Experimental Section

Melting points were taken on an Electrothermal melting point apparatus and are uncorrected. ^1H NMR spectra of deuteriochloroform solutions with Me_4Si as internal standard (δ 0) were recorded on a Varian FT 80 spectrometer. High-pressure liquid chromatography (HPLC) was performed on a Waters Model ALC-202 chromatograph equipped with a Model 440 UV detector monitoring at 254 nm and using a 3.9 × 300 mm μ-Porasil column.

Materials. Sodium benzenethiolate was prepared and Me_2SO was purified as previously reported[1,19] The preparations and characterization of the substrates and of the authentic samples necessary to the present investigation are described elsewhere.[1] All other commercial solvents and reagents were purified according to literature methods to match reported physical constants.

Photostimulated Reactions of 1a,b with Sodium Benzenethiolate (Experiments 1–12 of Tables I and II). In a Pyrex test tube was dissolved the sulfone **1a** or **1b** (0.15 mmol) in Me_2SO (5 mL) and this was deaerated with argon gas by using 5 freeze–pump–thaw cycles. To this solution either was added 1 mL of a Me_2SO solution of benzenethiol at the appropriate concentration or an additional 1 mL of Me_2SO (experiments 1, 5, and 9), followed by 3 mL of an 0.25 or 0.05 M solution of sodium benzenethiolate in the same solvent. The reaction mixture was deaerated again with argon and stoppered with a rubber septum. The reactions were then irradiated for 10 min in a homemade "merry-go-round" apparatus by a 300-W Osram sunlamp placed 10 cm from the reaction vessel. The successive workup involved dilution with water (5–6 volumes) and 3-fold extraction with Et_2O, followed by washing of the combined extracts with brine. The ether extract was dried (Na_2SO_4) and the solvent was removed on a rotoevaporator under reduced pressure. The residue, dissolved in CH_2Cl_2, was flash chromatographed on a silica gel column by first eluting with hexane, to remove some diphenyl disulfide and the benzenethiol, and then with CH_2Cl_2. All successive fractions (eluted with CH_2Cl_2) were collected together and concentrated on a rotoevaporator, and the residue was analyzed by TLC, ^1H NMR, and HPLC [eluants, CH_2Cl_2/*n*-hexane (4:1, v/v) at 1.7 mL/min for a good separation between **3a** and **5a**, CH_2Cl_2 at 2.0 mL/min or CH_2Cl_2/diisopropyl ether (10:1, v/v) at 0.8 mL/min for a quicker detection of other components of the reaction mixture].

The overall yields of the various experiments, estimated by NMR spectroscopy with 1,4-bis(chloromethyl)benzene as an internal standard, were almost quantitative in every case.

The relative yields reported in Tables I and II (average values of at least 5 independent experiments) were likewise obtained by NMR from the ratios of the integrated areas relative to the methyl absorptions. In the case of experiments 10–12, where some absorptions overlapped, a better reproducibility of the results was achieved by carrying out the NMR analysis first on the mixture of **1b**, **4b**, and **5b** and then, after removing the starting substrate by further chromatography, on the mixture of products alone.

1-(Phenylsulfonyl)-2,3,4,5-tetramethylbenzene (5b). Five independent reactions were carried out as above described on 0.1 g of **1b**, 1 molar equiv of PhSNa and 10 molar equiv of PhSH. After 1 h of irradiation, the reactions were poured together into brine and worked up as above. Column chromatography on silica gel (CH_2Cl_2as eluant) gave compound **5b** in 35% yield: mp 129.5–130.5 °C (EtOH); NMR ($CDCl_3$) δ 7.95 (s, 1 H, H-6), 7.82 (m, 2 H, H-2′ and H-6′ of $PhSO_2$), 7.50 (m, 3 H, H-3′, H-4′, and H-5′ of $PhSO_2$), 2.36, 2.31, 2.24, and 2.16 (4 overlapping s, 12 H in all, 4 CH_3). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.0; H, 6.6. Found C, 70.1; H, 6.7.

The successive fractions eluted from the column gave dibenzothiophene **4b** as well as small amounts of unreacted **1b**.

Quantum Yield Determination. A Me_2SO solution (8.4 mL) of equimolar amounts (3.2 10^{-5} mol) of **1b** and PhSNa was prepared, as reported above, in a Pyrex test tube wrapped in aluminium foil.[20] The solution was deaerated with argon gas and immediately sealed with a rubber stopper. After removal of the aluminium foil in a dark room, the test tube was placed (beside an identical test tube containing the actinometer) in a "merry-go-round" rotating within a Rayonet RPR-100 photochemical reactor equipped with 8 fluorescent lamps emitting maximally about 350 nm. A duplicate was run simultaneously; the deviations between duplicate runs did not exceed 2%. In order to test whether correction for a dark reaction had to be done, 2 unirradiated samples were prepared and quenched at the end of the irradiation time.

