OH, 4439-43-4; $CH_3(CH_2)_{11}OOH$, 3229-98-9; $CH_3(CH_2)_9OOH$, 4225-91-6; (*R*)-2-octyl-OOH, 68570-62-7; $CH_3(CH_2)_{10}CO_3H$, 2388-12-7; $CH_3(CH_2)_9CO_3H$, 676-08-4; (*E*)-PhCH=CHCO$_3$H, 137846-29-8; (*RS*)-$CH_3CH_2CH(Ph)CO_3H$, 137846-30-1; CsOH, 21351-79-1; H_2O_2, 7722-84-1; 2,3-dimethyl-2-butene, 563-79-1; (*S*)-2-bromooctane, 1191-24-8; 2-methoxyprop-2-yl hexadecyl peroxide, 137846-21-0; 2-methoxyprop-2-yl dodecyl peroxide, 137846-22-1; 2-methoxyprop-2-yl decyl peroxide, 137846-23-2; 2-methoxyprop-2-yl 2(*R*)-octyl peroxide, 137846-24-3; 2-methoxyprop-2-yl peroxydodecanoate, 137846-25-4; 2-methoxyprop-2-yl peroxyundecanoate, 137846-26-5; 2-methoxyprop-2-yl (*E*)-3-phenyl-2-peroxypropenoate, 137846-27-6; 2-methoxyprop-2-yl (*RS*)-2-phenylperoxybutanoate, 137846-28-7; (-)-*trans*-2-phenylcyclohexyl 2-propenyl ether, 116102-43-3; 2(*R*)-octyl 2-[(*trans*-(-)-2-phenylcyclohexyl)oxy]prop-2-yl peroxide, 126873-59-4.

Supplementary Material Available: ^{13}C NMR spectra for all perketals, hydroperoxides, peresters, and peracids and ^1H NMR spectra of *trans*-(-)-2-phenylcyclohexyl perketal (18 pages). This material is contained in many 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.

Synthesis of Some Ethylindeno[1,2,3-*cd*]pyrenes

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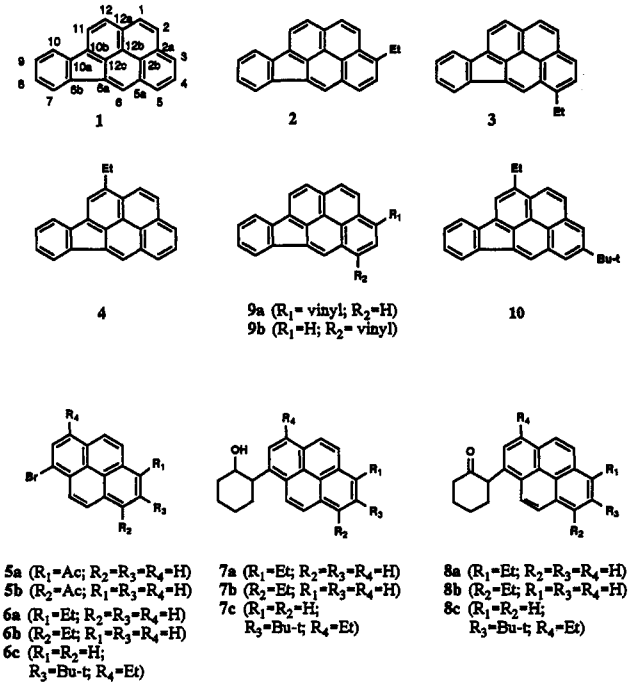
Received June 17, 1991

Indeno[1,2,3-*cd*]pyrene (**1**), a polycyclic aromatic compound (PAC) which possesses a fluoranthene framework, is an ubiquitous environmental pollutant that is generated by the combustion of fossil fuels and thus is present in direct emission sources like diesel exhaust.[1-3] Hydrocarbon **1** has also been shown to be both a mutagen and a carcinogen.[2,3] However, relatively little is known about its chemical and biological properties. For example, the results of Dewar-PI calculations predict that the reaction of **1** with electrophiles should yield products of C(3)- or C(5)-substitution.[4] Yet both bromination and Friedel–Crafts acetylation of **1** have yielded, predominantly, products of C(12) substitution, as the NMR spectra of the products have shown.[5] Additionally, the nitration of **1** by both acetyl nitrate and nitrogen dioxide have afforded the 12-nitro derivative[6] rather than the 8- or 9-nitro derivative.[7]

Here is described the synthesis of 3-ethyl- (**2**), 5-ethyl- (**3**) and 4-*tert*-butyl-12-ethylindeno[1,2,3-*cd*]pyrene (**10**) by the method of Cho and Harvey.[1] The ^1H and ^{13}C NMR spectroscopic characteristics were compared with those of the parent compound **1**. In addition, the results provide evidence of what sites of **1** are reactive toward electrophilic substitution.

Scheme I



Results and Discussion

Various bromoethylpyrenes were chosen as precursors of **2** and **3**. Thus, the Friedel–Crafts acetylation of 1-bromopyrene gave, as reported,[8] a ca. 2:3 mixture of 6- (**5a**) and 8-acetyl-1-bromopyrene (**5b**) (Scheme I). Attempts to separate the two isomers on a preparative scale were not successful. Therefore, the mixture was directly subjected to Wolff–Kishner reduction. Recrystallization of the mixture of products afforded pure 1-bromo-8-ethylpyrene (**6b**) (ca. 20%). What remained in the mother liquor was a mixture (ca. 1:1) of 1-bromo-6-ethylpyrene (**6a**) and **6b**.

