observed for 4, relative intensities differed. Anal. Cald for $C_{20}H_{19}F$: C, 86.28; H, 6.90; F, 6.83. Found: C, 85.96; H, 6.89; F, 6.68.

11-Fluoro-1,2,3,4-tetrahydro-7,12-dimethylbenz[*a*]anthracene (7). PAH 7 was synthesized from diol 38 (270 mg; 1.0 mmol) according to the procedure used for the synthesis of 4 employing low valent titanium prepared by reduction of $TiCl_3$ with $LiAlH_4$. The usual workup and chromatographic purification (silica gel/petroleum ether) followed by crystallization (CH_2Cl_2/MeOH) afforded 7 (180 mg; 75%) as yellow flakes: mp 82.5–83.5 °C; ^1H NMR (270 MHz) δ 1.65–1.75 (m, 2 H, H-3 or H-2), 1.90–2.00 (m, 2 H, H-2 or H-3), 2.95 (t, J = 6 Hz, 2 H, H-4), 3.0 (s, 3 H, 7-CH_3), 3.08 (d, $J_{CH_3,F\text{-}9}$ = 9 Hz, 3 H, 12-CH_3), 3.25 (t, J = 5.8 Hz, 2 H, H-1), 7.05–7.13 (m, 1 H, H-10), 7.17 (d, $J_{H\text{-}5,H\text{-}6}$ = 9.09 Hz, 1 H, H-5), 7.28–7.37 (m, 1 H, H-9), 8.00 (d, $J_{H\text{-}6,H\text{-}5}$ = $J_{H\text{-}8,H\text{-}9}$ = 9.0 Hz, 2 H, H-6 and H-8); MS was similar to those observed for 4 or 5. Anal. Calcd for $C_{20}H_{19}F$: C, 86.28; H, 6.90; F, 6.83. Found: C, 86.51; H, 7.10; F, 6.72.

11-Fluoro-1,2,3,4,7,12-hexahydro-12-methyl-7-methylenebenz[*a*]anthracene (45). Fifteen milligrams of *p*-TsOH was added to a solution of 11F-TH-DMBA (7) (60 mg, 0.22 mmol) in 25 mL of dry benzene ($CaCl_2$/distilled). The mixture was heated under gentle reflux in an oil bath at 80 °C for 1 h. The mixture was cooled and chromatographed on basic alumina (Woelm) using benzene as eluant. The eluate was concentrated in vacuo and the oily residue was rechromatographed over silica gel (100–200 mesh) by using petroleum ether as eluant. The eluate, upon concentration in vacuo followed by crystallization from CH_2Cl_2/anhydrous MeOH, afforded 51 mg (85%) of light yellow crystals: mp 72–73 °C; ^1H NMR (500 MHz) δ 1.20 (d, $J_{CH,H}$ = 6.95 Hz, 3 H, 12-CH_3), 1.65–1.9 (m, 4 H, H-2 and H-3), 2.65–2.95 (m, 4 H, H-1 and H-4), 4.55 (q, $J_{H,CH}$ = 7.0 Hz, 1 H, H-12), 5.5–5.6 (m, 2 H, H-7), 6.95–7.04 (m, 2 H, H-5 and H-10), 7.18–7.25 (m, 1 H, H-9), 7.43–7.47 (m, 2 H, H-8 and H-6); MS, m/e 278.1482 ($C_{20}H_{19}F$, M^+, 19.13), 263 ($C_{19}H_{16}F$, $M^+ - CH_3$, 100). Anal. Calcd for $C_{20}H_{19}F$: C, 86.28; H, 6.90; F, 6.83. Found: C, 86.29; H, 6.89; F, 6.55.

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Dicyclopenta[*ef*,*kl*]heptalene (Azupyrene) Chemistry. Electrophilic Substitution on 1- and 4-Substituted Azupyrenes. Substituent Spectral Effects for Mono- and Disubstitution Derivatives

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The orientation of electrophilic substitution on monosubstituted azupyrenes has been investigated by the trifluoroacetylation of 1-methylazupyrene, the acetylation of 1-acetylazupyrene, 1-(trifluoroacetyl)azupyrene, and methyl azupyrene-1-carboxylate, the bis(diaminomethylation) of azupyrene, and the nitration of 4-nitroazupyrene. The results only partially correlate with predictions based on simple (e.g., resonance structure) considerations of the intermediate arenium ions. ^1H NMR and ultraviolet/visible spectral shifts are correlated for a number of 1-, 4-, 1,2-, 1,4-, 1,6-, 1,7-, and 2,5-substituted derivatives.

Electrophilic Disubstitution. Previous studies[2,3] showed that electrophilic monosubstitution of azupyrene occurs at the 1- and 4-positions with the former favored (from 3:2 to 13:1) in protonation, acetylation, trifluoroacetylation, halogenation, thiocyanation, and aminomethylation, but the latter dominant (35:1) for nitration. MNDO calculations of E_a values for trifluoroacetylation and nitration correlated with the results for these reactions.[2] It was then desired to determine the position(s) of substitution on 1- and 4-substituted compounds.

The monosubstitution studies together with earlier observations on the behavior of a large number of 1-substituted azulenes[4] with electrophiles pointed to the open positions on the five-ring compounds and the 4- or 9-positions on the seven-ring compounds for the introduction of the second substituent on a 1-substituted azupyrene. Consideration of resonance stabilization or destabilization of the intermediate arenium ion by the group on the 1-position showed positions 2, 6, and 9 favored with an

(1) From the Ph.D. Theses of E.D.D. (1985) and L.G.K. (1981), University of Washington.

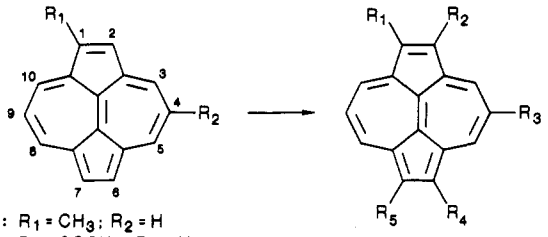
(2) Anderson, A. G., Jr.; Davidson, E. R.; Daugs, E. D.; Kao, L. G.; Lindquist, R. L.; Quenemoen, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 1896.

(3) Anderson, A. G., Jr.; Daugs, E. D. *J Org. Chem.* **1987**, *52*, 4391.

(4) Anderson, A. G., Jr.; Gale, D. J.; McDonald, R. N.; Anderson, R. G.; Rhodes, R. C. *J. Org. Chem.* **1964**, *29*, 1373. Anderson, A. G., Jr.; Anderson, R. G. *Ibid.* **1962**, *27*, 3578. Anderson, A. G., Jr.; Scotini, R., Jr.; Cowles, E. J.; Fritz, C. G. *Ibid.* **1957**, *22*, 1193 and references therein.

