

# 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):

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

in which  $E_{\text{ref}}$  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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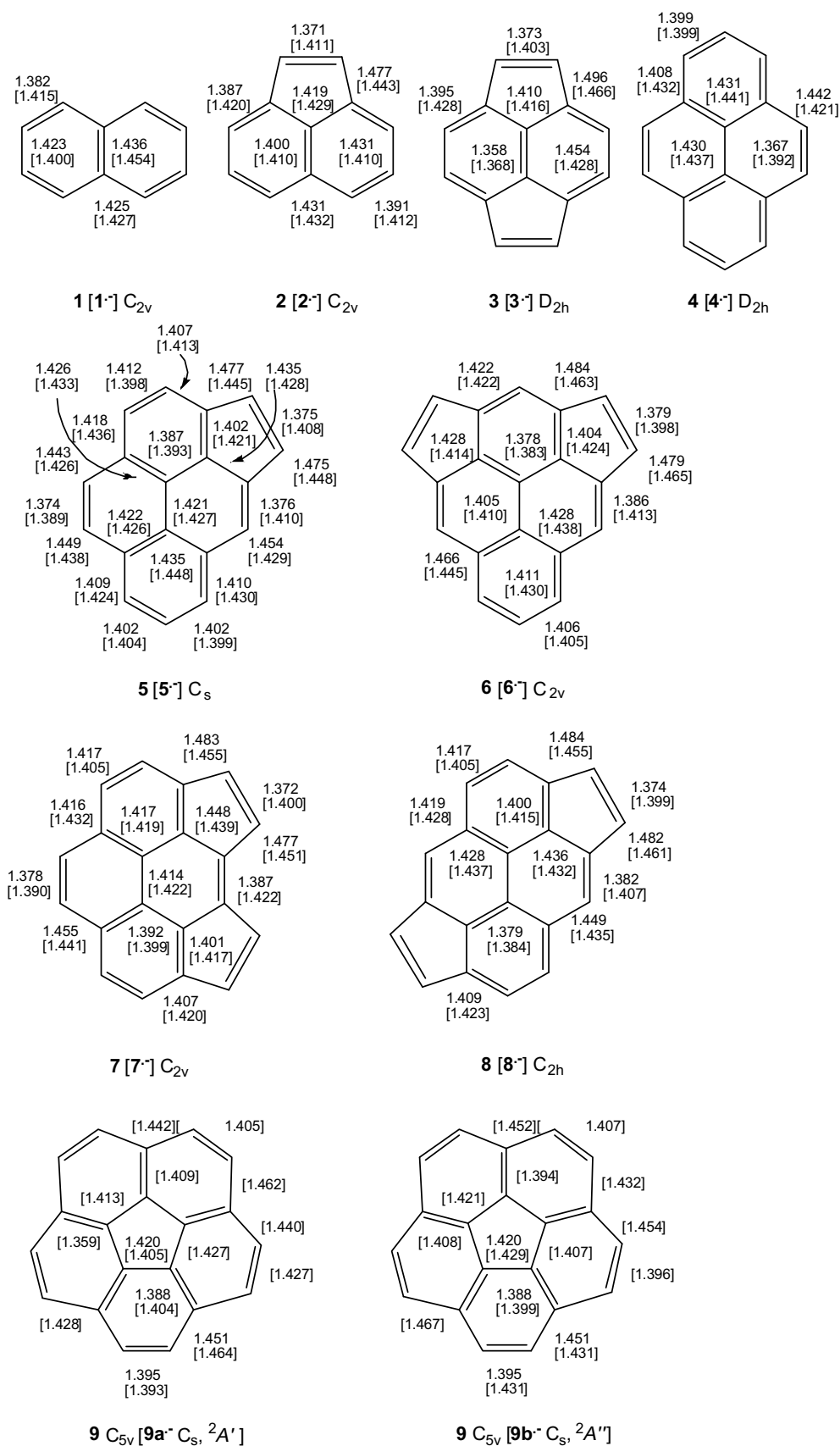


Fig. 1. B3LYP/DZP++ carbon-carbon bond lengths of the neutral (non)-alternant PAH 1–9 and their radical anions 1<sup>−</sup>–9<sup>−</sup> between square brackets.

