Origin of Pyrene under High Temperature Conditions in the Gas Phase. The Pivotal Role of Phenanthrene

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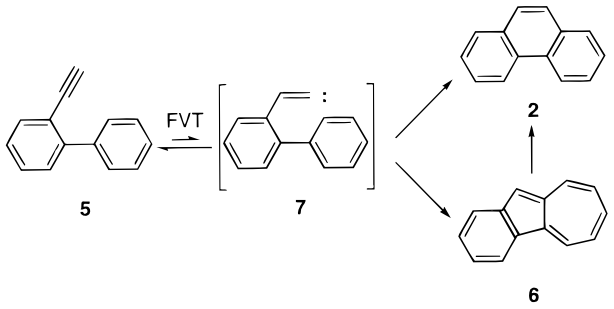
4-Ethynylphenanthrene (**15**), and the latent precursors for 2-ethynyl- (**18**) and 3-ethynylphenanthrene (**19**), viz., 2-(1-chloroethenyl)- (**16**) and 3-(1-chloroethenyl)phenanthrene (**17**), respectively, have been subjected to flash vacuum thermolysis (FVT). Whereas at 800 °C **15** is quantitatively converted into pyrene (**1**), **16** and **17** only give **18** and **19**, respectively. Both **18** and **19** contain redundant ethynyl substituents, i.e., after ethynyl−ethylidene carbene equilibration neither five- nor six-membered ring formation can occur by carbene C−H insertion. At $T \geq 1000$ °C **16** and **17** gave pyrolysates containing the same set of 11 (non)-alternant polycyclic aromatic hydrocarbons (PAH), albeit in a different ratio. The different product ratio suggests that redundant ethynyl substituents migrate along the phenanthrene periphery presumably via transient cyclobuta-PAH intermediates toward positions suitable for either five- or six-membered ring formation by carbene C−H insertion. The results provide an explanation for the ubiquitous formation of pyrene (**1**), acephenanthrylene (**9**), and fluoranthene (**3**) during (incomplete) combustion. Phenanthrene (**2**) appears to be a point of divergence in PAH growth by C_2 addition.

Introduction

The observation that (non)-alternant polycyclic aromatic hydrocarbons (PAH) are invariably formed during (incomplete) combustion of fossil fuels in combination with their potential genotoxic properties[1] has made the elucidation of their build-up under high-temperature conditions in the gas phase a topical issue.[2] Important processes proposed to be operational are radical reactions,[3] C_2 or ethyne (C_2H_2) additions to small PAH giving ethynylated PAH (E-PAH)[4] as well as PAH isomerizations and interconversions ("annealing").[5] An interesting result of combustion sample analysis is that only a distinct set of (non)-alternant PAH is formed. Examples of ubiquitous representatives are the PAH pyrene (**1**, $C_{16}H_{10}$) and phenanthrene (**2**, $C_{14}H_{10}$) as well as the CP-PAH [(cyclopentafused)-PAH] fluoranthene (**3**, $C_{16}H_{10}$) and acenaphthylene (**4**, $C_{12}H_8$). This has led to their use as probes for the identification of PAH samples from either biogenic or anthropogenic origin. Whereas soil samples containing primarily **2** signal a biogenic origin, those containing **1** and **2** as well as **3** as major PAH constituents are attributed to be of anthropogenic origin, viz., generated during combustion.[6]

Scheme 1



Flash vacuum thermolysis (FVT)[5,7] has proven to be an excellent method to gain insight into the mechanisms responsible for (non)-alternant PAH build-up.[8] For example, FVT of 2-ethynylbiphenyl (**5**) gave phenanthrene (**2**) and benzazulene (**6**, ratio **2**:**5**:**6**, 560 °C 3:94:3 and at 700 °C 72:0:28, Scheme 1).[9] The formation of **2** and **6** from **5** was explained by invoking ethynyl−ethylidene carbene equilibration (conversion **5** → **7** and *vice versa*) followed

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(1) Lafleur, A. L.; Longwell, J. P.; Shirnamé-Moré, L.; Monchamp, P. A.; Peters, W. A.; Plummer, E. F. *Energy Fuels*, **1990**, *4*, 307 and references cited. Howard, J. B.; Longwell, J. P.; Marr, J. A.; Pope, C. J.; Busby, W. F., Jr.; Lafleur, A. L.; Taghizadeh, K. *Combust. Flame* **1995**, *101*, 262 and references cited.

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(5) For recent reviews: Eastwood, F. W. In *Gas-Phase Reactions in Organic Synthesis*; Vallée, Y., Ed.; Gordon and Breach Science Publishers: New York, 1997; Chapter 1 and references cited. Wiersum, U. E.; Jenneskens, L. W. In *Gas-Phase Reactions in Organic Synthesis*, Vallée, Y., Ed.; Gordon and Breach Science Publishers: New York, 1997; Chapter 3 and references cited.

(6) For example: Tan, Y.L.; Kong, A.; Monetti, M. A. *Polycyclic Aromat. Compd*. **1996**, *9*, 185 and references cited.

(7) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980; Chapters 1 and 2.

(8) For reviews: Jenneskens, L. W.; Sarobe, M.; Zwikker, J. W. *Pure Appl. Chem*. **1996**, *68*, 219 and references cited. Scott, L. T. *Pure Appl. Chem*. **1996**, *68*, 291 and references cited.

(9) Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J.; McMullen, G. L. *Austr. J. Chem*. **1974**, *27*, 2393.