0022-3263/88/1953-0352$01.50/0

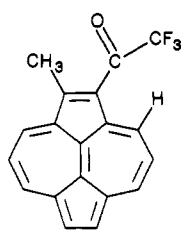
electron-donating group and positions 4 and 7 favored with an electron-withdrawing group. The nitro group at position 4 would direct (resonance effect) the electrophile to position 1(7) preferably over positions 2(6) or 9, but the factors which favored mononitration at position 4[2] could enhance the reactivity at position 9. Field effects would be most noticeable at positions near the substituents.



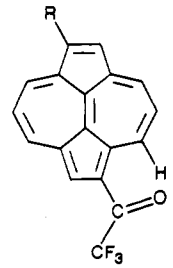
1: $R_1 = CH_3$; $R_2 = H$
5: $R_1 = COCH_3$; $R_2 = H$
9: $R_1 = H$; $R_2 = COCH_3$
11: $R_1 = COCF_3$; $R_2 = H$
14: $R_1 = CO_2CH_3$; $R_2 = H$
17: $R_1 = CH_2OCH_2CH_3$; $R_2 = H$
20: $R_1 = H$; $R_2 = NO_2$

2: $R_1 = CH_3$; $R_2 = COCF_3$; $R_3, R_4, R_5 = H$
3: $R_1 = CH_3$; $R_4 = COCF_3$; $R_2, R_3, R_5 = H$
4: $R_1 = CH_3$; $R_5 = COCF_3$; $R_2, R_3, R_4 = H$
6: $R_1, R_4 = COCH_3$; $R_2, R_3, R_5 = H$
7: $R_1, R_5 = COCH_3$; $R_2, R_3, R_4 = H$
8: $R_1, R_3 = COCH_3$; $R_2, R_4, R_5 = H$
10: $R_2, R_3 = COCH_3$; $R_1, R_4, R_5 = H$
12: $R_1 = COCF_3$; $R_4 = COCH_3$; $R_2, R_3, R_5 = H$
13: $R_1 = COCF_3$; $R_5 = COCH_3$; $R_2, R_3, R_4 = H$
15: $R_1 = CO_2CH_3$; $R_4 = COCH_3$; $R_2, R_3, R_5 = H$
16: $R_1 = CO_2CH_3$; $R_5 = COCH_3$; $R_2, R_3, R_4 = H$
18: $R_1, R_4 = CH_2OCH_2CH_3$; $R_2, R_3, R_5 = H$
19: $R_1, R_5 = CH_2OCH_2CH_3$; $R_2, R_3, R_4 = H$
21: $R_1, R_3 = NO_2$; $R_2, R_4, R_5 = H$
22: $R_2, R_3 = NO_2$; $R_1, R_4, R_5 = H$

Treatment of 1-methylazupyrene (1) with trifluoroacetic anhydride[5] gave predominantly (ca. 93%) substitution at the 2- and 6-positions (2, 3) in a 1:5 ratio with a small amount of 1,7-product (4) as determined from the ^1H NMR spectra. No product from reaction at position 9 was detected. The signal for H-3 in the spectrum of 2 was at δ 8.71, whereas the signals for the corresponding H-10 in 1-(trifluoroacetyl)azupyrene (11) and H-5 in 3 were at δ 9.91 and 9.83, respectively. This points to the preferred conformations of the trifluoroacetyl groups for 2, 3, and 11 as shown with the carbonyl in 2 directed away from H-3 because of the steric interaction between the 1-CH_3 and the CF_3 groups and with the opposite carbonyl orientation in 3 and 11.



2



3: R = CH_3
11: R = H

(5) Methylation or other alkylation, which would have given more symmetrical products, was not attempted as earlier experience with azulene had given polysubstitution.

(6) A crystal of azupyrene showed disorder such that meaningful X-ray data were not obtained. The monosubstituted compounds prepared thus far have not yielded suitable crystals.

Table I. Electrophilic Disubstitution Positions and Ratios

subst	substn positns	ratio
1-CH_3	2, 6, 7	1:5:small
1-$COCH_3$	4, 6, 7	small:3:7[a]
1-$COCH_3$	4, 6, 7	0.3:2:3[b]
1-$COCF_3$	6, 7	2:3
1-CO_2CH_3	6, 7	2:3
1-$CH_2NH(CH_3)_2^+$[d]	6, 7	9:11
4-$COCH_3$	1, 2	c
4-NO_2	1, 2	5:11

[a] With $CH_3COCl + AlCl_3$. [b] With $(CH_3CO)_2O + BF_3$–etherate. [c] Ratio not determined. [d] Presumed to be the monosubstitution product.

Acetylation of 1-acetylazupyrene (5) with acetyl chloride and aluminum chloride gave a 78% yield of 1,6- (6) and 1,7-diacetylazupyrene (7) in a 3:7 ratio. The ^1H NMR spectrum of the initial product showed a small absorption for the 1,4-isomer (8) but this was not isolated. When a sample of 5 containing some 4-acetylazupyrene (9) was acetylated, NMR evidence for the formation of 2,4-diacetylazupyrene (10) in addition to the expected 8 was obtained. Boron trifluoride–etherate catalysis of the acetylation of 5 with acetic acid anhydride gave (NMR analysis) a 37:57:6 ratio of a mixture of 6, 7, and 8, respectively.

Similarly, acetylation of 1-(trifluoroacetyl)azupyrene (11) gave a 93% yield of a mixture of the 1,6- (12) and 1,7-substitution (13) products in a ratio of ca. 2:3. The same ratio of the corresponding products (15 and 16) was obtained from the acetylation of methyl azupyrene-1-carboxylate (14), which was prepared from 5 in 45% yield by hypoiodite oxidation followed by esterification. The complexity of the spectra of these unsymmetrical compounds did not permit the detection of the small quantity of 1,4-isomer which might have been present.

Bis(dimethylaminomethylation) was accomplished directly from azupyrene as described for monodimethylaminomethylation[7] except that a higher temperature and longer reaction time were employed. The amine products were not isolated but converted directly to a mixture of quaternary iodides by treatment with methyl iodide, and the salt mixture in turn converted to the corresponding ethoxymethyl derivatives.[3] From this product were obtained the previously prepared 1-(ethoxymethyl)azupyrene (17, 42%), arising from the mono(dimethylamino)methyl compound, and a mixture of the 1,6- (18) and 1,7-bis(ethoxymethyl)azupyrenes (19) (32%) in a ratio of 9:11 by NMR analysis. The aminomethylation reaction mixture was acidic, so the reacting substrate for disubstitution was probably the protonated form of the mono(dimethylamino)methyl intermediate. This plus the relative bulkiness of the group would account for the absence of disubstitution at the 2-position, as found with 5, and the dominance of the 1,7-product.

