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Flash Vacuum Thermolysis of Acenaphtho[*1,2-a*]acenaphthylene. Thermal Behaviour of a Polycyclic Aromatic Hydrocarbon Containing Two Abutting Pentagons.

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Abstract: FVT of acenaphtho[*1,2-a*]acenaphthylene (**1**) gave acenaphtho[*1,2-e*]acenaphthylene (**2**), cyclopenta[*cd*]perylene (**3**) and cyclopenta[*rst*]benzo[*hi*]chrysene (**4**). The formation of **3** and **4** indicates that, besides ring contraction/ring expansion of **1** giving **2**, homolytic scission of a five-membered ring carbon-carbon single bond of **1** is an important competitive process.

In recent years it has been shown that Flash Vacuum Thermolysis (FVT) of (multi) ethynyl-substituted Polycyclic Aromatic Hydrocarbons (E-PAH) is an excellent method for the preparation of non-alternant externally (multi) cyclopentafused-PAH (CP-PAH).[1] Their availability has allowed their identification in combustion samples[2] and contributed to unravel the mechanisms responsible for the ubiquitous formation of those (CP)-PAH representatives invariably generated during incomplete combustion.[1,3] Moreover, many CP-PAH represent (planar) substructures of various fullerenes.[3] Of special relevance was the observation that CP-PAH possessing externally fused CP moieties selectively rearrange into isomers containing an internally fused CP unit by ring contraction/ring expansion involving 1,2-H/1,2-C shifts in the gas phase between 800-1000 °C. Examples are the conversions of acephenanthrylene into fluoranthene ($C_{16}H_{10}$),[4] cyclopenta[*cd*]pyrene into benzo[*ghi*]fluoranthene ($C_{18}H_{10}$)[1] and both benz[*j*]- and benz[*l*]acephenanthrylene into benzo[*j*]fluoranthene ($C_{20}H_{12}$),[5] respectively. However, until now only CP-PAH containing isolated CP rings externally fused to a PAH periphery were studied.

We here report on the FVT behaviour of acenaphtho[*1,2-a*]acenaphthylene (**1**, $C_{22}H_{12}$, Scheme 1).[6] Compound **1** contains two abutting CP moieties and represents a substructure of C_{50} and various possible C_{36} isomers.[7] Besides ring contraction/ring expansion, which converts **1** into the unknown CP-PAH acenaphtho[*1,2-e*]acenaphthylene (**2**, $C_{22}H_{12}$), homolytic scission of a five-membered ring carbon-carbon single bond of **1** is an important competitive process giving access to the transient diradical intermediate **5**. The latter is proposed to be a precursor for cyclopenta[*rst*]benzo[*hi*]chrysene (**4**, $C_{22}H_{12}$), which subsequently rearranges into cyclopenta[*cd*]perylene (**3**, $C_{22}H_{12}$, Scheme 1).

Aliquots of **1** (20 mg)[6] were subjected to FVT (unfilled quartz tube length 40 cm, diameter 2.5 cm, subl. temp. 120-140 °C, rate 20 mgh^{-1} and 10^{-2} Torr) in the temperature range 900-1200 °C. Whereas at 900 °C **1** was quantitatively recovered, at T ≥ 1000 °C red coloured pyrolysates were obtained; mass recoveries remained good to excellent throughout the applied temperature range (Table 1). Product analysis (HPLC, GC-MS) revealed that, besides **1**, up to three novel compounds of composition $C_{22}H_{12}$ (276 amu) were present in the 1000-1200 °C pyrolysates. Unfortunately, their separation by column chromatography using various conditions was thwarted due to co-elution of the products. Notwithstanding, ^{1}H NMR

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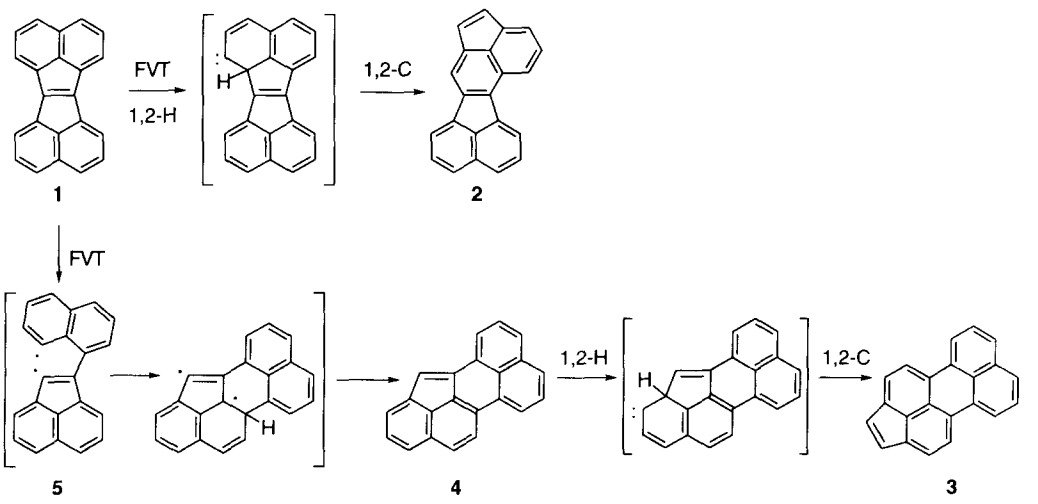
Scheme 1.



