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Cyclopentadiene Annulated Polycyclic Aromatic Hydrocarbons: Investigations of Electron Affinities

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Abstract: The adiabatic electron affinities of cyclopentadiene and 10 associated benzannelated derivatives have been predicted with both density functional and Hartree−Fock theory. These systems can also be regarded as benzenoid polycyclic aromatic hydrocarbons (PAHs) augmented with five-membered rings. Like the PAHs, the electron affinities of the present systems generally increase with the number of rings. To unequivocally bind an electron, cyclopentadiene must have at least two conventionally fused benzene rings. 1H-Benz[*f*]indene, a naphthalene-annulated cyclopentadiene, is predicted to have a zero-point energy corrected adiabatic electron affinity of 0.13 eV. Since the experimental E_A of naphthalene is negative (−0.19 eV), the five-membered ring appendage contributes to the stability of the naphthalene-derived 1H-benz-[*f*]indene radical anion significantly. The key to binding the electron is a contiguous sequence of fused benzenes, since fluorene, the isomer of 1H-benz[*f*]indene, with separated six-membered rings, has an electron affinity of −0.07 eV. Each additional benzene ring in the sequence fused to cyclopentadiene increases the electron affinity by 0.15−0.65 eV: the most reliable predictions are cyclopentadiene (−0.63 eV), indene (−0.49 eV), fluorene (−0.07 eV), 1H-benz[*f*]indene (0.13 eV), 1,2-benzofluorene (0.25 eV), 2,3-benzofluorene (0.26 eV), 12H-dibenzo[*b,h*]fluorene (0.65 eV), 13H-indeno[1,2-*b*]anthracene (0.82 eV), and 1H-cyclopenta[*b*]naphthacene (1.10 eV). In contrast, if the six-membered ring-fusion is across the $C_2−C_3$ cyclopentadiene single bond, only a single benzene is needed to bind an electron. The theoretical electron affinity of the resulting molecule, isoindene, is 0.49 eV, and this increases to 1.22 eV for 2H-benz[*f*]indene. The degree of aromaticity is responsible for this behavior. While the radical anions are stabilized by conjugation, which increases with the size of the system, the regular indenes, like PAHs in general, suffer from the loss of aromatic stabilization in forming their radical anions. While indene is 21 kcal mol⁻¹ more stable than isoindene, the corresponding radical anion isomers have almost the same energy. Nucleus-independent chemical shift calculations show that the highly aromatic molecules lose almost all aromaticity when an extra electron is present. The radical anions of cyclopentadiene and all of its annulated derivatives have remarkably low C−H bond dissociation energies (only 18−34 kcal mol⁻¹ for the mono-, bi-, and tricyclics considered). Hydrogen atom loss leads to the restoration of aromaticity in the highly stabilized cyclopentadienyl anion congeners.

I. Introduction

Vereecken et al.[1] have shown that benzenoid rings can react with C_3H_X to produce polycyclic aromatic hydrocarbons (PAHs) incorporating five-membered rings. Such five-membered ring systems are possible intermediates for the formation not only of higher planar but also nonplanar PAHs, including fullerenes.[2] Recent interest in PAHs with five-membered rings has spawned experimental work.[3]

Polycyclic aromatic hydrocarbons are among the most studied organic molecules in modern chemistry. A PAH was the first

molecule (as opposed to a microorganism) shown to be responsible for the onset of disease. Indeed, some PAHs are among the most carcinogenic substances known to humankind.[4,5] PAHs are known to be present in more than trace amounts in the earth's atmosphere,[6] soil,[7] and water,[8] particularly in developed areas. In addition, PAHs have been detected in meteorites,[9] and there is spectroscopic evidence that PAHs exist in interstellar space.[10] In fact, it has been estimated that 1−2%

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of all the available carbon in interstellar clouds is due to PAHs.[11] Polycyclic aromatic hydrocarbons have been frequent subjects for both experimental and theoretical analyses.[12-18] The electron affinities of PAHs show clear trends: benzene and naphthalene have negative electron affinities, but these become positive with at least three benzene rings.[18] We provide here a similar analysis of systems containing five-membered rings.

Density functional theory (DFT) generally computes electron affinities within 0.2 eV of experiment.[19-24] A rather exhaustive review of DFT electron affinities by Rienstra-Kiracofe and co-workers[25] is available. One of the factors involved is the loss of aromaticity caused by the addition of an electron.

The aromaticity of polybenzenoid hydrocarbons (PBHs) has been highly studied,[4,5,26,27] including a very recent contribution from Schleyer et al.[28] The widely used notion of the aromatic sextet is usually attributed to Armit and Robinson,[29] but was originally introduced in 1922 by Crocker.[30] Clar[26,27] employed the notion of the aromatic sextet to account for the aromaticity of PAHs. The key to this highly successful description of PAHs was the idea that the aromaticity depends on the multiple of six π electrons which are assigned without duplication. The principle can be applied to the benzannelated cyclopentadiene series, molecules which have been very instructive for the analysis of aromaticity, nonaromaticity, and antiaromaticity of the neutrals as well as the closed-shell cations and anions.[31-41] However, their radical anions and those of similar PAHs have

not been analyzed before. To what extent do the five-membered rings influence the ability to bind an electron?

The quantitative criteria commonly used to assess the aromaticity of molecules are based on energetic, geometric, and magnetic properties.[40,42-51] Energetic criteria are based on homodesmotic,[52] isodesmic,[53] or isomerization reactions.[54] Greater bond length alternation is assumed to be associated with a decrease in aromatic character. Geometric treatments such as HOMA[44-46] (harmonic oscillator model of aromaticity) are typically used to deduce the degree of aromaticity from bond distances.

