FEATURE ARTICLE

Electron Affinities of Polycyclic Aromatic Hydrocarbons

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The electron affinities of benzene and four polycyclic aromatic hydrocarbons (PAHs), naphthalene, anthracene, tetracene, and the perinaphthenyl radical, have been obtained using six common density functional theory (DFT) methods. When compared to experiment, the BHLYP, BLYP, and B3LYP functionals have average absolute errors of 0.17, 0.18, and 0.19 eV, respectively. The success of the BHLYP functional is dubious due to a fortuitous cancelation in error between the tendency for BHLYP to underestimate electron affinities and zero-point vibrational energy (ZPVE) corrections. We recommend the BLYP and B3LYP functionals for future studies of PAH anions. However, the computation of ZPVE corrections may be a limiting factor in the accuracy of any method seeking to predict electron affinities for large PAHs.

I. Introduction

Long recognized to be of great chemical importance, polycyclic aromatic hydrocarbons (PAHs)[1−7] have generated much recent attention because of evidence for their existence in interstellar space.[8−16] In particular, interstellar PAHs may play an important role in the burgeoning field of astrobiology.[13,14] The majority of evidence for interstellar PAHs results from emission bands in the infrared (IR, ≈6−17 μm) region of the interstellar spectrum.[9,12]

Due to the conditions in the interstellar medium, attention has primarily focused on cationic and neutral PAHs as possible interstellar molecules; however, it is quite possible that anionic PAHs also exist in interstellar space assuming a sufficiently strong electron binding energy, i.e., a large electron affinity ($>\approx$0.5 eV). Indeed, in infrared spectroscopy experiments designed to measure IR emission bands of PAHs, the pentacene anion has been observed.[17−20] However, not all PAHs are expected to bind an additional electron, thus making the electron affinities (EA) of polycyclic aromatic hydrocarbons of particular interest. Indeed, anions of PAHs have been the subject of numerous past experimental[21−28] and theoretical work.[19,29,30] Specifically, the most recent experimental values for the electron affinities of benzene, naphthalene, anthracene, tetracene, and pentacene (cf. Figure 1) are -1.12 ± 0.03,[23] -0.19 ± 0.03,[23] 0.530 ± 0.005,[25] 1.04 ± 0.04,[24] and 1.35 ± 0.04 eV,[24] respectively. It is clear that as size of linear-"acene", or "polyacene" PAHs increase from one to five (or more) aromatic rings, the electron affinity substantially increases.

Although the above-mentioned polyacenes are not expected to be the dominant PAHs in the interstellar medium,[17] they are still expected to be of some importance in interstellar space. In particular, as we have just noted, larger polyacenes can be expected to exhibit large electron affinities which may allow them to be a significant source of interstellar PAH anions, despite the lesser presence of the parent neutral polyacenes. Furthermore, on a more terrestrial note, very recent investigations of the fractional quantum Hall effect[7] make the electronic properties of tetracene and pentacene of particular interest.

Electronic structure theory investigations of PAHs have long been successful due to the ease of Hückel molecular orbital (MO) theory.[31] However, only in the past decade have more sophisticated correlated methods such as perturbation theory and density functional theory been applied on PAHs. Density functional theory (usually with the B3LYP functional) has been widely used in theoretical investigations of neutral and cationic PAH infrared spectra.[11,16,19,20,29,32] On the other hand, recent investigations[19,29,30] of PAH anions have used semiempirical theory (AM1) or B3LYP without diffuse functions on the basis sets.[19,29] During the past several years, work in our group has shown that density functional theory (DFT) can be an accurate (to within ≈0.2 eV with the B3LYP, BLYP, and BP86 functionals) method for predicting the electron affinities of simple hydrocarbons.[33−36] In this present work we extend our study of hydrocarbon electron affinities to larger, polycyclic aromatic hydrocarbons with an interest in whether DFT can be expected to give a similarly accurate theoretical description of PAHs and their corresponding anions. Specifically, we examine six different density functionals using a double-ζ basis with diffuse functions. Our results should suggest whether B3LYP or some other functional is the best choice for future studies of PAH anions.