Treatment of **6b** with, successively, BuLi and cyclohexene oxide yielded the corresponding substituted cyclohexanol **7b**. Similar treatment of the mixture of **6a** and **6b** described above and recrystallization of the mixture of products gave **7a**. The cyclohexanones **8a** and **8b** were obtained by the pyridinium dichromate (PDC) oxidation of **7a** and **7b**, respectively. The cyclodehydration of each ketone gave a mixture of hydrocarbons,[9] which was subjected to dehydrogenation without further purification.

The first attempt to prepare **2** from the products from the cyclodehydration of **8a**, by treatment with DDQ, gave only small amounts of **2** and 3-vinylindeno[1,2,3-*cd*]pyrene (**9a**). Similar treatment of the products from the cyclodehydration of **8b** gave **3** (in low yield) and its 5-vinyl analogue **9b**. A second attempt, which employed trityl trifluoroacetate (TTFA)[10] as the dehydrogenating reagent, was somewhat more successful. Byproducts like vinyl derivatives were not detected by TLC. However, isolating **2** (or **3**) from the dark green reaction mixture proved to be fairly difficult. A last attempt at aromatization, by Pd/C-catalyzed dehydrogenation, was more successful, although the yield of **2** depended on the reaction time.

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Table I. ^{1}H NMR Spectra of the Ethylindenopyrenes 1–4 and 10

	chemical shift,[a] δ, in ppm (J, in Hz)				
site	1	2	3	4	10
1	8.14 (d, 9.1)	8.17 (d, 9.3)	8.09 (d, 9.0)	8.30 (d, 9.4)	8.28 (d, 9.4)
2	8.10 (d, 9.1)	8.32 (d, 9.3)	8.04 (d, 9.0)	8.04 (d, 9.4)	8.08 (d, 9.4)
3	8.28 (d, 7.6)	(Et)	8.21 (d, 7.8)	8.25 (d, 7.7)	8.29 (s)
4	8.06 (t, 7.6)	7.93 (d, 7.6)	7.94 (d, 7.8)	8.03 (t, 7.7)	(*t*-Bu)
5	8.34 (d, 7.6)	8.36 (d, 7.6)	(Et)	8.39 (d, 7.7)	8.45 (s)
6	8.60 (s)	8.57 (s)	8.85 (s)	8.53 (s)	8.53 (s)
7	8.14 (m)	8.14 (m)	8.19 (m)	8.14 (m)	8.13 (m)
8	7.44 (m)	7.45 (m)	7.45 (m)	7.43 (m)	7.45 (m)
9	7.49 (m)	7.47 (m)	7.48 (m)	7.47 (m)	7.47 (m)
10	8.04 (m)	8.05 (m)	8.05 (m)	8.04 (m)	8.04 (m)
11	8.39 (d, 7.7)	8.39 (d, 7.8)	8.37 (d, 7.8)	8.27 (s)	8.24 (s)
12	8.25 (d, 7.7)	8.24 (d, 7.8)	8.22 (d, 7.8)	(Et)	(Et)
$-CH_2-$		3.44 (q, 7.6)	3.55 (q, 7.6)	3.47 (q, 7.5)	3.46 (q, 7.6)
-Me		1.53 (t, 7.6)	1.58 (t, 7.6)	1.55 (t, 7.5)	1.55 (t, 7.6)
t-Bu					1.62 (s)

[a] The signals due to the protons at C(7)–C(10) are typical of the protons of an AXX'M system. Consequently, the chemical shift that is reported is the midpoint of the signal.

However, the isolation and purification of the products were easy.

In order to sterically hinder the approach of electrophiles to the reactive sites, i.e., C(6) and C(8), of 1-ethylpyrene,[11] that compound was alkylated by treatment with *tert*-butyl bromide to yield 7-*tert*-butyl-1-ethylpyrene. This compound was then brominated in the usual manner to afford 1-bromo-7-*tert*-butyl-3-ethylpyrene (**6c**). Treatment of **6c** in the manner described above for **6b** eventually gave, via **7c** and **8c**, 4-*tert*-butyl-12-ethylindeno[1,2,3-*cd*]pyrene (**10**). However, attempts to de-*tert*-butylate **6c** and **10** failed: the employment of such reagents as Nafion-H membrane,[12] aluminum chloride, sulfuric acid, or trifluoroacetic acid in toluene met with no success.

On the other hand, hydrocarbon **4** could be formed by the Wolff-Kishner reduction of 12-acetylindeno[1,2,3-*cd*]pyrene,[5] which, in turn, was obtained by the electrophilic acetylation of its parent **1**.

The complete assignment of the signals in the ^{1}H (Table I) and ^{13}C NMR spectra (Table II) of **1–4** and **10** was facilitated by 2D NMR techniques, which included normal and long-range COSY and hetero-COSY procedures.[13] In the ^{1}H NMR spectra, the protons ortho and peri to the ethyl group resonate at higher ($\Delta\delta$ = −0.12 to −0.15 ppm) and lower fields ($\Delta\delta$ = +0.14 to +0.25 ppm), respectively, than do the corresponding protons of the parent compound **1**. The direction and magnitude of the changes in the chemical shift can be reasonably explained in terms of the diamagnetic effects of the ortho and peri substituents, which are similar to those seen in the spectra of methylpyrenes.[14] The ^3J coupling constants, $J_{H(1)-H(2)}$, in the spectra of **2**, **4**, and **10** are larger (ΔJ = 0.2–0.3 Hz) than that in the spectrum of **1**, due to the presence of a peri substituent. A similar trend is seen in the spectra of pyrene and its derivatives,[8,15] although the magnitudes of ΔJ are small. This observation indicates that the presence of a peri substituent increases the double bond character of the C(1)–C(2) bond.

