an ice–salt mixture. After 128 g (4.00 mol) of absolute methanol had been added dropwise through the dropping funnel, the reaction mixture was allowed to stir overnight to ensure evaporation of all the excess phosgene. The crude methyl chloroformate was washed with two 50-mL portions of ice water and dried over anhydrous sodium sulfate and calcium carbonate for 1 day. Distillation at atmospheric pressure yielded 280 g (75%) of methyl chloroformate, bp 70–72 °C (reported (2) bp 71.5 °C).

A 2-L, three-necked flask fitted with a water condenser, a dropping funnel, and a stirrer was charged with 120 g (0.76 mol) of bis(4-hydroxy-2-butenyl) ether (II), 400 mL of dry chloroform, and 200 g (2.5 mol) of dry pyridine. To the reaction flask cooled at 0 °C was added 235 g (2.5 mol) of freshly distilled methyl chloroformate over a period of 8 h. The reaction mixture was washed successively with 200 mL of water, 100 mL of 5% hydrochloric acid, and 100 mL of a saturated sodium bicarbonate solution. After the chloroform solution was dried over anhydrous magnesium sulfate overnight, the chloroform was removed by distillation under reduced pressure, and the residue was fractionally distilled through a 12-in., helix-packed column to yield 175 g (84%) of bis(4-hydroxy-2-butenyl) ether bis(methyl carbonate) (IV), bp 155–157 °C (0.8 mm), n^{30}_D 1.4564. Anal.

Calcd for $C_{12}H_{18}O_7$: C, 52.55; H, 6.56. Found: C, 52.74; H, 6.73.

An infrared spectrum analysis of bis(4-hydroxy-2-butenyl) ether bis(methyl carbonate) (IV) showed strong absorption bands at 958, 1100, 1275, 1450, 1760, and 3000 cm^{-1} indicative of the presence of an aliphatic ether, a covalent carbonate, and a double bond.

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Synthesis and Fluorescence Spectra of 1,4-Bis(phenylethynyl)anthracene

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The synthesis of the title compound, 1,4-BPEA, was accomplished in the same manner as for 9,10-BPEA, but with lower yield due to a side reaction. The compound is a fair fluorescer with 60% quantum yield in benzene. The emission peaks are at 449 and 478 nm in benzene—blue-shifted from 9,10-BPEA—but still red-shifted from 9,10-diphenylanthracene. Ethanol solutions peak at 443 and 472 nm with the same quantum yield.

Introduction

In a recent paper (3) we gave the fluorescence spectra of several substituted 9,10-bis(phenylethynyl)anthracenes. We have now synthesized a related fluorescer, 1,4-BPEA, measured the fluorescence and quantum yield, and noted how these are affected by this change in the position of the phenylethynyl groups.

Syntheses of 1,4-Bis(phenylethynyl)anthracene and 2-Phenylethynyl-1,4-dihydroxyanthracene

1,4-Anthraquinone (6.3 g, 0.0303 mol; mp 221–224 °C, reported (2)) was reacted with lithiophenylacetylide (6.8 g of phenylacetylene, 1.5 g of lithium amide, 85 mL of dry dioxane) in the same manner (1) used with 9,10-anthraquinone. The dark tarry product obtained when the reaction mixture was quenched with 4 g of ammonium chloride in 100 mL of water was separated from the liquid phase by decanting the latter. The crude product was triturated several times with pentane to remove excess phenylacetylene and then with water; after drying, the crude product was boiled with 100 mL of benzene and chilled overnight at 5 °C, and the solid (1.8 g) was removed and saved (A). When the benzene solution was diluted with 75 mL of n-hexane and further cooled, 3.6 g of olive green solid separated. The latter was filtered and redissolved in 25 mL of acetone and the solution chilled at −15 °C for 3 days, 0.14 g of solid (mp >320 °C; same IR spectrum as that for the following by-product) was removed. This acetone solution was diluted with 20 mL of acetone and added dropwise with stirring to 5.5 g of stannous chloride in 50 mL of 50% aqueous acetic acid. After overnight stirring at 25 °C, the mixture was diluted with 100 mL of water, slurried with some Celite, and centrifuged. The supernatant was discarded. The cake was resuspended in water and centrifuged, and the washings were discarded; this process was repeated twice more. After drying the cake, it was extracted with one 50-mL and two 25-mL portions of boiling benzene. The combined extracts were diluted with 250 mL of cyclohexane and 100 mL of n-hexane and chilled at −15 °C for several days; the supernatant was decanted from the dark resinous material, which had separated, and evaporated to leave 0.8 g of dark yellow 1,4-bis(phenylethynyl)anthracene. Sublimation at pump limit and a pot temperature of 160–170 °C gave felted yellow needles of 1,4-BPEA, mp 164–165 °C. Carbonyl absorptions were absent in the IR spectrum.

