Cyclopent[*fg*]acepyrylene, Cyclopent[*jk*]acepyrylene and Cyclopent[*mn*]acepyrylene: Novel $C_{20}H_{10}$ Cyclopenta-fused Polycyclic Aromatic Hydrocarbons

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Flash vacuum thermolysis of 1,8- (**2a**), 1,6- (**2b**) and 1,3-bis(1-chloroethenyl)pyrene (**2c**) gives the novel $C_{20}H_{10}$ cyclopenta-fused Polycyclic Aromatic Hydrocarbons (CP-PAHs) cyclopent[*fg*]- (**1a**), cyclopent[*jk*]- (**1b**) and cyclopent[*mn*]acepyrylene (**1c**), respectively; bis(cyclopenta-fusion) topology has a profound influence on their properties.

The non-alternant cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) have been recognized as major combustion effluents.[1] Despite their ubiquitous presence and potential mutagenic, carcinogenic and/or toxic activity,[2] little is known about their thermal build up and interconversions under high temperature conditions. Generally, their identification is hampered by the lack of well defined reference samples. Besides the above, non-alternant CP-PAHs may also possess interesting electronic properties for new organic materials[3] and are considered as model compounds for the rationalization of fullerene chemistry.[4]

The hitherto unknown $C_{20}H_{10}$ CP-PAHs cyclopent[*fg*]- (**1a**), cyclopent[*jk*]- (**1b**) and cyclopent[*mn*]acepyrylene (**1c**) have been proposed to be intermediates in carbon network formation at high temperatures[5] and, more recently, as important combustion effluents (Scheme 1).[6]

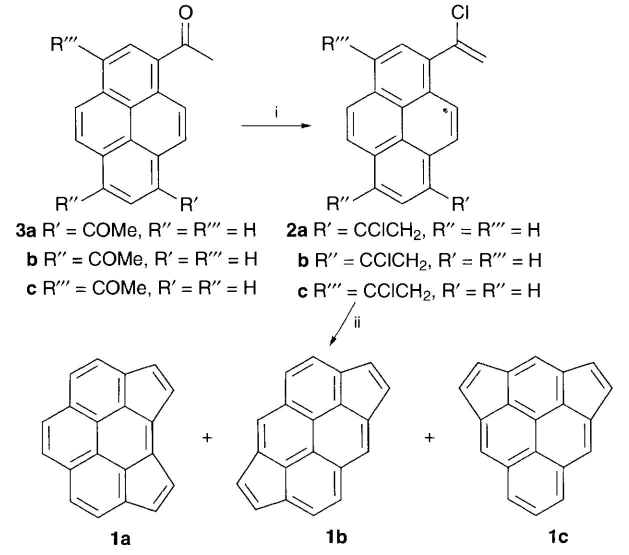
Here we report the synthesis of **1a–c** by Flash vacuum thermolysis (FVT) of bis(1-chloroethenyl)pyrenes **2a–c**. It is shown that bis(cyclopenta-fusion) topology has a marked influence on the properties of **1a–c**.

Precursors **2a–c** were obtained using the following procedure. Bisacetylation[7] of pyrene gave a mixture of 1,8- (**3a**), 1,6- (**3b**) and 1,3-bisacetylpyrenes (**3c**) in the ratio 3 : 1 : 1 from which pure **3a** and **3b** could be isolated by crystallization (Scheme 1).† Crystallization in the case of **3c** only gave an enrichment (75%; impurity **3b** 25%). Treatment of **3a**, **3b** and the enriched **3c** fraction with 2.5 equiv. of PCl_5[7] gave 1,8- (**2a**), 1,6- (**2b**) and and 1,3-bis(1-chloroethenyl)pyrene (**2c**), respectively.†

FVT of **2a–c** (50 mg, 10^{-2} Torr, sublimation temp. 140 °C, rate 100 mg h^{-1}) at the temperatures shown in Table 1, followed by ^1H NMR, GC-MS and HPLC analysis of the pyrolysates unequivocally shows that bis(cyclopenta-fusion) is a consecutive process.‡ Between 700–800 °C, pyrene derivatives **4a–c** containing both a 1-chloroethenyl and an ethynyl substituent were identified. At $T \geqslant 800$ °C they are converted into bisethynylpyrenes **5a–c**, subsequently into ethynylcyclopenta[*cd*]pyrenes (**6a–c**) and finally into cyclopent[*fg*]- (**1a**), cyclopent[*jk*]- (**1b**) and cyclopent[*mn*]acepyrylene (**1c**), respectively.† While FVT of **2a–b** at 1100 °C gave pure **1a** and **1b**, respectively, FVT of **2c** at 1100 °C yielded a pyrolysate containing **1c** (78%), **6c** (6%) and cyclopenta[*cd*]pyrene [**7** (16%),[7] Table 1]. The identification of **7** suggests that decomposition of **1c** occurs. Up to T = 900 °C the mass recoveries remain good to excellent.

