High-Temperature Behavior of 1,8-Diethynylanthracene. Benz[*mno*]aceanthrylene, a Transient Intermediate for Cyclopenta[*cd*]pyrene

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The awareness that the genotoxicity of combustion exhausts can be accounted for by the presence of a small number of polycyclic aromatic hydrocarbons (PAHs), of which cyclopenta-fused derivatives (CP-PAHs), such as cyclopenta[*cd*]pyrene (**6**),[1] pose an extraordinary biohazard,[2] has made the elucidation of CP-PAH formation mechanisms under high-temperature conditions a topical issue.[3] Additional impetus is given by the proposal that CP-PAHs also may play a role in fullerene build up under arc and flame conditions.[4]

The origin of cyclopenta[*cd*]pyrene (**6**) during combustion has been rationalized by invoking the intermediacy of 1-ethynylpyrene, thought to arise from either C_2 or ethyne (C_2H_2) addition to pyrene.[1,5] This proposal was supported by flash vacuum thermolysis (FVT) experiments using 1-(1-chloroethenyl)pyrene ("masked" 1-ethynylpyrene).[6,7] Under FVT conditions 1-(1-chloroethenyl)pyrene is quantitatively converted in situ into 1-ethynylpyrene, which subsequently gave **6** at $T > 1000$ °C (mass recovery 90%).[1] By similar approaches, important and abundant CP-PAH effluents have been prepared in reasonable to good yields as well as with good mass recoveries.[8]

Recently, other thermal pathways involving either selective (CP)-PAH isomerizations ("annealing")[9] or PAH interconversions[10] were disclosed. For example, ubiqui-

tous **6** is obtained from (CP)-PAHs such as benzo[*ghi*]-fluoranthene ($C_{18}H_{10}$, **7**)[9b,11] and benzo[*c*]phenanthrene ($C_{18}H_{12}$).[10b]

Here we wish to report that FVT of 1,8-bis(1-chloroethenyl)anthracene (**2**), which at $T > 800$ °C is quantitatively converted in situ into 1,8-diethynylanthracene (**3**),[12] gives an unexpected entry to the abundant combustion effluent cyclopenta[*cd*]pyrene (**6**). The presence of 10-ethynylaceanthrylene (**4**), besides **3**, in the temperature range 800−900 °C in combination with the identification of **6** as primary product at $T > 900$ °C suggests that **4** is converted into transient benz[*mno*]aceanthrylene (**5**),[13] which immediately rearranges into **6** under the high-temperature conditions in the gas phase.

FVT precursor **2** was prepared in two steps from anthracene. Bisacetylation of anthracene gave a 1:1 mixture of 1,5- and 1,8-diacetylanthracene (**1**); pure **1** was isolated using preparative column chromatography. Subsequently, 1,8-diacetylanthracene (**1**) was treated with PCl_5 to give crude 1,8-bis(1-chloroethenyl)anthracene (**2**), which was also purified by preparative column chromatography (yield 40% from **1**, see the Experimental Section).

Aliquots of **2** (0.1 g, 10^{-2} Torr, sublimation temperature 140 °C and sublimation rate 0.05 g h⁻¹) were transferred into the unpacked quartz tube (length, 40 cm; diameter, 2 cm; and temperature range, 800−1100 °C) of our FVT apparatus. The pyrolysate product composition was determined using ¹H NMR, capillary GC−MS, HPLC, and authentic samples of **3**,[12] **6**,[1] and **7**,[11] respectively, as reference compounds. At 800 °C, **2** is quantitatively converted into a mixture of 1,8-diethynylanthracene (**3**) and 10-ethynylaceanthrylene (**4**,[14] Scheme 1 and Table 1). Repyrolysis of the pyrolysate at 800 °C supported the consecutive conversion of **2** into **3** and **4**, respectively [initial composition, **3,** 65% and **4,** 35% (mass recovery ca. 100%); and after repyrolysis, **3,** 34%; **4,** 53%; and **6,** 13% (mass recovery 74%)]. Corresponding results were found upon FVT of **2** at 900 °C [pyrolysate composition, **3,** 13%; **4,** 40%; and **6,** 47% (mass recovery 33%)]. Above 900 °C, **6** was the major low molecular weight product,

