Registry No. CH_2Br_2, 74-95-3; cyclohexene, 110-83-8; bicyclo[4.1.0]heptane, 286-08-8; cyclooctene, 931-88-4; bicyclo[6.1.0]nonane, 286-60-2; α-pinene, 80-56-8; 2,7,7-trimethyltricyclo[4.1.1.$0^{2,4}$]octane, 32549-17-0; β-pinene, 127-91-3; 6′,6′-dimethylspiro[cyclopropane-1,2′-norpinane], 35117-81-8; 1-hexene, 592-41-6; butylcyclopropane, 930-57-4; 1-octene, 111-66-0; hexylcyclopropane, 4468-61-5; 3,4-dihydropyran, 110-87-2; 2-oxabicyclo[4.1.0]heptane, 286-16-8; *trans*-crotyl alcohol, 504-61-0; *trans*-2-methylcyclopropylcarbinol, 21003-36-1.

Condensation with Trifluoroacetonitrile: A Simple One Step Synthesis of 5-Cyano-6-(trifluoromethyl)uracil

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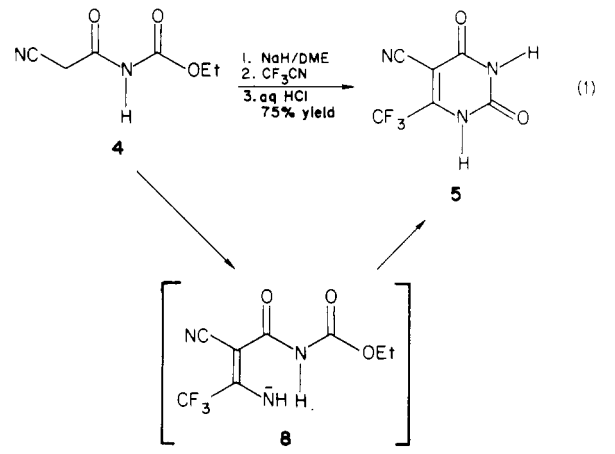
A number of fluorine-substituted uracil derivatives show interesting biological activity. For example, 5-fluorouracil derivatives are useful as antitumor agents, and 5-(trifluoromethyl)deoxyuridine shows marked antiviral activity.[1,2] The binding of 6-substituted uracil to thymidine phosphorylase has been studied. The 6-trifluoromethyl derivative has been reported to bind to this enzyme sevenfold better than the 6-methyl analogue. Presumably the increased activity was due to the increased acidity of the uracil.[3] The 3-substituted-6-(trifluoromethyl)uracils have also been reported as herbicides.[4]

It is noteworthy that the existing synthetic routes to the 6-(trifluoromethyl)uracils do not allow a facile derivation at the 5-position,[3-5] which is needed for the synthesis of various analogues for biological evaluations. An acid function such as a cyano group at the 5-position is highly desirable, since it would offer increased opportunities for derivation. However, the 5-cyano derivative was hitherto unknown. It has been reported that an active methylene compound reacted with trifluoroacetonitrile to give the corresponding 2-trifluoromethyl enamine.[6] By employing an active methylene compound with a γ-ester function, such as *N*-(cyanoacetyl)urethane (**4**), one should be able to prepare the corresponding uracil in one step. In fact, treatment of **4** with sodium hydride followed by reaction of the resulting anion with trifluoroacetonitrile gave 5-cyano-6-(trifluoromethyl)uracil (**5**) in 75% yield (eq 1). Presumably the reaction intermediate was enamine **6**, though it was not isolated. The structural assignment of **5** was supported by its spectral properties and combustion analysis. Trifluoroacetonitrile has been condensed with enamines or ynamines to give the corresponding 2,4-bis(trifluoromethyl)pyrimidine.[7] However, trifluoroacetonitrile has not been used for the synthesis of uracils.



(1)

Experimental Section

Melting points are uncorrected. ^{19}F NMR spectra were obtained on a Varian EM-360 spectrometer. ^1H NMR spectra were obtained on a Varian XL-300 spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer. Signals are reported in parts per million downfield from tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 727B infrared spectrophotometer. Mass spectra were obtained on a Finnigan MAT CH7A mass spectrometer. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

