the reactivity and produces a bathochromic shift.^{7a} Thus, higher members of this series have proved too reactive to isolate under ordinary conditions and only derivatives of octacene,^{21a,b} nonacene,^{21c} and undecacene^{21c} have been prepared. However, some authors²² believe that it will be possible to work with unsubstituted linear polyacenes under suitable conditions.

An interesting property of linear polyacenes is the possibility that they could be organic superconductors. Kivelson and Chapman²² have considered a microscopic model of "polyacene" similar to the model of "polyacetylene". They showed that polyacene is expected to be an unusual one-dimensional conductor with a novel electronic structure.

Proton affinity, PA, values for one-to-four-ring linear polyacenes, benzene (**1**), naphthalene (**2**), anthracene (**3**), and tetracene or naphthacene (**4**), are available in the literature.²³ There is also a qualitative study²⁶ on the proton affinities of benzene, naphthalene, and anthracene at atmospheric pressure by ion mobility spectrometry. In this work we have measured the intrinsic gas-phase basicity of pentacene (**5**) and derived its corresponding proton affinity value by proton-transfer equilibrium using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry.^{27–31}

To estimate the PAs of higher linear polyacenes and to extrapolate a value to "infinite polyacene", we have also carried out a theoretical study with linear polyacenes ranging from benzene (**1**) to pentaicosacene (**15**), with 25 benzenoid rings. All the studied compounds are shown in Figure 1. Because of the large number of orbitals involved only semiempirical quantum calculations were carried out.

Experimental Section

Pentacene (**5**), CAS Registry number [135-48-8], was a commercial product from Aldrich. Its purity was assessed by standard methods.

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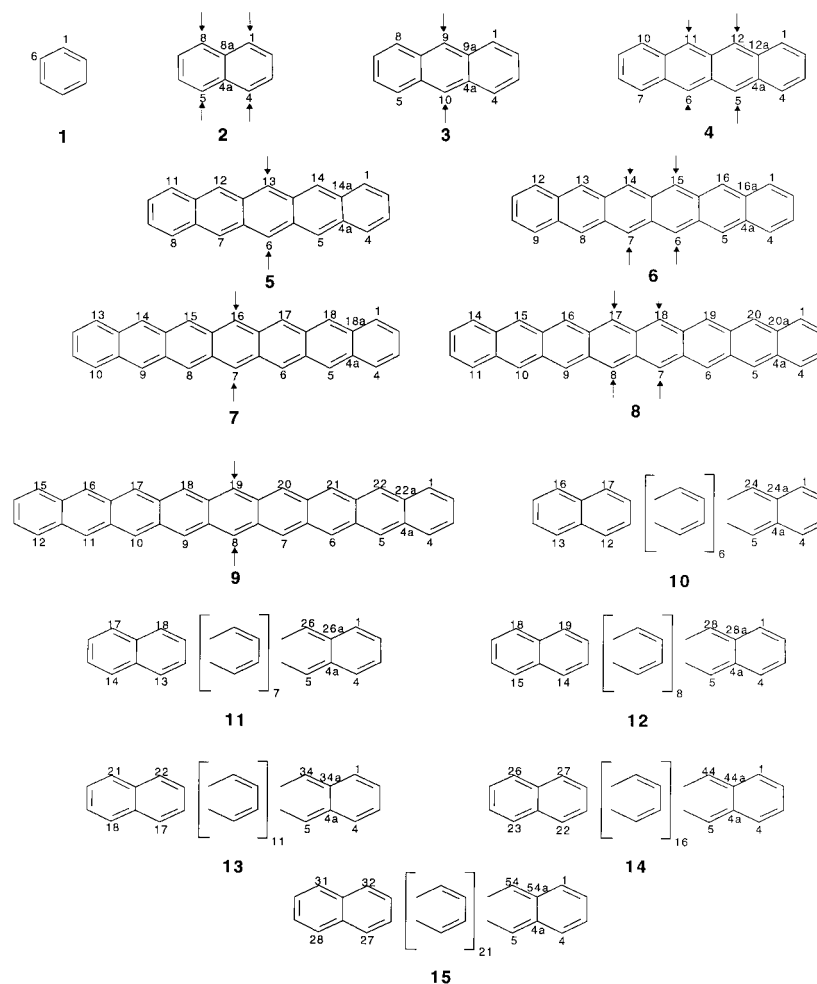
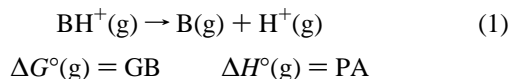


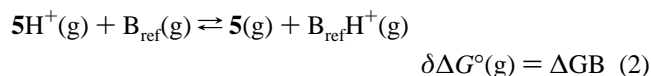
Figure 1. Studied linear polyacenes: **1**, benzene; **2**, naphthalene; **3**, anthracene; **4**, tetracene or naphthacene; **5**, pentacene; **6**, hexacene; **7**, heptacene; **8**, octacene; **9**, nonacene; **10**, decacene; **11**, undecacene; **12**, dodecacene; **13**, pentadecacene; **14**, icosacene; **15**, pentaicosacene. The numeration of the atoms is according to Chemical Abstracts. Arrows indicate the corresponding protonation sites.

