Flash Vacuum Thermolysis of Acenaphtho[1,2-*a*]acenaphthylene, Fluoranthene, Benzo[*k*]- and Benzo[*j*]fluoranthene − Homolytic Scission of Carbon−Carbon Single Bonds of Internally Fused Cyclopenta Moieties at $T \geq 1100$ °C

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Flash vacuum thermolysis (FVT, 1000 °C ≥ T ≥ 1200 °C) of acenaphtho[1,2-*a*]acenaphthylene (**3**, $C_{22}H_{12}$) gave the $C_{22}H_{12}$ cyclopenta-fused polycyclic aromatic hydrocarbon (CP-PAH) acenaphtho[1,2-*e*]acenaphthylene (**4**), cyclopenta-[*cd*]perylene (**5**) and cyclopenta[*def*]benzo[*hi*]chrysene (**6**). Whereas the formation of **4** is explained by a ring contraction/ring expansion rearrangement of **3**, the identification of **5** and **6** suggests that **3** also undergoes homolytic scission of a five-membered ring's carbon–carbon single bond furnishing the transient diradical intermediate **7**. Ring closure of **7** to form **8** after rotation around the carbon–carbon single bond of the intact five-membered ring followed by hydrogen shifts will give **6**. The latter can rearrange subsequently into **5** by ring contraction/ring expansion. The structural assignment of **4** and **5** was supported by independent FVT of 6,12-bis(1-chloroethenyl)chrysene (**14**) and 3-(1-chloroethenyl)perylene (**23**), respectively. FVT of **14** (900–1200 °C) gave in a consecutive process 6,12-bis(ethynyl)chrysene (**15**), 9-ethynylbenz[*j*]acephenanthrylene (**16**) and bis(cyclopenta[*hi,qr*])chrysene (**17**). Although at T ≥ 900 °C **17** selectively rearranges into **4** by ring contraction/ring expansion, at 1200 °C the latter is converted into **5** presumably via a diradical intermediate obtained by homolytic scission of a single carbon–carbon bond of a five-membered ring. FVT of **23** gave *in situ* 3-ethynylperylene (**25**), which at 1000 °C is nearly quantitatively converted into **5**. The propensity of internal cyclopenta moieties to undergo homolytic scission of a five-membered ring's carbon–carbon single bond was corroborated by independent FVT of benzo[*k*]- (**11**) and benzo[*j*]fluoranthene (**12**). Previously unknown thermal pathways to important (CP)-PAH combustion effluents are disclosed at T ≥ 1000 °C.

Introduction

The discovery[1] and subsequent isolation of fullerenes from soot obtained by either evaporating graphite in an arc,[2] from flames under appropriate conditions[3] and by pyrolysis of polycyclic aromatic hydrocarbons (PAH)[4] has revived (non)alternant PAH research. Besides considerable activities in the area of large curved PAH synthesis, *viz.* to obtain PAH which represent parts of fullerene surfaces,[5] the elucidation of possible fullerene growth mechanisms involving PAH as intermediates, *i.e.* under flame conditions[3] and upon PAH pyrolysis,[4] has become an important research issue. Additional impetus is given by the fact that PAH are ubiquitously generated during (incomplete) combustion and that many representatives have to be considered as environmental pollutants.[6]

Flash vacuum thermolysis (FVT)[7] has proven to be an excellent tool for the study of the build up of (non-)alternant PAH as well as the determination of their thermal properties under high-temperature conditions in the gas phase. Selective syntheses of various non-alternant (multi) cyclopenta-fused PAH (CP-PAH) were developed and their propensity to undergo either selective rearrangements or conversions under high-temperature conditions in the gas phase has been disclosed. From the results a trend emerged:[6][8] The conversion of CP-PAH containing external CP moieties into their internally CP-fused isomers, such as that of acephenanthrylene (**1**) into fluoranthene (**2**), by ring contraction/ring expansion (consecutive 1,2-H/1,2-C shift or *vice versa*), is in general thermodynamically favoured in the high-temperature range (Scheme 1).[9][10] Although these rearrangements are now established, until recently no data were available for CP-PAH containing (at least) two abutting CP moieties.[11] Insight in the thermal behaviour of this class of CP-PAH is of interest to rationalize the formation of the lower fullerene C_{50} and the recently identified C_{36}[12] and, more in general, the formation of fullerenes which do not fulfil the isolated-pentagon rule.[13]

In a preliminary account[11] we reported that FVT (10^{-2} Torr, 1000−1200 °C) of acenaphtho[1,2-*a*]acenaphthylene (**3**, $C_{22}H_{12}$),[14] which possesses two abutting CP moieties and represents a key substructure of C_{50} and various possible C_{36} isomers[12] gave the novel $C_{22}H_{12}$ CP-PAH acenaphtho[1,2-*e*]acenaphthylene (**4**), cyclopenta[*cd*]perylene (**5**)

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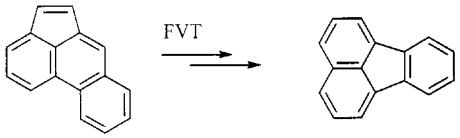


Scheme 1

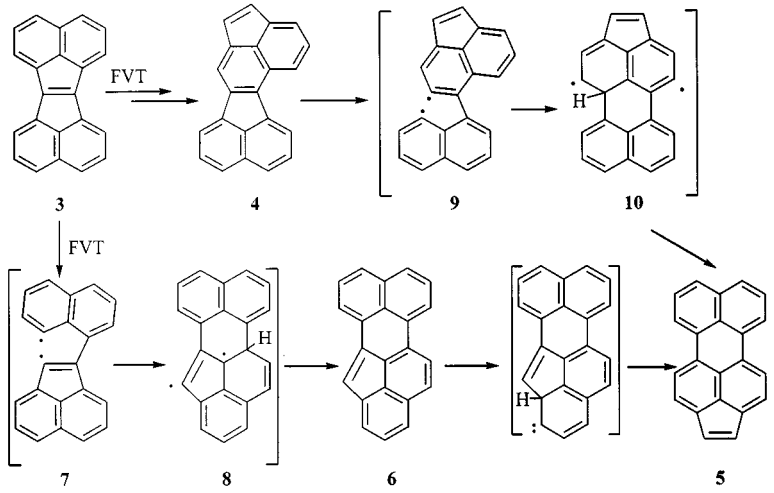
and cyclopenta[*def*]benzo[*hi*]chrysene (**6**). Whereas the conversion of **3** into **4** was explained by ring contraction/ring expansion,[9][10] the formation of **5** and **6** was tentatively explained by invoking another competitive process, *viz.* homolytic scission of a five-membered ring′s carbon−carbon single bond of **3**. Ring closure of the transient diradical intermediate **7** after rotation around the intact five-membered ring′s carbon−carbon single bond followed by ring closure into **8** and hydrogen shifts will give **6**, which subsequently can rearrange into **5** by ring contraction/ring expansion (Scheme 2 and *vide infra*).

