Electronically Excited States of Anistropically Extended Singly-Deprotonated PAH Anions

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) play a significant role in the chemistry of the interstellar medium (ISM) as well as in hydrocarbon combustion. These molecules can have high levels of diversity with the inclusion of heteroatoms and the addition or removal of hydrogens to form charged or radical species. There is an abundance of data on the cationic forms of these molecules, but there have been many fewer studies on the anionic species. The present study focuses on the anionic forms of deprotonated PAHs. It has been shown in previous work that PAHs containing nitrogen heteroatoms (PANHs) have the ability to form valence excited states giving anions electronic absorption features. This work analyzes how the isoelectronic pure PAHs behave under similar structural constructions. Singly-deprotonated forms of benzene, naphthalene, anthracene, and teteracene classes are examined. None of the neutral-radicals possess dipole moments large enough to support dipole-bound excited states in their corresponding closed-shell anions. Even though the PANH anion derivatives support valence excited states for three-ringed structures, it is not until four-ringed structures of the pure PAH anion derivatives that valence excited states are exhibited. However, anisotropically-extended PAHs larger than tetracene will likely exhibit valence excited states. The relative energies for the anion isomers are very small for all of the systems in this study.

Keywords: Astrochemistry; Electronically Excited States; Polycyclic Aromatic Hydrocarbons; Anions

Introduction

Polycyclic aromatic hydrocarbons (PAHs) hold significant promise in explaining various chemical phenomena, but they also can give rise to significant complexity in their chemical analysis. PAHs are significant products of fossil fuel combustion,[1–8] and they are believed to be of great importance in astrochemistry.[9–13] These remarkably stable structures have been hypothesized to exist in environments as varied as the circumstellar envelopes of dying, carbon-rich stars to the soot of simple fires on Earth.[6] Many PAHs are known carcinogens and environmental pollutants largely due to their remarkable stability.[14,15] However, their characteristics also bode well for the discovery of new physical and chemical phenomena. Their π clouds can play host to binding various charged and uncharged particles, their sheer number of degrees of freedom provides for a wide array of rovibronic spectroscopic features, and the myriad of slight (and not-so-slight) structural changes creates a vast continuum of closely related phenomena. As a result, their chemistry and physics is rich but also very complicated and somewhat daunting.

Removing a single hydrogen from a a PAH often does not lead to tremendous effects on the molecule's gross properties, but such a process can lead to some novel physics not present in the parent molecule.[16–22] In smaller chemical systems akin to PAHs, it has been shown that removal of a hydrogen atom can create a neutral radical that will readily retain an additional electron in a valence ground state.[23–34] In fact, all of the anions known to exist in the interstellar medium (ISM) are closed-shell anions in valence ground states.[35–41] It has been hypothesized that excited states of anions may be responsible[42–45] for some of the diffuse interstellar bands (DIBs), the series of surprisingly consistent electronic absorption features observed towards numerous astronomical sources for nearly a century[46–48] whose carriers of some lines have only recently been firmly established.[49]

The most common anionic excited state is a dipole-bound state where the additional electron is very loosely bound to the parent neutral molecule.[50–53] A fairly significant dipole moment in excess of 2.0 D or even 2.5 D for the corresponding neutral molecule is necessary to form such a state.[54] However, recent work has shown that some closed-shell anions may possess excited electronic, valence states independent of the dipole strength present in the neutral radical core.[30–34,55,56] Most notably, quantum chemical analysis of singly-deprotonated PAH anions with nitrogen heteroatoms (PANHs) has shown that many of these negatively charged molecules possess valence excited states in addition to potential (and more common) dipole-bound excited states.[55] While the presence of candidate dipole-bound excited states is interesting, the valence excited states of anions removes the neutral-radical dipolar strength criterion opening the door for the possibility of richer anionic electronic spectra. Of the singly-deprotonated PANH anion isomeric derivatives of quinoline, acridine, and pyrenidine tested, the larger acridine and pyrenidine derivative anions show regular valence excited states. The smaller quinoline and isoquinoline deprotonated anion derivatives exhibit only the potential for dipole-bound excited states if their respective dipole moments are large enough.[55] As a consequence, it appears as though the size of the deprotonated PAH/PANH anion may influence the molecule's ability to exhibit a valence excited state.