The gas-phase basicity, GB, of a compound B is formally defined as the standard Gibbs energy change for reaction 1, the corresponding proton affinity PA being the standard enthalpy change for the same reaction.



The gas-phase basicity of **5** was determined from equilibrium proton-transfer reactions conducted in a modified Bruker CMS-47 Fourier FT-ICR mass spectrometer³² used in previous studies.^{3,5,33} Working conditions were similar to those already described.^{33d} The average cell temperature is ca. 333 K. Due to the low volatility of **5**, the sample was introduced into the spectrometer through the direct insertion probe. It was necessary to heat the sample and allow a 24 h-stabilization period prior to the proton-exchange experiments.

FT-ICR measurements provide the standard Gibbs energy change $\delta\Delta G^\circ(\text{g})$ for the proton-exchange reaction 2:



where B_{ref} is a reference base.

For these equilibria,

$$\delta\Delta G^\circ(\text{g}) = -RT \ln K_p \quad (3)$$

In every case, the reversibility of reaction 2 was confirmed by means of double resonance-like experiments. The pressure readings for the various neutral reagents, as determined by the Bayard-Alpert gauge of the FT-ICR spectrometer, were corrected by means of the gauge sensitivity for each reactant. The gauge sensitivities relative to N_2 (S_r) have been estimated according to Bartmess and Georgiadis³⁴ using the average molecular polarizabilities, $\alpha(\text{ahc})$, calculated according to Miller.³⁵

Computational Details

Structures, energies, harmonic vibrational frequencies, and all the other properties were obtained by means of the AM1 semiempirical method,³⁶ as implemented in the Spartan 3.1 package of programs,³⁷ running on a Silicon Graphics "INDY" R4600SC workstation.

The proton affinities of the several polyacenes were calculated from the equation:

$$\text{PA} = \Delta_f H^\circ(\text{B}) + \Delta_f H^\circ(\text{H}^+) - \Delta_f H^\circ(\text{BH}^+) \quad (4)$$

$\Delta_f H^\circ(\text{B})$ and $\Delta_f H^\circ(\text{BH}^+)$ were calculated with AM1 Hamiltonian. Since AM1 gives very poor estimate of the heat of formation of H^+ , the experimental value³⁸ ($367.2 \text{ kcal mol}^{-1}$) has been used.

TABLE 1: Experimental Results Pertaining to the Determination of the Gas-Phase Basicity of Pentacene^a

| ref | GB(<i>B</i> _{ref}) ^b | ΔGB | GB (pentacene) | GB(pentacene) (average) |
|--|--|-------|-------------------|----------------------------|
| <i>t</i> -C ₄ H ₉ NH ₂ | 215.7 | 2.43 | 218.13 | 218.7 ± 0.5 |
| <i>t</i> -C ₅ H ₁₁ NH ₂ | 216.9 | 1.70 | 218.60 | |
| (CH ₂ =CHCH ₂) ₂ NH | 219.1 | 0.23 | 219.33 | |
| (C ₂ H ₅) ₂ NH | 219.7 | -0.89 | 218.81 | |

^a All values in kcal mol⁻¹. ^b All the GB values of reference bases are taken from ref 25.

Experimental Results

The experimental results of the measurement of the gas-phase basicity of **5** are summarized in Table 1.

For each reference base, GB(**5**) is obtained through eq 5:

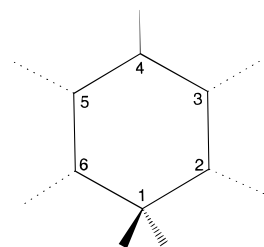
$$\text{GB}(\mathbf{5}) = \text{GB}(B_{\text{ref}}) + \Delta\text{GB} \quad (5)$$

GB(*B*_{ref}) were taken from the very recent update of Hunter and Lias.²⁵ From the data given in Table 1, an average value of 218.7 kcal mol⁻¹ is obtained for the gas-phase basicity of **5**, the standard deviation being 0.5 kcal mol⁻¹. According to the IUPAC criterion,^{39,40} the latter measures the precision of GB-(**5**). The accuracy of the GB(**5**) value at the 95% level can be estimated at ± 0.8 kcal mol⁻¹.⁴¹

To obtain the proton affinity of pentacene we have used the entropy values of the neutral and protonated molecule evaluated at AM1 level, 121.24 and 123.83 cal mol⁻¹ K⁻¹, respectively. For the enthalpy of the proton we have used a value of 26.04 cal mol⁻¹ K⁻¹.³⁸ From these data, a value of 225.7 kcal mol⁻¹ is obtained for the proton affinity of pentacene.

