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Electron Affinities of Polycyclic Aromatic Hydrocarbons by Means of B3LYP/6-31+G* Calculations

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The gas-phase experimental adiabatic electron affinities (AEAs) of the polycyclic aromatic hydrocarbons (PAHs) anthracene, tetracene, pentacene, chrysene, pyrene, benzo[*a*]pyrene, benzo[*e*]pyrene, and fluoranthene are well reproduced using the hybrid density functional method B3LYP with the 6-31+G* basis set, indicating that the smallest addition of diffuse functions to the basis set is suitable for a correct description of the stable PAH anion states. The calculated AEAs also give a very good linear correlation with available reduction potentials measured in solution. The AEAs (not experimentally available) of the isomeric benzo[*ghi*]fluoranthene and cyclopenta[*cd*]pyrene, commonly found in the environment, are predicted to be 0.817 and 1.108 eV, respectively, confirming the enhancement of the electron-acceptor properties associated with fusion of a peripheral cyclopenta ring. The calculated localization properties of the lowest unoccupied MO of cyclopenta[*cd*]pyrene, together with its relatively high electron affinity, account for a high reactivity at the ethene double bond of this PAH in reductive processes.

Introduction

Because of their impact on health and environment,[1] much attention is being devoted to polycyclic aromatic hydrocarbons (PAHs), some of them being mutagens and key intermediates in carcinogenic processes. PAHs are ubiquitous in the biosphere, primarily as a result of the incomplete combustion of biomass and fossil fuels from human activities.[2,3] PAHs are generally persistent in the environment and resistant to enzymatic degradation, tend to accumulate in the biota, and have been detected in the atmosphere, water, vegetables, soil, sediments, and food.[4−9]

As a compound class, PAHs comprise uncountable members and innumerable isomers as the molecular weight increases, with distinctive physical properties, chemical reactivity, and biological significance.[10] The knowledge of the structural characteristics is fundamental for understanding the role and fate in the environment of a given PAH, but may be difficult to achieve by experimental measurements. As an alternative or complementary approach, the acquisition of molecular parameters (i.e., descriptors) by means of theoretical calculations can provide relevant information to estimate (bio)chemical properties and establish quantitative structure−activity relationships (QSAR).[11,12]

A nonlinear relationship between the photoinduced toxicity and the energy of the triplet and singlet state of a set of PAHs has been proposed.[13] In agreement, Veith et al.[12] found that the best descriptor to distinguish phototoxic from nonphototoxic PAHs is the HOMO−LUMO energy gap, as evaluated with semiempirical calculations, while Lewis and Parke[14] correlated the carcinogenic and mutagenic activities of methyl-substituted benz[*a*]anthracenes only with the LUMO energy, that is, within the validity of Koopmans' theorem,[15] the electron affinity (EA). More recently, Ferreira and co-workers[11,16] found that the phototoxicity of PAHs is related to each of the electronic descriptors HOMO energy, LUMO energy, and HOMO−LUMO gap.

PAHs have recently created additional interest because of their presence in interstellar space and many celestial objects,[17,18] which seem to be responsible for emission bands in the infrared region of the interstellar spectrum.[19] Not only have neutral or cationic species been observed in the interstellar medium, but so also have anion states of PAHs with sufficiently large EA.[20]

This prompted researchers to test[21] whether density functional theory (DFT) methods are suitable to calculate EAs for this class of compounds. The experimental adiabatic EA (AEA, associated with formation of the geometrically relaxed anion) of benzene and the first three linear polyacenes is nicely reproduced[21] by the difference between the total energy of the neutral state and that of the anion state (each with its optimized geometry), evaluated with either the BLYP or the B3LYP functional and employing a double-ζ basis set (denoted as DZP++) with polarization and diffuse functions at both the carbon and hydrogen atoms.

The EA was found[22,23] to be an important descriptor also for modeling the gas-phase oxidation rates of PAHs in diesel combustion, thus indicating that the initial step in the destruction of PAHs is plausibly the capture of an electron. Rhead and co-workers[22,23] investigated the sources of PAHs in diesel exhaust emissions, and for mid-speed and mid-load conditions they observed a linear relationship between the extent to which individual PAHs survived combustion and the LUMO energy, as evaluated from Hückel calculations.

