0.4–1.8 (m, 18 H), 2.27 (s, 3 H), 2.1–3.5 (m, 4 H), 3.93 (s, 3 H), 6.63 (s, 1 H), 10.07 (s, 1 H); IR (KBr, cm$^{-1}$) 3420, 1660, 1220; MS, *m/z* (relative intensity) 318 (M$^{+}$, 49), 287 (49), 286 (100), 189 (33).

**13-(Methoxycarbonyl)-14-hydroxy[11]metacyclophane (17c).** Compound **17c** was obtained from **20c** by method D in 59% yield: mp 69–71 °C; $^{1}$H NMR (CDCl$_3$) 0.62–1.90 (m, 18 H), 2.40–2.67 (m, 2 H), 2.80–3.03 (m, 2 H), 3.83 (s, 3 H), 6.43 (s, 2 H), 10.70 (s, 1 H); IR (KBr, cm$^{-1}$) 3410, 1660, 1560, 1250; MS, *m/z* (relative intensity) 304 (M$^{+}$, 54), 273 (47), 272 (100), 91 (19).

**16-(Methoxycarbonyl)-17-hydroxy-20-methyl[14]metacyclophane (17d).** Compound **17d** was prepared from **20d** by method D in 54% yield: mp 102–105 °C; $^{1}$H NMR (CDCl$_3$) 0.70–1.90 (m, 24 H), 2.17 (s, 3 H), 2.43–3.20 (m, 4 H), 3.85 (s, 3 H), 6.54 (s, 1 H), 10.30 (s, 1 H); IR (KBr, cm$^{-1}$) 3410, 1650, 1430; MS, *m/z* (relative intensity) 360 (M$^{+}$, 71), 329 (60), 328 (100), 302 (22).

**(*S*)-*α*-Methoxy-*α*-(trifluoromethyl)phenylacetyl Chloride (21).** Compound **21** was prepared by a literature method[17] in 81% yield: bp 67–68 °C (2 mm) (lit.[17] bp 54–55 °C (1 mm)).

**Preparation and Separation of the Diastereomers 22a.** Compound **17a** was quantitatively converted into diastereomers **22a** with **21** by method B. The ratio of the two diastereomers was 1:1. They were separated by TLC mesh chromatography (eluted with petroleum ether and ethyl acetate, 35:1). From 180 mg of the mixture were obtained 66 mg of *α*-**22a** and 75 mg of *β*-**22a**: $^{1}$H NMR (CDCl$_3$, 200 MHz) *α*-**22a** 0.66–1.76 (m, 18 H), 2.20–3.00 (m, 4 H), 3.66 (s, 6 H), 4.25 (ABq, 2 H, *J* = 3 Hz), 6.82 (s, 1 H), 6.92–7.64 (m, 10 H); *β*-**22a** 0.66–1.76 (m, 18 H), 2.20–3.00 (m, 4 H), 3.58 (s, 3 H), 4.25 (ABq, 2 H, *J* = 3 Hz), 6.85 (s, 1 H), 6.92–7.64 (m, 10 H).

**(+)-13-(Hydroxymethyl)-14-hydroxy-17-benzyl[11]metacyclophane (23a).** Compound *α*-**22a** was reduced by method C to give (+)-**23a**: mp 138–139 °C; $[\alpha]^{20}_{D}$ 12.6° (*c* 0.012 g/2 mL acetone); $^{1}$H NMR (CDCl$_3$) 0.37–1.90 (m, 18 H), 2.0–3.1 (m, 4 H), 4.16 (s, 2 H), 4.93 (s, 2 H), 6.50 (s, 1 H), 6.80–7.5 (m, 5 H); IR (KBr, cm$^{-1}$) 3415, 1600, 1080; MS, *m/z* (relative intensity) 366 (M$^{+}$, 12), 350 (100), 348 (88), 91 (99); exact mass calcd for $C_{25}H_{34}O_2$ 366.2559, found 366.2521.

**(–)-13-(Hydroxymethyl)-14-hydroxy-17-benzyl[11]metacyclophane (23a).** Compound *β*-**22a** was reduced by method C to give (–)-**23a**: mp 138–140 °C; $[\alpha]^{20}_{D}$ 14.4° (*c* 0.006 g/2 mL acetone). Its $^{1}$H NMR and IR spectra were identical with those of (+)-**23a**.

**Preparation and Separation of Diastereomers 22b.** Compound **17b** was converted into the diastereomeric esters **22b** in 90% yield by method B with compound **21**. The two diastereoisomers were separated by TLC mesh chromatography on silica gel (eluted with petroleum ether and ethyl acetate, 35:1): $^{1}$H NMR (CDCl$_3$) *α*-isomer, 0.46–1.80 (m, 18 H), 2.32 (s, 3 H), 2.36–3.18 (m, 4 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 6.76 (s, 1 H, 7.44–7.65 (m, 5 H); *β*-isomer 0.46–1.80 (m, 18 H), 2.32 (s, 3 H), 2.31–3.18 (m, 4 H), 3.58 (s, 3 H), 6.80 (s, 1 H), 7.44–7.65 (m, 5 H).

**(+)-13-(Hydroxymethyl)-14-hydroxy-17-methyl[11]metacyclophane (23b).** The reduction of *α*-**22b** by method C gave (+)-**23b**: mp 123–158 °C; $[\alpha]^{20}_{D}$ +6.3° (*c* 0.036 g/2 mL, acetone); $^{1}$H NMR (CDCl$_3$) 0.3–1.9 (m, 18 H), 2.30 (s, 3 H), 2.40–3.30 (m, 4 H), 4.90 (s, 2 H), 6.53 (s, 1 H); IR (KBr, cm$^{-1}$) 3610, 3400, 3200, 1600, 960; MS, *m/z* (relative intensity) 290 (M$^{+}$, 9), 274 (99), 272 (82), 257 (33), 136 (100). Anal. Calcd for $C_{19}H_{30}O_2$: C, 78.62; H, 10.34. Found: C, 78.71; H, 10.32.