By fractionally crystallizing the solid A from benzene there was isolated a small amount of greenish yellow solid, mp >320 °C, whose infrared spectrum showed a CO absorption at 1680 cm^{-1}. Although this evidence might suggest a 1,4-anthraquinone derivative, the ^1H NMR spectrum is more consistent with the assumption that this material is the keto tautomer of 2-

Table I. Absorption and Emission Spectra of
1,4-BPEA in Ethanol

Absorbance[a]		Fluorescence emission[b]	
λ, nm	A, rel	λ, nm	Fq(λ), rel
280	73.4	410	0.0
282	69.5	420	2.2
286	74.8	430	21.7
290	64.4	440	89.1
296	58.0	*443*	100.0
300	61.9	450	69.6
310	79.9	457	47.8
321	90.2	460	50.0
330	51.5	*472*	80.4
340	30.9	480	58.7
350	30.1	490	34.8
360	35.2	500	32.6
370	36.6	502	32.6
380	50.4	510	26.1
390	63.4	520	17.4
400	85.6	530	12.0
408	100.0	540	9.8
410	99.2	550	7.6
420	78.9	560	5.4
431	97.6	570	3.3
440	58.5	580	2.2
450	7.3	590	1.7
460	1.6	600	1.1
		610	0.4
		620	0.0

[a] Slits, 10 nm; molecular absorbances $\epsilon(408)$ 1.64 × 10^4 cm^{-1} M^{-1}, $\epsilon(431)$ 1.60 × 10^4. [b] Slits, 10 nm; excitation at 408 nm, 0.412 μM.

phenylethynyl-1,4-dihydroxyanthracene which would result from the 1,4-addition of lithiophenylacetylide to the starting anthraquinone. ^{1}H NMR (Me$_2$SO-d_6, 100 MHz), δ 5.21 (s, 2 H, CH$_2$), 7.12 (s, 5 H), (C$_6$H$_5$), 7.71 (quartet, 2 H, H$_6$, H$_7$), 8.15 (quartet, 2 H, H$_5$, H$_6$), 8.48 (s, 2 H, H$_9$, H$_{10}$).

The sample for analysis was recrystallized from dimethyl sulfoxide.

Elemental analyses (C, H, O) were performed for the 1,4-BPEA and for this compound and were submitted for review.

Fluorescence Procedure and Results

The small amount (2.3 mg) of sublimed 1,4-BPEA was all used in 25 mL of ethanol to obtain the spectra and quantum yield. Then the ethanol was evaporated and the same material (estimated from ethanol solution proportions as 2.0 mg) was dissolved in 25 mL of benzene.

Tables I and II give the absorption and emission spectra of 1,4-BPEA in ethanol and benzene. The molecular absorbances are given at the peaks. The accuracy of these molecular absorbancies is limited by the accuracy of weighing the small samples and the estimation of the amount of 1,4-BPEA left from the ethanol evaporation. Figure 1 summarizes these data graphically.

Table III gives the excitation peaks which are close to the absorption peaks. Excitation spectra are quite noisy on this instrument and this accounts for the differences in the peak wavelengths. However, the peak heights of excitation show too large a variation from the corresponding absorption peak heights. The reason is an impurity which showed up as an emission band when we excited the benzene solution at the 323-nm peak. This impurity fluorescence bank peaked around 376 nm. The 1,4-BPEA emission was also present and undistorted. Evidently the excitation/absorption peak differences were due to the impurity absorption around 320 nm and did not affect the work

Table II. Absorption and Emission Spectra of
1,4-BPEA in Benzene

Absorbance[a]		Fluorescence emission[b]	
λ, nm	A, rel	λ, nm	Fq(λ), rel
290	93.1	410	0.0
300	79	420	1.2
310	93	430	8.3
320	110	440	55
323	112	*449*	*100*
330	93	460	50
340	47	465	48
350	37	470	60.7
360	32	*478*	*76*
370	34	480	74
380	44	490	43
390	60	500	29.8
400	73	*508*	*30.0*
411	100	510	29.8
420	88	520	21
425	84	530	14
430	92	540	11
434	98	550	8
440	89	560	6
450	30	570	5
460	5	580	4
470	1.5	590	2.4
480	0.0	600	1.9
		610	1.2
		620	0.5
		630	0.0

[a] Slits, 10 nm; molecular absorbances $\epsilon(411)$ 2.06 × 10^4 cm^{-1} M^{-1}, $\epsilon(434)$ 2.01 × 10^4, $\epsilon(323)$ 2.31 × 10^4. [b] Slits, 10 nm; excitation at 411 nm, 0.37 μM.