Magnetic criteria also are quite effective in discerning aromaticity, as the ability to sustain a diatropic ring current is the defining characteristic of aromatic species.[47-49] According to Jiao et al.,[40] "the magnetic criterion may be the most specific and unambiguous manifestation of aromaticity and antiaromaticity." The use of NICS, "nucleus-independent chemical shift," as a measure of aromaticity is straightforward and well established,[50,51] also for PAHs.[28] NICS values, typically based on absolute magnetic shieldings computed at the center of rings, or above ring centers, are a less ambiguous gauge of aromaticity than the more difficult-to-evaluate energetic criteria and will help to explain the trends in the electron affinities of the molecules studied here.

The goal of the present work is to compute the electron affinities of several benzannelated cyclopentadiene molecules (up to five fused rings) to determine how many rings are needed to achieve a positive electron affinity. These results are interpreted by an analysis of the change in aromaticity due to the conversion to a radical anion. The bond dissociation energies (BDE), that is, the energy necessary to cleave the tetravalent C−H bond homolytically, also are reduced by the addition of an electron.

II. Computional Methods

Absolute energetics, optimized geometries, and harmonic vibrational frequencies were computed using Hartree−Fock theory and three variants of density functional theory, B3LYP,[55,56] BLYP,[57,56] and BP86.[57,58] For all open-shell molecules the unrestricted formalism was utilized.

The 6-31G*, 6-31+G*, 6-311G*, 6-311+G*, 6-311++G*, and 6-311+G** basis sets were used for the smaller mono-, bi-, and tricyclic PAHs. Adding hydrogen atom polarization functions to these smaller PAHs resulted in only minor changes (less than 0.03 eV) in the adiabatic electron affinity (AEA). Thus, computations on the larger tetra- and

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Table 1. B3LYP/6-31+G* NICS Values at Ring Centers [NICS(0)], 1 Å above [NICS(1)], and HOMA Values[a] for the Neutral and Radical Anionic Mono-, Bi-, and Tricyclic Molecules

	ring I[b]	ring II	ring III		ring I[b]	ring II	ring III
	Cyclopentadiene **1**(**1**·⁻)				1H-Benz[f]indene **4**(**4**·⁻)		
NICS(0)	−2.7(−1.3)[c]	−	−	NICS(0)	−8.6(10.2)	−8.8(10.9)	0.5(−1.5)
NICS(1)	−4.7(−22.2)	−	−	NICS(1)	−10.5(5.9)	−10.5(6.2)	−2.5(−2.9)
HOMA	−0.90(−0.76)	−	−	HOMA	0.78(0.71)	0.70(0.60)	−1.06(−0.98)
	Benzene				Isondene **5**(**5**·⁻)		
NICS(0)	−8.8	−	−	NICS(0)	2.1(1.8)	−3.7(−2.0)	−
NICS(1)	−10.6	−	−	NICS(1)	−1.6(−0.5)	−5.3(−2.4)	−
HOMA	0.99	−	−	HOMA	0.15(0.47)	−0.80(−0.99)	−
	Indene **2**(**2**·⁻)				2H-Benz[f]indene **6**(**6**·⁻)		
NICS(0)	−8.2(10.3)	−0.3(−1.1)	−	NICS(0)	1.3(0.0)	1.0(1.3)	−4.3(−2.7)
NICS(1)	−10.0(6.3)	−3.1(−2.0)	−	NICS(1)	−2.1(−2.5)	−2.3(−1.5)	−5.9(−3.3)
HOMA	0.97(0.71)	−0.97(−1.08)	−	HOMA	0.21(0.58)	0.21(0.23)	−0.72(−0.97)
	Fluorene **3**(**3**·⁻)						
NICS(0)	−7.5(6.1)	1.2(1.9)	−7.5(6.1)				
NICS(1)	−9.5(2.7)	−2.1(0.9)	−9.5(2.7)				
HOMA	0.97(0.76)	−1.00(−1.11)	0.97(0.76)				

[a] HOMA values utilize the geometries listed in Figures 1−3. [b] For definitions of Rings I−III see Figures 1−3. [c] Values in parentheses refer to radical anions.

pentacyclic systems only employed polarization functions on the carbon atoms. Diffuse functions were not included for the tetra- and pentacyclic systems due to problems with grid size requirements (i.e., unreasonably large grids were required for SCF convergence) and with basis set linear dependencies. Rather, we approximated an upper bound of the effect of diffuse functions on one of the tetracyclic systems. The smaller 6-31G* and 6-311G* basis sets were used for the other tetra- and the pentacyclic systems.

The adiabatic electron affinities were computed as differences between the total energies of the neutral and the corresponding radical anion minima. Zero-point vibrational energy-corrected (ZPVE) electron affinities also were determined.

NICS calculations were performed at the GIAO/B3LYP/6-31+G* level for the mono-, bi-, and tricyclic systems; the 6-31G* basis set was used for the tetra- and pentacyclic systems. As pointed out by Schleyer et al.[51] NICS(1), that is, 1 Å above ring centers, is a better gauge of aromaticity than NICS(0), since local contributions are reduced. Both values are reported here in ppm. Most of the computations employed Gaussian 94.[59] For the 6-31+G* and 6-311+G* computations on 1,2-benzofluorene Q-Chem 2.0[60] was used. These values are utilized to place an upper limit on the effect of diffuse carbon functions on the AEA. The DFT grid employed 75 radial shells and 302 angular points per shell. HOMA values were obtained using the formalism of Krygowski and Cyrański.[46] The C−H distances are unimportant for the aromaticity and electron affinities. Cartesian coordinates of all molecules are provided in the Supporting Information.