**(–)-13-(Hydroxymethyl)-14-hydroxy-17-methyl[11]metacyclophane (23b).** Compound *β*-**22b** was similarly reduced to (–)-**23b**. Its $^{1}$H NMR and IR spectra were identical with those of (+)-**23b**: mp 123–125 °C; $[\alpha]^{20}_{D}$ –8° (*c* 0.024 g/2 mL acetone).

**Preparation of 22c.** Compound **22c** was prepared from **17c** by method B in 92% yield: $^{1}$H NMR (CDCl$_3$) 0.67–2.00 (m, 18 H), 2.50–2.87 (m, 4 H), 3.63 (s, 6 H), 6.80 (s, 1 H), 7.07 (s, 1 H), 7.33–7.73 (m, 5 H); IR (CCl$_4$, cm$^{-1}$): 205 (42.3), 189 (100); exact mass calcd for $C_{29}H_{35}F_3O_5$ 520.2437, found 520.2425.

**Preparation of 22d.** Compound **17d** was converted to **22d** in 90% yield by method B: $^{1}$H NMR (CDCl$_3$) 0.70–1.80 (m, 24 H), 2.27 (s, 3 H), 2.53–2.90 (m, 4 H), 3.60 (s, 6 H), 6.77 (s, 1 H), 7.23–7.70 (m, 5 H); IR (film, cm$^{-1}$) 3420, 1665, 1220; MS, *m/z* (relative intensity) 576 (M$^{+}$, 4), 545 (3), 374 (30), 189 (100).

**Acknowledgment.** We thank NSERC of Canada and FCAC of Quebec for financial support. GJK thanks the government of the People's Republic of China for the award of a scholarship.

**Registry No.** **9**, 87565-80-8; **11a**, 87968-80-7; (–)-**11a**, 87968-82-9; (+)-**11a**, 87968-83-0; **11b**, 87968-84-1; (–)-**11b**, 87968-86-3; (+)-**11b**, 87968-85-2; **12**, 34713-98-9; **13a** (isomer 1), 88034-40-6; **13a** (isomer 2), 87968-81-8; **13b** (isomer 1), 94294-14-1; **13b** (isomer 2), 94346-88-0; **14**, 67609-52-3; **17a**, 94294-21-0; **17b**, 94323-81-6; **17c**, 94323-82-7; **17d**, 94294-22-1; **18**, 3725-27-7; **19a**, 94294-15-2; **19b**, 3725-25-5; **19c**, 3725-27-7; **19d**, 94294-16-3; **20a**, 94294-17-4; **20b**, 94294-18-5; **20c**, 94294-19-6; **20d**, 94294-20-9; (*S*)-**21**, 20445-33-4; **22a** (isomer 1), 94294-23-2; **22a** (isomer 2), 94346-89-1; **22b** (isomer 1), 94294-26-5; **22b** (isomer 2), 94346-90-4; **22c**, 94294-29-8; **22d**, 94294-30-1; (+)-**23a**, 94294-24-3; (–)-**23a**, 94294-25-4; (+)-**23b**, 94294-27-6; (–)-**23b**, 94294-28-7; methyl 3-pyrrolidinocrotonate, 15424-17-6; (*R*)-(–)-*α*-methoxyphenylacetic acid, 3966-32-3; 1-morpholinocyclododecene, 3725-39-1; 1-morpholinocyclopentadecene, 3804-59-9.

**Supplementary Material Available:** Temperature dependent $^{1}$H NMR spectra of compounds **22b** and **22d** (2 pages). Ordering information is given on any current masthead page.

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# Nuclear Spin–Spin Coupling via Nonbonded Interactions. 4. F–F and H–F Coupling in Substituted Benzo[*c*]phenanthrenes[1]

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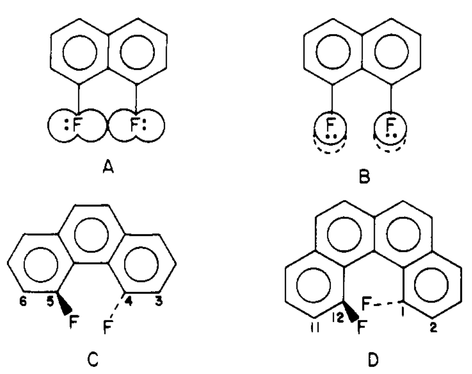
NMR measurements of the F–F coupling constants for a series of 4-substituted 1,12-difluorobenzo[*c*]phenanthrenes are reported. The results provide further support for earlier generalizations that intramolecular "through-space" F–F coupling, in contrast to its "through-bond" counterpart, is essentially insensitive to the electronic character of substituents even though they cause significant perturbations in the $^{19}$F chemical shifts. The large magnitude "through-space" H–F coupling between H-12 and F-1 for several 4- and 9-substituted 1-fluorobenzo[*c*]phenanthrenes shows a similar insensitivity to substituents. This is consistent with the notion that "through-space" H–F and F–F coupling have analogous origins in nonbonded overlap interactions.

