ChemComm

Triscyclopenta[*cd,fg,jk*]pyrene: another congener of the externally cyclopenta-fused pyrene series

Martin Sarobe,[a] **Remco W. A. Havenith**[ab] **and Leonardus W. Jenneskens***[a]

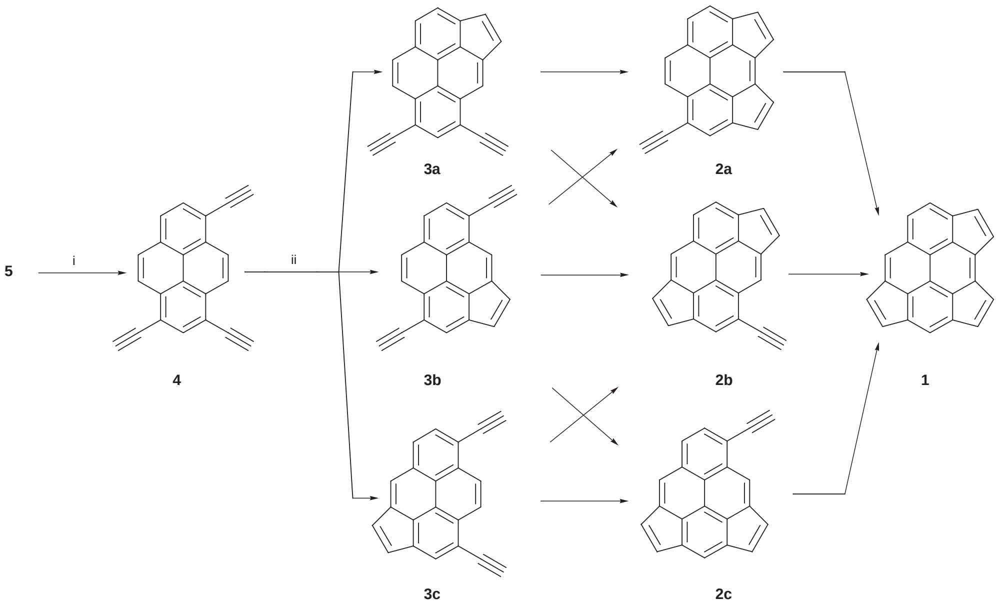
[a] *Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: jennesk@chem.uu.nl*
[b] *Debye Institute, Theoretical Chemistry Group, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received (in Liverpool, UK) 3rd March 1999, Accepted 23rd April 1999

Flash vacuum thermolysis of 1,3,6-tris(1-chloroethenyl)pyrene 5 between 900–950 °C gave the thermally labile triscyclopenta[*cd,fg,jk*]pyrene 1; in line with the 'conjugated circuits model' and supported by IGLO III//RHF/6-31G calculations, all hydrogen atoms of 1 are additionally shielded by 0.4–0.9 ppm (^{1}H NMR).