Table II. ^{13}C NMR Spectra of the Ethylindenopyrenes 1–4 and 10

	chemical shift (δ, in ppm)				
site	1	2	3	4	10
1	126.6	126.3	125.6	123.4	123.3
2	127.1	123.3	127.2	126.7	126.8
2a	130.4	127.9	128.9	130.2	129.9
2b	123.1	123.5	123.4	123.6	127.8
3	126.7	141.4	126.8	126.4	123.7
4	126.4	126.9	127.1	126.3	149.5
5	128.5	128.7	142.7	128.2	125.7
5a	132.0	130.4	129.3	132.2	132.1
6	121.3	121.6	117.4	120.5	120.7
6a	135.6	134.6	135.2	135.6	135.5
6b	138.9	138.8	139.0	139.0	139.1
7	122.4	122.3	122.2	122.3	122.2
8	126.7	126.6	126.5	126.6	126.5
9	128.2	127.9	128.0	128.0	127.9
10	121.5	121.4	121.4	121.3	121.2
10a	141.8	141.7	141.7	141.8	141.9
10b	133.0	132.7	132.6	132.9	132.6
11	119.6	119.5	119.4	119.8	119.4
12	124.8	124.4	124.6	139.7	139.5
12a	130.5	130.4	130.9	126.4	126.3
12b	121.7	122.0	121.9	122.0	121.8
12c	130.6	130.8	130.3	129.1	129.0
CH_2		26.2	26.8	26.7	26.7
Me		16.5	16.6	16.5	16.5
t-Bu					31.9/35.3

In the ^{13}C NMR spectra of the ethyl homologues **2–4** and **10**, the signals due to the various carbons appear at fields similar to those of the corresponding carbons of **1**, except the cases indicated below. Thus, the carbons which bear the ethyl group resonate at lower fields ($\Delta\delta$ = +14.2 to +14.9 ppm) than do the corresponding carbons of parent compound **1**. The same phenomenon is noticeable when the spectra of benzene and ethylbenzene ($\Delta\delta$ = +15.4 ppm) are compared. On the other hand, the signals due to the tertiary carbons peri to the ethyl group and the quaternary carbons ortho and para to the ethyl group are observed at higher fields ($\Delta\delta$ = −3.2 to −3.9, −2.5 to −4.2, and −1.5 to −1.6 ppm, respectively) than are the signals due to the corresponding carbons of **1**. Similar changes in chemical shift are seen when the spectra of methylpyrenes[14] and 1-methylnaphthalene[16] are compared with those of their parent compounds. These findings suggest that the chemical shift of a particular carbon of a complex alkyl-

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(12) The use of Nafion-H powder should be effective in bringing about trans-*tert*-butylation. In addition to ref 11, see: Miyazawa, A.; Yamato, T.; Tashiro, M. *J. Org. Chem.* **1991**, *56*, 1334. Miyazawa, A.; Tsuge, A.; Yamato, T.; Tashiro, M. *Ibid.* **1991**, *56*, 4312.

(13) Cho, B. P.; Harvey, R. G. *J. Org. Chem.* **1987**, *52*, 5679. Because the ^{1}H NMR spectrum of **1** that is described is that of a more concentrated solution, the signals appear at somewhat higher fields than do those of the spectrum that is recorded now.

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substituted PAC can be estimated by combining the chemical shift of the corresponding carbon of the parent PAC and the value of $\Delta\delta$ obtained by comparing the spectrum of a simpler PAC, e.g., naphthalene or pyrene, with those of its alkyl-substituted analogues.

Experimental Section

Melting points are uncorrected. IR spectra of KBr pellets were recorded with a JASCO IR Report-100. UV–vis spectra of EtOH solutions were recorded with a Shimadzu UV-180. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a Varian VXR-300. The concentrations of the solutions were ca. 2 mg/0.7 mL of solvent in the case of the ^1H NMR spectra and 20–30 mg/0.7 mL of solvent in the case of the ^{13}C NMR spectra. Mass spectra were recorded with a Hitachi M-80 equipped with a direct inlet and operated at an ionization voltage of 70 eV.