5-Cyano-6-(trifluoromethyl)uracil (5). To a solution of *N*-(cyanoacetyl)urethane (**4**) (100 g, 0.64 mol, Aldrich Co.) in 700 mL of anhydrous 1,2-dimethoxyethane under an atmosphere of nitrogen was added 34 g (0.7 mol) of sodium hydride (50% oil dispersion). The temperature of the exothermic reaction was kept below 45 °C by a water bath. The resulting muddy gray suspension was stirred for 30 min. After the exothermic reaction subsided, it was warmed to 35 °C by external heating. To this mixture, a stream of trifluroacetonitrile (Fairfield Co.) was added in slowly. At the end of 5.5 h, the uptake of trifluoroacetonitrile became very slow, and an excess amount of trifluoroacetonitrile was used. The resulting brown solution was poured into cold 6 N aqueous hydrochloric acid and extracted with ethyl acetate. The ethyl acetate layer was washed with water, dried ($MgSO_4$), and concentrated to give a solid. It was washed with chloroform/acetonitrile to give 97 g of a cream color solid (75% yield) as **5**: mp 245–253 °C; IR (Nujol) 2250 (m, C≡N), 1703 (s), 1630 (s) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 12.1 (s, N_4H, 1 H), 9.9 (br s, N_1H, 1 H; chemical shift and integration varied with the amount of moisture in Me_2SO-d_6); ^{13}C NMR (Me_2SO-d_6) δ 160.4 (C_4), 149.6 (C_2), 148.9 (C_6, q, J = 35.9 Hz), 118.3 (CF_3, q, J = 278.1 Hz), 111.6 (CN), 86.9 (C_5, q, J = 1.4 Hz); ^{19}F NMR (Me_2SO-d_6, CCl_3F) δ −67.53; mass spectrum, *m/e* (relative intensity) 205 (M^+, 40.3), 162 (40.0), 96 (12.3), 93 (59.9), 28 (100.0).

Anal. Calcd for $C_6H_2F_3N_3O_2$: C, 35.14; H, 0.98; N, 20.49. Found: C, 35.14; H, 0.92; N, 20.48.

Registry No. **4**, 6629-04-5; **5**, 98577-47-0; trifluoroacetonitrile, 353-85-5.

Synthesis and Fluorescence Spectra of Structural Analogues of Potential Benzo[*b*]fluoranthene-DNA Adducts[1,2]

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Benzo[*b*]fluoranthene (**1**), an environmental carcinogen[3-7] interacts in vivo with the DNA of mouse epidermis

(1) (a) Heidelberger, C.; Parsons, D. G.; Remy, D. C. *J. Am. Chem. Soc.* **1962**, *84*, 3597. (b) Heidelberger, C.; Parsons, D. G.; Remy, D. C. *J. Med. Chem.* **1964**, *7*, 1. (c) Ryan, K. J.; Acton, E. M; Goodmann, L. *J. Org. Chem.* **1966**, *31*, 1181.

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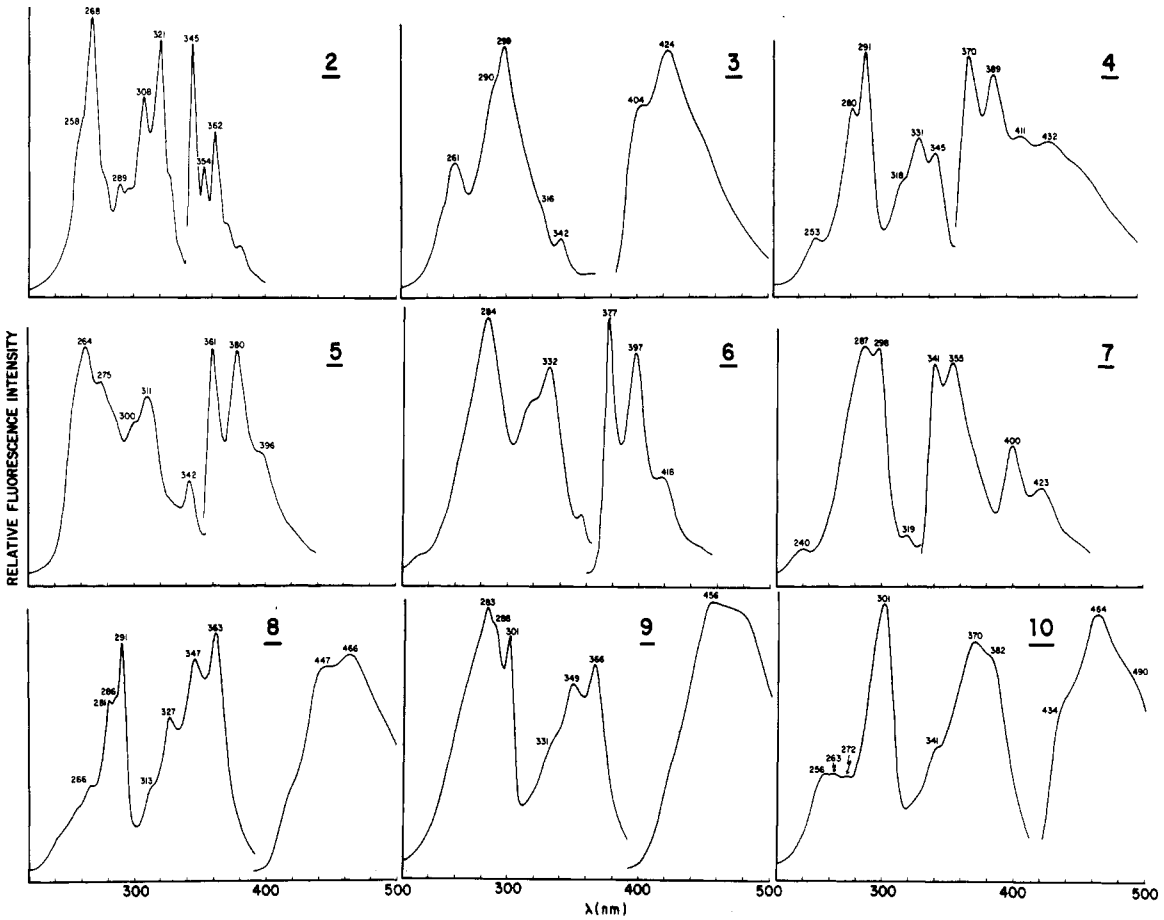