Deprotonated PAHs have been investigated recently for their structural and rovibrational properties,[18] but they show small dipole moments, impeding their ability to possess dipole-bound states. However, as it has been shown for deprotonated PANHs, valence excited states can still be present. In this work, the anisotropic class of PAHs beginning with benzene and stretching to tetracene are deprotonated to create similar closed-shell PAH anions to the PANHs examined previously.[55] The anisotropic expansion allows for the presence of valence excited states to be probed as a product of molecular length in order to begin forming a working hypothesis for the presence of valence excited states in PAH anions. The unique deprotonated isomers of each class of PAHs in this set (benzene, naphthalene, anthracene, and tetracene) are all examined for their vertical excited states. Again, higher amounts of deprotonation can be incorporated, but the present work is limited to single deprotonation as a first step in the analysis of closed-shell PAH anions. It is hoped that clear patterns can begin to emerge in order to enable predictions for the nature of excited states in closed-shell PAH anions.

Computational Details

The methods applied here mimic the previous approach used in the PANH analysis.[55] A total of 18 PAH molecules are analyzed here. There is only one unique deprotonated benzene anion to be studied, and the corresponding neutral-radical is also be included. However, there are two deprotonated naphthalene isomers, and three for both anthracene and tetracene. The neutral-radicals are also included for these species, as well. Geometry optimizations of the dehydrogenated neutral radicals and corresponding anions are computed using the B3LYP[57,58] density functional and the 6-31+G** basis set[59] as available on the PSI4 quantum chemistry program suite.[60] These computations provide relative energy data for the radicals and anions, the dipole moments, and the necessary molecular structures needed to compute vertical excitation energies.

The vertical excitation computations for the closed shell-anions also employ the PSI4 program, as well as spin-restricted Hartree-Fock reference wave functions[61] and the equation-of-motion coupled cluster theory at the singles and doubles level (EOM-CCSD).[62–65] In order for a dipole-bound excited state potentially to exist, the corresponding neutral-radical requires a minimum dipole moment of 2.0 D. Previous work[55,66] has shown that vertical computations of dipole-bound excited states are readily determined from further augmenting any basis set with four, highly-diffuse *s*-type basis functions labelled as "+4s" in the present shorthand. Dipole-bound vertical excitation energies are converged to 0.01 eV with these four functions; adding more, diffuse *s*-type functions does not influence the excitation energy further. The converged energy is beyond the expected limit of accuracy for computed electronic transition energies[30] and is nearly coincident with experimentally known electron binding energies/electron affinities (eBEs/EAs) for dipole-bound states.[53,67,68]

The presence of valence excited states in anions is produced from use of the standard aug-cc-pVDZ basis sets[69,70] (abbreviated as apVDZ in this work) since the electrons are closely bound by favorable orbital energetics and not loosely so by the strength of the neutral's dipole moment. Higher angular momentum functions are prohibitively costly for the larger systems in this molecular set, and they have not previously added any further qualitative understanding for anionic excited states.[30–32,34,56] As a result, only the double-zeta basis set results are reported here. The eBEs for the various valence ground state anion isomers are attempted using the CFOUR computational chemistry package[71] with the equation-of-motion ionization potential[72] formalism at the CCSD level of theory and the apVDZ basis set when possible.