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<sup>•−</sup>–9<sup>•−</sup>** 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<sub>18</sub>H<sub>12</sub>), 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<sup>•−</sup>** [14], the occurrence of near-linear dependencies were found during B3LYP/DZP++ geometry optimization of (CP)-PAH **2–9** and their radical anions **2<sup>•−</sup>–9<sup>•−</sup>**. 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<sup>−5</sup> were carefully projected out in the case of **2–9** and **2<sup>•−</sup>–9<sup>•−</sup>** (Table 1) after which all neutrals and radical anions gave stable convergence. For the radical anions **1<sup>•−</sup>–9<sup>•−</sup>** <*S*<sup>2</sup>> 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<sup>•−</sup>–9<sup>•−</sup>** were proper minima and to assess zero-point vibrational energies (ZPVEs) (Table 1). B3LYP/DZP++ AEAs with and without ZPVE correction [ $\Delta\text{ZPVE} = \text{ZPVE}(\text{neutral}) - \text{ZPVE}(\text{anion})$ ] of **1–9** were calculated following Eq. (2):

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

## 3. Results and discussion

Proper minima were successfully located for **1–9** and **1<sup>•−</sup>–9<sup>•−</sup>** after projecting out *N* MOs in the case of **2–9** and **2<sup>•−</sup>–9<sup>•−</sup>**. 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<sup>•−</sup>–8<sup>•−</sup>** (Table 2). In line with literature data [23], conversion of corannulene (**9**) into its radical anion **9<sup>•−</sup>** induces Jahn-Teller distortion [**9** (C<sub>5v</sub>) → **9<sup>•−</sup>** (C<sub>s</sub>)]. Note that for **9<sup>•−</sup>** two electronic states, <sup>2</sup>*A'* (**9a<sup>•−</sup>**) and <sup>2</sup>*A''* (**9b<sup>•−</sup>**) are accessible, which at the B3LYP/DZP++ level of theory possess a nearly identical *E*<sub>tot</sub> [ $\Delta E_{\text{tot}} = E_{\text{tot}}(\mathbf{9a}^{\bullet-}) - E_{\text{tot}}(\mathbf{9b}^{\bullet-}) = -0.78 \text{ kcal mol}^{-1}$ ] with **9a<sup>•−</sup>** being slightly more stable. The relative stability of **9a<sup>•−</sup>** and **9b<sup>•−</sup>**, 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<sup>•−</sup>** or **9b<sup>•−</sup>** (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<sup>•−</sup>–8<sup>•−</sup>**). This is illustrated by a comparison of corresponding carbon–carbon bond lengths ( $\Delta r$  *ca.* 0.03 Å, Fig. 1) and valence angles ( $\Delta^\circ$  *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<sup>•−</sup>**, **3<sup>•−</sup>** and **5<sup>•−</sup>–8<sup>•−</sup>** show strong anti-bonding character

Table 2  
B3LYP/DZP++ AEA (in eV) and *E*<sub>1/2</sub>(0/−1) vs. SCE (in V) [4] values for **1–9**

Compound <sup>a</sup> (point group)	AEA <sup>b</sup>	<i>E</i> <sub>1/2</sub> (0/−1) vs. SCE
<b>1</b> (D <sub>2h</sub> , C <sub>10</sub> H <sub>8</sub> )	−0.20 {−0.04} [14] (−0.19 ± 0.03 [25])	−2.66
<b>2</b> (C <sub>2v</sub> , C <sub>12</sub> H <sub>8</sub> )	0.76 {0.87}	−1.80
<b>3</b> (D <sub>2h</sub> , C <sub>14</sub> H <sub>8</sub> )	1.42 {1.51}	−1.06
<b>4</b> (D <sub>2h</sub> , C <sub>16</sub> H <sub>10</sub> )	0.46 {0.60} (0.41 ± 0.01 [26])	−2.22
<b>5</b> (C <sub>s</sub> , C <sub>18</sub> H <sub>10</sub> )	1.15 {1.26}	−1.56
<b>6</b> (C <sub>2v</sub> , C <sub>20</sub> H <sub>10</sub> )	1.47 {1.56}	−1.32
<b>7</b> (C <sub>2v</sub> , C <sub>20</sub> H <sub>10</sub> )	1.74 {1.81}	−1.02
<b>8</b> (C <sub>2h</sub> , C <sub>20</sub> H <sub>10</sub> )	1.65 {1.75}	−1.15
<b>9</b> (C <sub>5v</sub> , C <sub>20</sub> H <sub>10</sub> /C <sub>s</sub> ) <sup>c</sup>	<b>9a<sup>•−</sup></b> 0.70 {0.89} <sup>2</sup> <i>A'</i> <b>9b<sup>•−</sup></b> 0.67 {0.85} <sup>2</sup> <i>A''</i> (0.506 [27])	−1.99

<sup>a</sup> See Fig. 1.