II. Methods

Total energies, equilibrium geometries, harmonic vibrational frequencies, and ZPVE's were determined for the neutral and anion species of each PAH studied. Six different exchange-correlation density functionals were used and have been denoted B3LYP, B3P86, BHLYP, BLYP, BP86, and LSDA. The first five are generalized gradient approximations (GGA's) and

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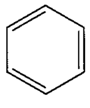
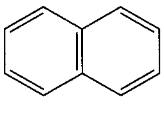
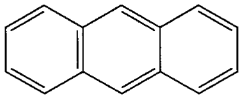


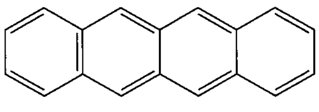
Benzene C_6H_6



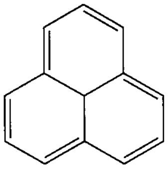
Naphthalene $C_{10}H_8$



Anthracene $C_{14}H_{10}$



Tetracene $C_{18}H_{12}$



Perinaphthenyl radical $C_{13}H_9$

Figure 1. Benzene and four polycyclic aromatic hydrocarbons (PAHs).

employ either the dynamical correlation functional of Lee, Yang, and Parr (LYP)[37] or that of Perdew (P86)[38,39] in conjunction with one of Becke's exchange functionals: the three-parameter HF/DFT hybrid exchange functional (B3),[40] a modification of the half-and-half HF/DFT hybrid method (BH) (the BH functional as implemented by Gaussian 94),[41] or the 1988 pure DFT exchange functional (B).[42] The sixth density functional scheme used in the study was the standard local-spin-density approximation (LSDA) which employs the 1980 correlation functional of Vosko, Wilk, and Nusair[43] along with the Slater exchange functional.[44−46]

All functionals employed a double-ζ basis set with polarization and diffuse functions, denoted DZP++. This basis set is identical to the basis set used in previous studies in our group,[33−36] and allows for direct comparison with our previous electron affinity results. The DZP++ basis was constructed by augmenting the Huzinaga−Dunning[47,48] set of contracted double-ζ Gaussian functions with one set of p polarization functions for each H atom and one set of five d polarization functions for each C atom ($\alpha_p(\mathrm{H}) = 0.75$, $\alpha_d(\mathrm{C}) = 0.75$). To complete the DZP++ basis, one even-tempered s diffuse function was added to each H atom and a set of even-tempered s and p diffuse functions to each C atom. These "even-tempered" orbital exponents were determined according to the guidelines of Lee and Schaefer.[49] That is, the s- or p-type diffuse function exponent, $\alpha_{\mathrm{diffuse}}$, for a given atom was determined by

$$\alpha_{\mathrm{diffuse}} = \frac{1}{2}\left(\frac{\alpha_1}{\alpha_2} + \frac{\alpha_2}{\alpha_3}\right)\alpha_1$$

where α_1 is the smallest, α_2 the second smallest, and α_3 the third smallest Gaussian orbital exponent of the s- or p-type primitive functions of that atom. All polarization and diffuse orbital exponents were not scaled. There are a total of six DZP++ basis functions per H atom and 19 per C atom.

The quantum chemical computations of this study were conducted with the Gaussian 94[50] system of DFT programs. Spin-unrestricted Kohn−Sham orbitals were used for all computations. Both the neutral and anion geometries were optimized via analytic gradients with each of the six density functionals. Numerical integration of the functionals was carried out using the Gaussian 94[50] default pruned grid consisting of 75 radial shells with 302 angular points per shell. The mass-weighted Hessian matrix, and hence the harmonic vibrational frequencies, were determined analytically for all DFT methods.

The adiabatic electron affinities (AEA) for the molecules studied were computed by differences between the total energy of the geometry-optimized neutral and the total energy of the corresponding geometry optimized anion. ZPVE-corrected electron affinities were also determined by adding the corresponding harmonic ZPVE to these total energies before subtracting the energy of the anion from that of the neutral. Vertical attachment energies (VAE) for benzene and naphthalene are computed by differences between the total energy of the optimized neutral and the anion single point energy at the optimized neutral geometry.

III. Results

A. Electron Affinities. Electron affinities for benzene, naphthalene, anthracene, tetracene, and the perinaphthenyl radical (cf. Figure 1) with each density functional are reported in Table I. In general, we do not discuss optimized geometries, because differences between the optimized neutral and optimized anion structures are small. For example, with the B3LYP functional the greatest change between any neutral C−C bond and the corresponding anion C−C bond is only 0.03 Å in naphthalene and anthracene, 0.02 Å in tetracene, and 0.01 Å in the perinaphthenyl radical.

