Pergamon

Tetrahedron Letters 43 (2002) 3833–3836

TETRAHEDRON
LETTERS

Externally-fused cyclopenta moieties in non-alternant CP-PAHs act as *peri*-substituents

Carola Koper, Leonardus W. Jenneskens* and Martin Sarobe

Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received 26 February 2002; revised 27 March 2002; accepted 5 April 2002

Abstract—The Hammett constants σ_m for the externally fused cyclopenta moiety in the CP-PAHs **1**(1,8-CP), **2**(1,9-CP), **3**(1,10-CP) and **4**(3,5-CP) have been determined. The σ_m values for these structurally different CP-PAHs are nearly identical. This gives evidence that the cyclopenta moiety acts as a *peri*-substituent with $\sigma_m = 0.4 \pm 0.07$. © 2002 Elsevier Science Ltd. All rights reserved.

Non-alternant polycyclic aromatic hydrocarbons containing cyclopenta moieties fused to their perimeter (CP-PAHs) are an abundant group of compounds from which several representatives possess genotoxic properties.[1,2] This is of considerable relevance as they are inadvertently formed during incomplete combustion processes.[3] In addition, CP-PAHs represent topological substructures of fullerenes and some of them have been proposed as building blocks for fullerenes under flame conditions.[3,4] Another illustrative property of CP-PAHs, which is in line with their non-alternant character, is their enhanced electron affinity. This is also a property of fullerenes.[5]

Although a qualitative survey of all possible closed-shell Kekulé resonance structures of CP-PAHs indicates that the π-electrons of the cyclopenta moiety are in conjugation with those of the aromatic core, experimental evidence suggests that this moiety has to be regarded as a *peri*-substituent. For example, CP-PAHs undergo addition reactions to the cyclopenteno double bond.[6] Unambiguous evidence for the presence of a localized cyclopenteno-like double bond is found in the available single-crystal X-ray structures. In the five-membered ring typical sp^2–sp^2 hybridized single (1.46 Å) and double (1.36 Å) carbon–carbon bonds are found.[7] In addition, in asymmetric CP-PAHs, which contain magnetically inequivalent cyclopenteno protons, the characteristic $^3J_{HH}$ coupling constant ($^3J_{HH} \sim$ 5.1–5.4 Hz) for cyclopentenes is observed.[8]

These results prompted us to study the electronic effect of annelation of a cyclopenta moiety to alternant PAH cores in more detail by cyclic voltammetry (CV). In Fig. 1, the cyclic voltammograms[9] of acenaphthylene [**1**(1,8-CP)], aceanthrylene [**2**(1,9-CP)], cyclopenta[*cd*]pyrene [**3**(1,10-CP)] and cyclopenta[*cd*]fluoranthene [**4**(3,5-CP)] are shown (see also Chart 1).

All CP-PAHs possess a (*pseudo*)-*reversible* first reduction wave [$E_{1/2}$ (0/−1) in V versus SCE]. Whereas for **1**(1,8-CP) the second reduction wave [$E_{1/2}$ (−1/−2) in V versus SCE] is not discernible within the available potential window (−2.5 to +3 V[9]), it is *irreversible* for **2**(1,9-CP) and **3**(1,10-CP), and (*pseudo*)-*reversible* for **4**(3,5-CP). If the redox potentials of these $C_{12}H_{18}$, $C_{16}H_{10}$ and $C_{18}H_{10}$ CP-PAHs are compared with those of corannulene ($C_{20}H_{10}$), a non-alternant PAH with an

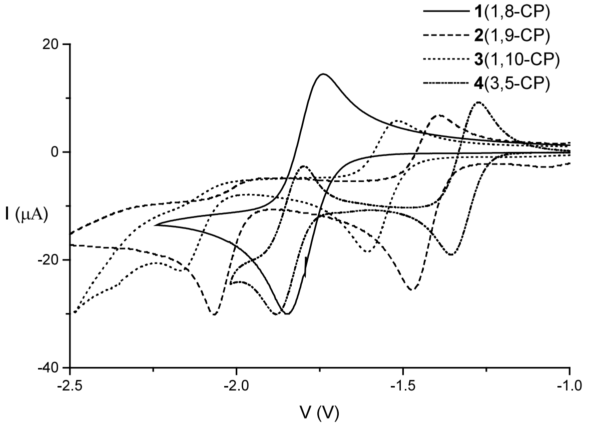

Figure 1. Reduction waves of **1**(1,8-CP), **2**(1,9-CP), **3**(1,10-CP) and **4**(3,5-CP) (in V versus SCE, scan rate is 50 mV s^{-1}).[9]