In this paper we present a full account on the FVT of **3**, *i.e.* its conversion into **4**, **5** and **6**. To support the initial structural assignment of **6**, which was based on its ^{1}H NMR data, IGLOIII//6−31G[15] calculations were done; a satisfactory agreement between the experimental and theoretical data was found (Table 1). Furthermore, independent FVT routes for the hitherto unknown CP-PAH **4** and **5** were developed in order to enable their unequivocal identification in pyrolysates obtained by FVT of **3**. The propensity of **4** and **5** to undergo selective rearrangements or conversions under FVT conditions is discussed. The suggestion that upon FVT of **3** homolytic scission of one of the five-membered ring′s carbon−carbon single bonds is an important competitive process besides ring contraction/ring expansion prompted us to subject fluoranthene (**2**), benzo[*k*]- (**11**) and benzo[*j*]fluoranthene (**12**) to similar FVT conditions. Whereas at $T \geq 1100$ °C **2** only gave a small amount of **1**, both **11** and **12** undergo conversions presumably involving diradical intermediates giving ultimately access to (CP)-PAH, which have all been identified as important combustion effluents (*vide infra*).[16]

Results and Discussion

FVT of Acenaphtho[1,2-*a*]acenaphthylene (3)

Aliquots of **3** (20 mg) prepared according to a literature procedure[14] were sublimed into the unpacked quartz tube (length 40 cm, diameter 2 cm and temperature range 1000−1200 °C) of our FVT apparatus (10^{-2} Torr, subl. temp. 120−140 °C and rate 20 mg h^{-1}, see Experimental Section). The pyrolysate product composition was determined with ^{1}H NMR, HPLC, capillary GC and GC-MS. Whereas at 900 °C **3** was recovered quantitatively, at 1000 °C besides **3** two novel compounds of composition $C_{22}H_{12}$ (276 amu, GC/MS) were found (mass recovery 79%). In going to 1100 °C (mass recovery 62%) the amount of these products increase at the expense of **3**. At 1200 °C (mass recovery 50%) another product of composition $C_{22}H_{12}$ as well as some perylene (**13**, $C_{20}H_{12}$, 252 amu, GC/MS) were identified besides **3** and the two initial $C_{22}H_{12}$ compounds (Table 2). Unfortunately, isolation of the $C_{22}H_{12}$ CP-PAH by column chromatography under a variety of conditions was unsuccessful due to the occurrence of co-elution. Notwithstanding, a survey of the ^{1}H NMR spectra of the pyrolysates suggested that one of $C_{22}H_{12}$ products possesses both an externally fused CP moiety and a benzo[*j*]fluoranthene-like framework. Hence, **3** apparently rearranges into acenaphtho[*1,2-e*]acenaphthylene (**4**) by ring contraction/ring expansion (Scheme 2). However, since **4** represents a new CP-PAH, an independent synthesis was required for its unambiguous identification (*vide infra*). According to the ^{1}H NMR data one of the other novel $C_{22}H_{12}$ products possesses a symmetrical perylene-like structure with a fused CP moiety. Its structure was tentatively assigned to the hitherto unknown CP-PAH cyclopenta[*cd*]perylene (**5**) and was also verified by an independent synthesis (Scheme 2 and *vide infra*). Tedious preparative HPLC of the 1200 °C pyrolysate gave access to an analytical amount (*ca.* 5 mg) of the third novel product of composition $C_{22}H_{12}$ (Figure 1). ^{1}H NMR showed twelve distinct ^{1}H signals, which in combination with ^{1}H-homonuclear decoupling experiments strongly sug-



Scheme 2

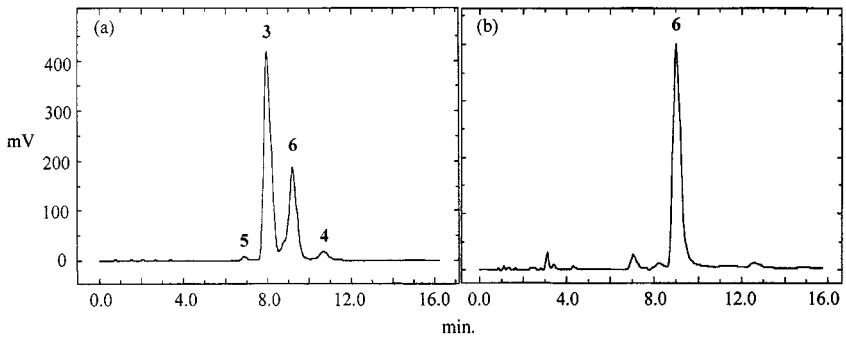


Figure 1. HPLC (eluent $CH_3CN:H_2O$, 80%:20%, detection UV, λ = 254 nm) trace of the 1200°C pyrolysate of **3** before (a) and after (b) isolation of **6**

gested that its structure corresponds to cyclopenta[*def*]benzo[*hi*]chrysene (**6**, Scheme 2 and Figure 2).

Additional support for the structural assignment of **6** was obtained by a comparison of its experimental ^{1}H NMR chemical shifts and those calculated at the IGLOIII//6−31G[15] level of theory (Table 1). Satisfactory agreement was found between theory and experiment; in general the theoretical ^{1}H NMR chemical shifts are calculated to be positioned *ca.* 0.3−0.6 ppm downfield from the experimental values. In addition, the IGLOIII//6−31G ^{1}H chemical shifts enable the unambiguous assignment of the hydrogen atoms at positions 1 and 6, and 2 and 5 which on the basis of the ^{1}H-homonuclear decoupling experiments[11] remained interchangeable (Table 1 and Figure 2). The nucleus independent chemical shifts (NICS)[17] values calculated 0.5 Å above the center of the five- and each six-membered rings, which are probes for the aromatic, non-aromatic or anti-aromatic character of the distinct rings, reveal that the five-membered ring *c* is nonaromatic [NICS(*c*) = 0.78 ppm], the six-membered ring *d* [NICS(*d*) = 4.24 ppm] moderately anti-aromatic and the six-membered rings *a*, *b*, *e* and *f* aromatic [NICS values: *a*, −8.34, *b*, −9.79, *e*, −9.95 and *f*, −9.00 ppm (Figure 2)].[17]

Table 1. Theoretical (IGLOIII//6−31G) *versus* experimental [^{1}H NMR (300.13 MHz, [D_6]acetone)] ^{1}H NMR chemical shifts of **6** (Figure 2)

H atom [position]	$\delta(^1$H NMR$)_{IGLO}$ [ppm]	$\delta(^1$H NMR$)_{exp.}$ [ppm]	$\Delta\delta$[a] [ppm]
1	9.14	8.59	0.55
2	8.17	7.78	0.39
3	8.58	8.07	0.51
4	8.55	8.06	0.49
5	8.08	7.75	0.33
6	8.91	8.53	0.38
7	8.72	8.42	0.30
8	8.65	8.13	0.52
9	8.45	7.92	0.53
10	8.09	7.70	0.39
11	8.27	7.91	0.36
12	7.94	7.61	0.33

[a] $\Delta\delta = \delta(^1$H NMR$)_{IGLO} - \delta(^1$H NMR$)_{exp.}$

A comparison of the pyrolysate product composition concomitant with increasing temperature suggested that both **4** and **6** are primary products, *viz.* a decrease in the amount of **3** corresponds to an increase of **4** as well as **6** (Table 2). Whereas the amount of **4** increased with increasing temperature, that of **6** levels of at 1100°C. However, the formation of **5** and **6** from **3** cannot be explained by ring contraction/ring expansion. Hence, apparently another process, *i.e.* homolytic scission of a five-membered ring′s carbon−carbon single bond giving transient diradical **7**, is also operational under the applied FVT conditions (Scheme 2). In line with the thermal behaviour of related diradicals,[18] ring closure of **7** into **8** after rotation around the intact five-membered ring′s carbon−carbon single bond followed by hydrogen shifts will give access to **6**, which subsequently can yield **5** by ring contraction/ring expansion (*vide infra*). AM1[19] calculations gave heats of formation (ΔH_f°) for **5** and **6** of 129.0 and 133.6 kcal mol^{-1}, respectively, *i.e.* the conversion of **6** into **5** is calculated to be exothermic (ΔH_r −4.6 kcal mol^{-1}).

