High temperature gas phase syntheses of $C_{20}H_{12}$ cyclopenta-fused polycyclic aromatic hydrocarbons: benz[*l*]acephenanthrylene and benz[*j*]acephenanthrylene and their selective rearrangement to benzo[*j*]fluoranthene

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The novel $C_{20}H_{12}$ cyclopenta-fused polycyclic aromatic hydrocarbon benz[*l*]acephenanthrylene (2) and its isomer benz[*j*]acephenanthrylene (3) have been obtained by flash vacuum thermolysis of 2-(1-chloroethenyl)benzo[*c*]phenanthrene (6) and 6-(1-chloroethenyl)chrysene (7), respectively. At $T \geqslant 900$ °C 2 and $T \geqslant 1000$ °C 3 rearrange selectively to the abundant combustion effluent benzo[*j*]fluoranthene (1). No evidence for the presence of the related rearrangement products benz[*l*]aceanthrylene (12) and benz[*j*]aceanthrylene (13), respectively, is found. Semi-empirical AM1 calculations provide a rationalization for these observations; the conversion of 2 and 3 into 1, instead of 12 and 13, respectively, ***via*** **consecutive ring-contraction–ring-expansion processes and** ***vice versa*** **is favoured.**

Introduction

Polycyclic aromatic hydrocarbons (PAH) have been recognized as environmental contaminants which are invariably generated during incomplete combustion processes. Among PAH the non-alternant cyclopenta-fused PAH (CP-PAH) represent a special class, due to the fact that several representatives possess extraordinary genotoxicity.[1] Examples of CP-PAH are acephenanthrylene, fluoranthene, the benzo-fused fluoranthenes, cyclopenta[*cd*]pyrene,[2] benzo[*ghi*]fluoranthene and cyclopent[*hi*]acephenanthrylene.[3] Consequently, the elucidation of CP-PAH build up processes under high temperature conditions as well as the preparation of reference compounds are important research issues. Additional impetus has been given by the proposal that CP-PAH are precursors for fullerenes such as C_{60}.[4]

With regard to the origin of CP-PAH under high temperature conditions in the gas phase, ethynyl-PAH thought to arise from either C_2 or ethyne (C_2H_2) addition to PAH,[5] have been postulated as penultimate precursors.[6] Ample evidence for CP-PAH formation from ethynyl-PAH *via* ethynyl–ethylidene carbene equilibration[7] followed by carbene C–H insertion has been obtained using flash vacuum thermolysis (FVT) experiments.[4,8] Other high temperature pathways to CP-PAH involve selective CP-PAH rearrangements (isomerizations)[3] and conversions[8] of PAH.

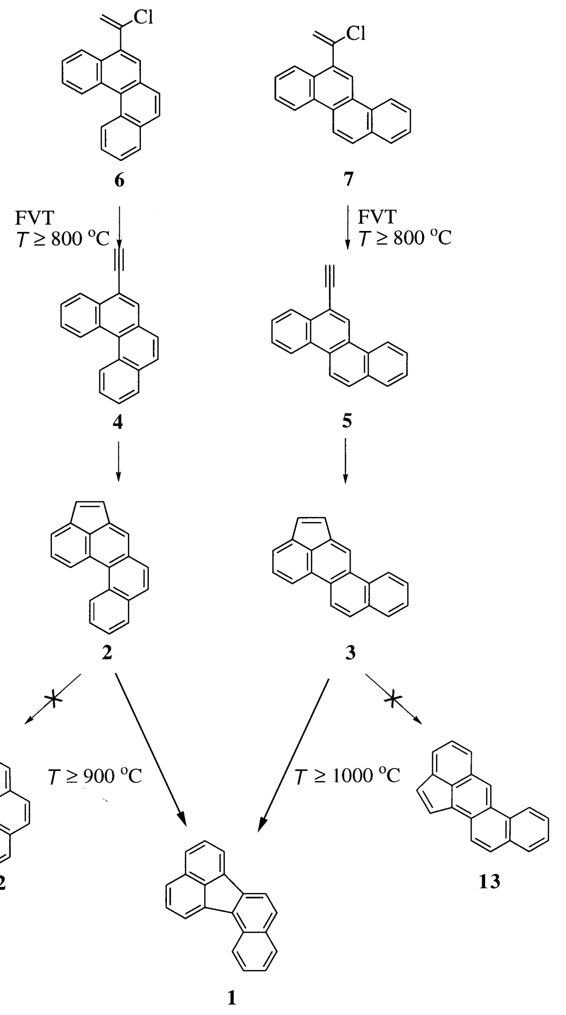
Here we report high temperature gas phase FVT syntheses of the hitherto unknown $C_{20}H_{12}$ CP-PAH benz[*l*]acephenanthrylene (**2**) and its isomer benz[*j*]acephenanthrylene[9] (**3**) from 2-(1-chloroethenyl)benzo[*c*]phenanthrene (**6**) and 6-(1-chloroethenyl)chrysene (**7**), respectively. In addition, it is shown that at $T \geqslant 900$ °C **2** and $T \geqslant 1000$ °C **3** selectively rearrange to the ubiquitous combustion effluents benzo[*j*]fluoranthene[10] (**1**, Scheme 1). These results are of three-fold interest: (*i*) the previously reported interconversions of the $C_{16}H_{10}$ CP-PAH aceanthrylene (**20**), acephenanthrylene (**19**) and fluoranthene (**21**) under flow pyrolysis (N_2 carrier gas, filled quartz tube) conditions (*vide infra*),[11] which have been proposed to occur *via* ring-contraction–ring-expansion processes, *viz.* 1,2-C/1,2-H shifts and *vice versa*, are also operational for the benzannulated $C_{20}H_{12}$ derivatives. (*ii*) In contrast to the $C_{16}H_{10}$ flow pyrolysis results of acephenanthrylene (**19**),[11] **2** and **3** only rearrange into **1**, *viz.* the related benzannulated aceanthrylenes benz[*l*]aceanthrylene[12] (**12**) and benz[*j*]aceanthrylene[12] (**13**) are absent (*vide infra*). (*iii*) Novel high temperature pathways to benzo[*j*]fluoranthene[10] (**1**) are disclosed, which are of interest for the rationalization of the ubiquitous formation of **1** during combustion processes and for the formation of C_{60} *via* pyrolysis of naphthalene.[4]

