where X_0 = initial concentration of 2-bromopyridine, Y_0 = initial concentration of the substituted 2-bromopyridine, Z_0 = initial concentration of the nucleophilic reagent, and R = ratio of the isomers formed. Similar runs were carried out using mixtures of 2-bromo- and 2-bromo-5-methylpyridine and a ternary mixture of 2-bromo-, 2-bromo-3-methyl-, and 2-bromo-5-methylpyridine.

Kinetic Procedures. A. Potassium Thiophenoxide in Methanol.—The runs were carried out in sealed tubes under nitrogen using 15-ml portions of solution containing equimolar ($\equiv$0.00461 mol) proportions of potassium thiophenoxide and the 2-bromopyridine. Aliquots were quenched in halide-free nitric acid and the solution was allowed to stand for 24 hr in air so that the unreacted thiophenol which was liberated was oxidized and did not interfere with the titration. Liberated bromide ion was titrated against silver nitrate. To check this procedure an aliquot was also quenched with hydrochloric acid and back-titrated with baryta to determine the amount of thiophenoxide consumed; data indicating that halide liberated is equivalent to thiophenoxide consumed [time in hours, titer for bromide determination *vs.* 0.0202 N $AgNO_3$ (a = 12.1 ml), titer for thiophenoxide determination after addition of aliquot of HCl *vs.* 0.0312 N $Ba(OH)_2$ (a = 18.72 ml)]: 0, 0.02, 11.00; 7.6, 0.78, 11.55; 24, 2.03, 12.25; 48, 3.42, 13.24; 73, 4.38, 13.95; 100, 5.40, 14.52; k_2 (from Br^- determination) = 4.853×10^{-5} l. mol^{-1} sec^{-1}; k_2 (from acid–base titration) = 4.942×10^{-5} l. mol^{-1} sec^{-1}.

B. Thiophenol in Methanol.—Equimolar amounts of the 2-bromopyridine and thiophenol in methanol were sealed in glass tubes under nitrogen. The rates were initially followed by pouring the reaction mixture into halide-free nitric acid, extraction with two portions of chloroform and then the addition of a few drops of hydrogen peroxide. After a few hours the solution was extracted with ether, the ether layer washed with water and the aqueous extracts combined and analyzed for bromide ion. This did not lead to consistent titration values, and the method was abandoned in favor of that of Bevan and Hirst.[23] The contents of the sample tube were added to 25 ml of 1 N hydrochloric acid, to which solid potassium iodide was added followed by a known volume of standard potassium iodate. The excess iodine was titrated against sodium thiosulfate solution.

C. Thiophenol in Dimethyl Sulfoxide.—DMSO liberated iodine from acid solutions of iodide and iodate so that this method of assaying was discarded. Equimolar amounts (0.00275–0.00500 mol) of the 2-bromopyridine and potassium thiophenoxide in DMSO were heated under nitrogen in sealed tubes. Aliquots were quenched in hydrochloric acid and the excess acid was back-titrated with baryta.

Registry No.—Thiophenoxide ion, 13133-62-5; 2-bromopyridine, 109-04-6; 2-bromo-3-methylpyridine, 3430-17-9; 2-bromo-5-methylpyridine, 3510-66-5; 2,3-dibromopyridine, 13534-89-9; 2,5-dibromopyridine, 624-28-2; 2-thiophenoxypyridine (picrate), 19520-21-9; 3-methyl-2-thiophenoxypyridine, 19520-22-0; 3-methyl-2-thiophenoxypyridine (picrate), 19520-23-1; 5-methyl-2-thiophenoxypyridine, 19541-52-7; 5-methyl-2-thiophenoxypyridine (picrate), 19520-24-2; 3-bromo-2-thiophenoxypyridine, 19520-25-3; 3-bromo-2-thiophenoxypyridine (picrate), 19520-26-4; 5-bromo-2-thiophenoxypyridine, 19520-27-5; 5-bromo-2-thiophenoxypyridine (picrate), 19520-28-6.