7-*tert*-Butyl-1-ethylpyrene. To a mixture of 1-ethylpyrene[17] (9.20 g, 40 mmol), $AlCl_3$ (5.70 g, 42.8 mmol), and CH_2Cl_2 (80 mL) at 5–10 °C under Ar was added *t*-BuBr (4.8 mL, 41 mmol) over 30 min. The mixture was stirred for an additional 45 min, whereupon ice was added to quench the reaction. The two liquid layers were separated. The organic layer was washed with aq $NaHSO_3$ and water, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane) to give 7-*tert*-butyl-1-ethylpyrene (6.52 g, 66%): mp 123–125 °C (hexane); IR 2964, 2868, 866 cm^{-1}; UV λ_{max} (log ϵ) 343 (4.70), 327 (4.48), 313 (4.07), 278 (4.68), 267 (4.42), 256 (4.12), 247 (4.94), 237 nm (4.71); ^1H NMR δ 1.48 (3 H, t, J = 7.6 Hz), 1.58 (9 H, s), 3.37 (2 H, q, J = 7.6 Hz), 7.85 (1 H, d, J = 7.6 Hz, H_2), 7.99 (1 H, d, J = 6.3 Hz, H_4), 7.99 (1 H, d, J = 6.3 Hz, H_5), 8.08 (1 H, d, J = 7.6 Hz, H_3), 8.08 (1 H, d, J = 9.3 Hz, H_9), 8.18 (1 H, d, J = 1.9 Hz, H_6), 8.19 (1 H, d, J = 1.9 Hz, H_8), 8.26 (1 H, d, J = 9.3 Hz, H_{10}); ^{13}C NMR δ 16.0 (Me), 26.4 (–CH_2–), 31.8 (Me_3), 35.1, 121.7 (C_8), 122.0 (C_6), 123.1 (C_{10}), 123.2 (C_{10c}), 124.6 (C_3), 124.9 (C_{10b}), 125.9 (C_2), 126.6 (C_5), 127.2 (C_9), 127.3 (C_4), 128.1 (C_{10a}), 129.4 (C_{3a}), 130.7 (C_{8a}), 131.2 (C_{5a}), 138.3 (C_1), 148.7 (C_7); MS m/z 286 (M^+), 271, 214.

1-Bromo-7-*tert*-butyl-3-ethylpyrene (6c). A solution of bromine (1.52 g, 9.5 mmol) in CH_2Cl_2 (10 mL) was added over 40 min to a mixture of 7-*tert*-butyl-1-ethylpyrene (2.28 g, 8 mmol), powdered Fe (112 mg, 2 mmol), and CH_2Cl_2 (40 mL) at 15–20 °C. After 1 h of stirring the mixture was treated as described above. Column chromatography of the crude product on Florisil gave 2.58 g (88%) of **6c**: mp 246–249 °C dec (PhH); IR 2980, 1595, 1225, 870 cm^{-1}; UV λ_{max} (log ϵ) 351 (4.66), 334 (4.48), 320 (4.07), 283 (4.58), 272 (4.37), 260 (4.12), 250 (4.79), 243 nm (4.59); ^1H NMR δ 1.48 (3 H, t, J = 7.6 Hz), 1.58 (9 H, s), 3.33 (2 H, q, J = 7.6 Hz), 8.08 (1 H, d, J = 9.5 Hz, H_9), 8.10 (1 H, d, J = 9.1 Hz, H_5), 8.10 (1 H, s, H_2), 8.21 (1 H, d, J = 9.1 Hz, H_4), 8.23 (2 H, s, H_6, H_8), 8.36 (1 H, d, J = 9.5 Hz, H_{10}); ^{13}C NMR δ 15.7 (Me), 26.1 (CH_2), 31.8 (Me_3), 35.1, 119.6 (C_1), 122.6 (C_6), 122.6 (C_8), 122.9 (C_4), 125.7 (C_{10}), 126.6 (C_{10b}), 127.5 (C_5), 127.7 (C_{3a}, C_{10a}, or C_{10b}), 127.8, 128.1 (C_9), 128.2, 129.8 (C_2), 130.8 (C_{5a}), 131.0 (C_{8a}), 139.1 (C_3), 149.4 (C_7); MS m/z 366, 364 (M^+), 351, 349.

1-Bromo-6-ethyl- (6a) and 1-Bromo-8-ethylpyrene (6b). A mixture of the isomers **5a** and **5b** (2:3 mixture, 6.23 g, 19 mmol), KOH (1.28 g, 20 mmol), 95% $N_2H_4 \cdot H_2O$ (5.0 mL, 100 mmol), and diethylene glycol (200 mL) was heated at 100 °C for 2 h, then at 200 °C for 6 h. The cooled mixture was diluted with water, and the organic matter was purified by column chromatography on silica gel (PhH) to afford 5.26 g (88%) of a mixture of **6a** and **6b**: IR 841, 838 cm^{-1}. The mixture was recrystallized from EtOH to give pure **6b** (20%): mp 129–130 °C; IR 841 cm^{-1}; UV λ_{max} (log ϵ) 351 (4.67), 334 (4.55), 279 (4.74), 268 (4.48), 244 nm (4.87); ^1H NMR δ 1.49 (3 H, t, J = 7.6 Hz, Me), 3.40 (2 H, q, J = 7.6 Hz), 7.92 (1 H, d, J = 7.8 Hz, H_7), 7.96 (1 H, d, J = 9.0 Hz, H_4), 7.98 (1 H, d, J = 8.2 Hz, H_3), 8.05 (1 H, d, J = 9.0 Hz, H_5), 8.15 (1 H, d, J = 7.8 Hz, H_6), 8.21 (1 H, d, J = 8.2 Hz, H_2), 8.40 (1 H, d, J = 9.6 Hz, H_9), 8.46 (1 H, d, J = 9.6 Hz, H_{10}); ^{13}C NMR δ 16.0 (Me), 26.5, 119.4 (C_1), 124.3 (C_{10c}), 124.8 (C_9), 125.2 (C_3), 125.5 (C_{10}), 125.6 (C_6), 126.1 (C_4), 126.1 (C_{10b}), 126.9 (C_7), 127.7 (C_5), 128.1 (C_{8a}), 129.3 (C_{10a}), 129.6 (C_{5a}), 129.8 (C_2), 130.8 (C_{3a}), 139.2 (C_8); MS m/z 310, 308 (M^+), 295, 293, 214.