Concurrent with the decrease in mass recovery at $T \geqslant 900$ °C (Table 1), besides **1a–c**, an intractable polymer film is deposited immediately behind the hot zone. The resemblance of the polymer IR spectra, in combination with a strong band at 2900 cm^{-1} [ν(C–H) stretch vibrations] and the absence of ν(C≡C) [2100 cm^{-1}] and ν(≡C–H) [3310 cm^{-1}] stretch vibrations indicates that the cyclopentene alkenic bonds of **1a–c** are susceptible to polymerization. This is supported by the properties of **1a–c**; either upon standing in solution or upon heating in the solid state (140–160 °C) a similar intractable polymer is obtained (IR).[8]

A survey of the ^1H NMR chemical shifts of the cyclopenta-protons reveals the profound influence of bis(cyclopenta-fusion) topology.† Although according to their $^3J_{HH}$ coupling constants (5.1–5.4 Hz) **1a–c** possess cyclopentene-type double bonds, substantial differences are found between their chemical



Scheme 1 *Reagents and conditions*: i, 2.5 equiv. PCl_5, CH_2Cl_2, 5 h, reflux; −2HCl; ii, FVT (700–1100 °C, 10^{-2} Torr), −2HCl; 1,2 H shift, intramolecular C–H insertion

Table 1 Product composition of the pyrolysates obtained by FVT of **2a–c**[a]

Reactant	T/°C	Products (%) **2**	**4**	**5**	**6**	**7**	**1**	Mass recovery (%)
2a	700	3	24	70	3	—	—	96
	800	—	1	86	12	—	1	94
	900	—	—	38	29	—	33	26
	1000	—	—	5	13	—	82	16
	1100	—	—	—	—	—	100	6
2b	700	13	37	48	2	—	—	98
	800	—	—	76	18	—	6	98
	900	—	—	20	26	—	54	79
	1000	—	—	—	3	—	97	59
	1100	—	—	—	—	—	100	27
2c	700	3	8	78	11	—	—	98
	800	—	—	51	39	—	10	98
	900	—	—	—	13	—	87	88
	1000	—	—	—	14	8	78	76
	1100	—	—	—	6	16	78	26

[a] The product composition of the pyrolysates was established from ^1H NMR integral ratios, capillary GC and HPLC.

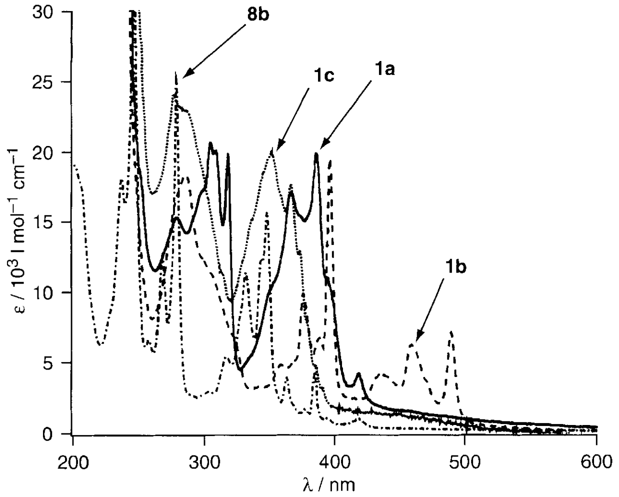


Fig. 1 UV–VIS spectra (solvent hexane) of **1a**, **1b**, **1c** and **8b**

shifts (**1a**, δ 7.01 and 6.78, **1b**, δ 6.70 and 6.61 and **1c**, δ 7.50 and 7.22). Compared to cyclopenta[*cd*]pyrene (**7**, δ 7.45 and 7.23, $^3J_{HH}$ 5.3 Hz)[7] these protons become more shielded in the series **1c**, **1a** to **1b**.[9]

The effect of bis(cyclopenta-fusion) is also reflected by the UV–VIS spectra of **1a–c** (Fig. 1).† Qualitatively the spectra of **1a** (C_{2v}) and **1c** (C_{2v}) resemble those of cyclopent[*hi*]acephenanthrylene (C_{2v})[10] and **7** (C_1),[11] respectively. In contrast, **1b** (C_{2h}) possesses a markedly different UV–VIS spectrum. Considerable bathochromic shifts of the bands are observed and vibronic couplings are discernible. The spectral features of **1a–c** are qualitatively well reproduced by PPP-SCI calculations.[12] Hydrogenation [5% Pd/C, C_2H_5OH, $p(H_2)$ 1 Torr, 20 °C] of **1a–c** gave quantitatively the related bisdihydrocyclopentacepyrylenes **8a–c**, respectively, which all possess pyrene-like UV–VIS spectra (for **8b** see Fig. 1). Preliminary steady-state fluorescence spectroscopy shows that **1a** and **1c** fluoresce, while **1b** is inactive. In contrast to cyclopenta[*cd*]pyrene (**7**),[11] the Kasha–Vavilov rule[13] applies for **1a** and **1c**, *i.e.* their fluorescence is independent on the excitation wavelength.