---

* Corresponding author. Fax: +31-30-2534533; e-mail: jennesk@chem.uu.nl

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(02)00683-4

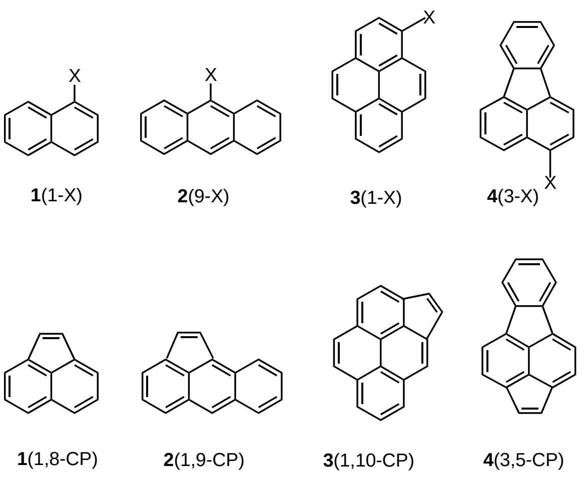

Chart 1.

internal cyclopenta moiety, known for its high electron affinity [$E_{1/2}$ (0/−1) in V versus SCE = −2.51 V],[10] it must be concluded that **1**(1,8-CP)–**4**(3,5-CP) possess higher electron affinities, albeit corannulene can accept up to four electrons.

A comparison of the $E_{1/2}$ (0/−1) values of **1**(1,8-CP), **2**(1,9-CP), **3**(1,10-CP) and **4**(3,5-CP) with those of the related parent PAHs shows an interesting feature (Table 1).[11] The annelation of a cyclopenta moiety leads to a shift of $E_{1/2}$ (0/−1) of ca. 0.9 V for **1**(1,8-CP) and ca. 0.6 V for **2**(1,9-CP)–**4**(3,5-CP). The nearly identical positive shift for **2**(1,9-CP)–**4**(3,5-CP) suggests that annelation of the cyclopenta moiety perturbs the core of the topologically different alternant PAHs in a systematic fashion. The larger shift of $E_{1/2}$ (0/−1) for **1**(1,8-CP) indicates that its core is more affected by external cyclopenta fusion. To verify the difference in $\Delta E_{1/2}$ (0/−1) between **1**(1,8-CP) and **2**(1,9-CP)–**4**(3,5-CP), the electron affinities (EA) of **1**(1,8-CP)–**4**(3,5-CP) and their related parent PAHs were calculated using AM1.[12] The difference, ΔEA [= EA(CP-PAH)−EA(PAH)], is 0.7 eV for **1**(1,8-CP) and 0.5 eV for **2**(1,9-CP)–**4**(3,5-CP), which reflects the trend [factor 1.4 increase for **1**(1,8-CP)] observed in the shift of $E_{1/2}$ (0/−1) values. Note that for **1**(1-H)–**4**(3-H) the LUMO has the correct orbital phase relationship to interact strongly with the LUMO of ethene. Thus, in the case of **1**(1,8-CP)–**4**(3,5-CP) the LUMO resembles the *in-phase* (bonding) combination of the LUMO of the corresponding alternant PAH cores and that of ethene. This gives a new LUMO level, whose energy is lower than that of its contributors.[13] The strongest interaction occurs in the case of **1**(1,8-CP). These results show that the externally-fused cyclopenta moiety in non-alternant PAHs can indeed be described as an electron accepting substituent.

To quantify the electronic effect exerted by the external cyclopenta moiety, the substituent constant σ_m for the externally-fused cyclopenta moiety was determined using the Hammett relation. Although both σ_m and σ_p constants were used for the Hammett relations, it will be shown that σ_m gives the better correlation (see also Ref. 14a).

