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Migration of Redundant Ethynyl Substituents Along Polycyclic Aromatic Hydrocarbon Peripheries. Consequences for Polycyclic Aromatic Hydrocarbon Build Up.

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Abstract: The formation of cyclopenta[*cd*]pyrene (**5**) and benzo[*ghi*]fluoranthene (**6**) upon FVT of 3,9-*bis*ethynylphenanthrene (**1**) and 8-ethynylfluoranthene (**2**), respectively, suggests that redundant ethynyl substituents, which cannot give five- and/or six-membered ring formation *via* ethynyl ethylidene carbene equilibration followed by carbene C-H insertion, can migrate along the PAH periphery at high temperatures.

Ethynylated Polycyclic Aromatic Hydrocarbons (E-PAH), thought to arise from C_2 or ethyne (C_2H_2) addition to small PAH, are frequently postulated as important precursors for the build up of (non)-alternant PAH during combustion.[1] This proposal has been substantiated by Flash Vacuum Thermolysis (FVT) experiments using (multiple) ethynylated PAH (E-PAH). With an appropriate substitution pattern they are efficiently converted into PAH containing additional fused five- and/or six-membered rings.[2] Their formation under unimolecular FVT conditions is rationalized by invoking ethynyl ethylidene carbene equilibration followed by carbene C-H insertion.[2] Although in general this process appears to be *irreversible*, *i.e.* upon repyrolysis of the fused product no E-PAH are formed, evidence for *reversible* carbene C-H insertion has been reported recently.[3] Furthermore, the fused products subsequently may undergo selective rearrangements or conversions *via* ring-contraction/ring-expansion,[2] C_2 extrusion,[2,4] etc. at high temperatures in the gas phase.

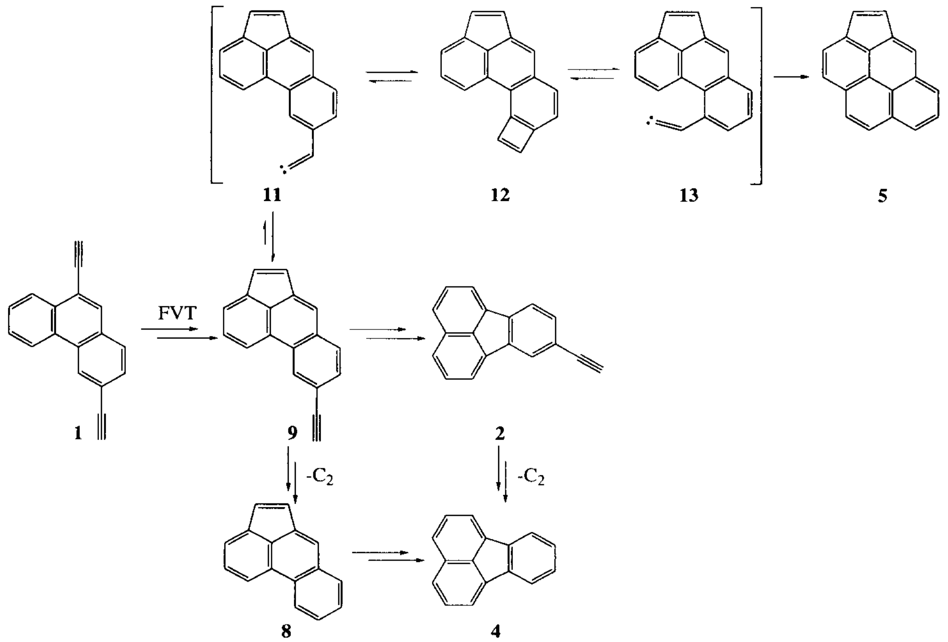
An intriguing issue remains to be addressed. What is the fate of redundant ethynyl substituents, *i.e.* those incapable of five- or six-membered ring formation, *viz.* by carbene C-H insertion after ethynyl ethylidene carbene equilibration?

We here report the results of FVT experiments using 3,9-*bis*ethynylphenanthrene (**1**)[5] and 8-(1-chloroethenyl)fluoranthene (**10**),[6] *i.e.* a facile FVT precursor for 8-ethynylfluoranthene (**2**),[6,7] which were designed to give an answer to this question. Compounds **1** and **2** were selected for the following two reasons. 1) They are ethynylated derivatives of the abundant combustion effluents phenanthrene (**3**; $C_{14}H_{10}$) and fluoranthene (**4**; $C_{16}H_{10}$). 2) They are representatives of the $C_{18}H_{10}$ potential energy surface, which also comprises the ubiquitous PAH effluents cyclopenta[*cd*]pyrene (**5**)[8] and benzo[*ghi*]fluoranthene (**6**).[9] For **1** we anticipated that, in analogy with the efficient FVT conversion of 9-ethynylphenanthrene (**7**) into acephenanthrylene (**8**),[10] the 9-ethynyl substituent will give cyclopenta-fusion, *i.e.* **1** will be converted into 9-ethynylacephenanthrylene (**9**). In contrast, the 3-ethynyl substituent of **1** will be redundant for ring formation.