By comparing the ^1H NMR spectrum of the mixture of isomers with that of pure **6b**, the signals due **6a** could be identified. **6a**: ^1H NMR δ 1.49 (3 H, t, J = 7.6 Hz, Me), 3.41 (2 H, q), 7.92 (1 H, d, J = 7.8 Hz, H_7), 7.99 (1 H, d, J = 8.2 Hz, H_3), 8.05 (1 H, d, J = 9.3 Hz, H_4), 8.13 (1 H, d, J = 9.2 Hz, H_9), 8.16 (1 H, d, J = 7.8 Hz, H_8), 8.21 (1 H, d, J = 8.2 Hz, H_2), 8.32 (1 H, d, J = 9.3 Hz, H_5), 8.38 (1 H, d, J = 9.2 Hz, H_{10}).

2-(6-Ethyl-1-pyrenyl)cyclohexanol (7a) and Its Isomer 7b. To a solution of **6b** (2.16 g, 7 mmol) in Et_2O (50 mL) at –10 °C was added BuLi (15.9 mL of a 1.1 M solution in hexane, 17.5 mmol) over 20 min. The mixture was allowed to warm to rt. Then, after 4.5 h, cyclohexene oxide (1.77 mL, 17.5 mmol) in Et_2O (10 mL) was added. The mixture was stirred at rt overnight. Column chromatography on silica gel (PhH) gave 1.82 g (79%) of **7b**: mp 168–169 °C (cyclohexane); IR 3400, 1049, 837 cm^{-1}; UV λ_{max} (log ϵ) 349 (4.59), 332 (4.45), 318 (4.08), 278 (4.67), 268 (4.39), 257 (4.04), 245 (4.79), 236 nm (4.60); ^1H NMR δ 1.48 (3 H, t, J = 7.6 Hz, Me), 1.53–1.80 (5 H, m), 1.85–1.93 (1 H, m), 1.97–2.12 (2 H, m), 2.26–2.34 (1 H, m), 3.39 (2 H, q, J = 7.6 Hz), 3.65–3.76 (1 H, m, benzylic), 4.06–4.16 (1 H, m, carbinolic), 7.89 (1 H, J = 7.8 Hz, H_7), 7.98 (1 H, d, J = 8.9 Hz, H_4), 8.00 (1 H, d, J = 8.9 Hz, H_5), 8.03 (1 H, d, J = 8.0 Hz, H_2), 8.11 (1 H, d, J = 7.8 Hz, H_6), 8.19 (1 H, d, J = 8.0 Hz, H_3), 8.35 (1 H, d, J = 9.7 Hz, H_9), 8.49 (1 H, d, J = 9.7 Hz, H_{10}); ^{13}C NMR δ 16.2 (Me), 25.3 (C_5), 26.5 (C_4), 26.6 (–CH_2–), 34.1 (C_3), 34.9 (C_6), 47.2 (C_2), 74.7 (C_1), 122.6 (C_{10}), 123.2 (C_2), 123.6 (C_9), 125.1 (C_6), 125.3 (C_3), 125.4 (C_{10c}), 125.6 (C_{10b}), 126.5 (C_7), 126.5 (C_4), 127.3 (C_5), 128.2 (C_{3a}), 129.6 (C_{10a}), 130.1 (C_{5a}), 130.3 (C_{3a}), 136.8 (C_1), 138.4 (C_8); MS m/z 328 (M^+), 243.

A ca. 1:1 mixture of **6a** and **6b** (2.47 g, 8 mmol) was treated in a manner similar to that described above to give 1.61 g (61%) of a mixture of the corresponding cyclohexanols. Recrystallization from cyclohexane afforded 0.57 g (22%) of **7a**: mp 183–184 °C; IR 3360, 1059, 832 cm^{-1}; UV λ_{max} (log ϵ) 348 (4.68), 331 (4.50), 317 (4.12), 278 (4.71), 267 (4.41), 257 (4.02), 245 (4.82), 235 nm (4.61); ^1H NMR δ 1.45–1.80 (5 H, m), 1.48 (3 H, t, J = 7.6 Hz, Me), 1.85–1.92 (1 H, m), 1.97–2.04 (1 H, m), 2.04–2.11 (1 H, m), 2.26–2.33 (1 H, m), 3.38 (2 H, q, J = 7.6 Hz), 3.64–3.75 (1 H, m, benzylic), 4.05–4.17 (1 H, m, carbinolic), 7.89 (1 H, d, J = 7.8 Hz, H_7), 8.03 (1 H, d, J = 8.0 Hz, H_2), 8.04 (1 H, d, J = 8.9 Hz, H_4), 8.08 (1 H, d, J = 9.5 Hz, H_9), 8.12 (1 H, d, J = 7.8 Hz, H_8), 8.20 (1 H, d, J = 8.0 Hz, H_3), 8.28 (1 H, d, J = 8.9 Hz, H_5), 8.39 (1 H, d, J = 9.5 Hz, H_{10}); ^{13}C NMR δ 16.2 (Me), 25.2 (C_5), 26.5 (C_4), 26.8 ($MeCH_2$–), 34.1 (C_3), 34.9 (C_6), 47.3 (C_2), 74.7 (C_1), 121.9 (C_{10}), 123.0 (C_5), 123.2 (C_2), 124.8 (C_8), 125.1 (C_3), 125.4 (C_{10c}), 125.6 (C_{10b}), 126.5 (C_7), 127.2 (C_4), 127.8 (C_9), 128.7 (C_{5a}), 129.4 (C_{8a}), 129.7 (C_{3a}), 130.1 (C_{10a}), 136.9 (C_1), 138.6 (C_6); MS m/z 328 (M^+), 243.