Figure 1. Fluorescence spectra of compounds **2–10**. Excitation and emission wavelengths were respectively as follows (nm): **2** (320, 344); **3** (301, 425); **4** (292, 370); **5** (264, 380); **6** (318, 395); **7** (288, 340); **8** (363, 446); **9** (364, 450); **10** (375, 464).

to form at least five covalently bound adducts.[8] Their structures are not known. By analogy to other polynuclear aromatic hydrocarbons, the reactive intermediates formed metabolically from **1** could be epoxides or dihydro diol epoxides.[9,10] The DNA adducts would result from attack of a nucleophilic center of a DNA base, such as N^2 of deoxyguanosine, on the epoxide or dihydro diol epoxide, yielding a product in which either one or two of the double bonds of **1** was saturated. The fluorescence spectra of such products have been used in studies on other polynuclear aromatic hydrocarbons to determine the positions involved in DNA adduct formation. For example, 7,12-dimethylbenz[*a*]anthracene–DNA adducts have anthracene-like fluorescence spectra and benzo[*a*]pyrene–DNA adducts have pyrene-like spectra.[11,12] These spectra were important in the assignment of dihydrodiol epoxides as major ultimate carcinogens of these two hydrocarbons. In this report, we present the fluorescence spectra of compounds **2–10** (Figure 1). An improved synthesis of acephenanthrylene (**5**) was developed for this study, and syntheses of the previously unknown vinyl compounds **3**, **6**, **9**, and **10** are also described. In addition, we have assessed the mutagenicity toward *S. typhimurium* of **5**, which has been detected in the environment.

11-Ethylidene-11*H*-benzo[*b*]fluorene (**3**) was prepared by reaction of ethylmagnesium bromide with 11*H*-benzo[*b*]fluoren-11-one, followed by dehydration. This gave a mixture of isomers, 50% *E* and 50% *Z*, which were assigned by the positions of the methyl resonances (2.40 and 2.46 ppm, respectively) in the NMR spectrum of **3**.

The synthesis of acephenanthrene, which can be aromatized to **5**, was first reported in 1932.[13] It was prepared in erratic yields by succinoylation of acenaphthene, Clemmensen reduction, cyclization to 7-oxo-7,8,9,10-tetrahydroacephenanthrene, reduction, and aromatization. Yields in this synthesis were reported to be somewhat higher in a recent study.[14] An alternate synthesis of **5** was achieved by photolysis of 1-(*o*-iodobenzylidene)indane, followed by aromatization.[15] Acephenanthrylene has also been prepared as an analytical standard, but no details were given.[16] We found that 9-methylphenanthrene (**13**)

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(2) Supported by NIEHS Grant ES-02030.
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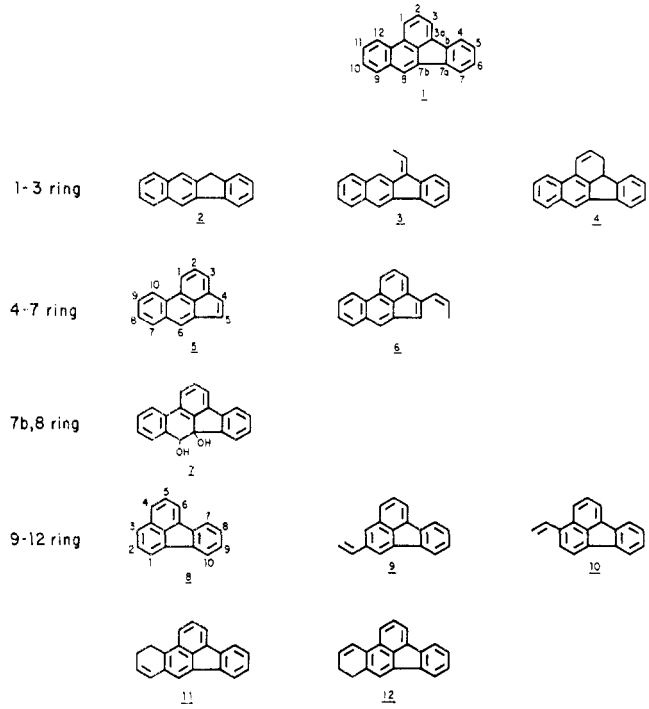
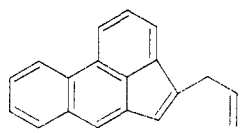


was the most convenient starting point for preparation of **5** (Scheme I). Treatment with *N*-bromosuccinimide gave 9-(bromomethyl)phenanthrene (**14**), which was converted to 9-(cyanomethyl)phenanthrene (**15**) by reaction with KCN. Hydrolysis and cyclization gave 4-oxo-4,5-dihydroacephenanthrylene (**17**), which was reduced and dehydrated, yielding **5** in approximately 30% overall yield from **13**.