Results and discussion

Flash Vacuum Thermolysis (FVT)

FVT precursors **6** and **7** were obtained in two steps from benzo[*c*]phenanthrene[13] (**10**) and chrysene (**11**), respectively. In agreement with previously reported data,[14] acetylation of **10** and **11** gave 2-acetylbenzo[*c*]phenanthrene (**8**, yield 45%) and 6-acetylchrysene (**9**, yield 57%), respectively, which were converted into **6** (yield 48%) and **7** (yield 81%) by treatment with PCl_5 (Scheme 1, see Experimental section). The 1-chloroethenyl derivatives **6** and **7** are 'masked' ethynyl derivatives; they are converted *in situ* to 2-ethynylbenzo[*c*]phenanthrene (**4**) and 6-ethynylchrysene (**5**) by facile HCl elimination at relatively low temperatures under FVT conditions (Table 1).[3,8,15] To enable the unequivocal identification of **4** and **5** in the pyrolysates obtained upon FVT of **6** and **7**, respectively, both compounds were independently synthesized from 2-bromobenzo[*c*]phenanthrene (**14**) and 6-bromochrysene (**16**), respectively, by treatment with ethynyltrimethylsilane furnishing **15** and **17**, followed by removal of the trimethylsilyl functionality (Scheme 2, see Experimental section).

FVT at 800 °C of **6** and **7** (25 mg, 10^{-2} Torr, sublimation temp. 140 °C, rate 50 mg h^{-1}; see Experimental section) gave **4** and **5**, respectively, which were converted into the previously unknown benz[*l*]acephenanthrylene (**2**) and benz[*j*]acephenanthrylene[9] (**3**). The formation of CP-PAH **2** and **3** from *in situ* generated **4** and **5**, respectively, under high temperature conditions is rationalized by the occurrence of an ethynyl–ethylidene carbene equilibration[7] followed by carbene C–H insertion of the latter.[4,8] Note that the structure of **2** could be unambiguously assigned on the basis of a comparison of its ^1H NMR



Scheme 1

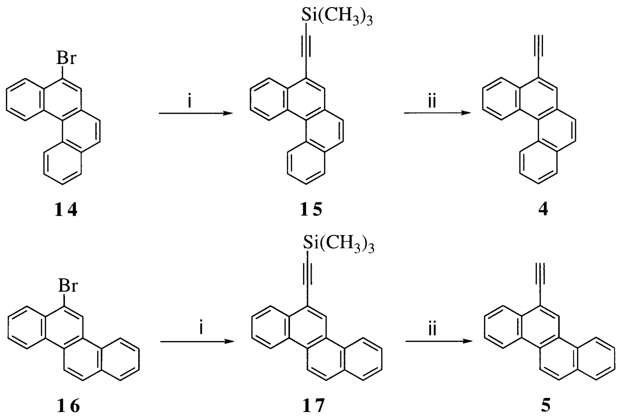
Table 1 Product composition of the pyrolysates obtained by FVT of **6** and **7**[a]

Precursor	T/°C	Pyrolysate product composition (%)				Mass recovered (%)
		6	**4**	**2**	**1**	
6	800	2	57	41	—	88
	900	—	—	91	9	86
	1000	—	—	80	20	77
	1100	—	—	47	53	71
7		**7**	**5**	**3**	**1**	
	800	—	36	64	—	80
	900	—	20	80	—	80
	1000	—	—	90	10	79
	1100	—	—	84	16	73

[a] ^{1}H NMR integral ratios, capillary GC and HPLC gave identical results. Compounds **4** and **5** were unambiguously identified by independent syntheses (see text).

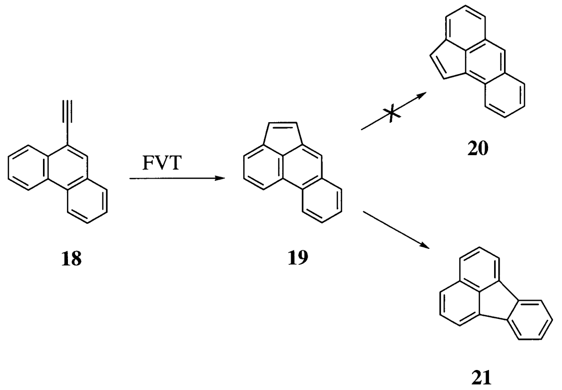
spectral data with those available for other benzo[*c*]phenanthrene derivatives (see Experimental section). At $T \geqslant 900$ °C, besides **2** and **3**, benzo[*j*]fluoranthene[10] (**1**) was unambiguously identified in the pyrolysates (Scheme 1). Good to excellent mass recoveries are obtained throughout the temperature range applied (Table 1). A survey of the temperature conversion data indicates that FVT is also a suitable method for the preparative synthesis of **2** and **3**, respectively (see Experimental section and Table 1).