<sup>b</sup> ZPVE-corrected AEAs between brackets and experimental gas phase AEAs between parentheses.

<sup>c</sup> See text and [23].

Table 1

B3LYP/DZP++ lowest eigenvalues of the overlap matrix multiplied by 10<sup>4</sup> and number of MOs (*N*, in parentheses) projected out for stable convergence of **2–9** and **2<sup>•−</sup>–9<sup>•−</sup>**, and, B3LYP/DZP++ ZPVE energies (in eV) and  $\Delta\text{ZPVE}$  corrections (in eV) for **1–9** and **1<sup>•−</sup>–9<sup>•−</sup>**

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

<sup>a</sup> See also Figs. 1 and 2, and Table 2.

<sup>b</sup> For **9a<sup>•−</sup>** and **9b<sup>•−</sup>**, see text and [23].

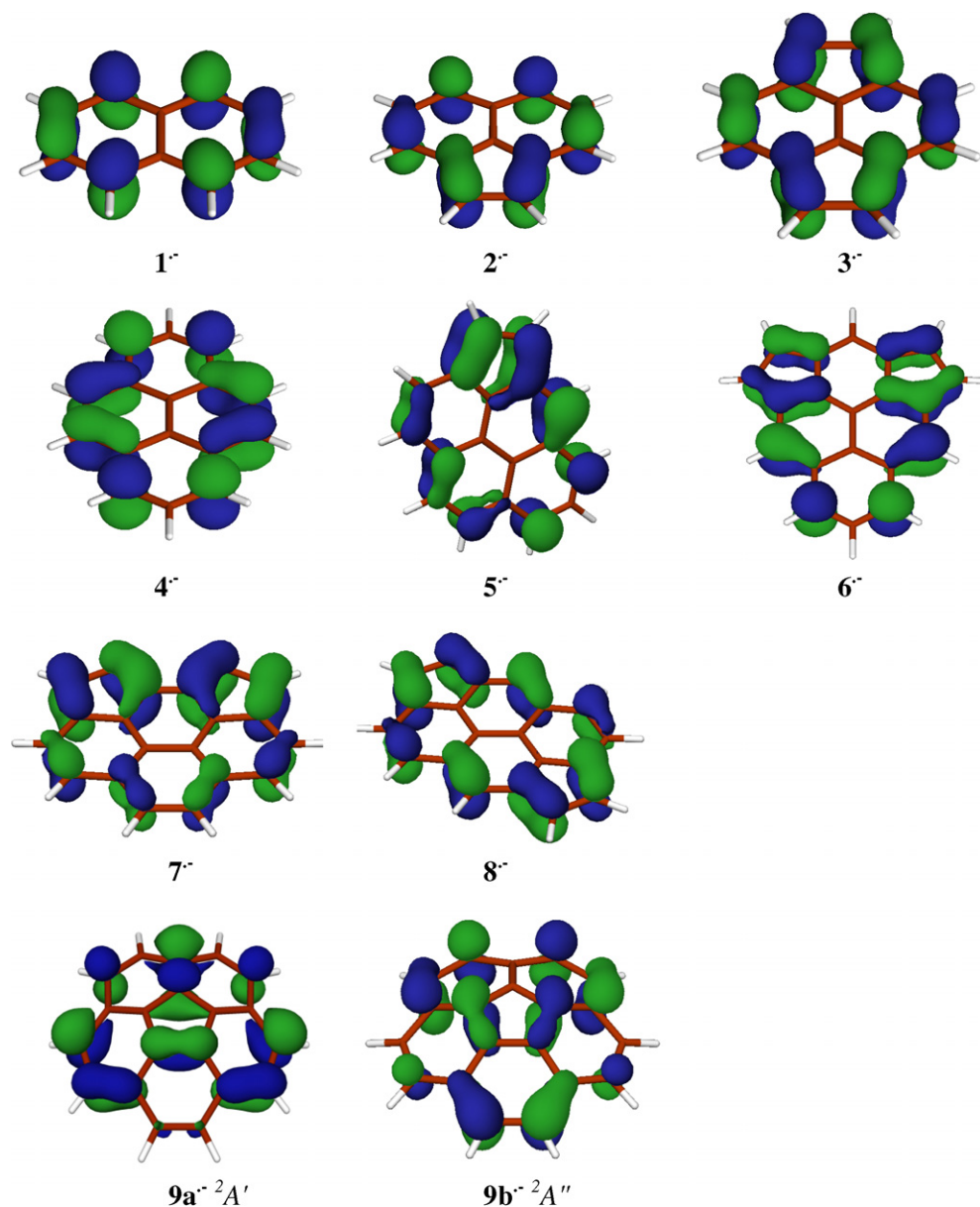


Fig. 2. B3LYP/DZP++ Singly occupied molecular orbitals (SOMOs) of  $1^{\bullet-}$ – $9^{\bullet-}$ . Note that the SOMOs are nearly identical to the LUMOs of the neutrals 1–9.