7c: 84% yield; mp 60–65 °C (crude); IR 3415, 1054, 873 cm^{-1}; UV λ_{max} 350, 334, 319, 282, 270, 259, 249, 240 nm; ^1H NMR δ 1.49 (3 H, t, J = 7.6 Hz, Me), 1.58 (9 H, s), 1.45–1.63 (4 H, m), 1.65–2.35 (5 H, m), 3.37 (2 H, q, J = 7.6 Hz), 3.62–3.74 (1 H, m, benzylic), 4.05–4.18 (1 H, m, carbinolic), 7.89 (1 H, s, H_2), 8.03 (1 H, d, J = 9.3 Hz, H_9), 8.06 (1 H, d, J = 9.2 Hz, H_5), 8.17 (2 H, s, H_6, H_8), 8.24 (1 H, d, J = 9.2 Hz, H_4), 8.39 (1 H, d, J = 9.3 Hz, H_{10}); ^{13}C NMR δ 16.1 (Me), 25.1 (C_4), 26.4 ($MeCH_2$–), 26.8 (C_5), 31.8 (Me_3), 33.9, 34.6 (C_3), 35.1 (C_6), 47.0 (C_2), 74.6 (C_1), 121.8 (C_8), 121.9 (C_9), 122.6 (C_{10}), 123.0 (C_2, C_4), 123.5 (C_{10c}), 125.5 (C_{10b}), 126.8 (C_9), 127.0 (C_5), 127.0 (C_{10a}), 128.2 (C_{3a}), 130.9 (C_{8a}), 131.0 (C_{5a}), 136.5 (C_1), 138.4 (C_3), 148.8 (C_7); MS m/z 384 (M^+), 299.

2-(6-Ethyl-1-pyrenyl)cyclohexanone (8a) and Its Isomers. A solution of **7a** (0.5 g, 1.5 mmol) in DMF (5 mL) was added to PDC (1.69 g, 4.5 mmol) in DMF (15 mL) at rt. The mixture was then stirred for 15 h. Upon dilution of the mixture with water, a precipitate formed. This was collected by filtration and was purified by column chromatography on silica gel (PhH) to give 0.40 g (82%) of **8a**: mp 167–168 °C; IR 1714, 833 cm^{-1}; UV λ_{max} (log ϵ) 348 (4.64), 322 (4.46), 317 (4.05), 278 (4.64), 267 (4.35), 257 (3.79), 244 (4.77), 235 nm (4.56); ^1H NMR δ 1.48 (3 H, t, J = 7.6 Hz, Me), 1.94–2.22 (3 H, m), 2.26–2.56 (3 H, m), 2.69–2.75 (2 H, m, H_6), 3.38 (2 H, q, J = 7.6 Hz), 4.67 (1 H, dd, J = 12.5, 5.4 Hz, benzylic), 7.88 (1 H, d, J = 7.3 Hz, H_7), 7.88 (1 H, d, J = 8.1 Hz, H_2), 7.93 (1 H, d, J = 9.4 Hz, H_{10}), 8.03 (1 H, d, J = 9.4 Hz, H_9), 8.08 (1 H, d, J = 9.3 Hz, H_4), 8.10 (1 H, d, J = 7.3 Hz, H_8), 8.17 (1 H, d, J = 8.1 Hz, H_3), 8.27 (1 H, d, J = 9.3 Hz, H_5); ^{13}C NMR δ 16.1 (Me), 26.1 (C_4 or C_5), 26.7 ($MeCH_2$–), 27.8 (C_5 or C_4), 35.2

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(C_3), 42.7 (C_6), 53.8 (C_2), 121.8 (C_{10}), 123.0 (C_5), 124.6 (C_3), 124.9 (C_8), 125.4 (C_{10b} or C_{10c}), 125.4 (C_{10c} or C_{10b}), 125.8 (C_7), 126.4 (C_2), 127.3 (C_4), 127.7 (C_9), 128.6 (C_{5a}), 129.2 (C_{10a}), 129.3 (C_{8a}), 130.2 (C_{3a}), 132.8 (C_1), 138.7 (C_6), 210.2 (CO); MS m/z 326 (M^+), 298, 283, 269, 243, 240.

8b: 69% yield; mp 183–184 °C; IR 1714, 842 cm^{-1}; UV λ_{max} (log ϵ) 349 (4.54), 332 (4.39), 318 (3.99), 279 (4.60), 268 (4.31), 257 (3.94), 244 (4.74), 236 nm (4.53); ^1H NMR δ 1.47 (3 H, t, J = 7.6 Hz, Me), 1.95–2.23 (3 H, m), 2.26–2.57 (3 H, m), 2.69–2.75 (2 H, m, H_6), 3.37 (2 H, q, J = 7.6 Hz), 4.66 (1 H, dd, J = 12.2, 5.6 Hz, benzylic), 7.87 (1 H, d, J = 7.8 Hz, H_7), 7.87 (1 H, d, J = 8.0 Hz, H_2), 7.98 (1 H, d, J = 8.9 Hz, H_4), 7.99 (1 H, d, J = 8.9 Hz, H_5), 8.02 (1 H, d, J = 9.7 Hz, H_{10}), 8.11 (1 H, d, J = 7.8 Hz, H_8), 8.15 (1 H, d, J = 8.0 Hz, H_3), 8.30 (1 H, d, J = 9.7 Hz, H_9); ^{13}C NMR δ 16.1 (Me), 26.0 (C_4 or C_5), 26.5 ($MeCH_2$–), 27.8 (C_5 or C_4), 35.0 (C_3), 42.7 (C_6), 53.8 (C_2), 122.6 (C_{10}), 123.5 (C_9), 124.7 (C_3), 125.2 (C_6), 125.4 (C_{10b} or C_{10c}), 125.5 (C_{10c} or C_{10b}), 125.7 (C_7), 126.3 (C_2), 126.6 (C_4), 127.3 (C_5), 128.0 (C_{8a}), 128.7 (C_{10a}), 129.9 (C_{3a}), 130.7 (C_{5a}), 132.6 (C_1), 138.5 (C_8), 210.2 (CO); MS m/z 326 (M^+), 298, 283, 269, 243, 240.