Flash vacuum thermolysis (FVT, 10^{-2} Torr, 1000 °C) of 1-(1-chloroethenyl)pyrene, *viz.* 'masked' 1-ethynylpyrene, quantitatively gave the ubiquitous and genotoxic combustion effluent cyclopenta[*cd*]pyrene **8** [mass recovery (MR) 90%].[1] This result supports the proposal[2] that ethynyl-substituted polycyclic aromatic hydrocarbons (E-PAH) play a pivotal role in the formation of externally cyclopenta-fused PAH (CP-PAH) effluents under high temperature conditions in the gas phase, *viz.* during combustion. Since 1-ethynylpyrene is thought to arise from C_2 and/or C_2H_2 addition to pyrene **7**,[3] we anticipated that multiple ethynyl-substituted pyrenes might be precursors for congeners of **8** containing multiple externally fused cyclopenteno units, that may represent hitherto unidentified combustion effluents. FVT of 1,6-, 1,8- and 1,3-bis(1-chloroethenyl)pyrene gave in reasonable to good yields dicyclopenta[*cd,jk*]- (**6a**), dicyclopenta[*cd,fg*]- (**6b**) and dicyclopenta[*cd,mn*]pyrene (**6c**), respectively,[4,5] which were all stable up to 1100 °C.† Subsequently, **6a–c** were indeed identified in flames as the three most abundant $C_{20}H_{10}$ CP-PAH combustion effluents.[6] Furthermore, it was shown that dicyclopenta-fusion topology markedly affects the electronic and magnetic properties of **6a-c**. Their gross ^{1}H NMR features, *i.e.* their average five- [$\delta(5)_{av}$] and six-membered ring [$\delta(6)_{av}$] ^{1}H chemical shifts, revealed that all hydrogen atoms of **6a,b** are 0.4–0.8 ppm more shielded than those of **6c** and **8** [$CDCl_3$; $\delta(5)_{av}/\delta(6)_{av}$: **6a**, 6.90/7.58, **6b**, 6.66/7.55, **6c**, 7.36/8.32 and **8**, 7.34/8.19].[4,5] These results were qualitatively rationalized using the obsolete ring perimeter model of Platt.[7] Whereas for **6a**,**b** two of the seven Kekulé resonance structures are anti-aromatic (16π-electron ring perimeter), similar anti-aromatic, ring perimeter resonance structures are unavailable for **6c** and **8**.[5,8] However Randić's conjugated circuits model,[9] which takes into account contributions of *all* possible [4*n*+2] and [4*n*] π-electron conjugated circuits, gives a better interpretation. It is readily shown that in the case of **6c** and **8** [4*n*] π-electron conjugated circuits are absent in their possible Kekulé resonance structures.

Here we report the synthesis of triscyclopenta[*cd,fg,jk*]pyrene **1** ($C_{22}H_{10}$) by FVT of 1,3,6-tris(1-chloroethenyl)pyrene **5**, *viz.* 'masked' 1,3,6-trisethynylpyrene **4** (Scheme 1),‡ and its salient spectroscopic properties. FVT (10^{-2} Torr, sublimation at 180 °C, rate 50 mg h^{-1}) of **5** (50 mg aliquots) was done at 800, 900, 950 and 1000 °C.§ In the 800 °C pyrolysate (MR 50%) the $C_{22}H_{10}$ (CP)-PAH **4** (30%),‡ the bisethynylcyclopenta[*cd*]pyrenes (**3a–c**, 20%) and traces of the ethynyldicyclopentapyrenes (**2a–c**) were identified [^{1}H NMR, GC-MS (Scheme 1)]. Surprisingly, the known $C_{20}H_{10}$, $C_{18}H_{10}$ and $C_{16}H_{10}$ (CP)-PAHs, 1,6-, 1,8- and 1,3-bisethynylpyrene (combined yield 20%),[4] 1-, 6- and 8-ethynylcyclopenta[*cd*]pyrene (combined yield 16%),[4] **6a–c** (1%),[4,5] **7** (7%) and **8** (5%),[1] respectively, were also found as side products (^{1}H NMR, GC-MS, GC-IR, HPLC). Hence, fragmentation reactions, *viz.* C_2 extrusions,[10] are competitive. At 900 °C (MR 20%) and 950 °C (MR 15%),§ instead of **4**, a novel compound (900 °C, 30% and 950 °C, 40%) was identified besides the fragmentation products



Scheme 1 *Conditions*: i, FVT (10^{-2} Torr, 800 °C); ii, FVT (10^{-2} Torr, $900 \leqslant T < 1000$ °C).