The amount of light absorbed by the reaction mixtures was measured by the ferrioxalate method.[21] The measurements were performed in duplicate during the irradiation of the reaction mixtures and compared with an unirradiated sample. The values obtained for the flux that entered the test tubes were about 1.5 10^{-5} einstein/min. After 15 s of irradiation the reaction mixtures were poured into brine and carefully worked up as previously described. The residue obtained by evaporation of the ether extracts was dissolved in CH_2Cl_2 and quantitatively transferred into a 10-mL volumetric flask. The amount of reacted substrate was determined by HPLC (CH_2Cl_2/diisopropyl ether (10:1, v/v) as eluant at 0.8 mL/min) with phenol as internal standard. While the irradiated reactions gave an average conversion value of 47%, in the unirradiated samples a 98% recovery of **1b** was determined.

The number of moles of reacted substrate divided by the total amount of light (in einsteins) absorbed by the solution during irradiation gave an average value of the quantum yield of 4.

Registry No. **1a**, 81064-10-0; **1b**, 81064-11-1; **3a**, 81095-45-6; **4a**, 23018-39-5; **4b**, 81064-13-3; **5a**, 2548-26-7; **5b**, 90481-86-0; PhSNa, 930-69-8; PhSH, 108-98-5.

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[19] Novi, M.; Guanti, G.; Thea, S.; Sancassan, F.; Calabrò, D. *Tetrahedron* **1979**, *35*, 1783.

[20] At these concentrations of **1b** and PhSNa light absorption at 350 nm was almost complete.

[21] Parker, C. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 104. Hatchard, C. G.; Parker, C. A. *Ibid.* **1956**, *235*, 518. Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1960; pp 783–786.

Fluorination of Polycyclic Aromatic Hydrocarbons: Charge vs. Frontier Orbital Control in Substitution Reactions of Radical Cations

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The anodic fluorination of perylene and pyrene in acetonitrile occurred at potentials consistent with the intermediacy of dications, but that of triphenylene with its radical cation. Fluorination of anthracene compounds at a meso position occurred by the action of iodine/silver(I) fluoride in acetonitrile via radical cation intermediates. Phenanthrene, 9-nitroanthracene, perylene, and pyrene failed to react. These results support the view that the reaction of fluoride-providing anions with cationic species occurs primarily by a charge controlled mechanism.

The anodic fluorination of aromatic hydrocarbons in acetonitrile has been reviewed by Rozhkov,[1] whose group has studied primarily the fluorination of naphthalene, benzene, and their derivatives. We have applied the me-

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Table I. Anodic and Chemical Fluorination of PAH

substrate				products		
hydrocarbon	class[a]	E^{ox}, V[b,c]	anode pot[b]	electrolysis	% yield[e]	I_2/AgF (% yield)[k]
perylene	pericondensed	0.55	0.65	trace fluoro monomer	<1	
		0.75[f]	0.75	1-F, 3-F, di-F isomer	15[d]	
9-methylanthracene	cene	0.66	0.66[g]	10-F	37	10-F (56%), trace iodo, dimer (7%)
anthracene	cene	0.84	1.0[g]	9-F	36[d]	9-F (10%), iodo (2%), trace dimer
pyrene	pyrene	0.86	1.0	trace fluoro monomer	<1	no fluoro, trace iodo, trace dimer
		1.12	1.2	1-F, 1,2-, 1,6-, 1,8-di-F	25[d]	
9-phenylanthracene	cene	0.91	1.0[g]	9-F, 9,9,10-tri-F-di-H		10-F (30%), iodo (10%), trace dimer, tri-F
benz[*a*]anthracene	dibenzacene	0.92	1.0[j]	7-F, 12-F, 7,12-di-F	40	7-F (10%), trace iodo, dimer (5%), trace di-F, tri-F
9,10-diphenylanthracene	cene	0.98[i]	0.95[h]	9,10-di-F-9,10-di-H	80	
triphenylene	starphene	1.13	1.25	1-F, 1,4-di-F, 1,1,4,4-tetra-F	30[d]	no fluoro, trace iodo, trace dimer
phenanthracene	benzenoid dibenzacene	1.23				none
9-nitroanthracene	cene	1.25				none

