Table IV. Quantum Yields

Run no.	408 nm	431 nm
Ethanol Solution (Excitation wavelength)		
A	0.675	
B	0.651	0.627
C	0.661	
	$q = 0.66 \pm 0.07$	0.63
Benzene Solution (Excitation wavelength)	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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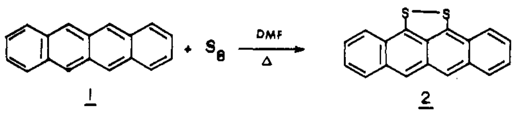
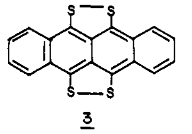
A single-step synthesis of the π-electron donor naphthaceno[5,6-*cd*]-1,2-dithiole is reported as well as polarographic data and its formation of a semiconducting salt with tetracyanoquinodimethane.

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**).



$1 + S_8 \xrightarrow[\Delta]{DMF} 2$



3

(DTT)(TCNQ)

4

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

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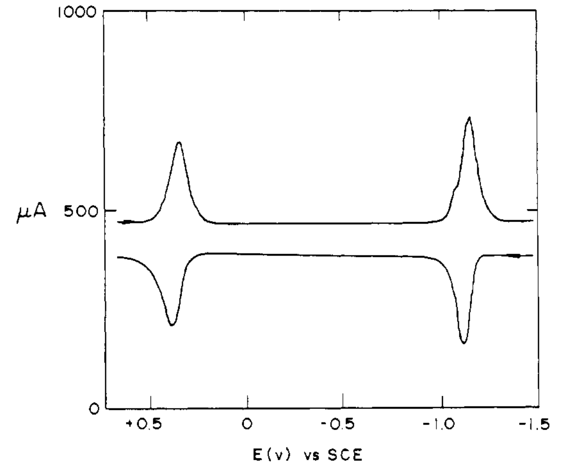

Figure 1. Differential pulse polarogram of DTT (10^{-5} M in CH_3CN) at glassy carbon electrode.

attachment. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer in acetonitrile (Burdick & Jackson) solutions. Infrared spectra (IR) were recorded on a Perkin-Elmer 225 spectrophotometer in KBr. Nuclear magnetic resonance (NMR) spectra were run in $CDCl_3$ solution containing Me_4Si as internal standard using a Varian 220-MHz instrument. Mass spectra were obtained using a Hitachi/Perkin-Elmer RMH-2 instrument. Polarographic measurements were performed in MeCN on a Princeton Applied Research Model 174A polarographic analyzer using a glassy carbon working electrode and a $Ag|Ag^+$ reference electrode. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

***Naphthaceno[5,6-cd]-1,2-dithiole* (2).** A mixture of 1 (0.50 g) and sublimed sulfur (0.14 g) in anhydrous dimethylformamide (25 mL) was refluxed for 24 h under argon. The reaction mixture was cooled and filtered and filtrate was concentrated. The combined solid obtained above (0.56 g) was gradient sublimed (195 °C, 3 × 10^{-5} Torr) three times with only successive middle fractions retained for subsequent sublimations to give 0.2 g (31%) of **2** as a violet crystalline solid: mp 212.7–214.6 °C; IR 1610, 1580, 1485, 1303, 1290, 938, 860, 829, 770, 750, 729, and 559 cm^{-1}; λ_{max} 214 nm (log ϵ 6.47), 236 (6.60) 297 (6.99), 402 (sh) (5.29), 425 (5.63), and 561 (5.63); NMR δ 8.00 (2 H, s, 11- and $12H_2$), 7.82 (2 H, d, J = 2 Hz, 4- and $7H_2$), 7.55 (2 H, d, J = 8 Hz, 1- and $10H_2$), and 7.48–7.23 (4 H, m, 2-, 3-, 8-, and $9H_2$); mass spectrum m/e (relative intensity) 290 (M, 100), 145 (M/2, 7).

Anal. Calcd for $C_{18}H_{10}S_2$: C, 74.44; H, 3.48; S, 22.08. Found: C, 74.43; H, 3.43; S, 22.29.

***Naphthaceno[5,6-c,d]-1,2-dithiole (tetracyanoquinodimethane)* (4).** A hot saturated solution of **2** in dichlorobenzene (Burdick & Jackson) was added to a hot equimolar solution of TCNQ in acetonitrile (Burdick & Jackson). The resulting mixture was allowed to cool, filtered, and vacuum dried to give **4** as black needles: mp 219.3 °C dec; IR 2210, 1615, 1575, 1530, 1345, 1285, 1115, 929, 865, 835, 768, 730, 612, 468, and 458 cm^{-1}.

Anal. Calcd for $C_{30}H_{14}N_4S_4$: C, 72.85; H, 2.86; N, 11.83; S, 12.96. Found: C, 72.73; H, 2.99; N, 11.60; S, 13.02.

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Aldol-Condensation Products from the Multiple Anions of Oximes, Benzanilides, a Benzamide, and *o*-Tolylanilides

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Several new β-hydroxyoximes, γ-hydroxyamides and δ-hydroxyamides were prepared from respective multiple anions by an aldol-type condensation with an aldehyde or ketones.

In connection with our work with $C(\alpha),O$-dilithiooximes (*2–4, 7–10*), several new β-hydroxyoximes were prepared by condensation of the dianion with ketones, such as 2-benzoyl-

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[†] Deceased.

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