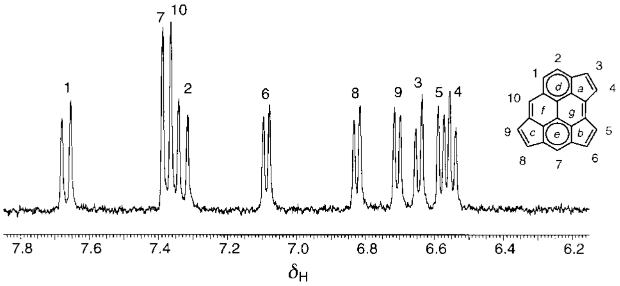


Fig. 1 ^{1}H NMR (300.13 MHz, acetone-d_6) spectrum of **1** (Table 1). See text for NICS(IGLO III//RHF/6-31G) (ref. 13) values *a*–*f*. Selected RHF/6-31G carbon–carbon bond lengths (in Å) (C_s): 1-2, 6a-7, 7-7a 1.41; 1-1a 1.40; 1a-10 1.48; 2-2a 1.39; 4a-5a 1.37; 9a-10, 1.36; 3-4, 5-6, 8-9 1.35; 2a-3, 4-4a, 5a-5, 6-6a, 7a-8, 9-9a 1.49 [*cf.* **7** (D_{2h}): 1-2, 1-1a, 1.39; 9-10, 1.34; 1a-10 1.44 and **8** (C_s): 1-2, 1-1a 1.40; 2-2a, 5a-6, 6-7, 7-8, 8-8a, 1.39; 2a-3 4-4a, 1.48; 3-4, 4a-5, 9-10 1.35; 5-5a 1.46; 8a-9, 1a-10, 1.45].

Table 1 δ_H (exp) *vs.* δ_H (IGLO) values of **1**

H atom[a]	δ_H(exp) [J/Hz][b]	δ_H (IGLO)[c]	$\Delta\delta$[d] (ppm)
1	7.67 [7.5]	8.35	0.68
2	7.33 [7.5]	7.87	0.54
3	6.65 [5.4]	7.32	0.67
4	6.54 [5.4]	7.23	0.69
5	6.58 [5.1]	7.28	0.70
6	7.09 [5.1]	7.77	0.68
7	7.39	8.03	0.64
8	6.82 [5.1]	7.51	0.69
9	6.71 [5.1]	7.24	0.53
10	7.36	7.99	0.63

[a] Fig. 1. [b] $^3J_{HH}$ coupling constants. [c] IGLO III//RHF/6-31G (ref. 12); Me$_4$Si at σ_H 32.1 or σ_C 196.1 ppm. [d] $\Delta\delta = \delta_H - \delta_H$(exp); mean deviation = 0.65 ppm.

(^{1}H NMR). Column chromatography (silica, *n*-hexane) of the 950 °C pyrolysate gave a pure sample (*ca.* 5 mg) that could be assigned to **1** [^{1}H, ^{13}C NMR, (HR)FAB-MS (Fig. 1)].¶ Whereas in the 950 °C pyrolysate besides **1** (40%) the $C_{20}H_{10}$ CP-PAH **6a**[4,5] (40%) is the other major product, the latter is the sole product upon FVT of **5** at 1000 °C [(MR *ca.* 10%) ^{1}H NMR, GC-MS]. In contrast with the prediction[11] that **1** represents a high temperature 'stabilomer', and the thermal stability of **6a-c**[4,5] and **8**,[1]† as well as their E-PAH precursors,[1,4] **1** and **4** are susceptible to fragmentation (C$_2$ extrusions[10]) under the FVT conditions.

The ^{1}H NMR chemical shifts of **1** resemble those of **6a**,**b** {Fig. 1 and Table 1 [$\delta(5)_{av}/\delta(6)_{av}$: **1** (acetone-$d_6$) 6.74/7.44, **6a** (CDCl$_3$) 6.90/7.58 and **6b** (CDCl$_3$) 6.66/7.55.[4,5]]}. This gives further credence to the applicability of the 'conjugated circuits model'.[9] Although **1** with its 17-carbon atom ring perimeter does not have any *closed shell* [4*n*] π-electron ring perimeter resonance structures, many [4*n*] (with n = 3, 4, 5) π-electron conjugated circuits can be distinguished in its available Kekulé resonance structures. Consequently, in analogy with **6a**–**b**, all its hydrogen atoms are 0.4–0.9 ppm more shielded than those of **6c** and **8** [$\delta(5)_{av}/\delta(6)_{av}$: **6c** (CDCl$_3$) 7.36/8.32[4,5] and **8** (CDCl$_3$) 7.34/8.19[1]]. This qualitative interpretation is further corroborated by *ab initio* calculations.