In summary, the availability of the $C_{20}H_{10}$ CP-PAHs **1a–c** allows their assessment as combustion effluents and their biological as well as their photophysical properties.

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Note added in proof: Compounds **1a–c** have also been prepared independently by L. T. Scott and coworkers (Boston College, USA).

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Footnotes

† For bisacetylation (**3a–c**) and bischlorination (**2a–c**) procedures see ref. 7. Compound **3a** (2.30 g, 8 mmol) was obtained by recrystallization of crude product (ratio **3a** : **3b** : **3c** = 3 : 1 : 1) from toluene at 20 °C. Compound **3b** (1.83 g, 6 mmol) was isolated by recrystallization of 7.70 g (26 mmol) of crude product from nitrobenzene at 4 °C. Crystallization from benzene at 20 °C gave a precipitate containing **3c** (75%) and **3b** (25%). Yields of **2**: **2a** (0.56 g, 1.73 mmol, 50%), **2b** (0.58 g, 1.80 mmol, 51%) and **2c** (0.11 g, 0.35 mmol, 10% by crystallization from diethyl ether at 4 °C). **4a–c**: **a** 1-(1-chloroethenyl)-8-, **b**, 1-(1-chloroethenyl)-6- and **c**, 1-(1-chloroethenyl)-3-ethynylpyrene; **5a–c**: **a**, 1,8-, **b**, 1,6- and **c**, 1,3-bisethynylpyrene; **6a–c**: **a**, 6-, **b**, 8- and **c**, 1-ethynylcyclopenta[*c,d*]pyrene and **8a–c**: **a**, bisdihydrocyclopent[*fg*]-, **b**, bisdihydrocyclopent[*jk*]- and **c**, bisdihydrocyclopent[*mn*]acepyrylenes. Satisfactory analytical data (^{1}H, ^{13}C NMR, GC-MS, IR) were obtained. *Selected data* for **1a**, λ_{max} (hexane)/nm (log ε) 457 (3.17), 419 (3.60), 394 (4.03), 386 (4.28), 367 (4.22), 351 (4.00), 318 (4.28), 309 (4.29), 305 (3.30), 298 (4.22), 279 (4.17) and 238 (4.79); ^{1}H NMR ($CDCl_3$): δ 7.69 and 7.61 (4 H, AB system, $^3J_{AB}$ 7.6 Hz), 7.45 (2 H, s), 7.01 (2 H, d, $^3J_{HH}$ 5.4 Hz) and 6.78 (2 H, d, $^3J_{HH}$ 5.4 Hz); *m*/*z* 250 (M^+) and 125 (M^{2+}). For **1b**, λ_{max} (hexane)/nm (log ε) 490 (3.84), 459 (3.78), 435 (3.62), 396 (4.29), 388 (3.82), 376 (3.99), 359 (3.68), 322 (3.83), 299 (4.09), 285 (4.26), 239 (4.66) and 216 (4.70); ^{1}H NMR ($CDCl_3$): δ 7.70 (2 H, d, $^3J_{HH}$ 7.5 Hz), 7.50 (2 H, s), 7.46 (2H, d, $^3J_{HH}$ 7.5 Hz) and 6.70 and 6.61 (4 H, AB system ($^3J_{AB}$ 5.1 Hz); *m*/*z* 250 (M^+) and 125 (M^{2+}). For **1c**, λ_{max} (hexane)/nm (log ε) 429 (3.28), 366 (4.35), 352 (4.41), 337 (4.30), 286 (4.47), 277 (4.49) and 225 (4.89); ^{1}H NMR ($CDCl_3$): δ 8.51 (2 H, d, $^3J_{HH}$ 7.8 Hz), 8.36 (2 H, s), 8.14 (1 H, s), 8.05 (1 H, t, $^3J_{HH}$ 7.8 Hz), 7.50 (2 H, d, $^3J_{HH}$ 5.1 Hz) and 7.22 (2 H, d, $^3J_{HH}$ 5.1 Hz); *m*/*z* 250 (M^+) and 125 (M^{2+}).

‡ Cyclopenta-fusion occurs *via* an ethynyl–ethylidene carbene rearrangement followed by an intramolecular carbene insertion into a *peri*-C–H bond.[7]

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