Synthesis of 4-alkenylacephenanthrylenes presented problems associated with the instability of these compounds, which decomposed or polymerized at room temperature. Reaction of 4-oxo-4,5-dihydroacephenanthrylene (**17**) with vinylmagnesium bromide gave the expected alcohol, but all attempts at dehydration to 4-vinylacephenanthrylene resulted in polymerization. In a second approach, **17** was allowed to react with allylmagnesium bromide. Dehydration gave 4-(2-propenyl)acephenanthrylene (**19**). However, we were unsuccessful in



19

attempts to convert **19** to **6** by a variety of methods including treatment with *n*-butyllithium, sodium hydride, or trityl tetrafluoroborate. The unstable compound **6** was prepared, in low yield, by reaction of **17** with either 1-propenyllithium or 1-propenylmagnesium bromide, followed by dehydration. The configuration of the double bond in **6** is not known.

2-Vinylfluoranthene (**9**) was synthesized from 2-(bromomethyl)fluoranthene by treatment with hexamethylenetetramine to give fluoranthene-2-carboxaldehyde (**20**), followed by Wittig reaction with methyltriphenylphosphonium bromide. 3-Vinylfluoranthene (**10**) was prepared by reduction of 3-(carboxymethyl)fluoranthene with $LiAlH_4$ to 3-(2-hydroxyethyl)fluoranthene (**21**), reaction with $SOCl_2$, and dehydrohalogenation.

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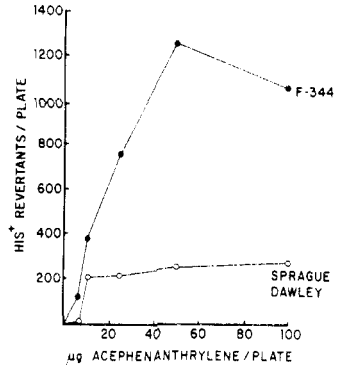
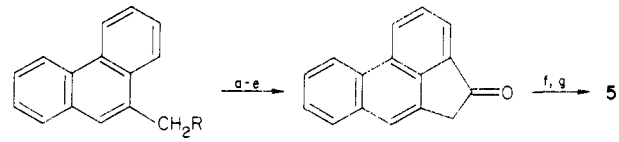


Figure 2. Mutagenicity of acephenanthrylene (**5**) toward *S. typhimurium* TA100 in the presence of liver 9000*g* supernatants from F344 (●) or Sprague–Dawley (○) rats that had been pretreated with Aroclor 1254. Spontaneous revertants (143/plate) have been subtracted.

Scheme I. Synthesis of Acephenanthrylene (**5**)[a]



13, R=H
14, R=Br
15, R=CN
16, R=CO_2H

[a] (a) NBS, CCl_4; (b) KCN, EtOH; (c) KOH, EtOH; (d) $(COCl)_2$, CH_2Cl_2; (e) $AlCl_3$, CS_2; (f) $LiAlH_4$, Et_2O; (g) *p*-toluenesulfonic acid.

The fluorescence spectra of compounds **2**–**10** are presented in Figure 1. The spectra of **11** and **12** were similar to those of **9** and **10**, respectively, which indicates that vinyl derivatives such as **3** and **6** are appropriate model compounds. The spectra illustrated are all distinct from one another, which suggests that they will be useful for identification of DNA adducts of **1**.

Since acephenanthrylene has been detected in combustion effluents, we tested its mutagenicity toward *S. typhimurium* TA100. As illustrated in Figure 2, acephenanthrylene was mutagenic, when the assay was carried out with liver 9000*g* supernatant from F344 rats which had been pretreated with Aroclor 1254. When the assay was carried out with liver 9000*g* supernatant from identically pretreated Sprague–Dawley rats, significant mutagenic activity was not observed. In a previously reported assay of acephenanthrylene, in which a *S. typhimurium* forward mutation assay was used with activation by Aroclor 1254 induced Sprague–Dawley rat liver supernatant, acephenanthrylene was found to be inactive, in agreement with the present results.[16] The reason for the difference in response between Sprague–Dawley and F344 rats is not known.