Although the identification of **1** is in line with the previously reported rearrangement of the $C_{16}H_{10}$ CP-PAH acephenanthrylene (**19**) and aceanthrylene (**20**) into fluoranthene (**21**) under flow pyrolysis conditions,[11] a striking difference is the absence of the related isomers benz[*l*]aceanthrylene[12] (**12**) and benz[*j*]aceanthrylene[12] (**13**), respectively (Scheme 1). Hence, our results suggest that **2** and **3** rearrange selectively under high temperature FVT conditions, presumably *via* ring-contraction–ring-expansion processes (1,2-C/1,2-H shifts).[3,8] Moreover, the temperature conversion data indicate that **2** rearranges more readily than **3** (Table 1, *vide infra*). Since **2** and **3** are benzannulated derivatives of the $C_{16}H_{10}$ CP-PAH acephenanthrylene (**19**), which under flow pyrolysis conditions gave both aceanthrylene (**20**) and fluoranthene (**21**), 9-ethynylphenanthrene (**18**) was subjected to FVT ($T \geqslant 1000$ °C) (Scheme 3). Analysis of the pyrolysates showed the presence of acephenanthrylene (**19**) and fluoranthene (**21**). In contrast to the flow pyrolysis results of Scott and Roelofs,†[11] aceanthrylene (**20**) could not be identified even in trace amounts (GC–MS comparison with an authentic sample)! Similar results were found upon FVT ($T \geqslant 1000$ °C) of **19** itself. This strongly indicates that in going from flow pyrolysis (N_2 carrier gas, filled quartz tube) to FVT (10^{-2} Torr, unfilled quartz tube) conditions thermal reaction pathways are affected apparently as a consequence of changes in contact time and heat exchange.‡[15] Note that the pyrolysate



i: $(CH_3)_3SiC{\equiv}CH$, $(PH_3P)_2PdCl_2$, CuI in $N(CH_2CH_3)_3$; ii: K_2CO_3 in CH_3OH

Scheme 2



Scheme 3

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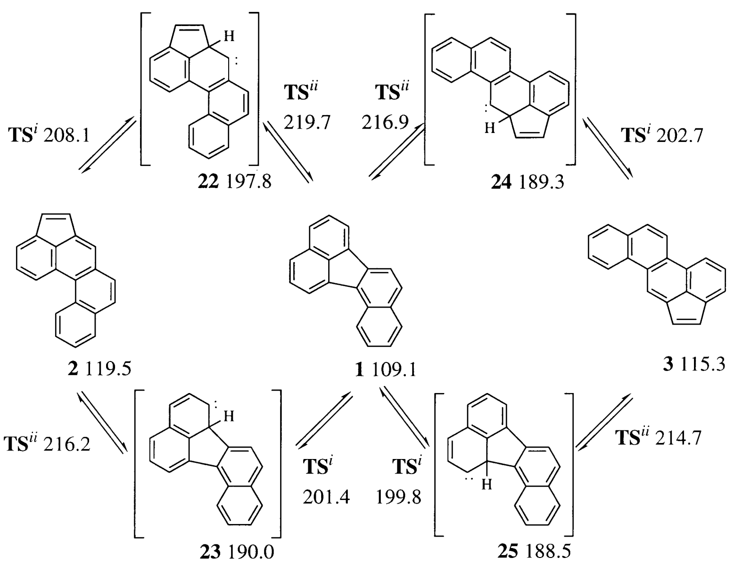
† In contrast to **5**, compound **18** is readily sublimed into the hot zone of the quartz tube and no evidence for thermal decomposition is found.

‡ The formation of **19** and **20** under FVT conditions using 9-ethynylphenanthrene (**18**) and 9-ethynylanthracene, respectively, as well as Meldrum's acid precursors, and the propensity of **19** and **20** to interconvert and ultimately rearrange to **21** and *vice versa*, are the subject of an investigation. The results will be reported in the near future. Notwithstanding, in our opinion the occurrence of unimolecular reactions is better secured under FVT conditions.[15]



Scheme 4 §

product composition as a function of temperature reveals that the rearrangement of **19** to **21** takes place to a similar extent as the rearrangement of **3** to **1** (ratio **19**:**21**; 1000 °C, 97:3, and 1100 °C, 86:14 with mass recoveries of 94 and 92%, respectively, and see Table 1).

In this context it should be stipulated that the application of the (1-chloroethenyl)-substituted PAH **6** and **7** for the *in situ* generation of ethynyl-PAH **4** and **5**, respectively, under FVT conditions is a prerequisite for the successful gas phase syntheses of **2** and **3**. This is vividly demonstrated by independent FVT experiments using 6-ethynylchrysene (**5**). FVT of **5** at 900 °C gave an intractable black solid in the sample flask during attempted sublimation (10^{-2} Torr and sublimation temperature 140 °C) into the hot zone of the FVT apparatus. The thermal instability of **5** is supported by differential scanning calorimetry (DSC; N_2 atmosphere); two irreversible exotherms at 141 and 155 °C are found. Comparison of FTIR spectra before and after heat treatment unambiguously showed the disappearance of the triple bond ≡C–H (3277 cm^{-1}) and –C≡C– (2098 cm^{-1}) stretching vibrations.