[a] Reference 8. [b] vs. Ag/Ag^+. [c] Reference 10. [d] Remainder of mass balance was a trace of tri- and tetra-fluoro, about 10–20% starting material, dimer, and fluoro dimer and fluoro polymer. [e] Combined yields. [f] Dication formation. [g] Reference 2c. [h] Reference 12. [i] Reference 2a. [j] Reference 2b. [k] The remainder of the mass balance was starting material.

thod to the fluorination of anthracene compounds.[2] Although a general applicability of the method has been implied,[3] competing reactions reduce its effectiveness.[2c] The synthesis of fluorobenz[*a*]anthracenes,[2b] required for carcinogenic studies, indicates its usefulness in specific cases. A mechanism involving attack by fluoride-providing anions ($H_nF_{n+1}^-$) on radical cations formed at the anode—an ECEC pathway[4]—was assumed.[1,2] Failure to repeat the fluorination of naphthalene and other substrates[5] and the slow reaction of isolated perylene radical cations with fluoride ions[6] have led to doubt that radical cations can react with fluoride-providing anions[7a] or that only certain types can react.[7b]

In order to include examples of each of the five classes of polycyclic aromatic hydrocarbons (PAH) as defined by Clar,[8] the electrolyses of perylene, pyrene, and triphenylene in $R_4NH_nF_{n+1}$ solutions in aprotic solvents are described here.

Radical cations of PAH can also be formed by chemical methods, in particular, by the reaction of iodine and silver(I) salts.[6] In this study PAH were treated with acetonitrile solutions of iodine and silver(I) fluoride that also contained $(CH_3)_4NH_2F_3$.[9]

Results

Electrolytic Fluorination. At or near the oxidation half-wave potential, perylene and pyrene gave only a trace of monofluoro derivatives. Dimers, fluoro dimers, and polymers were the principal products. Near the potential of the second wave of the current–voltage curve, 15–25% of a mixture of fluoro derivatives was obtained. On the other hand, triphenylene gave 30% of a mixture of fluoro derivatives at or near the oxidation half-wave potential. These results along with those of previous investigations, are summarized in Table I.

Chemical Fluorination. Anthracene, 9-methylanthracene, 9-phenylanthracene, and benz[*a*]anthracene were fluorinated. The results are summarized in Table I. Both the major and minor products were the same as those formed by anodic fluorination.[2] Perylene, pyrene, 9-nitroanthracene, and phenanthrene failed to yield fluoro derivatives, presumably for different reasons.

Discussion

A rather extensive discussion of the reaction of fluoride-providing anions with radical cations has appeared despite the few experimentally verified examples that have been described.[11] The fluorination of 9,10-diphenylanthracene[2a] was first accomplished at a potential that did not exclude the possibility that the dication was the reactive intermediate,[6a] but successful fluorinations of several polycyclic aromatic hydrocarbons at their first oxidation half-wave potentials,[2,b,c] including 9,10-diphenylanthracene,[12] support the involvement of radical cations. The most recent effort to provide a general and consistent theory of aromatic hydrocarbon radical cation reactivity with fluoride ion[7b] predicts that fluorination is possible for benzene and naphthalene, but highly unlikely for 9,10-diphenylanthracene and perylene. This theory is based on thermodynamic considerations. From this point of view

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(6) (a) Ristagno, C. V.; Shine, H. J. *J. Org. Chem.* **1971**, *36*, 4050–4055. (b) Shine, H. J.; Bandlish, B. K.; Stephenson, M. T. *Tetrahedron Lett.* **1978**, 733–736. (c) Stephenson, M. T.; Shine, H. J. *J. Org. Chem.* **1981**, *46*, 3139–3141.

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reaction can be expected when the orbital energy of the radical cation approaches that of the fluoride ion. In light of the results of more recent anodic fluorinations, which include examples of each of the five classes of aromatic hydrocarbons, we believe that successful fluorinations are predominantly charge controlled rather than frontier orbital controlled. Any explanation must consider the diverse results shown in Table I. Certain classes of radical cations react with fluoride-providing anions, while others require higher potentials, suggesting that the latter react only through the intermediacy of dications.

The reaction of inorganic ionic nucleophiles with organic electrophiles has been considered by Klopman.[13] Three factors were included: (1) the coulombic interactions of the two species, (2) solvation energy changes,[14] (3) electron-transfer interactions. The terminology of hard and soft acids and bases was used. Hard–hard reactions are described as being fast because large coulombic interaction dictates the chemical outcome; the reaction is said to be charge controlled. The soft–soft reaction is described as being fast because of large interactions between the HOMO of the nucleophile and the LUMO of the electrophile. As these orbital energies come closer together, the reaction becomes frontier orbital controlled.