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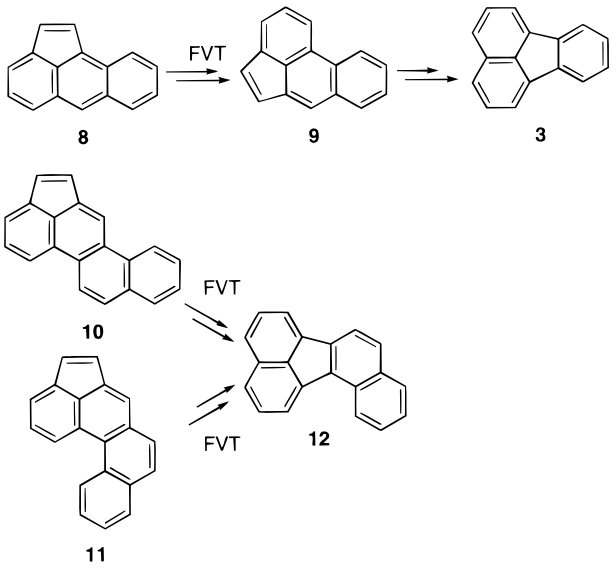
Scheme 2



by either carbene C−H insertion (conversion **7** → **2**) or carbene 1,2-addition (conversion **7** → **6**) under the high temperature conditions in the gas phase. Following a similar approach, FVT of (multi) ethynylated PAH (E-PAH) precursors, gave previously unknown externally cyclopentafused PAH (CP-PAH). Their availability has enabled their identification in combustion samples, the study of their genotoxic properties, and their use as reference compounds for the elucidation of CP-PAH thermal stability as a function of composition and in particular CP topology.[2,5,8,10] An intriguing outcome of these investigations is that CP-PAH containing a CP moiety externally fused to an alternant PAH framework rearrange with high selectivity into isomers containing an internally fused CP moiety. Examples are the consecutive conversion of aceanthrylene (**8**) into acephenanthrylene (**9**) and finally fluoranthene (**3**),[11,12] and the rearrangement of benz[*j*]- (**10**) and benz[*l*]acephenanthrylene (**11**) into benzo[*j*]fluoranthene (**12**), which were all proposed to occur by ring contraction/ring expansion processes under FVT conditions (Scheme 2).[13]

Surprisingly, the build-up of pyrene (**1**), which is one of the most ubiquitous PAH formed during (incomplete) combustion, is still unresolved. In line with the formation of phenanthrene (**2**) from 2-ethynylbiphenyl (**5**),[9] 2,2′-diethynylbiphenyl (**13**) has been frequently put forward as the pivotal precursor.[14] We have recently shown,[15] however, that FVT of **13** only gave **1** as a minor product (2−7%) in the temperature range 600−1100 °C (pyrolysate mass recoveries 98−37%). Instead of **1**, the major products were 9-ethynylphenanthrene (**14**), acephenanthrylene (**9**), and fluoranthene (**3**, Scheme 3)![15] Furthermore, since independent FVT of **14** gave **9** in almost quantitative yield, and **9** at $T \geq 900$ °C rearranged selectively into **3**,[12] it is clear that **13** is not the pivotal precursor for **1** under high-temperature conditions in the gas phase.

Scheme 3

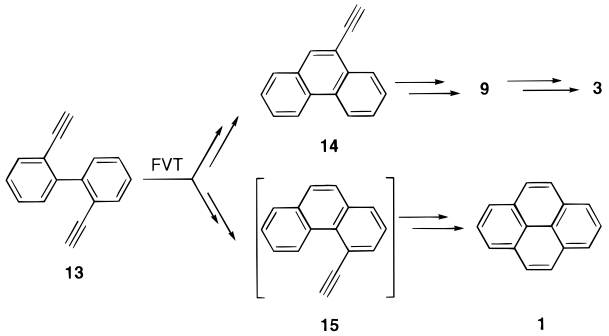


Table 1. Pyrolysate Product Composition (%) Obtained upon FVT of 15[a]

T/°C	**1**	**15**	mass recovery/%
600	12	88	100
700	67	33	100
800	100	–	100

[a] ^{1}H NMR integral ratios and capillary GC gave identical results (see Scheme 4).

Table 2. Pyrolysate Product Composition (%) Obtained upon FVT of 16 and 17[a]

FVT	**T**/°C	**1**	**2**	**3**	**4**	**9**	**18**	**19**	**20**	**21**	**22**	**23**	mass recovery/%
16	900	–	–	–	–	–	*100*	–	–	–	–	–	96
	1000	2	14	–	–	4	*74*	*4*	–	2	–	–	86
	1100	4	18	5	11	7	*33*	*3*	1	6	6	6	49[b]
	1200	7	17	10	23	10	*14*	*1*	2	8	7	1	30[b]
17	900	–	–	–	–	–	–	*100*	–	–	–	–	99
	1000	5	13	–	1	2	*2*	*71*	–	2	2	2	60
	1100	15	22	3	6	3	*2*	*26*	1	10	6	6	48[b]
	1200	20	15	6	28	4	*3*	*7*	2	6	5	4	24[b]

[a] ^{1}H NMR integral ratios, capillary GC and GC-FT-IR (1100 °C pyrolysates, Figure 1) gave identical results (see Chart 1). [b] Carbonization occurs.[24]

Here we report on the FVT behavior of 4-ethynylphenanthrene (**15**), and the latent precursors for 2-ethynyl- (**18**) and 3-ethynylphenanthrene (**19**), viz., 2-(1-chloroethenyl)- (**16**) and 3-(1-chloroethenyl)phenanthrene (**17**), respectively. Whereas at $T < 1000$ °C **16** and **17** are quantitatively converted into **18** and **19**, respectively, **15** gave **1** in quantitative yield already at 800 °C (Tables 1 and 2)! In contrast to **15**, both **18** and **19** contain redundant ethynyl substituents,[16] i.e., after ethynyl−ethylidene carbene equilibration neither a fused five- nor six-membered ring can be formed by carbene C−H insertion.[17] Notwithstanding, at $T \geq 1000$ °C both **16** and **17** gave pyrolysates containing the same set of 11 CP-PAH, albeit in a different ratio. The three $C_{16}H_{10}$ CP-PAH **1**, **3**, and **9**,[12] the two E-PAH **18** and **19**, the $C_{14}H_{10}$ PAH phenanthrene (**2**), the four $C_{14}H_8$ CP-PAH pyracylene (**20**), and 1-ethynyl- (**21**), 3-ethynyl- (**22**), and 5-ethynylacenaphthylene (**23**) as well as the $C_{12}H_8$ CP-

(10) For an example: Sarobe, M.; Flink, S.; Jenneskens, L. W.; van Poecke, B. L. A.; Zwikker, J. W. *J. Chem. Soc., Chem. Commun.* **1995**, 2415. Scott, L. T.; Necula, A. *J. Org. Chem.* **1996**, *61*, 386.