Semi-empirical AM1 calculations

To rationalize the propensity of CP-PAH isomers to interconvert ring-contraction–ring-expansion processes involving consecutive 1,2-H and 1,2-C shifts or *vice versa* have been invoked.[11] Both semi-empirical (MNDO)[16] and *ab initio* (MP3/6-31G) calculations gave credence to this mechanism in the case of the rearrangement of azulene into naphthalene[17] and the automerization (degenerate isomerization) of acenaphthylene[3] and benzene,[18] respectively. Here we present an extensive survey of the $C_{20}H_{12}$ potential energy surface using semi-empirical AM1[19] calculations (Schemes 4 and 5).§ In agreement with the experimental results the theoretical data equivocally show the conversion of **2** and **3** into **1** is preferred over that of **2** and **3** into **12** and **13**, respectively.

Rearrangement of benz[*l*]acephenanthrylene (2) and benz[*j*]acephenanthrylene[9] (3) into benzo[*j*]fluoranthene[10] (1)

AM1 predicts that the conversion of **2** ($\Delta_f H^\circ$ 119.5 kcal mol^{-1}) to **1** ($\Delta_f H^\circ$ 109.1 kcal mol^{-1}) is 4.2 kcal mol^{-1} more exothermic than that of **3** ($\Delta_f H^\circ$ 115.3 kcal mol^{-1}) to **1**. This is attributed to the fact that benzo[*l*]-fusion in the case of **2** will lead to additional steric strain in the fjord region (Scheme 4). Moreover, the activation enthalpies $\Delta H^{\ddagger}$; for the possible 1,2-C shifts in the case of **2**, *i.e.* either $\Delta H^{\ddagger}$(**2**→**23**) of 96.7 kcal mol^{-1} or $\Delta H^{\ddagger}$(**22**→**1**) of 21.9 kcal mol^{-1}, are more favourable than the related values found for **3** [$\Delta H^{\ddagger}$(**3**→**25**) 99.4 kcal mol^{-1} and $\Delta H^{\ddagger}$(**24**→**1**) 27.6 kcal mol^{-1}]. Nearly identical $\Delta H^{\ddagger}$ values are found for the related 1,2-H shift processes of **2** [$\Delta H^{\ddagger}$(**2**→**22**) 88.6 kcal mol^{-1} and $\Delta H^{\ddagger}$(**23**→**1**) 11.4 kcal mol^{-1}] and **3** [$\Delta H^{\ddagger}$(**3**→**24**) 87.4 kcal mol^{-1} and $\Delta H^{\ddagger}$(**25**→**1**) 11.3 kcal mol^{-1}]. Note that $\Delta_f H^\circ$ for the transition state of the 1,2-H shift will be overestimated by AM1.[3,19] Hence, the AM1 calculations predict that for both the conversion of **2** into **1** and **3** into **1** the 1,2-C shift process is the rate-limiting step. Furthermore in line with experiment, AM1 predicts that the rearrangement of **2** occurs more readily than that of **3**. Notwithstanding for the conversion of **2** and **3** into **1**, the consecutive 1,2-H/1,2-C shift pathway (**2**→**22**→**1** and **3**→**24**→**1**) is preferred over the reverse 1,2-C/1,2-H pathway (**2**→**23**→**1** and **3**→**25**→**1**, Scheme 4).§

Rearrangement of benz[*l*]acephenanthrylene (2) and benz[*j*]acephenanthrylene[9] (3) into benz[*l*]aceanthrylene (12) and benz[*j*]aceanthrylene (13)[12]

The absence of the alternative rearrangement products of **2** and **3**, *i.e.* benz[*l*]aceanthrylene (**12**) and benz[*j*]aceanthrylene (**13**),[12] respectively, is in line with our FVT results for 9-ethynylphenanthrene (**18**). No aceanthrylene could be identified in the pyrolysates (*vide supra*). These experimental observations are corroborated by AM1 calculations. Whereas $\Delta\Delta_f H^\circ$(**2**→**1**) is −10.4 kcal mol^{-1} (exothermic), $\Delta\Delta_f H^\circ$(**2**→**12**) [$\Delta_f H^\circ$(**12**) 121.2 kcal mol^{-1}] is 1.7 kcal mol^{-1} (endothermic; Schemes 4 and 5). For **3**, $\Delta\Delta_f H^\circ$(**3**→**1**) and $\Delta\Delta_f H^\circ$(**3**→**13**) [$\Delta_f H^\circ$(**13**) 119.0 kcal mol^{-1}] are −6.2 kcal mol^{-1} and 3.7 kcal mol^{-1}, respectively.§ Furthermore, the conversion of **2** to either **26** [$\Delta\Delta_f H^\circ$(**2**→**26**) 83.1 kcal mol^{-1}] or **27** [$\Delta\Delta_f H^\circ$(**2**→**27**) 79.3 kcal mol^{-1}] and **3** to either **28** [$\Delta\Delta_f H^\circ$(**3**→**28**) 83.5 kcal mol^{-1}] or **29** [$\Delta\Delta_f H^\circ$(**3**→**29**) 81.7 kcal mol^{-1}] is less favourable than that of **2** to either **22** [$\Delta\Delta_f H^\circ$(**2**→**22**) 78.3 kcal mol^{-1}] or **23** [$\Delta\Delta_f H^\circ$(**2**→**23**) 70.5 kcal mol^{-1}] and **3** to either **24** [$\Delta\Delta_f H^\circ$(**3**→**24**) 74.0 kcal mol^{-1}] or **25** [$\Delta\Delta_f H^\circ$(**3**→**25**) 73.2 kcal mol^{-1}], respectively (Schemes 4 and 5).§ The same applies to the activation enthalpies $\Delta H^{\ddagger}$ for both the 1,2-H [$\Delta H^{\ddagger}$(**2**→**26**) 92.2 kcal mol^{-1}, $\Delta H^{\ddagger}$(**27**→**12**) 13.1 kcal mol^{-1}, $\Delta H^{\ddagger}$(**3**→**28**) 92.7 kcal mol^{-1} and $\Delta H^{\ddagger}$(**29**→**13**) 13.0 kcal mol^{-1}, respectively] and 1,2-C shift [$\Delta H^{\ddagger}$(**2**→**27**) 107.1 kcal mol^{-1}, $\Delta H^{\ddagger}$(**26**→**12**) 20.1 kcal mol^{-1}, $\Delta H^{\ddagger}$(**3**→**29**) 108.0 kcal mol^{-1} and $\Delta H^{\ddagger}$(**28**→**13**) 21.4 kcal mol^{-1}, respectively]

