Gas phase adiabatic electron affinities of cyclopenta-fused polycyclic aromatic hydrocarbons

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Abstract

The B3LYP/DZP++ adiabatic electron affinity (AEA) of nine (non)-alternant polycyclic aromatic hydrocarbons are reported and discussed. Calculations became feasible for molecules this size by projecting out the near-linearly dependent part of the one-electron basis. Non-alternant PAH consisting of an alternant PAH core modified by *peri*-annulation with unsaturated five-membered rings (CP-PAHs) possess markedly enhanced AEAs.
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1. Introduction

Non-alternant cyclopenta-fused PAHs (CP-PAHs) consisting of an alternant PAH core modified by *peri*-annulation with (at least) one unsaturated five-membered ring (CP moiety) are of considerable chemical importance and biological relevance. This stems from their identity as sub-structures of fullerenes and carbon nanotubes [1,2], their potential to show unusual (photo)physical properties, e.g. facile (consecutive) one-electron reduction processes [3], anomalous fluorescence [4] and deviant aromatic character [5], and, their alleged presence (in charged form) in the interstellar medium [6]. In addition, CP-PAHs were found to possess bio-activity [7]. This is of interest since CP-PAHs have been identified as prevalent environmental pollutants that are invariably generated during incomplete combustion processes [8]. Recently, the dicyclopentapyrenes **7** and **8** [9,10] (Fig. 1) were unexpectedly found to exert direct-acting mutagenicity in bacterial assays [11]. To explain their unexpected activity, one-electron reduction was proposed as a key step (see also [12]).

Cyclic voltammetry experiments [3] have shown that CP-PAHs when compared to their related alternant PAH cores lacking the *peri*-annulated CP moiety undergo more facile (successive) one-electron reduction steps [*ca.* 0.5–0.7 V for both $\Delta E_{1/2}(0/-1)$ and $\Delta E_{1/2}(-1/-2)$]. In addition, $E_{1/2}(0/-1)$ and $E_{1/2}(-1/-2)$ values were found to be strongly dependent on the number and the topology of the *peri*-annulated CP moieties (*vide infra*, Table 2).

Since there is ample empirical evidence [8,13], that the first reduction potential $E_{1/2}(0/-1)$ is proportional to the gas-phase adiabatic electron affinity (AEA) following Eq. (1):

$$E_{1/2}(0/-1) = \text{AEA} - \Delta\Delta G_{\text{sol}} + E_{\text{ref}} \qquad (1)$$

in which E_{ref} equals -4.71 V (if $E_{1/2}(0/-1)$ is referenced to SCE) and $-\Delta\Delta G_{\text{sol}}$ is the free energy difference between the neutral molecule and its radical anion in the gas phase and in solution, CP-PAHs must possess substantially more positive gas phase AEA values than their corresponding alternant PAH cores. Unfortunately, experimental AEAs of CP-PAHs are not available [8]. Therefore, we were prompted to compute AEAs of a representative series of (CP)-PAHs at the *ab initio* B3LYP/DZP++ level of theory [14–17].

We here report and discuss the gas phase AEAs with and without zero-point vibrational energy (ZPVE)