(11) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461.[12]

(12) Sarobe, M.; Jenneskens, L. W.; Wesseling, J.; Snoeijer, J. D.; Zwikker, J. W.; Wiersum, U. E. *Liebigs Ann./Recueil* **1997**, 1207 and references cited.

(13) Sarobe, M.; Jenneskens, L. W.; Wesseling, J.; Wiersum, U. E. *J. Chem. Soc., Perkin 2* **1997**, 703 and references cited.

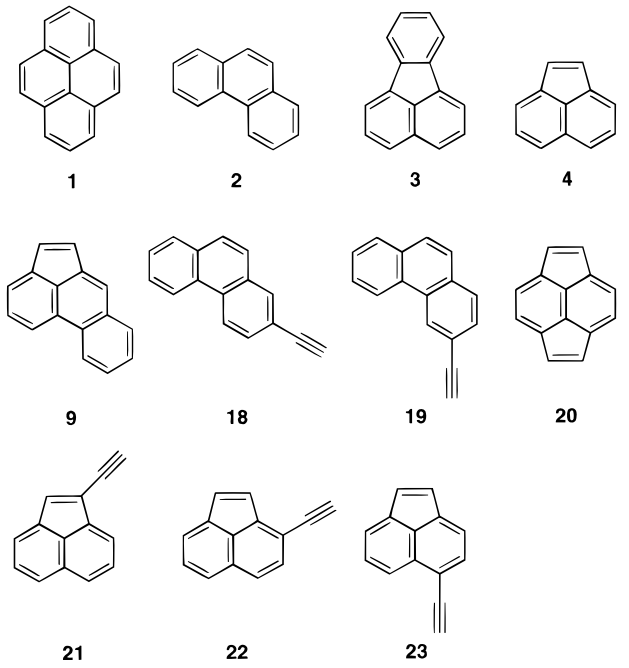
(14) For a recent example: Hofmann, J.; Zimmermann, G.; Guthier, K.; Hebgen, P.; Homann, K.-H. *Liebigs Ann.* **1995**, 631 and references cited.

(15) Sarobe, M.; van Heerbeek, R.; Jenneskens, L. W.; Zwikker, J. W. *Liebigs Ann./Recueil* **1997**, 2499 and references cited.

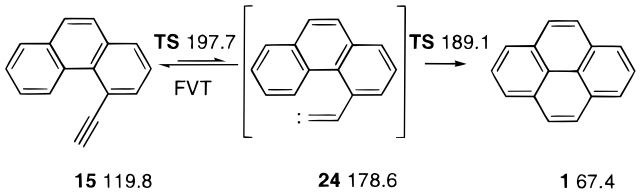
(16) Sarobe, M.; Jenneskens, L. W.; Kleij, A.; Petroutsa, M. *Tetrahedron Lett.* **1997**, *38*, 7255.

(17) See also: Hofmann, J.; Zimmerman, G.; Findeisen, M. *Tetrahedron Lett.*, **1995**, *36*, 3831. Scott, L. T.; Necula, A. *Tetrahedron Lett.* **1997**, *38*, 1877.

Chart 1. Products Identified in the 1100 °C Pyrolysates of 16 and 17 Using ^{1}H NMR, GC-MS, and GC−IR (see Figure 1 and text)



Scheme 4



PAH acenaphthylene (**4**) were unequivocally identified (Chart 1)![18,19] The presence of **1**, **3**, **9**, **18**, and **19** indicates that under the applied FVT conditions[7] the redundant ethynyl groups migrate along the phenanthrene periphery presumably via transient cyclobuta-PAH intermediates toward positions from which their ethylidene carbene tautomers can give either a fused five- or six-membered ring by carbene C−H insertion.[15−17] Semiempirical AM1[20] calculations support this interpretation (vide infra).

Results and Discussion

FVT of 4-Ethynylphenanthrene (**15**). Since FVT of 2,2′-diethynylbiphenyl (**13**) in the temperature range 600−1100 °C, gave, instead of **1** (minor product, 2−7%), 9-ethynylphenanthrene (**14**), acephenanthrylene (**9**), and fluoranthene (**3**) as major products concomitant with increasing temperature,[15] we envisaged that 4-ethynylphenanthrene (**15**) had to be the penultimate thermal precursor of **1** (Scheme 4). To substantiate this conjecture, **15** was prepared according to a literature procedure[21] and subjected to FVT (10^{-2} Torr, subl temp 160 °C, rate 50 mg h^{-1}). While at 600 °C **1** (12%) was the only novel product besides starting material (**15**, 88%), at 800 °C **15** is quantitatively converted into **1** (600−800 °C; mass recoveries 100%, Scheme 4 and Table 1).