1. Benzene. It is well-known that benzene does not bind an additional electron. Experimental electron transmission studies by Burrow, Michejda, and Jordan of the temporary benzene negative ion result in a vertical attachment energy of −1.12 eV.[23] Experimental data places the additional electron in the e_{2u} LUMO of benzene and all six density functionals in this present study yield an e_{2u} LUMO. Our computed vertical attachment energies are all within 0.32 eV of the experimental value, with the exception of the B3P86 and LSDA functionals, which greatly miscalculate the VAE. The best agreement with experiment is found for B3LYP which is within 0.24 eV of the experimental value.

2. Naphthalene. The electron affinity of naphthalene is very close to zero. In 1986, Zlatkis, Lee, Wentworth, and Chen reported an EA(naphthalene) = 0.14 eV using the electron capture method.[22] In contrast, Burrow et al. report a VAE(naphthalene) of −0.19 ± 0.03 eV,[23] and recent photoelectron spectroscopy results by Lyapustina, Xu, Nilles, and Bowen suggest an adiabatic electron affinity of −0.20 eV.[28] Indeed, one expects VAE(naphthalene) ≈ AEA(naphthalene) as the electron transmission spectrum of naphthalene displayed no evidence for a substantial geometry change between neutral and anionic naphthalene.[23] We likewise observe only small geometric changes between in our optimized neutral and anion structures. For example, with both the B3LYP and BLYP functionals, the greatest change between any C−C bond in neutral naphthalene and anionic naphthalene is 0.03 Å, with most C−C bonds changing by only 0.01−0.02 Å.

Our results for AEA(naphthalene), without ZPVE correction, with the B3LYP, BLYP, and BP86 functionals are all negative and within 0.18 eV of the values reported by Burrow et al. and Lyapustina et al., with the B3LYP and BLYP functionals nearly reproducing the experimental values. Although ZPVE corrections tend to raise the EA(naphthalene) by about 0.16 eV, applying a ZPVE correction is not necessarily warranted because a negative EA for naphthalene suggests a temporary anion (as with benzene), and thus ZPVE corrections obtained from fully optimized naphthalene anions are not of physical significance. Furthermore, we computed a VAE(naphthalene) = −0.33 eV with the BLYP functional. This suggests only a small relaxation energy (≈0.1 eV) for the anion, after attachment of an electron to neutral naphthalene. Thus it now appears that both theory and experiment favor a negative, vertical electron attachment energy for naphthalene and that no bound, isolated naphthalene anion exists.

3. Anthracene. In 1997, Schiedt and Weinkauf used photodetachment photoelectron spectroscopy to report an EA(anthracene) = 0.530 ± 0.005 eV.[25] With ZPVE corrections (which raise the AEA by about 0.13 eV), the B3LYP, BHLYP, and BLYP functionals are within 0.19 eV of the experimental value.

4. Tetracene. From measurements of gas-phase electron attachment free energies, ΔG°_a, where $\Delta G^\circ_a \approx$ AEA, Crocker, Wang, and Kebarle obtained EA(tetracene) = 1.04 ± 0.04 eV.[24] Recent photoelectron spectroscopy work by Weinkauf and co-workers reports an EA(tetracene) ≈ 1.1 eV.[51] As with naphthalene and anthracene, our computed harmonic ZPVE corrections are large for tetracene, about 0.11 eV. With these corrections, the B3LYP, BHLYP, and BLYP functionals are within 0.2 eV of the experimental value of Crocker et al. and even closer to the value of Weinkauf and co-workers.

5. Pentacene and Larger Polyacenes. An EA(pentacene) = 1.35 eV was also obtained in the gas-phase electron attachment experiments of Crocker et al.[24] Unfortunately, DFT computations on pentacene with our DZP++ basis set were not possible due to near-linear dependencies in the basis set. One solution to this problem is to project out the problematic dependencies from the basis set; however, this option is not available in the Gaussian 94 program system. Use of a basis set other than DZP++ would not allow direct comparison to our results for benzene−tetracene; thus we did not compute an electron affinity for pentacene. We do note a recent study by Halasinski, Hudgins, Salama, Allamandola, and Bally which presented B3LYP/6-31G* computations of pentacene.[20] We also note that experimental values for the EA of larger polyacenes, such as hexacene, are not currently known.