Table III. Excitation Peaks of 1,4-BPEA

Ethanol[a]		Benzene[b]	
λ, nm	I, rel	λ, nm	I, rel
323	92.1	323	87.5
411	98.2	413	96.7
432	100.0	435	100.0

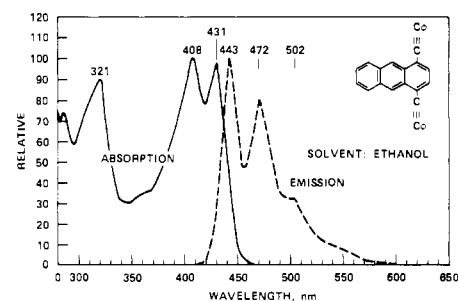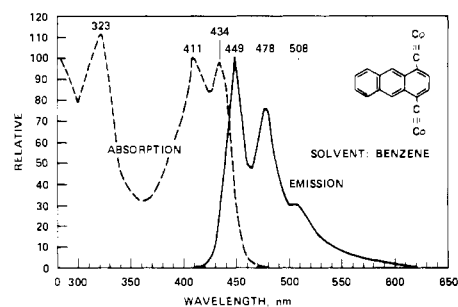[a] Slits, 10 nm; 0.412 μM. [b] Slits, 10 nm; 0.37 μM.

Figure 1. Absorption and emission spectra of 1,4-BPEA: (top) in benzene, (bottom) in ethanol.

Table IV. Quantum Yields

	Ethanol Solution	
	Excitation wavelength	
Run no.	408 nm	431 nm
A	0.675	
B	0.651	0.627
C	0.661	
	$q = 0.66 \pm 0.07$	0.63
	Benzene Solution	
	Excitation wavelength	
Run no.	411 nm	434 nm
A	0.641	
B	0.629	
B	0.657	
C	0.714	
C	0.677	0.633
	$q = 0.66 \pm 0.03$	0.63

above 400 nm where we measured quantum yields. We therefore did not pursue the impurity further.

The quantum yields in both solvents are given in Table IV. These are in air-saturated solutions. Solutions in air but in the dark were stable for 3 days in terms of spectra and quantum yields.

Discussion

In our earlier paper (*3*) we discussed the problem of corrected spectra and errors in quantum yield. With 1,4-BPEA its spectra are in the same region as the comparison compound (quinine sulfate at 457 nm) so this error is minimized.

The emission spectrum structure of 1,4-BPEA is much like that of 9,10-diphenylanthracene (DPA), but the peaks are strongly blue shifted from those of 9,10-BPEA. The absorption spectrum of 1,4-BPEA is different from both the other compounds. The quantum yield, 60%, is lower than that of the 9,10-BPEA (81%) (*3*).

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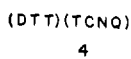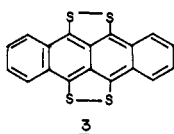
Synthesis of Naphthaceno[5,6-*cd*]-1,2-dithiole

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A single-step synthesis of the π-electron donor naphthaceno[5,6-*cd*]-1,2-dithiole is reported as well as polarographic data and its formation of a semiconducting salt with tetracyanoquinodimethane.

Considerable interest in the synthesis of planar, aromatic compounds containing exocyclic sulfur or selenium (*2*, *6*, *8*) as potential π donors has prompted our investigation of the reaction of sulfur with tetracene in refluxing dimethylformamide (DMF) to form naphthaceno[5,6-*cd*]-1,2-dithiole (DTT, **2**).

Tetracene (**1**) is known to react with excess sulfur, when refluxed with trichlorobenzene (*3*) or DMF (*7*), to give the well known naphthaceno[5,6-*cd*:11,12-*c'd'*]bis(1,2-dithiole) (TTT, **3**). The synthesis of the corresponding dithio derivative, DTT, however, has not been reported in the literature although Marschalk (*4*) first observed a violet solution when 5-chloronaphthacene reacted with sulfur but was unable to isolate the product. Goodings (*1*) later was able to isolate **2** in 4% yields from the gradient sublimation of crude **3**. We wish to report here a convenient, single stage, preparative route for the synthesis of **2**.

Gradient sublimed (*5*) tetracene reacts with 0.25 equiv of sulfur when refluxed for 24 h in anhydrous DMF to give after multiple gradient sublimation, in a 30% yield, **2**, mp 212.7–214.6 °C as violet needles. Attempts to prepare **2** using more than 0.25 equiv of sulfur resulted in the appearance of traces of **3** in the gradient sublimate while using less than 0.25 equiv gave **2** in poor yields (<10%) and required long reaction times.

In contrast to **3**, DTT is readily soluble in most organic solvents to give intense violet colored solutions. The differential pulse polarogram (Figure 1) of **2** exhibits one reversible oxidation step ($E^1_{1/2} = +0.37$ V vs. SCE) in acetonitrile with tetraethylammonium perchlorate as the support electrolyte. The peak shapes and reversibility are consistent with a one-electron process. Additionally **2** exhibits a reduction step at -1.17 V which is partially reversible and with the presence of a shoulder at -1.09 V appears to suggest a two–one electron process. The products(s) can be reoxidized at -1.14 V.

DDT reacts with the π-acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) to give the 1:1 TCNQ salt, **4**, as a black crystalline material. Single crystals, isolated as needles, appear yellow under optical transmission microscopy and extinguish polarized light along the needle axis. The four-probe room temperature electrical conductivity measured on single crystals of **4** was 3.0×10^{-6} (Ω cm)$^{-1}$ characteristic of an organic semiconductor.

Experimental Section

Melting points were determined using a Mettler FP5 melting point apparatus with a Mettler FP52 microscope hot stage