The facile conversion of **15** into **1** resembles that of 2-ethynylbiphenyl (**5**) into phenanthrene (**2**) under similar FVT conditions (Scheme 1).[9] Semiempirical AM1[20] calculations gave for the conversions of **15** [ΔH_f^0 (**15**) 119.8 kcal mol^{-1})] into **1** [ΔH_f^0 (**1**) 67.4 kcal mol^{-1}] and **5** [ΔH_f^0 (**5**) 104.5 kcal mol^{-1}] into **2** [ΔH_f^0 (**2**) 57.5 kcal mol^{-1}] enthalpies of reaction (ΔH_r) of −52.4 kcal mol^{-1} (**15** → **1**) and −47.0 kcal mol^{-1} (**5** → **2**), respectively, viz., both reactions have a similar exothermicity. As anticipated, six-membered ring formation (for example: the conversion of **5** into **2**, and **15** into **1**) is both thermodynamically and kinetically favored over five-membered ring formation {for example: the conversion of either 1-ethynyl- [**25**, ΔH_f^0 (**25**) 113.1 kcal mol^{-1}] or 9-ethynylphenanthrene [**14**, ΔH_f^0 (**14**) 113.3 kcal mol^{-1}][12] into acephenanthrylene [**9**, ΔH_f^0 (**9**) 95.6 kcal mol^{-1}]}.[12] For five-membered ring formation ΔH_r(AM1) values were found of −17.7 kcal mol^{-1} (**14** → **9**) and −17.5 kcal mol^{-1} (**25** → **9**), respectively, which are considerably less exothermic than the corresponding values in the case of six-membered ring formation [ΔH_r (**15** → **1**) −52.4 kcal mol^{-1} and ΔH_r(**5** → **2**) −47.0 kcal mol^{-1}]. In agreement with an increase in strain in going from a six- to a five-membered ring, the AM1 activation enthalpy ($\Delta H^{\ddagger}$) for the ethylidene carbene C−H insertion reaction of **24** leading to **1** [$\Delta H^{\ddagger}$ (**24** → **1**) 10.5 kcal mol^{-1}] is 4.1 kcal mol^{-1} smaller than that for the conversion of the ethylidene carbene tautomer of **14**, *viz*. **32**, giving **9** [$\Delta H^{\ddagger}$ 14.6 kcal mol^{-1}][12] (Schemes 3−5, see also AM1 Calculations Section).

An important consequence of these results is that for the build-up of pyrene (**1**) under high-temperature conditions in the gas phase, phenanthrene (**2**) appears to be the pivotal precursor. Ethynylation at the 4-position of **2**, presumably by formal C_2 addition, will give **15**, which after ethynyl−ethylidene carbene equilibration is converted quantitatively into **1** by carbene C−H insertion. It should be stipulated, however, that C_2 addition is an exothermic process.[4] Hence, upon ethynylation of **2**, a reaction mixture containing all possible ethynylated phenanthrenes, viz., 1- (**25**), 2- (**18**), 3- (**19**), 4- (**15**), and 9-ethynylphenanthrene (**4**), respectively, is expected. Since it is documented that under FVT conditions **15** is converted into **1** (vide supra), 9-ethynylphenanthrene (**14**) into acephenanthrylene (**9**),[12] and that 1-ethynylphenanthrene (**25**) will be a precursor for **9**, too, the thermal properties of 2-ethynyl- (**18**) and 3-ethynylphenanthrene (**19**) remain to be elucidated.

FVT of 2-(1-Chloroethenyl)- (16) and 3-(1-Chloroethenyl)phenanthrene (17). To gain insight in the thermal behavior of **18** and **19**, their latent FVT precursors 2-(1-chloroethenyl)- (**16**) and 3-(1-chloroethenyl)-phenanthrene (**17**), respectively, were prepared and subjected to FVT. Both **16** and **17** were readily accessible from 2-acetyl-[22] and 3-acetylphenanthrene[22] (see Experimental Section) and subjected to FVT (10^{-2} Torr, subl temp 160 °C, rate 50 mg h^{-1}) between 800 and 1200 °C. Up to 1000 °C **16** and **17** were quantitatively converted into **18** and **19**, respectively (Table 2, mass recoveries ≥ 96%). However, at $T \geq 1000$ °C both precursors gave

(18) Sarobe, M.; Flink, S.; Jenneskens, L. W.; Zwikker, J. W.; Wesseling, J. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2125 and references cited.

(19) See also: Brown, R. F. C.; Eastwood, F. W.; Wong, N. R. *Tetrahedron Lett.* **1993**, *34*, 1223 and references cited.

(20) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(21) Mallory, F. B.; Baker, M. B. *J. Org. Chem.* **1984**, *49*, 1323.

(22) Gore, P. H. In *Friedel Crafts and Related Reactions*, Olah, G. A., Ed.; Interscience: New York, 1964; Vol. III, pp 78−80.