6. Electronic Structure Observations. In solution, polarographic half-wave reduction potentials, $-\epsilon_{1/2}$, are directly related to the gas-phase electron affinities through a correction for free energies of solvation, i.e., $-\epsilon_{1/2} \propto$ EA.[31] Measurements of half-wave reduction potentials in particular solvents are known for many PAHs. Additionally, because at a zeroth-order approximation electron affinities may be estimated as the energy of the LUMO in the parent neutral molecule (via Koopmans' theorem), relationships between a neutral molecule's LUMO energy and its $-\epsilon_{1/2}$ and/or EA can be made. Indeed, Streitwieser has shown a nearly linear correlation between $-\epsilon_{1/2}$ and Hückel MO LUMO energies for many PAHs.[31] In the standard Hückel MO approximation, with all α's and β's equal, the LUMO energies in units of the resonance delocalization parameter, β, for benzene through pentacene are −1.0, −0.618, −0.414, −0.295, and −0.220, which correlate to the now known experimental EAs of −1.12 ± 0.03,[23] −0.19 ± 0.03,[23] 0.530 ± 0.005,[25] 1.04 ± 0.04,[24] and 1.35 ± 0.04 eV,[24] respectively.

This relationship between Hückel MO energies and electron affinities has been used by Crocker, Wang, and Kebarle to estimate ΔG°_a(naphthalene) < 0.0, implying a negative EA-(naphthalene).[24] Likewise, the HOMO−LUMO gap of neutral PAHs, which is equivalent to |2β|, also correlates to EAs. Although the HOMO−LUMO gap is not as easily defined in Hartree−Fock and Kohn−Sham theories, one can still expect a strong correlation between HUMO−LUMO gaps and electron affinities. Indeed, with the B3LYP functional our neutral HUMO−LUMO gaps for benzene through tetracene are (in eV) 6.5, 4.7, 3.5, and 2.7 and linearly correlate (correlation coefficient squared, $R^2 = 0.98$) to B3LYP electron affinities (in eV, without zero-point correction) of −0.88, −0.20, 0.58, and 1.13. There is no reason to assume that this relationship will not hold for larger polyacenes, and thus EA(pentacene, hexacene, etc.) will be greater than 1.1 eV, which, vida supra, is indeed the case for pentacene. Eventually, as the size of linear polyacenes reaches infinity, the changes in the HOMO−LUMO gap will plateau. Notario and Abboud have estimated the EA of an infinite polyacene to be greater than 2.8 eV, based on extrapolations of AM1 semiempirical computations.[30]

B. The Perinaphthenyl Radical and Other PAHs. In the preceding discussion we have focused primarily on the electron affinities of the polyacenes. However, other "nonlinear" and/or open-shell PAH systems may also have significant electron affinities.[21,26,27,31] To test the applicability of DFT to other PAHs we have obtained EA results for the nonlinear, open-shell perinaphthenyl radical.

In 1979, Gygax, McPeters, and Brauman reported an EA-(perinaphthenyl radical) = 1.07 ± 0.1 eV using photodetachment spectroscopy.[21] With the exception of the BHLYP functional, our DFT results overestimate the experimental value by at least 0.24 eV. Whether this discrepancy might be due to the open-shell nature of the neutral species and/or its nonlinear topology is unclear. However, it should also be noted that the experimental value has larger error bars than the experimental values for some other polyacenes.

More recent experiments are extending photoelectron spectroscopy methods to larger PAHs, such as perylene ($C_{20}H_{12}$),[26] and the coronene ($C_{24}H_{12}$) monomer, dimer, and trimer.[27] The EAs of these species are 0.973 ± 0.005, 0.47 ± 0.09, 0.67 ± 0.09, and 0.75 ± 0.13 eV, respectively. From these results, it is clear that PAHs other than polyacenes may have significant electron affinities.

C. Functional Performance. Using our computed values for VAE(benzene), the non-ZPVE corrected EA values for naphthalene, and ZPVE corrected EA values for anthracene, tetracene, and the perinaphthenyl radical, and comparing to experimental values, we obtain an average absolute error for each gradient-corrected functional of (in eV): 0.17 (BHLYP), 0.18 (BLYP), 0.19 (B3LYP), 0.31 (BP86), and 0.72 (B3P86). The non-gradient-corrected LSDA functional grossly miscalculates the electron affinity for every species studied. Although the BHLYP functional results in the lowest overall error, our previous work has shown that BHLYP has a tendency to underestimate electron affinities.[33−36] If this is the case, as it seems to be upon examining the non-ZPVE corrected BHLYP EAs, then the large ZPVE corrections encountered in each of the five species help to offset low BHLYP EAs, resulting in a fortuitous cancelation of errors. Nonetheless, the low average absolute errors of the BLYP and B3LYP functionals clearly