The redox properties of PAHs determined in solution by means of cyclic voltammetry have shown that peripheral cyclopenta fusion notably enhances their EA and suggested a large localization of the added electron in the peripheral

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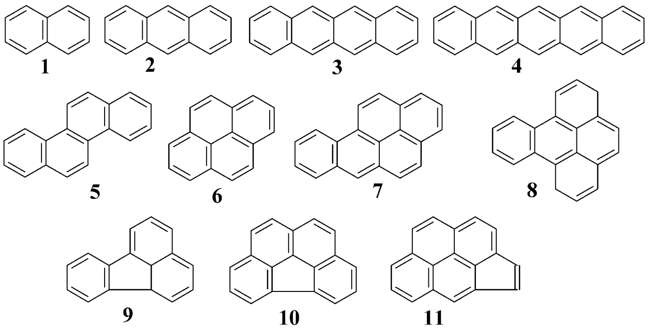
TABLE 1: B3LYP/6-31+G* VEAs and AEAs Obtained as the Neutral/Anion Total Energy Difference[a]

		6-31+ G*		DZP++	expt
		VEA	AEA	AEA	AEA
1	naphthalene	−0.378	−0.260	−0.20[b]	−0.05 ± 0.05(eval.[c])
2	anthracene	0.433	0.530	0.58[b]	0.57 ± 0.04; 0.53 ± 0.005[e]
3	tetracene	1.000	1.080	1.13[b]	1.04 ± 0.04
4	pentacene	1.408	1.479		1.35 ± 0.04[d]
5	chrysene	0.187	0.290		0.397 ± 0.008[f]; 0.33[g]; 0.32 ± 0.01[h]
6	pyrene	0.306	0.411		0.500 ± 0.030[i]; 0.39[g]
7	benzo[*a*]pyrene	0.674	0.772		0.78 ± 0.04[d]
8	benzo[*e*]pyrene	0.355	0.452		0.534 ± 0.008[f]
9	fluoranthene	0.599	0.722		0.630[j]
10	benzo[*ghi*]fluoranthene	0.716	0.817		
11	cyclopenta[*cd*]pyrene	0.986	1.108		

[a] AEAs calculated[21] with the DZP++ basis set and available experimental values are also reported for comparison; all values in eV. [b] Ref 21. [c] Ref 36, see text. [d] Ref 37. [e] Ref 38. [f] Ref 39. [g] Ref 40. [h] Ref 41. [i] Ref 42. [j] Ref 43.

SCHEME 1



pentagon.[24] Otero-Lobato et al.[25] showed that in cyclopenta[*cd*]pyrene (**11**, see Scheme 1) the olefinic bond of the externally fused five-membered ring is of importance for a positive mutagenic response through epoxide formation, in line with its high chemical and biological reactivity.[26,27]

The isomeric $C_{18}H_{10}$ cyclopenta[*cd*]pyrene (**11**) and benzo[*ghi*]fluoranthene (**10**), with a peripheral and an internal five-membered ring, respectively, are among the most concentrated contaminants (including also pyrene and fluoranthene) found[9] in sediments of a coastal lagoon (Piallassa Baiona, Ravenna, Italy) of the Adriatic sea. In a study[28] of PAH bioaccumulation in mussels it was demonstrated that the concentration ratio **11**/**10** in biota was much smaller than in sediments, in contrast with the nearly unchanged ratio between pyrene and fluoranthene. The lower bioaccumulation of cyclopenta[*cd*]pyrene was ascribed to its chemical and biological reactivity at the ethene double bond.

A theoretical approach adequate for describing the energetics and nature of anion states involves difficulties not encountered for neutral or cation states. A proper description of the spatially diffuse electron distributions of anions requires a basis set with diffuse functions.[29] On the other hand, inclusion of diffuse functions in the basis set can generate low-energy solutions with no physical significance with regard to anion formation,[30−32] mainly for anion states which are unstable with respect to the neutral molecule (i.e, when the neutral molecule possesses a negative EA). For example, in the above-mentioned B3LYP results[21] for benzene not only is the agreement between calculated (−0.88 eV) and experimental (−1.12 eV) vertical EA (VEA, associated with formation of the anion with the geometry of the neutral state) the least satisfactory, but also the singly occupied MO (SOMO) of the benzene anion is predicted to be a spatially diffuse $\sigma^*(a_{1g})$ MO instead of the valence $\pi^*(e_{2u})$ MO. The EA (−1.16 eV) calculated[33] at the B3LYP/6-311+G* level (here fewer diffuse functions are added to the basis set than those of the DZP++ basis) is very close to experiment, but again the SOMO of the benzene anion is wrongly identified so that this energy comparison is irrelevant, whereas B3LYP/6-31G* calculations (without diffuse functions) predict correctly the SOMO to be a valence MO of π^* symmetry, but the computed EA (−2.31 eV) is far too small.[33]

However, except for naphthalene which possesses an AEA close to zero, the first anion state of the PAHs constituted by fused benzene rings is quite stable, so that the choice of the basis set might not be as crucial as for the unstable anion states. In fact, a study[32] of the dependence of calculated EAs of phosphabenzenes upon the basis set employed showed that the energy calculated for stable anion states changes only slightly with further addition of diffuse functions to the 6-31+G* basis set.