For the construction of the Hammett plots (Eq. (1))[15] the first reduction potential of the *mono*-substituted PAHs **1**(1-X), **2**(9-X), **3**(1-X) and **4**(3-X) was measured using CV (Chart 1).[16,17] Unfortunately, most *mono*-substituted PAHs gave either a (*pseudo*)-*reversible* or *irreversible* first reduction wave. Therefore, instead of $E_{1/2}$ (0/−1) or E_{pc} (0/−1) values, E_{onset} (0/−1) values were used, which gives a reliable estimate of the substituent effect (Table 2).[18]

$$(n/0.059)E_{onset}\ (\mathrm{X}) = \rho\sigma + (n/0.059)E_{onset}\ (\mathrm{X}=\mathrm{H}) \qquad (1)$$

For all derivatives of compounds **1**–**4** the E_{onset} (0/−1) values were plotted against the appropriate substituent constants σ_m, which mainly contain inductive effects.[19] The Hammett relation with σ_m gives an excellent linear correlation over the complete σ range for all compounds **1**–**4** studied [Fig. 2, cf. Table 3 for correlation coefficients (r^2)]. The quality of the linear free energy relationship between E_{onset} (0/−1) and σ_m is substantiated by the intercepts, which have to correspond to the E_{onset} (0/−1) values of the parent PAHs **1**(1-H)–**4**(3-H) (Chart 1). They are indeed in close agreement with the experimental values (Tables 2 and 3). The Hammett parameter ρ, which is positive, i.e. reduction will be facilitated by electron-withdrawing substituents X, reflects the sensitivity of E_{onset} (0/−1) towards substitution (Table 3). For the series of compounds **2**–**4** similar ρ values are found, which are comparable to the ρ values reported in literature for Hammett relations between the first reduction potential of alkyl-substituted PAHs and σ^*.[14c,d] The Hammett relation derived for the *mono*-substituted 1-naphthalenes **1**(1-X) yields a significantly larger ρ value (factor 1.5). This is in agreement with the enhanced interaction of the naphthalene core and the ethene-like substituent, which

Table 1. Reduction potentials (in V versus SCE) of alternant PAHs **1**(1-H)–**4**(3-H) and the corresponding non-alternant CP-PAHs **1**(1,8-CP)–**4**(3,5-CP) (Chart 1)[a]

Parent PAH	$E_{1/2}$ (0/−1)	ΔE[b]	CP-PAH	$E_{1/2}$ (0/−1)	ΔE[b]	$\Delta E_{1/2}$ (0/−1)
1(1-H)	−2.66	0.10	**1**(1,8-CP)	−1.80	0.15	0.86
2(9-H)	−2.10	0.08	**2**(1,9-CP)	−1.47	0.09	0.63
3(1-H)	−2.22	0.08	**3**(1,10-CP)	−1.56	0.16	0.66
4(3-H)	−1.92	0.08	**4**(3,5-CP)	−1.33	0.11	0.59

[a] E_{red} (−1/−2): **2**(1,9-CP) −2.06 V and **3**(1,10-CP) −2.22 V, and $E_{1/2}$ (−1/−2): **4**(3,5-CP) −1.86 V, ΔE = 0.25 V.

[b] $\Delta E = E_{pc} - E_{pa}$.[9]

Table 2. E_{onset} (0/−1) values (in V versus SCE) for **1**(1-X), **2**(9-X), **3**(1-X) and **4**(3-X) (Chart 1)

X	σ_m	σ_p	E_{onset} (0/−1)			
			1	**2**	**3**	**4**
H	0	0	−2.54	−2.02	−2.13	−1.81
NH_2	−0.16	−0.66	[a]	−2.14	−2.27	−1.20
CH_3	−0.06	−0.14	−2.59	−2.05	[b]	[b]
C_2H_5	−0.08	−0.13	−2.73	[b]	−2.18	[b]
C≡CH	0.20	0.23	−2.20	−1.72	−1.87	−1.59
$COCH_3$	0.36	0.47	−1.85	[b]	−1.47	−1.41
NO_2	0.71	0.81	−1.11	−1.01	−1.07	−0.89
CP			−1.70	−1.37	−1.49	−1.24

[a] Not measured due to available potential window.[9]

[b] Not determined.