8c: 55% yield; mp 128–130 °C; IR 1710, 871 cm^{-1}; UV λ_{max} (log ϵ) 350 (4.68), 333 (4.52), 319 (4.13), 281 (4.66), 270 (4.44), 259 (4.17), 249 (4.89), 240 nm (4.69); ^1H NMR δ 1.48 (3 H, t, J = 7.6 Hz, Me), 1.57 (9 H, s), 1.95–2.10 (2 H, m), 2.15–2.22 (1 H, m), 2.27–2.32 (1 H, m), 2.38–2.56 (2 H, m, H_3), 2.68–2.71 (2 H, m, H_6), 3.36 (2 H, q, J = 7.6 Hz), 4.60 (1 H, dd, J = 12.1, 5.8 Hz, H_2), 7.72 (1 H, s, H_2), 7.92 (1 H, d, J = 9.4 Hz, H_{10}), 7.98 (1 H, d, J = 9.4 Hz, H_9), 8.04 (1 H, d, J = 9.3 Hz, H_5), 8.14 (1 H, s, H_8), 8.17 (1 H, s, H_6), 8.24 (1 H, d, J = 9.3 Hz, H_4); ^{13}C NMR δ 15.9 (Me), 25.9 (C_4), 26.7 ($MeCH_2$–), 27.6 (C_5), 31.8 (Me_3), 35.0, 35.0 (C_3), 42.6 (C_6), 53.7 (C_2), 121.8 (C_8), 122.0 (C_6), 122.6 (C_{10}), 123.1 (C_4), 123.5 (C_{10c}), 125.3 (C_{10b}), 126.1 (C_2), 126.6 (C_9), 126.7 (C_5), 127.1 (C_{10a}), 127.4 (C_{3a}), 130.7 (C_{8a}), 130.9 (C_{5a}), 132.5 (C_1), 137.7 (C_3), 148.5 (C_7), 210.0 (CO); MS m/z 382 (M^+), 354.

Cyclodehydration of Ketones 8 and Attempted Dehydrogenation of the Products. (i) Dehydrogenation by DDQ. A mixture of ketone **8a** (206 mg, 0.63 mmol) and PPA (31 g) was heated at 100 °C for 2.5 h. The mixture was then added to crushed ice, and the whole was extracted with benzene. The extract was washed with aq $NaHCO_3$ and water then was passed through a short column of Florisil. After removal of a small amount of benzene by azeotropic distillation, DDQ (0.48 g, 2.1 mmol) was added to the eluate and the solution was refluxed for 1 h under Ar. After the mixture cooled to rt, it was passed through a short column of alumina. The red eluate was concentrated, and the residue was recrystallized from hexane to give 21 mg (12%) of **2**: mp 121–122 °C; IR 1440, 1382, 833 cm^{-1}; UV λ_{max} (log ϵ) 390 (4.36), 368 (4.30), 318 (4.40), 300 (4.52), 278 (4.48), 252 (4.81), 247 (4.73), 242 nm (4.69); MS m/z 304 (M^+), 289, 276.

A small quantity (1.7 mg, 1%) of **9a** was also isolated. **9a**: mp 170–171 °C; IR 1512, 913, 890, 835 cm^{-1}; ^1H NMR δ 5.63 (1 H, dd, J = 11.0, 1.2 Hz, cis), 6.02 (1 H, dd, J = 17.4, 1.2 Hz, trans), 7.36–7.44 (1 H, m, H_8), 7.39–7.46 (1 H, m, H_9), 7.80 (1 H, dd, J = 17.4, 11.0 Hz, –CH=), 7.97–8.00 (1 H, m, H_{10}), 8.06–8.09 (1 H, m, H_7), 8.12 (1 H, d, J = 9.4 Hz, H_1), 8.19 (1 H, d, J = 7.8 Hz, H_{12}), 8.20 (1 H, d, J = 7.6 Hz, H_4), 8.33 (1 H, d, J = 7.8 Hz, H_{11}), 8.34 (1 H, d, J = 7.6 Hz, H_5), 8.34 (1 H, d, J = 9.4 Hz, H_2), 8.51 (1 H, s, H_6); MS m/z 302 (M^+), 289, 276.

Similar treatment of **8b** (136 mg, 0.42 mmol) afforded **3** (9.0 mg, 8%) and **9b** (4.3 mg, 3%). **3**: mp 117–118 °C; IR 1440, 1432, 1401, 837 cm^{-1}; UV λ_{max} (log ϵ) 380 (4.17), 362 (4.18), 317 (4.40), 305 (4.53), 280 (4.38), 252 (4.78), 246 (4.68), 242 nm (4.63); MS m/z 304 (M^+), 289.