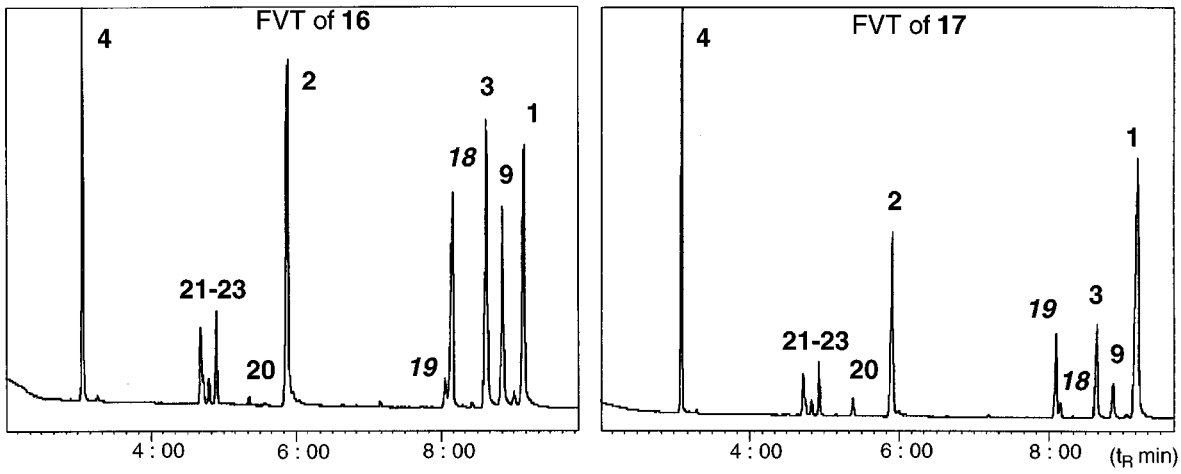
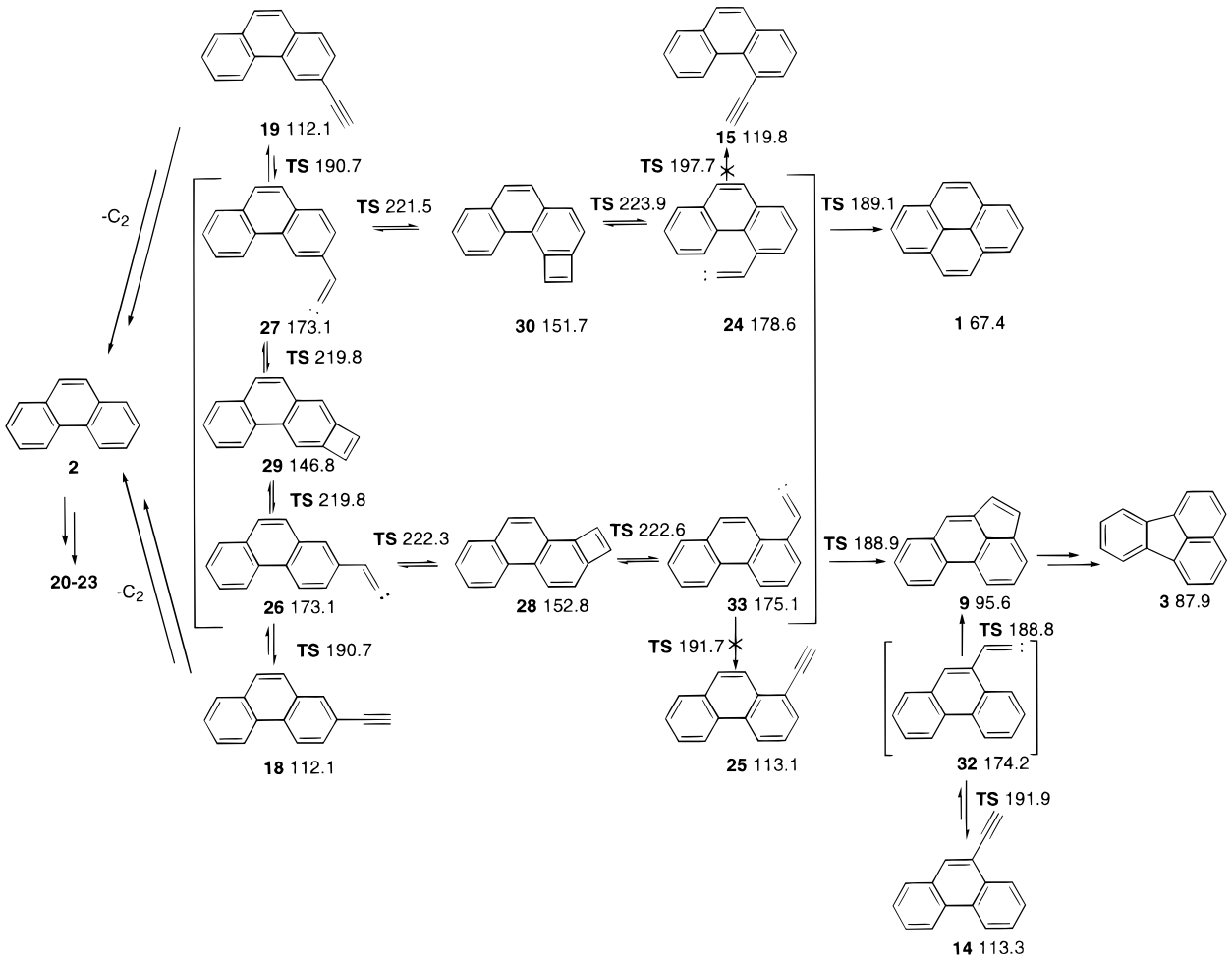


Figure 1. Gas chromatogram of the 1100 °C pyrolysates of **16** and **17** using GC-MS.

Scheme 5



pyrolysates containing the same set of 11 CP-PAH, albeit in a different ratio. The three $C_{16}H_{10}$ CP-PAH **1**, **3**, **9**,[12] the two $C_{16}H_{10}$ E-PAH **18** and **19**, the $C_{14}H_{10}$ PAH **2**, the four $C_{14}H_8$ CP-PAH pyracylene (**20**), and 1-ethynyl- (**21**), 3-ethynyl- (**22**), and 5-ethynylacenaphthylene (**23**) as well as the $C_{12}H_8$ CP-PAH acenaphthylene (**4**) were unequivocally identified (mass recoveries 86−24%, Chart 1 and Table 2).[8,18,19] This is further substantiated by GC-MS (Figure 1) as well as a GC-FT-IR analyses of the 1100 °C pyrolysates of **16** and **17**, respectively; all cryotrapped IR spectra of the identified products were in excellent agreement with those of authentic samples.[23] It is noteworthy that the product ratio of **1**, **3**, **9**, **18**, and **19** varied concomitant with the applied FVT precursors, i.e., **16** and **17**, respectively (vide infra). The identification of **2** in the pyrolysates suggests that at $T > 1000$ °C C_2 extrusion[24] also occurs. It is noteworthy that in situ generated **18** as well as **19** apparently possesses a similar propensity to undergo C_2 extrusion (Table 2). The forma-

(23) Visser, T.; Sarobe, M.; Jenneskens, L. W.; Wesseling, J. *Fuel* **1998**, *77*, 913.

tion of compounds **18**−**22** is rationalized by the established conversion of **2** into **20** and the rearrangement of the latter into **19**−**21** involving cyclopenta[*bc*]acenaphthylene as a transient intermediate.[8,18,19,23] The formation of **4** is explained by the occurrence of C_2 extrusion from **20** under FVT conditions.[8,18]