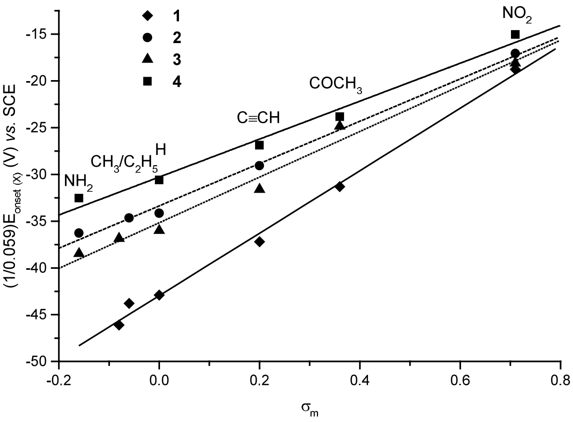

Figure 2. Hammett plots of **1**(1-X), **2**(9-X), **3**(1-X) and **4**(3-X); (1/0.059) E_{onset} (0/−1) (in V versus SCE) versus σ_m.

Table 3. Hammett parameters obtained for E_{onset} (0/−1) (in V versus SCE) versus σ_m for series **1**–**4** and σ_m values for **1**(1,8-CP), **2**(1,9-CP), **3**(1,10-CP) and **4**(3,5-CP)

	r^2[a]	a[b]	ρ (V)[c]	s (ρ)[d]	σ_m	s (σ)[d]
1	0.995	−2.54	2.0	0.09	0.42	0.04
2	0.995	−1.97	1.3	0.05	0.45	0.03
3	0.983	−2.07	1.4	0.09	0.41	0.04
4	0.985	−1.79	1.2	0.09	0.46	0.05

[a] Correlation coefficient.

[b] a is E_{onset} (0/−1) for X = H (in V versus SCE), see also Table 2.

[c] Slope×0.059.[9,15]

[d] Standard deviation.

was advanced to explain the increased shift of $E_{1/2}$ (0/−1) for **1**(1-CP) (ΔE (0/−1) in Table 1 and ΔEA (AM1),[12] vide supra).

From the linear free energy relationships in combination with the measured E_{onset} (0/−1) of the CP-PAHs **1**(1,8-CP), **2**(1,9-CP), **3**(1,10-CP) and **4**(3,5-CP), σ_m values for the externally-fused cyclopenta moiety were estimated. Interestingly, despite the substantial structural variation of **1**(1,8-CP), **2**(1,9-CP), **3**(1,10-CP) and **4**(3,5-CP), the values derived for σ_m are 0.42, 0.45, 0.41 and 0.46, respectively; they are nearly identical. Apparently, the effect of the cyclopenta moiety on the different aromatic cores is indeed similar. This gives compelling evidence that the externally-fused cyclopenta moiety indeed acts as a *peri*-substituent.

In contrast to the excellent Hammett relations found between E_{onset} (0/−1) and σ_m for the series **1**–**4**, no single correlation spanning the whole σ range was found if σ_p was used. In this case the NH_2 derivatives deviate markedly, presumably due to a dominating resonance effect. This resonance effect will influence the mode of charge distribution and thereby ρ. As a consequence, the Hammett relation between the reduction potential and σ_p yields two lines, one for $\sigma_p<0$ and one for $\sigma_p>0$, of which the first has a smaller ρ value. Since the reduction potential E_{onset} (0/−1) of the cyclopenta-fused PAHs falls in the same range as the acetyl-substituted PAHs, the line for $\sigma_p>0$ will be of interest. We noted that the linear relationship for $\sigma_p>0$ is comparable to the one obtained for the relation between the E_{onset} (0/−1) and σ_m.