Results and Discussion

Relative Energies and Dipole Moments

The range of PAHs within this study spans anistropically from the one-ring system of benzene up to the four-ringed tetracene. The isomers of the systems are named for deprotonation of a specific carbon atom. The carbon atoms are numbered from the exterior of the ring toward the interior. In other words, the most exposed carbon atom is the lowest numbered. The naphthalene isomers H1 and H2 are named for deprotonation of the carbon atoms numbered in Figure 1. This continues for the three symmetry-unique deprotonation sites for anthracene (Figure 2) and tetracene (Figure 3). The doubly-occupied orbital in each anion associated with the extra electron is localized within the region formerly occupied by the carbon-hydrogen bond. This orbital functions like a lone pair creating a carbene carbon. The related deprotonated PANH anion derivatives behave in a similar fashion.[55] Depending on the molecule, these localized lone pair (*lp*) orbitals are either the highest-occupied molecular orbital (HOMO) or the HOMO-1 if the highest energy occupied π orbital is less stable than the carbene, doubly-occupied orbital.

Data for the relative anionic and radical energies as well as the dipole moments for all of the radical isomers are located in Table 1. Since benzene has only one deprotonated anion and radical isomer, there are no comparative structural and subsequent relative energetic data. The phenyl radical's dipole moment is computed to be 0.81 D, in line with previous work.[73] The naphthalene radicals differ by only 0.056 eV with the structure having the more exposed lone pair (H1) being lower in energy. The relative energies invert for the anion, but the energy splitting between isomers is very small at less than 0.001 eV. Additionally, the dipole moments for the phenyl or naphthyl radicals are not large enough to support dipole-bouned excited states.

The energy differences for the anthracene and tetracene dehydrogenated radicals, also given in Table 1, further corroborate that the centralized carbon atoms are more stable upon removal of their hydrogen atoms. However, the energy splittings are larger than for naphthalene. H1 anthracene is 0.213 eV above the H3 minimum with H2 in the middle at 0.153 eV. A similar trend is present for tetracene with the H1 isomer 0.276 eV above the H3 minimum with H2 again in between these two at 0.213 eV. The H1 anion isomers with their lone pairs more exposed on the molecular exterior are, again, the lowest energy closed-shell anion isomers for the anthracene and tetracene sets. H2 is in the middle with H3 highest in energy. However, the difference between H1 and H3 for the deprotonated anthracene derivative anions is a mere 9.12 meV and is 8.31 meV for H1 and H3 tetracene. The H2 anion energies fall between these, again. All of the dipole moments for the anthracene and tetracene radical isomers are also well below the necessary requirement to be considered candidates for dipole bound excited states. Therefore, only valence excited states can be considered and will be discussed for these PAHs.

Vertical Excitation Energies

The excitation energies for the various states of the examined deprotonated PAH anion derivatives are given in Table 2. The excitation energy for the 2 $^1A_1$ state of the phenyl radical of the benzene class clearly shows dipole-bound behavior. Inclusion of the highly-diffuse basis functions lowers the energy from 2.23 eV with apVDZ to 1.50 for apVDZ+4s. Additionally, the oscillator strength decreases by three orders of magnitude. The 1 $^1B_1$ state has more valence character but still has non-negligible excitation components coming from the diffuse orbitals. Hence, it is not a true valence state. Regardless, its energy is significantly higher than the clear dipole-bound 2 $^1A_1$ state. Since, the dipole moment of this molecule is too small to support a dipole-bound excited state, the phenyl anion will not possess an electronically excited state of any kind.

The 1 $^1A''$ states of the two naphthalene isomers are valence states as evidenced from both the little change brought about by the inclusion of the four diffuse functions and by analysis of the orbitals involed. However, the eBEs at 1.80 eV and 1.85 eV, respective of the H1 and H2 isomers, are 0.75 eV and 0.96 eV below the valence excitations. Consequently, no valence excited states are present for the deprotonated naphthalene derivative anions. Similar behavior has also been shown for deprotonated quinoline and isoquinoline anion derivatives.[55]