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(14) A ¹H NMR chemical shift difference ($\Delta\delta$ 1.42 ppm) is found for the two cyclopentene protons of **4** as a consequence of deshielding of H(1) by the ethynyl substituent at C(10) (see the Experimental Section); Hesse, M.; Meier, H.; Zeeh, B. *Spektroscopische Methoden in der Organischen Chemie*; Thieme Verlag: Stuttgart, 1991.

Table 1. Pyrolysate Product Composition Obtained upon FVT of 2[a]

T/°C	mass recovery/%	3/%	4/%	6/%	7/%
800	100	65	35		
	74[b]	34[b]	53[b]	13[b]	
900	33[c]	13	40	47	
1000	32[c]			>99	<1
1100	31[c]			95	5

[a] ^{1}H NMR integral ratios, capillary GC, and HPLC gave identical results. [b] Mass recovery and pyrolysate product composition after repyrolysis at 800 °C. [c] Carbonization occurs (see text).
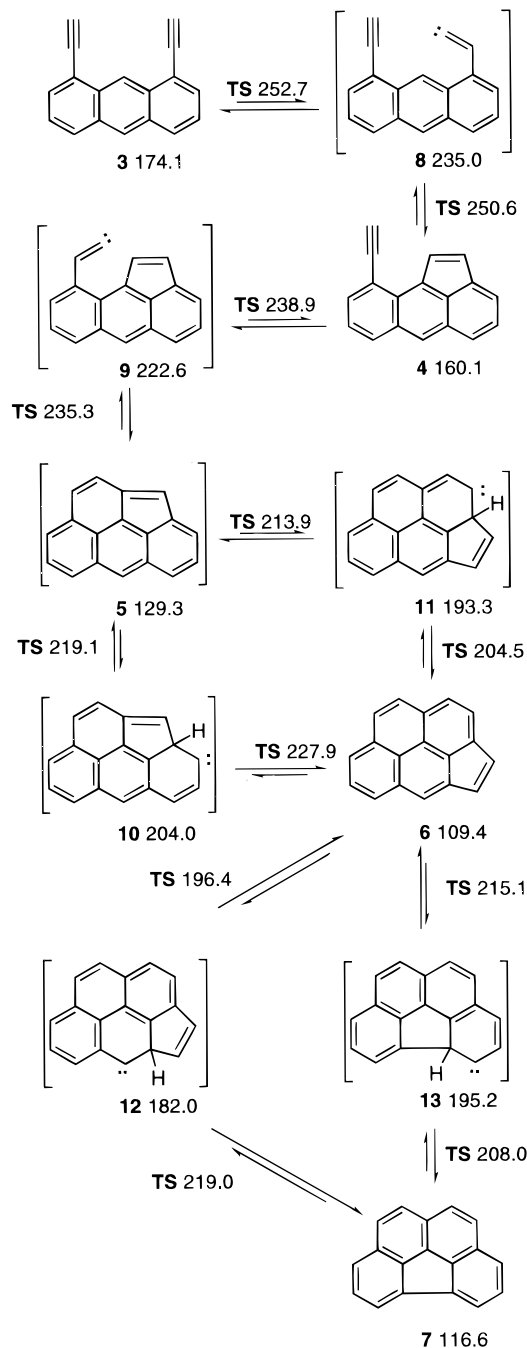
Scheme 1
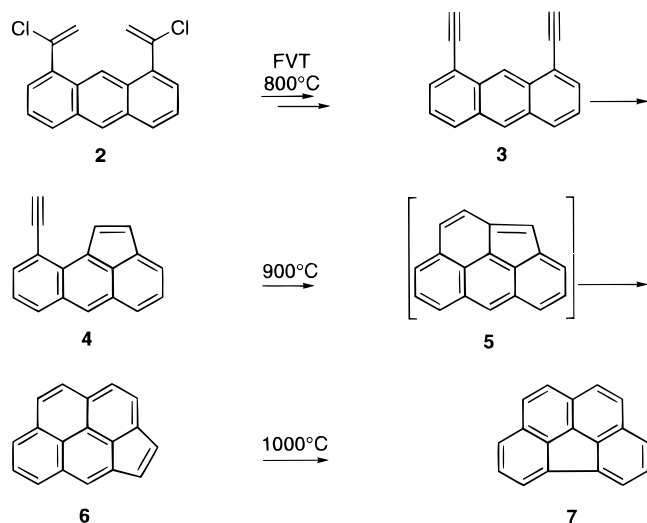
Scheme 2