Theoretical Results and Discussion

Structures. To check the reliability of our calculations, we have compared the AM1-calculated structures of linear polyacenes with the available experimental data and with a recent theoretical study⁴² using density functional theory (DFT) at B3LYP/6-311G** level. To our knowledge, there are experimental geometries for linear polyacenes up to pentacene.⁴³

**Figure 2.** Numeration of the atoms in the central ring of the studied linear polyacenes that it is used in Tables 1S and 2S.

Theoretical and experimental C–C bond lengths for linear polyacenes from benzene to pentacene are collected in Table 2.

As shown in Table 2, semiempirical structures are comparable to those obtained with DFT calculations, and both agree well with structures experimentally determined. As Wiberg⁴² points out, X-ray data are in somewhat better agreement with the calculated structures than electron diffraction results. Notice that the latter give the gaseous structures, directly comparable to the calculated ones, but have the disadvantage that the individual C–C bond lengths cannot be resolved separately, but must be inferred from the nonbonded C–C distances.⁴²

Protonation of the linear polyacenes takes place in the central rings at the positions indicated in Figure 1, as it is explained below. We can compare the geometries of the rings where protonation occurs, both before and after protonation. In Table 1S (Supporting Information), geometries of the central ring for all the studied compounds are collected. The numeration of the atoms is that indicated in Figure 2.

Also given in Table 1S is the geometry of the ring where the protonation takes place extrapolated to a linear polyacene with an infinite number of benzenoid rings. As shown there, C1–C2 and C6–C1 bond lengths significantly lengthen after protonation at C1, the other C–C bond lengths being nearly constant. More significant is the behavior of the bond angles. Thus, C2C1C6 bond angle is reduced by almost 5° because of the formal change in the hybridization of C1-atom (sp² to sp³). Mulliken bond orders follow a trend opposite to that of the bond lengths. C1–C2 and C6–C1 bond orders decrease after the protonation, the other C–C bond orders varying very slightly.

TABLE 2: Theoretical and Experimental C–C Bond Lengths in Linear Polyacenes. All Values in angstroms

| compound | method | C1–C2 | C2–C3 | C4–C4a | C4a–C8a | C4a–C9a | C9–C9a | C5–C4a | C5–C5a | C4–C12a | C5–C11a | C6–C5a | C4a–C14a | C5a–C13a |
|-----------------|--------------------|-------|-------|--------|---------|---------|--------|--------|--------|---------|---------|--------|----------|----------|
| (1) benzene | AM1 ^a | 1.395 | | | | | | | | | | | | |
| | DFT ^b | 1.394 | | | | | | | | | | | | |
| | X-ray ^c | 1.392 | | | | | | | | | | | | |
| | ED ^d | 1.399 | | | | | | | | | | | | |
| | IR ^e | 1.390 | | | | | | | | | | | | |
| | R ^f | 1.397 | | | | | | | | | | | | |
| (2) naphthalene | AM1 ^a | 1.373 | 1.416 | 1.422 | 1.419 | | | | | | | | | |
| | DFT ^b | 1.375 | 1.415 | 1.420 | 1.431 | | | | | | | | | |
| | X-ray ^g | 1.378 | 1.421 | 1.425 | 1.426 | | | | | | | | | |
| | ED ^h | 1.381 | 1.417 | 1.422 | 1.412 | | | | | | | | | |
| | | | | | | | | | | | | | | |
| (3) anthracene | AM1 ^a | 1.365 | 1.426 | 1.433 | | 1.429 | 1.399 | | | | | | | |
| | DFT ^b | 1.367 | 1.424 | 1.429 | | 1.443 | 1.398 | | | | | | | |
| | X-ray ^g | 1.369 | 1.431 | 1.434 | | 1.441 | 1.403 | | | | | | | |
| | ED ⁱ | 1.397 | 1.422 | 1.437 | | 1.437 | 1.392 | | | | | | | |
| | | | | | | | | | | | | | | |
| (4) tetracene | AM1 ^a | 1.361 | 1.431 | 1.438 | | | | 1.387 | 1.413 | 1.437 | 1.431 | | | |
| | DFT ^b | 1.364 | 1.429 | 1.433 | | | | 1.390 | 1.409 | 1.450 | 1.450 | | | |
| | X-ray ^j | 1.38 | 1.46 | 1.42 | | | | 1.39 | 1.40 | 1.44 | 1.46 | | | |
| | | | | | | | | | | | | | | |
| (5) pentacene | AM1 ^a | 1.358 | 1.434 | 1.441 | | | | 1.381 | 1.421 | | | 1.401 | 1.442 | 1.435 |
| | DFT ^b | 1.361 | 1.434 | 1.437 | | | | 1.385 | 1.415 | | | 1.401 | 1.454 | 1.453 |
| | X-ray ^k | 1.35 | 1.43 | 1.42 | | | | 1.38 | 1.40 | | | 1.39 | 1.44 | 1.45 |

^a This work. ^b B3LYP/6-311G** computed values taken from ref 42. ^c X-ray data taken from ref 44. ^d Electron diffraction data taken from ref 45. ^e Infrared data taken from ref 46. ^f Raman data taken from ref 47. ^g X-ray data taken from ref 48. ^h Electron diffraction data taken from ref 49a. ⁱ Electron diffraction data taken from ref 49b. ^j X-ray data obtained in ref 50a and reevaluated in ref 43. ^k X-ray data obtained in ref 50b and reevaluated in ref 43.