The only 4-substituted compound readily available is the nitro derivative (20).[2] It was felt that the introduction of a second nitro group might provide the symmetrical 4,9-dinitro compound for possible use in the determination of ring bond lengths by X-ray structural analysis.[6] Nitration of 20 with nitronium tetrafluoroborate, however, gave only the 1,4- (21) and 2,4-dinitro (22) products (73%) in a 5:1 ratio. Thus the presence of the 4-NO_2 group completely dominates the factors proposed to account for the exclusive mononitration at the 4-position[2] to the extent that none of the 4,9-dinitro compound was detected.

(7) Anderson, A. G., Jr.; Daugs, E. D.; Kao, L. G.; Wang, J.-F. *J. Org. Chem.* 1986, *51*, 2961.

Table II. ^{1}H Chemical Shifts for 1-Substituted Azupyrenes[a]

	H								
subst	2	3	4	5	6	7	8	9	10
$COCH_3$	+0.31	−0.15	−0.23	−0.17	−0.14	−0.17	−0.08	+0.05	+1.28
$COCF_3$	+0.50	−0.09	−0.17	−0.14	−0.13	−0.16	−0.01	+0.18	+1.26
CO_2CH_3	+0.51	−0.05	−0.14	−0.08	−0.08	−0.10	0.00	+0.11	+1.20
Cl	−0.10	−0.05	−0.06	−0.14	−0.05	−0.01	−0.01	−0.01	+0.04
Br	+0.02	−0.04	−0.07	−0.13	−0.05	+0.01	−0.01	+0.01	+0.04
SCN	+0.11	−0.06	−0.13	−0.06	−0.10	−0.10	−0.11	+0.01	−0.19
NO_2	+0.40		−0.20			−0.18		+0.05	+0.93
CH_3	−0.16	−0.10	−0.06	−0.03	−0.01	+0.02	+0.02	−0.04	−0.13
CH_2OEt	+0.01	−0.06	−0.07	−0.02	−0.02	0.00	−0.01	−0.02	+0.05
$CH_2N(CH_3)_2$	−0.03	−0.04	−0.05	−0.01	−0.01	+0.01	+0.03	0.00	+0.18

[a] Shifts in δ relative to azupyrene: 7.40 (H-4,9), 8.40 (H-1,2,6,7), 8.68 (H-3,5,8,10). $CDCl_3$ solvent.

The structures of the disubstitution products were assigned by analysis of the ^{1}H NMR spectra. The chemical shifts previously found for the various monosubstitution compounds were used along with structural symmetry considerations (e.g., the 1,6-diacetyl product, containing a center of symmetry, would show a single triplet, whereas the 1,7-diacetyl product, containing a plane of symmetry through C-4 and C-9, wouuld have two triplets for H-4 and H-9).

The results are summarized in Table I. The departures from those predicted (i.e., no reaction at position 9 on the 1-methyl compound and appreciable reaction at position 6 on the 1-acetyl compounds and at the 2-position on the 4-acetyl and 4-nitro derivatives) may be taken to indicate that the qualitative considerations used were not sufficient for the relatively complex π-electron structure involved.

The studies on electrophilic mono- and disubstitution of azupyrene have provided the ^{1}H NMR and ultraviolet/visible spectra of a number of 1- and 4-monosubstitutions[2,3,7] and 1,2-, 1,4-, 1,6-, 1,7-, and 2,4-disubstitution derivatives. The effects of these substituents on certain corresponding absorptions for azupyrene are correlated here.

^{1}H NMR Spectra. Substituent chemical shift differences of ring hydrogens have been studied for substituted benzenes.[8] These shifts are attributed to both inductive and resonance effects.[9] These considerations together with H–H decoupling, to connect triplets with doublets for example, enabled the assignment of all separated signals for the mono- and disubstituted azupyrenes. In the spectra of some isomeric mixtures, all the peaks of the minor component were not resolved and no δ value could be assigned.

Table II gives the results for the 1-substituted compounds and Table III for the 4-substituted compounds. The largest shifts were found for H-10 with a carbonyl group at C-1, in agreement with the results of an NOE experiment which placed the methyl group of the 1-acetyl derivative toward H-2, and with planarity of the ring and carbonyl as indicated by the H-10–CF_3 coupling in the trifluoroacetyl compound.[3] The next largest shift was for H-3(5) in the 4-NO_2 and H-10 in the 1-NO_2 compounds. This is consistent with the planarity of the nitro group with the ring, in contrast to the nonplanar orientations of the 4-acetyl and 4-trifluoroacetyl groups.[3]

Halogen substituents effected smaller chemical shift differences, and a combination of inductive and resonance considerations was used for the specific assignments. The 1-CH_2G series also showed small differences, but in the expected order, for H-2. For all compounds except 1-SCN, the substituent caused detectable differences between all nonequivalent hydrogens at 500 MHz. In the 1-SCN spectrum, the signal for the nonequivalent H-3 and H-5 was one doublet, and the signal for H-6 and H-7 was a singlet.

Table III. ^{1}H NMR Chemical Shifts for 4-Substituted Azupyrenes[a]

	H				
subst	1(7)	2(6)	3(5)	8(10)	9
$COCH_3$	−0.08	+0.03	+0.62	−0.03	+0.08
$COCF_3$	+0.02	+0.15	+0.71	+0.09	+0.28
Cl	0.00	−0.10	+0.07	−0.01	−0.04
Br	−0.07	−0.01	+0.22		
SCN	−0.09	−0.02	+0.12	−0.01	+0.07
NO_2	+0.03	+0.13	+1.04	+0.08	+0.25

[a] Shifts in δ relative to azupyrene: 7.40 (H-4,9), 8.40 (H-1,2,6,7), 8.68 (H-3,5,8,10). $CDCl_3$ solvent.

Disubstitution has thus far afforded one example for the 1- and 2-positions, five examples for the 1- and 6-positions, four examples for the 1- and 7-positions, and two examples each for the 1- and 4-positions and 2- and 4-positions (Table IV). Inspection of the ^{1}H chemical shifts shows a good correlation with the effect of substituent group (acetyl, carboxylate, trifluoroacetyl, nitro) on the adjacent or nearly adjacent hydrogens consistent with the findings for the monosubstituted compounds. These correlations support the structural assignments given.