For **1** (C_s symmetry) a pyrene-like *ab initio* RHF/6-31G structure containing three cyclopenteno moieties with distinct sp^2–sp^2 carbon–carbon double (1.35 Å) and single (1.49 Å) bonds was obtained (Fig. 1). In addition, the IGLO III//RHF/6-31G[12] δ_H and δ_C chemical shifts of **1** were in good agreement with the experimental data (Table 1).¶ A comparison of the IGLO III//RHF/6-31G anisotropy of the diamagnetic magnetic susceptibility $\Delta\chi$ ($= \chi_{\text{out-of-plane}} - \chi_{\text{in-plane}}$)‖ of **1**, **7** and **8**, respectively, showed that **7** ($\Delta\chi$ −248.5 ppm cgs) and **8** ($\Delta\chi$ −267.2 ppm cgs) possess similar values. In contrast, $\Delta\chi$ of **1** (−206.5 ppm cgs) is substantially less negative due to changes of $\chi_{\text{out-of-plane}}$ and $\chi_{\textit{in-plane}}$ (ratio $\chi_{\text{out-of-plane}}/\chi_{\text{in-plane}}$: **1**; −314.2/−107.7 = 2.9, **7**; −359.9/−92.7 = 3.9 and **8**; −333.7/−85.2 = 3.9). Hence, **1** will have a reduced ring current[12] leading to additional shielding of all hydrogen atoms. The magnetic properties of the individual rings of polycyclic **1** using the nucleus independent chemical shift criterion [NICS(IGLO III//RHF/6-31G); 0.5 Å above each ring center[13]] reveal that the five-membered rings are anti-aromatic (*a*: 10.7, *b*: 4.8 and *c*: 5.3 ppm), the top/bottom six-membered rings are aromatic (*d*: −9.6 and *e*: −9.4 ppm) and the central ones are nearly non-aromatic [*f*: 1.3 and *g*: 0.5 ppm (Fig. 1)]. The NICS results indicate that **1**, like **7** and **8**,‖ is best represented by a Clar-type[14] structure. In going from **7** to **8** and finally **1**, the related NICS values of the five- (six-) membered rings become more positive (less negative); their anti-aromatic (aromatic) character increases (decreases).

Financial support [M. S. Basque Government (Beca de Formacion de Investigadores)], discussions with Dr J. H. van Lenthe (Utrecht University) and fruitful suggestions from a referee are acknowledged.

Notes and references

† At 1100 °C **6c** gave some **8** (16%) (ref. 4).

‡ Independent synthesis for **4**: Treatment of **5** with Na/NH$_3$ (l) (ref. 15) at −40 °C gave **4** (yield 40%). For **5**: Acetylation (3.5 equiv.) of **7** gave 1,3,6-trisacetylpyrene (ref. 16), which by treatment with PCl$_5$ (3.5 equiv. (ref. 1,4) gave **5** (overall yield 16%). Satisfactory analytical data [^{1}H, ^{13}C NMR, FT-IR, (HR)MS and/or EA] were found for **4** and **5**.

§ Only *ca.* 50% w/w of **5** sublimed into the hot zone, the remainder gave an intractable solid in the sample flask. At T ⩾ 900 °C carbonization became a competitive process. Pure **4** could not be sublimed into the hot zone; upon heating it gave an intractable solid.