Previous theories of PAH radical cation reactivity centered on the orbital symmetry[7a] and orbital energy[7b] aspects and did not include the charge or coulombic interactions. For this reason, describing the interaction of a hard $H_nF_{n+1}^-$ ion with various PAH radical cations in terms of charge as well as orbital control has appeal.

Table II compares the charge distribution in pairs of PAH radical cations, matched by relative orbital energies. Correlation between HOMO orbital energies and anodic potentials[7b] allows us to contrast these PAH radical cations of nearly identical orbital energies but opposite reactivities.

The radical cations of all of these four compounds would be predicted unreactive toward fluoride ion on the basis of their orbital energies.[7b] However, unlike pyrene and perylene, with their more delocalized charge density, anthracene and 9-methylanthracene do react with fluoride-providing anions because of coulombic interactions. Otherwise, the major reaction pathway for all is the orbital-controlled dimerization reaction. This is entirely expected since the LUMO energy of the radical cation and the HOMO energy of the parent hydrocarbon are nearly identical. When perylene and pyrene are further oxidized to the highly charged dications the reaction with fluoride-providing ion is productive because of coulombic interactions. Benz[*a*]anthracene, with charge buildup on the carbon atoms at the 7- and 12-positions, and 9-phenylanthracene, with charge on the 10-position, afford modest and high yields of fluoromonomers as a result of coulombic interactions with the $H_nF_{n+1}^-$ ions. These materials would have been predicted unreactive by previous theories.[7] Prediction of the reactivity of a PAH radical cation with $H_nF_{n+1}^-$ ions[16] requires a knowledge of the electronic profile of the radical cation as well as the relative orbital energies.

Chemical Fluorination. Bergmann and Shahak[17] reported the preparation of iodobenzene and *p*-iodoanisole by the use of iodine and silver(I) fluoride in acetonitrile. The reaction of iodine with silver(I) fluoride in acetonitrile has been shown to produce iodine monofluoride.[18] It has also been prepared from the elements in $CFCl_3$ at −75 °C where its addition to olefins was regio- and stereospecific.[19]

Assuming that iodine monofluoride was the reactive species in the reaction of iodine and silver(I) fluoride with the aromatic compounds, two possible modes of action were possible. Electrophilic substitution of iodine by the polar I–F molecule would account for the formation of iodobenzene and *p*-iodoanisole.[17] The fluorination of the polycyclic aromatic hydrocarbons could be accomplished by oxidation of the substrates to radical cations followed by nucleophilic attack as in the electrolytic reaction.

Anthracene, 9-methylanthracene, 9-phenylanthracene, and benz[*a*]anthracene, whose $E_{1/2}$ values are about 1.0 V vs. Ag/Ag^+ (0.10 M) or lower, were able to form radical cations by electron transfer.

Fluorination of phenanthrene and 9-nitroanthracene did not occur[20] here because of their relatively high oxidation potentials. Their radical cations can be formed at an anode, whose potential may be increased to the appropriate value, but not by iodine and silver(I) fluoride (I–F) in acetonitrile.

An alternative pathway for anthracene compounds would be the addition of the elements of I–F across the central ring followed by the loss of HI. Although such a reaction is possible for substitution in anthracene and benz[*a*]anthracene, it is unlikely for those compounds substituted in the 9-position of anthracene. Since the products resulted from fluorination at the 10-position, electrophilic attack by the electropositive iodine at that position can be eliminated. Huckel MO calculations[15] for the 9-substituted anthracenes reveal that the 10-carbon has the highest electron density and iodination via electrophilic attack not fluorination at that position could be expected.

Experimental Section

Electrolysis. General Procedure. A resin flask type glass vessel (ca. 250 mL) served as a single compartment cell. The cap had ports for three electrodes, a condenser, and inlet for nitrogen or argon. The anodes were of graphite cloth (Union Carbide Grade WCA) or platinum[21] and the cathodes were platinum or stainless steel. The reference electrode was Ag/Ag^+ (0.1 M) in acetonitrile separated from the electrolysis solution by a "thirsty glass" plug. The acetonitrile solvent was added through a 4-cm plug of activity I basic alumina to the cell which was previously dried at 100 °C for 6 h. The supporting electrolyte was added in a dry box. The residual current was measured and found to be very low. The organic substrate was added under an atmosphere of nitrogen or argon, which was maintained throughout the electrolysis. The reaction was followed by approximate coulometry and thin-layer chromatography. The reaction was stopped when all starting material had been consumed or the current was too low to be useful. After removal of the solvent, the residue was partitioned between petroleum ether (30–60 °C) and water. The organic layer was washed with water and saline and dried over calcium sulfate prior to solvent removal.