TABLE 1: Vertical Attachment Energies for Benzene and Adiabatic Electron affinities for Four Polycyclic Aromatic Hydrocarbons[a]

molecule	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	Exp.
benzene (D_{6h})	−0.88	−0.47	−1.39	−1.44	−1.26	−7.41	−1.12 ± 0.03[b]
C_6H_6 ($^1A_{1g} \leftarrow {}^2E_{2u}$)							
naphthalene (D_{2h})	−0.20	0.35	−0.49	−0.23	−0.01	0.47	−0.19 ± 0.03[b]
$C_{10}H_8$ ($^1A_g \leftarrow {}^2B_{1g}$)	(−0.04)	(0.51)	(−0.31)	(−0.07)	(0.15)	(0.62)	
anthracene (D_{2h})	0.58	1.16	0.30	0.53	0.78	1.29	
$C_{14}H_{10}$ ($^1A_g \leftarrow {}^2B_{3u}$)	(0.72)	(1.29)	(0.45)	(0.67)	(0.90)	(1.41)	0.530 ± 0.005[c]
tetracene (D_{2h})	1.13	1.71	0.86	1.06	1.32	1.85	
$C_{18}H_{12}$ ($^1A_g \leftarrow {}^2B_{1g}$)	(1.24)	(1.83)	(0.96)	(1.18)	(1.43)	(1.95)	1.04 ± 0.04[d]
perinaphthenyl radical (D_{3h})	1.29	1.86	0.92	1.23	1.47	2.07	
$C_{13}H_9$ ($^2A_1'' \leftarrow {}^1A_1'$)	(1.36)	(1.93)	(0.97)	(1.31)	(1.54)	(2.14)	1.07 ± 0.1[e]

[a] The harmonic zero-point vibrational energy (ZPVE) corrected adiabatic electron affinities are listed in parentheses. All results are with a DZP++ basis set and given in eV. [b] Vertical attachment energy as determined by electron transmission spectroscopy, ref 23. [c] Photodetachment photoelectron spectroscopy, ref 25. [d] Gas-phase electron attachment free energy, ref 24. [e] Laser threshold detachment, ref 21.

show that DFT can be successfully applied to the study of PAH electron affinities. However, it is surprising that the BP86 functional has a rather large average absolute error—upon examining eight medium-ring hydrocarbon compounds, Rienstra-Kiracofe, Graham, and Schaefer found an average absolute error of only 0.12 eV with BP86.[34] It is not clear why BP86 performs so poorly on PAHs.

As density functional theory and other correlated methods are applied to larger and larger systems, a complicating factor in the determinations of AEAs will be the ZPVE correction. Our previous studies of electron affinites[33−36] have shown that for most small molecules, ZPVE corrections to the classical EA are usually small (on the order of a few hundredths of an electronvolt). This current study suggests that ZPVE corrections in PAHs are likely to be an order of magnitude larger. Indeed, nearly all ZPVE corrections in Table 1 are greater than 0.1 eV and positive, corresponding to lower vibrational frequencies in the anions, which could be contributed to the additional electron residing in an antibonding orbital, though certainly some vibrations will be affected more than others.

Could the large magnitude of the ZPVE corrections for PAHs be attributed to the sum of many ($3N - 6$) small changes in frequencies between the neutral and anion species? To further investigate this, we have computed the B3LYP/DZ harmonic ZPVE correction between coronene and its anion to be 0.2 eV (cf. ref 27), which accounts for nearly 40% of the overall AEA! Because of the large ZPVE corrections in PAHs, the usually insignificant errors in harmonic frequencies obtained by DFT (or any other method) now become significant, and may limit the method's overall accuracy. A possible solution to this problem would be to devise a scale factor for DFT zero-point vibrational energies. Such a scale factor will necessarily be different from already used harmonic-to-fundamental scale factors, as the ZPVE is not equal to half the sum of the fundamental vibrational frequencies.[52] Certainly more investigations into the nature of ZPVE changes between neutral and charged PAH species are warranted.

IV. Conclusion

We have examined the electron affinities of benzene and four PAHs with six different density functionals. Our results show that the BLYP and B3LYP functionals have low average absolute errors of only 0.18 and 0.19 eV when compared to experimental values, and we recommend these functionals in future studies of PAH anions. However, it appears that EA computations for larger PAHs may be affected by the accuracy of the harmonic ZPVE correction, regardless of the method employed.

Future theoretical and experimental studies of PAH anions are certainly justified. It is all but certain that more-extended polyacenes (hexacene or higher) will have large electron affinities. Furthermore, many nonlinear PAHs may also have large electron affinities. Our work indicates that electronic structure methods (specifically, DFT) are suitable for the study and identification of PAH anions which may have an interstellar presence.

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