III. Results and Discussion

The variations in geometries with the various methods and basis sets are very small; hence we only report B3LYP bond distances and angles with our largest basis set. We emphasize

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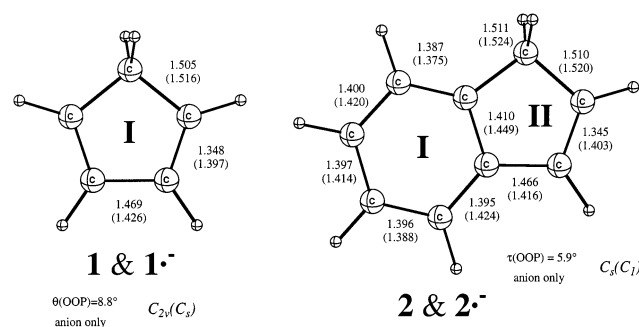
Figure 1. B3LYP/6-311+G** geometries of cyclopentadiene and indene, as well as their radical anions. Neutral bond lengths (in Å) and symmetries are listed first, with anionic quantities in parentheses. In cyclopentadiene the radical anion has an out-of-plane angle, namely the angle by which the tetravalent carbon is pushed out of the plane of the other four carbons. The indene radical anion has a torsional angle between the benzene ring and three cyclopentadiene carbons. Roman numerals identify the rings.

B3LYP electron affinities, as this functional is known to give the best results compared with experiment.[21,23,24,61−64]

III. A. Mono-, Bi-, and Tricyclic Systems. Nyulászi and Schleyer[65] found cyclopentadiene to be marginally aromatic, due to the π contribution of CH_2 group hyperconjugation. Neutral cyclopentadiene and its radical anion (**1** and **1**·⁻ in Figure 1) have varying bond distances, consistent with the small NICS values listed in Table 1. Like those in all other five-membered rings, the HOMA values are very negative, and will not be discussed further. Note that the carbon framework of the cyclopentadiene radical anion is puckered (C_s), rather than planar (C_{2v}). The tetravalent carbon is bent out of the plane of the other carbons by 9°. As discussed in more detail below, the radical anion can eject a hydrogen to form the aromatic closed-shell cyclopentadienyl anion relatively easily.

The electron affinity of cyclopentadiene (Table 2) is essentially unaffected by aromaticity considerations. Cyclopentadiene does not bind an electron; it is predicted to have a

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Table 2. Theoretical Electron Affinities for Mono-, Bi-, and Tricyclic Molecules, in eV

basis set	B3LYP	BLYP	BP86	HF
	Cyclopentadiene (**1**)			
6-31G*	−1.79(−1.59)[a]	−1.91(−1.71)	−1.61(−1.41)	−2.64(−2.43)
6-31+G*	−1.06(−0.90)	−1.08(−0.93)	−0.90(−0.74)	−2.03(−1.84)
6-311G*	−1.43(−1.23)	−1.51(−1.31)	−1.24(−1.05)	−2.37(−2.16)
6-311+G*	−1.04(−0.88)	−1.06(−0.91)	−0.87(−0.72)	−2.03(−1.84)
6-311++G*	−0.66(−0.63)	−0.69(−0.79)	−0.57(−0.51)	−1.09(−1.02)
6-311+G**	−1.02(−0.85)	−1.03(−0.88)	−0.85(−0.69)	−2.01(−1.82)
	Indene (**2**)			
6-31G*	−1.22(−1.04)	−1.31(−1.12)	−1.00(−0.81)	−2.08(−1.86)
6-31+G*	−0.69(−0.50)	−0.71(−0.52)	−0.50(−0.31)	−1.67(−1.44)
6-311G*	−0.91(−0.71)	−0.96(−0.75)	−0.69(−0.49)	−1.85(−1.63)
6-311+G*	−0.63(−0.41)	−0.69(−0.50)	−0.47(−0.27)	−1.65(−1.44)
6-311++G*	−0.55(−0.49)	−0.52(−0.44)	−0.39(−0.27)	−1.65(−1.43)
6-311+G**	−0.64(−0.45)	−0.66(−0.47)	−0.44(−0.25)	−1.63(−1.42)
	Fluorene (**3**)			
6-31G*	−0.81(−0.64)	−0.87(−0.71)	−0.55(−0.39)	−1.62(−1.40)
6-31+G*	−0.31(−0.14)	−0.32(−0.15)	−0.32(N/A)	−1.27(−1.05)
6-311G*	−0.49(−0.31)	−0.53(−0.34)	−0.24(−0.06)	−1.40(−1.17)
6-311+G*	−0.27(−0.08)	−0.29(−0.09)	−0.05(0.13)	−1.24(−0.99)
6-311++G*	−0.27(−0.07)	−0.28(−0.10)	−0.05(0.15)	−1.24(−0.99)
6-311+G**	−0.24(−0.07)	−0.25(−0.07)	−0.02(0.15)	−1.23(−0.99)
	1H-Benz[*f*]indene (**4**)			
6-31G*	−0.56(−0.39)	−0.62(−0.46)	−0.30(−0.14)	−1.45(−1.20)
6-31+G*	−0.10(0.06)	−0.11(0.05)	0.12(0.28)	−1.11(−0.86)
6-311G*	−0.26(−0.08)	−0.29(−0.12)	0.00(0.17)	−1.24(−0.99)
6-311+G*	−0.08(0.11)	−0.09(0.10)	0.16(0.33)	−1.10(−0.82)
6-311++G*	−0.08(0.12)	−0.09(0.12)	0.16(0.35)	−1.10(−0.82)
6-311+G**	−0.05(0.13)	−0.06(0.12)	0.19(0.36)	−1.08(−0.82)
	Isoindene (**5**)			
6-31+G*	0.30(0.44)	−	−	−
6-311+G**	0.35(0.49)	−	−	−
	2H-Benz[*f*]indene (**6**)			
6-31+G*	1.05(1.18)	−	−	−
6-311+G**	1.10(1.22)	−	−	−

[a] Electron affinities in parentheses are zero-point corrected.