The acridine class of deprotonated PANH derivative anions posses valence excited states. However, the inclusion of the nitrogen heteroatom appears to influence this phenomenon since none of the three deprotonated anthracene derivative anions examined here seems to possess valence excited states. The 2 $^1A'/^1A_1$ states are all excitations out of the lone pair into the dipole-bound orbitals. The EOMIP computations could not converge for the aug-cc-pVDZ basis set for the larger anthracene and tetracene anions. Even though the acridine derivatives cannot possess dipole-bound excited states, it can be assumed from previous work[30–34] that the eBEs and these dipole-bound-like excitation energies are close enough to be used interchangeably for vertical computations. The 1 $^1A''/^1B_1$ states of the anthracene derivatives are valence in character. The accepting virtual orbital is the lowest energy π virtual orbital making these valence $lp \rightarrow \pi^*$ excitations much like the behavior observed for the related deprotonated acridine PANH anion derivative valence excited states.[55] At the apVDZ+4s basis level, the eBEs determined from the 2 $^1A'/^1A_1$ excited states are 0.01 eV, 0.11 eV, and 0.14 eV, respectively of H1, H2, and H3, lower in energy the valence excited states. Hence, the valence excited states are likely not accessed, and no excited states can exist.

It is worth noting that the difference between the valence excitation energy and the presumed eBE has decreased substantially as the number of anistropically-extended rings has increased. Since the related PANH anions have valence excited states for the isoelectronic acridine class, it appears to be the presence of the destabilizing nitrogen heteroatom[74] that reduces the $lp \rightarrow \pi^*$ excitation energy down below the eBE threshold. As a result, the larger deprotonated tetracene anion derivatives should possess valence excited states from a particle-in-a-box argument. Since the length of the "box" (the π cloud in the aromatic rings) has increased, the excitation energy into the lowest unoccupied π orbital should decrease. Indeed, such appears to be the case for the deprotonated tetracene derivative anions.

The $1\ ^1A''$ states for the H1, H2, and H3 tetracene anion isomers are valence excited states, the result of $lp \rightarrow \pi^*$ excitations. The eBEs (determined from the $2\ ^1A'$ dipole-bound excited states) are all $\sim 0.45 - 0.50$ eV above the valence $1\ ^1A''$ excited states. The H1 valence excitation at 1.64 eV is the lowest of the set, and H3 at 1.99 eV is the highest giving a fairly narrow range of excitation energies. These energy values also happen to follow the stability pattern shown for the ground state anions' relative energies. The tetracene-class valence excitation energies are also lower in energy than the three anthracene anion derivative valence excitations. Hence, only the deprotonated tetracene anion derivatives from our set can support excited states, and they must be valence.

The pattern in valence excitation energy that emerges from this family of deprotonated PAH derivative anions leads to the conclusion that the singly deprotonated pentacene anions and longer PAHs of this class will all possess valence excited states. The oscillator strengths (f) for the determined valence excited states are not exceptionally great but are consistent between the apVDZ and apVDZ+4s basis sets. The relatively small f values are likely to continue for the large PAHs, but these molecules are almost certainly present in relatively high abundances in various interstellar environments. Deprotonation of neutral, closed-shell PAHs through radiation or collisional forces is highly likely creating enough deprotonated anionic material to overcome the small oscillator strengths. As a result, these molecules can thus be possible contributors for the less strong DIBs, given their low oscillator strengths.

Conclusions

Since the chemistry of PAHs can be quite dense due to the various relatively minor modifications that can be made to the chemical structure, the present study has been limited to the analysis of PAH anions that are closed-shell, singly-deprotonated, and anistropically extended rings ranging from the phenyl anion to the tetracenyl anion isomers. The dipole moments for the neutral radicals are all too small for the corresonding PAH anions to possess dipole-bound excited states. Unlike their isoelectronic PANH cousins where three-ringed anion derivatives could support valence excited states, four rings are necessary for the PAH deprotonated anion derivatives. However, the larger five, six, seven, etc. ringed closed-shell PAH anions should all possess valence excited states. The valence excitation energies for the closed-shell PAH anions are higher in energy than the related PANH molecules due to the destabilizing nitrogen heteroatom. The tetracene class of PAH anion derivatives supports valence excited states, and they all fall within 0.35 eV of one another in the low-energy, sub 2.0 eV ($>$ 600 nm) visible range. Regardless of their spectral features, proton rearrangement in the singly-deprotonated PAH anions should be fairly rapid due to the low relative energies. This is unlike the PANH anion derivatives.[55]

Larger singly-deprotonated PAH anion derivatives will possess absorption features that may play a role in interstellar absorption spectra. Moreover, all of these anions are stable structures that may serve as necessary intermediates in various hydrocarbon reactions.