Experimental Section

Infrared spectra were run on a Perkin-Elmer Model 267 grating infrared spectrophotometer. NMR spectra were determined with a JEOL Model FX90Q spectrometer in $CDCl_3$ solution unless otherwise stated and are reported as parts per million downfield from Me_4Si as an internal reference. UV spectra were determined in CH_3OH with a Cary Model 118 instrument. Fluorescence spectra were obtained with a Perkin-Elmer Model 650-10S fluorescence spectrophotometer. HPLC was carried out with a Waters Associates Model ALC/GPC-204 high-speed liquid chromatograph equipped with a Model 660 solvent programmer, a Model LC-25 UV–vis detector, and a 4.6 mm (i.d.) × 250 mm EM 10-μm column eluted from 70% CH_3OH in H_2O to 100%

CH_3OH in 30 min at 2 mL/min. MS were run with a Hewlett-Packard Model 5982A dual-source instrument using a membrane separator. Microanalyses were performed by Galbraith Laboratories.

Benzo[*b*]fluorene (**2**),[17] 11*H*-benzo[*b*]fluoren-11-one,[18] 2-(bromomethyl)fluoranthene,[19] 3,3a-dihydrobenzo[*b*]fluoranthene (**4**),[19] *cis*-7b,8-dihydroxy-7b,8-dihydrobenzo[*b*]fluoranthene (**7**),[20] 3-fluoranthenylacetic acid,[21] 11,12-dihydrobenzo[*b*]fluoranthene (**11**),[22] 9,10-dihydrobenzo[*b*]fluoranthene (**12**),[19] and 9-methylphenanthrene (**13**)[23] were prepared according to published procedures.

11-Ethylidene-11*H*-benzo[*b*]fluorene (3). Ethylmagnesium bromide (0.26 g, 0.002 mol, 2 M solution in Et_2O; Aldrich), was added dropwise to a solution of 11*H*-benzo[*b*]fluorene-11-one (0.46 g, 0.002 mol) in 50 mL of Et_2O under N_2, and the solution was stirred for 1 h at room temperature. Conventional workup yielded 0.3 g of crude alcohol, which was directly dehydrated by using *p*-toluenesulfonic acid in benzene. The crude olefin was purified by chromatography on silica gel. Elution with hexane–CH_2Cl_2 (90:10) afforded **3** as a yellow solid (0.15 g, 30%): mp 133–134 °C; NMR δ 2.40 (d, 1.5 H, J = 9 Hz, *E* isomer, CH_3), 2.46 (d, 1.5 H, J = 6 Hz, *Z* isomer, CH_3), 6.6–6.95 (m, 1 H), 7.2–7.45 (m, 4 H), 7.55–8.25 (m, 6 H); MS, m/e (relative intensity) 242 (M^+, 100); UV λ_{max} (ϵ) 357 (4330), 322 (7560), 294 (34 300), 286 (33 240), 275 (24 300), 253 (55 900), 244 (46 080), 225 (25 700).

Anal. Calcd for $C_{19}H_{14}$: C, 94.17; H, 5.82. Found: C, 93.93; H, 5.72.

9-(Bromomethyl)phenanthrene (14). A suspension of NBS (17.8 g, 0.1 mol), 9-methylphenanthrene (**13**) (19.2 g, 0.1 mol), and benzoyl peroxide (10 mg) in CCl_4 (200 mL) was heated at reflux under a heat lamp for 1 h. Conventional workup provided **14** (25.4 g, 92%) as a light yellow solid: mp 120 °C (lit.[24] mp 118–119 °C); NMR δ 4.7 (s, 2 H), 7.2–8.1 (m, 7 H), 8.1–8.5 (m, 2 H); MS, m/e (relative intensity) 272 (M^+,10), 270 (10), 191 (100).

9-(Cyanomethyl)phenanthrene (15). To a suspension of the bromide **14** (10.0 g, 0.036 mol) in EtOH (100 mL) was added KCN (6.5 g, 0.1 mol) in H_2O (10 mL). The reaction mixture was heated under reflux for 3 h, poured into H_2O, extracted with Et_2O (2 × 150 mL), dried, and concentrated to give **15** (7.0 g, 89%): mp 104–106 °C; NMR δ 4.0 (s, 2 H), 7.5–7.8 (m, 7 H), 8.4–8.8 (m, 2 H); MS, m/e (relative intensity) 217 (M^+, 100).

Anal. Calcd for $C_{16}H_{11}N$: C, 88.47; H, 5.06. Found: C, 88.46; H, 5.08.

9-Phenanthrylacetic Acid (16). A solution of the nitrile **15** (10.8 g, 0.05 mol) and KOH (11.2 g, 0.2 mol) in EtOH was heated under reflux for 20 h. The reaction mixture was diluted with H_2O and acidified with dilute HCl. The precipitate was collected by filtration, washed with H_2O, and dried to give **16** as a white solid (11.0 g, 93%): mp 222 °C (lit.[25] mp 221 °C; MS, m/e (relative intensity) 236 (M^+, 14.5), 235 (44.7), 191 (100).