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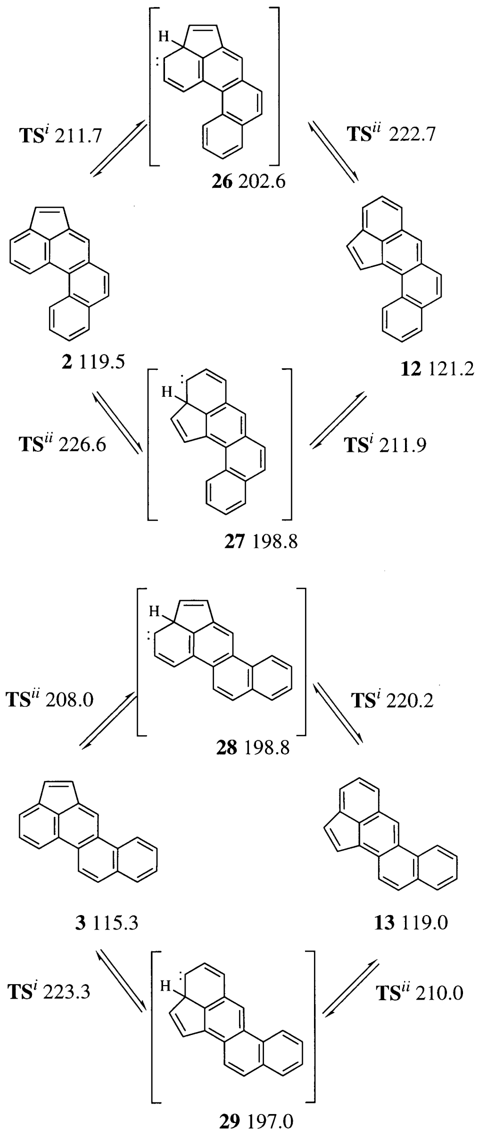
§ Units are in kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). Data concerning the geometry optimization, optimized geometries and the Hessian calculations are available upon request from one of the authors (L. W. J.); **TS**^{i}, transition state for 1,2-H shift and **TS**^{ii}, transition state for 1,2-C shift.



Scheme 5 §

compared with the $\Delta H^\ddagger$ values for the 1,2-H [$\Delta H^\ddagger(\mathbf{2}\rightarrow\mathbf{22})$ 88.6 kcal mol^{-1}, $\Delta H^\ddagger(\mathbf{23}\rightarrow\mathbf{1})$ 11.4 kcal mol^{-1}, $\Delta H^\ddagger(\mathbf{3}\rightarrow\mathbf{24})$ 87.4 kcal mol^{-1} and $\Delta H^\ddagger(\mathbf{25}\rightarrow\mathbf{1})$ 11.3 kcal mol^{-1}, respectively] and 1,2-C shift [$\Delta H^\ddagger(\mathbf{2}\rightarrow\mathbf{23})$ 96.7 kcal mol^{-1}, $\Delta H^\ddagger(\mathbf{22}\rightarrow\mathbf{1})$ 21.9 kcal mol^{-1}, $\Delta H^\ddagger(\mathbf{3}\rightarrow\mathbf{25})$ 99.4 kcal mol^{-1} and $\Delta H^\ddagger(\mathbf{24}\rightarrow\mathbf{1})$ 27.6 kcal mol^{-1}, respectively] in the conversion of **2** and **3** to **1**. Thus, the AM1 results support the experimental observations that **2** and **3** rearrange selectively into **1** under the high temperature conditions in the gas phase.

Conclusions

The ubiquitous combustion effluent benzo[*j*]fluoranthene (**1**),[10] which has been proposed to play a prominent role in fullerene build-up,[4] is accessible *via* rearrangement of **2** and **3**[9] under high temperature conditions in the gas phase. Our results support the idea that either C_2 or excess ethyne (C_2H_2) and PAH present in the gas phase during combustion[5] will combine to form ethynyl-PAH. In the case of appropriate ethynyl substitution, CP-PAH are obtained which in turn can undergo further CP-PAH rearrangements.