FVT of 6,12-Bis(1-chloroethenyl)chrysene (14) − The Formation of Bis(cyclopenta[*hi*,*qr*])chrysene (17) and Its Selective Rearrangement into Acenaphtho[1,2-*e*]-acenaphthylene (4)

Since **4** is an externally CP-fused benzo[*j*]fluoranthene derivative, we referred to earlier FVT results for its independent synthesis. FVT of 6-(1-chloroethenyl)chrysene (**18**) at $T \leq 1000$°C gave *in situ* 6-ethynylchrysene (**19**), which after ethynyl-ethylidene carbene equilibration followed by carbene C−H insertion, gave benz[*j*]acephenanthrylene (**20**). At 1100°C **20** selectively rearranged into **12** (Scheme 3).[20]

Therefore, we envisaged that FVT of 6,12-bis(ethynyl)-chrysene (**15**) should give in a consecutive process 9-ethynylbenz[*j*]acephenanthrylene (**16**) and bis(cyclopenta[*hi,qr*])-chrysene (**17**), which ultimately will rearrange into **4** (Scheme 4). To substantiate this hypothesis **15** was prepared in three steps from chrysene. Bromination with an excess of alumina-supported copper(II) bromide[21] gave 6,12-dibromochrysene (**21**, yield 74%). Treatment of **21** with two equiv. of ethynyltrimethylsilane in the presence of a catalyst[22] gave 6,12-bis(trimethylsilylethynyl)chrysene (**22**, yield 80%), which after deprotection gave pure **15** (yield 61%, see Experimental Section). Unfortunately, however, FVT (10^{-2} Torr, subl. temp. 120−160°C) of **15** was

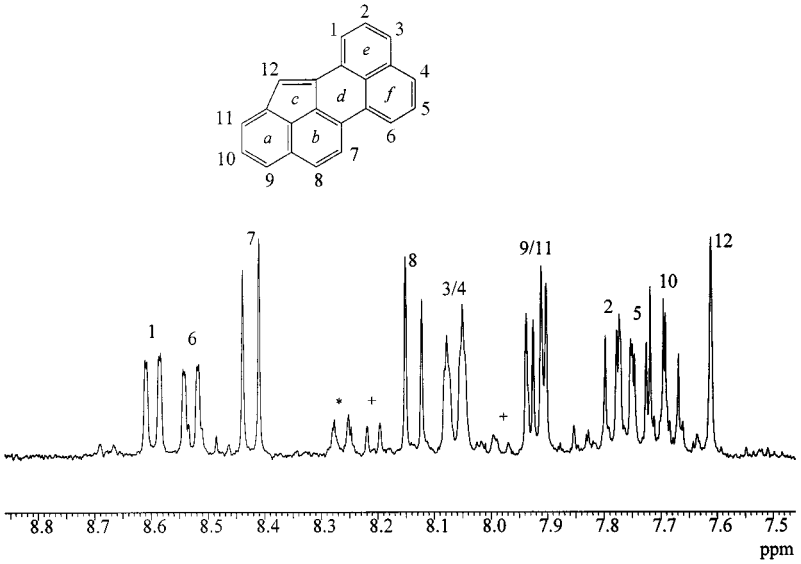


Figure 2. ^{1}H NMR (300.13 MHz, [D_6]acetone) of **6** isolated by preparative HPLC; * and + traces of cyclopenta[*cd*]perylene (**5**) and perylene (**13**)

Table 2. Product composition of the pyrolysates obtained upon FVT of **3**[a]

T [°C]	**3** [%]	**4** [%]	**5** [%]	**6** [%]	Mass Recovery [%]
1000	85	4	–	11	79
1100	77	9	–	14	62
1200[b]	45	34	6	15	50

[a] ^{1}H NMR integral ratios and capillary GC gave identical results. – [b] The 1200°C pyrolysate contains some perylene (**13**, *ca.* 1%) presumably obtained by 'C_2' extrusion from **5**.

thwarted, *i.e.* **15** could not be sublimed into the hot zone of our FVT apparatus. Instead of sublimation a colour change of **15** in the sample flask from yellow to dark brown was observed and an intractable solid was obtained. Extraction experiments of heat-treated **15** revealed that no soluble, low molecular weight compounds were present. Solid-state FT-IR showed that after heat treatment only a minute amount of free ethynyl substituents [ν(≡C–H) 3265 cm^{-1} and ν(C≡C) 2097 cm^{-1}] was still present. Hence, under the sublimation conditions **15** apparently undergoes oligo- or polymerization presumably involving the ethynyl substituents. Additional evidence for the occurrence of oligo- *cq.* polymerization was obtained by differential scanning calorimetry (DSC) and thermogravimetry [TGA(N_2), see Experimental Section]. In the DSC curve of **15** (0.65 mg) only one exotherm (175–230°C with ΔH –31.8 kcal mol^{-1}) was observed in the first heating run! In subsequent cooling and heating runs neither endotherms nor exotherms were discernible (Figure 3). TGA(N_2) revealed that during the exothermic process in the first DSC heating curve a weight loss $\Delta w/w$ of *ca.* 8% occurred.

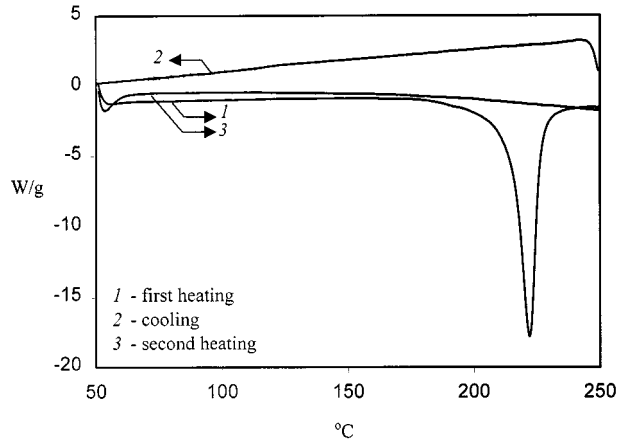
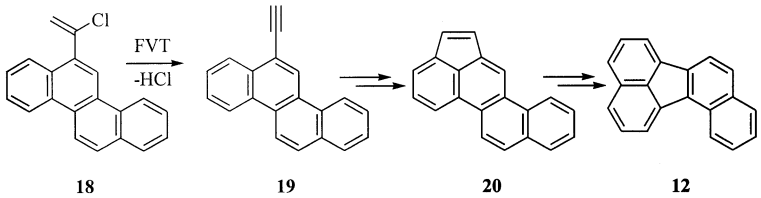