4-Oxo-4,5-dihydroacephenanthrylene (17). To a suspension of **16** (11.0 g, 0.046 mol) in 150 mL of CH_2Cl_2 was added dropwise under N_2 oxalyl chloride (7.7 g, 0.06 mol). The reaction mixture was stirred at room temperature for 3 h, and the CH_2Cl_2 was removed under reduced pressure. The crude product was dissolved in 100 mL of CS_2, and the solution was cooled to 0 °C. $AlCl_3$ (10.6 g, 0.08 mol) was added in portions, and the mixture was stirred for 1 h at 0 °C and then refluxed for 10 min. The mixture was cooled and then poured into cold H_2O containing 100 mL of 4 N HCl. The resulting mixture was extracted with $CHCl_3$. The usual workup yielded a yellow solid (9.0 g). Column chromatography of this material on silica gel with CH_2Cl_2 as eluant gave 8.0 g (80%) of **17**: mp 158–160 °C; NMR δ 3.7 (s, 2 H), 7.5–8.1 (m, 6 H), 8.4–8.7 (m, 2 H); MS, m/e (relative intensity) 218 (M^+, 92.5), 189 (100).

Anal. Calcd for $C_{16}H_{10}O$: C, 88.07; H, 4.58. Found: C, 87.96; H, 4.60.

Acephenanthrylene (5). To a stirred suspension of $LiAlH_4$ (1.3 g, 0.035 mol) in anhydrous Et_2O (100 mL) was added dropwise a solution of **17** (5.9 g, 0.027 mol) in 30 mL of Et_2O. The mixture was stirred at 0 °C for 1 h and then at room temperature for 1 h. The reaction mixture was poured onto ice. The organic layer was collected, washed with H_2O, dried, and concentrated to yield crystalline 4-hydroxy-4,5-dihydroacephenanthrylene (**18**) (4.8 g, 81%): mp 148–150 °C; MS, m/e (relative intensity) 220 (M^+, 100) 202 (43.6). The alcohol was used in the next step without further purification.

To a solution of **18** (4.5 g, 0.027 mol) in benzene was added 30 mg of *p*-toluenesulfonic acid. The mixture was heated under reflux for 1 h with a Dean–Stark trap. Removal of the benzene gave 3.5 g of a light yellow solid, which was purified on silica gel with elution by hexane–CH_2Cl_2 (80:20) to give pure **5** (3.0 g, 55%): mp 140–141 °C (lit.[15] mp 143–144 °C); MS, m/e (relative intensity) 202 (100); UV λ_{max} (ϵ) 365 (9340), 347 (8510), 329 (8540), 315 (7680), 299 (11 080), 288 (9190), 270 (172 600), 262 (31 100), 232 (33 100).

4-(2-Propenyl)acephenanthrylene (19). Allylmagnesium bromide (0.7 g, 0.005 mol, 1.0 M in Et_2O; Aldrich) was added dropwise under an N_2 atmosphere to a solution of **17** (1.1 g, 0.005 mol) in 30 mL of THF. The reaction mixture was stirred for 2 h. After dilution with H_2O, the mixture was worked up as usual to yield 0.4 g of the oily alcohol, which was used directly in the next step.

A solution of the above alcohol and *p*-toluenesulfonic acid (5 mg) in benzene was heated at 60 °C for 10 min. Conventional workup followed by chromatography on silica gel, eluting with hexane–CH_2Cl_2 (90:10) afforded **19** as a yellow oil: NMR δ 3.5 (dd, 2 H), 5.0–5.4 (m, 2 H), 5.9–6.4 (m, 1 H), 6.7 (s, 1 H), 7.3–8.0 (m, 6 H), 8.2–8.4 (m, 1 H), 8.5–8.7 (m, 1 H); MS, m/e (relative intensity) 242 (M^+, 42.5), 215 (100).

4-(1-Propenyl)acephenanthrylene (6). Anhydrous Et_2O (10 mL) and Mg turnings (0.072 g) were placed in a 100-mL flask under N_2 followed by the dropwise addition of 1-bromopropene (0.36 g, 0.003 mol) in 10 mL of Et_2O. After being stirred for 30 min, the mixture was heated at 60 °C for 1 h. After the formation of the Grignard reagent, the reaction mixture was cooled to 0 °C for 10 min, and the ketone **17** (0.42 g, 0.002 mol) in THF (2 mL) was added dropwise. Stirring was continued at 0 °C for 30 min. The reaction was allowed to warm to room temperature and then added to a mixture of 50 mL of ice–water and 4 mL of 2 N HCl. The organic layer was separated, washed with brine, dried ($MgSO_4$), and evaporated to give the crude alcohol. This was dissolved in anhydrous benzene (50 mL) and 5 mg of *p*-toluenesulfonic acid was added. The mixture was heated at 60 °C for 1 h. Removal of the benzene gave 0.050 g of a light yellow solid, which was purified by chromatography on silica gel with elution by hexane to give pure **6** as a yellow oil (0.03 g, 4.1%): NMR δ 2.0 (d, 3 H, CH_3), 6.5–6.65 (m, 2 H), 6.85 (s, 1 H), 7.4–8.0 (m, 6 H), 8.35 (d, 1 H), 8.5–8.65 (m, 1 H); MS, m/e (relative intensity) 242 (M^+, 100); UV λ_{max} (ϵ) 376 (10 600), 358 (10 100), 340 (8330), 311 (17 800), 302 (14 500), 274 (19 300), 264 (34 600), 256 (39 500), 249 (41 400).