Experimental

All reactions were carried out under an N_2 atmosphere. All solvents were purified and dried by standard procedures. Column chromatography was performed on Merck Kieselgel 60 silica (230–400 ASTM). Melting points are uncorrected. ^{1}H (300.13 MHz) and ^{13}C (75.47) NMR spectra were obtained on a Bruker AC 300 spectrometer. *J* values are given in Hz. IR spectra were recorded with an FTIR Mattson Galaxy FTIR 5000 using a diffuse reflection accessory; samples were diluted in optically pure potassium bromide. GC–MS spectra were measured on an ATI Unicam Automass System 2 quadrupole mass spectrometer (column: J&W Scientific DB-17, length 30 m, id 0.32 mm and film thickness 0.25 µm; injector temperature, 300 °C; temperature program, 2 min 200 °C, (10 °C min^{-1})→280 °C; carrier gas He). HPLC: column reverse phase C_{18} (3 µm particles, diameter 4.6 mm and length 10 cm), Thermo Separation Products Spectra Series 200 gradient pump, Spectra-Physics UV2000 UV detector (λ 254 nm) and eluent acetonitrile–water either 60:40 or 80:20, flow rate 1 ml min^{-1}. Differential scanning calorimetry (DSC) was performed on a Mettler DSC 12E under an N_2 atmosphere (heating and cooling rate 10 °C min^{-1}). Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Syntheses

2-Acetylbenzo[*c*]phenanthrene (8).[14] To a cooled suspension (0 °C, ice bath) of anhydrous $AlCl_3$ (0.19 g, 1.42 mmol) in CH_2Cl_2 (10 ml), 0.09 g (1.15 mmol) acetylchloride was added under stirring. Subsequently, 0.25 g (1.1 mmol) of benzo[*c*]phenanthrene (**10**)[13] was added in small portions at room temperature. After stirring for 3 h the reaction mixture was cooled (0 °C, ice bath) and a 0.5 M HCl solution (10 ml) was added. The organic layer was separated, washed with a saturated sodium bicarbonate solution (15 ml) and water (15 ml), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Crude 2-acetylbenzo[*c*]phenanthrene (**8**) was purified by column chromatography (silica, eluent chloroform). Pure **8** was obtained as a white solid (yield 0.17 g, 0.63 mmol, 57%). Mp 109–111 °C; δ_H(300.13 MHz, $CDCl_3$) 9.05 (2 H, m), 8.81 (1 H, m), 8.28 (1 H, s), 8.04 (1 H, m), 7.95 (1 H, AB system, *J* 8.5), 7.86 (1 H, AB system, *J* 8.5), 7.69 (4 H, m) and 2.88 (3 H, s); δ_C(75.47 MHz, $CDCl_3$) 201.6, 134.5, 130.9, 130.4, 130.1, 129.8, 129.6, 128.8, 128.6, 128.5, 128.4, 128.1, 127.2, 127.0, 126.7, 126.65, 126.56, 126.5, 126.4 and 29.9; *m/z* (MS) 270 ($M^{\cdot+}$).

6-Acetylchrysene (9).[14] To a cooled suspension (0 °C, ice bath) of anhydrous $AlCl_3$ (2.45 g, 13.2 mmol) in CH_2Cl_2 (50 ml), 1.08 g (13.7 mmol) acetylchloride was added under stirring. Subsequently, 3.00 g (13.2 mmol) of chrysene (**11**) was added in small portions at room temperature. After heating at reflux for 3 days the reaction mixture was cooled (0 °C, ice bath) and a 0.5 M HCl solution (50 ml) was added. The organic layer was separated, washed with a saturated sodium bicarbonate solution (15 ml) and water (15 ml), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Crude 6-acetylchrysene (**9**) was purified by column chromatography (silica, eluent chloroform). Pure **9** was obtained as a yellow solid (yield 1.62 g, 6.0 mmol, 45%). Mp 129–130 °C; δ_H(300.13 MHz, $CDCl_3$) 9.12 (1 H, s), 8.79 (3 H, m), 8.67 (1 H, d, *J* 9.1), 8.08 (1 H, d, *J* 9.1), 8.01 (1 H, dd, *J* 7.9 and 2.1), 7.73 (4 H, m) and 2.93 (3 H, s); δ_C(75.47 MHz, $CDCl_3$) 201.6, 134.9, 132.2, 131.1, 130.7, 130.6, 129.8, 128.8, 128.6, 127.6, 127.3, 127.2, 126.8, 126.7, 126.2, 124.2, 123.3, 122.7, 120.9 and 30.2; *m/z* (MS) 270 ($M^{\cdot+}$).

2-(1-Chloroethenyl)benzo[*c*]phenanthrene (6). A mixture of **8** (0.14 g, 0.52 mmol) in CH_2Cl_2 and PCl_5 (0.17 g, 0.82 mmol) in CH_2Cl_2 (10 ml) was heated at reflux for 2 h. After cooling to room temperature, water (10 ml) was added. The organic layer was separated, washed with a saturated sodium bicarbonate solution (15 ml) and water (15 ml), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Crude 2-(1-chloroethenyl)benzo[*c*]phenanthrene (**6**) was purified by column chromatography (silica, eluent dichloromethane). Yield **6**, 0.12 g (0.42 mmol, 81%, brownish oil). δ_H(300.13 MHz, $CDCl_3$)

9.10 (2 H, m), 8.36 (1 H, m), 8.03 (1 H, dd, *J* 7.8 and 1.7), 7.92 (1 H, AB system, *J* 8.5), 7.89 (1 H, s), 7.82 (1 H, AB system, *J* 8.5), 7.67 (4 H, m), 5.92 (1 H, d, *J* 1.1) and 5.73 (1 H, d, *J* 1.1); δ_C(75.47 MHz, $CDCl_3$) 138.6, 135.5, 133.9, 130.6, 130.4, 129.9, 129.8, 128.6, 128.4, 128.2, 128.1, 127.9, 127.5, 126.6, 126.4 (two isochronous carbon atoms), 126.3 (two isochronous carbon atoms), 126.0 and 117.9; *m/z* (MS) 290 and 288 ($M^{\cdot+}$ with isotope pattern).