Hence, other processes, such as ring-contraction/ring-expansion[2,10] of **9** giving 8-ethynylfluoranthene (**2**)[6] or C_2 extrusion[2,4] furnishing **8** followed by its rearrangement into **4**,[10] will occur. Although in the case of **2**, the 8-ethynyl substituent will also be redundant for ring formation, its fluoranthene core is known to be highly resistent to rearrangement at high temperatures in the gas phase.[10]

FVT (quartz tube length 40 cm, diameter 2.5 cm, subl. temp. 130 °C, rate 50 mgh^{-1} and 10^{-2} Torr) of **1** at 1000 °C gave a pyrolysate (mass recovery 50%) consisting mainly of 9-ethynylacephenanthrylene (**9**, 85%). This suggests that the primary thermal process is indeed cyclopenta-fusion involving the 9-ethynyl substituent, whereas the 3-ethynyl substituent remains unchanged. Besides **9**, 8-ethynylfluoranthene (**2**, 8%), fluoranthene (**4**, 2%), cyclopenta[*cd*]pyrene (**5**, 1%) and acephenanthrylene (**8**, 4%), were unequivocally identified (Scheme 1). Similar to the thermal rearrangement of **8** into **4**,[10] **2** has to be derived from **9**. The presence of the $C_{16}H_{10}$ PAH **4** and **8** indicates that C_2 extrusion[2,4] is apparently a competitive process. The formation of **5**, however, is less straightforward. Under unimolecular FVT conditions it formally requires the unprecedented migration of the redundant 9-ethynyl substituent of **9** to the 10-position followed by ethynyl ethylidene carbene equilibration and carbene C-H insertion, *i.e.* six-membered ring formation! Additional support for the viability of this process is obtained upon FVT of **1** at 1025 °C (mass recovery 31%). Besides an increase in yield of **2** (12%), **4** (7%) and **8** (16%), the amount of **5** (8%) also increases considerably. Unfortunately, FVT of **1** at higher temperatures is thwarted as a consequence of the onset of carbonization in the hot zone of the quartz tube.

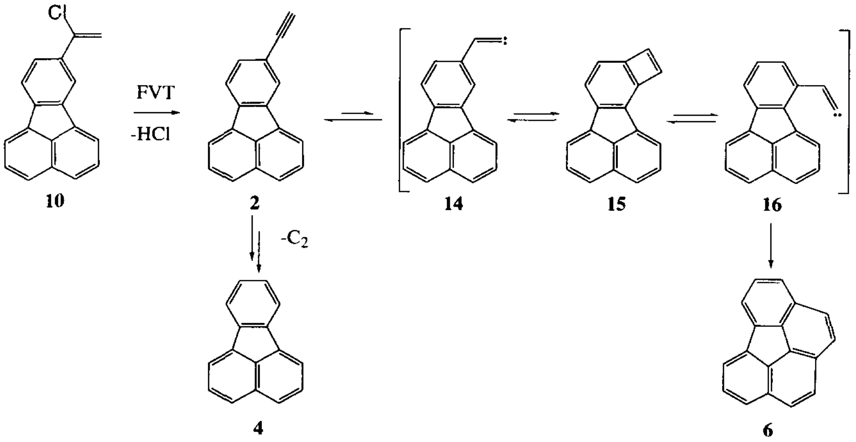
Scheme 1



To gain further insight in the propensity of redundant ethynyl substituents towards migration 8-(1-chloroethenyl)fluoranthene (**10**)[6] was subjected to FVT (subl. temp. 90 °C, rate 50 mgh^{-1} and 10^{-2} Torr). Whereas at T $\leq$ 1000 °C (mass recoveries > 50%) only 8-ethynylfluoranthene (**2**) was obtained,[6] at 1100 °C (mass recovery 25 %), besides **2** (60%), **4** (28%) and, more interestingly, benzo[*ghi*]fluoranthene (**6**; 12%) were unambiguously identified (Scheme 2). At 1200 °C (mass recovery 21 %) concomitant with increased conversion of **2** (52%) the yields of both **4** (31%) and **6** (17%) increase. The presence of **4** suggests that **2** is also susceptible to C_2 extrusion.[2,4] However, like the formation of **5** from **1**, the identification of **6** points to the occurrence of ethynyl migration along the PAH periphery!