whereas at $T >$ 1000 °C minor amounts of benzo[*ghi*]-fluoranthene (**7**)[11] were also identified (Scheme 1 and Table 1). The presence of **7**, besides **6**, indicates that the latter rearranges presumably by a ring-contraction/ring-expansion process (1,2-C/1,2-H shift).[8c,9b] It is noteworthy that at $T \geq$ 900 °C the mass recoveries decrease due to carbonization ($T =$ 800 °C, ca. 100% and $T >$ 900 °C, ca. 30%); a thin carbon lining is deposited on the wall of the quartz tube inside the furnace.[15]

No evidence for the rearrangement of **4** into 10-ethynylacephenanthrylene, which is also a potential FVT precursor of **6** by ring-contraction/ring-expansion, was found. This is in line with FVT experiments using either 9-ethynylanthracene or aceanthrylene in the temperature range 800–1100 °C. At $T >$ 1000 °C, both precursors gave, besides aceanthrylene, acephenanthrylene in only small amounts (ca. 5%).[9e] These results further corroborate that, at least under FVT conditions, cyclopenta-fusion occurs more readily than ring-contraction/ring-expansion.[8a–c,9e–f]

To rationalize the formation of **6** from **4**, benz[*mno*]-aceanthrylene (**5**)[13] is invoked as transient intermediate. In going from **4** to **5**, the ethynyl substituent at C(10) has to undergo ethyne–ethylidene carbene equilibration followed by carbene C–H insertion (Scheme 1).[15] Apparently, **5** is susceptible to rearrangement by ring-contraction/ring-expansion[9a,16] under the high-temperature conditions in the gas phase.

This interpretation is corroborated by AM1[17] calculations (Scheme 2). Benz[*mno*]aceanthrylene (**5**) is predicted to be less stable than either **6** or **7** [$\Delta H_f°$(**5**) = 129.3 kcal mol^{-1}, $\Delta H_f°$(**6**) = 109.4 kcal mol^{-1}, and $\Delta H_f°$(**7**) = 116.6 kcal mol^{-1}]. In addition, the activation enthalpy ($\Delta H^{\ddagger}$) for C–H carbene insertion in going from **9** to **5** [$\Delta H^{\ddagger}$(**9**→**5**) = 12.7 kcal mol^{-1}] is smaller than that in going from **8** to **4** [$\Delta H^{\ddagger}$(**8**→**4**) = 15.6 kcal mol^{-1}].[18] These results give credence to our proposal that the consecutive conversion of **3** into **4** and **5** will be viable under FVT conditions. The fleeting existence of **5** is rationalized by the AM1 $\Delta H^{\ddagger}$ values connecting **5** to **9**, **10**, and **11**, respectively [$\Delta H^{\ddagger}$(**5**→**9**) = 106.0 kcal mol^{-1}, $\Delta H^{\ddagger}$(**5**→**10**, 1,2-

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(18) For the C–H carbene insertion of 1-ethylideneanthracene to aceanthrylene, $\Delta H^{\ddagger}$(AM1) = 14.1 kcal mol^{-1}.[9e]