6-(1-Chloroethenyl)chrysene (7). A mixture of **9** (1.50 g, 5.6 mmol) in CH_2Cl_2 and PCl_5 (1.50 g, 7.2 mmol) in CH_2Cl_2 (50 ml) was heated at reflux for 48 h. After cooling to room temperature, water (50 ml) was added. The organic layer was separated, washed with a saturated sodium bicarbonate solution (50 ml) and water (50 ml), dried over magnesium sulfate, filtered and concentrated under reduced pressure. Crude 6-(1-chloroethenyl)chrysene (**7**) was purified by column chromatography (silica, eluent diethyl ether–hexane 2:1 v/v). Yield **7**, 0.77 g (2.7 mmol, 48%, brownish solid). Mp 151–154 °C; δ_H(300.13 MHz, $CDCl_3$) 8.80 (2 H, m), 8.76 (1 H, s), 8.70 (1 H, d, *J* 9.1), 8.34 (1 H, m), 8.04 (1 H, d, *J* 9.1), 8.00 (1 H, dd, *J* 7.9 and 1.4), 7.70 (4 H, m), 5.96 (1 H, d, *J* 1.1) and 5.74 (1 H, d, *J* 1.1); δ_C(75.47 MHz, $CDCl_3$) 139.8, 135.7, 132.2, 130.8, 130.5, 129.2, 128.9, 128.6, 128.3, 127.2 (two isochronous carbon atoms), 127.0, 126.7, 126.3, 126.2, 123.5, 123.0, 122.3, 120.9 and 118.0; *m/z* (MS) 290 and 288 ($M^{\cdot+}$ with isotope pattern).

2-Bromobenzo[*c*]phenanthrene (14). 70.0 mg (0.31 mmol) of benzo[*c*]phenanthrene (**10**) was treated with 0.62 g (0.91 mmol) of alumina supported copper(II) bromide in carbon tetrachloride (25 ml)[20] at 35 °C for 2 days. After filtration the residue was washed with 20 ml of carbon tetrachloride. The combined filtrate was concentrated under reduced pressure and the residue purified by column chromatography (silica, eluent hexane) giving 70.0 mg (0.23 mmol, 74%) of pure **14** as pale yellow oil. δ_H(300.13 MHz, $CDCl_3$) 9.11 (1 H, m), 9.04 (1 H, d, *J* 8.6), 8.50 (1 H, m), 8.18 (1 H, s), 8.02 (1 H, dd, *J* 7.5 and 1.8), 7.91 (1 H, d, *J* 8.5) and 7.70 (5 H, m); δ_C(75.47 MHz, $CDCl_3$) 133.6, 131.5, 131.4, 131.1, 130.7, 130.4, 130.0, 128.7, 128.3, 128.2, 128.0, 127.7, 126.9, 126.8, 126.5, 126.2, 125.7 and 121.8; *m/z* (MS) 306 ($M^{\cdot+}$ with isotope pattern).

2-Ethynylbenzo[*c*]phenanthrene (4). Bis(triphenylphosphine)-palladium dichloride (8.0 mg, 0.01 mmol) and copper(I) iodide (4 mg, 0.03 mmol) was added to a deaerated solution of 60.0 mg (0.20 mmol) of **14** and 40.0 mg (0.40 mmol) of ethynyltrimethylsilane in anhydrous triethylamine (20 ml) and the reaction mixture was stirred for two days.[21] After filtration the residue was washed with triethylamine (10 ml) and the combined filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica, eluent hexane) giving 25.9 mg (0.08 mmol, 40%) of pure 2-(trimethylsilylethynyl)benzo[*c*]phenanthrene (**15**) as yellow oil. δ_H(300.13 MHz, $CDCl_3$) 9.09 (2 H, m), 8.58 (1 H, m), 8.10 (1 H, s), 8.01 (1 H, dd, *J* 7.6 and 1.7), 7.89 (1 H, AB system, *J* 8.5), 7.77 (1 H, AB system, *J* 8.5), 7.70 (4 H, m) and 0.38 (9 H, s). Compound **15** (20.0 mg, 0.06 mmol) was converted into **4** by treatment with anhydrous potassium carbonate (5 mg) in methanol (5 ml) at room temperature for 4 h. After removal of the solvent under reduced pressure chloroform (10 ml) was added and the resulting solution washed with water (2 × 10 ml). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Pure **4** was obtained as a brown oil (14 mg, 0.05 mmol, 95%). δ_H(300.13 MHz, $CDCl_3$) 9.10 (2 H, m), 8.60 (1 H, m), 8.14 (1 H, s), 8.02 (1 H, dd, *J* 7.5 and 1.8), 7.91 (1 H, AB system, *J* 8.5), 7.78 (1 H, AB system, *J* 8.5), 7.70 (4 H, m) and 3.54 (1 H, s); δ_C(75.47 MHz, $CDCl_3$) 134.0, 132.7, 132.5, 130.1, 129.9, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 126.6, 126.6, 126.5, 126.4, 126.4, 126.3, 118.8, 82.2 and 81.8; ν/cm^{-1} 3300 (≡C–*H* stretch), 2100 (*C*≡*C*–H stretch); *m/z* (MS) 252 ($M^{\cdot+}$) (Found: C, 95.16; H, 4.75. Calc. for $C_{20}H_{12}$: C, 95.21; H, 4.79).