The similar σ_m values derived for the different CP-PAHs suggest that the cyclopenta moiety is well described using a substituent constant that mainly consists of inductive effects. This is in agreement with recent ab initio valence bond calculations on **1**(1,8-CP), **3**(1,10-CP), **4**(3,5-CP) and other CP-PAHs in which the relative energies and weights of all possible closed shell Kekulé resonance structures are taken into account.[20] In all cases the results show that Kekulé resonance structures in which the cyclopenta moiety participates in π electron delocalization have higher energies and negligible weights.

References

1. Howard, J. B.; Longwell, J. P.; Marr, J. A.; Pope, C. J.; Busby, W. F., Jr.; Lafleur, A. L.; Taghizadeh, K. *Combust. Flame* **1995**, *101*, 262–270.
2. Lafleur, A. L.; Longwell, J. P.; Marr, J. A.; Monchamp, P. A.; Pummer, E. F.; Thilly, W. G.; Mulder, P. P. Y.; Boere, B. B.; Cornelisse, J.; Lugtenburg, J. *Environ. Health Perspect.* **1993**, *101*, 146–153.
3. Lafleur, A. L.; Howard, J. B.; Taghizadeh, K.; Plummer, E. F.; Scott, L. T.; Necula, A.; Swallow, K. C. *J. Phys. Chem.* **1996**, *100*, 17421–17428.