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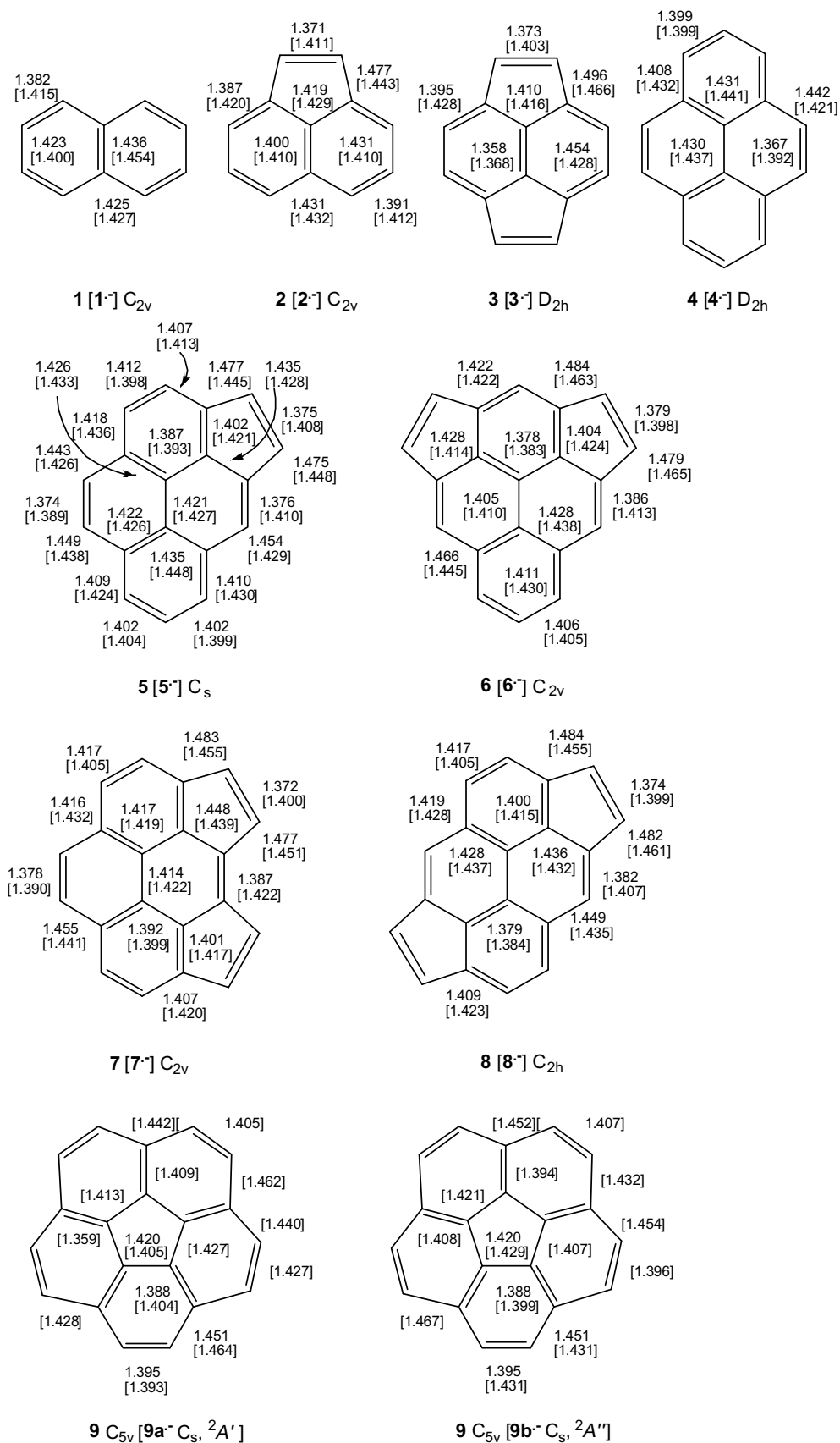 *E-mail address:* l.w.jenneskens@uu.nl (L.W. Jenneskens).

Fig. 1. B3LYP/DZP++ carbon–carbon bond lengths of the neutral (non)-alternant PAH **1–9** and their radical anions **1·⁻–9·⁻** between square brackets.

correction of the (non)-alternant (CP)-PAHs naphthalene (**1**, see also [14]), acenaphthylene (**2**), pyracylene (**3**), pyrene (**4**), cyclopenta[*cd*]- (**5**), [18] dicyclopenta[*cd,mn*]- (**6**) [9,10], dicyclopenta[*cd,fg*]- (**7**) [9,10], dicyclopenta[*cd,jk*]pyrene (**8**) [9,10] and the bowl-shaped corannulene (**9**) [19,20] (Fig. 1). It is shown that CP-PAHs possess markedly enhanced AEAs when compared to the AEAs of related alternant PAH cores lacking peripheral CP moieties.