Pairs of fluorine atoms that are crowded against one another intramolecularly are well documented to exhibit unusually large nuclear spin–spin coupling constants as measured by $^{19}$F NMR spectroscopy.[2,3] Such F–F cou-

0022-3263/85/1950-0457$01.50/0

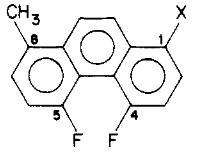
Chart I



A: σ overlap of in-plane 2p orbitals
B: π overlap of out-of-plane 2p orbitals
C: slight helical distortion
D: pronounced helical distortion

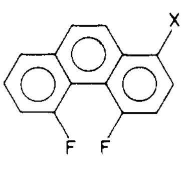
pling, which has a strong inverse dependence on the F–F distance, has been attributed theoretically to "through-space" nonbonded interactions involving overlap of lone-pair orbitals from the two fluorine atoms.[2c]

In a study of four 1-substituted 8-methyl-4,5-difluorophenanthrenes **1a–d**,[4] Servis and Fang observed that although the $^{19}F$ chemical shift of F-4 depends strongly on the nature of the substituent X ($\Delta\delta_F$ = 22 ppm for **1c** compared to **1d**), the magnitude of the coupling constant between F-4 and F-5 is almost invariant ($J_{FF}$ = 170 ± 2 Hz for **1a** and **1b**, and $J_{FF}$ = 167 ± 2 Hz for **1c** and **1d**).

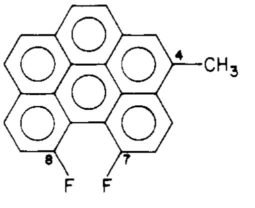


1a, X = $CH_2Br$
1b, X = $CH_2OH$
1c, X = $CO_2CH_2CH_3$
1d, X = $NH_2$

Our results for 1-methyl-4,5-difluorophenanthrene (**2a**, $J_{FF}$ = 174 Hz), 1-chloro-4,5-difluorophenanthrene (**2b**, $J_{FF}$ = 177 Hz), and 4-methyl-7,8-difluorobenzo[*ghi*]perylene (**3**, $J_{FF}$ = 174 Hz) also seem to fit this pattern.



2a, X = $CH_3$
2b, X = Cl



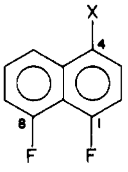
**3**

Servis and Fang suggested that insensitivity of $J_{FF}$ to substitution that *does* result in $\delta_F$ variation might be a characteristic of "through-space" F–F coupling that could distinguish it from ordinary "through-bond" F–F coupling.[4,5] Subsequently, we carried out a study[2b] of a series of seven 4-substituted 1,8-difluoronaphthalenes of type **4** (with X = H, $CH_3$, $NH_2$, $NHCOCH_3$, Cl, CN, and $NO_2$) from which we concluded that although the C-4 substituent appears to exert a substantial *steric* effect of $J_{FF}$,[6] it seems to have no more than a slight *electronic* effect on $J_{FF}$, in agreement with the generalization of Servis and Fang.[4]

Table I. NMR Data for Various Substituted 1,12-Difluorobenzo[*c*]phenanthrenes[a]

| no. | X | $\delta_{F\text{-}1}$, ppm[b] | $\delta_{F\text{-}12}$, ppm[b] | $J_{FF}$, Hz[c] |
|---|---|---|---|---|
| **5a** | 4-$CH_3$ | 3.03 | 6.06 | 42.7 |
| **5b** | 4-$CH_3O$ | −3.77 | 6.14 | 44.4 |
| **5c** | 4-Br | *d* | *d* | 45–46[e] |
| **5d** | 4-CN | 15.39 | 5.12 | 45.6 |

[a] Spectra were measured at 84.6 MHz in $C_6D_6$ at 25 °C unless otherwise noted. [b] Chemical shifts are given in ppm downfield from internal TTC. [c] The coupling constants for **5a**, **5b**, and **5d** were reproducible within ±0.2 Hz. [d] At 188.3 MHz in $CDCl_3$ the observed chemical shifts are 5.29 and 5.16 ppm; we have no basis for a choice between the two possible assignments. [e] With such a small chemical shift difference, only an approximate determination of $J_{FF}$ was possible.



**4**

In the 1,8-difluoronaphthalene system, the σ overlap of the in-plane 2p fluorine lone-pair orbitals should be much greater in magnitude than the π overlap of the out-of-plane 2p fluorine lone-pair orbitals as pictured in Chart I. Using as a guide the theory linking F–F coupling with lone-pair orbital overlap,[2c] one can then hypothesize that the large F–F coupling observed in such molecules ($J_{FF}$ ranges from 59 to 75 Hz in the **4** series[2b]) depends more on the overlap interactions of the in-plane lone pairs than on those of the out-of-plane lone pairs. In the 4,5-difluorophenanthrene system, the overlap interactions of the fluorine lone-pair orbitals are less easily described because the system probably has a slight helical distortion of the type indicated in Chart I as judged by X-ray crystallographic studies on phenanthrene itself.[7] For purposes of this discussion we define a local plane at F-4 containing F-4, C-4, and C-3, and a local plane at F-5 containing F-5, C-5, and C-6. It seems likely that the helical distortion is sufficiently small that the dominant lone-pair overlap interactions that are believed[2c] to be responsible for the very large F–F coupling in the 4,5-difluorophenanthrenes ($J_{FF}$ ranges from 167 to 177 Hz in the **1** and **2** series) are those involving the 2p fluorine lone-pair orbitals with local in-plane orientation rather than those with local out-of-plane orientation. In the 1,12-difluorobenzo[c]phenanthrene system, however, helical distortions of the type indicated in Chart I appear to be sufficiently large[8] that the major overlap interactions of interest in the present context involve locally out-of-

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(1) Taken in part from the Ph.D. Thesis of W. R. Ricker, Bryn Mawr College, 1974.