6-Ethynylchrysene (5). Bis(triphenylphosphine)palladium chloride (0.14 g, 0.2 mmol) and copper(I) iodide (0.01 g, 0.05 mmol) was added to a deaerated solution of 6-bromochrysene (**16**, 0.4 g, 1.3 mmol)[22] and ethynyltrimethylsilane (0.19 g, 1.9 mmol) in triethylamine (40 ml) and the reaction mixture was heated at reflux for 48 h.[21] After cooling to room temperature the reaction mixture was filtered and the filtrate was concentrated *in vacuo*. Crude 6-(trimethylsilylethynyl)chrysene (**17**) was purified by column chromatography [silica, eluent light petroleum (40–60)–ethyl acetate 15:1 v/v]. Yield **17** (0.28 g, 0.9 mmol, 69%, brownish waxy solid). δ_H(300.13 MHz, $CDCl_3$) 9.00 (1 H, s), 8.77 (2 H, m), 8.68 (1 H, d, *J* 9.1), 8.53 (1 H, m), 8.02 (1 H, d, *J* 9.1), 7.98 (1 H, dd, *J* 8.0 and 1.3), 7.70 (4 H, m) and 0.40 (9 H, s). Compound **17** (0.28 g, 0.9 mmol) was converted into **5** by treatment with anhydrous potassium carbonate (0.03 g) in methanol (30 ml) at room temperature for 5 h. After removal of the solvent under reduced pressure dichloromethane (60 ml) was added, the organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. Pure **5** was obtained as a brownish solid (yield 0.14 g, 0.56 mmol, 65%). Mp 146 °C (decomp.); δ_H(300.13 MHz, $CDCl_3$) 9.05 (1 H, s), 8.77 (3 H, m), 8.57 (1 H, dd, *J* 6.5 and 2.4), 8.03 (2 H, m), 7.72 (4 H, m) and 3.58 (1 H, s); δ_C(75.47 MHz, $CDCl_3$) 132.2, 131.5, 130.3, 128.8, 128.6 (two isochronous carbon atoms), 127.3, 127.2 (two isochronous carbon atoms), 127.1, 127.0, 126.8, 126.7, 126.4, 123.3, 123.0, 121.2, 120.9, 118.9 and 81.9; ν/cm^{-1} 3277 (≡C–*H* stretch), 2100 (*C*≡*C*–H stretch); *m/z* (MS) 252 ($M^{\cdot+}$) (Found: C, 95.05; H, 4.76. Calc. for $C_{20}H_{12}$: C, 95.21; H, 4.79).

Benz[*l*]acephenanthrylene (2). Compound **2** was initially purified from the 900 °C pyrolysate by column chromatography (silica, eluent hexane–benzene 7:3 v/v) followed by recrystallization from ethanol. Analytically pure **2** was obtained using preparative HPLC. Mp 175–177 °C; δ_H(300.13 MHz, $CDCl_3$) 9.21 (1 H, d, *J* 8.4), 8.95 (1 H, m), 8.09 (1 H, s), 8.02 (1 H, dd, *J* 7.9 and 1.2), 7.95 (1 H, AB system, *J* 8.7), 7.92 (1 H, AB system, *J* 8.7), 7.74 (3 H, m), 7.64 (1 H, m), 7.23 (1 H, AB system, *J* 5.3) and 7.14 (1 H, AB system, *J* 5.3); δ_C(75.47 MHz, $CDCl_3$) 140.0, 139.0, 134.0, 133.3, 131.9, 131.3, 129.0, 128.7, 128.4, 128.0, 127.9, 127.3, 126.9, 126.6, 126.5, 126.4, 126.0 and 122.6 (two ^{13}C resonances are not resolved); *m/z* (MS) 252 ($M^{\cdot+}$) (Found: C, 94.89; H, 4.77. Calc. for $C_{20}H_{12}$: C, 95.21; H, 4.79).

Benz[*j*]acephenanthrylene (3). Compound **3** was isolated from the 1000 °C pyrolysate by column chromatography (silica, eluent hexane–benzene 9:1 v/v) followed by recrystallization from ethanol. Mp 172–173 °C (mp 170–171 °C);[9] all analytical data were in agreement with those previously reported.[9]

Benzo[*j*]fluoranthene (1). All analytical data were in agreement with those previously reported.[10]

General flash vacuum thermolysis procedure

A commercial Thermolyne 21100 tube furnace containing an unpacked quartz tube (length 40 cm and diameter 2.5 cm) was used for all FVT experiments. Temperature–conversion curves were determined by evaporating 50 mg aliquots of either **6** or **7** (sublimation temperature 140 °C and sublimation rate 50 mg h^{-1}) into the quartz tube at a pressure of 10^{-2} Torr and the temperatures are shown in Table 1. In the case of FVT of **5** and **19** 50 mg aliquots were used (**5**; sublimation temperature 140 °C and **19**; sublimation temperature 90 °C and sublimation rate 60 mg h^{-1}). The pyrolysate product composition was determined with ^1H, ^{13}C NMR spectroscopy, capillary GC, capillary GC–MS and HPLC.

Semi-empirical AM1 calculations

Calculations were performed with AM1 as implemented in MOPAC 6.0.[19] Geometry optimization was performed without symmetry constraints (keyword PRECISE). Transition states (TS)§ were located using a reaction coordinate and, subsequently, refined using the Eigenvector Following routine (keyword TS) until GNORM $\leqslant$ 0.5. All minima and transition states were characterized by a Hessian calculation (keywords FORCE and LARGE); either none or only one imaginary vibration, respectively, was found. Heats of formation ($\Delta_f H^\circ$) of the minima and transition states (**TS**) are presented in Schemes 4 and 5; $\Delta_f H^\circ$ and $\Delta H^\ddagger$ are reported in kcal mol^{-1}.§

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