Figure 2. B3LYP/6-311+G** geometries of fluorene and 1H-benz[*f*]indene, as well as the radical anions. Neutral bond lengths (in Å) and symmetries are listed first, with radical anionic quantities in parentheses. Roman numerals identify the rings.

negative electron affinity of −0.63 eV at B3LYP/6-311++G*. The basis set dependence is considerable. In particular, diffuse functions on both carbon and hydrogen are very important. The BP86 electron affinities for all basis sets are about 0.2 eV larger than those for the other functionals. This tendency for BP86 to overshoot electron affinities is consistent with the results of the systematic computations of Rienstra-Kiracofe et al.[25]

Indene (**2** and **2**•−, Figure 1) has a single benzene fused to cyclopentadiene, across a C═C double bond. The C−C bond lengths in the six-membered ring are nearly the same, whereas the cyclopentadiene portion of indene has widely alternating C−C bond distances, ranging from 1.345 to 1.511 Å, as in cyclopentadiene itself. Benzannelation generally increases the length of a cyclopentadiene double bond, in **2** from 1.348 Å to 1.410 Å. The NICS(1) value of −10.0 for the benzene moiety of indene contrasts with the −3.1 value for the five-membered ring. For comparison, benzene has a NICS(1) value of −10.6 (PW91/IGLO-III//B3LYP/6-311+G**).[51]

The indene radical anion (**2**•−) has C_1 symmetry, alternating bond lengths, and a positive NICS(1) value of 6.3 in the six-membered ring. Like the cyclopentadiene radical anion, the indene radical anion is nonplanar, and has a 6° torsional angle between the three cyclopentadiene carbons and the benzene plane. Indene also has a negative electron affinity, but the B3LYP/6-311++G* value, −0.49 eV, is larger (more positive) than the −0.88 eV vertical attachment energy for benzene (no AEA is available for benzene). The indene AEA is much more negative than the −0.04 value for the bicyclic naphthalene,[18]
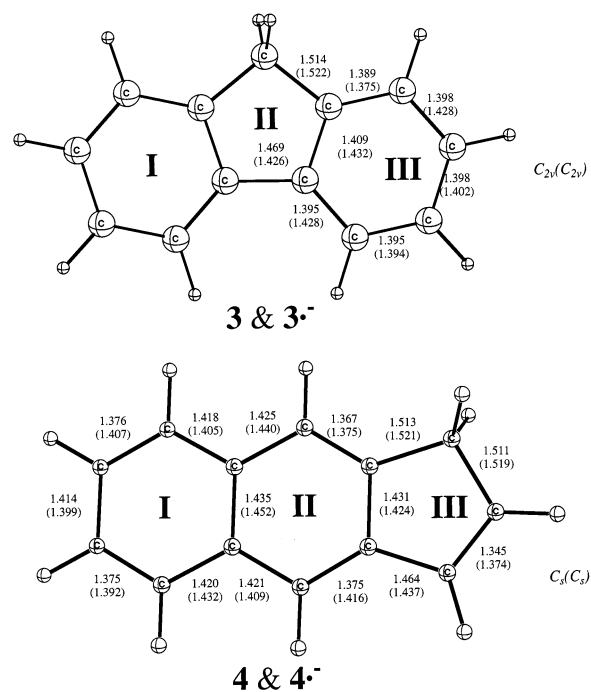
and 0.14 eV less negative than that computed for cyclopentadiene. This behavior is due to the unfavorable loss of indene aromaticity.

The structures of neutral and radical anionic fluorene (**3** and **3**•−) and 1H-benz[*f*]indene (**4** and **4**•−) are given in Figure 2. Fluorene (**3**) has aromatic benzene rings fused to both cyclopentadiene double bonds. The C_{2v} neutral exhibits classic aromatic character: highly similar C−C bond distances (HOMA = 0.968) in the six-membered rings, with negative NICS(1) values (−9.5).

The fluorene radical anion (**3**•−) retains C_{2v} symmetry (see Figure 2), but the benzene rings exhibit substantial bond length variations. The HOMA decreases to 0.76, again consistent with the nonaromatic 2.7 NICS(1) value. The electron affinity of fluorene, −0.07 eV at B3LYP/6-311+G**, approaches a positive value. Thus, the fluorene radical anion may be "quasistable". The tricyclic molecule is better able to delocalize the electron density over the larger carbon framework.

The last tricyclic in this set, 1H-benz[*f*]indene (**4** and **4**•−), with C_s symmetry, corresponds to a naphthalene-fused cyclopentadiene (Figure 2) (the notations used here are those of Harvey;[5] 1H indicates that carbon 1 in **4** is tetravalent and *f* is the site of benzene annelation). The Clar model predicts that 1H-benz[*f*]indene, with only one full aromatic sextet, is higher in energy than fluorene, which has two full sextets. The computations agree. Fluorene is roughly 9 kcal mol⁻¹ lower, and the radical anion, 5 kcal mol⁻¹ lower in energy than **4** and **4**•−, respectively. The structures for 1H-benz[*f*]indene follow some of the same trends as indene, but the cyclopentadiene double bond fused to the aromatic ring is increased in length even more, to 1.431 Å (vs 1.409 Å). As in naphthalene, the bond lengths in neutral (**4**) alternate significantly. Nevertheless, the NICS values are the same, −10.5, for both six-membered
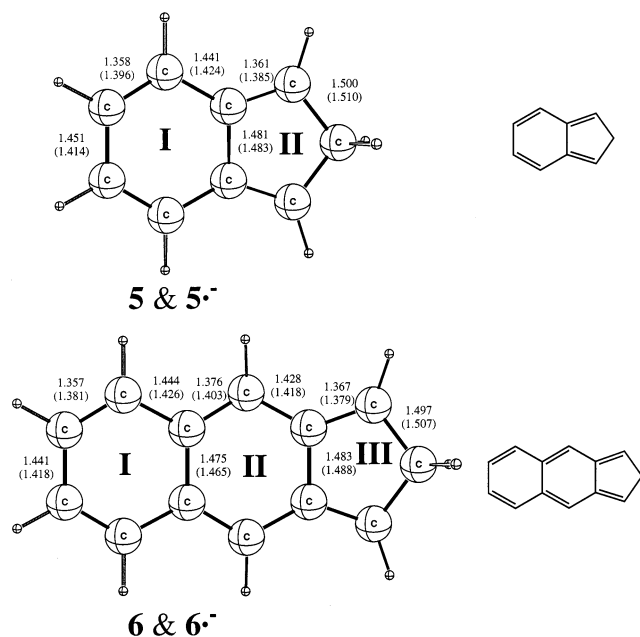
Figure 3. B3LYP/6-311+G** geometrical structures of isoindene (top) and 2H-benz[*f*]indene (bottom), as well as their radical anions, all in $C_{2\nu}$ symmetry. Neutral bond lengths (in Å) are listed first, with radical anion bond lengths in parentheses. A Kekulé structure is included for both molecules, to emphasize their nonaromatic nature. Roman numerals identify the rings.