The residue was chromatographed by medium-pressure chromatography[22] on silica with petroleum ether as eluent. Because

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[13] Klopman, G. *J. Am. Chem. Soc.* **1967**, *90*, 223–234.

[14] In the work described here comparison is made between systems in which the solvation energy changes are similar to each other.

[15] Coulson, C. A.; Streitweiser, A. "Dictionary of π Electron Calculations"; W. H. Freeman: San Francisco, 1965. See also ref 4.

[16] The reported cases of anodic fluorination via radical cations have involved solvated hydrogen fluoride ions, $H_2F_3^-$ and $H_3F_4^-$, not fluoride ions.

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[19] Rozen, Z.; Brand, M. *Tetrahedron Lett.* **1980**, *21*, 4543–4546.

[20] Phenanthrene has been fluorinated by electrolysis in CH_3CN solution of $(CH_3)_4NH_2F_3$ but the products proved difficult to separate and purify.

[21] Since all three substances coated a platinum anode, graphite cloth was used for pyrene and triphenylene. A more convenient method was used for perylene. A device was constructed that reversed the current every 15 s.

[22] The medium-pressure apparatus was assembled from two 3.0 × 100 cm Altex glass columns preceded by a glass scrubber column (1.5 × 25 cm). Pressure was applied by a Fluid Metering, Inc. pump.

of the low solubility of perylene and triphenylene in acetonitrile solutions of $(CH_3)_4NH_2F_3$, $(C_4H_9)_4NH_3F_4$ was used as the supporting electrolyte.

Tetrabutylammonium Trihydrogen Tetrafluoride (TBAF). Tetrabutylammonium bromide (TBAB) (100 g) was dried in a vacuum oven for 12 h at 100 °C (0.5 mm). The contents of a lecture bottle of hydrogen fluoride was condensed at −78 °C and added to the TBAB. When the evolution of HBr ceased, the excess HF was allowed to evaporate overnight and approximately 100 g of a clear liquid remained.

Titration with 0.1 N NaOH revealed the presence of three moles of HF per mole of fluoride salt. Anal. Calcd for $C_{16}H_{39}H_3F_4$: F, 23.60. Found: F, 23.03.[23]

1-Fluoropyrene. Only one monofluoro isomer was detected. This result differs from fluorination with xenon difluoride, which gave three monofluoro isomers and no higher fluoro derivatives.[22] The physical properties of this material: mp 135.5–136.5 °C (lit.[25] mp 136–137 °C); UV (cyclohexane) 232 nm (log ϵ 4.33), 242 (4.78), 264 (4.30), 272 (4.53), 322 (4.20), 338 (4.30); IR (KBr, cm^{-1}) 1602, 1496, 1460, 1435, 1250, 832; NMR ($CDCl_3$, Me_4Si) 8.3–7.5 (m), 8.1 (s), 7.89 (s); ^{19}F NMR ($CDCl_3$, $CFCl_3$) (44, 46) −127.02 (dd, J_{HF} = 5 Hz, J_{HF} = 9 Hz).

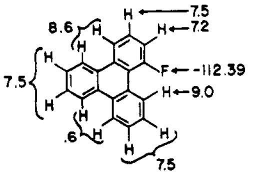
Fluoroperylenes. Because of the low solubility of perylene in acetonitrile solutions of $(C_4H_9)_4NH_3F_4$, TBAF in *n*-butyronitrile was used as the reaction medium. Electrolysis of a solution of perylene (0.5 g) and TBAF (10 g) at 0.55 V vs. Ag/Ag^+ (0.1 M), the $E_{1/2}^{ox}$, gave chiefly intractable residues, a small quantity of fluorodimers, and about 30% recovery of perylene and polymer. The trace of fluoroperylene was detected by a mass ion at 270 in the mass spectrum of recovered perylene. At an anodic potential of 0.80 V vs. Ag/Ag^+ (0.1 M), the 1- and 3-fluoroperylenes were obtained in approximately equal amounts. The 1-fluoro isomer had an ^{19}F NMR peak at −112.3, the 3-fluoro isomer at −126.52.[26]

The 1-fluoro isomer assignment was based on the ^{19}F chemical shift of 1-fluorotriphenylene, since each is a bay region substituent. The 3-fluoro isomer chemical shift was compared with that of 1-fluoropyrene (−127.02).[24]

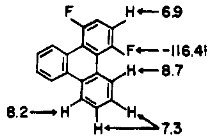
Difluoroperylenes. A mixture of difluoroperylenes, deemed clean by mass spectral examination, was not resolved. ^{19}F NMR peaks at −113.1, −125.62, −126.80, and −135.55 were recorded.