H) = 89.8 kcal mol⁻¹, and $\Delta H^{\ddagger}$(**5→11**, 1,2-C) = 84.6 kcal mol⁻¹]. These theoretical results suggest that the conversion of **5** to either **10** [$\Delta H^{\ddagger}$(**5→10**, 1,2-H)] or **11** [$\Delta H^{\ddagger}$(**5→11**, 1,2-C)] is considerably more favorable than the back-conversion of **5** to **9** [$\Delta H^{\ddagger}$(**5→9**), *retro*-carbene C−H insertion, Scheme 2]. In addition, the AM1 $\Delta H^{\ddagger}$ values for the rearrangement of **5** to **6** by either a consecutive 1,2-C/1,2-H shift process or *vice versa* [1,2-C/1,2-H, $\Delta H^{\ddagger}$(**5→11**, 1,2-C) = 84.6 kcal mol⁻¹ and $\Delta H^{\ddagger}$(**11→6**, 1,2-H) = 11.2 kcal mol⁻¹; 1,2-H/1,2-C, $\Delta H^{\ddagger}$(**5→10**, 1,2-H) = 89.8 kcal mol⁻¹ and $\Delta H^{\ddagger}$(**10→6**, 1,2-C) = 23.9 kcal mol⁻¹] indicate that the 1,2-C/1,2-H shift process is preferred over the 1,2-H/1,2-C shift process, i.e. **5** presumably rearranges to **6** via carbene **11**. Furthermore in line with our experimental observations, the AM1 $\Delta H^{\ddagger}$ values for the rearrangement of **5** to **6** are smaller than those for the conversion of **6** into **7** [1,2-C/1,2-H, $\Delta H^{\ddagger}$(**6→13**, 1,2-C) = 105.7 kcal mol⁻¹ and $\Delta H^{\ddagger}$(**13→7**, 1,2-H) = 12.8 kcal mol⁻¹; 1,2-H/1,2-C, $\Delta H^{\ddagger}$(**6→12**, 1,2-C) = 87.0 kcal mol⁻¹ and $\Delta H^{\ddagger}$(**12→7**, 1,2-C) = 37.0 kcal mol⁻¹]. This is in agreement with our temperature conversion data; **7** is obtained at the expense of **6** at *T* > 1000 °C (Table 1).[8c,9b,19]

In summary, under FVT conditions, in situ generated 1,8-diethynylanthracene (**3**) is consecutively converted into 10-ethynylaceanthrylene (**4**) and benz[*mno*]aceanthrylene (**5**). Under the high-temperature conditions in the gas phase, **5** instantaneously rearranges into cyclopenta[*cd*]pyrene (**6**).[1,2] Hence, a novel entry to the abundant combustion effluent **6** from a previously unexpected $C_{18}H_{10}$ PAH precursor, viz. **3**, involving consecutive carbene C−H insertion reactions followed by isomerization ("annealing") processes has been disclosed. These results contribute to the understanding of the formation processes responsible for the ubiquitous formation of a specific (CP)-PAH, such as **6**, during combustion.

Experimental Section

General Procedures. All reactions were carried out under a N₂ atmosphere. Column chromatography was performed on Merck Kiesegel 60 silica (230−400 ASTM). Melting points are uncorrected. ¹H (300.13 MHz) and ¹³C (75.47 MHz) NMR spectra were recorded in CDCl₃ with TMS as internal standard.

Caution: Many polycyclic aromatic hydrocarbons are potential mutagens and carcinogens. Hence, they should be handled with care.