Figure 4. B3LYP/6-311+G* geometries of 1,2-benzofluorene (top) and 2,3-benzofluorene (bottom), as well as their radical anions. All structures are of C_s symmetry. Neutral bond lengths (in Å) are listed first, with radical anionic bond lengths in parenthesis. Roman numerals identify the rings.

Table 3. C–H Bond Dissociation Energies (Zero-Point Corrected) for the Radical Anions of the Mono-, Bi-, and Tricyclic Molecules, in kcal mol^{-1}

	B3LYP/6-31+G*	B3LYP/6-311+G**
cyclopentadiene (1•⁻)	17.8	17.5
indene (2•⁻)	24.8	24.6
fluorene (3•⁻)	32.8	32.8
1H-benz[*f*]indene (4•⁻)	34.6	34.4
isoindene (5•⁻)	25.2	24.9
2H-benz[*f*]indene (6•⁻)	29.9	29.5

rings. Clearly these rings are aromatic, but the geometric criterion is less persuasive: HOMA for the six-membered rings is 0.78 and 0.70 for Rings I and II, respectively, smaller than the values in fluorene (**3**).

Density functional theory predicts **4** to have a positive electron affinity: the B3LYP/6-311+G** zero-point corrected adiabatic electron affinity is 0.13 eV. This is consistent with the trend in polybenzenoid molecules.[18] The electron affinity of naphthalene is −0.04 eV;[18] thus, the fusion of the five-membered ring increases the electron affinity by 0.17 eV.

Besides fusing benzene rings to cyclopentadiene at a double bond, a different type of attachment is possible, for example as in isoindene (**5** and **5•⁻**) and 2H-benz[*f*]indene (**6** and **6•⁻**) (see Figure 3). These molecules are not aromatic, since six-membered ring fusion along the unique cyclopentadiene single bond results in quinoid structures. The loss of aromaticity results in a large energy difference between isoindene and indene, 22.0 kcal mol^{-1}, and between 1H-benz[*f*]indene and 2H-benz[*f*]indene, 31.5 kcal mol^{-1} (B3LYP/6-311+G**). Since neither of the radical anions (**5•⁻** and **6•⁻**) are aromatic, the energy difference between the radical anion isomers is much smaller, −0.7 and 4.9 kcal mol^{-1} for indene (**2**) vs isoindene (**5**) and 1H- (**4**) vs 2H-benz[*f*]indene (**6**), respectively.

The neutral isoindene (**5**) and its radical anion (**5•⁻** are both essentially nonaromatic with slightly negative NICS(1) values between −1.5 and −5.9. Remarkably, isoindene has a *positive* electron affinity, 0.49 eV at B3LYP/6-311+G**, whereas the value for indene is −0.45 eV. The difference is almost 1 eV! This emphasizes the considerable importance of the aromatic stabilization in these systems. The added electron destroys the aromaticity of the conventional benzenoid system, thus eliminating the aromatic stabilization energy. This is not the case for the conjugated isomers such as **5**; hence the "iso" systems have larger electron affinities.
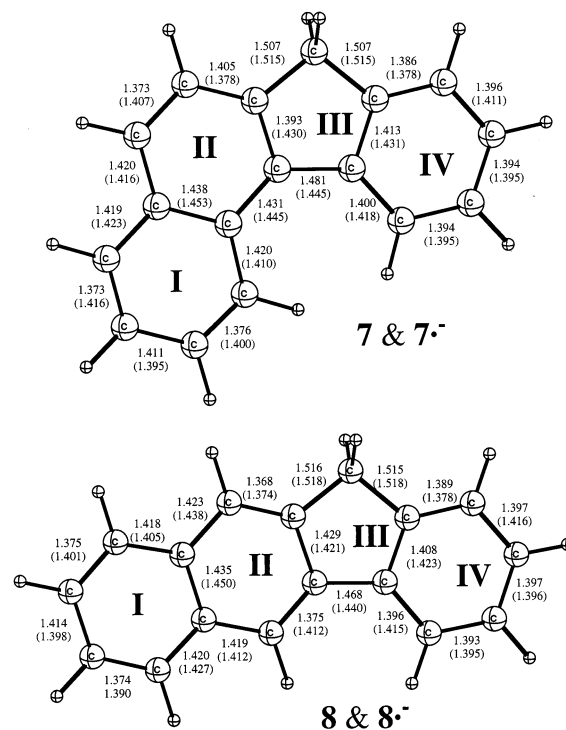
This trend is even more pronounced for 2H-benz[*f*]indene (**6**). Again the NICS(1) values indicate little or no aromaticity for either the neutral or the radical anion (**6•⁻**). The negative (−5.9) neutral Ring III NICS(1) of **6**, may be attributed to local π effects.[51] NICS(1) is reduced to −3.3 in **6•⁻**. The electron affinity of tricyclic **6**, 1.22 eV, is significantly larger than any of the systems yet considered. The 0.13 eV value for 1H-benz-[*f*]indene (**4**) is over 1 eV smaller.