2. Computational details

For the computation of gas phase AEAs of (CP)-PAH **1**–**9** the geometries of the neutral compounds **1**–**9** and their radical anions **1**$^{\cdot-}$–**9**$^{\cdot-}$ were optimized at the B3LYP/DZP++ level of theory [14–17] using GAMESS-UK [21]. As noted previously in the linear acene series [14], application of the DZP++ basis set has one major drawback. For representatives of a certain size, e.g. tetracene ($C_{18}H_{12}$), the DZP++ basis set gave near-linear dependencies [22] resulting in severe numerical problems during the self-consistent field convergence process. With the exception of **1** and its radical anion **1**$^{\cdot-}$ [14], the occurrence of near-linear dependencies were found during B3LYP/DZP++ geometry optimization of (CP)-PAH **2**–**9** and their radical anions **2**$^{\cdot-}$–**9**$^{\cdot-}$. The standard technique that will reduce this numerical instability is to project out the problematic dependencies from the basis set. To this end part (N) of the molecular orbitals (MOs) with eigenvalues of the overlap matrix smaller than *ca.* 10^{-5} were carefully projected out in the case of **2**–**9** and **2**$^{\cdot-}$–**9**$^{\cdot-}$ (Table 1) after which all neutrals and radical anions gave stable convergence. For the radical anions **1**$^{\cdot-}$–**9**$^{\cdot-}$ $<S^2>$ values were found in the expected range of 0.76–0.77. Hessian calculations were run to test whether the optimized geometries of **1**–**9** and **1**$^{\cdot-}$–**9**$^{\cdot-}$ were proper minima and to assess zero-point vibrational energies (ZPVEs) (Table 1). B3LYP/DZP++ AEAs with and without ZPVE correction [ΔZPVE = ZPVE(neutral) − ZPVE(anion)] of **1**–**9** were calculated following Eq. (2):

$$AEA = [E_{tot}(neutral) + ZPVE(neutral)]$$
$$- [E_{tot}(anion) + ZPVE(anion)] \quad (2)$$

3. Results and discussion

Proper minima were successfully located for **1**–**9** and **1**$^{\cdot-}$–**9**$^{\cdot-}$ after projecting out N MOs in the case of **2**–**9** and **2**$^{\cdot-}$–**9**$^{\cdot-}$. The calculated positive definite Hessians confirmed that no symmetry breaking occurs for (CP)-PAHs **1**–**8** upon addition of the extra electron, i.e. formation of the radical anions **1**$^{\cdot-}$–**8**$^{\cdot-}$ (Table 2). In line with literature data [23], conversion of corannulene (**9**) into its radical anion **9**$^{\cdot-}$ induces Jahn-Teller distortion [**9** (C_{5v}) → **9**$^{\cdot-}$(C_s)]. Note that for **9**$^{\cdot-}$ two electronic states, $^2A'$ (**9a**$^{\cdot-}$) and $^2A''$ (**9b**$^{\cdot-}$) are accessible, which at the B3LYP/DZP++ level of theory possess a nearly identical E_{tot} [$\Delta E_{tot} = E_{tot}($**9a**$^{\cdot-}$$) - E_{tot}($**9b**$^{\cdot-}$$) = -0.78$ kcal mol^{-1}] with **9a**$^{\cdot-}$ being slightly more stable. The relative stability of **9a**$^{\cdot-}$ and **9b**$^{\cdot-}$, however, was previously noted to be dependent on the applied level of theory [23].