The spectra of three of the disubstitution compounds provided the first observations of non-nearest-neighbor hydrogen coupling in azupyrene derivatives. For the 1,4- and 2,4-dinitro derivatives values of 2.5 and 2.1 Hz, respectively, for J_{3-5} were found. This coupling was recorded as J = 1.7 Hz for the 2,4-diacetyl product, but was too small to be resolved in the spectrum of the corresponding 1,4-compound. An increase in coupling constants is a general finding with the presence of electron-withdrawing substituents.[10]

Ultraviolet–Visible Spectra. Solvent polarity has little effect on the position of λ_{max} in carbocyclic benzenoid aromatic compounds[11] but causes a shift in λ_{max} for nonalternant aromatic molecules because a difference in electron distributions in the ground and excited states leads to respective differences in stabilization depending on solvent polarity.[12] Comparison of hexane and chloroform with azulene, for example, showed a shift of 580 to 577 nm,[13] and analogous effects have been found for

(8) Hayamizu, K.; Yamamoto, O. *J. Mol. Spectrosc.* **1965**, *25*, 442; **1968**, *28*, 89; **1969**, *29*, 183.
(9) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159. Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Ibid.* **1973**, *10*, 1.
(10) Barfield, M.; Chakrabarti, R. *Chem. Rev.* **1969**, *69*, 757.
(11) Hohlneicher, G. In *DMS UV Atlas of Organic Compounds*; Butterworths: London, 1971; Vol. V, F1.
(12) Jaffe, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; Wiley: New York, 1962;, p 338.
(13) Cowles, E. J. *J. Am. Chem. Soc.* **1957**, *79*, 1093.

Table IV. ^{1}H Chemical Shifts for Disubstituted Azupyrenes[a]

subst	H 1	2	3	4	5	6	7	8	9	10
1-CH_3-2-$COCF_3$			+0.03	−0.03	−0.17	−0.13	−0.13	−0.11	−0.15	−0.11
1-CH_3-6-$COCF_3$		−0.42	−0.43	+0.07	+1.15		+0.33	−0.27	−0.27	−0.27
1,6-$(COCH_3)_2$		+0.36	−0.06	+0.01	+1.28		+0.36	−0.06	+0.01	+1.28
1-$COCH_3$-6-CO_2CH_3		+0.51	−0.08	−0.02	+1.23		+0.32	−0.10	+0.05	+1.21
1-$COCH_3$-6-$COCF_3$		+0.28	−0.13	−0.06	+1.16		+0.42	−0.09	+0.03	+1.20
1,7-$(COCH_3)_2$		+0.25	−0.16	+0.28	−0.16	+0.25		+1.26	+0.20	+1.26
1-$COCH_3$-7-CO_2CH_3		+0.51	−0.14	−0.26	−0.14	+0.29		+1.24	+0.28	+1.24
1-$COCH_3$-7-$COCF_3$		+0.25	−0.14	−0.25	−0.12	+0.40		+1.26	+0.25	+1.19
1,6-$(CH_2OC_2H_5)_2$		0.00	−0.04	−0.05	+0.02		0.00	−0.04	−0.05	+0.02
1,7-$(CH_2OC_2H_5)_2$		−0.02	−0.07	−0.09	−0.07	+0.02		+0.06	0.00	+0.06
1,4-$(COCH_3)_2$		+0.43	+0.54		+0.52	−0.07	−0.14	−0.04	+0.22	+1.30
1.4-$(NO_2)_2$		+0.92	+1.22		+1.09	+0.20	+0.11	+0.25	+0.57	+1.34
2,4-$(COCH_3)_2$	+0.33		+2.00		+0.70	−0.14	−0.02	−0.06	0.00	−0.02
2,4-$(NO_2)_2$	+0.83		+1.25		+1.18	+0.24	+0.16	+0.22	+0.33	+0.22

[a] Shifts in δ relative to azupyrene: 7.40 (H-4,9), 8.40 (H-1,2,6,7), 8.68 (H-3,5,8,10). $CDCl_3$ solvent.

Table V. Long-Wavelength Shifts for Monosubstituted Azupyrenes

subst	λ_{max}[a]	$\Delta\lambda_{max}$	log ϵ
none	482	0	3.99
1-CH_3	484	+2	3.60
1-$CH_2N(CH_3)_2$	484	+2	3.69
1-CH_2OEt	484	+2	4.03
1-Cl	486	+4	4.06
1-Br	486	+4	4.10
1-SCN	488	+6	4.02
1-$COCH_3$	498	+16	4.14
1-CO_2CH_3	506	+24	3.73
1-$COCF_3$	510	+28	3.32
4-NO_2	508	+26	3.84
4-$COCH_3$	480	−2	3.52
4-$COCF_3$	480[b]	−2[b]	2.95
4-Cl	492	+10	3.86
3-NO_2	522	+40	2.71

[a] In nm. Hexanes as solvent. [b] Uncertain due to presence of 1-$COCF_3$ isomer.

heteroanalogues of azulene.[14] Examination of the spectrum of azupyrene for the solvent series hexane, cyanomethane, dichloromethane, ethyl ether, and ethanol showed essentially no change in λ_{max} values.

Ring substitution in the benzenoid compounds always produces a bathochromic absorption shift which is larger for groups which can electronically conjugate with the ring π electrons.[15] With nonbenzenoid systems, both batho- and hypsochromic shifts are observed, depending on the position and nature of the substituent.[14e] Jaffe and Orchin have discussed the contributions of inductive and mesomeric effects for benzene and nonalternant compounds.[16] As would be expected, the picture is some less clear for the latter with, for example, either an increase or a decrease in transition energy possible from the inductive effect depending on ring position. Also, the nature of the substituent can cause unequal ground and excited state stabilizations.[14e]

Data for the longest wavelength maxima are given in Table V. There was little change in the general appearance of the UV–vis spectra of the 1-substituted compounds, but bathochromic shifts of 2–28 nm were observed for the 482-nm absorption in the order of substituent

Table VI. Long-Wavelength Shifts for Disubstituted Azupyrenes

subst	λ_{max}[a]	$\Delta\lambda_{max}$	log ϵ
none	482[b]	0	3.99
1-CH_3-2-$COCF_3$	504[c]	22	3.53
1-CH_3-6-$COCF_3$	511[c]	29	3.60
1,6-$(COCH_3)_2$	520[d]	38	3.75
1,7-$(COCH_3)_2$	506[d]	24	3.84
1,4-$(NO_2)_2$	498[e]	16	3.57
2,4-$(NO_2)_2$	508[e]	26	3.49

[a] In nm. [b] Hexanes solvent. [c] *n*-Hexane solvent. [d] Cyanomethane solvent. [e] Dichloromethane solvent.

electron withdrawal. This observation correlates with a change in polarization in the excited state and an enhanced negative charge in the five-membered ring(s). In contrast, the general appearance of the spectra for the 4-NO_2, 4-$COCH_3$, and 4-$COCF_3$ compounds, while similar within the group, differed markedly from that of the 1-substituted compounds. All showed a substantial decrease in the intensity of the long-wavelength absorption[17] and an intensity increase for the band at 350–400 nm. Wavelength shifts of +26 and −2 nm were found for 4-NO_2 and 4-$COCH_3$, respectively. The value of −2 nm for 4-$COCF_3$ is uncertain because of the presence of the 1-$COCF_3$ isomer. With the 4-Cl group, the long wavelength intensity was unchanged (no steric effect) and a bathochromic shift (10 nm) was found. The spectrum of the 3-NO_2 isomer[18] was very similar to that of the 4-NO_2, except for a larger bathchromic shift of 40 nm.

