Synthesis and Characterization of the Three Dicyclopentapyrenes[1]

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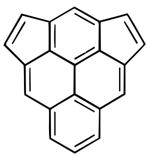
Polycyclic aromatic hydrocarbons containing fully unsaturated five-membered rings as integral components of their trigonal carbon networks (CP-PAHs) have attracted considerable attention recently in a variety of scientific circles.[2−10] Some of these novel nonalternant hydrocarbons exhibit unusual photophysical behavior, *e.g.*, anomalous fluorescence,[3] and/or pronounced biological activity, *e.g.*, acute cyctotoxicity.[4] Many have been identified or are believed to be formed as products of incomplete combustion, either in flames[5] or in cigarette smoke,[6] and a few have been produced by flash pyrolyses of other hydrocarbons.[7,8] Five-membered rings fully encircled by benzene rings impart a curvature to the trigonal carbon network that gives rise to the bowl-shaped geometry of corannulene[9] and to the closed polyhedral surfaces of the fullerenes.[10] Herein we report the syntheses and a preliminary spectroscopic examination of the three isomeric dicyclopentapyrenes **1**, **2**, and **3**, all of which were unknown until now. The ^{1}H NMR properties of isomer **1** differ markedly from those of **2** and **3** (Table 1).



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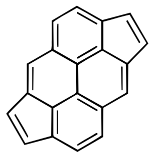

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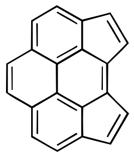

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The key step in our syntheses takes advantage of the intramolecular trapping of vinylidenes generated thermally from terminal acetylenes, a powerful method for ring construction first reported by R. F. C. Brown.[11]

Table 1. ^{1}H NMR Patterns for Dicyclopentapyrenes 1, 2, and 3[a]

compd	average chemical shifts[b] 6-membered rings	 5-membered rings
1	8.26	7.35
2	7.55	6.66
3	7.58	6.91

[a] Measured in $CDCl_3$. [b] In ppm downfield from tetramethylsilane.

Several years ago, we extended the synthetic utility of this method by introducing the 1-chlorovinyl side chain as a superior “masked ethynyl group” for flash pyrolyses (Scheme 1) and exploited this technology in a three-step synthesis of corannulene.[12] We have subsequently employed the same methodology for the synthesis of numerous CP-PAHs,[1,7] including those reported here, and other workers have adopted our method to prepare such compounds as cyclopentapyrene[13] and a $C_{30}H_{12}$ double corannulene.[14]

Friedel−Crafts acylation of pyrene with excess acetyl chloride and aluminum chloride in carbon disulfide gives 1,3-diacetylpyrene (**4**), 1,6-diacetylpyrene (**5**), and 1,8-diacetylpyrene (**6**), all of which can be isolated in usable quantities through a combination of crystallization and chromatographic purification methods.[15] Separate treatment of each diketone with PCl_5 in dichloromethane at room temperature gives the corresponding bis(1-chlorovinyl)pyrenes **7**, **8**, and **9**, and flash vacuum pyrolysis of these at 1000 °C/0.75−1.0 mmHg in separate experiments gives the title compounds **1**, **2**, and **3**, respectively (Scheme 2).

A full listing of all the ^{1}H NMR chemical shifts and coupling constants for the title compounds can be found together with the ^{13}C NMR data in the Experimental Section; however, the striking difference in the gross ^{1}H NMR spectroscopic properties of isomer **1** vis-à-vis those of **2** and **3** (Table 1) deserves comment. Even a casual inspection of the NMR spectra reveals that the resonances of all the hydrogens in **2** and **3** are shifted upfield