1,8-diacetylanthracene (1).[20] To a cooled suspension (0 °C, ice bath) of fresh AlCl₃ (5.29 g, 40 mmol) in CH₂Cl₂ (30 mL) was added 2.94 g (38 mmol) acetyl chloride. After stirring until a clear solution was obtained, powdered anthracene (2.67 g, 15 mmol) was added in small portions at room temperature. After stirring overnight, the reaction mixture was cooled to 0 °C (ice bath) and hydrolyzed with 0.5 M HCl [30 mL (0 °C, ice bath)]. After standard work up a mixture of 1,5-di- and 1,8-diacetylanthracene (**1**) (ratio 1:1) was obtained (yield 3.2 g, 12 mmol, 80%). The 1,8-diacetyl isomer was isolated and purified using preparative column chromatography (silica, eluent chloroform). Yield of **1**: 1.12 g (4 mmol, 27%). Mp: 174−176 °C (lit.[20] mp: 178 °C). ¹H NMR: δ 10.17 (s, 1H), 8.43 (s, 1H), 8.10 (d, ³*J*(H,H) = 8.5 Hz, 2H), 7.94 (d, ³*J*(H,H) = 6.9 Hz, 2H), 7.48 (dd, ³*J*(H,H) = 6.9 Hz, ³*J*(H,H) = 8.5 Hz, 2H), 2.84 (s, 6H) ppm. ¹³C NMR: δ 201.6, 136.5, 133.0, 131.7, 129.2, 128.8, 127.5, 124.5, 124.4 and 30.0 ppm. GC/MS: *m/z* (%) 262 (55) [M•⁺], 247 (100) [M − CH₃⁺], 219 (80) [M − C₂H₃O⁺].

1,8-Bis(1-chloroethenyl)anthracene (2). A mixture of **1** (1.10 g, 4.2 mmol) and PCl₅ (2.19 g, 10.5 mmol) in CH₂Cl₂ (100 mL) was heated to reflux for 5 h. After cooling to room temperature, water (100 mL) was added. After standard workup and purification by preparative column chromatography (silica, eluent chloroform), **2** is isolated as a yellow solid. Yield of **2**: 0.51 g (1.7 mmol, 40%). Mp: 108−109 °C. ¹H NMR: δ 9.10 (s, 1H), 8.48 (s, 1H), 8.02 (d, ³*J*(H,H) = 8.6, 2H), 7.57 (d, ³*J*(H,H) = 7.2 Hz, 2H), 7.45 (dd, ³*J*(H,H) = 7.2 Hz, ³*J*(H,H) = 8.6 Hz, 2H), 5.94 (d, ²*J*(H,H) = 1.1 Hz, 2H), 5.69 (d, ²*J*(H,H) = 1.1 Hz, 2H). ¹³C NMR: δ 138.5, 137.1, 131.2, 129.7, 128.6, 127.4, 126.7, 124.9, 122.8, and 118.0 ppm. GC/MS: *m/z* (%) 298 (50) [M•⁺ with isotope pattern], 263 (40) [(M − Cl)⁺ with isotope pattern]. Elemental analysis calcd for $C_{18}H_{12}Cl_2$: C, 72.26; H, 4.04. Found: C, 72.08; H, 4.07.

1,8-Diethynylanthracene (3) ¹H NMR: δ 9.44 (s, 1H), 8.46 (s, 1H), 8.03 (d, ³*J*(H,H) = 8.6 Hz, 2H), 7.79 (d, ³*J*(H,H) = 6.9 Hz, 2H), 7.45 (dd, ³*J*(H,H) = 8.6 Hz, ³*J*(H,H) = 6.9 Hz, 2H), 3.62 (s, 2H). ¹³C NMR: δ 131.6, 131.5, 131.4, 129.5, 127.5, 125.0, 123.8, 120.4, 82.6 and 81.7 ppm. GC/MS: *m/z* (%) 226 (100) [M•⁺]. The spectrocopic results are in agreement with available literature data.[12]