Here, B3LYP calculations are carried out to evaluate the VEAs and AEAs of the 11 PAHs represented in Scheme 1, as the difference between the total energies of the neutral and anion states. Our objectives in the present work are 2-fold. The first is to test whether the positive EAs of PAHs can be accurately reproduced using a basis set (6-31G*) without diffuse functions or a basis set (6-31+G*) which includes the smallest addition of diffuse functions, with the consequent advantages in computer time with respect to larger basis sets.

Following this, the EAs (not experimentally available) of the isomeric $C_{18}H_{10}$ cyclopenta[*cd*]pyrene (**11**) and benzo[ghi]fluoranthene (**10**) are compared to each other to verify whether the peripheral five-membered ring of the former enhances the electron-acceptor properties, and the localization properties of the LUMO and geometrical changes upon anion formation are analyzed to obtain further insight into the high reactivity of the ethene double bond of cyclopenta[*cd*]pyrene upon electron addition.

Results and Discussion

The total energy of the neutral molecules **1**−**11** and of their vertical (with the same geometry as the neutral states) and adiabatic (with their optimized geometries) anion states were calculated with the Gaussian 98 set of programs[34] using the B3LYP hybrid functional[35] with the standard 6-31G* and the 6-31+G* basis set, the latter including the smallest addition of diffuse functions (3*s* and 3*p* functions on the carbon atoms). The VEAs and AEAs obtained with the 6-31+G* basis set are reported in Table 1 together with the AEAs of **1**−**3** calculated[21] with the DZP++ basis set (which includes more diffuse functions than the 6-31+G* basis set) and experimental AEAs available for PAHs **1**−**9**.

Except for naphthalene (**1**) which possesses an AEA close to zero and a negative VEA (−0.19 eV[36]), the ground anion states of the PAHs considered lie well below the energy of the neutral state molecule. Table 1 shows that the positive AEAs supplied by the B3LYP/6-31+G* calculations match very well the corresponding measured values. The calculated AEAs of anthracene (**2**), tetracene (**3**), chrysene (**5**), pyrene (**6**), and benzo[*a*]pyrene (**7**) reproduce the average experimental values within 0.05 eV, the AEA of benzo[*e*]pyrene (**8**) is slightly (0.08 eV) underestimated, while those of fluoranthene (**9**) and pentacene (**4**) are slightly overestimated, the largest error (0.13 eV) occurring for the latter. Due to the relatively small geometrical changes caused by electron addition on these π-systems, the calculated VEAs (see Table 1) are not much smaller than the AEAs, the differences ranging from 0.08 to 0.12 eV.

For all PAHs, the B3LYP/6-31+G* calculations correctly predict the LUMO of the neutral molecules, as well as the SOMO of the ground anion states, to be valence π^* MOs, and their localization properties essentially correspond to those obtained with the 6-31G* basis set (i.e., without inclusion of diffuse functions).

Comparison of the present results with the AEAs reported[21] for **2** and **3** using the DZP++ basis set (see Table 1) shows that inclusion of more diffuse functions produces only a small (0.05 eV) EA increase and does not improve agreement with experiment. It can also be noticed that zero-point vibrational energy corrections, which further increase the AEA by about 0.13 eV,[21] would worsen the agreement with experiment. These findings indicate that the stable anion states of PAHs are much less spatially diffuse than unstable anion states, and thus they can be properly described with a basis set which includes the smallest addition of diffuse functions.

In agreement, for all the PAHs considered, both the VEAs and AEAs (not reported) supplied by the 6-31G* basis set (which does not include diffuse functions) are only about 0.4 eV smaller than the corresponding values obtained with the 6-31+G* basis set. This difference is relatively small when compared to that found[32] for the (unstable) anion states of benzene (about 1 eV) and pyridine (0.7 eV).