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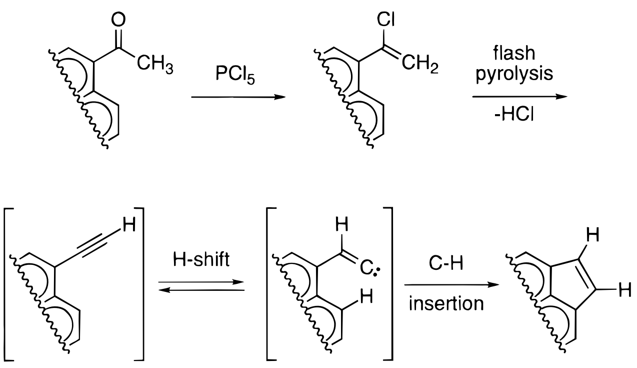
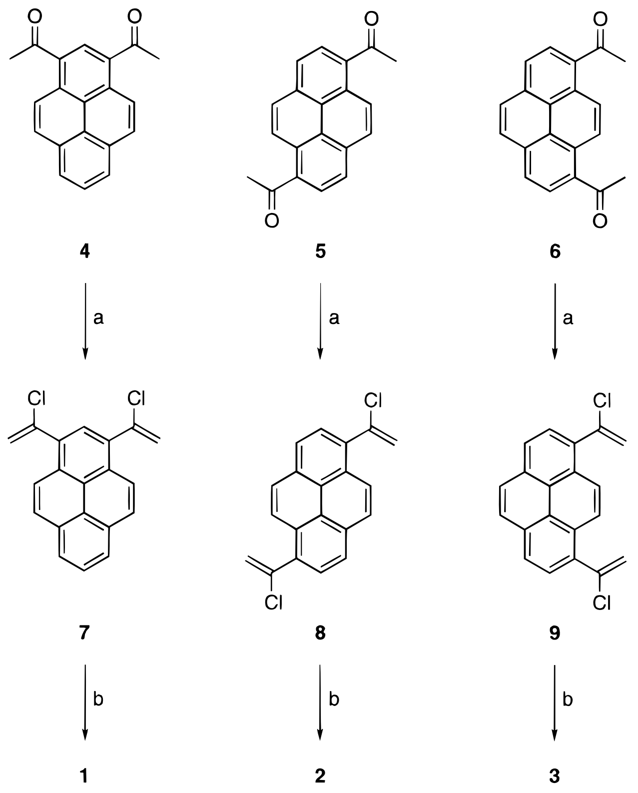
Scheme 1



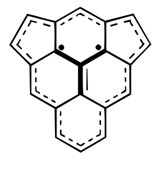
Scheme 2



(a) PCl_5, CH_2Cl_2 (b) flash pyrolysis, 1000 °C, 0.75 - 1.0 mmHg

by 0.4−0.7 ppm relative to the resonances of the corresponding hydrogens in **1**.

As a first-order explanation for this curious difference, we note that two of the seven resonance structures of isomers **2** and **3** can be viewed as antiaromatic [16]-annulene perimeters with a closed-shell butadiene moiety in the core (*s-trans* and *s-cis*, respectively).[16−18] Isomer **1**, on the other hand, has no resonance structures with an antiaromatic [16]annulene perimeter that leave a closed-shell moiety in the core; perimeter delocalization in **1** would leave a trimethylenemethane core (contrast **10** with **11** and **12**).



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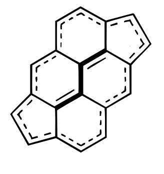

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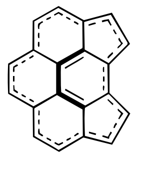

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In this respect, isomers **2** and **3** resemble dicyclopentanaphthalene (pyracylene), in which the hydrogens are significantly shielded by the paramagnetic ring current contribution of an antiaromatic $4N$ π-electron perimeter.[19] Isomer **1** should feel no such paramagnetic ring current effect, and this may well contribute to the lower-field resonances of its protons. High-level molecular orbital calculations ought to shed further light on the differences between these isomers.

The syntheses described herein make it possible to confirm or refute experimentally the presence of these dicyclopentapyrenes in flames and smoke as well as to test their carcinogenicity. The possibility that hydrocarbon **3** might isomerize to corannulene (also $C_{20}H_{10}$) by a Stone−Wales-type rearrangement[20] under suitable conditions can now also be tested.

Experimental Section

General. High-resolution mass spectra were obtained from the Mass Spectroscopy Laboratory, School of Chemical Sciences, University of Illinois.

General Procedure for the Preparation of Bis(1-chlorovinyl)pyrenes. A mixture of 0.1 g (0.35 mmol) of the diacetylpyrene,[15] 0.218 g (1.05 mmol) of phosphorous pentachloride, and 10 mL of methylene chloride was stirred at room temperature for 3 h. The reaction was quenched with water and extracted with methylene chloride. The crude product was purified by column chromatography on silica gel with pentane. A small amount (2−7%) of over-chlorinated product could generally be detected in the chromatographed material by ^{1}H NMR spectroscopy (singlet at 6.6−6.7 ppm), but this minor contaminant caused no apparent problem in the next step.

1,3-Bis(1-chlorovinyl)pyrene (7): yield of 66 mg (44%) from 135 mg of 1,3-diacetylpyrene; mp = 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, 2H, $J = 9.2$ Hz), 8.25 (d, 2H, $J = 7.7$ Hz), 8.18 (d, 2H, $J = 9.2$ Hz), 8.08 (s, 1H), 8.06 (t, 1H, $J = 7.6$ Hz), 6.01 (d, 2H, $J = 1.3$ Hz), 5.71 (d, 2H, $J = 1.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 133.2, 130.7, 128.8, 127.1, 126.4, 126.1, 124.1, 118.8; HRMS calcd for $C_{20}H_{12}Cl_2$ 322.0316, found 322.0315.