Acknowledgements

The work undertaken by RCF is supported by start-up funds provided by Georgia Southern University. European Research Council Grant 246976 supports work on interstellar PAHs done at Leiden Observatory. This material is based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement Notice NNH13ZDA017C issued through the Science Mission

Directorate. The figures are produced with the CheMVP program developed at the Center for Computational Quantum Chemistry at the University of Georgia.

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Figure 1: Naphthalene with the carbons numbered for deprotonation or dehydrogenation.

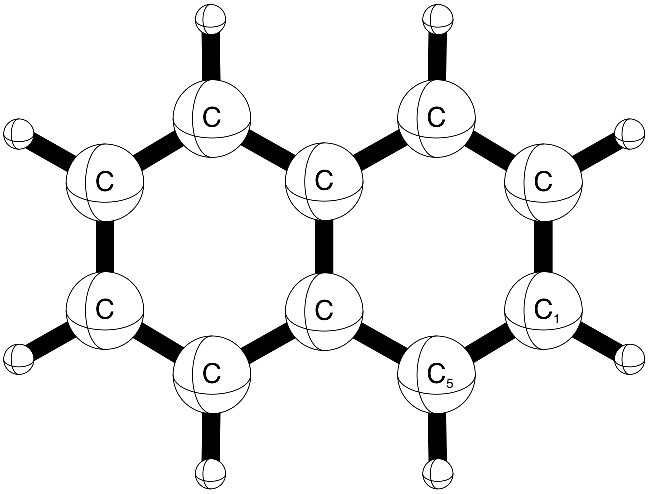

Figure 2: Anthracene with the carbons numbered for deprotonation or dehydrogenation.

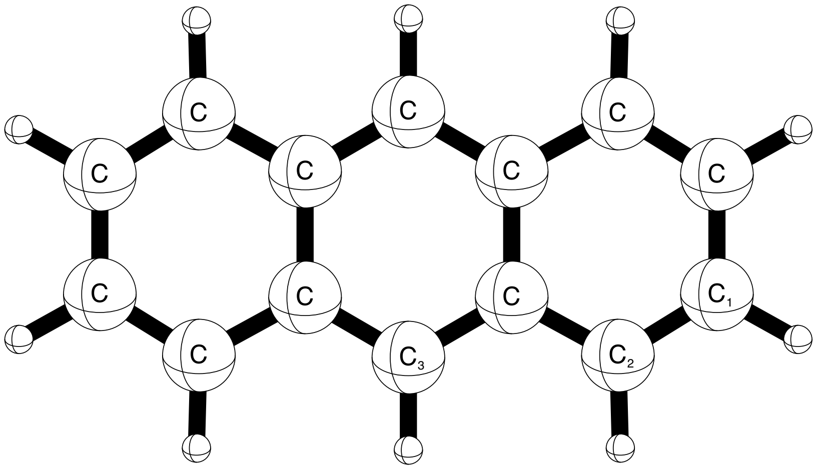

Figure 3: Tetracene with the carbons numbered for deprotonation or dehydrogenation.