The available data for disubstituted derivatives is given in Table VI. The shift is essentially additive for the 1-CH_3-6-$COCF_3$ compound (+30 calcd), only approximately for 1,6- and 1,7-$(COCH_3)_2$ groups, (+32 calcd) and definitely not for the 1-CH_3-2-$COCF_3$ substituents. The 1- and 2-NO_2 derivatives are not known, so no calculated additive values are possible for the dinitro compounds.

Experimental Section

General. Chemicals were reagent grade and not further purified unless otherwise indicated. N_2, Ar, $CHCl_3$, CH_2Cl_2, and hexanes were purified and dried. Precoated TLC plates were obtained from MCB Manufacturing Chemists, Inc., Cincinnati, OH. Analytical plates (0.25 mm) were prepared with silica gel 60F-254. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Canadian

(14) (a) Anderson, A. G., Jr.; Ko, R. P. *J. Org. Chem.* **1984**, *49*, 4769. (b) Anderson, A. G., Jr.; Forkey, D. M.; Grina, L. D. *Ibid.* **1972**, *37*, 3499. (c) Anderson, A. G., Jr.; Forkey, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 924. (d) Anderson, A. G., Jr.; Harrison, W. F.; Anderson, R. G. *Ibid.* **1963**, *85*, 3448. (e) Anderson, A. G., Jr.; Steckler, B. M. *Ibid.* **1959**, *81*, 4941.

(15) Friedel, R. A.; Orchin, M. *Ultraviolet Spectra of Aromatic Compounds*; Wiley: New York, 1951; p 17ff.

(16) Reference 12, pp 247–344.

(17) Reference 12, pp 434–437.

(18) Kao, L. G. Ph.D. Thesis, University of Washington, 1981. Anderson, A. G., Jr.; Kao, L. G. *J. Org. Chem.* **1982**, *47*, 3584.

Microanalytical Service Ltd., Vancouver, Brisith Columbia. Spectral data were recorded on the following instruments: UV–vis, Hewlett-Packard 8450A spectrophotometer (1.0-cm quartz cells); NMR, Brucker CXP-200 or Brucker WM 500 cryospec spectrometer with Me_4Si as internal standard; mass spectra, Hewlett-Packard 5985 GC/MS system with 30-m (DB-5) fused silica capillary or, for exact mass, V.G. Micromass 7070 M GC/M5 and associated VG 2035 F/B Data System[8] with perfluorokerosene as the standard. Reaction flasks for anhydrous reactions were flame-dried and condensers, etc. were oven-dried. Because of the small quantities involved and the inability to achieve complete separations, a number of compounds were not obtained analytically pure.

Trifluoroacetylation of 1-Methylazupyrene (1). To a cold (ice bath) stirred solution of 0.47 mL (3.36 mmol) of triethylamine and 147 mg (0.676 mmol) of 1-methylazupyrene in 10 mL of CH_2Cl_2 under N_2 was added 0.51 mL (3.4 mmol) of trifluoroacetic acid anhydride. The solution gradually became brown-red in color. Stirring was continued at room temperature for 4 days. The mixture was filtered (short neutral Al_2O_3 column), and the concentrate from the filtrate was chromatographed (silica gel CC-7). Hexane removed unchanged **1** (ca. 2 mg) and products were eluted with 1:1 $HCCl_3$–hexane. Multiple-development TLC (silica gel G, hexane) of the eluate residue gave two fractions. The gold-brown band afforded 32.1 mg (15.2%) of 1-methyl-2-(trifluoroacetyl)azupyrene (**2**) as orange-bronze needles: mp 116–117 °C; UV–vis(hexane) λ_{max} (log ϵ) 240 (4.18), 246 (4.19), 251 (4.19), 258 (4.19), 267 (4.20), 287 (4.01), 317 (4.00), 380 (3.40), 416 (2.81), 445 (2.92), 490 (sh, 3.38), 504 nm (3.53); ^{1}H NMR ($CDCl_3$) δ 3.06 (s, 3, CH_3), 7.25 (t, 1, H-9), 7.37 (t, 1, H-4), 8.27 (dd, 2, H-6,7), 8.51 (d, 1, H-5), 8.57 (d, 2, H-8,10), 8.71 (d, 1, H-3); mass spectrum, m/e (relative intensity) 312.1 (M^+, 54.5), 313.1 ($M^+ + 1$, 11.1), 243.1 ($M^+ - 69$, 35.7); exact mass, m/e 312.0775 ($C_{19}H_{11}OF_3$ requires 312.0761).

From the orange-brown band was obtained 165.8 mg (78.6%) of 1-methyl-6-(trifluoroacetyl)azupyrene (**3**) as dark bronze needles: mp 104–105 °C; UV–vis (hexane) λ_{max} (log ϵ) 240 (4.18), 245 (4.17), 252 (4.16), 258 (4.19), 264 (4.21), 302 (4.05), 316 (3.94), 336 (3.83), 355 (sh, 3.36), 372 (sh, 3.33), 389 (3.65), 402 (3.40), 412 (3.32), 438 (2.97) 450 (sh, 2.86), 474 (2.96), 484 (2.96), 511 nm (3.60); ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 2, CH_3), 7.13 (t, 1, H-9), 7.47 (t, 1, H-4), 7.98 (s, 1, H-2), 8.25 (d, 1, H-3), 8.41 (d, 2, H-8,10), 8.77 (q, 1, H-7), 9.83 (d, 1, H-5) (small satellite peaks were interpreted to arise from the presence of a small amount of the isomeric 1-methyl-7-(trifluoroacetyl)azupyrene (**4**)); mass spectrum, m/e (relative intensity) 312.1 (M^+, 100), 313.1 ($M^+ + 1$, 20.5), 243.1 ($M^+ - 69$, 94.7), 215.1 ($M^+ - 97$, 47.4). Anal. Calcd for $C_{19}H_{11}OF_3$: C, 73.08; H, 3.55. Found: C, 73.25; H, 3.63.