Anal. Calcd for $C_{19}H_{14}$: C, 94.17; H, 5.84. Found: C, 93.92; H, 5.77.

Fluoranthene-2-carboxaldehyde (20). A mixture of hexamethylenetetramine (0.7 g, 0.005 mol) and 2-(bromomethyl)-fluoranthene (0.14 g, 0.0005 mol) in wet EtOH (30 mL) was heated under reflux for 4 h. After the mixture had cooled, dilute HCl was added, and then the mixture was extracted with 100 mL of Et_2O. The organic layer was washed with H_2O, dried, and evaporated, and then the residue was filtered with CH_2Cl_2–hexane (30:70) through a short column of silica gel. The product was recrystallized from Et_2O–hexane to give 60 mg (50%) of light yellow product: mp 154–155 °C; NMR δ 7.3–8.0 (m, 7 H), 8.1–8.25 (dd, 2 H), 10.1 (s, 1 H); MS, m/e (relative intensity) 230 (M^+, 100), 201 (62.9).

2-Vinylfluoranthene (9). To a slurry of methyltriphenylphosphonium bromide (0.17 g, 0.0005 mol) in 10 mL of anhydrous THF at 0 °C was added *n*-BuLi (0.0005 mol). After the mixture

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was stirred for 1 h, **20** (0.1 g, 0.0004 mol) in 2 mL of anhydrous THF was added dropwise, and the mixture was stirred for 1.5 h at room temperature. The reaction mixture was filtered, and the solvent was removed to give crude **9**. Purification by silica gel chromatography using hexane as the eluant gave pure **9** (30 mg, 33%): mp 81–82 °C; NMR δ 5.25 (d, 1 H, J = 12 Hz), 5.8 (d, 1 H, J = 18 Hz), 6.65–7.0 (m, 1 H), 7.1–7.9 (m, 9 H); MS, m/e (relative intensity) 228 (M^+, 100). UV λ_{max} (ϵ) 360 (8390), 344 (7930), 329 (5520), 295 (18 400), 283 (24 800), 278 (34 100), 267 (37 800), 253 (43 400).

Anal. Calcd for $C_{18}H_{12}$: C, 94.69; H, 5.30. Found: C, 94.37; H, 5.11.

3-(2-Hydroxyethyl)fluoranthene (21). The alcohol **21** was prepared from 3-fluoranthenylacetic acid (2.6 g, 0.01 mol) and $LiAlH_4$ (0.36 g, 0.01 mol) under conditions similar to those described for reduction of **17**: yield 85%; mp 91–93 °C; NMR δ 1.7 (br s, 1 H, OH), 3.3 (t, 2 H, CH_2), 3.8 (t, 2 H, CH_2) 7.2–8.0 (m, 9 H); MS, m/e (relative intensity) 246 (M^+, 6.7), 215 (100).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.72. Found: C, 87.51; H, 5.88.

3-(2-Chloroethyl)fluoranthene (22). A solution of $SOCl_2$ (3 mL) in 10 mL of dry benzene was added slowly to a stirred solution of alcohol **21** (0.49 g, 0.0022 mol) in 10 mL of dry benzene. After being stirred for 1 h, the mixture was then heated at reflux for 12 h. The reaction mixture was cooled, washed with H_2O, aqueous $NaHCO_3$, and H_2O, dried ($MgSO_4$), and concentrated. The resulting yellow solid was preabsorbed onto silica gel and purified by chromatography on a column of silica gel with hexane–CH_2Cl_2 (90:10) as eluant to yield 0.2 g (37%) of the chloride **22** as light yellow crystals: mp 89–90 °C; NMR δ 3.6 (d, 2 H, CH_2), 3.85 (d, 2 H, CH_2Cl), 7.2–7.5 (m, 4 H), 7.6–8.0 (m, 5 H); MS, m/e (relative intensity) 229 (M^+ – Cl, 34.4), 215 (100).