TABLE 3: AM1-Calculated and Experimental Enthalpies of Formation and Proton Affinities, in kcal mol⁻¹, for Selected Linear Polyacenes. PA(AM1) Values Given in Parentheses are Corrected through Eq 7

| compound | neutral | | protonated | | PA(AM1) | PA(exp) |
|---------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------|--------------------|
| | $\Delta_f H^\circ(\text{AM1})$ | $\Delta_f H^\circ(\text{exp})$ | $\Delta_f H^\circ(\text{AM1})$ | $\Delta_f H^\circ(\text{exp})$ | | |
| (1) benzene | 22.0 | 19.82 ^a | 206.0 | 207.6 ^d | 183.3 (179.0) | 179.4 ^g |
| (2) naphthalene | 40.6 | 35.99 ^a | 213.2 | 211.3 ^d | 194.6 (192.1) | 191.9 ^g |
| (3) anthracene | 62.9 | 55.17 ^a | 221.3 | 214.4 ^d | 208.9 (208.4) | 208.0 ^g |
| (4) tetracene | 86.9 | 69.6 ^b | 238.2 | 220.4 ^e | 215.9 (216.6) | 216.5 ^g |
| (5) pentacene | 111.9 | (85) ^c | 255.5 | 226.5 ^f | 223.5 (225.3) | 225.7 ^h |
| (6) hexacene | 137.3 | (101) ^c | 276.5 | | 228.0 (230.4) | |
| (7) heptacene | 163.0 | | 297.7 | | 232.5 (235.6) | |
| (8) octacene | 188.9 | | 320.8 | | 235.3 (238.9) | |
| (9) nonacene | 215.0 | | 344.0 | | 238.2 (242.2) | |
| (10) decacene | 241.2 | | 368.2 | | 240.2 (244.4) | |
| (11) undecacene | 267.4 | | 392.5 | | 242.1 (246.7) | |
| (12) dodecacene | 293.7 | | 417.5 | | 243.4 (248.2) | |
| (13) pentadecacene | 372.8 | | 493.3 | | 246.6 (251.9) | |
| (14) icosacene | 504.8 | | 622.6 | | 249.4 (255.1) | |
| (15) pentaicosacene | 637.0 | | 753.3 | | 250.9 (256.7) | |

^a Value taken from ref 51. ^b Value taken from ref 52. ^c Estimated value taken from ref 53. ^d Value obtained from eq 6 using experimental enthalpy of formation of the neutral molecule taken from ref 51 and the experimental proton affinity value taken from ref 25. ^e Value obtained from eq 6 using experimental enthalpy of formation of the neutral molecule taken from ref 52 and the experimental proton affinity value taken from ref 25. ^f Value obtained from eq 6 using estimated enthalpy of formation of the neutral molecule taken from ref 53 and the experimental proton affinity measured in this work. ^g Value taken from ref 25. ^h This work.

Charges of the carbon and hydrogen atoms of the central ring in linear polyacenes evaluated at AM1 level are shown in Table 2S. Also extrapolated charges for an infinite linear polyacene are collected in the same table. More significant changes occur in C4, the C-atom opposite to the protonation site. C4 has a negative charge in the neutral molecules and a positive charge after protonation.

Heats of formation and proton affinities. Calculations of the standard enthalpies of formation by AM1 method have been carried out for neutral and protonated aromatic hydrocarbons shown in Figure 1. The standard enthalpies of formation calculated for neutral and protonated molecules are listed in Table 3, together with the available experimental data.

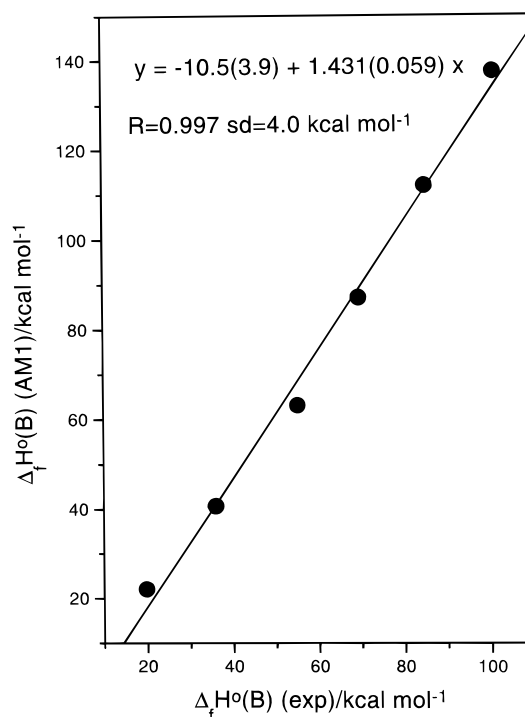
AM1-calculations of the heats of formation of compounds 1–4 have been reported in the literature.^{54,55}

There is a good linear correlation (see Figure 3) between the experimental and the AM1-calculated heats of formation of compounds from benzene to hexacene (note that the values for pentacene and hexacene are estimated values⁵³).