Figure 3. DSC trace of **15** (first and second heating run as well as first cooling run, see Experimental Section; –W/g exothermic)

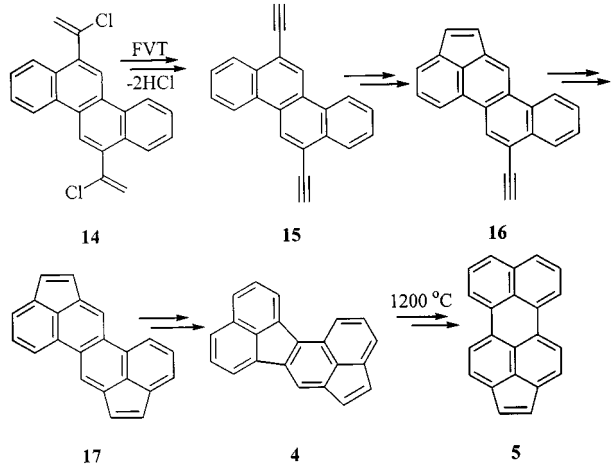
To alleviate this problem, **15** was converted into 6,12-bis(1-chloroethenyl)chrysene (**14**), *viz.* a 'masked' ethynyl precursor,[8] by treatment with HCl(g) in acetic acid (Scheme 4). Aliquots of **14** (50 mg) were subjected to FVT (10^{-2} Torr, subl. temp. 150–160°C and rate 50 mg h^{-1}).



Scheme 3

Although some oligo- or polymerization of **14** still occurred in the sample flask during sublimation, good to moderate mass recoveries were obtained in the temperature range 900−1200°C (Table 3). At 900°C the hitherto unknown bis(cyclopenta[*hi,qr*])chrysene (**17**, 85%) was the major product besides small amounts of 6,12-bis(ethynyl)chrysene (**15**, 2%), 9-ethynylbenzo[*j*]acephenanthrylene (**16**, 5%) and acenaphtho[1,2-*e*]acenaphthylene (**4**, 8%, Scheme 4). Pure **17** was readily isolated from the 900−1000°C pyrolysates by recrystallization from toluene (yield 31%, see Experimental Section). At 1000°C **17** (91%) and **4** (9%) were the only products (Table 3). This is in line with the consecutive conversion of **15** into **16** and finally into **17** followed by rearrangement of the latter into **4** (1100°C; ratio **4**:**17** 22%:78%). Tedious column chromatography of the 1100°C pyrolysate gave a fraction which besides some **17** mainly contained **4** (ratio **4**:**17** 90%:10%, ^{1}H NMR, GC-MS, HPLC, HRMS). No evidence for the presence of **3** even in trace amounts in any of these pyrolysates was found (^{1}H NMR, GC-MS, HPLC). Hence, **4** does not appear to rearrange into **3** by ring contraction/ring expansion under the applied FVT conditions. This is in line with the results of AM1[19] calculations. Whereas the conversion of **17** (ΔH_f^0 153.8 kcal mol^{-1}) into **4** (ΔH_f^0 147.5 kcal mol^{-1}) is calculated to be exothermic (ΔH_r −6.3 kcal mol^{-1}), that of **4** into **3** (ΔH_f^0 153.3 kcal mol^{-1}) is found to be endothermic (ΔH_r 5.8 kcal mol^{-1}).

The spectroscopic data of **4** derived from the enriched fraction of the 1100°C pyrolysate of **14** were identical to those found in the pyrolysates of **3**. It should be stipulated



Scheme 4

Table 3. Product composition of the pyrolysates obtained upon FVT of **14**[a]

T [°C]	**4** [%]	**5** [%]	**15** [%]	**16** [%]	**17** [%]	Mass recovery [%]
900	8	–	2	5	85	97
1000	9	–	–	–	91	44
1100	22	–	–	–	78	42
1200	55	5	–	–	40	39

[a] ^{1}H NMR integral ratios and capillary GC gave identical results.

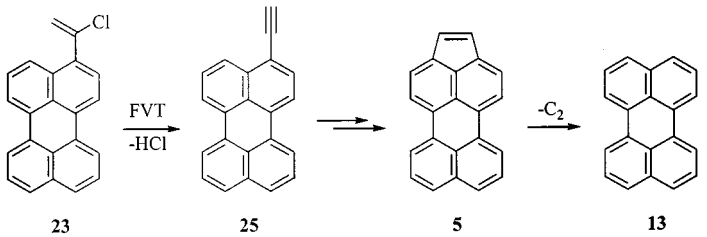
that the 900−1100°C pyrolysates of **14** contained neither **5** nor **6**. However in the 1200°C pyrolysate a small amount of **5** (5%) was unequivocally identified (Table 3). This suggests that, at 1200°C **4** can be converted into **5** presumably by a diradical mechanism involving homolytic scission of a five-membered ring′s carbon−carbon single bond of **4** furnishing transient diradical **9**. After rotation around the intact five-membered ring′s carbon−carbon single bond followed by ring closure **9** will give **10**, which after hydrogen shifts will yield **5** (Schemes 2 and 4 and *vide infra* for related results).

FVT of 3-(1-Chloroethenyl)perylene (23) − Formation of Cyclopenta[*cd*]perylene (5)

3-(1-Chloroethenyl)perylene (**23**) was obtained in two steps from perylene (**13**). Friedel−Crafts acetylation of **13** gave 3-acetylperylene (**24**, yield 40%),[23] which upon treatment with PCl_5/PCl_3 gave **23** (yield 93%, Scheme 5 and see Experimental Section). FVT of **23** (10^{-2} Torr, subl. temp. 120−140°C, rate 50 mg h^{-1}), *viz.* ′masked′ 3-ethynylperylene (**25**), at 1000°C gave cyclopenta[*cd*]perylene (**5**, 95%) and a small amount of **13** (5%; mass recovery 77%). Pure **5** was isolated by recrystallization from ethanol (yield 51% and see Experimental Section). A comparison of its spectral data with that found in the pyrolysates of **3** unequivocally revealed the presence of **5**. Since upon FVT of **23** no evidence for the formation of either **4** or **6**, even in trace amounts, was found, neither **23** nor **5** are FVT precursors for **4** and **6**.