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Electronic Absorption and Fluorescence of Phenylethynyl-Substituted Acenes

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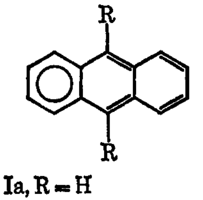
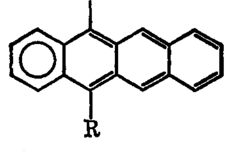
Substitution of acenes Ia, IIa and IIIa with the phenylethynyl group substantially increased quantum yields of fluorescence, and produced large shifts to longer wavelengths in the visible absorption and fluorescence spectra. A nearly constant displacement toward the red of 100 mμ in the fluorescence emission was observed for the *meso*-substituted bis(phenylethynyl)acenes Ib, IIb, and IIIb, when compared with the parent hydrocarbons. The spectral data indicate that the ethynyl group is a better conductor of electronic effects in the excited state than in the ground state.

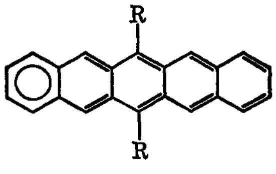
An extensive study of the fluorescence efficiencies of 9,10-disubstituted anthracenes has shown that the relative effectiveness of the phenyl group in intensifying fluorescence is considerably greater than that for such substituents as halo, hydroxy, alkoxy, alkyl, amino, acyl and nitro.[1] We have found that 9,10-bis(phenylethynyl)anthracene (Ib), a bright yellow-green fluorescer,[2] has an absolute fluorescence quantum yield (ϕ_F) = 0.96, which is even higher than ϕ_F = 0.84 for 9,10-diphenylanthracene (Ic). Thus the fluorescence efficiency of Ib is greater than any of the 9,10-disubstituted anthracenes previously reported. A comparison of the absorption and emission properties of Ib with those of the parent hydrocarbon, anthracene (Ia), shows that in addition to enhancing the fluorescence efficiency, the mild electron accepting phenylethynyl group[3] has also produced unusually large red shifts (see Table I).



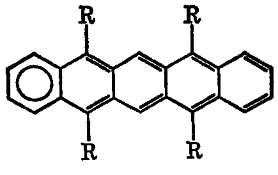
Ia, R = H
b, R = $-C \equiv CC_6H_5$
c, R = $-C_6H_5$
d, R = $-CH{=}CHC_6H_5$



IIa, R = H
b, R = $-C \equiv CC_6H_5$



IIIa, R = H
b, R = $-C \equiv CC_6H_5$



IVb, R = $C \equiv CC_6H_5$

To test the generality of the effect of phenylethynyl substitution on excited state behavior, phenylethynylacenes IIb, IIIb and IVb were prepared (see Table II for visible absorption spectra) and evaluated. 5,12-Bis(phenylethynyl)naphthacene (IIb), and 6,13-bis-

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TABLE I

ABSORPTION AND FLUORESCENCE OF THE ACENES I–IV

	Absorption,[a] Long-wavelength band			Fluorescence,[a] short-wavelength band,		Quantum yields (ϕ_F),
Compd	λ_{max}, mμ	Log ε	Δλ, mμ	λ_{max}, mμ	Δ λ_{max}	einstein/mol
Ia	382	3.80		388		0.25
Ib	455	4.52	73	486	98	0.96
Ic	395	4.13	13	407	19	0.84
IIa	476	3.98		483		0.21
IIb	548	4.37	72	580	97	0.66
IIIa	576	3.72		578		<0.01
IIIb	655	4.41	79	680	102	0.34
IVb[b]	705	4.43	129	740	162	0.08

[a] Solvent was benzene. [b] Solvent was o-dichlorobenzene.