Some authors^{55,56} have previously noted the serious discrepancy between calculated and experimental heats of formation for tetracene. There is a general agreement that the experimental $\Delta_f H^\circ$ of tetracene is in error, probably due to susceptibility of the compound to oxidation. From the correlation line with the first three linear polyacenes and using the AM1-calculated value, a value of 76.0 kcal mol⁻¹ for the heat of formation of tetracene is obtained.

To obtain the heat of formation of protonated molecules, we have carried out preliminary calculations at AM1 level protonating some of the polyacenes at all the possible protonation sites. The results are collected in Table 4.

As shown in Table 4, the protonation in linear polyacenes occurs in the “meso” positions, in the ring situated in the middle of the molecule in the case of polyacenes with an odd number of rings, and in one of the two central rings of the molecule when the polyacenes have an even number of rings. Sites of protonation in the studied linear polyacenes are indicated in Figure 1. The sites of protonation reflect the decrease in aromatic character as the length of the molecule is increased,^{7a,57} corresponding to the localization of π electrons on those carbons marked with an arrow in Figure 1. These are the positions at which the molecules show an increasing tendency to undergo

**Figure 3.** AM1-calculated versus experimental heats of formation of neutral linear polyacenes.

addition reactions, such as halogenation and addition of maleic anhydride.⁵⁸ They are also the positions at which the proton nuclear magnetic resonance (NMR) chemical shifts show the greatest deshielding.⁵⁹

Steiner and Fowler⁵⁸ have computed and mapped very recently the electron current densities induced in planar hydrocarbons by an external magnetic field. Their diagrams show that the strength of the π circulation in tetracene is largest within the central two-ring naphthalenic system, while that in pentacene and heptacene is largest in the central three-ring anthracenic system. The larger π current in the central region of the longer molecules results in increased deshielding of the protons there, whereas the terminal protons have relatively constant shieldings throughout the series.⁵⁸

TABLE 4: Influence of the Site of Protonation^a on the AM1-Calculated Heats of Formation, in kcal mol⁻¹, for Some of Protonated Linear Polyacenes. Absolute Values of HOMO Coefficients for All the Sites are Given in Parentheses

| compound | site of protonation | | | | | | | |
|----------|---------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | C1 | C2 | C4a | C5 | C5a | C6 | C6a | C9 |
| 2 | 213.2 (0.42) | 216.7 (0.28) | 231.9 (0.00) | | | | | |
| 3 | 229.6 (0.30) | 233.8 (0.23) | 249.5 (0.12) | | | | | 221.3 (0.43) |
| 4 | 249.9 (0.22) | 254.0 (0.19) | 268.7 (0.15) | 238.2 (0.37) | 273.0 (0.00) | | | |
| 5 | 272.3 (0.17) | 276.0 (0.16) | 289.6 (0.16) | 258.9 (0.31) | 294.8 (0.07) | 255.5 (0.37) | | |
| 6 | 295.9 (0.14) | 299.3 (0.14) | 311.9 (0.15) | 281.6 (0.26) | 316.7 (0.10) | 276.5 (0.33) | 320.1 (0.00) | |

^a Protonations at positions such as C4a, C5a, and C6a leads to a loss of planarity and to greatly reduced stability.

Lowe and Silverman⁶⁰ examined the perturbation expression for the delocalization energy, attempting to understand the difference between sites in PAHs. They concluded that the delocalization energy is largest at sites where the occupied molecular orbitals highest in energy have their largest coefficients. One needs to examine only the HOMO in order to qualitatively predict the variation of ΔE_{deloc} with attachment of H^+ to different ring positions. As discussed by Lowe and Silverman,⁶⁰ it is expected that the HOMO shall have small coefficients on fusion site atoms and large coefficients at sites adjacent to fusion sites and intermediate coefficients at sites which are second neighbors to fusion sites. In Table 4, AM1-calculated coefficients of the HOMO for linear polyacenes up to pentacene are collected. It can be seen that sites with the largest HOMO coefficients coincide with the sites where AM1-calculated enthalpies of formation of the corresponding protonated structures are smallest. In all the other polyacenes, sites with the largest HOMO coefficients are situated in the central rings of the compounds.

Very recently, Lehner et al.⁶¹ have calculated $\Delta E/\beta$ values, an index of carbonium ion formation and stability, for a series of polynuclear aromatic hydrocarbons from perturbational molecular orbital (PMO) theory. Greater $\Delta E/\beta$ values correspond to increased ability to delocalize electrons. They have calculated values for all the positions in linear polyacenes from naphthalene to nonacene, and the positions with greater values of this index are coincident with the corresponding sites of protonation.