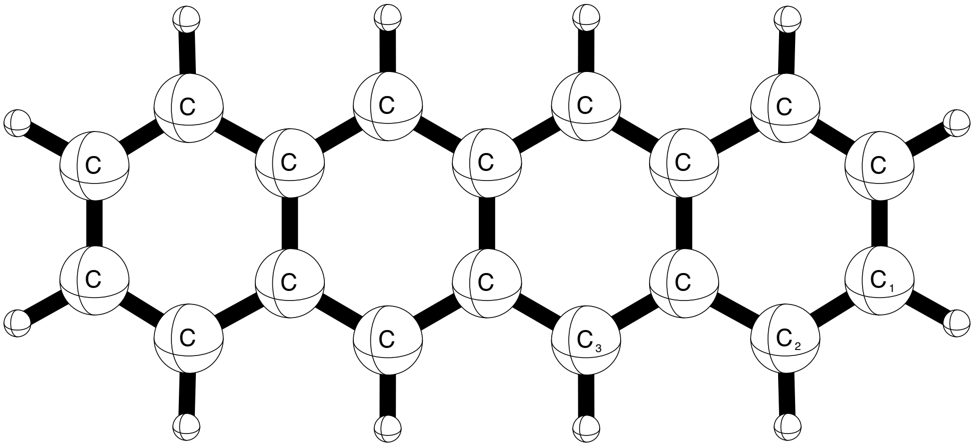

Table 1: Relative anionic and radical energies (in eV) and dipole moments (D) for the dehydrogenated/deprotonated PAH derivatives.

	Isomer	Relative Anionic Energy	Relative Radical Energy	Dipole Moment
Benzene/Phenyl	–	–	–	0.81
Naphthalene	H1	0.056	0.000	0.85
	H2	0.000	9.45×10^{-4}	0.74
Anthracene	H1	0.213	0.000	0.92
	H2	0.153	9.86×10^{-4}	0.77
	H3	0.000	9.12×10^{-3}	0.64
Tetracene	H1	0.276	0.000	0.98
	H2	0.213	2.88×10^{-4}	0.81
	H3	0.000	8.31×10^{-3}	0.63

Table 2: Vertical Excitation Energies (in eV), eBEs (in eV), and Oscillator Strengths (f) for the PAH Derivative Anions

	Isomer	State	apVDZ	apVDZ+4s	apVDZ f	apVDZ+4s f	eBE
Benzene/Phenyl	–	$2\ ^1A1$	2.23	1.50	2×10^{-2}	2×10^{-5}	–
		$1\ ^1B1$	3.18	3.55	0.0	0.0	
Naphthalene	H1	$2\ ^1A'$	2.75	1.81	1×10^{-2}	2×10^{-5}	1.80
		$1\ ^1A''$	2.55	2.55	2×10^{-3}	2×10^{-3}	
	H2	$2\ ^1A'$	2.70	1.86	2×10^{-3}	1×10^{-5}	1.85
		$1\ ^1A''$	2.82	2.81	2×10^{-3}	2×10^{-3}	
Anthracene	H1	$2\ ^1A'$	2.85	2.01	1×10^{-2}	3×10^{-5}	–
		$1\ ^1A''$	2.02	2.02	2×10^{-3}	2×10^{-3}	
	H2	$2\ ^1A'$	2.87	2.07	7×10^{-4}	7×10^{-4}	–
		$1\ ^1A''$	2.18	2.18	1×10^{-3}	1×10^{-3}	
	H3	$2\ ^1A_1$	2.94	2.24	3×10^{-5}	3×10^{-6}	–
		$1\ ^1B_1$	2.38	2.38	0.0	0.0	
Tetracene	H1	$2\ ^1A'$	2.72	2.15	3×10^{-2}	4×10^{-5}	–
		$1\ ^1A''$	1.64	1.64	1×10^{-3}	1×10^{-3}	
	H2	$2\ ^1A'$	2.94	2.21	3×10^{-2}	–	–
		$1\ ^1A''$	1.75	1.75	5×10^{-4}	–	
	H3	$2\ ^1A'$	3.19	2.47	4×10^{-2}	5×10^{-4}	–
		$1\ ^1A''$	1.99	1.99	1×10^{-3}	1×10^{-3}	