The negative electron affinities for the smaller mono-, bi-, and tricyclic PAHs (**1**−**3**) indicate that the radical anions are unstable. Besides electron ejection, restoring the neutral, a second possible stabilization mechanism is ejection of a methylene hydrogen atom, forming the aromatic closed-shell cyclopentadienyl, indenyl, and fluorenyl anions.[40]

The cyclopentadiene radical anion (**1•⁻**) has distorted C_s symmetry, compared with the $C_{2\nu}$ structure of the neutral (**1**). The "axial" radical anion methylene C–H bond is elongated, 1.136 Å and weakened due to hyperconjugation. It is as if the radical anion is attempting to eject this hydrogen. Table 3 lists the homolytic bond dissociation energies (BDE) for the radical anions of **1**−**6**. The BDE of a tetravalent C–H bond in neutral

Table 4. B3LYP/6-31G* NICS Values at Ring Centers [NICS(0)], 1 Å above [NICS(1)] and HOMA Values[a] for the Neutral and Radical Anionic Tetra- and Pentacyclic PAHs

	Ring I[b]	Ring II	Ring III	Ring IV	Ring V
			1,2-Benzofluorene **7(7•⁻)**		
NICS(0)	−9.7(1.6)[c]	−9.0(5.5)	0.8(0.4)	−8.9(−4.4)	−
NICS(1)	−11.3(−1.2)	−10.7(2.1)	−2.4(−2.2)	−10.4(−5.9)	−
HOMA	0.77(0.71)	0.75(0.55)	−0.92(−1.00)	0.96(0.85)	−
			2,3-Benzofluorene **8(8•⁻)**		
NICS(0)	−9.5(2.8)	−9.3(5.8)	1.5(0.7)	−8.5(−2.5)	−
NICS(1)	−11.2(−0.2)	−11.0(2.1)	−2.1(−2.3)	−10.2(−4.5)	−
HOMA	0.78(0.75)	0.72(0.63)	−1.10(−0.99)	0.97(0.87)	−
			12H-Dibenzo[b,h]fluorene **9(9•⁻)**		
NICS(0)	−9.4(−2.1)	−9.1(0.7)	2.0(1.2)	−9.1(0.7)	−9.4(−2.1)
NICS(1)	−11.1(−4.4)	−10.8(−2.3)	−1.6(−1.9)	−10.8(−2.3)	−11.1(−4.4)
HOMA	0.78(0.78)	0.72(0.64)	−1.17(−0.28)	0.72(0.64)	0.78(0.78)
			13H-Indeno[1,2-b]anthracene **10(10•⁻)**		
NICS(0)	−8.7(−1.7)	−12.0(0.5)	−8.3(1.1)	1.6(0.5)	−8.4(−6.0)
NICS(1)	−10.5(−4.0)	−13.4(−2.7)	−10.1(−1.8)	−1.9(−2.5)	−10.1(−7.6)
HOMA	0.64(0.76)	0.71(0.57)	0.54(0.63)	−1.14(−1.01)	0.97(0.93)
			1H-Cyclopenta[b]naphthacene **11(11•⁻)**		
NICS(0)	−7.9(−3.4)	−12.5(−2.2)	−12.1(−1.9)	−7.6(−3.0)	0.3(−1.3)
NICS(1)	−9.8(−5.4)	−13.8(−4.9)	−13.5(−4.7)	−9.5(−5.1)	−2.7(−3.2)
HOMA	0.55(0.72)	0.65(0.57)	0.61(0.53)	0.41(0.63)	−1.16(−1.08)

[a] HOMA values utilize the geometries listed in Figures 4 and 5. [b] For definitions of Rings I−V see Figures 4 and 5. [c] Values in parentheses refer to the radical anions.

Table 5. Theoretical Electron Affinities, in eV, of Tetra- and Pentacyclic PAHs

	B3LYP	BLYP	BP86	HF
		1,2-benzofluorene (**7**)		
6-31G*	−0.21(−0.06)[a]	−0.27(−0.12)	0.06(0.21)	−0.98(−0.72)
6-31+G*	0.13	N/A	N/A	−0.68
6-311G*	0.08(0.25)	0.05(0.22)	0.35(0.51)	−0.78(−0.52)
6-311+G*	0.16	N/A	N/A	−0.66
		2,3-benzofluorene (**8**)		
6-31G*	−0.20(−0.05)	−0.26(−0.11)	0.08(0.23)	−1.02(−0.77)
6-311G*	0.10(0.26)	0.08(0.24)	0.38(0.54)	−0.81(−0.56)
		12H-dibenzo[b,h]fluorene (**9**)		
6-31G*	0.20(0.34)	−	−	−
6-311G*	0.50(0.65)	−	−	−
		13H-indeno[1,2-b]anthracene (**10**)		
6-31G*	0.39(0.52)	−	−	−
6-311G*	0.68(0.82)	−	−	−
		1H-cyclopenta[b]naphthacene (**11**)		
6-31G*	0.69(0.82)	−	−	−
6-311G*	0.97(1.10)	−	−	−

[a] Electron affinities in parentheses are zero-point corrected.

cyclopentadiene is 71.1 kcal mol⁻¹,[66] much greater than that of cyclopentadiene radical anion (**1•⁻**), where the homolytic BDE is only 17.5 kcal mol⁻¹. Hydrogen ejection from the cyclopentadiene radical anion gives the very aromatic cyclopentadienyl anion, $C_5H_5^-$ (NICS(0) value of −19.4).[40] Thus, the gain of aromatic stabilization energy lowers the BDE considerably. The situation is analogous for the **2•⁻** through **6•⁻** radical anions. They all have methylene C−H bond dissociation energies between 24 and 35 kcal mol⁻¹, much smaller than expected for the neutrals. In each case, the closed shell anion is highly aromatic,[40] resulting in a much reduced BDE.