4. (a) Jenneskens, L. W.; Sarobe, M.; Zwikker, J. W. *Pure Appl. Chem.* **1996**, *68*, 219–224 and references cited therein; (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291–300 and references cited therein.
5. (a) Haddon, R. C. *Phil. Trans. R. Soc. Lond. A* **1993**, *343*, 53–62; (b) Ruoff, R. S.; Kadish, K. M.; Boulas, P.; Chen, E. C. M. *J. Phys. Chem.* **1995**, *99*, 8843–8850; (c) Fowler, P. W.; Ceulemans, A. *J. Phys. Chem.* **1995**, *99*, 508–510.
6. (a) Trost, B. M.; Bright, G. M. *J. Am. Chem. Soc.* **1967**, *89*, 4244–4245; (b) Nyholm, S. H.; Alexander, J.; Lundanes, E.; Frandsen, H.; Andersson, R.; Grivas, S.; Nesnow, S.; Holme, J. A. *Carcinogenesis* **1996**, *117*, 1111–1120; (c) Gold, A.; Eisenstadt, E. *Cancer Res.* **1980**, *40*, 3940–3944.
7. (a) Freiermuth, B.; Gerber, S.; Riesen, A.; Wirz, J.; Zehnder, M. *J. Am. Chem. Soc.* **1990**, *112*, 738–744; (b) Lutz, M.; Spek, A. L.; Sarobe, M.; Jenneskens, L. W. *Acta Crystallogr.* **1999**, *C55*, 659–661; (c) Dang, H.; Levitus, M.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 136–143.
8. Brügel, W. *Handbook of NMR Spectral Parameters*; Heyden & Son, Ltd., 1979; Vol. 1.
9. Cyclic voltammetry (CV) was performed using an EG&G Potentiostat/Galvanostat Model 263A in CH_3CN (freshly distilled from CaH_2) containing 0.1 M Bu_4NPF_6 as supporting electrolyte at scanning rates of 50 and 100 mV s^{-1} (potential window −2.5 to +3 V). Redox potentials were determined relative to an $Ag/AgNO_3$ reference electrode (0.1 M in CH_3CN) and were referenced to SCE by measuring the oxidation potential of the $FeCp_2/FeCp_2^{\bullet +}$ couple (0.31 V versus SCE).
10. See for example: Seiders, T. J.; Baldridge, K. K.; Siegel, J. S.; Gleiter, R. *Tetrahedron Lett.* **2000**, *41*, 4519–4522 and references cited therein.
11. E_{onset} (0/−1) and $\Delta E = E_{pc} - E_{pa}$ values were determined at a scanning rate of 50 mV s^{-1}. At a higher scanning rate (100 mV s^{-1}) an increase of ΔE (ca. 10 mV) is found, which is in line with the (*pseudo*)-*reversible* behavior of the compounds. For a review: Heinze, J. *Angew. Chem.* **1984**, *96*, 823–840 and references cited therein.
12. AM1 calculations (MOPAC 7); all minima were characterized using a Hessian calculation. The EAs of (CP)-PAHs were calculated as the difference in ΔH_f° values of the optimized (CP)-PAHs and their corresponding radical-anions. The radical anions were optimized using the RHF half-electron method. See also Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
   PAH: ΔH_f° (kcal mol^{-1}): **1**(1-H) 40.6; **2**(1-H) 62.9; **3**(1-H) 67.3; **4**(3-H) 87.9. $PAH^{\bullet -}$: ΔH_f° (kcal mol^{-1}): **1**(1-H) 26.2; **2**(1-H) 35.3; **3**(1-H) 39.2; **4**(3-H) 56.8. CP-PAH: ΔH_f° (kcal mol^{-1}): **1**(1,8-CP) 80.7; **2**(1,9-CP) 103.2; **3**(1,10-CP) 109.1; **4**(3,5-CP) 140.8. CP-$PAH^{\bullet -}$: ΔH_f° (kcal mol^{-1}): **1**(1,8-CP) 50.2; **2**(1,9-CP) 63.0; **3**(1,10-CP) 70.2; **4**(3,5-CP) 98.7. ΔEA = EA(CP-PAH)-EA(PAH) **1**, 0.70, **2**, 0.55, **3**, 0.46, **4**, 0.48 eV.
13. See also: Plummer, B. F. *J. Phys. Chem.* **1987**, *91*, 5035–5037.
14. (a) For example: Choy, N.; Kim, C.-S.; Ballestro, C.; Artigas, L.; Diez, C.; Lichtenberger, F.; Shapiro, J.; Russell, K. C. *Tetrahedron Lett.* **2000**, *41*, 6955–6958; (b) Keshavarz, K. M.; Knight, B.; Haddon, R. C.; Wudl, F. *Tetrahedron* **1996**, *52*, 5149–5159; (c) Klemm, L. H.; Koilik, A. J.; Desai, K. B. *J. Org. Chem.* **1963**, *28*, 625–630; (d) Klemm, L. H.; Koilik, A. J. *J. Org. Chem.* **1963**, *28*, 2044–2049.
15. In Eq. (1) *n* stands for the number of electrons involved in the redox process.
16. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980.
17. Compounds **1**–**4** (X = C≡CH, $COCH_3$, CP) were synthesized according to literature procedures.[21] Compounds **1**–**4** (X = NH_2) were obtained by catalytic reduction of the corresponding compounds with X = NO_2. All other compounds were purchased commercially. *Caution:* (CP)-PAHs are potential genotoxic compounds.
18. The use of peak potentials (E_{pc}) for irreversible processes will give unreliable information due to the strong dependence of E_{pc} on factors such as solvent, electrolyte, scan rate and the concentration of the analyte. In contrast, E_{onset} (0/−1) is virtually independent of these factors and therefore will provide a proper estimate of the substituent effect.[16]
19. Exner, O. *Correlation Analysis of Chemical Data*; Plenum Press: New York, 1988.
20. (a) Havenith, R. W. A.; van Lenthe, J. H.; Dijkstra, F.; Jenneskens, L. W. *J. Phys. Chem. A* **2001**, *105*, 3838–3845; (b) Havenith, R. W. A.; van Lenthe, J. H.; Jenneskens, L. W., manuscript in preparation.
21. (a) Sarobe, M. *Consequences for Carbon Build up during Combustion and Fullerene Formation Processes. Polycyclic Aromatic Hydrocarbons under High Temperature Conditions*; Utrecht University: Utrecht, The Netherlands, 1998; (b) Sarobe, M.; Jenneskens, L. W.; Wesseling, J.; Snoeijer, J. D.; Zwikker, J. W.; Wiersum, U. E. *Liebigs. Ann./Recueil* **1997**, 1207–1213; (c) Sarobe, M.; Zwikker, J. W.; Snoeijer, J. D.; Wiersum, U. E.; Jenneskens, L. W. *J. Chem. Soc., Chem. Commun.* **1994**, 89–90; (d) Sarobe, M.; Snoeijer, J. D.; Jenneskens, L. W.; Slagt, M. Q.; Zwikker, J. W. *Tetrahedron Lett.* **1995**, *36*, 8489–8492.