¶ *Selected data* for **1**: δ_C(75.46 MHz, acetone-d_6) 139.1 (*C*H), 137.8 (*C*H), 135.3 (*C*H), 133.0 (*C*H), 130.6 (*C*H), 129.6 (*C*H), 126.9 (*C*H), 126.3 (*C*H), 124.6 (*C*H), 119.8 (*C*H), quaternary C not resolved; *m/z* (FAB-MS) 274 (**1**$^+$); (HRFAB-MS: calc. for $C_{22}H_{10}$ 274.0783, found 274.0750); λ_{max}(n-C_6H_{14})/nm (log ε) 550.0 (2.27), 485.0 (2.92), 455.0 (2.94), 420.5 (3.19), 397.0 (3.22), 338.5 (3.63), 297.5 (3.70), 240.0 (4.06), 205.0 (4.10); E_{tot} (a.u.) [RHF/6-31G (IGLO III//RHF/6-31G)] −838.595341 (−839.154631); δ_C(IGLO) 152.2, 148.9 (*C*H), 147.2, 145.8, 145.6 (*C*H), 145.5, 145.2, 144.7 (*C*H), 143.3, 140.8, 140.4, 140.2, 139.9, 139.1 (*C*H), 138.9 (*C*H), 136.9 (*C*H), 132.9 (*C*H), 132.6 (*C*H), 129.0, 128.5 (*C*H), 125.3 (*C*H), 122.7.

‖ $\chi_{\text{out-of-plane}} = \chi_{zz}$ and $\chi_{\text{in-plane}} = 0.5(\chi_{xx} + \chi_{yy})$ in ppm cgs; −/+ $\Delta\chi$ = dia-/para-magnetic (ref. 12). NICS(IGLO III//RHF/6-31G; 0.5 Å) (ref. 13) values: **7**, *d/e* −14.6 and *f/g* −5.5 ppm and **8**, *a* 2.0, *d* −13.2, *e* −13.4, *f* −4.9 and *g* −4.7 ppm.

1 M. Sarobe, J. W. Zwikker, J. D. Snoeijer, U. E. Wiersum and L. W. Jenneskens, *J. Chem. Soc., Chem. Commun.*, 1994, 89.
2 For a recent review: U. E. Wiersum and L. W. Jenneskens, in *Gas Phase Reactions in Organic Synthesis*, ed. Y. Vallée, Gordon and Breach, Amsterdam, The Netherlands, 1997, ch. 3, pp. 143–194.
3 H. Bockhorn, F. Fetting and H. W. Wenz, *Ber. Bunsenges. Phys. Chem.*, 1983, **87**, 1067 and references cited therein.
4 M. Sarobe, S. Flink, L. W. Jenneskens, B. L. A. van Poecke and J. W. Zwikker, *J. Chem. Soc., Chem. Commun.*, 1995, 2415.
5 L. T. Scott and A. Necula, *J. Org. Chem.*, 1996, **61**, 386.
6 A. L. Lafleur, J. B. Howard, K. Taghizadeh, E. F. Plummer, L. T. Scott, A. Necula and K. C. Swallow, *J. Phys. Chem.*, 1996, **100**, 17421 and references cited therein.
7 J. R. Platt, *J. Chem. Phys.*, 1954, **22**, 1448.
8 M. Kataoka, *Tetrahedron*, 1997, **53**, 12 875.
9 M. Randić, *Tetrahedron*, 1977, **33**, 1905 and references cited therein.
10 R. F. C. Brown, K. J. Coulston and F. W. Eastwood, *Tetrahedron Lett.*, 1996, **37**, 6819.
11 S. E. Stein and A. Fahr, *J. Phys. Chem.*, 1985, **89**, 3714.
12 U. E. Fleischer, W. Kutzelnigg, P. Lazzaretti and V. Mülhenkamp, *J. Am. Chem. Soc.*, 1994, **116**, 5298 and references cited therein.
13 P. von Rague Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317.
14 E. Clar, in *Polycyclic Hydrocarbons*, Academic Press, London, 1964.
15 W. Ried and V.B. Saxema, *Angew. Chem.*, 1968, **80**, 366.
16 P. H. Gore, in *Friedel and Crafts and Related Reactions*, ed. G. A. Olah, Interscience, New York, vol. III, 1964, pp. 74–80.

Communication 9/01717H