Fluorination of Triphenylene. An acetonitrile solution of triphenylene (1.5 g, 6.5 × 10^{-3} mol) and TBAF (10 g) was electrolyzed at 1.35 V vs. Ag/Ag^+ (0.1 M) for 12 h; 0.69 g of a mixture of fluoromonomers was isolated.

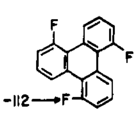
1-Fluorotriphenylene. As with the pyrene experiments the yields of this product depended on the reaction time. Shorter reaction times produced larger amounts of this isomer relative to higher order fluoro derivatives. The physical properties of this material: mp 167–168 °C (lit.[27] 174–175 °C); IR (KBr, cm^{-1}) 1438, 1422, 1428, 742, 720; UV (cyclohexane) 252 nm (log ϵ 4.9), 260 (5.1), 276 (4.27), 287 (4.2); NMR ($CDCl_3$, Me_4Si) 9.0 (1 H, m), 8.6 (4 H, m), 7.5 (5 H, m), 7.2 (1 H, m); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −112.39. Anal. Calcd for $C_{18}H_{11}F$: C, 87.78; H, 4.51; F, 7.71. Found: C, 87.81, H, 4.49, F, 7.81.

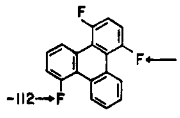


1,4-Difluorotriphenylene. While the crude reaction mixture of an exhaustive electrolysis preparative reaction contained only small amounts of this compound and large percentages of the 1,1,4,4-tetrafluoro isomer, each application of the mixture to column chromatography yielded the same results, namely a large amount of the 1,4-difluoro compound and very little or none of the tetrafluoro material. This material was assigned as the 1,4-isomer over the 2,3-isomer since the proton integration for the 1-, 4-, 5-, 8-, 9-, and 12-protons decreased relative to the 2-, 3-, 6-, 7-, 10-, and 11-proton integration, combined with the fact that the material which was assigned as the 1,1,4,4-tetrafluoro isomer yielded this difluoro isomer on degradation. The physical characteristics of this material: mp 128–129 °C; IR (KBr, cm^{-1}) 1432, 1218, 822, 758, 722; UV (cyclohexane) 254 nm (log ϵ 4.99), 262 (5.02), 278 (4.27), 289 (4.29); NMR ($CDCl_3$, Me_4Si) 8.7 (2 H, m), 8.2 (2 H, m), 7.3 (4 H, m), 6.9 (2 H, dd, J_{HF} = 8.10 Hz); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −116.41 (decoupled, s, coupled, t, J = 8.5 Hz). Anal. Calcd for $C_{18}H_{10}F_2$: C, 81.80; H, 3.82; F, 14.38. Found: C, 81.78; H, 3.92; F, 14.59.

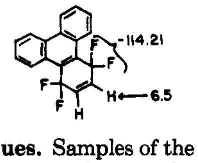


Trifluorotriphenylene. The small samples of this material generated were characterized by mass spectroscopy (*m*/*e* 282) and a dilute ^{19}F NMR. ^{19}F NMR ($CDCl_3$, $CFCl_3$) −112.45, −112.48, −116.10. These lines were consistent with a mixture of the 1,5,9- and 1,4,8-isomers. The 1,4,5-, 1,5,12-, and 1,8,12-isomers are ruled out since the three lines are nearly identical with the lines in 1-fluoro and 1,4-difluoro isomers based on the assumption that these other isomers would have different unique chemical shifts based on their unique chemical environment. Namely, they lack any 14-bay region through space interactions.[28] This interaction disturbs the axial symmetry of the C–F bond, reducing diamagnetic currents in the bond, and causing a paramagnetic shift to lower field.





1,1,4,4-Tetrafluorotriphenylene. This material was always the major product in electrolysis experiments allowed to go to completion. As mentioned earlier this material tended to decompose to form the 1,4-difluoro isomer when it was applied to chromatography. Samples pure enough to afford clean ^{19}F NMR and NMR spectra were derived by purification of the crude mixture on a short (30 × 100 mm) silica column. As before this resulted in a loss of 1,1,4,4-tetrafluoro material but small relatively pure samples were obtained. These limited samples were characterized by NMR, ^{19}F NMR, IR, and UV and combustion analysis: IR (KBr, cm^{-1}) 1460, 1382, 1344, 1287, 1120, 1118, 760, 724; UV (isooctane) 224 nm (log ϵ 4.35), 248 (4.57), 256 (4.71), 282 (3.80), 292 (3.79), 304 (3.8); NMR ($CDCl_3$, Me_4Si) 8.6 (4 H, m), 716 (4 H, m), 6.5 (2 H, m); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −114.21 (decoupled, s). Anal. Calcd for $C_{18}H_{10}F_4$: C, 71.99; H, 2.70; F, 25.31. Found: C, 74.09; H, 3.6; F, 22.38. This analysis reveals the high degree of fluorination although it is evidently contaminated with some of the 1,4-difluoro isomer.