10-Ethynylaceanthrylene (4).[14] Compound **4** was isolated from the 800 °C pyrolysate (50 mg) by column chromatography (silica, eluent *n*-hexane). Mp: 82−84 °C. ¹H NMR: δ 8.51 (d, ³*J*(H,H) = 5.3 Hz, 1H), 8.48 (s, 1H), 8.11 (d, ³*J*(H,H) = 8.7 Hz, 1H), 7.96 (d, ³*J*(H,H) = 8.4 Hz, 1H), 7.86 (d, ³*J*(H,H) = 7.0 Hz, 1H), 7.80 (d, ³*J*(H,H) = 6.6 Hz, 1H), 7.59 (dd, ³*J*(H,H) = 8.4 Hz, ³*J*(H,H) = 6.6 Hz, 1H), 7.38 (dd, ³*J*(H,H) = 8.7 Hz, ³*J*(H,H) = 7.0 Hz, 1H), 7.09 (d, ³*J*(H,H) = 5.3 Hz, 1H), 3.58 (s, 1H). GC/MS: *m/z* (%) 226 (100) [M•⁺]. HRMS calcd for $C_{18}H_{10}$ 226.0783, found 226.0780. It is noteworthy that upon standing at room temperature solutions of **4** appear to undergo dimerization (¹H NMR: characteristic multiplet at δ 4.22 ppm).[21] Consequently, the ¹³C NMR spectrum of **4** had to be obtained from ¹³C NMR spectrum of the 900 °C pyrolysate (22 mg) by comparison with the ¹³C NMR data of pure **3** and **6** (See Table 1 and Supporting Information). ¹³C NMR δ 139.9, 135.5, 134.5, 132.2, 131.3, 130.8, 129.5, 128.9, 127.8, 127.7, 126.7, 126.3, 126.1, 126.0, 123.7, 118.7, 84.9 and 82.0 ppm.

Cyclopenta[*cd*]pyrene (6). ¹H NMR: δ 8.43 (d, ³*J*(H,H) = 7.7 Hz, 1H), 8.40 (s, 1H), 8.30 (d, ³*J*(H,H) = 7.6 Hz, 1H) 8.11 (m, 3H), 8.03 (m, 2H), 7.43 (d, ³*J*(H,H) = 5.1 Hz, 1H), 7.25 (d, ³*J*(H,H) = 5.3 Hz, 1H). ¹³C NMR: δ 138.9, 135.3, 133.3, 131.7, 130.6, 130.3, 130.0, 128.3, 127.5, 127.1, 126.7, 126.6, 126.4, 126.2, 124.1, 122.4, 122.0 and 120.5 ppm. The spectrocopic results are in agreement with available literature data.[1]

Benzo[*ghi*]fluoranthene (7). ¹H NMR: δ 8.14 (d, ³*J*(H,H) = 7.0 Hz, 2H), 7.95 (m, 6H), 7.70 (t, ³*J*(H,H) = 7.0 Hz, 2H). ¹³C NMR: δ 137.4, 133.2, 128.3, 127.7, 126.7, 126.6, 126.4, 125.0 and 123.4 ppm. The spectrocopic results are in agreement with available literature data.[11]

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 in all FVT experiments. The temperature conversion data was determined by evaporating aliquots (0.05 g h⁻¹) of **2** into the quartz tube at a pressure of 10⁻² Torr (Table 1). The product composition of the pyrolysates was determined using ¹H NMR integration ratios, capillary GC, and HPLC.

AM1 Calculations. AM1 geometry optimization (MOPAC 6.0) was executed without imposing symmetry constraints until GNORM = 0.5.[17] Transition states (**TS**) were located using a reaction coordinate and, subsequently, refined using the Eigenvector Following routine (keyword TS) until GNORM = 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. $\Delta H_f°$ and $\Delta H^{\ddagger}$ values are reported in kcal mol⁻¹ (1 cal = 4.184 J, Scheme 2).

(19) For the rearrangement of **6** to **7**, AM1 calculations suggest that the 1,2-H/1,2C route is preferred (see also Scheme 2). It is noteworthy that AM1 overestimates the activation enthalpy $\Delta H^{\ddagger}$ for 1,2-H shifts.[8c,17]

(20) Bassilios, H. F.; Shawky, M.; Salem, A. Y. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 298.

(21) For the photodimerization of a related CP-PAH, viz. aceanthrylene, see: Plummer, B. F.; Singleton, S. F. *Tetrahedron Lett.* **1987**, *28*, 4801 and references cited.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **1**−**4**, **6**, **7** and the 900 °C pyrolysate of **2**, as well as AM1 Archive files for all minima (**3**−**13**) and related transition states (**TS**) presented in Scheme 2 (64 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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