3-Vinylfluoranthene (10). A suspension of 3-(2-chloroethyl)fluoranthene (0.26 g, 0.001 mol) and KOH (200 mg) in ethanol was heated at reflux for 1 h. Conventional workup followed by chromatography on silica gel eluting with hexane–CH_2Cl_2 (90:10) afforded **10** as a yellow solid: mp 100 °C (0.15 g, 66%); NMR δ 5.45 (dd, 1 H, J = 1.2 Hz, J = 11.0 Hz), 5.8 (dd, 1 H, J = 1.2 Hz, J = 19 Hz), 7.1–7.9 (m, 9 H), 8.0 (d, 1 H); MS, m/e (relative intensity) 228 (M^+, 100); UV λ_{max} (ϵ) 376 (1110), 363 (1200), 335 (79 701), 293 (22 000), 238 (34 400).

Anal. Calcd for $C_{18}H_{12}$: C, 94.69; H, 5.30. Found: C, 94.35; H, 5.54.

Mutagenicity Assays. Mutagenicity assays were performed as previously described[26] using *S. typhimurium* TA100 (TA 1535/pKm 1101) provided by Dr. Bruce Ames of the University of California, Berkeley, CA. Male F344 rats or Sprague–Dawley rats (250–350 g) were treated with a single ip injection of 500 mg/kg Aroclor 1254, 5 days prior to sacrifice, and the liver 9000g supernatants were prepared for use as the metabolic activation system.[27] Reported values are the means of triplicate assays. Standard deviations were less than 10% of the means.

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Registry No. **2**, 243-17-4; (*E*)-**3**, 98677-74-8; (*Z*)-**3**, 98677-86-2; **4**, 88746-54-7; **5**, 201-06-9; **6**, 98677-75-9; **7**, 98677-76-0; **8**, 206-44-0; **9**, 98677-77-1; **10**, 98677-78-2; **11**, 77061-03-1; **12**, 88746-65-0; **13**, 883-20-5; **14**, 24471-57-6; **15**, 50781-52-7; **16**, 25177-46-2; **17**, 98677-79-3; **18**, 98677-80-6; **19**, 98677-81-7; **20**, 98677-82-8; **21**, 98677-83-9; **22**, 98677-84-0; 11*H*-benzo[*b*]fluoren-11-one, 3074-03-1; 11-ethyl-11-hydroxybenzo[*b*]fluorene, 98677-85-1; 9-phenanthreneacetyl chloride, 98677-87-3; 4-hydroxy-4-(2-propenyl)-4,5-dihydroacephenanthrylene, 98677-88-4; 4-hydroxy-4-(1-propenyl)-4,5-dihydroacephenanthrylene, 98677-89-5; 1-bromopropene, 590-14-7; 4-ethenyl-4-hydroxy-4,5-dihydroacephenanthrylene, 98677-90-8; 2-(bromomethyl)fluoranthene, 88746-58-1; methyltriphenylphosphonium bromide, 1779-49-3; 3-fluoranthenylacetic acid, 24827-02-9.

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A Convenient Synthesis of Hexamethylenetetraselenafulvalene (HMTSF)

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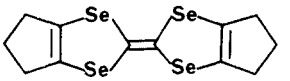
Hexamethylenetetraselenafulvalene (HTMSF, **1**)[1] is known to form electrically conducting charge-transfer complexes with TCNQ (tetracyanoquinodimethane) (σ_{RT} = 2000 cm^{-1} Ω^{-1})[2] and with TNAP (tetracyanonaphthoquinodimethane) (σ_{RT} = 2900 cm^{-1} Ω^{-1})[3], with the TCNQ complex remaining metallic as $T \rightarrow 0$ K.[4] However, widespread studies of HMTSF complexes have been hindered by the lack of availability of the π-donor molecule **1**. We wish to provide a new synthetic pathway to HMTSF and report for the first time the physical properties of this interesting donor component for organic metals.



1

HMTSF was first synthesized from CSe_2[5] via piperidinium diselenocarbamate, which was reacted with α-halocyclopentanone (**2**). The resulting selenocarbamate was then taken through two synthetic steps to yield the appropriate 2-selenoxo-1,3-diselenole (**3**) (Scheme I). Triethylphosphite-induced coupling of the resulting selone (**3**) provided HMTSF. Later,[6] HMTSF was obtained through the same basic synthetic pathway, except that formation of the piperidinium diselenocarbamate was accomplished via consecutive H_2Se reactions with *N,N*-dimethylphosgeneimminium chloride, in the presence of piperidine.

These routes to HMTSF are not only long and inefficient but also involve the use of expensive, highly toxic, and malodorous CSe_2 or H_2Se.

In our approach to **1**, we adopted a procedure similar to those used to synthesize the sulfur and tellurium donors: DBTTF,[7] DBTTeF,[8] HMTTeF,[9] and BDMT-TTeF.[10]

(1) Recommended IUPAC name: 5,5′,6,6′-Tetrahydro-$\Delta^{2,2'}$-bi-4*H*-cyclopenta-1,3-diselenole. Current Chemical Abstracts name: 2-(5,6-Dihydro-4*H*-cyclopenta-1,3-diselenol-2-ylidene)-5,6-dihydro-4*H*-cyclopenta-1,3-diselenole.

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