The computed changes in geometry in going from **9** to either **9a**$^{\cdot-}$ or **9b**$^{\cdot-}$ (Fig. 1) are in agreement with those previously reported [23]. In the case of (CP)-PAH **1**–**8** only small changes in geometry are found upon addition of the extra electron (**1**$^{\cdot-}$–**8**$^{\cdot-}$). This is illustrated by a comparison of corresponding carbon–carbon bond lengths (Δr *ca.* 0.03 Å, Fig. 1) and valence angles (Δ° *ca.* 0.5°). For CP-PAHs **2**, **3** and **5**–**8**, most prominent structural changes occur in the *peri*-annulated CP moieties, e.g. the ethene-like carbon–carbon bond lengthens and the *ipso* carbon–carbon bonds shorten (Fig. 1). This suggests that upon addition of the extra electron 6π-electron cyclopentadienide sub-structures contribute [4]. This is supported by the B3LYP/DZP++ Singly Occupied MOs (SOMOs, Fig. 2) which for **2**$^{\cdot-}$, **3**$^{\cdot-}$ and **5**$^{\cdot-}$–**8**$^{\cdot-}$ show strong anti-bonding character

Table 1
B3LYP/DZP++ lowest eigenvalues of the overlap matrix multiplied by 10^4 and number of MOs (N, in parentheses) projected out for stable convergence of **2**–**9** and **2**$^{\cdot-}$–**9**$^{\cdot-}$, and, B3LYP/DZP++ ZPVE energies (in eV) and ΔZPVE corrections (in eV) for **1**–**9** and **1**$^{\cdot-}$–**9**$^{\cdot-}$

Compound[a]	DZP++ (N)	ZPVE	ΔZPVE
1/1$^{\cdot-}$	0.05 (0)	4.01/3.85	0.16
2/2$^{\cdot-}$	0.03 (4)	4.33/4.22	0.11
3/3$^{\cdot-}$	0.01 (4)	4.66/4.57	0.09
4/4$^{\cdot-}$	0.01 (10)	5.64/5.50	0.13
5/5$^{\cdot-}$	0.002 (20)	5.96/5.86	0.10
6/6$^{\cdot-}$	0.003 (20)	6.28/6.18	0.10
7/7$^{\cdot-}$	0.0002 (20)	6.28/6.20	0.08
8/8$^{\cdot-}$	0.003 (20)	6.27/6.17	0.10
9/9a$^{\cdot-}$ $^2A'$[b]	0.0003 (20)	6.28/6.10	0.18
9b$^{\cdot-}$ $^2A''$	0.0003 (20)	6.10	0.18

[a] See also Figs. 1 and 2, and Table 2.
[b] For **9a**$^{\cdot-}$ and **9b**$^{\cdot-}$, see text and [23].

Table 2
B3LYP/DZP++ AEA (in eV) and $E_{1/2}(0/-1)$ vs. SCE (in V) [4] values for **1**–**9**

Compound[a] (point group)	AEA[b]	$E_{1/2}(0/-1)$ vs. SCE
1 (D_{2h}, $C_{10}H_8$)	−0.20 {−0.04} [14] (−019 ± 0.03 [25])	−2.66
2 (C_{2v}, $C_{12}H_8$)	0.76 {0.87}	−1.80
3 (D_{2h}, $C_{14}H_8$)	1.42 {1.51}	−1.06
4 (D_{2h}, $C_{16}H_{10}$)	0.46 {0.60} (0.41 ± 0.01 [26])	−2.22
5 (C_s, $C_{18}H_{10}$)	1.15 {1.26}	−1.56
6 (C_{2v}, $C_{20}H_{10}$)	1.47 {1.56}	−1.32
7 (C_{2v}, $C_{20}H_{10}$)	1.74 {1.81}	−1.02
8 (C_{2h}, $C_{20}H_{10}$)	1.65 {1.75}	−1.15
9 (C_{5v}, $C_{20}H_{10}/C_s$)[c]	**9a**$^{\cdot-}$ 0.70 {0.89} $^2A'$ **9b**$^{\cdot-}$ 0.67 {0.85} $^2A''$ (0.506 [27])	−1.99