1,6-Bis(1-chlorovinyl)pyrene (8): yield of 69 mg (62%) from 100 mg of 1,6-diacetylpyrene; mp = 185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, 2H, $J = 9.2$ Hz), 8.18 (d, 2H, $J = 7.8$ Hz), 8.13 (d, 2H, $J = 9.2$ Hz), 8.07(d, 2H, $J = 7.9$ Hz), 6.01 (d, 2H, $J = 1.2$ Hz), 5.68 (d, 2H, $J = 1.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.4, 131.4, 128.3, 127.9, 126.8, 125.2, 124.9, 124.7, 110.5; HRMS calcd for $C_{20}H_{12}Cl_2$ 322.0316, found 322.0315.

1,8-Bis(1-chlorovinyl)pyrene (9): yield of 58 mg (52%) from 100 mg of 1,8-diacetylpyrene; mp = 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H), 8.16 (d, 2H, $J = 7.8$ Hz), 8.07 (d, 2H, $J = 7.3$ Hz), 8.06 (s, 2H), 6.02 (d, 2H, $J = 1.2$ Hz), 5.68 (d, 2H, $J = 1.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.2, 131.8, 127.9, 127.8, 126.8, 125.2, 125.0, 124.6, 118.5; HRMS calcd for $C_{20}H_{12}Cl_2$ 322.0316, found 322.0315.

General Procedure for the Preparation of Dicyclopentapyrenes. Compounds **7**, **8**, and **9** were submitted to flash vacuum pyrolysis at 1000 °C, with a slow bleed of nitrogen

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[16] Though the "perimeter model" of Platt[17] has fallen into disfavor as a method for predicting the overall aromaticity of PAHs, the presence or absence of closed conjugated circuits around the perimeter of a PAH in one or more of its valence bond resonance structures does make a weighted contribution to the overall electronic properties of the molecule.[18]

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carrier gas (final pressure: 0.75−1.0 mmHg), as previously described.[12] The dicyclopentapyrenes were purified by flash vacuum chromatography on silica gel with pentane. All three dicyclopentapyrenes are sensitive to air oxidation, but decomposition can be retarded by storage under nitrogen in the dark at −20 °C.

Dicyclopenta[*cd*,*mn*]pyrene (1): yield of 30 mg (78%) from 60 mg of 1,3-bis(1-chlorovinyl)pyrene; brick red crystals; mp = 180 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, 2H, J = 7.7 Hz), 8.30 (s, 2H), 8.11 (s, 1H), 7.99 (t, 1H, J = 7.7 Hz), 7.49 (d, 2H, J = 5.0 Hz), 7.20 (d, 2H, J = 5.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 135.6, 134.9, 132.6, 131.4, 127.9, 126.9, 126.4, 125.6, 120.0, 118.6, 114.6; UV−vis (hexane) λ_{max} (log ϵ) 367 (3.30), 350 (3.26), 332 (3.04), 278 (3.50), 232 (3.67); HRMS calcd for $C_{20}H_{10}$ 250.0782, found 250.0781.

Dicyclopenta[*cd*,*jk*]pyrene (2): yield of 62 mg (80%) from 100 mg of 1,6-bis(1-chlorovinyl)pyrene; dark brown crystals; mp = 210 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 7.7 Hz), 7.49 (s, 2H), 7.45 (d, 2H, J = 7.7 Hz), 6.69 (d, 2H, J = 5.1 Hz), 6.61 (d, 2H, J = 5.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.2, 133.2, 131.8, 131.3, 130.4, 129.3, 125.4, 122.1, 121.2; UV−VIS (hexane) λ_{max} (log ϵ) 490 (3.47), 459 (3.42), 435 (3.21), 398 (3.97), 388 (3.50), 376 (3.68), 355 (3.30), 323 (sh, 3.53), 308 (sh, 3.75), 287 (3.94), 240 (4.40); HRMS calcd for $C_{20}H_{10}$ 250.0782, Found 250.0784. Anal. Calcd for $C_{20}H_{10}$: C, 95.97; H, 4.03. Found: C, 95.66; H, 4.31.

Dicyclopenta[*cd*,*fg*]pyrene (3): yield of 40 mg (51%) from 100 mg of 1,8-bis(1-chlorovinyl)pyrene; brown crystals; mp = 190 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 7.6 Hz), 7.61 (d, 2H, J = 7.6 Hz), 7.45 (s, 2H), 7.02 (d, 2H, J = 5.3 Hz), 6.79 (d, 2H, J = 5.3 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 141.2, 138.7, 138.2, 131.6, 131.4, 128.6, 128.1, 127.8, 124.5, 121.3; UV−vis (hexane) λ_{max} (log ϵ) 418 (3.58), 400 (3.96), 386 (4.30), 366 (4.21), 350 (3.88), 319 (4.32), 304 (4.40), 296 (4.36), 279 (4.39), 239 (4.80); HRMS calcd for $C_{20}H_{10}$ 250.0782, found 250.0784.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1**, **2**, **3**, **7**, **8**, and **9** (22 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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