(2) References to many previous studies of this phenomenon by other workers are cited in the three earlier parts in this series: (a) Mallory, F. B.; Mallory, C. W.; Ricker, W. M. *J. Am. Chem. Soc.* **1975**, *97*, 4770–4771. (b) Mallory, F. B.; Mallory, C. W.; Fedarko, M.-C. *Ibid.* **1974**, *96*, 3536–3542. (c) Mallory, F. B. *Ibid.* **1973**, *95*, 7747–7752.

(3) (a) Hilton, J.; Sutcliffe, L. H. *Progr. Nucl. Magn. Reson. Spectrosc.* **1975**, *10*, 27–39. (b) Matthews, R. S.; Preston, W. E. *Org. Magn. Reson.* **1980**, *14*, 258–263. (c) Schaefer, T.; Marat, K.; Lemire, A.; Janzen, A. F. *Ibid.* **1982**, *18*, 90–91. (d) Matthews, R. S. *Ibid.* **1982**, *18*, 226–230.

(4) Servis, K. L.; Fang, K.-N. *J. Am. Chem. Soc.* **1968**, *90*, 6712–6717.

(5) For examples of the dependence of "through-bond" F–F coupling on substituents, see ref 4 and the following: (a) Abraham, R. J.; Macdonald, D. B.; Pepper, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 147–153. (b) Hogben, M. G.; Graham, W. A. G. *Ibid.* **1969**, *91*, 283–291. (c) Cohen, E. A.; Bourn, A. J. R.; Manatt, S. L. *J. Magn. Reson.* **1969**, *1*, 436–449.

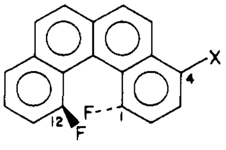
(6) We argued that large C-4 substituents in these naphthalenes cause molecular distortions that decrease the distance between F-1 and F-8 and thereby increase the F–F coupling constant. Matthews[3d] has reached a similar conclusion.

(7) Cheney, B. V. *J. Am. Chem. Soc.* **1968**, *90*, 5386–5390.

(8) For benzo[c]phenanthrene itself, H-1 lies about 0.8 Å above (and H-12 about 0.8 Å below) the average molecular plane as judged by X-ray crystallographic studies: Herbstein, F. H.; Schmidt, G. M. J. *J. Chem. Soc.* **1954**, 3302–3313.

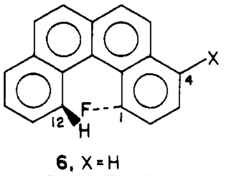
plane rather than locally in-plane 2p fluorine lone-pair orbitals.[9] Explicitly, for the 1,12-difluorobenzo[*c*]phenanthrene system as it is drawn in Chart I, we believe that the most important nonbonded interaction for F–F coupling involves the $\sigma$ overlap of the front face lobe of the locally out-of-plane 2p lone-pair orbital on the rearward pointing F-1 fluorine atom and the rear face lobe of the locally out-of-plane 2p lone-pair orbital on the frontward pointing F-12 fluorine atom.

It seemed conceivable to us initially that the earlier conclusions[2b,4] about the insensitivity of "through-space" F–F coupling to substituent effects might apply only to systems such as 1–4, in which we think the coupling involves in-plane lone-pair orbitals that are *orthogonal* to the corresponding aromatic $\pi$ systems, and not to a system such as **5**, in which we think the coupling involves lone-pair orbitals that are *conjugated* through the aromatic $\pi$ system with the C-4 substituent. To test this idea, we synthesized compounds **5a–d** and measured their $^{19}$F NMR spectra. From the narrow range of the observed F–F coupling constants for **5a–d** given in Table I (about 43–46 Hz) we conclude that insensitivity to electronic substituent effects appears to be characteristic of "through-space" F–F coupling in a nonplanar system like benzo[*c*]phenanthrene as well as in planar or essentially planar systems like naphthalene and phenanthrene.

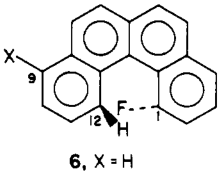


**5a**, X = $CH_3$
**5b**, X = $CH_3O$
**5c**, X = Br
**5d**, X = CN

Evidence from several studies supports the notion that "through-space" H–F coupling, like its F–F counterpart, also involves nonbonded overlap interactions.[2a,10] It appears that H–F coupling arises, at least in part and perhaps predominantly, from interactions of lone-pair orbitals on the fluorine atom with filled $\sigma$ or $\pi$ orbitals on the *carbon* atom to which the coupled hydrogen atom is bonded rather than from direct interactions between the fluorine atom and the hydrogen atom.[2a,10] To explore whether "through-space" H–F coupling exhibits an insensitivity to substituents similar to that found for the analogous F–F coupling, we have synthesized 1-fluorobenzo[*c*]phenanthrene (**6**) and a series of its 4-substituted (**7a–c**) and 9-substituted (**8a–c**) derivatives and have measured the exceptionally large coupling constants for the interaction of H-12 and F-1 in each of these seven molecules.