spectroscopy of the 1000-1200 °C pyrolysates indicated that two of the novel products correspond to the hitherto unknown CP-PAH acenaphtho[*1,2-e*]acenaphthylene (**2**)[8] and cyclopenta[*cd*]perylene (**3**),[9] respectively. Unequivocal evidence for their structural assignment was obtained by independent FVT syntheses of **2** and **3** (Scheme 2).

Table 1. Pyrolysate product composition upon FVT of **1** between 900-1200 °C (Scheme 1).[a]

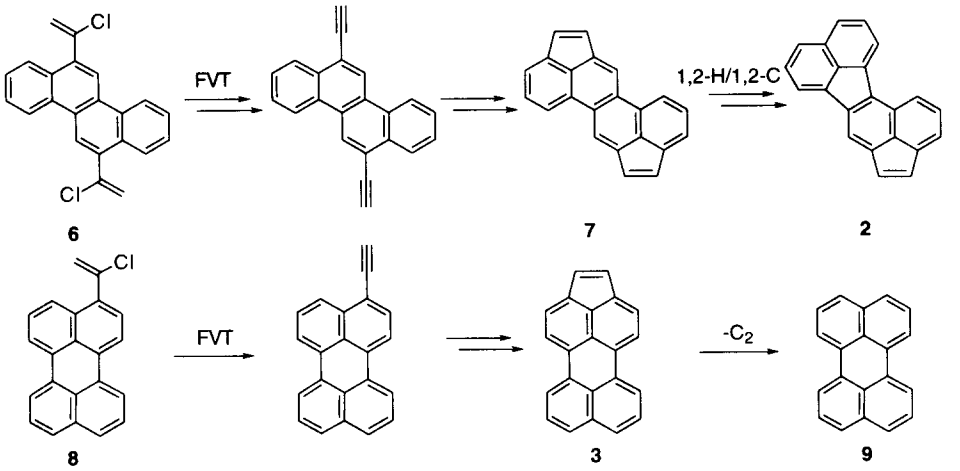
T (°C)	**1** (%)	**2**[8] (%)	**3**[9] (%)	**4**[13] (%)	Mass Recovery (%)
900	100	-	-	-	100
1000	85	4	-	11	79
1100	77	9	-	14	62
1200[b]	45	34	6	15	50

[a] ^{1}H NMR integral ratios, HPLC as well as capillary GC gave almost identical results. [b] The 1200 °C pyrolysate contains a trace of perylene (**9**, *ca.* 1%) presumably due to C_2 extrusion from **3** (Scheme 2).

The different approach towards **2** was inspired on earlier results, *viz.* FVT (T ≥ 1000 °C) of 6-(1-chloroethenyl)chrysene gave benz[*j*]acephenanthrylene and its rearrangement product benzo[*j*]fluoranthene (1000 °C, ratio 90%:10% and 1100 °C, ratio 84%:16% with mass recoveries of 79% and 73%, respectively).[5] Hence, we anticipated that FVT of 6,12-*bis*(1-chloroethenyl)chrysene (**6**)[10] should give the hitherto unknown *bis*cyclopenta[*hi,qr*]chrysene (**7**), which by ring contraction/ring expansion should selectively rearrange into **2**. Indeed, FVT of **6** (50 mg) at 1100 °C (subl. temp. 150-160 °C, rate 50 mgh^{-1}) gave a pyrolysate containing only **7**[11] and **2**[8] (ratio **7**:**2** 78%:22%; mass recovery 42%, Scheme 2). An enriched fraction consisting primarily of **2** and some **7** (ratio **2**:**7** 90%:10%) could be isolated by column chromatography (silica, eluent *n*-hexane).