TABLE II

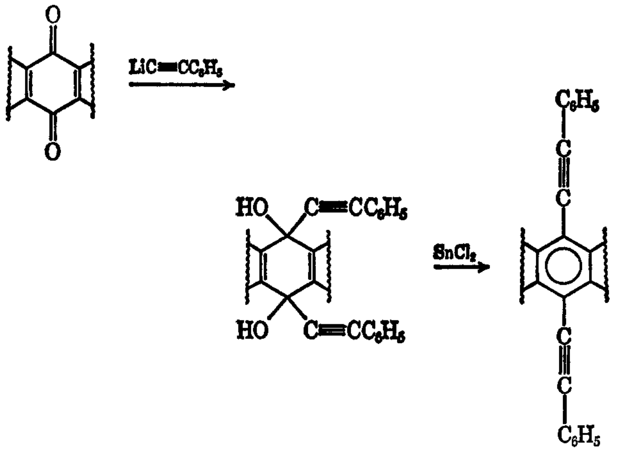
VISIBLE ABSORPTION SPECTRA OF PHENYLETHYNYL-SUBSTITUTED ACENES[a]

Compd	λ_{max}, mμ (log ε)
Ib	439 (4.50), 455 (4.52)
IIb	478 (3.90), 512 (4.24), 548 (4.37)
IIIb	560 (3.74), sh 604 (4.16), 655 (4.41)
IVb[b]	430 (3.60), 461 (3.46), 597 (371), 645 (4.18), 705 (4.43)

[a] Determined in benzene with a Cary 15 spectrophotometer. [b] Solvent was o-dichlorobenzene.

(phenylethynyl)pentacene (IIIb), and 5,7,12,14-tetrakis(phenylethynyl)pentacene (IVb), were prepared from 5,12-naphthacenequinone,[4] 6,13-pentacenequinone[5] and 5,7,12,14-pentacenediquinone,[6] respectively, according to the procedure described by Ried for making Ib—phenylethynylation with lithium phenylacetylide, followed by reduction of the corresponding quinols with stannous chloride[7] (see Scheme I).

SCHEME I



The spectral data presented in Table I point out the generality of the large shifts to longer wavelengths and the increased fluorescence efficiencies. In particular, the fluorescence emission of *meso*-substituted acenes Ib, IIb and IIIb is displaced from that of the parent hydrocarbons by a nearly constant value of 100 mμ. Substitution of four phenylethynyl groups in the 5, 7, 12, and 14 positions of pentacene (*i.e.*, IV), however, gave a bathochromic shift of only 162 mμ.

Comparison of the yellow-green fluorescence of Ib with the observed blue fluorescence of 9,10-diethynylanthracene[8] illustrates the essential character of the phenyl group in causing a bathochromic shift. The large spectral shifts in the phenylethynyl-substituted acenes indicate substantial electron delocalization through the –C≡C– group in the excited state, and a significant lowering of the first excited singlet relative to the ground state. This observation is in direct contrast to the proposal that the delocalized system of γ-phenylpropargyl radical does not include the benzene ring,[9] and points out the difference in the conjugative characteristics of the –C≡C– group in excited and ground-state systems.

The absence of a sizable red shift in the absorption and fluorescence spectra of 9,10-diphenylanthracene reflects the noncoplanarity of the phenyl groups with the anthracene ring in the ground and excited states. Similarly, steric effects appear to account for the small red shift in the absorption spectrum of *trans,trans*-9,10-distyrylanthracene (Id), which has a single broad band centered at 410 mμ. The steric strain in the vibrationally equilibrated first excited singlet state of Id evidently is relieved by a conformational change, as indicated by a substantial shift in fluorescence (λ_{max} 615 mμ, shoulder at 560 mμ). In the related phenylethynylacene Ib, it is clear from the absorption and fluorescence spectra that neither the ground nor excited state is sterically hindered. Moreover, it is apparent that the –CH═CH– group is a better conductor of electronic effects in the excited state than is –C≡C–, since the yellow-orange fluorescence of 9,10-distyrylanthracene (ϕ_F = 0.23) is at longer wavelengths than the fluorescence of Ib, which is centered at 513 mμ. This is qualitatively in agreement with the conclusion that acetylenes have a lower aptitude than ethylenes for conjugation with electron deficient systems in the ground state.[3]