To compare the AM1-calculated heats of formation of protonated linear polyacenes with experimental values, we have obtained indirect experimental values from the relation:

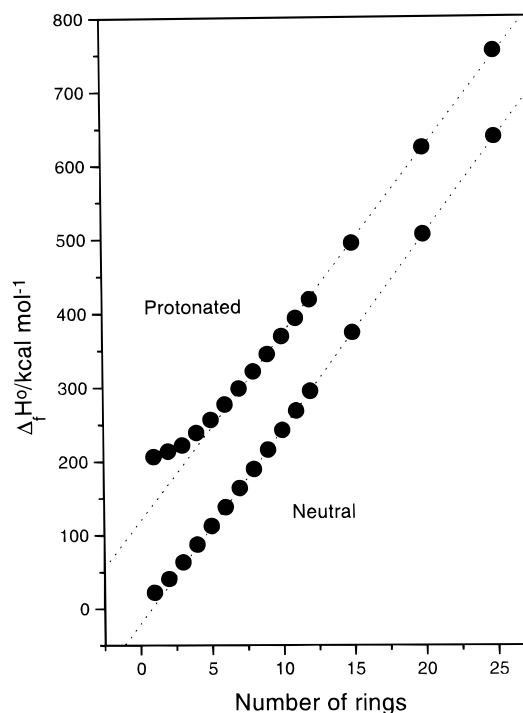
$$\Delta_f H^\circ(\text{BH}^+) = \Delta_f H^\circ(\text{B}) + \Delta_f H^\circ(\text{H}^+) - \text{PA} \quad (6)$$

and using the corresponding experimental values of the enthalpies of formation of the neutral molecules and of the proton (367.2 kcal mol⁻¹),³⁸ as well as the experimental proton affinity values. There is a good linear correlation ($r = 0.998$) between the AM1-calculated and experimental enthalpies of formation of the protonated molecules.

The evolution of the heats of formation of neutral and protonated linear polyacenes with the number of rings is shown in Figure 4.

Theoretical PA values at AM1 level are calculated through eq 3. They are collected in Table 4 together with the available experimental data. There is a very good linear correlation (see Figure 5) between AM1-calculated and experimental proton affinity values for linear polyacenes from benzene to pentacene.

From this correlation we obtain eq 7. It permits a correction of the AM1-calculated PAs in order to estimate more reliable "experimental" values for the proton affinities of linear polyacenes.

**Figure 4.** Evolution of the heats of formation of neutral and protonated linear polyacenes with the number of rings.

$$\text{PA} = 1.150 \text{ PA(AM1)} - 31.74 \quad (7)$$

PA values thus corrected for all the linear polyacenes studied herein are collected in Table 3. We can plot now these corrected PA values against the number of rings n of each polyacene (See Figure 6).

As it is shown in Figure 6, there is a clear correlation between proton affinities and the number of benzenoid rings in linear polyacenes. The curve can be fitted by the empirical eq 8:

$$\text{PA} = 157.3 + 19.0 (1 - e^{-n/22}) + 86.7 (1 - e^{-n/3.8}) \quad (8)$$

that gives a slightly better description ($\text{sd} = 0.8 \text{ kcal mol}^{-1}$) of the data than a single-exponential expression ($\text{sd} = 1.1 \text{ kcal mol}^{-1}$). From this expression it is easy to extrapolate a PA value for a linear polyacene of infinite number of rings. If $n \rightarrow \infty$, a proton affinity value of 263 kcal mol⁻¹ is obtained. Meot-Ner²⁴ extrapolated a value of 278 kcal mol⁻¹ for the PA of an edge-hydrogenated graphite monolayer from hydrogen atom affinities of the radical ions of several PAHs. Also, Stein and Brown⁶² have estimated a range of PA for a single-layer graphite of $\sim 239\text{--}279 \text{ kcal mol}^{-1}$.

Electronic structures. The energies of the highest occupied molecular orbital (HOMO) and of the lowest unoccupied molecular orbital (LUMO) computed at AM1 semiempirical level for all the linear polyacenes studied in this work are

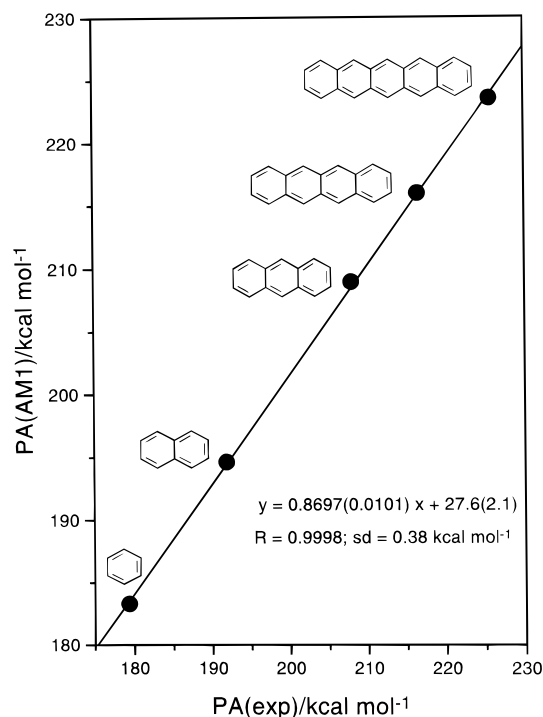


Figure 5. AM1-calculated versus experimental proton affinities of linear polyacenes.