FVT of 3-(1-chloroethenyl)perylene (**8**, 50 mg)[12] at 1000 °C (subl. temp. 120-140 °C, rate 50 mgh^{-1}) gave a pyrolysate (mass recovery 77%) containing **3**[9] and a trace of perylene (**9**, Scheme 2).

Scheme 2.



Although the conversion of **1** into **2** can be explained by a ring contraction/ring expansion,[1,3-5] the formation of **3** from **1** is less straightforward (Scheme 1). Fortunately, a small amount of the third $C_{22}H_{12}$ product (*ca.* 5 mg) could be isolated from the 1200 °C pyrolysate by tedious preparative HPLC. Its NMR (^1H, ^{13}C and ^1H decoupling experiments) data were in line with that expected for the hitherto unknown CP-PAH cyclopenta[*rst*]benzo[*hi*]chrysene (**4**, Figure 1).[13] The identification of **4** suggests that upon FVT of **1**, besides ring contraction/ring expansion,[1,3-5] *viz.* the conversion of **1** into **2**, homolytic scission of a five-membered ring carbon-carbon single bond giving transient diradical **5** is an important competitive process. It is expected[14] that **5** after hydrogen shifts and rotation around the other carbon-carbon single bond or *vice versa* will finally give **4** upon ring closure. Subsequently, **4** can rearrange into **3** by ring contraction/ring expansion.[1,3-5,15]

The propensity of **1** to undergo homolytic scission next to the documented five/six-membered ring exchange[1,3-5] under FVT (1000-1200 °C) conditions is attributed to the presence of two abutting CP moieties which will impose pentalene-like character and, thus, additional strain. AM1 calculations predict **1** to be 5.8, 24.3 and 19.7 kcalmol^{-1} less stable than **2**, **3** and **4**, respectively (Scheme 1).[16] Furthermore,

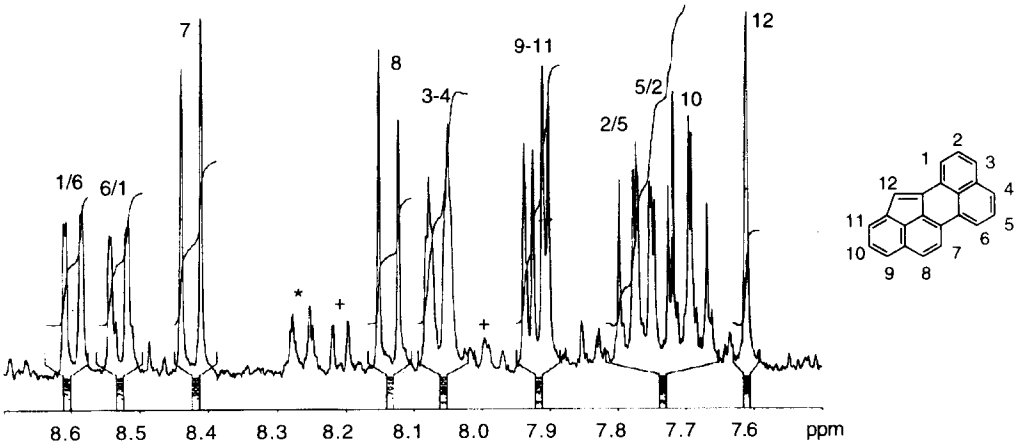


Figure 1. ^1H NMR(acetone-d_6, 300 MHz) of **4** isolated by preparative HPLC (* and + traces of **3** and **9**, respectively). The assignments 1/6 *vs.* 2/5 can be reversed.[13]

the availability of the previously unknown CP-PAH **2**, **3** and **4** will enable their identification as possible combustion effluents as well as the assessment of their genotoxic properties.