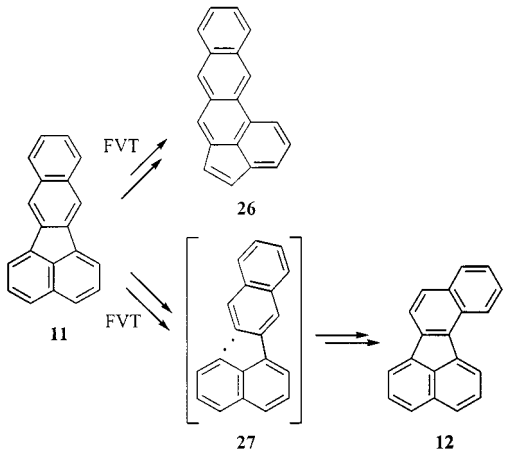
FVT of Fluoranthene (2), Benzo[*k*]fluoranthene (11) and Benzo[*j*]fluoranthene (12) at $T \geq 1100$°C

Since upon FVT of **3** homolytic scission of a five-membered ring′s carbon−carbon single bond appears to be an



Scheme 5

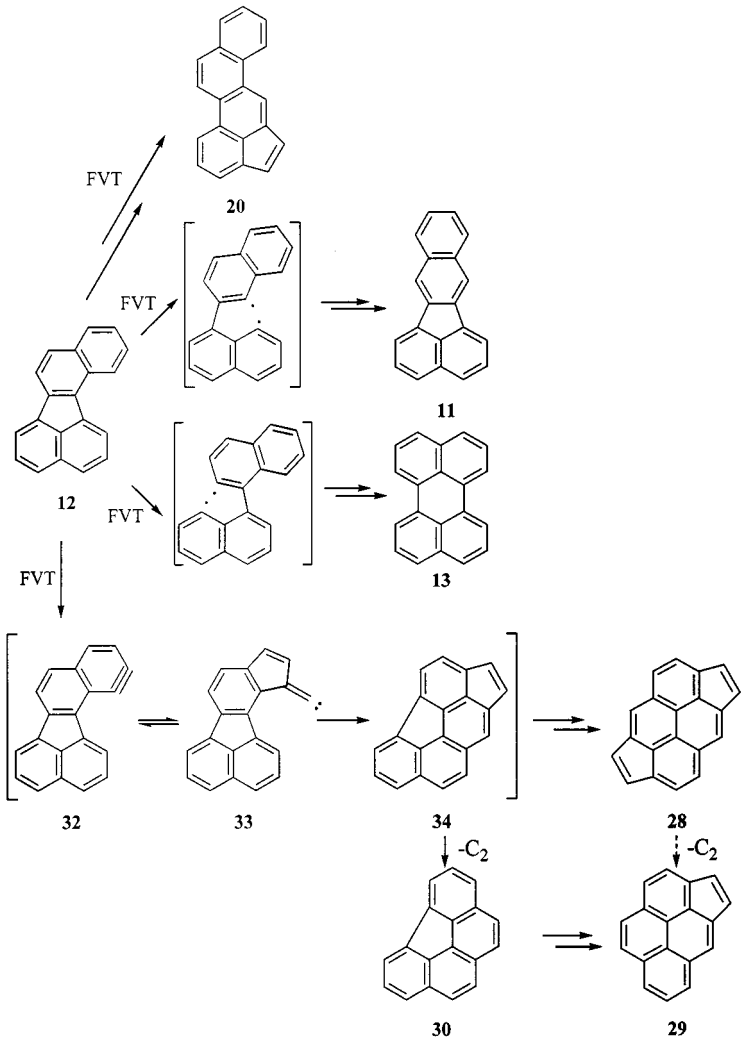
important competitive process besides ring contraction/ring expansion, we were prompted to reinvestigate the thermal stability of CP-PAH fluoranthene (**2**, $C_{16}H_{10}$) and, benzo[*k*]- (**11**, $C_{20}H_{12}$) and benzo[*j*]fluoranthene (**12**, $C_{20}H_{12}$) under similar FVT conditions. Both **2** and **12** were previously shown to be thermally stable under FVT conditions at $T \leq 1000\,^{\circ}C$.[10][20]



Scheme 6

FVT of **2** (20 mg) at 1100°C (10^{-2} Torr, subl. temp. 80−100°C, rate 20 mg h^{-1}) gave pyrolysates containing besides starting material **2** (94%) a small amount of acephenanthrylene (**1**, 6%, mass recovery 74%). The reverse process depicted in Scheme 1 rationalizes the formation of **1** from **2**, *viz.* **2** undergoes a 1,2-H shift followed by a 1,2-C shift or *vice versa*. At 1200°C an identical product distribution was found (mass recovery 55%). Note that in the case of **2** homolytic scission of a five-membered ring's carbon−carbon single bond followed by ring closure and hydrogen shifts represents a degenerate process.

In contrast, FVT of **11** (20 mg) at 1100−1200°C (10^{-2} Torr, subl. temp. 100−120°C, rate 20 mg h^{-1}) gave pyrolysates which, besides **11**, contained two other $C_{20}H_{12}$ CP-PAH, *viz.* benz[*k*]acephenanthrylene (**26**)[24] and benzo[*j*]fluoranthene (**12**, ratio **11**:**12**:**26**; 1100°C, 90%:6%:4% and 1200°C, 84%:11%:5% with mass recoveries of 60% and



Scheme 7

38%, respectively, Scheme 6). Although in going from 1100°C to 1200°C the amount of **26** did not change significantly, that of **12** increased concomitantly with a decrease of **11**. Whereas the formation of **26** from **11** can be rationalized by a ring contraction/ring expansion rearrangement,[9][10] that of **12** from **11** corroborates that homolytic scission of a five-membered ring′s carbon−carbon single bond leading to the transient diradical **27** indeed occurs. After rotation around the other five-membered ring′s carbon−carbon single bond followed by ring closure and a hydrogen shift the latter will give **12**.

Since we have previously shown that benz[*j*]acephenanthrylene (**20**) between 1000−1100°C selectively rearranges into benzo[*j*]fluoranthene (**12**, Scheme 3),[20] we have subjected **12** to FVT at 1200°C (10^{-2} Torr, subl. temp. 140°C, rate 50 mg h^{-1}). A pyrolysate was obtained containing seven different (CP)-PAH (mass recovery 45%, Scheme 7)! Starting material (**12**, 57%, $C_{20}H_{12}$), benz[*j*]acephenanthrylene (**20**, 4%, $C_{20}H_{12}$),[20] benzo[*k*]fluoranthene (**11**, 15%, $C_{20}H_{12}$), perylene (**13**, 7%, $C_{20}H_{12}$), cyclopent[*jk*]acepyrylene (**28**, 6%, $C_{20}H_{10}$),[25] cyclopenta[*cd*]pyrene (**29**, 7%, $C_{18}H_{10}$)[26] and benzo[*ghi*]fluoranthene (**30**, 4%, $C_{18}H_{10}$)[27] were all unambiguously identified.

The formation of **11** and **13** from **12** further supports the occurrence of a homolytic scission of a five-membered ring′s carbon−carbon single bond, put forward to rationalize the formation of **6** and **12** upon FVT of **3** and **11**, respectively (*vide supra*). The formation of **20**[20] is explained by a ring contraction/ring expansion of **12** under the severe FVT conditions. However, the formation of **28**, **29** and **30** is less straightforward. Note that benzo[*c*]phenanthrene (**31**, $C_{18}H_{12}$) gave both **29** and **30** under related FVT conditions.[27] The formation of **29** was explained by invoking the initial formation of 1,2-dehydrobenzo[*c*]phenanthrene, *viz.* a benzyne homologue, *via* homolysis of a *peri* aryl C−H bond followed by loss of a vicinal hydrogen, which after benzyne-cyclopentadienylidene carbene equilibration and an intramolecular carbene C−H insertion will give **29**. Note that **30** will rearrange under the FVT conditions into **29** and *vice versa*.[27] Recently, the results of *ab initio* calculations were reported which strongly favour the latter mechanism.[28] If an analogous process is operational for **12**, initial formation of benzyne derivative **32** after equilibration with its cyclopentadienylidene carbene tautomer **33** followed by intramolecular carbene C−H insertion will give transient cyclopenta[*cd*]benzo[*ghi*]fluoranthene (**34**). Compound **34** can either rearrange into **28** by ring contraction/ring expansion or undergo ′C_2′ extrusion directly furnishing **30** (Scheme 7). Semi-empirical AM1[19] calculations predict ΔH_f^o values for and **28**, **30** and **34** of 154.6 kcal mol^{-1}, 116.6 kcal mol^{-1} and 176.6 kcal mol^{-1}, respectively, *i.e.* a facile conversion from **34** into **30** and **28** is expected. In this context, it is noteworthy that **28** is thermally stable up to 1100°C.[25] Hence, we anticipate that transient **34** will be the precursor for both **28** and **30**. The latter, subsequently, will rearrange into **29** under the applied FVT conditions.