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 ( $9a^{\bullet-}$  and  $9b^{\bullet-}$ ).

In Table 2 the B3LYP/DZP++ AEAs for 1–9 calculated according to Eq. (2) [ $\text{AEA} = (E_{\text{tot}}(\text{neutral}) + \text{ZPVE}(\text{neutral})) - (E_{\text{tot}}(\text{anion}) + \text{ZPVE}(\text{anion}))$ ] 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 ( $\Delta\text{ZPVE}$ , 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  $1^{\bullet-}$ – $9^{\bullet-}$  (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  $E_{\text{tot}}$  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

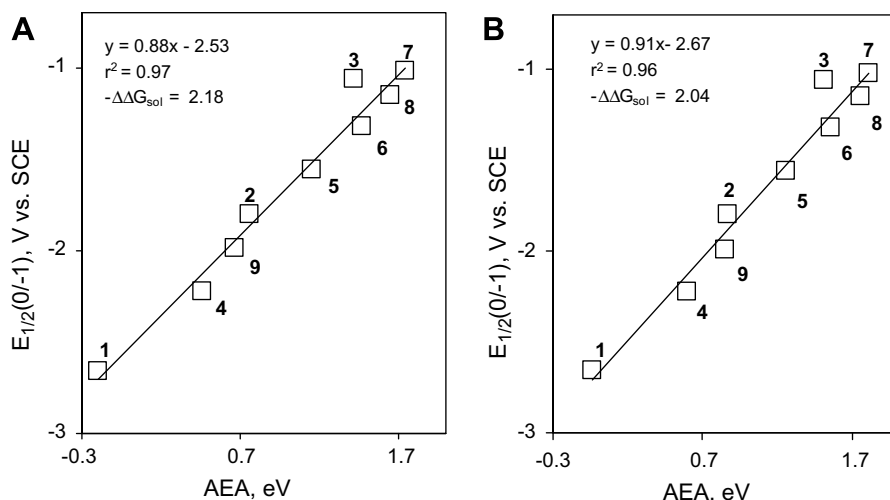


Fig. 3. Linear correlation between B3LYP/DZP++ AEA values without ZPVE (in eV, **A**) and with ZPVE (in eV, **B**) correction and  $E_{1/2}(0/-1)$  vs. SCE (in V) values [4] of 1–9.

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  $-\Delta\Delta G_{\text{sol}} + E_{\text{ref}}$  (with  $E_{\text{ref}} -4.71$  V [8,13]) a  $-\Delta\Delta G_{\text{sol}} = 2.18$  eV is calculated that is close to the value of  $1.99 \pm 0.05$  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  $-\Delta\Delta G_{\text{sol}}$  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 ( $1^{\cdot-}$ ) the extra electron is not bound [14,25], it is bound in the acenaphthylene radical anion ( $2^{\cdot-}$ ). 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  $\Delta\text{AEA}$  of 0.96 eV is found. A similar  $\Delta\text{AEA}$  (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 ( $\Delta\text{AEA}$ : 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  $\text{C}_{20}\text{H}_{10}$ , Fig. 1), unequivocally shows that 6–8 possess markedly more positive AEAs (Table 2). Hence, 6–8 are *inherently* better electron acceptors than 9 (see also [30]). Interestingly, the AEAs of 3 and 5–8 (Table 2), which are surface sub-structures of  $\text{C}_{60}$  and  $\text{C}_{70}$ , correspond to *Ca.* 53% (3) of the AEA of  $\text{C}_{60}$  ( $2.65 \pm 0.05$  eV [31]), and, *Ca.* 52% (3), 42% (5), 54% (6), 64% (7) and 61% (8) of that of  $\text{C}_{70}$  ( $2.72 \pm 0.05$  eV [31]). In contrast, the AEA of 9 corresponds to only *ca.* 25% of the AEAs of  $\text{C}_{60}$  and  $\text{C}_{70}$  [31].

The effect of a peripheral CP moiety also compares favourably to that exerted by *benz*-annulation in the alternant linear acene series ( $\Delta\text{AEA}$  *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 ( $\Delta\text{AEA}$  *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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