Acetylation of 1-Acetylazupyrene (5). Method A. A 0.75-mL (0.30 mmol) portion of a solution of 0.07 mL (0.98 mmol) of acetyl chloride and 0.17 g (0.80 mmol) of $AlCl_3$ in 2 mL of CH_2Cl_2 was added to 37.5 mg (0.16 mmol) of **5** in 10 mL of CH_2Cl_2 under Ar. The solution became deep red in color. After 5 min, 5 mL of H_2O was added, and the separated organic layer was washed with 10% $NaHCO_3$ and dried (Na_2SO_4). The solvent was removed, and flash chromatography (1 in. × 1 in. silica gel) with CH_2Cl_2 separated 7.0 mg (19%) of unchanged **5**. Elution with 1:1 ether–CH_2Cl_2 gave 35.0 mg (79%, 97% net) of diacetylazupyrenes containing (high-field ^{1}H NMR analysis) 1,6- (**6**) and 1,7-diacetylazupyrene (**7**) in a ratio of 3:7 plus a trace of 1,4-diacetylazupyrene (**8**): mass spectrum, m/e (relative intensity) 287 ($M^+ + 1$, 21), 286 (M^+, 91), 272 ($M^+ - 14$, 19), 271 ($M^+ - 15$, 100), 228 ($M^+ - 58$, 20), 200 ($M^+ - 86$, 27); exact mass, m/e 286.1013 ($C_{20}H_{14}O_2$ requires 286.0944).

Flash chromatography (3 in. × 1 in. silica gel column, CH_2Cl_2) gave partial separation with **6** in a broad, pink front band and **7** in a narrower trailing band. The latter was found to contain appreciable amounts of **6** and was subjected to repeated rechromatography until TLC showed only traces of **6**. Final flash chromatography (6 in. × 1 in. silica gel) afforded **7** free of **6** but still containing a few percent of **8**. Sublimation (150 °C, 0.1 Torr) of a sample gave material richer in **8**. Compound **6** was obtained as red needles: mp 285–287 °C; UV–vis (CH_3CN) λ_{max} (log ϵ) 243 (4.24), 252 (4.27), 269 (4.28), 294 (4.17), 306 (4.00), 327 (3.88), 369 (3.48), 384 (3.71), 484 (3.00), 508 (3.52), 520 nm (3.75); ^{1}H NMR ($CDCl_3$) δ 2.9 (s, 6, CH_3), 7.41 (t, 2, H-4,9, J = 9.9 Hz), 8.62 (d, 2, H-3,8 J = 9.9 Hz), 8.76 (s, 2, H-2,7), 9.96 (d, 2, H-5,10, J = 9.9 Hz). Compound **7** was obtained as green needles: mp 258–259 °C; UV–vis (log ϵ) 234 (4.23), 253 (4.25), 269 (4.32), 300 (4.21), 312 (4.12), 323 (3.94), 333 (3,88), 3.64 (3.81), 492 (3.36), 506 nm (3.84); ^{1}H NMR ($CDCl_3$) δ 2.9 (s, 6, CH_3), 7.12 (t, 1, H-4, J = 9.7 Hz), 7.60 (t, 1, H-9, J = 9.9 Hz), 8.52 (d, 2, H-3,5, J = 9.7 Hz), 8.65 (s, 2, H-2,6), 9.94 (d, 2, H-8,10, J = 9.9 Hz). ^{1}H NMR for **8** ($CDCl_3$) δ 2.9 (s, 6, CH_3), 7.62 (t, 1, H-9, J = 9.7 Hz), 8.26 (d, 1, H-7, J = 4.6 Hz), 8.34 (d, 1, H-6, J = 4.6 Hz), 8.64 (d, 1, H-8, J = 9.7 Hz), 8.83 (s, 1, H-2), 9.34 (s, 1, H-5), 9.22 (s, 1, H-3), 9.98 (d, 1, H-10, J = 9.7 Hz).

Repetition of the procedure with a sample of **5** which contained **9** gave, in addition to **6**, **7** and **8** as described above. ^{1}H NMR peaks in the spectrum of the product from the sublimation of the material containing mostly **8** were indicative of the presence of **10**: ($CDCl_3$) δ 2.9 (s, 6, CH_3), 7.40 (t, 1, H-9, J = 9.9 Hz), 8.26 (d, 1, H-7, J = 4.7 Hz), 8.38 (d, 1, H-6, J = 4.7 Hz), 8.62 (d, 1, H-8, J = 9.9 Hz), 8.66 (d, 1, H-10, J = 9.9 Hz), 8.73 (s, 1, H-1), 9.38 (d, 1, H-5, J = 1.7 Hz), 10.68 (d, 1, H-3, J = 1.7 Hz).

Method B. A mixture of 8.0 mg (0.33 mmol) of **5**, 0.20 mL (2.1 mmol) of acetic anhydride, 1.0 mL (0.8 mmol) of BF_3–etherate, and 10 mL of CH_2Cl_2 under Ar was refluxed for 4 h. Then 10 mL of H_2O was added to the cooled solution, and the separated organic phase was washed with 10% $NaHCO_3$, dried (Na_2SO_4), and concentrated. Workup as described in method A for the separation of unchanged **5** gave a product which contained **6** and **7** in a ratio of 2:3 plus a few percent of **8** by high-field ^{1}H NMR analysis.