Fluorination Residues. Samples of the lower R_f residues were submitted for combustion analysis to determine if the solvent (acetonitrile) had reacted to yield acetamide compounds or if the residue was not just fluoropolymer in nature. Anal. Found: C, 53.82; H, 4.89; N, 0.93; F, 21.18. These results support the latter assumption. IR (KBr, cm^{-1}) indicated no carbonyl absorptions.

Iodine/Silver(I) Fluoride Reactions.[29] 9-Methylanthracene (0.5 g, 2 × 10^{-3} mol), silver(I) fluoride (2.5 g, 2 × 10^{-2} mol) and

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(23) The analysis does not meet the usual standards for compound characterization, but it is sufficient to illustrate the nature of the supporting electrolyte.

(24) Bergman, E. D.; Selig, H.; Lin, C.-H.; Rabinovits, M.; Agranat, I. *J. Org. Chem.* **1975**, *40*, 3793–3794.

(25) Bavin, P. M. G.; Dewar, M. J. S. *J. Chem. Soc.* **1955**, 4486–4487.

(26) Stephenson, M. T., and Shine, H. J. (ref 6c), reported ^{19}F NMR chemical shifts at 90 °C in naphthalene of 106 for the 1-fluoro and 119.2 for the 3-fluoro isomers.

(27) Bavin, P. M. G.; Dewar, M. J. S. *J. Chem. Soc.* **1956**, 169.

(28) Dewar, M. J. S.; Kelemen, J. *J. Chem. Phys.* **1968**, *49*, 499.

Table II. Simple HMO Positive Charge Distribution in Radical Cations

unreactive			reactive		
compd	atom	C^2	compd	atom	C^2
pyrene	1	0.1358	anthracene	1	0.0967
	2	0.000		2	0.0484
	4	0.0873		9	0.1936
perylene	1	0.0835	9-methylanthracene	1	0.0776
	2	0.0130		2	0.0554
	3	0.1076		9	0.1694
				10	0.2215

TMAF (2.5 g, 1.9×10^{-2} mol) were combined in dry acetonitrile (100 mL) in a 200-mL Erlenmeyer flask wrapped in aluminum foil, under a blanket of nitrogen with a magnetic stirrer.

Solid iodine (1.25 g, 3.5×10^{-3} mol) was added in one portion to the stirred suspension. The reaction was followed by TLC and deemed complete after 2 h. The solution was diluted with ether (100 mL) and the solid silver iodide collected by filtration. The filtrate was added to water (100 mL) and ether (100 mL) and the layers were separated. The organic phase was washed with saturated sodium bicarbonate solution, 10% sodium thiosulfate solution, water, and brine prior to drying over sodium sulfate and evaporation in vacuo. The crude product was purified by medium-pressure column chromatography on silica gel (30–60 m particle size, 10 × 1000 mm column) to yield 0.28 g (56%) of a yellow product along with 0.175 g of starting material, 0.05 g of a mixture of dimers, and a trace of an iodo compound. 9-Fluoro-10-methylanthracene: mp 109.5–110.5 °C; IR (KBr, cm^{-1}) 1625 (w), 1390 (s), 1075 (m), 742 (s); UV (cyclohexane) 248 nm (log ε 5.0), 256 (5.49), 356 (3.84), 375 (4.5), 396 (4.01); NMR ($CDCl_3$, Me_4Si) 3.02 (d, 3 H, $J = 5$ Hz), 7.5 (m, 4 H), 8.3 (m, 4 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −137.79. Anal. Calcd for $C_{15}H_{11}F$: C, 85.7; H, 5.24; F, 9.05. Found: C, 85.6; H, 5.25; F, 9.17.