**6**, X = H
**7a**, X = $CH_3O$
**7b**, X = Br
**7c**, X = CN



**6**, X = H
**8a**, X = $CH_3O$
**8b**, X = Br
**8c**, X = CN

**Table II. NMR Data for Various Substituted 1-Fluorobenzo[*c*]phenanthrenes**[a]

| no. | X | $\delta_{F\text{-}1}$, ppm[b] | $\delta_{H\text{-}12}$, ppm[b] | $J_{F\text{-}1,H\text{-}12}$, Hz[c] |
|---|---|---|---|---|
| **6** | H | 15.2 | 8.45 | 14.4 |
| **7a** | 4-$CH_3O$ | 5.40 | 8.53[d] | 14.8[d] |
| **7b** | 4-Br | 14.7 | 8.21 | 14.6 |
| **7c** | 4-CN | 24.6 | 8.10 | 14.1 |
| **8a** | 9-$CH_3O$ | 15.6 | 8.13 | 14.7 |
| **8b** | 9-Br | 15.0 | 8.16 | 14.9 |
| **8c** | 9-CN | 14.0 | 8.24 | 14.1 |

[a] Spectra were measured at 84.6 MHz for $^{19}$F and 90 MHz for $^1$H in $C_6D_6$ at 25 °C unless otherwise noted. [b] Chemical shifts are given in ppm downfield from internal standards: TTC for $^{19}$F and $Me_4Si$ for $^1$H. [c] The tabulated coupling constants were reproducible within ±0.2 Hz. [d] See ref 9. [e] Owing to low solubilities of nitriles **7c** and **8c** at 25 °C, their spectra were measured at 75 °C and 65 °C, respectively.

The H-12 signals in the $^1$H NMR spectra of **6–8** are easily recognizable by their unusually low field chemical shifts ($\delta$ = 8.1–8.5 ppm) and their especially elaborate splitting patterns.[11] By homonuclear decoupling experiments involving selective irradiation in the region of the upfield aromatic signals, we were able to collapse the H-12 multiplet in each case to a simple doublet resulting from the coupling between H-12 and F-1.[12] From the results given in Table II, we conclude that "through-space" H–F coupling in systems **6–8**, like "through-space" F–F coupling in systems **1–5**, is essentially independent of the electron-supplying or electron-withdrawing character of the substituent.[13]

## Experimental Section

**General Methods.** Melting points were measured with a Thomas-Hoover oil bath apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories. $^1$H NMR spectra were obtained either with a Perkin-Elmer R-32 (90 MHz) spectrometer or with a Varian A-56/60A (60 MHz) spectrometer. $^{19}$F NMR spectra were obtained either with a Perkin-Elmer R-32 (84.6 MHz) spectrometer or an IBM WP-200 SY (188.3 MHz) spectrometer. Chemical shifts, reproducible to ±0.01 ppm, were measured in ppm downfield from internal standards: tetramethylsilane ($Me_4Si$) for $^1$H nuclei, and 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TTC) for $^{19}$F nuclei. Analyses by combined gas chromatography and mass spectrometry (GC/MS) were carried out with a Hitachi Perkin-Elmer RMS-4 mass spectrometer interfaced with a Perkin-Elmer 990 gas chromatograph. An F&M 402 gas chromatograph was used for simple GC analyses. UV absorption spectra were obtained with a Perkin-Elmer 202 spectrometer. The term ligroin refers to petroleum ether with bp 60–70 °C. Sublimations at reduced pressure were carried out as described previously.[14]

**2-X-5-fluorobenzaldehydes.** 2-Methyl-5-fluorobenzaldehyde was prepared from commercially available 4-fluoro-2-iodotoluene by a Grignard reaction with triethyl orthoformate according to a procedure described previously.[4]

2-Methoxy-5-fluorobenzaldehyde, mp 45.0–46.5 °C (lit.[15] mp 47 °C), was prepared by a Sommelet reaction[16] of 2-(chloro-

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(9) The local plane at F-1 contains F-1, C-1, and C-2; the local plane at F-12 contains F-12, C-12, and C-11.

(10) Myrhe, P. C.; Edmonds, J. W.; Kruger, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 2459–2466. (b) Jefford, C. W.; Hill, D. T.; Ghosez, L.; Toppet, S.; Ramey, K. C. *Ibid.* **1969**, *91*, 1532–1534. (c) Gribble, G. W.; Douglas, J. R., Jr. *Ibid.* **1970**, *92*, 5764–5765. (d) Servis, K. L.; Jerome, F. R. *Ibid.* **1971**, *93*, 1535–1537. (e) Gribble, G. W.; Kelly, W. J. *Tetrahedron Lett.* **1981**, *22*, 2475–2478. (f) Yamamoto, G.; Ōki, M. *J. Org. Chem.* **1984**, *49*, 1913–1917.

(11) In each of these molecules, H-12 has significant coupling to four other nuclei: F-1, H-11, H-10, and H-8. The only other low field signals are simple double doublets for H-5 in compounds **7a–c** and for H-8 in compounds **8a–c**.

(12) The H-12 doublet in the decoupled $^1$H spectrum of the 4-methoxy compound **7a** was partly obscured by the H-5 signal; this complication in the analysis of the spectrum of **7a** was removed by the addition of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium, which shifted the H-5 signal (but not the H-12 signal) to lower fields.

(13) An analogous conclusion can be drawn from the observation[10c] that the methyl protons in 4-fluoro-5-methylfluorene and 4-fluoro-5-methylfluorenone have very similar H–F coupling constants (8.3 and 7.3 Hz, respectively).