These results suggest that upon FVT of **16** and **17** at $T \geq 1000$ °C the in situ generated **18** and **19**, respectively, undergo ethynyl migrations[16] along their phenanthrene periphery (Scheme 5)! This is corroborated by the unambiguous identification of **1**, **3**, **9**, **18**, and **19** in the pyrolysates. Independent FVT experiments have revealed that **1** and **9** are obtained from 4-ethynyl- (**15**) and 9-ethynylphenanthrene (**14**), respectively, and that **3** is obtained by rearrangement of **9** via ring contraction/ring expansion.[12]

Although the formation of **1** and **9** from either in situ **18** or **19** can also be rationalized by consecutive C_2 extrusion/C_2 addition, i.e., the formation of **2** followed by a random C_2 addition giving the appropriate ethynylated phenanthrene FVT precursors for **1** and **9**, this is unexpected since FVT generally occurs under unimolecular[7] conditions. Moreover, if consecutive C_2 extrusion/C_2 addition would occur, the amounts of **1** and **9** obtained by FVT of either **16** or **17** under similar conditions should be approximately identical. Since upon FVT of **16**, **9** and its rearrangement product **3** are more abundant than **1** and the amount of **18** exceeds that of **19**, whereas opposite ratios are found upon FVT of **17**, consecutive C_2 extrusion/C_2 addition is highly unlikely (Table 2 and Figure 1). Furthermore, with increasing temperature the yields of **1**, **3**, and **9** increase at the expense of **18** and **19**, respectively. This suggests that ethynyl migration[16] is an important competitive process next to C_2 extrusion[24] (Scheme 5 and Table 2).

Interestingly, the products obtained by FVT of **16** and **17**, viz., **1**, **2**, **3**, **4**, **9**, and **18**−**23** (Chart 1), all represent ubiquitous CP-PAH combustion effluents.[1,3−5,23,25] Hence, unexpected thermal pathways for some of these representatives are disclosed.

AM1[20] Calculations. Whereas ethylidene carbene C−H insertions in the case of five/six-membered ring formation require temperatures between 600 and 900 °C, for ethynyl migrations temperatures of at least 1000 °C are needed.[16,23] Hence, the latter process has to have a higher activation enthalpy ($\Delta H^{\ddagger}$). We previously proposed that ethynyl migration along PAH peripheries involves cyclobuta-PAH as transient intermediates, followed by ring opening into a carbene (retro-carbene C−H insertion) and carbene C−H insertion.[15,16,23] Hence, the ethylidene carbene tautomers of **18** and **19**, viz. **26** and **27**, are precursors for transient cyclobuta[*a*]- (**28**) as well as cyclobuta[*b*]phenanthrene (**29**), and **29** as well as cyclobuta[*c*]phenanthrene (**30**), respectively (Scheme 5). AM1 calculations gave activation enthalpies for cyclobutaphenanthrene formation of 49.2 kcal mol^{-1} [$\Delta H^{\ddagger}$ (**26** → **28**)], 46.7 kcal mol^{-1} [$\Delta H^{\ddagger}$ (**26** → **29**)], 46.7 kcal mol^{-1} [$\Delta H^{\ddagger}$ (**27** → **29**)], and 48.4 kcal mol^{-1} [$\Delta H^{\ddagger}$ (**27** → **30**)], respectively (Scheme 5). These $\Delta H^{\ddagger}$ values are considerably larger than those calculated for ethylidene carbene C−H insertions giving either a fused five- or six-membered ring [$\Delta H^{\ddagger}$ (**32** → **9**) 14.6 kcal mol^{-1} and $\Delta H^{\ddagger}$ (**24** → **1**) 10.5 kcal mol^{-1}, Scheme 5].

A comparison of the ΔH_f^0 values of the transient cyclobuta-PAH **28** [ΔH_f^0 (**28**) 152.8 kcal mol^{-1}], **29** [ΔH_f^0 (**29**) 146.8 kcal mol^{-1}], and **30** [ΔH_f^0 (**30**) 151.7 kcal mol^{-1}] and those of E-PAH **18** [ΔH_f^0 (**18**) 112.1 kcal mol^{-1}], **19** [ΔH_f^0 (**19**) 112.1 kcal mol^{-1}], **14** [ΔH_f^0 (**14**) 113.3 kcal mol^{-1}], and **15** [ΔH_f^0 (**15**) 119.8 kcal mol^{-1}],[26] respectively, suggests that the cyclobutaphenanthrene isomers will open into the related E-PAH, viz., **18** and/or **25** from **28**, **18** and/or **19** from **29**, and **15** and/or **19** from **30**, respectively. Evidence for the occurrence of such a process was found earlier during FVT of 2,2′-diethynylbiphenyl (**13**); transient cyclobuta[*l*]phenanthrene (**31**) gave ultimately 9-ethynylphenanthrene (**14**).[15] However at $T \geq 800$ °C in the gas phase, E-PAH **14**, **15**, and **25** will equilibrate with their ethylidene carbene tautomers **32**, **24**, and **33**, respectively, and give pyrene (**1**) and acephenanthrylene (**9**) by facile carbene C−H insertion (vide supra, Table 1 and refs 12 and 15). Since transient cyclobuta[*a*]phenanthrene (**28**), viz., the penultimate precursor of **9**, is only accessible from **26**, **9** is expected to be a more abundant product in pyrolysates derived from **16** (and, thus, in situ generated **18**). Analogously, cyclobuta[*c*]phenanthrene (**30**), viz., the penultimate precursor of **1**, has to be derived from **27** which will be more abundant product in pyrolysates of **17** (and, thus, in situ generated **19**). This is in excellent agreement with our experimental observations (Table 2). In line with the higher activation enthalpies for cyclobuta-PAH formation,[27] ethynyl migration only occurs at $T > 1000$ °C where C_2 extrusion[24] is an important competitive process.