Hence, we propose that another process with apparently a higher activation energy involving the formation of transient cyclobuta-PAH intermediates,[11] followed by *retro*-carbene C-H insertion, becomes operational. For **1** and **2**, this leads to the conversion of 9-ethynylacephenanthrylene (**9**) and 8-ethynylfluoranthene (**2**) ultimately into the ethylidene carbene tautomers of 10-ethynylacephenanthrylene (**13**, see Scheme 1) and 9-ethynylfluoranthene (**16**, see Scheme 2), respectively, which are FVT precursors for **5** and **6**.[2] It is noteworthy that for **2** this conjecture is fully corroborated by semiempirical AM1 calculations.[12]

Scheme 2



In summary, our data suggest that in E-PAH redundant ethynyl substituents, which cannot participate in direct five- and/or six-membered ring formation migrate along the PAH periphery presumably *via* transient cyclobuta-PAH intermediates. These results are of particular importance for the rationalization of the build up of ubiquitous PAH effluents during combustion.[1,2]

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References and Notes.

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5. 3,9-*Bis*ethynylphenanthrene (**1**): A deaerated solution of 3,9-dibromophenanthrene[13] (0.23 g, 0.7 mmol) and ethynyltrimethylsilane (0.35 g, 3.5 mmol) in dry triethyl amine (30 ml) was treated with *bis*(triphenylphosphine)palladium dichloride (20 mg) and copper(I) iodide (3 mg) and heated at reflux temperature for 72 h. The reaction mixture was filtered, the filtrate concentrated *in vacuo* and the residue purified by column chromatography (silica, eluent *n*-hexane) giving 3,9-*bis*(trimethylsilylethynyl)-phenanthrene (**17**) as a yellow orange oil (0.14 g, 0.4 mmol, 57 %). ^1H NMR (300.13 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.66 (m, 1H), 8.42 (m, 1H), 7.97 (s, 1H), 7.73 (d, 1H, *J* = 8.2 Hz), 7.70 (m, 2H), 7.63 (dd, 1H, *J* = 1.4, 8.2 Hz), 0.36 (s, 9H), 0.31 (s, 9H). Compound **17** (0.14 g, 0.4 mmol) was converted into **1** by treatment with anhydrous potassium carbonate (0.12 g) in methanol (40 ml) at 25 °C for 2 h. After work up[10] pure **1** (0.09 g, 0.4 mmol, 100 %, yellow waxy solid) was obtained. ^1H NMR (300.13 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.65 (m, 1H), 8.45 (m, 1H), 8.01 (s, 1H), 7.76 (d, 1H, *J* = 8.2 Hz), 7.72 (m, 2H), 7.67 (dd, 1H, *J* = 1.4, 8.2 Hz), 3.51 (s, 1H), 3.25 (s, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 132.3, 131.3, 130.8, 130.1, 129.9, 129.4, 128.5, 127.6, 127.5, 127.0, 126.9, 122.8, 121.2, 119.7, 84.0, 82.3, 81.7, 78.3. HRMS calcd. for $C_{18}H_{10}$ 226.0782, found 226.0778.
6. 8-(1-Chloroethenyl)fluoranthene (**10**): 8-Acetylfluoranthene[14] (0.89 g, 3.6 mmol), PCl_5 (1.14 g, 5.4 mmol) and PCl_3 (7.3 ml) were heated for 2 h at 60 °C. After cooling to room temperature water (10 ml) was added and the reaction mixture was extracted (diethyl ether 3 x 25 ml). The combined organic fractions were dried ($MgSO_4$), filtered, concentrated *in vacuo* and the residue was purified by column chromatography (silica, eluent $CHCl_3$). Yield **10** (0.20 g, 0.8 mmol, 22 %, yellow oil). ^1H NMR (300.13 MHz, $CDCl_3$): δ 8.80 (d, 1H, *J* = 1.8 Hz), 7.98 (m, 2H), 7.87 (m, 3H), 7.67 (m, 3H), 5.90 (d, 1H, *J* = 1.8 Hz), 5.60 (d, 1H, *J* = 1.8 Hz). MS (EI) *m/z* (%): 262 $M^{+\cdot}$ and 264 $M{+}2^{+\cdot}$ with isotope pattern (60), 227 $M\text{-}Cl^{+}$ (100). HRMS calcd. for $C_{18}H_{11}{}^{35}Cl$ 262.0548, found 262.0543.
   8-Ethynylfluoranthene (**2**): δ 8.05 (d, 1H, *J* = 1.4 Hz), 7.96 (d, 2H, *J* = 6.9 Hz), 7.88 (d, 2H, *J* = 8.1 Hz), 7.87 (d, 1H, *J* = 7.8 H), 7.66 (dd, 2H, *J* = 8.1, 6.9 Hz), 7.53 (dd, 1H, *J* = 7.8, 1.4 Hz), 3.17 (s, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 139.7, 139.4, 136.2, 136.1, 132.8, 131.5, 130.0, 128.1 (two isochronous resonances), 127.2, 127.1, 125.2, 121.3, 120.9, 120.7, 120.5, 84.3, 77.3. HRMS calcd. for $C_{18}H_{10}$ 226.0782, found 226.0779.
7. Upon FVT 1-chloroethenyl groups readily undergo hydrogen chloride elimination.[2]
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