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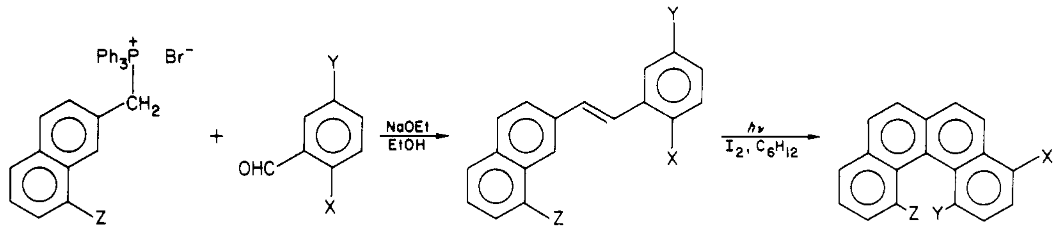
**Table III. Syntheses of Substituted *trans*-2-Styrylnaphthalenes and Benzo[*c*]phenanthrenes**[a]



| substituents | | | *trans*-2-styrylnaphthalenes | | | benzo[*c*]phenanthrenes | | | |
|---|---|---|---|---|---|---|---|---|---|
| X | Y | Z | yield, % | recryst solvent | mp, °C | no. | yield, % | recryst solvent | mp, °C |
| $CH_3$ | F | F | 74 | ligroin | 99.8–100.6 | **5a** | 48[b] | methanol | 112.6–113.6[c] |
| $CH_3O$ | F | F | 81 | ligroin | 83.7–84.7 | **5b** | 48[b] | benzene–ligroin | 107.7–108.5 |
| Br | F | F | 91 | ligroin | 119.5–120.4 | **5c** | 39[b] | benzene–ligroin | 129.2–130.0 |
| CN | F | F | | | | **5d** | 65[d] | benzene–ligroin | 174.5–175.5 |
| H | H | F | 93 | benzene–ethanol | 132.3–132.8 | **6** | 40 | pentane | 61.8–63.0 |
| $CH_3O$ | F | H | 80 | ligroin | 63.4–64.2 | **7a** | 43[b] | ethanol | 129.8–130.6 |
| Br | F | H | 85 | methanol | 118.8–119.4 | **7b** | 43[b] | ligroin | 147.2–147.6 |
| CN | F | H | | | | **7c** | 56[d] | *e* | 185.3–186.0 |
| $CH_3O$ | H | F | 76 | *e* | 104.3–105.0 | **8a** | 35[b] | *e* | 134.0–135.0 |
| Br | H | F | 80 | ethanol | 100.0–100.6[f] | **8b** | 50[b] | *e* | 135.0–135.4 |
| CN | H | F | | | | **8c** | 92[d] | benzene–ligroin | 179.0–179.5 |

[a] Satisfactory elemental analyses for C and H were obtained for all nineteen tabulated compounds. [b] In addition, products from ring closure at the X-bearing carbon and loss of HX were obtained in 5–15% yield as shown by GC/MS. [c] A phase transition occurs at some temperature between 70 and 100 °C. [d] From the preceding bromo compound. [e] Purified by sublimation. [f] A phase transition occurs around 90.5 °C.

methyl)-5-fluoroanisole, which was obtained by chloromethylation of 4-fluoroanisole.[15]

2-Bromo-5-fluorotoluene was treated with *N*-bromosuccinimide and the resulting bromomethyl compound was subjected to a Sommelet reaction.[16] The product was isolated by steam distillation and purified by sublimation at 50 °C (0.01 torr) to give 2-bromo-5-fluorobenzaldehyde as white crystals, mp 53.0–54.8 °C. Anal. Calcd for $C_7H_4BrFO$: C, 41.41; H, 1.99. Found: C, 41.20; H, 2.17.

2-Chloro-5-fluorobenzaldehyde was prepared as described previously.[17]

**Phosphonium Salts.** 7-(Bromomethyl)-1-fluoronaphthalene[17] and 2-(bromomethyl)naphthalene[18] were converted to the corresponding phosphonium salts in high yields by treatment with 1 equiv of triphenylphosphine in refluxing dry xylene.

***trans*-2-Styrylnaphthalenes.** In a typical procedure, 10 mmol of one of the aforementioned phosphonium salts (dried at 100 °C for 1 h immediately before use) was added in one portion under $N_2$ to a solution prepared by dissolving 0.23 g (10 mmol) of sodium metal in 30 mL of specially dried[19] ethanol. The resulting yellow reaction mixture was stirred magnetically for 20 min and then a solution of 10 mmol of the appropriate aldehyde in 8 mL of dry ethanol was added dropwise over 15 min. After the reaction mixture had been stirred and maintained under $N_2$ overnight and its yellow color had faded, it was diluted by the addition of 27 mL of water.[20] The crude 2-styrylnaphthalene derivative was then isolated, either by suction filtration or by extracting with several portions of ligroin, drying the extracts over anhydrous $MgSO_4$, filtering the dried ligroin solution through a column of alumina, eluting the column with additional ligroin, and rotary evaporating the eluate. The crude product, which was shown by GC to contain a mixture of the cis and trans isomers of the 2-styrylnaphthalene, was dissolved in 100 mL of benzene. A small crystal of iodine was added and the solution was irradiated with an ordinary 100-W light bulb until the cis → trans isomerization was complete as judged by GC. The benzene was removed by rotary evaporation and the residue was dissolved in ligroin and chromatographed on alumina to remove iodine and polar impurities. Evaporation of the eluate and purification of the residue by recrystallization and/or sublimation at reduced pressure gave the *trans*-2-styrylnaphthalene in good yield. Details for individual compounds are given in Table III.

**Benzo[*c*]phenanthrenes.** Typically, a solution of 5 mmol of the *trans*-2-styrylnaphthalene in 500 mL of cyclohexane containing $1 \times 10^{-3}$ M iodine was irradiated[21] in an immersion apparatus with a 450-W Hanovia medium-pressure mercury arc lamp contained in a water cooled quartz probe. The solution was stirred magnetically and the progress of the photocyclization reaction was monitored by GC. After the reaction was judged to be essentially complete, the reaction mixture was chromatographed on alumina to remove iodine and polar impurities. The crude product was isolated by rotary evaporation of the eluate and was purified by sublimation at reduced pressure and/or recrystallization to give the substituted benzo[*c*]phenanthrene in modest yield. Details for individual compounds are given in Table III.