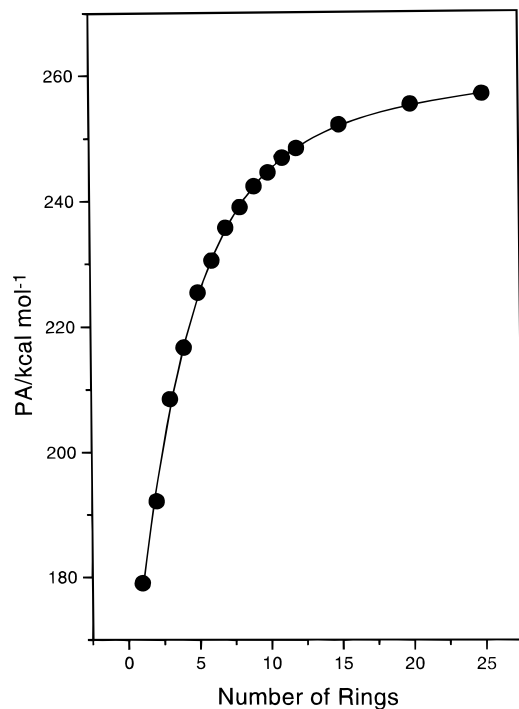


Figure 6. Evolution of the proton affinities of linear polyacenes with the number of rings.

collected in Table 3S, together with the HOMO–LUMO energy separation or HOMO–LUMO gap E_g .

According to Koopmans' theorem,⁶³ the ionization potentials IP and electron affinities EA correspond approximately to the negatives of the energies of the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively:

$$\text{IP} \equiv -\epsilon_{\text{HOMO}} \quad \text{and} \quad \text{EA} \equiv -\epsilon_{\text{LUMO}}$$

Also given are in Table 3S the IP and EA experimental values when available. In agreement with the above, there is a very

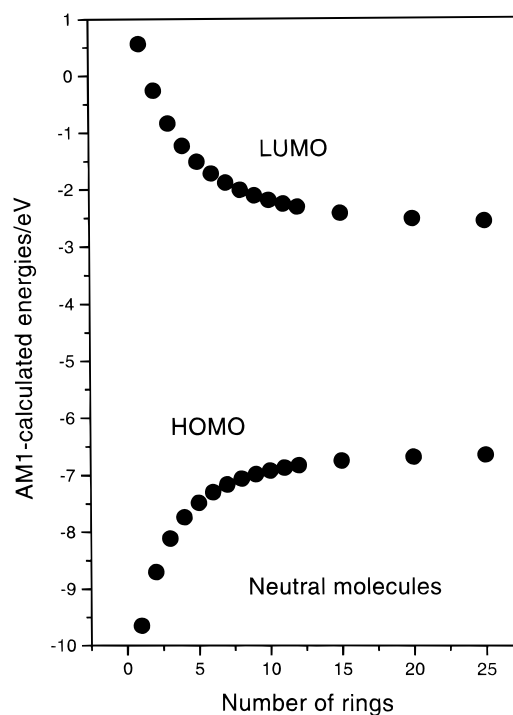


Figure 7. Evolution of the AM1-calculated energies of HOMO and LUMO of neutral linear polyacenes with the number of rings.

good linear relationship between ϵ_{HOMO} and experimental IP values:

$$-\epsilon_{\text{HOMO}} = 0.818(0.013)\text{IP}(\text{exp}) + 2.07(0.10) \quad (9)$$

$$\text{in eV; } n = 6; \quad r = 0.9995; \quad \text{sd} = 0.03 \text{ eV}$$

Similarly, there is another very good correlation between ϵ_{LUMO} and experimental EA values:

$$-\epsilon_{\text{LUMO}} = 0.789(0.025)\text{EA}(\text{exp}) + 0.399(0.023) \quad (10)$$

$$\text{in eV; } n = 4; \quad r = 0.9990; \quad \text{sd} = 0.03 \text{ eV}$$

From eqs 9 and 10 we can derive two relations providing IP and EA values for all the linear polyacenes from their HOMO and LUMO energies, respectively:

$$\text{IP} = -(1.22 \epsilon_{\text{HOMO}} + 2.53) \quad (11)$$

$$\text{EA} = (1.27 \epsilon_{\text{LUMO}} + 0.506) \quad (12)$$

IP and EA values obtained from eqs 11 and 12 are shown in parentheses in Table 3S. Molecules possessing high-lying occupied and low-lying unoccupied orbitals, that is low first IPs and high first EAs, are highly reactive.⁶⁴ This is the case of linear polyacenes.