[a] See Fig. 1.
[b] ZPVE-corrected AEAs between brackets and experimental gas phase AEAs between parentheses.
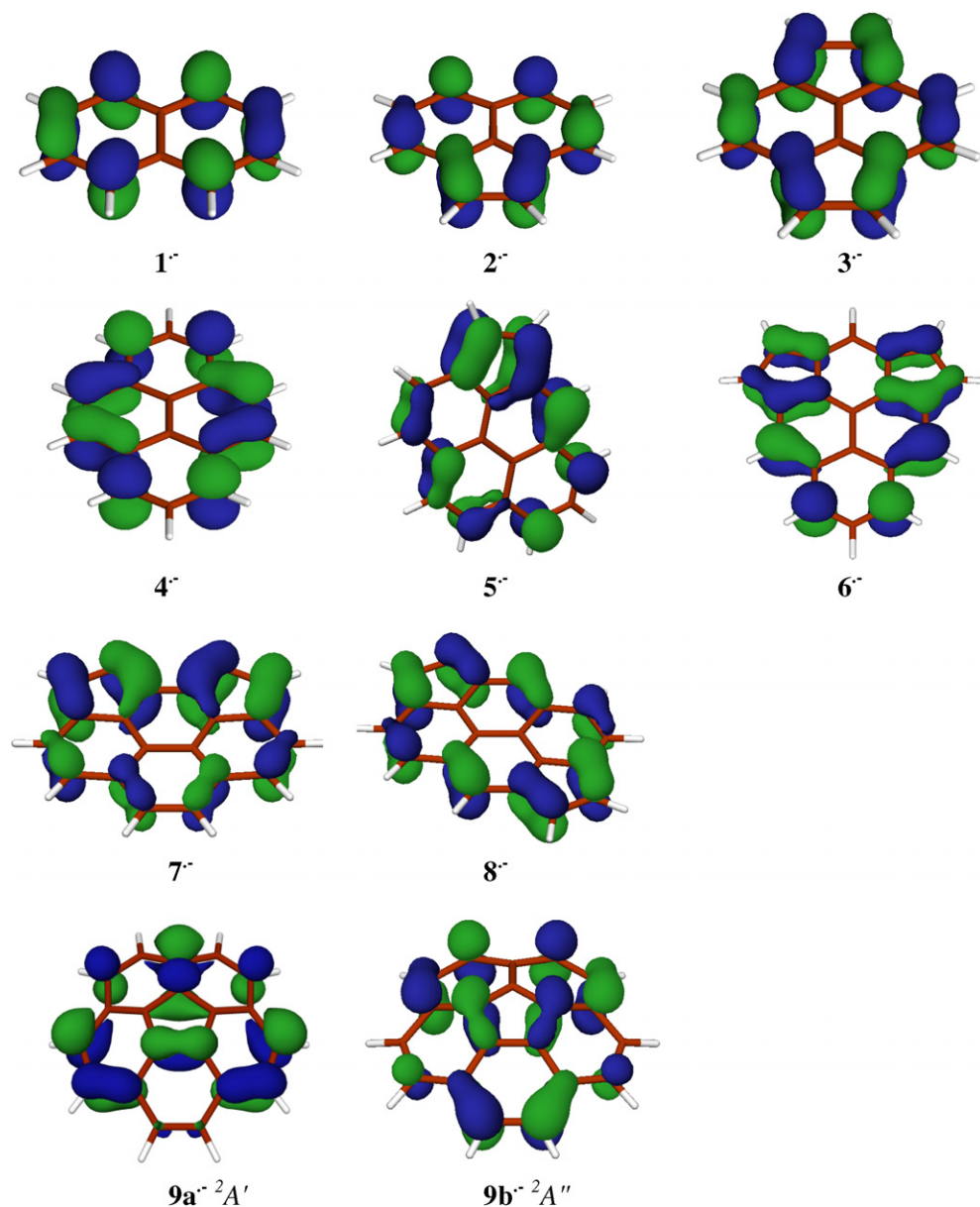[c] See text and [23].