**Cyanobenzo[*c*]phenanthrenes.** Cyanobenzo[*c*]phenanthrenes were prepared by heating a magnetically stirred mixture of 1.5 mmol of the corresponding bromobenzo[*c*]phenanthrene, 1.6 mmol of cuprous cyanide, 9 mL of dimethylformamide, and 4 drops of pyridine under reflux for 20 h.[22] An additional 1 mmol of cuprous cyanide was then added and the mixture was heated under reflux for 5 h more or until the reaction was judged complete by GC analysis. The reaction mixture was then cooled to room temperature and poured into a mixture of 12 mL of concentrated ammonium hydroxide and 12 g of crushed ice. The resulting solid was collected by suction filtration, washed with water, air-dried, and purified by sublimation at reduced pressure to give the cyanobenzo[*c*]phenanthrene as white or very pale yellow crystals. See Table III.

**1-Methyl-4,5-difluorophenanthrene (2a) and 1-Methyl-4,7-difluorophenanthrene.** A Wittig reaction of (3-fluorobenzyl)triphenylphosphonium chloride and 2-methyl-5-fluorobenzaldehyde gave an oil shown by GC/MS to contain a mixture of the cis and trans isomers of 3′,5-difluoro-2-methylstilbene. This oil was heated briefly along with a small crystal of iodine to effect cis → trans isomerization and then was distilled to give material with bp 110–115 °C (0.05 torr). Trituration of the distillate with

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(20) The triphenylphosphine oxide byproduct is soluble in ethanol containing up to 40% water: Maercker, A. *Org. React.* (*N.Y.*) **1965**, *14*, 270–490.

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pentane at 0 °C gave a sample of 3′,5-difluoro-2-methylstilbene as a crystalline solid that melted below room temperature: MS, *m/e* 230 (M$^+$). Anal. Calcd for $C_{15}H_{12}F_2$: C, 78.25; H, 5.25. Found: C, 78.15; H, 5.15.

A solution of 1.4 g (6 mmol) of the stilbene in 300 mL of cyclohexane containing 3 × 10$^{-3}$ M iodine was irradiated and worked up as described generally above to give as the crude product a mixture of 1-methyl-4,5-difluorophenanthrene and 1-methyl-4,7-difluorophenanthrene. These two isomers were separated by chromatography on a 16-cm × 2-cm column of alumina using as eluent 180 mL of pentane followed by 100 mL of a 9:1 mixture of ligroin and benzene and 100 mL of a 3:1 mixture of ligroin and benzene. The pentane eluate was collected as 18 10-mL fractions; evaporation of the pentane from combined fractions 8–12 yielded 0.2 g of the previously described[4] 1-methyl-4,7-difluorophenanthrene: $^1$H NMR (60 MHz, $CCl_4$) $\delta$ 8.88 (apparent quintet, 1 H, H-5), 7.62–6.78 (complex m, 6 H), 2.45 (s, 3 H). Material obtained by evaporation of fractions 17–18 of the pentane eluate and all of the ligroin–benzene eluates was purified sequentially by rechromatography on alumina in pentane, chromatography on silicic acid in ligroin, and rechromatography on silicic acid in pentane to give 0.1 g of solid 1-methyl-4,5-difluorophenanthrene shown by GC to be about 94% pure; this material was used for all NMR measurements. Fractional sublimation at reduced pressure gave a 6-mg sample of 1-methyl-4,5-difluorophenanthrene (**2a**) as white crystals with no significant impurities as judged by GC and with mp 58.0–58.6 °C: $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 7.85–7.05 (complex m, 7 H), 2.61 (s, 3 H); $^{19}$F NMR (188.3 MHz, $CDCl_3$) 12.80 and 9.17 ppm downfield from TTC (AB type quartet of ddd, $J_{FF}$ = 174 Hz); MS, *m/e* 228 (M$^+$). Anal. Calcd for $C_{15}H_{10}F_2$: C, 78.94; H, 4.42. Found: C, 78.91; H, 4.29.

**1-Chloro-4,5-difluorophenanthrene (2b) and 1-Chloro-4,7-difluorophenanthrene.** A Wittig reaction of (3-fluorobenzyl)triphenylphosphonium chloride and 2-chloro-5-fluorobenzaldehyde gave an oil shown by GC/MS to contain a mixture of the cis and trans isomers of 2-chloro-3′,5-difluorostilbene: MS, *m/e* 250, 252 (M$^+$). This mixture of stilbene isomers (2.0 g, 9 mmol) was dissolved in 500 mL of cyclohexane containing 2 × 10$^{-3}$ M iodine, irradiated, and worked up in the usual way. GC/MS analysis of the crude product indicated the formation of two isomeric chlorodifluorophenanthrenes (*m/e* 248, 250) and a small amount of a difluorophenanthrene (*m/e* 214). Two recrystallizations of this mixture from methanol gave 0.8 g (40%) of 1-chloro-4,7-difluorophenanthrene as white crystals, mp 119.0–120.6 °C. Sublimation at reduced pressure and an additional recrystallization from methanol gave 0.6 g of material with mp 123.5–124.2 °C: $^1$H NMR (60 MHz, $CDCl_3$) $\delta$ 9.2–8.8 (apparent quintet, 1 H, H-5), 8.3–8.0 (dd, 1 H, H-10, $J_{9,10}$ = 9.5 Hz, $J_{4,10}$ = 2.2 Hz), 7.8–7.0 (m, 5 H, H-2,3,6,8,9); MS, *m/e* 248, 250 (M$^+$). Anal. Calcd for $C_{14}H_7ClF_2$: C, 67.62; H, 2.84. Found: C, 67.49; H, 2.93.