9-Fluoro-10-phenylanthracene.[30] When the same procedure as for 9-methylanthracene was used, a mixture was obtained that contained a large quantity of starting material, an iodo derivative, and a trace of a trifluoro compound. This crude mixture was combined with lithium aluminum hydride (0.2 g, 5.3×10^3 mol) in tetrahydrofuran and allowed to stand at ambient temperature overnight.[31] A 10% solution of hydrochloric acid (25 mL) was added cautiously to the reaction solution with stirring. The solution was partitioned between ether and water and the phases were separated. The organic phase was dried over calcium sulfate prior to evaporation in vacuo to yield about 0.5 g of a mixture of the product and the starting material. This mixture was separated by medium-pressure chromatography to yield 0.16 g (30%) of the product along with 0.35 g of the starting material. Product: NMR ($CDCl_3$, Me_4Si) 8.3 (m, 2 H), 7.7–7.2 (m, 1 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −135.20. Anal. Calcd for $C_{20}H_{13}F$: F, 6.98. Found: F, 6.71.

9-Fluoroanthracene. The same procedure as for 9-phenylanthracene yielded traces of difluoroanthracene (and, before reduction, traces of iodoanthracene) as determined by mass spectroscopy, 0.05 g (10%) of 9-fluoroanthracene, and 0.4 g of anthracene. 9-Fluoroanthracene: IR (KBr, cm^{-1}) 2940, 1635 (w), 1360 (s), 1075 (m), 725 (s); NMR ($CDCl_3$, Me_4Si) 8.6–7.4 (m, 9 H); ^{19}F NMR ($CDCl_3$, $CFCl_3$) −135.14.

7-Fluorobenz[*a*]anthracene. The same procedure as for 9-methylanthracene yielded 0.04 g (10%) of 7-fluorobenz[*a*]anthracene and 0.35 g (70%) of recovered benz[*a*]anthracene along with trace amounts of an iodo derivative, a difluoro derivative, and a trifluoro derivative as determined by mass spectroscopy of the crude reaction mixture. The 7-fluorobenz[*a*]anthracene was identical by ^{19}F NMR to authentic material. ^{19}F NMR ($CDCl_3$, $CFCl_3$) −134.98; NMR ($CDCl_3$, Me_4Si) 6.65 (s, 1 H), 8.55 (m, 1 H), 8.1 (m, 1 H), 7.85 (m, 2 H), 7.7–7.2 (m, 6 H).

Acknowledgment. We thank Dean E. Turner for his assistance.

Registry No. Perylene, 198-55-0; 9-methylanthracene, 779-02-2; anthracene, 120-12-7; pyrene, 129-00-0; 9-phenylanthracene, 602-55-1; benz[2]anthracene, 56-55-3; 9,10-diphenylanthracene, 1499-10-1; triphenylene, 217-59-4; phenanthrene, 85-01-8; 9-nitroanthracene, 602-60-8; pyrene radical cation, 34506-93-9; perylene radical cation, 12576-62-4; anthracene radical cation, 34512-28-2; 9-methylanthracene radical cation, 34467-27-1; 1-fluoropyrene, 1691-65-2; 1-fluorotriphenylene, 438-44-8; 1,4-difluorotriphenylene, 90670-31-8; 1,5,9-trifluorotriphenylene, 90670-32-9; 1,1,4,4-tetrafluorotriphenylene, 90670-33-0; 9-fluoro-10-methylanthracene, 27705-31-3; 9-fluoro-10-phenylanthracene, 2022-42-6; 9-fluoroanthracene, 529-85-1; 7-fluorobenz[*a*]anthracene, 23683-26-3; 1,4,8-trifluorotriphenylene, 90670-34-1.

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(29) All experiments were run under an atmosphere of dry nitrogen or argon. Acetonitrile was HPLC grade, protected from moisture, and dried by passing through an alumina plug. Chromatography solvents were distilled prior to use. Silica gel (0.032–0.063 m) was used as chromatography support unless stated otherwise. All melting points were taken on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. IR spectra were recorded on a Cary 15. Proton NMR were recorded on a Varian EM390 in $CDCl_3$ solutions with Me_4Si as internal standard. Fluorine NMR were recorded on a Varian FT80A in $CDCl_3$ solutions with $CFCl_3$ as external standard. Mass spectra were recorded on a Micromass Model 7070F from V.G. Micromass Ltd., Winsford, England. Combustion analysis were performed by Galbraith Laboratories, Inc.

(30) Purification of the fluoro derivatives of anthracene and 9-phenylanthracene was hampered by the presence of small amounts of the monoiodo isomers. These iodo derivatives had nearly the same R_f as the fluoro derivatives and were extremely difficult to remove by chromatography. Since pure samples of the fluoro derivatives for characterization were sought, selective reduction of the iodo isomer to the parent hydrocarbon was accomplished by reduction with 4 equiv of lithium aluminum hydride.

(31) Brown, H. C.; Krishnamurty, S. *J. Org. Chem.* **1969**, *34*, 3918.