Acetylation of 1-(Trifluoroacetyl)azupyrene (11). A 0.5 mL (0.077 mmol) portion of reagent prepared from 0.11 mL (1.55 mmol) of acetyl chloride and 0.102 g (0.77 mmol) of $AlCl_3$ in 5 mL of CH_2Cl_2 was added to 8.0 mg (0.027 mmol) of **11** in 10 mL of CH_2Cl_2 under Ar with stirring. After 30 min, 5 mL of H_2O was added, and the separated organic phase was washed (10% $NaHCO_3$) and dried (Na_2SO_4) before solvent removal. The residue was chromatographed on a 5 in. × 0.75 in. silica gel column. CH_2Cl_2 eluted a trace of **11** as a red band and then a second red band which yielded 8.5 mg (0.025 mmol, 93%) of a mixture of 1-acetyl-6-(trifluoroacetyl)azupyrene (**12**) and 1-acetyl-7-(trifluoroacetyl)azupyrene (**13**) in a ratio of 2:3 (high-field NMR) as a red solid, mp 200–209 °C: ^{1}H NMR ($CDCl_3$) for **12** δ 2.96 (s, 3, CH_3), 7.34 (t, 1, H-4, J = 9.7 Hz), 7.43 (t, 1, H-9, J = 9.7 Hz), 8.55 (d, 1, H-3, J = 9.7 Hz), 8.59 (d, 1, H-8, J = 9.7 Hz), 8.68 (s, 1, H-2), 8.82 (q, 1, H-7), 9.84 (d, 1, H-5, J = 9.7 Hz), 9.88 (d, 1, H-10, J = 9.7 Hz); for **13** δ 2.96 (s, 2, CH_3), 7.15 (t, 1, H-4, J = 9.7 Hz), 7.65 (t, 1, H-9, J = 7.65 Hz), 8.54 (d, 1, H-3, J = 9.7 Hz), 8.56 (d, 1, H-5, J = 9.7 Hz), 8.65 (s, 1, H-2), 8.80 (q, 1, H-6), 9.87 (d, 1, H-10, J = 9.7 Hz), 9.94 (d, 1, H-8, J = 9.7 Hz); mass spectrum, m/e (relative intensity) 341 ($M^+ + 1$, 22), 340 (M^+, 100), 325 ($M^+ - 15$, 34), 271 ($M^+ - 69$, 82), 228 ($M^+ - 112$, 29), 200 ($M^+ - 140$, 35); exact mass m/e 340.0691 ($C_{20}H_{11}O_2F_3$ requires 340.0711).

Methyl Azupyrene-1-carboxylate (14). A mixture of 19 mg (0.078 mmol) of **5** dissolved in 10 mL of tetrahydrofuran, 5 mL of 10% NaOH, and 1 mL of a solution containing 10% I_2 and 20% KI was stirred at room temperature for 3 h. Excess I_2 was destroyed with aqueous $Na_2S_2O_3$ and the aqueous solution was washed with ethyl ether (3 × 15 mL), then chilled (ice bath), and acidified (concentrated $H_3O^+Cl^-$). The acidified solution was extracted with ethyl ether (4 × 10 mL). The concentrated (to 30 mL), combined extracts were treated with excess (ca. 3 mmol) CH_2N_2[9] in ethyl ether (10 mL). Excess CH_2N_2 was destroyed (acetic acid), and the green solution was washed with H_2O and 10% $NaHCO_3$. The residue, after drying (Na_2SO_4) and solvent removal, was taken up in CH_2Cl_2 and filtered through a 1 in. × 0.5 in. silica gel column. Sublimation (160 °C, 0.5 Torr) of the filtrate residue gave 9 mg (45%) of **14** as red-brown needles: mp 138–140 °C; UV–vis (hexanes) λ_{max} (log ϵ) 231 (431), 262 (4.39), 296 (4.12), 310 (4.05), 379 (4.61), 410 (3.04), 438 (3.04), 480 (3.11), 506 nm (3.73); ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 3, CH_3), 7.26 (t, 1, H-4, J = 9.5 Hz), 7.51 (t, 1, H-9, J = 9.7 Hz), 8.30 (d, 1, H-7, J = 4.5 Hz), 8.32 (d, 1, H-6, J = 4.5 Hz), 8.60 (d, 1, H-5, J = 9.5 Hz), 8.63 (d, 1, H-3, J = 9.5 Hz), 8.68 (d, 1, H-8, J = 9.7 Hz), 8.91 (s, 1, H-2), 9.88 (d, 1, H-10, J = 9.7 Hz); mass spectrum, m/e (relative intensity) 260 (M^+, 100), 229 ($M^+ - 31$, 36), 201 ($M^+ - 59$, 33), 200 ($M^+ - 60$, 27); exact mass, m/e 260.0835 ($C_{18}H_{12}O_2$ requires

260.0837). Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.75; H, 4.79.

Acetylation of Methyl Azupyrene-1-carboxylate (14). To a solution of 9.0 mg (0.035 mmol) of **14** in 10 mL of CH_2Cl_2 were added, under anhydrous conditions, 50 μL (0.53 mmol) of acetic acid anhydride and 50 μL (0.41 mmol) of BF_3–etherate, and the mixture was stirred overnight at room temperature. Water (10 mL) was added, and the solvent was removed from the separated, washed (10% $NaHCO_3$), and dried (Na_2SO_4) organic layer. Chromatography of the residue on a 3 in. × 1 in. silica gel column with CH_2Cl_2 (trace of green material) and then 3:1 CH_2Cl_2–ether gave 6.0 mg (57%) of a red solid, mp 205–212 °C. High-field NMR analysis indicated the presence of methyl 6-acetylazupyrene-1-carboxylate (**15**) and methyl 7-acetylazupyrene-1-carboxylate (**16**) in a ratio of 2:3: ^{1}H NMR ($CDCl_3$) for **15** δ 2.95 (s, 3, CH_3), 4.10 (s, 3, OCH_3), 7.38 (t, 1, H-4, J = 9.7 Hz), 7.45 (t, 1, H-9, J = 9.7 Hz), 8.58 (d, 1, H-8, J = 9.7 Hz), 8.60 (d, 1, H-3, J = 9.7 Hz), 8.72 (s, 1, H-7), 8.91 (s, 1, H-2), 9.89 (d, 1, H-10, J = 9.7 Hz), 9.91 (d, 1, H-5, J = 9.7 Hz); for **16** δ 2.95 (s, 3, CH_3), 4.10 (s, 3, OCH_3), 7.14 (t, 1, H-4, J = 9.7 Hz), 7.68 (t, 1, H-9, J = 9.7 Hz), 8.54 (d, 2, H-3,5, J = 9.7 Hz), 8.69 (s, 1, H-6), 8.91 (s, 1, H-2), 9.92 (d, 1, H-10, J = 9.7 Hz), 9.99 (d, 1, H-8, J = 9.7 Hz); exact mass, m/e 302.0901 ($C_{20}H_{14}O_3$ requires 302.0943).