B. Tetra- and Pentacyclic Systems. Two isomeric tetracyclic systems studied, both with C_s symmetry, are 1,2-benzofluorene (**7** and **7•⁻**) and 2,3-benzofluorene (**8** and **8•⁻**). As shown in Figure 4, these have benzene rings annelated to fluorene. Diffuse functions were only included for 1,2-benzofluorene, but this
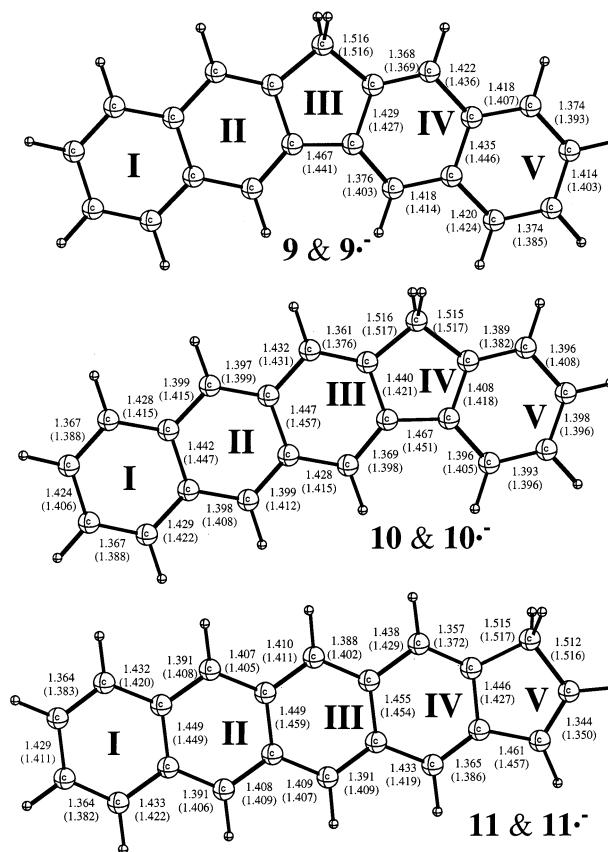
(66) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

Figure 5. B3LYP/6-311+G* geometries of the pentacyclic systems, 12H-dibenzo[b,h]fluorene (top, C_{2v}), 13H-indenol[1,2-b]anthracene (middle, C_s), and 1H-cyclopenta[b]napthacene (bottom), C_s), as well as their radical anions. Neutral bond lengths (in Å) are listed first, with radical anionic bond lengths in parenthesis. Roman numerals identify the rings.

gives an upper bound on their effect for the other tetra- and pentacyclic systems.

Neutral 1,2-benzofluorene (**7**) shows many of the classic characteristics of aromaticity. The three benzenoid rings all have
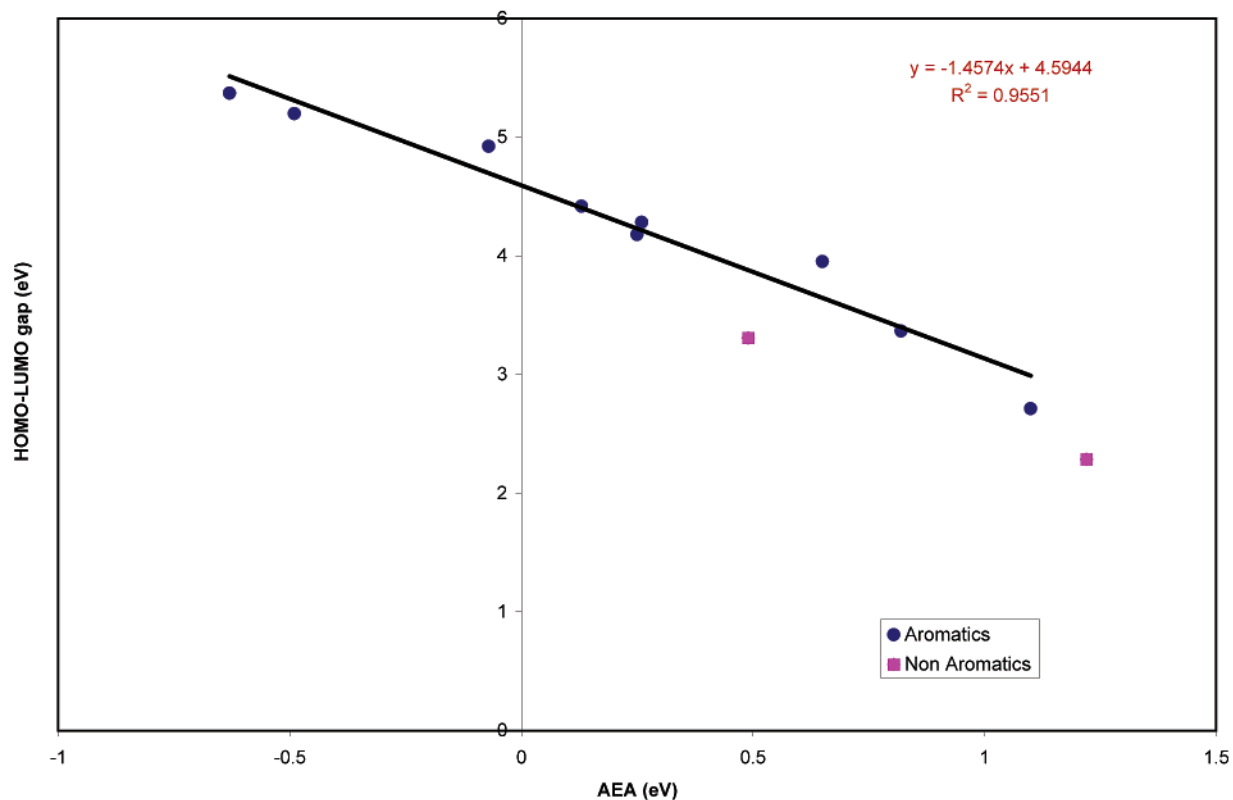
Figure 6. Graphical plot of HOMO−LUMO gap vs adiabatic electron affinity for molecules considered in this study. All values utilize the basis set associated with the previous structures. The linear fit is only for the aromatic neutrals.