Naphthalene (**1**) possesses an AEA close to zero, the measurements performed with different techniques ranging from a positive value (0.134 eV,[44] using an electron capture detector) to a negative value (−0.20 eV,[45] from the binding energies of naphthalene anions stabilized by a number of water molecules and extrapolation to zero water molecules). An independent evaluation can be obtained by adding 0.12 eV (the difference between the adiabatic and vertical EAs calculated here) to the negative VEA (−0.19 ± 0.05 eV) measured[36] with electron transmission spectroscopy. Superposition of the high energy side of the intense electron beam signal at zero energy with the resonance observed in the electron transmission spectrum could increase the apparent resonance energy by some hundredths of an eV, thus leading to −0.05 ± 0.05 eV as a reasonable assessment of the AEA of naphthalene, nearly midway between the two extremes mentioned above. The adiabatic ground anion state of naphthalene would thus be slightly unstable with respect to the neutral molecule and, in any case, is substantially less stable than those of PAHs **2**−**9**, thus accounting for a somewhat larger error (an underestimation of 0.2 eV) in the calculated EA.

For the eight PAHs **2**−**9**, the average (absolute) difference between the B3LYP/6-31+G* and experimental AEA is 0.058 eV (standard deviation = 0.041 eV). This gives confidence on the reliability of the AEAs predicted for the $C_{18}H_{10}$ isomers benzo[*ghi*]fluoranthene (**10**) and cyclopenta[*cd*]pyrene (**11**), containing an annelated five-membered ring, for which experimental values are not available. The AEA (1.108 eV) calculated for **11**, where the pentacycle is peripheral, is 0.3 eV larger than that of **10**.

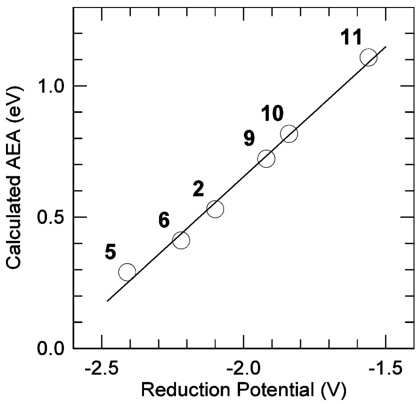


Figure 1. Plot of B3LYP/6-31+G* gas-phase AEAs vs the corresponding reduction potentials measured in solution for PAHs **2**, **5**, **6**, **9**, **10**, and **11**.

Further support to the reliability of the AEAs calculated for **10** and **11** comes from comparison with one-electron reduction potentials ($E_{1/2}$) measured in CH_3CN, reported by Koper et al.[24] Figure 1 interestingly shows that a plot of the AEAs calculated for **2**, **5**, **6**, **9**, **10**, and **11** versus the corresponding $E_{1/2}$ values (in V) gives a very good linear correlation (AEA = $0.987E_{1/2} + 2.629$, correlation coefficient = 0.996) with a slope close to one, so that the EA differences are nearly equal to the $E_{1/2}$ differences. The present results thus confirm the conclusions drawn from cyclic voltammetry data in solution by Koper et al.[24] on the enhancement of the electron-acceptor properties associated with peripheral cyclopenta fusion.

Moreover, when $E_{1/2}$ (−2.66 V) measured[24] for naphthalene is introduced into this linear equation, a corresponding AEA of 0.00 eV is extrapolated, in very good agreement (equal within experimental error) with the above evaluation of −0.05 eV.

The larger EA of cyclopenta[*cd*]pyrene (**11**) with respect to benzo[*ghi*]fluoranthene (**10**) implies a more pronounced tendency of the former to reduction, but this does not necessarily account for the high chemical and biological reactivity[9,26,27] of its ethene double bond. On the other hand, **11** is not only a better electron-acceptor than **10**, but also a better electron-donor at one and the same time. To our knowledge, experimentally determined ionization energies for **10** and **11** are not available in the literature. However, we have found[46] a very good linear correlation between the HOMO energy supplied by either Hartree−Fock (HF) or semiempirical calculations for a large number of PAHs and the corresponding measured ionization energies. Such empirically calibrated scalings predict the ionization energy of **11** to be sizably smaller (0.5 eV) than that of **10**.

However, according to the charge distributions predicted by HF and B3LYP calculations, the HOMO of both **10** and **11** is essentially nonbonding between carbon atoms labeled 2 and 3 in Scheme 2, so that ionization is expected to only slightly affect the C(2)−C(3) bond strength. Figure 2 shows the localization properties of the LUMO of **10** and **11** (those predicted for the anion SOMO are quite similar), as supplied by B3LYP/6-31G* calculations. In both compounds the LUMO is largely localized on the C(2) and C(3) carbon atoms, but an important difference between the two PAHs is apparent. The LUMO of **10** is strongly C(2)−C(3) bonding and nearly nonbonding on the adjacent C−C bonds of the five-membered ring, whereas the LUMO of

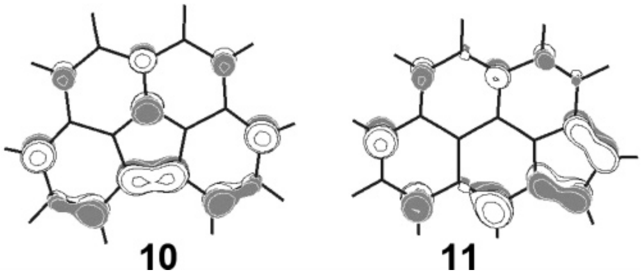


Figure 2. Representation of the LUMO of **10** and **11** as supplied by B3LYP/6-31G* calculations.