Conclusions

The FVT results presented in this paper provide evidence that the presence of two abutting five-membered rings in the case of acenaphtho[1,2-*a*]acenaphthylene (**3**), markedly affects its propensity to undergo rearrangements and conversions under high-temperature conditions in the gas phase. Whereas CP-PAH containing externally fused CP moieties, which in general rearrange into isomers containing an internally fused CP moieties with high selectivity by ring contraction/ring expansion, **3** also appears to undergo another independent process, *viz.* homolytic scission of a five-membered ring′s single carbon−carbon. The latter process is operational under FVT conditions at $T \geq 1100$°C in the case of the benzofluoranthene derivatives **4**, **11** and **12**. Whereas **4** is converted into **5** and **11** into **12**, **12** gave its isomers **11**, **13** and **20** as well as the CP-PAH **28**, **29** and **30**.

Experimental Section

General: All reactions were carried out under a N_2 atmosphere. − Column chromatography was performed on Merck Kieselgel 60 silica (230−400 ASTM). − Melting points were uncorrected. − ^1H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded in $CDCl_3$ with TMS as internal standard except in the case of **6**, which was recorded in [D_6]acetone. − GC-MS; 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 150°C− (10°C min^{-1}) → 280°C; carrier gas He). − Differential scanning calorimetry (DSC) was performed on a Mettler DSC 12E under a N_2 atmosphere (heating and cooling rate 20°C min^{-1}). − Thermogravimetry (TGA) was done under a N_2 atmosphere on a Perkin−Elmer TGS-2 with an autobalance AR-2 (temperature range 50−850°C and a heating rate of 20°C min^{-1}). 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 and Spectra Physics UV2000 UV detector (λ = 254 nm) with eluent CH_3CN:H_2O 80%:20%. − Elemental analysis was carried out by H. Kolbe Mikroanalytisches Laboratorium Mülheim a.d. Ruhr, Germany.

Caution! Many (cyclopenta-fused) polycyclic aromatic hydrocarbons (CP)-PAH are potential mutagens and carcinogens; they should be handled with care.

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 for **3** and **14** were determined by subliming 20 mg (subl. temp. 120−140°C, rate 20 mg h^{-1}) and 50 mg aliquots (subl. temp. 150−160°C, rate 50 mg h^{-1}), respectively, into the quartz tube at 10^{-2} Torr and the temperatures shown in Tables 2 and 3. Compound **23** (50 mg) was only subjected to FVT (subl. temp. 120−140°C, rate 50 mg h^{-1}) at 1000°C. In the case of **2**, **11** and **12** FVT (20 mg aliquots) was done at 1000−1100°C (subl. temp. 80−100°C, rate 20 mg h^{-1}), 1100−1200°C (subl. temp. 100−120°C, rate 20 mg h^{-1}) and 1200°C (subl. temp. 140°C, rate 20 mg h^{-1}), respectively. Pyrolysate product compositions were determined by ^1H and ^{13}C NMR, HPLC, capillary GC, and GC-MS.

Acenaphtho[1,2-*a*]acenaphthylene (3): Compound **3** was prepared according to a literature procedure; all spectroscopic and analytical data were in agreement with those earlier reported.[14]

Acenaphtho[1,2-*e*]acenaphthylene (4): An enriched fraction containing **4** (90%) and **17** (10%) was obtained by preparative column chromatography (silica, eluent *n*-C_6H_{14}) of the 1000°C pyrolysate of **14**. − ^{1}H NMR: δ = 8.49 (d, ^3J(H,H) = 7.8 Hz, 1 H), 8.41 (d, ^3J(H,H) = 7.0 Hz, 1 H), 8.19 (s, 1 H), 8.02 (d, ^3J(H,H) = 6.8 Hz, 1 H), 7.88 (d, ^3J(H,H) = 8.0 Hz, 1 H), 7.86 (d, ^3J(H,H) = 8.2 Hz, 1 H), 7.75−7.65 (m, 3 H), 7.62 (d, ^3J(H,H) = 6.9 Hz, 1 H), 7.12 (A part of AB system, *J*(AB) = 5.2 Hz, 1 H) and 7.08 (B part of AB system, *J*(AB) = 5.2 Hz, 1 H) ppm. − ^{13}C NMR: 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 (ten quaternary C atoms not resolved). − GC/MS *m*/*z* (%) 276 (100) [M$^{\cdot+}$]. − HRMS ($C_{22}H_{12}$) Calcd. 276.0939; found 276.0910.

Cyclopenta[*cd*]perylene (5): Pure **5** was isolated from the 1000°C pyrolysate of **23**. The pyrolysate was collected with CH_2Cl_2 (10 mL) followed by removal of the solvent *in vacuo*. Addition of C_2H_5OH (0.02 g mL^{-1}) gave a deeply red coloured solution from which **5** crystallized at 4°C. Yield 51%, red crystals, m.p. > 300°C (dec.). - ^{1}H NMR: δ = 8.46 (d, ^3J(H,H) = 7.5 Hz, 2 H), 8.28 (d, ^3J(H,H) = 7.5 Hz, 2 H), 7.85 (d, ^3J(H,H) = 7.6 Hz, 2 H), 7.81 (d, ^3J(H,H) = 7.5 Hz, 2 H), 7.61 (dd, ^3J(H,H) = 7.5 Hz and 7.6 Hz, 2 H) and 7.13 (s, 2 H). − ^{13}C NMR: δ = 138.0, 131.7, 129.8, 129.7, 128.9, 128.3, 126.5, 125.2, 122.5 and 120.0 (three quaternary C atoms not resolved). − GC/MS *m*/*z* (%) 276 (100) [M$^{\cdot+}$]. − $C_{22}H_{12}$ (276.34): calcd. C 95.62, H 4.38; found C 95.39, H, 4.34.