Fig. 2. B3LYP/DZP++ Singly occupied molecular orbitals (SOMOs) of **1**$^{\cdot-}$–**9**$^{\cdot-}$. Note that the SOMOs are nearly identical to the LUMOs of the neutrals **1–9**.

along the ethene-like bond and bonding character along the two *ipso* carbon–carbon bonds. The charge distribution of the extra electron (e) as obtained by Natural Population Analysis as well as the spin density distribution [24], shows that *ca.* 0.2–0.3 e is concentrated in the *peri*-annulated CP moieties. In contrast, only *ca.* 0.1 e is found in the *internal* circumscribed unsaturated five-membered ring of the corannulene radical anion (**9a**$^{\cdot-}$ and **9b**$^{\cdot-}$).

In Table 2 the B3LYP/DZP++ AEAs for **1–9** calculated according to Eq. (2) [AEA = (E_{tot}(neutral) + ZPVE(neutral)) − (E_{tot}(anion) + ZPVE(anion))] with and without inclusion of ZPVE correction are reported. A comparison of the computed AEAs with scarcely available experimental gas-phase AEAs of the (non)-alternant PAHs, naphthalene (**1**) [25], pyrene (**4**) [26], and corannulene (**9**) [27],

shows that especially the B3LYP/DZP++ AEAs without ZPVE correction are in good agreement. Inclusion of ZPVE correction tends to overestimate the computed AEAs by *ca.* 0.1–0.2 eV (ΔZPVE, Table 2, see also [14]). This can be attributed to the difference in B3LYP/ DZP++ ZPVE energy of the neutral (CP)-PAHs **1–9** and their related radical anions **1**$^{\cdot-}$–**9**$^{\cdot-}$ (Table 1). The fortuitous agreement of the B3LYP/DZP++ AEAs without ZPVE correction with experimental AEAs is apparently a consequence of an overestimation of the E_{tot} of the radical anions which compensates a lack of ZPVE correction (see also [14,28]).

To gain insight in the reliability of the calculated B3LYP/DZP++ AEA values for CP-PAHs **2–8** we have assessed whether a correlation similar to Eq. (1) exists
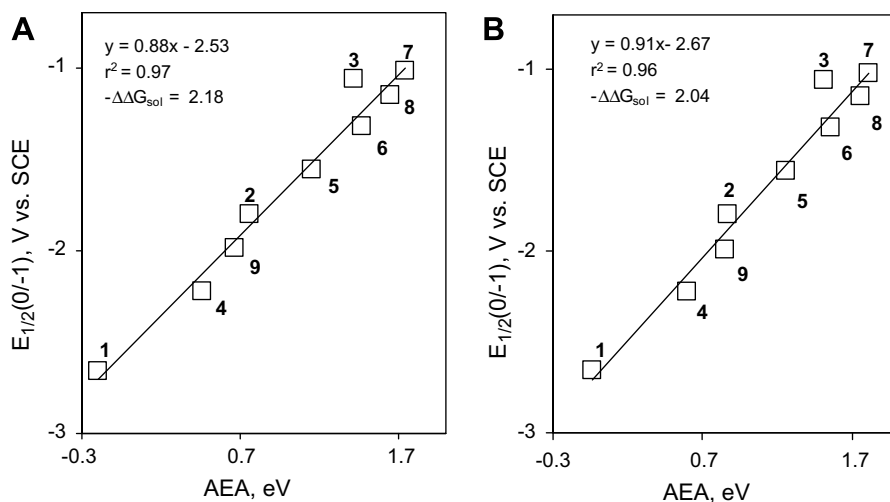
Fig. 3. Linear correlation between B3LYP/DZP++ AEA values without ZPVE (in eV, **A**) and with ZPVE (in eV, **B**) correction and $E_{1/2}(0/-1)$ vs. SCE (in V) values [4] of **1–9**.