The combined filtrates from all the methanol recrystallizations were evaporated and the residue was chromatographed on alumina with ligroin as eluent. All the fractions of the eluate were analyzed by GC, and appropriate fractions were combined and rotary evaporated to give 0.5 g (25%) of material shown by GC to contain 60% of the 4,5-difluoro isomer. Eight recrystallizations of this material from pentane gave 0.05 g of 1-chloro-4,5-difluorophenanthrene (**2b**) as white crystals with less than 0.5% contamination by the 4,7-difluoro isomer as judged by GC and with mp 74.2–74.6 °C: $^1$H NMR (90 MHz, $CDCl_3$) $\delta$ 8.14 (br d, 1 H, H-10, $J_{9,10}$ = 9 Hz), 7.76 (br d, 1 H, H-9, $J_{9,10}$ = 9 Hz), 7.70–7.15 (complex m, 5 H, H-2,3,6,7,8); $^{19}$F NMR (188.3 MHz, $CDCl_3$) 13.34 and 11.98 ppm downfield from TTC (AB type quartet of br d, $J_{FF}$ = 177 Hz); MS, *m/e* 248, 250 (M$^+$). Anal. Calcd for $C_{14}H_7ClF_2$: C, 67.62; H, 2.84. Found: C, 67.67; H, 2.90.

**4-Methyl-7,8-difluorobenzo[*ghi*]perylene (3) and 1-Methyl-9,12-difluorodibenzo[*c,g*]phenanthrene.** The phosphonium salt derived from 3-(bromomethyl)-6-fluorophenanthrene and triphenylphosphine, prepared as described previously[17] (8.32 g, 15 mmol), was subjected to a Wittig reaction with 2.35 g (17 mmol) of 4-fluoroacetophenone according to the general procedures described above. The crude product was recrystallized from a 9:1 mixture of diethyl ether and methanol to give 3.6 g (72%) of a mixture of the *E* and *Z* isomers of 1-(6-fluoro-3-phenanthryl)-2-(4-fluorophenyl)propene: $^1$H NMR (60 MHz, $CDCl_3$) $\delta$ 2.33 (d, $J \sim 2$ Hz, methyl), 2.23 (d, $J \sim 2$ Hz, methyl); MS, *m/e* 330 (M$^+$). Anal. Calcd for $C_{23}H_{16}F_2$: C, 83.62; H, 4.88. Found: C, 83.66; H, 4.89.

A sample of 0.66 g (2 mmol) of the aforementioned mixture of *E* and *Z* isomers was dissolved in 400 mL of benzene containing 1.4 × 10$^{-3}$ M iodine and was subjected to the usual photocyclization procedure. Recrystallization of the crude product from benzene gave 0.15 g (23%) of 4-methyl-7,8-difluorobenzo[*ghi*]perylene (**3**) as pale yellow-green needles, mp 199.9–200.8 °C: $^{19}$F NMR (94.1 MHz,[23] dimethylformamide) 14.06 and 13.20 ppm downfield from TTC (AB type quartet of dd, $J_{FF}$ = 174 Hz); MS, *m/e* 326 (M$^+$); UV max (benzene) 293, 304, 360, and 389 nm. Anal. Calcd for $C_{23}H_{12}F_2$: C, 84.68; H, 3.71. Found: C, 84.83; H, 3.62.

By a modification of the general procedure for photocyclization in which the quartz probe was replaced by a Pyrex probe to filter out short wavelength light, it was possible to stop the photocyclization of the mixture of the *E* and *Z* isomers of 1-(6-fluoro-3-phenanthryl)-2-(4-fluorophenyl)propene at the dibenzo[*c,g*]phenanthrene stage. Thus irradiation through Pyrex of a solution of 1.65 g (5 mmol) of the *E,Z* mixture in 400 mL of benzene containing 6 × 10$^{-4}$ M iodine gave 1.04 g (64%) of crude yellow product. Purification of this material by recrystallization from ethanol and two sublimations at reduced pressure gave 1-methyl-9,12-difluorodibenzo[*c,g*]phenanthrene as pale yellow crystals, mp 176.2–178.8 °C: $^1$H NMR (60 MHz, $CDCl_3$) $\delta$ 8.28–7.07 (complex m, 11 H), 2.72 (br s, 3 H); $^{19}$F NMR (56.4 MHz, $C_6D_6$) 2.19 ppm upfield from TTC (ddd, F-9, $J_{9,10}$ = 12.1 Hz, $J_{8,9}$ = 8.1 Hz, $J_{7,9}$ = 6.4 Hz, $J_{FF}$ < 0.5 Hz), 3.20 ppm upfield from TTC (ddd, F-12, $J_{11,12}$ = 12.1 Hz, $J_{12,13}$ = 7.8 Hz, $J_{12,14}$ = 6.4 Hz, $J_{FF}$ < 0.5 Hz); MS, *m/e* 328 (M$^+$); UV max (ethanol) 226, 264, and 296 nm. Anal. Calcd for $C_{23}H_{14}F_2$: C, 84.13; H, 4.30. Found: C, 83.99; H, 4.32.

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(23) We are grateful to Professor David R. Dalton of Temple University for obtaining this spectrum.