Cyclopenta[*def*]benzo[*hi*]chrysene (6): A small amount of analytically pure **6** (*ca.* 5 mg) was obtained by tedious preparative HPLC of the 1200°C pyrolysate of **3**. − ^{1}H NMR ([D$_6$]acetone): δ = 8.59 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.0 Hz, 1 H), 8.53 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.0 Hz, 1 H), 8.42 (d, ^3J(H,H) = 8.6 Hz, 1 H), 8.13 (d, ^3J(H,H) = 8.6 Hz, 1 H), 8.07 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.0 Hz, 1 H), 8.06 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.0 Hz, 1 H), 7.92 (d, ^3J(H,H) = 8.1 Hz, 1 H), 7.91 (d, ^3J(H,H) = 6.9 Hz, 1 H), 7.78 (dd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 7.2 Hz, 1 H), 7.75 (dd, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 8.4 Hz, 1 H), 7.70 (dd, ^3J(H,H) = 8.1 Hz and ^3J(H,H) = 6.9 Hz, 1 H) and 7.61 (s, 1 H). − ^{13}C NMR ([D$_6$]acetone): 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 (ten quaternary C atoms not resolved) (see IGLOIII//6−31G Calculations). − GC/MS *m*/*z* (%) 276 (100) [M$^{\cdot+}$]. − HRMS ($C_{22}H_{12}$): calcd. 276.0939; found 276.0906.

6,12-Bis(1-chloroethenyl)chrysene (14): Compound **15** (0.48 g, 1.1 mmol) was converted into **14** by treatment with HCl gas in acetic acid (50 mL) at 80°C for 1 h. Subsequently, water (100 mL) was added and the resulting mixture extracted with $CHCl_3$ (3 × 50 mL). The organic layer was washed with a saturated solution of $NaHCO_3$ in water, dried over magnesium sulfate and concentrated under reduced pressure. Pure **14** was obtained as yellow solid (0.40 g, 1.1 mmol, 100%). − M.p. 188°C (dec.). − ^{1}H NMR: δ = 8.80 (dd, ^4J(H,H) = 1.4 Hz, ^3J(H,H) = 9.1 Hz, 2 H), 8.73 (s, 2 H), 8.33 (dd, ^4J(H,H) = 1.7 Hz, ^3J(H,H) = 7.7 Hz, 2 H), 7.74 (m, 4 H), 5.97 (d, ^2J(H,H) = 0.8 Hz, 2 H) and 5.75 (d, ^2J(H,H) = 0.8 Hz, 2 H). − ^{13}C NMR: δ = 139.0, 126.7, 130.8, 129.3, 127.9, 127.2, 127.0, 126.3, 123.4, 122.0 and 118.2. − GC/MS *m*/*z* (%) 348 (100), 350 (67), 352 (12) [M$^{\cdot+}$ with appropriate isotope pattern].

6,12-Bis(ethynyl)chrysene (15): Bis(triphenylphosphane)palladium dichloride (0.28 g, 0.4 mmol), and copper(I) iodide (0.02 g, 0.1 mmol) was added to a deaereated solution of 0.40 g (1.04 mmol) of 6,12-dibromochrysene (**20**) and 0.30 g (3.1 mmol) of ethynyltrimethylsilane in anhydrous triethylamine (40 mL).[22] The reaction mixture was heated at reflux temperature for 5 days. After cooling to room temperature the solid was filtered off and the filtrate concentrated under reduced pressure. The residue was purified by column chromatography (silica, eluent *n*-C_6H_{14}:$CHCl_3$, 2:1) giving 0.35 g (0.8 mmol, 80%) of pure 6,12-bis(trimethylsilylethynyl)chrysene (**22**) as a yellow solid. − M.p. 130−131°C. − ^{1}H NMR: δ = 8.93 (s, 2 H), 8.76 (m, 2 H), 8.50 (m, 2 H), 7.73 (m, 4 H) and 0.40 (s, 6 H). − ^{13}C NMR: δ = 131.5, 129.8, 127.7, 127.4, 127.2, 126.9, 126.4, 123.3, 120.8, 103.6, 100.4 and 0.1. − GC/MS *m*/*z* (%) 420 (100) [M$^{\cdot+}$]. Compound **22** (0.35 g, 0.8 mmol) was converted into **15** by treatment with anhydrous K_2CO_3 (0.06 g) in CH_3OH (30 mL) at room temperature for 3 hours. After removal of the solvent under reduced pressure $CHCl_3$ (50 mL) was added and the resulting solution washed with water (2 × 20 mL). The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Pure **15** was obtained as an off white solid (0.14 g, 0.5 mmol, 61%). Even upon storage at −20°C **15** slowly oligo *cq.* polymerizes. − DSC; m.p. endotherm not discernible, *i.e.* in the first heating run only one exotherm (175−230°C with Δ*H* −31.8 kcal mol^{-1}, see text and Figure 3) was found. − ^{1}H NMR: δ = 8.99 (s, 2 H), 8.77 (m, 2 H), 8.54 (m, 2 H), 7.75 (m, 4 H) and 3.60 (s, 2 H). − ^{13}C NMR: δ = 131.6, 129.8, 127.7, 127.6, 127.3, 127.0, 126.9, 123.2, 120.1, 82.6 and 82.2. − GC/MS *m*/*z* (%) 276 (100) [M$^{\cdot+}$]. − $C_{22}H_{12}$ (276.34): calcd. C 95.62, H 4.38; found C 95.42, H 4.32.

9-Ethynylbenz[*j*]acephenanthrylene (16): Selected spectral data for **16** were derived from the 900°C pyrolysate of **14** by comparison with available spectroscopic data of **4**, **15** and **17** (Table 3). − ^{1}H NMR: δ = 8.95 (s, 1 H), 8.94 (s, 1 H), 8.84 (dd, ^4J(H,H) = 1.7 Hz, ^3J(H,H) = 7.2 Hz, 1 H), 8.60 (m, 1 H), 8.45 (dd, ^4J(H,H) = 1.7 Hz, ^3J(H,H) = 7.2 Hz, 1 H), 7.75 (m, 4 H), 7.24 (AB system, *J*(AB) = 5.3 Hz, 1 H), 7.22 (AB system, *J*(AB) = 5.3 Hz, 1 H) and 3.59 (s, 1 H). − GC/MS *m*/*z* (%) 276 (100) [M$^{\cdot+}$].

Bis(cyclopenta[*hi*,*qr*])chrysene (17): Pure **17** was isolated from the 900−1000°C pyrolysate of **14** by recrystallization from toluene (10 mg mL^{-1}). Isolation of **17** from the *T* > 1000°C pyrolysates is thwarted due to co-precipitation of **4** and **17**. Yield 31%, orange crystals, m.p. 235°C (dec.). − ^{1}H NMR: δ = 8.94 (s, 2 H), 8.55 (dd, ^4J(H,H) = 1.7 Hz, ^3J(H,H) = 7.2 Hz, 2 H), 7.74 (m, 4 H), 7.25 (AB system, *J*(AB) = 5.3 Hz, 2 H) and 7.22 (AB system, *J*(AB) = 5.3 Hz, 2 H). − ^{13}C NMR: δ = 139.8, 139.1, 131.9, 131.2, 129.0, 128.2, 127.1, 126.8, 123.2, 122.6 and 120.6. − GC/MS *m*/*z* (%) 276 (100) [M$^{\cdot+}$]. − $C_{22}H_{12}$ (276.34): calcd. C 95.62, H 4.38; found: C 95.36; H 4.46.