between the $E_{1/2}(0/-1)$ vs. SCE values of **1–9** [3] and their AEAs (Table 2). As shown in Fig. 3A, a good quality linear fit (r^2 0.97 and slope 0.88) is obtained that indeed follows Eq. (1) [8,13]. From the intercept, which equals $-\Delta\Delta G_{sol} + E_{ref}$ (with E_{ref} −4.71 V [8,13]) a $-\Delta\Delta G_{sol} = 2.18$ eV is calculated that is close to the value of 1.99 ± 0.05 eV derived from a comprehensive correlation [13] of experimental $E_{1/2}(0/-1)$ vs. SCE and AEA values of a series of alternant PAHs. Inclusion of ZPVE correction in the AEA values does not significantly affect the quality of the fit (r^2 0.96, slope 0.91 with $-\Delta\Delta G_{sol}$ 2.04 eV, Fig. 3B). These observations give confidence that reliable estimates of the experimental gas phase AEAs of the non-alternant (CP)-PAHs **2**, **3**, **5–8** and **9** are obtained at the B3LYP/DZP++ level of theory.

A survey of the computed AEAs of **1–9** in Table 2 demonstrates the effect exerted by *peri*-annulation of CP moieties. Whereas in the naphthalene radical anion (**1**·⁻) the extra electron is not bound [14,25], it is bound in the acenaphthylene radical anion (**2**·⁻). The AEA of **2** (0.76 eV) is unusually high [*Cf.* AEAs of **4** and **9**, Table 2]; in going from **1** to **2** a ΔAEA of 0.96 eV is found. A similar ΔAEA 0.69 eV) is obtained in going from **4** to **5**, (see also [29]). The AEAs of **2** and **5** can be further improved by *peri*-annulation of a second CP moiety (ΔAEA: **2→3**, 0.66 eV, **5→6**, 0.32 eV, **5→7**, 0.59 eV and **5→8**, 0.50 eV, Table 2). Clearly, the number and topology of the peripheral CP moieties controls their AEAs. A comparison of the AEAs of the CP-PAHs **6–8** with that of corannulene (**9**) (all $C_{20}H_{10}$, Fig. 1), unequivocally shows that **6–8** possess markedly more positive AEAs (Table 2). Hence, **6–8** are *inherently* better electron acceptors then **9** (see also [30]). Interestingly, the AEAs of **3** and **5–8** (Table 2), which are surface sub-structures of C_{60} and C_{70}, correspond to *Ca.* 53% (**3**) of the AEA of C_{60} (2.65 ± 0.05 eV [31]), and, *Ca.* 52% (**3**), 42% (**5**), 54% (**6**), 64% (**7**) and 61% (**8**) of that of C_{70} (2.72 ± 0.05 eV [31]). In contrast, the AEA of **9** corresponds to only *ca.* 25% of the AEAs of C_{60} and C_{70} [31].

The effect of a peripheral CP moiety also compares favourably to that exerted by *benz*-annulation in the alternant linear acene series (ΔAEA *ca.* 0.65 eV) [14]. It also matches *ca.* 60% of the increase in AEA predicted upon *per*-fluorination, *i.e.* substitution of all perimeter hydrogens by fluorines of linear acenes (ΔAEA *ca.* 1.20 eV), [32].

4. Conclusions

Our results indicate that reliable estimates of the AEAs of CP-PAHs are obtained at the B3LYP/DZP++ level of theory. The computed AEAs show that CP-PAHs represent an interesting class of electron acceptors. Since CP-PAHs are readily accessible [1,2,9,10,18] and their AEAs can be enhanced further by substitution of the perimeter hydrogens [32,33], (functionalized) CP-PAHs are timely synthetic targets for novel *n*-type materials, viz. strong oxidants. In addition, the AEAs of CP-PAHs warrant further investigations of the properties of their radical anions in connection with their possible occurrence in the interstellar medium [6] and as an aid for the identification of bio-active representatives [7,11,12].

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