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8. Enriched fraction of **2**: ^{1}H NMR($CDCl_3$, 300 MHz) δ 8.49 (1H, d *J* 7.5 Hz), 8.41 (1H, d *J* 7.0 Hz), 8.19 (1H, s), 8.02 (1H, d *J* 6.8 Hz), 7.88 (1H, d *J* 8.0 Hz), 7.86 (1H, d *J* 8.2 Hz), 7.75-7.65 (3H, m), 7.62 (1H, d *J* 6.9 Hz), 7.12 (1H, A part of AB system *J* 5.2 Hz) and 7.08 (1H, B part of AB system *J* 5.2 Hz) ppm. ^{13}C NMR($CDCl_3$, 75.47 MHz) δ 129.6, 129.5, 128.4, 128.2, 128.0, 127.4, 127.3, 124.6, 124.1, 123.8, 121.0 and 118.7 (quarternary ^{13}C resonances not resolved) ppm. MS (EI, 70 eV): *m/z* (%) 276 (100). HRMS ($C_{22}H_{12}$) Calcd. 276.0939. Found 276.0910.
9. **3**: Recrystallization (C_2H_5OH), red crystals, m.p. > 300 °C (dec.). ^{1}H NMR($CDCl_3$, 300 MHz) δ 8.46 (2H, d *J* 7.5 Hz), 8.28 (2H, d *J* 7.5 Hz), 7.85 (2H, d *J* 7.6Hz), 7.81 (2H, d *J* 7.5 Hz), 7.61 (2H, dd *J* 7.5, 7.6 Hz) and 7.13 (2H, s) ppm. ^{13}C NMR($CDCl_3$, 75.47 MHz) δ 138.0, 131.7, 129.8, 129.7, 128.9, 128.3, 126.5, 125.2, 122.5 and 120.0 ppm (three quarternary ^{13}C resonances not resolved). MS (EI, 70 eV): *m/z* (%) 276 (100). $C_{22}H_{12}$ (276.34) Calcd. C 95.62, H 4.38. Found C 95.39, H 4.34.
10. 6,12-*Bis*(1-chloroethenyl)chrysene (**6**) was prepared in three steps from chrysene. Bromination of chrysene using the procedure of Kodomari, M.; Satoh, H.; Yoshitomi, S. *J. Org. Chem.*, **1988**, *53*, 2093-2094 gave 6,12-dibromochrysene (yield 74%). After its conversion into 6,12-*bis*(trimethylsilylethynyl)chrysene according to Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis*, **1980**, 627-630 (yield 80%) treatment with HCl(g) in acetic acid gave **6** (yield 100%).[5] All compounds gave satisfactory analytical data (^{1}H, ^{13}C NMR, MS and elemental analysis).
11. **7**: Recrystallization (toluene), orange crystals, m.p. 235 °C (dec.). ^{1}H NMR($CDCl_3$, 300 MHz) δ 8.94 (2H, s), 8.55 (2H, dd *J* 1.7, 7.2 Hz), 7.74 (4H, m), 7.25 (2H, A part of AB system *J* 5.3 Hz) and 7.22 (2H, B part of AB system *J* 5.3 Hz) ppm. ^{13}C NMR($CDCl_3$, 75.47 MHz) δ 139.8, 139.1, 131.9, 131.2, 129.0, 128.2, 127.1, 126.8, 123.2, 122.6 and 120.6 ppm. MS (EI, 70 eV): *m/z* (%) 276 (100). $C_{22}H_{12}$ (276.34) Calcd. C 95.62, H 4.38. Found C 95.36, H 4.36.
12. 3-(1-Chloroethenyl)perylene (**8**) was prepared from 3-acetylperylene (Zieger, H.E. *J. Org. Chem.*, **1966**, *31*, 2977-2981) by treatment with PCl_5/PCl_3 (yield 93%).[4,5] All compounds gave satisfactory analytical data (^{1}H, ^{13}C NMR, MS and elemental analysis).
13. **4**: ^{1}H NMR(acetone-d_6, 300 MHz) δ 8.59 (1H, dd *J* 1.0, 7.2 Hz), 8.53 (1H, dd *J* 1.0, 8.4 Hz), 8.42 (1H, d *J* 8.6 Hz), 8.13 (1H, d *J* 8.6 Hz), 8.07 (1H, dd *J* 1.0, 8.3 Hz), 8.06 (1H, dd *J* 1.0, 8.3 Hz), 7.92 (1H, d *J* 8.1 Hz), 7.91 (1H, d *J* 6.9 Hz), 7.78 (1H, dd *J* 7.2, 8.3 Hz), 7.75 (1H, dd *J* 8.3, 8.4 Hz), 7.70 (1H, dd *J* 6.9, 8.1 Hz) and 7.61 (1H, s) ppm. ^{13}C NMR(acetone-d_6, 75.47 MHz) δ 131.6, 130.7, 129.8, 129.6, 127.8, 127.3, 126.0, 125.4, 125.2, 125.1, 120.0 and 119.9 (quarternary C-atoms not resolved) ppm. MS (EI, 70 eV): *m/z* (%) 276 (100). HRMS ($C_{22}H_{12}$) Calcd. 276.0939. Found 276.0906.
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16. AM1 (MOPAC 6.0) gave ΔH_f^o values of 153.3, 147.5, 129.0, 133.6 and 153.8 kcalmol^{-1} for **1**, **2**, **3**, **4** and **7**, respectively.