Rapid quantitative prediction of ionization energies and electron affinities of polycyclic aromatic hydrocarbons

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Abstract

Quantitative structure–activity relationship (QSAR) studies of polycyclic aromatic hydrocarbons (PAHs) often employ rapid semi-empirical calculations to evaluate ionization energy (IE) and electron affinity (EA) values, assuming they are equal (but of opposite sign) to the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), respectively. However, regardless of the assumption of validity of Koopmans' theorem, the reliability of this simple theoretical approach for reproducing the experimental IE and EA trends has not been tested, except for a few linear PAHs.

Here the measured IEs and EAs of 17 PAHs are plotted *vs.* the HOMO and LUMO energies obtained with semiempirical AM1 calculations and, for comparison, HF/6-31G calculations. Good linear relationships are obtained with both methods, with correlation coefficients $r > 0.98$ for the IEs and $r > 0.96$ for the EAs. The IEs and EAs predicted by scaling the corresponding MO energies with the appropriate empirical linear equation are compared with experimental values available in the literature for PAHs (28 IEs and 22 EAs). The average (absolute) difference between evaluated and measured IEs is found to be 0.07 eV (s.d. = 0.05 eV), while for the EAs the average difference is slightly larger. The accuracy of both AM1 and HF/6-31G methods are essentially equal, the former having the significant advantage of being 60 times faster.

The present study demonstrates the ability of rapid semiempirical calculations carried out on the neutral molecules to parallel the experimental IE and EA values of PAHs, and provides simple linear equations which can be routinely employed for their quantitative prediction in this class of compounds.
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the biosphere, primarily as a result of anthropogenic activities (incomplete combustion of biomass and fossil fuels) [1,2]. PAHs have been detected in the atmosphere, water, vegetables, soil, sediments and food [3–8] and tend to accumulate in the biota. Because of their impact on health and the environment [9] much attention is being devoted to this class of compounds, some of them being mutagens and key intermediates in carcinogenic processes.

PAHs have recently created additional interest because of their probable presence in interstellar space and many celestial objects [10,11], being the best candidates to explain the emission bands in the infrared region of the interstellar spectrum [12]. Not only have neutral or cationic species been observed in the interstellar medium, but also anion states of species having sufficiently large electron affinities (EAs) [13].

The PAH family comprises uncountable members and isomers as the molecular weight increases, with different

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physical properties and chemical reactivity [14]. The role and fate in the environment of a given PAH depends upon its structural characteristics, which may be difficult to obtain experimentally. As an alternative 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) [15,16].

Newsted and Giesy [17] found that the toxicity of a series of PAHs is induced by exposure to sunlight and found a non-linear relationship between phototoxicity and energy of the neutral excited state. In agreement, Veith et al. [16] found that the best descriptor to distinguish phototoxic from non-phototoxic PAHs is the energy gap between the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals, as evaluated with semiempirical calculations, while Lewis and Parke [18] correlated the carcinogenic and mutagenic activities of methyl substituted benz[*a*]anthracenes only with the LUMO energy obtained with CNDO/2 calculations. More recently, Ferreira and co-workers [15,19] found that the phototoxicity of PAHs, with some exceptions, is related to each of the electronic descriptors HOMO energy, LUMO energy and HOMO–LUMO gap, evaluated with semiempirical MNDO or AM1 calculations.

Rhead and coworkers [20,21] found the LUMO energy to be an important descriptor for modelling the gas-phase oxidation rates of PAHs in diesel combustion. 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 obtained with Hückel calculations.

The frontier MO structure seems therefore to be strictly related to important properties of the PAHs, directly associated with their environmental impact. Due to the large number of data required to test the suitability of the descriptors, it is reasonable that the QSAR studies reported in the literature employ quick methods, such as semiempirical calculations, to evaluate the HOMO and LUMO energies.

Less reasonable, however, is the (often tacitly made) assumption that the measurable physical properties ionization energy (IE) and EA are equal (with opposite sign) to the corresponding filled and empty MO energies, respectively, of the neutral molecules. This is true only within the limits of the approximation of Koopmans' theorem (KT) [22], where the relaxation effects occurring on the time scale of electron ejection or addition are neglected. In addition, no mention is usually made of the fact that the numerical values obtained for the MO energies depend on the computational method employed. Even more importantly, to our knowledge, attempts to check the reliability of these simple theoretical methods for reproducing (if not the absolute values) at least the measured IE and EA trends of PAHs have never been made, except for some linear polyacenes [23]. For this reason, it cannot be ruled out

that anomalies found in the descriptor/property relationships are to be ascribed to inadequacy of the semiempirical calculations in predicting the relative IE and/or EA values for some PAHs.

The first EA (associated with electron addition to the LUMO) of a molecular system can, in principle, be obtained as the total energy difference between the ground neutral state and the lowest-lying anion state. However, 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 [24]. 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 [25–27], especially for anion states which are unstable with respect to the neutral molecule (i.e, when the neutral molecule possesses a negative EA).

The experimental adiabatic EA (AEA, associated with formation of the geometrically relaxed anion) of the first three linear polyacenes is nicely reproduced [28] by the difference between the total energy of the neutral state and that of the anion state (each with its optimized geometry), evaluated with the B3LYP functional (an exchange-correlation functional within the framework of density functional theory) employing a double-ζ basis set with polarization and diffuse functions at both the carbon and hydrogen atoms. However, it has been demonstrated [29–32] that the EAs of PAHs can be accurately reproduced by B3LYP/6-31+G* calculations, i.e., using a basis set which includes the smallest addition of diffuse functions, with the consequent advantages in computer time with respect to larger basis sets. Nevertheless, even with the 6-31+G* basis set, evaluation of a single AEA value for a PAH containing four fused rings takes about two days with a modern personal computer. Thus, although it can be employed to predict IEs and AEAs for a large number of PAHs [30–32], this approach is not well-suited for QSAR studies.

Correlations of the measured IEs and EAs of conjugated π-systems with the corresponding orbital energies calculated for the neutral molecules have been made over several decades [33]. In particular, good linear correlations have been found between the energies of virtual π^* MOs obtained with the Hartree–Fock (HF) [26,34] and B3LYP [35] methods with the corresponding measured energies of vertical electron attachment (i.e., negative vertical EAs, associated with unstable anion states). As far as semiempirical calculations are concerned, to our knowledge, the only test available in the literature was reported by Notario and Abboud [23]. They found very good linear correlations between the AM1 [36] HOMO and LUMO energies and the experimental IEs and AEAs, respectively, of PAHs, but their investigation was limited to a small number of linear polyacenes.

Our objective in the present work is to extend previous work to a large sample of PAHs. Experimental IEs and