Experimental Section

9,10-Dihydroxy-9,10-bis(phenylethynyl)-9,10-dihydroanthracene.—Recrystallization of the product obtained from the reaction of 9,10-anthraquinone and lithium phenylacetylide[10] from acetonitrile gave colorless crystals, mp 220° (lit.[10] mp 206–207°). The two peaks at 3550 and 3410 cm^{-1} in the infrared spectrum ($CHCl_3$) established the *cis* relationship of the two hydroxy groups.

9,10-Bis(phenylethynyl)anthracene (Ib).—The procedure described by Ried, Donner, and Schelegelmilch[10] was used without modification.

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5,12-Dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene.—To lithium phenylacetylide, made from 14.85 g (0.146 mol) of phenylacetylene and 2.80 g (0.122 mol) of lithium amide in 100 ml of dioxane, was added 15.7 g (0.061 mol) of 5,12-naphthacenequinone[4] in 150 ml of dioxane. The mixture was refluxed for 4 hr, then cooled and treated with 350 ml of 0.5 *M* aqueous ammonium chloride solution. Recrystallization of the product from benzene gave 15.95 g (57%) of colorless crystals, mp 216.5–218° dec. The infrared spectrum ($CHCl_3$) had a single peak at 3610 cm^{-1} for *trans* OH, and two peaks at 3550 and 3400 cm^{-1} corresponding to *cis*-hydrogen-bonded OH. The ratio of *cis* to *trans* was 4:1.

Anal. Calcd for $C_{34}H_{22}O_2$: C, 88.31; H, 4.77. Found: C, 87.97; H, 4.83.

5,12-Bis(phenylethynyl)naphthacene (IIb).—To 29 g of stannous chloride dihydrate in 200 ml of 50% aqueous acetic acid was slowly added 14.4 g of 5,12-dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene in 300 ml of dioxane. The mixture was stirred at room temperature for 2 hr, then diluted to a volume of 1500 ml with water. Recrystallization of the crude product from benzene gave 8.1 g (63%) of dark red-purple needles, mp 248° dec.

Anal. Calcd for $C_{34}H_{20}$: C, 95.33; H, 4.67. Found: C, 95.45; H, 4.78.

6,13-Dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene.—To lithium phenylacetylide, made from 10.20 g (0.10 mol) of phenylacetylene and 2.30 g (0.10 mol) of lithium amide in 100 ml of anhydrous dioxane, was added 3.08 g (0.01 mol) of 6,13-pentacenequinone[5] in 100 ml of dioxane. The mixture was refluxed for 4 hr, then treated with 600 ml of 0.5 *M* aqueous ammonium chloride solution. The crude product was washed with benzene, then washed with water. Recrystallization in chloroform gave 3.47 g (68%) of colorless solid, mp 230° dec. The infrared spectrum ($CHCl_3$) had a single peak at 3610 cm^{-1} for *trans* OH, and two peaks at 3550 and 3400 cm^{-1} corresponding to *cis*-hydrogen-bonded OH. The ratio of *cis* to *trans* was 1:1.

Anal. Calcd for $C_{38}H_{24}O_2$: C, 89.06; H, 4.69. Found: C, 89.32; H, 4.80.

6,13-Bis(phenylethynyl)pentacene (IIIb).—To 30 g of stannous chloride dihydrate in 25 ml of 50% aqueous acetic acid was added 1.38 g of 6,13-dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene in 90 ml of dioxane and the mixture was stirred at room temperature for 2 hr. Dilution with water gave 1.18 g of crude product. Recrystallization from xylene gave 0.91 g (63%) of deep blue crystals, which sublimed at 195°.