Also in Table 3S are the HOMO–LUMO energy gaps of linear polyacenes. There is a negative dependence with the number of rings, as previously pointed out by Clar.^{7a} Trinajstić et al.⁶⁵ predicted a zero band gap for an infinite linear polyacene. This points to linear infinite polyacene as a potential quasi one-dimensional organic conductor. This prediction has been known for polyacene for sometime,^{23,66} but it has never been tested because high members of the polyacene family are too reactive to be isolated under ordinary conditions.⁷ Extended π -conjugated systems represent the simplest models for molecular wires.⁶⁷ In Figure 7 HOMO and LUMO energies of linear polyacenes are represented against the number of rings. The HOMO–LUMO gap extrapolated to an infinite linear polyacene

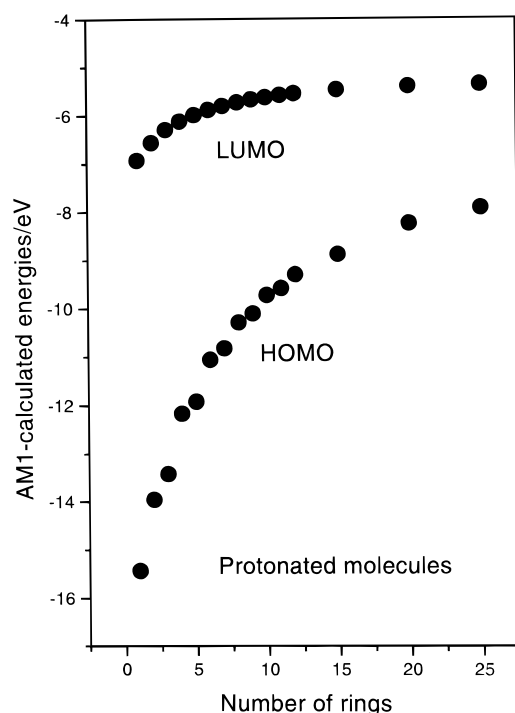


Figure 8. Evolution of the AM1-calculated energies of HOMO and LUMO of protonated linear polyacenes with the number of rings.

is about 3.8 eV, but if we correct this energy gap with the experimental IPs and EAs, the HOMO–LUMO gap decreases to 2.5 eV.

A similar study has been carried out for the case of protonated linear polyacenes. The HOMO and LUMO energies and the energy gap computed at AM1 level are shown in Table 4S. The evolution of HOMO and LUMO energies with the number of rings is represented in Figure 8. The HOMO–LUMO energy gap extrapolated to an infinite protonated linear polyacene is about 2.4 eV.

The reactivity and the energy of the UV transition energies can be linked. A low transition energy (long wavelength) implies a low HOMO–LUMO gap, and the latter frequently results in high reactivity.⁴² Linear polyacenes are characterized by remarkably large shifts in their UV p-bands. Clar^{7,68} was the first to notice a striking parallelism between Diels–Alder reactivity (a “para” reactivity, as he termed it) and the position of the p band (hence the name)⁶⁹ in many homologous series.^{64a} Clar noted^{7a} that the more highly colored a benzenoid hydrocarbon, the less stable it generally is. He ascribed this relationship to a bathochromic shift of the p band as the stability decreases. The p band is due to an allowed electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).^{7a} Experimental energies of the p absorption bands in the gas phase for linear polyacenes up to hexacene are collected in Table 3S.

As it can be expected, there is a very good linear correlation between AM1-calculated HOMO–LUMO gap energies and the experimental p absorption band energies:

$$E_g = 1.1406(0.0047)E_p + 3.426(0.017) \quad (13)$$

in eV; $n = 6$; $r = 0.99997$; $sd = 0.016$ eV

From this correlation we can obtain p band energy values for all the linear polyacenes studied here. They are shown in Table 3S. From the extrapolated value of the HOMO–LUMO

gap energy for an infinite linear polyacene we obtain a value of only 0.30 eV for the energy of its corresponding p absorption band.

Conclusions

(1) The excellent correlation between experimental thermodynamic and spectral magnitudes and the AM1 calculated values strongly supports the main conclusions of this study. (2) Our work includes a number of “long” polyacenes. This allows us to directly approach the “plateau values” of several important properties such as HOMO and LUMO energies and PA values. (3) The combination of experimental data and theoretical calculations allow us to estimate the maximum extent of thermodynamic stabilization of protonated linear polyacenes provided by charge delocalization through annelation. The effect is quite large. Thus, the difference in PA between benzene and an “infinitely long” polyacene amounts to some 84 kcal mol^{−1}. The difference between the experimental PAs of benzene and pentacene already equals 46.3 kcal mol^{−1}. Pentacene has an intrinsic basicity comparable to that of aliphatic primary and secondary amines and our results predict octacene and longer hydrocarbons to be “superbases” in the gas phase.

Supporting Information Available: AM1-calculated bond lengths and angles, charges, and HOMO and LUMO energies (6 pages). Ordering information is given on any current masthead page.

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