Conclusions

FVT of 4-ethynyl- (**15**), and the latent precursors for 2-ethynyl- (**18**) and 3-ethynylphenanthrene (**19**), viz., 2-(1-chloroethenyl)- (**16**) and 3-(1-chloroethenyl)phenanthrene (**17**), respectively, revealed that **15** is a selective precursor for pyrene (**1**) already at 800 °C. In contrast at $T < 1000$ °C **16** and **17** are only quantitatively converted into **18** and **19**, respectively. At $T \geq 1000$ °C both **16** and **17**, however, gave pyrolysates containing the same set of 11 constituents, albeit in a different ratio. The change in product ratio suggests that at $T \geq 1000$ °C the redundant ethynyl moieties of **18** and **19** migrate along the phenanthrene framework via transient cyclobuta-PAH intermediates toward positions suitable for either a fused five- or six-membered ring formation by a carbene C−H insertion. However, due to the high activation enthalpy required for ethynyl migration, C_2 extrusion is a competitive process.

These results are of relevance for the ubiquitous formation of pyrene (**1**), acephenanthrylene (**9**), and

(24) Brown, R. F. C.; Coulston; K. J.; Eastwood, F. W. *Tetrahedron Lett.* **1996**, *37*, 6819. The occurrence of fragmentation reactions is supported by the observation of carbonization in the hot zone concomitant with a decrease in mass recovery.

(25) Lafleur, A. L.; Howard, J. B.; Taghizadeh, K.; Plummer, E. F.; Scott. L. T.; Necula, A.; Swallow, K. C. *J. Phys. Chem.* **1996**, *100*, 17421 and references cited.

(26) The increase of ΔH_f^0 **15** [ΔH_f^0 (**15**) 119.8 kcal mol^{-1}] compared with the ΔH_f^0 values of **14** [ΔH_f^0 (**14**) 113.3 kcal mol^{-1}], **18** [ΔH_f^0 (**18**) 112.1 kcal mol^{-1}], **19** [ΔH_f^0 (**19**) 112.1 kcal mol^{-1}] and **25** [ΔH_f^0 (**25**) 113.1 kcal mol^{-1}] is attributed to steric strain between the ethynyl substituent and the phenanthrene hydrogen atom at the 5-position, respectively (see also ref 21).

(27) Cyclobuta-PAH formation is expected to occur in the dilute gas phase. Cf. the stability of benzocyclobutadiene, which dimerizes above −190 °C; Chapmann, O. L.; Chang, C. C.; Rosenquist, N. R., *J. Am. Chem. Soc.* **1976**, *98*, 261. For recent ab initio calculations on benzocyclobutadiene: Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.*, **1993**, *115*, 11153 and references cited.

fluoranthene (**3**) during (incomplete) combustion, i.e., phenanthrene (**2**) appears to be a point of divergence in PAH growth. Whereas ethynylation of **2** at the 1- or 9-position will give **9** and, subsequently, **3** by a ring contraction/ring expansion rearrangement,[12] ethynylation at the 4-position will only give **1**. Although ethynylation at the 2- or 3-position will give among others the $C_{16}H_{10}$ CP-PAH **1**, **3**, and **9**, the latter two compounds are preferentially formed from in situ generated 2-ethynylphenanthrene (**18**), whereas 3-ethynylphenanthrene (**19**) will preferentially give **1**.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere. All solvents were purified and dried by standard procedures. Melting points are uncorrected. Column chromatography: Merck kieselgel 60 silica (230−400 ASTM). ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra: δ values in ppm (reference tetramethylsilane) and J values in hertz. Infrared spectra: FT-IR, using a diffuse reflection accessory. The samples were diluted in optically pure potassium bromide. GC-MS; column: DB-17, length 30 m, 0.32 mm i.d., and film thickness 0.25 μm; injector temperature, 300 °C; temperature program, 2 min at 150 °C (10 °C min^{-1}) and then increased to 280 °C; carrier gas He and MS (EI 70 eV) quadrupole mass spectrometer. GC−FTIR: GC separations (column: HP-5MS, length 25 m, 0.25 mm i.d., and film thickness 0.25 μm; injector temperature 275 °C, temperature program, 2 min at 80 °C and then increased to 290 °C (10 °C min^{-1}); carrier gas He) and cryotrapped FT-IR-detection.[23]

Caution: Many (non)-alternant polycyclic aromatic hydrocarbons (CP-PAH) are potential mutagens and carcinogens; they should be handled with care.

Acephenanthrylene (9),[12] **Pyracylene (20),**[18,23] **and 1-Ethynyl- (21),**[18,19,23] **3-Ethynyl- (22),**[18,19,23] **and 5-Ethynylacenaphthylene (23).**[18,23] The spectroscopic and analytical data of **9** and **20**−**23** were in agreement with available literature data.

Pyrene (1), Fluoranthene (3), and Acenaphthylene (4). The spectroscopic and analytical data of **1**, **3**, and **4** were in agreement with those of commercially available samples.

4-Ethynylphenanthrene (15).[21] The synthesis of **15** was carried out using a literature procedure; all spectroscopic and analytical data of **15** were in agreement with those previously reported.[21] Overall yield of **15**: 0.45 g, 2.23 mmol, off white crystals; mp 43−45 °C (colorless oil[21]); ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.34 (1H, m), 7.93 (1H, dd, J 1.4, 7.3), 7.88 (2H, m), 7.73 (1H, AB system, J 8.8), 7.69 (1H, AB system, J 8.8), 7.65 (2H, m), 7.50 (1H, t, J 7.7), 3.68 (1H, s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.1, 133.0, 132.9, 130.5, 130.2, 130.0, 128.4, 127.9, 127.2, 127.0, 126.2, 125.9, 125.4, 118.1, 86.4, 83.4 ppm; GC/MS: m/z (%) (MS) 202 (100) [M$^{+\cdot}$].