Anal. Calcd for $C_{38}H_{22}$: C, 95.39; H, 4.60. Found: C, 95.23; H, 4.75.

5,7,12,14-Tetrahydroxy-5,7,12,14-tetrakis(phenylethynyl)-5,-7,12,14-tetrahydropentacene.—A mixture of 10.20 g (0.10 mol) of phenylacetylene, 2.30 g (0.10 mol) of lithium amide and 75 ml of anhydrous dioxane was refluxed for 1 hr. More dioxane (100 ml) was added to the cooled mixture. 5,7,12,14-Pentacenediquinone[6] (1.69 g, 0.005 mol) was added all at once and the mixture was refluxed for 4.5 hr. Aqueous ammonium chloride solution (0.2 *N*, 400 ml) was added, followed by an addition of 200 ml of benzene. A tan solid, mp 400°, was collected after stirring the aqueous and benzene layers for 15 min. Recrystallization from chloroform gave 2.77 g (72%) of colorless crystals, infrared 3300 cm^{-1} (Nujol).

Anal. Calcd for $C_{54}H_{34}O_4$: C, 86.86; H, 4.56. Found: C, 87.16; H, 4.52.

5,7,12,14-Tetrakis(phenylethynyl)pentacene (IVb).—To a solution of 1.69 g (7.5 mmol) of stannous chloride dihydrate in 15 ml of 50% acetic acid was added 1.12 g (1.5 mmol) of the tetrol in 50 ml of dioxane. A dark green color formed as the mixture was stirred at room temperature for 5 hr. Filtration gave 0.98 g of solid which was insoluble in most organic solvents. Recrystallization from 1,2,4-trichlorobenzene gave dark green needles, mp >300°.

Anal. Calcd for $C_{54}H_{30}$: C, 95.58; H, 4.42. Found: C, 95.50; H, 4.28.

Fluorescence Measurements.—The techniques and instrumentation used for obtaining absolute emission intensities, spectra and quantum yields in the visible region have been described elsewhere.[11a] An instrument similar in design, but with sensitivity out to 1.0 μ, was constructed and used to obtain fluorescence data in the long-wavelength visible and near-infrared regions.[11b]

Registry No.—Ia, 120-12-7; Ib, 10075-85-1; Ic, 1499-10-1; Id, 10273-82-2; IIa, 92-24-0; *cis*-5,12-dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene, 18826-28-3; *trans*-5,12-dihydroxy-5,12-bis(phenylethynyl)-5,12-dihydronaphthacene, 18826-65-8; IIb, 18826-29-4; IIIa, 135-48-8; *cis*-6,13-dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene, 18826-30-7; *trans*-6,13-dihydroxy-6,13-bis(phenylethynyl)-6,13-dihydropentacene, 18826-66-9; IIIb, 18826-31-8; 5,7,12,14-tetrahydroxy-5,7,12,14-tetrakis(phenylethynyl)-5,7,12,14-tetrahydropentacene, 18841-60-6; IVb, 18826-38-5.

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Reactions of Pentafluorophenylcopper Reagent

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A pentafluorophenylcopper reagent containing magnesium halide was prepared from the reaction between pentafluorophenylmagnesium bromide and cuprous chloride. The reagent underwent reactions representative of both organocopper and perfluoroaryl organometallic compounds. Reactions with H_2O, CO_2, O_2, C_6H_5I, *p*-$C_6F_5OC_6F_4Br$, *p*-$CH_3OC_6F_4I$, $CF_2{=}CFI$, and $C_7F_{15}I$ have been studied. The effect of the magnesium halide content on the reactivity of the pentafluorophenylcopper reagent was examined.

The method for the preparation of decafluorobiphenyl from bromopentafluorobenzene and copper-bronze[1] suggests the intervention of a pentafluorophenylcopper intermediate. Reports have indicated that pentafluorophenylmercury,[2] zinc,[3] and cadmium[4] and more recently perfluoroalkylcopper compounds[5]

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