NICS(1) values near the benzene result (see Table 4). The radical anion ($7^{•-}$) clearly loses aromaticity, with rings I−III becoming nonaromatic, while ring IV is only slightly aromatic This may help explain why 1,2-benzofluorene has a positive electron affinity (Table 5). The B3LYP/6-311G* zero-point corrected AEA is 0.25 eV, 0.12 eV larger than for the tricyclic 1H-benz[ƒ]indene (**4**). Larger carbon frameworks augmented by five-membered rings are able to delocalize the extra electron more effectively, increasing the electron affinities.

The closely related 2,3-benzofluorene (**8**) exhibits many of the same characteristics. The neutral structure has alternating bond lengths (differing by as much as 0.055 Å in ring II) but significantly negative NICS values, indicating aromatic character for the benzenoid rings, the 2,3-benzofluorene radical anion. According to the Clar model, both **7** and **8** have two aromatic sextets, but **8** is more stable by 2.7 kcal mol^{-1}.

In view of the large number of possible pentacyclic systems we chose three representative linear chains (**9**−**11**), in which the cyclopentadiene ring is moved from the center to the edge (see Figure 5). These illustrate the importance of chains of fused benzene rings in increasing the electron affinity.

12H-Dibenzo[b,h]fluorene (**9** and $9^{•-}$) has a cyclopentadiene ring with naphthalene fused on both sides. Both the C_{2v} neutral and its radical anion have alternating benzenoid bond distances, with the largest difference being 0.067 Å in rings II and IV for the neutral and 0.077 for the radical anion. The neutral is highly aromatic, but the radical anion has lost this aromaticity; NICS-(1) values are −2.3 in the internal benzene rings and −4.4 in the external rings. Consistent with the larger number of rings, the zero-point corrected electron affinity, 0.65 eV at B3LYP/

6-311G*, is almost 0.4 eV larger than that computed for the tetracyclic benzofluorenes.

While the isomeric 13H-indeno[1,2-b]anthracene (**10** and $10^{•-}$) has an anthracene moiety, the radical anion appears to lose most of its aromaticity. However, the NICS(1) of −7.6 and HOMA value of 0.93 of $10^{•-}$ indicates that some aromaticity remains in Ring V. The computed zero-point corrected electron affinity of **10** (0.82 eV) is increased by almost 0.2 eV compared to that of **9** due to the longer anthracene moiety. The electron affinity of anthracene is 0.72 eV;[18] the additional five-membered ring increases this value.

1H-Cyclopenta[b]naphthacene (**11** and $11^{•-}$) has the cyclopentadiene at an external position. Again the neutral and its radical anion have alternating bond distances (the largest difference is 0.098 Å in ring IV of the neutral and 0.082 in the radical anion). The radical anionic benzenoid rings of $11^{•-}$ have slightly negative NICS(1) values (−4.7 to −5.4), indicating that this radical anion maintains a small degree of aromaticity. The chain of four straight benzene rings binds an electron rather well, and the zero-point corrected electron affinity of **11** is 1.10 eV. This is almost a full eV larger than the electron affinities of the benzofluorenes, and only 0.14 eV smaller than the value for tetracene.[18] The ability of this PAH to retain some aromatic character, that is, to lose less aromatic stabilization, explains its larger electron affinity. The characteristics of the pentacyclic rings are consistent with Clar's model: while **11** has only one aromatic sextet, it has the highest relative energy and the most olefinic terminal benzene ring. This arrangement binds an electron better. Both **9** and **10** have two aromatic sextets and are 18.8 and 15.0 kcal mol^{-1} more stable, respectively, than **11**.

IV. Summary and Conclusions

The addition of benzene rings to cyclopentadiene dramatically improves the ability to bind an electron. Consider the increase of electron affinities from **1** to **11**: −0.63 (**1**), −0.49 (**2**), −0.07 (**3**), 0.13 (**4**), 0.25 (**7** and **8**), 0.65 (**9**), 0.82 (**10**), and 1.10 eV (**11**). Chains of fused benzene rings bind an electron best. The benzofluorenes and 1H-benz[*f*]indene all have a chain of two fused benzene rings and positive electron affinities.

However, while it takes two fused six-membered rings bound across the cyclopentadiene C═C double bond to cyclopentadiene to obtain a positive electron affinity, positive electron affinities can be obtained with only one six-membered ring when the cyclopentadiene fusion is along the unique single C−C bond (as in **5**). Isoindene has an adiabatic electron affinity (zero-point corrected) of 0.49 eV, higher even than any of the conventional tetracyclics considered. The AEA of the analogous tricyclic molecule, 2H-benz[*f*]indene (**6**) (1.22 eV) is higher than any PAH studied in this work.

The contribution of the cyclopentadiene moiety to the electron affinities decreases as the molecules increase in size. Conventional fusion of cyclopentadiene to benzene increases the electron affinity by 0.4 eV, while fusion to naphthalene increases the electron affinity by 0.17 eV. For tetracene, cyclopentadiene attachment decreases the electron affinity by 0.14 eV. The larger linear acenes are more olefinic in nature,[28] and thus the electron affinities are less affected by the cyclopentadiene fusion.

The results reveal several important computational conclusions. While diffuse functions are necessary to compute electron affinities of small molecules accurately, this is less so for the large systems studied here. Although not diffuse, the additional functions improve the overall description of the electron affinity in going from 6-31G* to 6-311G*.

Finally, the HOMO−LUMO gap shows a quasi-linear relationship ($R^2 = 0.955$) vs adiabatic electron affinities (Figure 6) for the aromatic molecules. Note that the nonaromatic conjugated systems do not appear to fit this relationship.

The electron affinities depend markedly on the aromatic nature of the PAH molecules. The PAH radical anions no longer have the Hückel number of π electrons, and thus aromaticity is diminished or even destroyed. This loss of resonance energy results in much smaller electron affinities, by as much as 1 eV, than the nonaromatic "isoindene" isomers.

Supporting Information Available: Tables of B3LYP/biggest basis set Cartesian coordinates, as well as absolute energetics and zero-point vibrational energies for all stationary points (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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