2-Ethynylphenanthrene (18).[28] Pure **18** was obtained in nearly quantitative yield upon FVT of 2-(1-chloroethenyl)-phenanthrene (**16**, 0.1 g, 0.4 mmol) at 900 °C (mass recovery 96%, Table 2). All spectroscopic and analytical data of **18** were in agreement with those previously reported.[28] Yield of **18**: 0.08 g, 0.39 mmol, 98%, off-white crystals; mp 75−77 °C (77−78 °C[28]); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (1H, d, J 6.9), 8.63 (1H, d, J 8.1), 8.05 (1H, d, J 1.8), 7.89 (1H, dd, J 1.8, 7.8), 7.70 (5H, m), 3.19 (1H, s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.6, 132.4, 131.7, 130.3, 129.9, 129.6, 128.7, 127.8, 127.1, 126.9, 126.3, 122.9, 122.8, 120.1, 83.8, 77.8 ppm; GC/MS: m/z (%) 202 (100%) [M$^{+\cdot}$].

3-Ethynylphenanthrene (19).[28] Pure **19** was obtained in nearly quantitative yield upon FVT of 3-(1-chloroethenyl)-phenanthrene (**17**, 0.1 g, 0.4 mmol) at 900 °C (mass recovery 99%, Table 2). All spectroscopic and analytical data of **19** were in agreement with those previously reported.[28] Yield of **19**: 0.08 g, 0.39 mmol, 98%, off-white crystals; Mp 107−108 °C (109 °C[28]); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (1H, s), 8.65 (1H, d, J 8.1), 7.88 (1H, dd, J 0.9, 7.2), 7.83 (1H, d, J 8.4), 7.76 (1H, d, J 9.0), 7.67 (4H, m), 3.21 (1H, s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.2, 132.0, 130.0, 129.7, 129.5, 128.7, 128.6, 128.1, 127.1, 127.0, 126.9, 126.4, 122.7, 120.0, 84.3, 77.6 ppm; GC/MS: m/z (%) 202 (100%) [M$^{+\cdot}$].

2-(1-Chloroethenyl)phenanthrene (16). 2-Acetylphenanthrene (0.87 g, 4.0 mmol),[22] PCl_5 (1.06 g, 5.1 mmol), and PCl_3 (75 mL) were stirred at room temperature for 24 h. Subsequently, water (250 mL) was added, and the reaction mixture was extracted (diethyl ether 3 × 50 mL). The combined organic fractions were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica, eluent $CHCl_3$). Yield of **16**: 0.54 g, 2.3 mmol, 57%, light red solid; mp 132−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.67 (1H, d, J 7.8), 8.66 (1H, d, J 8.8), 8.17 (1H, d, J 2.0), 7.90 (1H, dd, J 2.0, 8.8), 7.88 (1H, d, J 8.8) 7.77 (2H, s), 7.65 (2H, m), 5.97 (1H, d, J 1.8), 5.65 (1H, d, J 1.8) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.7, 134.7, 132.3, 131.7, 130.5, 129.8, 128.6, 127.6, 126.9, 126.7, 126.6, 126.5, 124.1, 122.8, 122.7, 113.0 ppm; GC/MS: m/z (%) 238 (97), 240 (32) [M$^{+\cdot}$, with appropriate isotope pattern]. Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.64. Found: C, 80.22; H, 4.69.

3-(1-Chloroethenyl)phenanthrene (17). 3-Acetylphenanthrene (0.57 g, 2.6 mmol),[22] PCl_5 (0.72 g, 3.5 mmol), and PCl_3 (75 mL) were stirred at room temperature for 24 h. Subsequently water (250 mL) was added, and the reaction mixture was extracted (diethyl ether 3 × 50 mL). The combined organic fractions were dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica, eluent $CHCl_3$). Yield of **17**: 0.43 g, 1.8 mmol, 69%, waxy reddish brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.95 (1H, s), 8.70 (1H, dd, J 0.6, 7.8), 7.87 (1H, dd, J 1.2, 7.5), 7.83 (1H, AB system, J 0.6, 8.1), 7.80 (1H, AB system, J 1.8, 8.1), 7.74 (1H, AB system, J 9.0), 7.69 (1H, AB system, J 9.0), 7.62 (2H, m), 5.95 (1H, d, J 1.8) and 5.66 (1H, d, J 1.8) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.4, 134.8, 132.3, 132.2, 130.0, 128.7, 128.6, 128.0, 126.9, 126.8, 126.3, 124.3, 122.7, 121.2, 113.2 (one quaternary carbon atom not resolved) ppm; GC/MS: m/z (%) 238 (87), 240 (28) [M$^{+\cdot}$, with appropriate isotope pattern]. Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.64. Found: C, 80.24; H, 4.66

General Flash Vacuum Thermolysis Procedure. A Thermolyne 21100 furnace containing an unpacked quartz tube (length 40 cm and diameter 2.5 cm) was used for all FVT experiments. Conversion curves were determined by subliming 0.1 g aliquots of the FVT precursors **15**, **16**, and **17**, respectively (sublimation temperature and rate; 160 °C and 50 mg h^{-1}), into the quartz tube at a pressure of 10^{-2} Torr and the temperatures shown in Tables 1 and 2. Pyrolysate product compositions were determined by ^{1}H and ^{13}C NMR as well as capillary GC and GC-MS. In the case of **16** and **17** the product composition of the 1100 °C pyrolysates was also studied using GC−FT-IR; identical results were found.

AM1[20] **Calculations.** Semiempirical AM1 geometry optimization (MOPAC 7.0) was executed without imposing symmetry constraints until GNORM ≤ 0.5 using the eigenvector-following routine (keywords EF/TS). All minima and transition states (**TS**) were characterized by a Hessian calculation (keywords Force and Large); either none or only one imaginary vibration, respectively, was found. ΔH_f^0 and $\Delta H^{\ddagger}$ values are reported in kcal mol^{-1} (1 cal = 4.184 J, Scheme 5, see also Supporting Information).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **15**−**19** as well as AM1 archive files for all minima and transition states (**TS**) presented in Scheme 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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