6,12-Dibromochrysene (21): Chrysene (1.00 g, 4.4 mmol) was treated with 15.0 g (22.4 mmol) of alumina-supported copper (II) bromide[21] in CCl_4 (50 mL) at reflux temperature for four days. After filtration the residue was washed with 200 mL hot CCl_4. The combined filtrate was concentrated under reduced pressure and the remaining solid was recrystallized from $CHCl_3$ giving pure **21** (1.25 g, 3.2 mmol, 74%) as white crystals. − M.p. 260°C (dec.). − ^{1}H NMR: δ = 9.00 (s, 2 H), 8.70 (m, 2 H), 8.44 (m, 2 H) and 7.78 (m, 4 H). − ^{13}C NMR: δ = 130.8, 130.5, 128.2, 128.1, 127.9, 127.8, 125.2, 123.3 and 123.2. − $C_{22}H_{10}Br_2$ (434.13): calcd. C 56.00, H 2.61; found C 55.76, H, 2.60.

3-(1-Chloroethenyl)perylene (23): A mixture of **24** (0.71 g, 2.4 mmol) and PCl_5 (0.70 g, 3.6 mmol) in PCl_3 (50 mL) was heated at 40°C for 3 h. After cooling to room temperature water (100 mL) was added. After standard workup, and purification by preparative column chromatography (silica, eluent $CHCl_3$/*n*-C_5H_{12}, 1:1) **23** was isolated as a yellow solid. Yield 0.68 g (2.2 mmol, 93%). − M.p. 140°C (dec.). − ^{1}H NMR: δ = 8.22 (m, 3 H), 8.14 (d, ^3J(H,H) = 7.8 Hz, 1 H), 8.03 (d, ^3J(H,H) = 8.4 Hz, 1 H), 7.71 (d, ^3J(H,H) = 8.1 Hz, 1 H), 7.70 (d, ^3J(H,H) = 8.0 Hz, 1 H), 7.53 (m, 4 H), 5.85 (d, ^2J(H,H) = 1.1 Hz, 1 H) and 5.61 (d, ^2J(H,H) = 1.1 Hz, 1 H).

− ^{13}C NMR: δ = 138.6, 134.6, 132.5, 131.8, 131.5, 131.0, 130.7, 128.5, 128.4, 128.0, 127.4, 127.0, 126.7, 126.6, 125.3, 120.7, 120.6, 120.5, 119.4 and 117.8 (two quaternary C atoms not resolved). − GC/MS *m/z* (%) 312 (100), 314 (35) [$M^{\cdot+}$ with appropriate isotope pattern].

3-Acetylperylene (24):[23] To a cooled suspension (0°C, ice bath) of fresh $AlCl_3$ (1.41 g, 10.7 mmol) in CH_2Cl_2 (20 mL), 0.62 g (7.9 mmol) acetyl chloride was added. After stirring until a clear solution was obtained, perylene (**13**, 1.88 g, 7.5 mmol) was added in small portions at room temperature. The reaction mixture was heated at reflux temperature for two hours, cooled to 0°C (ice bath) and, subsequently, hydrolysed with 0.5 M HCl [20 mL (0°C, ice bath)]. After standard workup a mixture of **13** (59%), **24** (40%) and 3,9-diacetylperylene (1%) was obtained. Compound **24** was isolated and purified by preparative column chromatography (silica, eluent $CHCl_3$). Yield 0.88 g (3.0 mmol, 40%). − M.p. 277−278°C (m.p. 277−278°C[23]). − ^{1}H NMR: δ = 8.69 (d, ^3J(H,H) = 8.6 Hz, 1 H), 8.23 (m, 3 H), 8.14 (d, ^3J(H,H) = 7.9 Hz, 1 H), 7.91 (d, ^3J(H,H) = 7.9 Hz, 1 H), 7.75 (d, ^3J(H,H) = 8.1 Hz, 1 H), 7.71 (d, ^3J(H,H) = 8.1 Hz, 1 H), 7.60 (t, ^3J(H,H) = 8.1 Hz, 1 H), 7.50 (t, ^3J(H,H) = 7.9 Hz, 2 H) and 2.75 (s, 3 H). − ^{13}C NMR: δ = 201.6, 135.6, 134.4, 134.1, 132.0, 131.2, 131.0, 130.2, 129.7, 129.2, 128.3, 128.2, 128.1, 127.8, 126.8, 126.6, 120.0, 121.8, 121.1, 120.8, 118.8 and 29.8. − GC/MS *m/z* (%) 294 [$M^{\cdot+}$].

IGLOIII//6−31G Calculations: The ^{1}H and ^{13}C NMR chemical shift values of **6** were calculated at the IGLOIII//6−31G[15] level of theory. For the IGLO calculation the implemented basis set III and a 6−31G-optimized geometry of **6** (C_s) was used (Figure 4). The absolute chemical shifts σ(^{1}H) and σ(^{13}C) of tetramethylsilane (TMS) calculated at the same level of theory [IGLOIII//6−31G; σ(^{1} H) 32.1 ppm and σ(^{13}C) 193.6 ppm] were used to convert the σ(^{1}H) and σ(^{13}C) values, respectively, of **6** to δ(^{1}H) and δ(^{13}C) values. Nucleus independent chemical shifts (NICS)[17] were calculated for each distinct five- and six-membered ring 0.5 Å above each ring center. $E_{tot.}$(6−31G) −839.829356 a.u. and $E_{tot.}$(IGLOIII6-31G) −840.384362 a.u. See Table 1 for IGLOIII//6−31G ^{1}H NMR chemical shifts of **6**. IGLOIII//6−31G ^{13}C NMR chemical shifts of **6:** δ = 150.12, 147.04, 144.83, 141.89, 140.17, 139.25, 138.09 (CH), 138.04 (CH), 138.01, 137.89, 137.74 (CH), 136.30, 136.36, 135.23 (CH), 134.19 (CH), 134.14 (CH), 133.30 (CH), 132.67 (CH), 131.21 (CH), 131.03 (CH), 128.27 (CH) and 121.54 (CH). For comparison similar IGLOIII//6−31G NICS calculations were done for acenaphthylene and perylene (**13**).[17] Pertinent data (6−31G geometry, Hessian calculation, IGLOIII output) of **6**, acenaphthylene and perylene (**13**) are available upon request (L.W.J.).

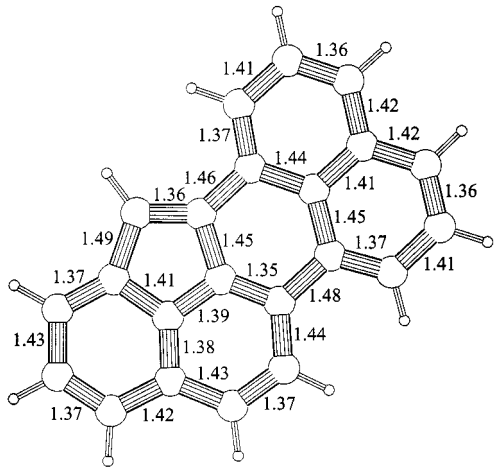


Figure 4. Optimized 6−31G geometry of **6** (C_s; bond lengths in Å)

AM1 Calculations: AM1 geometry optimization (MOPAC 6.0) was executed without imposing symmetry constraints until GNORM ≤ 0.5 using the eigenvector following routine (keywords EF).[19] All minima were characterized by a Hessian calculation (keywords Force and Large); no imaginary vibrations were found. ΔH_f^o values are reported in kcal mol^{-1} (1 cal = 4.184 J). Pertinent data (AM1 geometries, Hessian calculations) are available upon request (L.W.J.).

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