Bis(dimethylaminomethylation). 1,6- and 1,7-Bis(ethoxymethyl)azupyrene (18 and 19). The reaction was carried out with 24.0 mg (0.199 mmol) of azupyrene as previously described for monoaminomethylation[7] except that the temperature was ca. 100 °C and the reaction time 3 h. The mixture of amine products was converted directly to the quaternary iodide salts (45.0 mg) by treatment with 15 μL (0.241 mmol) of CH_3I in 10 mL of CH_2Cl_2. A 22.5 mg portion of the salts was treated with 1.0 mL of 0.70 M sodium ethoxide as previously described[3] to give a mixture of 1-(ethoxymethyl)azupyrene (**17**) and bis(ethoxymethyl)azupyrenes as indicated by TLC (CH_2Cl_2, R_f 0.80 and 0.48, respectively). Chromatography on a 12 in. × 0.5 in. silica gel column (10% hexanes in CH_2Cl_2) gave 6.5 mg (42%) of **17** (^{1}H NMR identical to that of an authentic sample)[3] and 6.0 mg (32%) of a product which crystallized from CH_2Cl_2 as brown needles, mp 35–38 °C. High field NMR indicated the composition to be **18** and **19** in a ratio of 9:11: ^{1}H NMR ($CDCl_3$) for **18** δ 1.33 (t, 6, CH_3, J = 7.1 Hz), 3.71 (q, 4, CH_2, J = 7.1 Hz), 5.39 (s, 4, CH_2), 7.35 (t, 2, H-4,9, J = 9.5 Hz), 8.40 (s, 2, H-2,7), 8.64 (d, 2, H-3,8, J = 9.5 Hz), 8.70 (d, 2, H-5,10, J = 9.5 Hz); for **19** δ 1.33 (t, 6, CH_3, J = 7.1 Hz), 3.71 (q, 4, CH_2, J = 7.1 Hz), 5.39 (s, 4, CH_2), 7.31 (t, 1, H-4, J = 9.5 Hz), 7.40 (t, 1, H-9, J = 9.5 Hz), 8.38 (s, 2, H-2,6), 8.61 (d, 2, H-3,5, J = 9.5 Hz), 8.74 (d, 2, H-8,10, J = 9.5 Hz); mass spectrum, m/e (relative intensity) 319 (M^+ + 1, 23), 318 (M^+, 100), 273 (M^+ – 45, 79), 229 (M^+ – 90, 40), 228 (M^+ – 91, 32), 215 (M^+ – 104, 35), 202 (M^+ – 117, 15); exact mass, m/e 318.1626 ($C_{22}H_{22}O_2$ requires 318.1620).

Nitration of 4-Nitroazupyrene (20). To 0.225 g (1.7 mmol) of a solution of vacuum-dried nitronium tetrafluoroborate in 3 mL of CH_3CN was added 0.15 mL (1.85 mmol) of pyridine with stirring. A 0.15 mL (0.085 mmol) portion of this reagent was added to a solution of 11.0 mg (0.045 mmol) of **20** in 40 mL of CH_2Cl_2 under Ar. The progress of the reaction was monitored by TLC (benzene; R_f(**20**) 0.71; R_f(**21**) 0.58; R_f(**22**) 0.49). After 30 min, 5 mL of H_2O was added, and the solvent was removed from the separated, washed (20-mL portions of H_2O, 1 N $H_3O^+Cl^-$, 10% $NaHCO_3$), filtered (glass wool), and dried (Na_2SO_4) organic layer. Flash chromatography of a CH_2Cl_2 solution of the residue on a 14 in. × 1 in. silica gel column (benzene) gave a trace of **20** and then 9.5 mg (73%) of 1,4-dinitroazupyrene (**21**) as a yellow solid, mp 287–289 °C, followed by 1.8 mg (14%) of 2,4-dinitroazupyrene (**22**) as a pink solid, mp 195–197°C: UV–vis (CH_2Cl_2) λ_{max} (log ε) for **21** 232 (4.13), 259 (4.35), 273 (sh, 4.28), 298 (4.08), 340 (sh, 3.91), 367 (4.13), 382 (sh, 4.06), 404 (4.00), 498 nm (3.57); for **22** 236 (4.31), 261 (4.20), 297 (sh, 3.92), 308 (3.93), 355 (sh, 394), 367 (4.03), 410 (3.64), 430 (3.64), 476 (3.30), 508 nm (3.49); ^{1}H NMR ($CDCl_3$) for **20**, δ 7.97 (t, 1, H-9, J = 9.5 Hz), 8.51 (d, 1, H-7, J = 4.4 Hz), 8.60 (d, 1, H-6, J = 4.4 Hz), 8.93 (d, 1, H-8, J = 9.5 Hz), 9.32 (s, 1, H-2), 9.77 (d, 1, H-5, J = 2.5 Hz), 9.90 (d, 1, H-3, J = 2.5 Hz), 10.02 (d, 1, H-10, J = 9.5 Hz); for **22** δ 7.73 (t, 1, H-9, J = 9.5 Hz), 8.56 (d, 1, H-7, J = 4.4 Hz), 8.64 (d, 1, H-6, J = 4.4 Hz), 8.90 (d, 2, H-8,10, J = 9.5 Hz), 9.23 (s, 1, H-1), 9.86 (d, 1, H-5, J < 2 Hz), 9.93 (d, 1, H-3, J < 2 Hz); mass spectrum for **21**, m/e (relative intensity) 292 (M^+, 50), 246 (M^+ – 46, 6), 200 (M^+ – 92, 37); exact mass, m/e 292.0444 ($C_{16}H_8N_2O_4$ requires 292.0484).

Registry No. 1, 102830-05-7; 1 (R_1 = Cl), 102830-03-5; 1 (R_1 = Br), 109801-98-1; 1 (R_1 = SCN), 109802-00-8; 1 (R_2 = $COCF_3$), 95193-27-4; 1 (R_2 = Cl), 102830-04-6; 1 (R_2 = Br), 109801-99-2; **2**, 111794-63-9; **2** (R_1 = CH_2NMe_2), 102830-07-9; **2** (R_1, R_4 = CH_2NMe_2), 111794-79-7; **2** (R_1, R_5 = CH_2NMe_2), 111794-80-0; **2** (R_1 = $CH_2NMe_3^+ \cdot I^-$), 102830-08-0; **2** (R_1, R_4 = $CH_2NMe_3^+ \cdot 2I^-$), 111794-81-1; **2** (R_1, R_5 = $CH_2NMe_3^+ \cdot 2I^-$), 111794-82-2; **3**, 111794-64-0; **4**, 111794-65-1; **5**, 109801-96-9; **6**, 111794-66-2; **7**, 111794-67-3; **8**, 111794-68-4; **9**, 109801-97-0; **10**, 111794-69-5; **11**, 72541-89-0; **12**, 111794-70-8; **13**, 111794-71-9; **14**, 111794-72-0; **15**, 111794-73-1; **16**, 111794-74-2; **17**, 109802-02-0; **18**, 111794-75-3; **19**, 111794-76-4; **20**, 95193-28-5; **21**, 111794-77-5; **22**, 111794-78-6; azupyrene, 193-85-1; 3-nitroazupyrene, 82510-91-6.