9b: mp 142–144 °C; IR 1548, 903, 844 cm^{-1}; ^1H NMR δ 5.73 (1 H, dd, J = 11.0, 1.2 Hz, cis), 6.07 (1 H, dd, J = 17.3, 1.2 Hz, trans), 7.41–7.49 (1 H, m, H_8), 7.43–7.51 (1 H, m, H_9), 7.98 (1 H, dd, J = 17.3, 11.0 Hz, –CH=), 8.01–8.05 (1 H, m, H_{10}), 8.04 (1 H, d, J = 8.9 Hz, H_2), 8.11 (1 H, d, J = 8.9 Hz, H_1), 8.13–8.17 (1 H, m, H_7), 8.23 (1 H, d, J = 7.8 Hz, H_{12}), 8.23 (2 H, s, H_3, H_4), 8.36 (1 H, d, J = 7.8 Hz, H_{11}), 8.93 (1 H, s, H_6); MS m/z 302 (M^+), 289, 276.

(ii) Dehydrogenation by TTFA. A mixture of ketone **8a** (100 mg, 0.31 mmol) and PPA (3.6 g) was heated at 110 °C for 2.5 h. After treatment as described above, a mixture of the crude product (0.1 g), trityl alcohol (0.21 g, 0.81 mmol), and TFA (2 mL) was refluxed for 8.5 h. The mixture was then added to crushed ice, and the whole was extracted with benzene. The extract was dried and concentrated. Triphenylmethane was removed from the solid residue by vacuum sublimation at 100 °C. The residual solid was recrystallized from EtOH to give 5 mg (5%) of **2**, which was identical in all respects with the specimen obtained earlier.

(iii) Dehydrogenation by Pd/C. Ketone **8c** (2.85 g, 7.4 mmol) was treated with PPA (98 g) as described above. A mixture of the crude products, 5% Pd/C (660 mg), and *p*-cymene (15 mL) was refluxed for 155 h. After removal of Pd/C by filtration and *p*-cymene by steam distillation, the residue was purified by column chromatography on silica gel (hexane) to give 1.28 g (48%) of **10**: mp 148–150 °C; IR 1443, 878, 738 cm^{-1}; UV λ_{max} (log ϵ) 429 (3.78), 388 (3.76), 365 (4.11), 319 (4.22), 305 (4.54), 277 (4.47), 254 nm (4.88); MS m/z 360 (M^+), 345.

Similarly, **8a** (370 mg, 1.13 mmol) gave 137 mg (39%) of **2**, mp 120–122 °C, and **8b** (417 mg, 1.28 mmol) afforded 85 mg (22%) of **3**, mp 116–118 °C.

Hydrocarbon 4. A mixture of 12-acetylindeno[1,2,3-*cd*]pyrene (95 mg, 0.3 mmol), diethylene glycol (55 mL), 95% $N_2H_4 \cdot H_2O$ (1 mL, 19 mmol), and NaOH (135 mg, 3 mmol) was heated at 100 °C for 2 h then at 210 °C for 2 h. Workup gave 55 mg (60%) of **4**: mp 122–124 °C; IR 1447, 1378, 824 cm^{-1}; UV λ_{max} (log ϵ) 413 (3.88), 377 (4.12), 360 (4.15), 317 (4.27), 304 (4.58), 277 (4.38), 251 nm (4.83); MS m/z 304 (M^+), 289, 287, 276.

Acknowledgment. The work described here was supported in part by a Grant-in-Aid for Scientific Research (No. 02640381) from the Ministry of Education, Science and Culture, to whom the authors' thanks are due. The authors also thank Professor T. Toda of Utsunomiya University for helpful discussions and Mr. H. Kaneda and Mr. K. Kon for their assistance.

Registry No. 1, 193-39-5; 2, 138060-63-6; 3, 138060-64-7; 4, 138060-65-8; 5a, 123348-29-8; 5b, 123348-30-1; 6a, 138060-66-9; 6b, 138060-67-0; 6c, 138060-68-1; 7a, 138060-69-2; 7b, 138060-70-5; 7c, 138060-71-6; 8a, 138060-72-7; 8b, 138060-73-8; 8c, 138060-74-9; 9a, 138060-75-0; 9b, 138060-76-1; 10, 138060-77-2; 1-ethylpyrene, 17088-22-1; 7-*tert*-butyl-1-pyrene, 138060-78-3; cyclohexene oxide, 286-20-4; 12-acetylindeno[1,2,3-*cd*]pyrene, 120362-67-6.

Supplementary Material Available: ^1H NMR spectra of 7-*tert*-butyl-1-ethylpyrene, **2–4**, **6b**, **6c**, and **7–10** (15 pages). This material is contained in many 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.

A Highly Rigid Capped Porphyrin

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Received September 23, 1991

Introduction

Cytochrome c oxidase is a polymetallic enzyme which is responsible for dioxygen reduction at the end of the mitochondrial respiratory chain of eukaryotic organisms.[1] The monomeric unit contains four metals, two iron atoms Fe_a and Fe_{a3}, respectively, associated with two copper atoms Cu_A and Cu_B. The catalytic process $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ seems to be a consequence of a cooperative interaction between the heme iron, cyt a_3 and copper, Cu_B, located at a distance of 3 Å according to recent EXAFS

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0022-3263/92/1957-1015$03.00/0