SCHEME 2

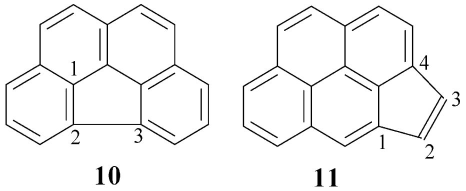


TABLE 2: Bond Distances (Å) Supplied by B3LYP/6-31+G* Calculations for the Neutral Molecules (left) 10 and 11 and Their Anion States (right)

	d (1−2)	*d* (2−3)	d (3−4)
10	1.4241 → 1.4376	1.5067 ad 1.4666	
11	1.4746 → 1.4446	1.3701 → 1.4034	1.4722 → 1.4412

11 is strongly antibonding between C(2) and C(3) and bonding on the adjacent C−C bonds, in agreement with previous Hückel calculations.[24]

The ethene double bond of **11** is thus expected to be substantially weakened upon electron addition. Table 2 reports B3LYP/6-31+G* bond distances of the five-membered ring of the neutral molecules **10** and **11** and their optimized anion states. The calculated C(2)−C(3) distance (1.507 Å) of the neutral molecule **10** is close to that (1.519 Å[47]) of the single C−C bond of cyclopentene, and it is notably reduced (0.04 Å) in the anion. In contrast, the C(2)−C(3) distance of **11** (1.370 Å, to be compared with 1.342 Å for the C═C double bond of cyclopentene[47]) increases by 0.03 Å upon anion formation, while the adjacent C−C bonds are shortened by about the same amount. The present results are therefore consistent with a high reactivity of the ethene double bond of **11** in reductive processes.

Conclusions

An adequate theoretical description of anion states (energy and localization properties) poses problems not encountered for neutral or cation states. A proper description of the spatially diffuse electron distributions of anions requires a basis set with diffuse functions. However, literature results[32] show that for anion states which are unstable with respect to the neutral molecule the calculated energies strongly depend on the choice of the basis set, the energy becoming increasingly smaller as the basis set is enlarged. In addition, inclusion of diffuse functions in the basis set can generate low-energy solutions with no physical significance with regard to anion formation, so that it becomes difficult to decide a priori which basis set will be reliable for reproducing the energy and localization properties of anion states.

Because of the increasing impact on health and the environment of PAHs, ubiquitous pollutants of anthropogenic origin, and the importance of their EA as a descriptor for modeling structure−activity relationships, B3LYP/6-31+G* calculations were used to determine whether the use of a basis set which includes the smallest addition of diffuse functions is suitable for a correct description of the stable PAH anion states. The calculated positive AEAs reproduce the corresponding measured values, ranging from 0.3 eV (chrysene) to 1.4 eV (pentacene), with an accuracy very close to experimental data, whereas the values obtained with the 6-31G* basis set are systematically about 0.4 eV too small. Both basis sets predict the AEAs to be only about 0.1 eV larger than the corresponding VEAs, due to relatively small geometrical changes produced by the added electron. Comparison with the AEAs obtained[21] for anthracene and tetracene using B3LYP/DZP++ calculations indicates that addition of more diffuse functions to the 6-31+G* basis set leads to an EA increase of only 0.05 eV and does not improve agreement with experiment.

A very good linear correlation is also found between the B3LYP/6-31+G* AEAs and available reduction potentials measured[24] in solution. Extrapolation of this linear dependence leads to 0.00 eV for the AEA of naphthalene, for which values obtained from different experimental methods range from +0.13 to −0.20 eV.

The AEAs (not experimentally available) of the $C_{18}H_{10}$ isomers benzo[*ghi*]fluoranthene and cyclopenta[*cd*]pyrene, commonly found in the environment, are predicted to be 0.817 and 1.108 eV, respectively, confirming the enhancement of the electron-acceptor properties associated with the fusion of a peripheral five-membered ring. Moreover, the calculated localization properties of the lowest unoccupied MO of cyclopenta[*cd*]pyrene are consistent with its high reactivity at the ethene double bond in reductive processes.

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