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The Formation of Substituted Dibenzothiophene Dioxides by Sulfonation of *meta-* and *para-*Terphenyls

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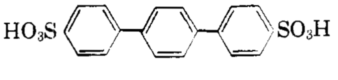
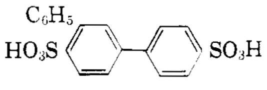
The sulfonation of *m-* and *p-*terphenyl results in the unexpected formation of sulfonated dibenzothiophene-5,5-dioxides 4′,4″-Bis(alkoxybenzamido)-*p*-terphenyls may be sulfonated with or without sulfone formation, depending on the reaction conditions. The structures of the sulfonated materials are determined. These materials are characterized by their exceptionally strong blue-green fluorescence.

INTRODUCTION

It is known that sulfonation of *p*-terphenyl with chlorosulfonic acid in tetrachloroethane at 70° gives 4′,4″-*p*-terphenyldisulfonic acid (I),[1] whereas *m*-terphenyl with concentrated sulfuric acid at 100° gives predominantly 4,4′-*m*-terphenyldisulfonic acid (II),[1] and *o*-terphenyl gives a mono-, di-, and tri-sulfonic acid.[2] It has now been found that 20 percent oleum or chlorosulfonic acid at 90–100° converts *p*-terphenyl into 4′,7-disulfo-3-phenyldibenzothiophene dioxide (III) and *m*-terphenyl into x,x′-disulfo-10,12-dithiaindeno[2,1*b*]fluorene 10,12-bisdioxide (IV).



I



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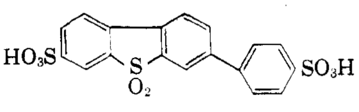
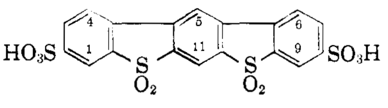
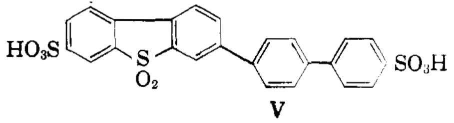


III

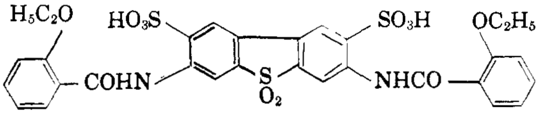


IV

In a similar manner, sulfonation of quaterphenyl with either 20 percent oleum at 100° or with concentrated sulfuric acid at 189–190° gives 3-(4′-sulfobiphenylyl)-7-sulfodibenzothiophene dioxide (V).



V



VI

The empirical formulae of III, IV, and V have been established by converting them to their di-*o*-tolylguanidine salts and di-*o*-toluidine salts which were then analyzed for all elements. The analytical data are in agreement with the postulated structures. The similarity of the ultraviolet spectra of III and V to that of VI, which is a known compound,[3] is evidence for the presence of the dibenzothiophene dioxide nucleus. The additional conjugation which V and VI have, by virtue of their added

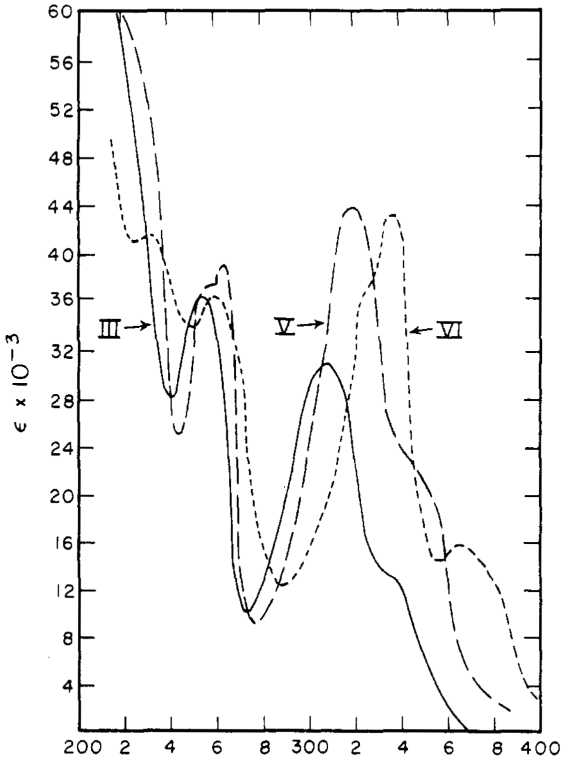


FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA OF THE DI-*o*-TOLYLGUANIDINE SALTS OF III AND V AND OF THE DI-*p*—TOLUIDINE SALT OF VI IN METHANOL.

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(1) C. Wulff and E. Roell (to I. G. Farbenindustrie A.-G.), U. S. Patent 2,004,546 (1935); *Chem. Abstr.*, **29**, 5282 (1935).

(2) C. F. H. Allen and D. M. Burness, *J. Org. Chem.*, **14**, 163 (1949).

(3) M. Scalera and D. R. Eberhart (to Amer. Cyanamid Co.), U. S. Patent 2,563,493 (1951); *Chem. Abstr.*, **46**, 273 (1952).

substituents, produces a bathochromic shift with respect to III in the whole absorption spectrum, as shown in Figure 1.

The spectrum of IV (see Fig. 2) is notable in respect to the high value of the extinction coefficient and the presence of considerable fine structure which may be indicative of strain in the molecule. The linear isomer has been chosen arbitrarily. The sulfonic acids are probably in the 2,8-position since further sulfonation of II gives IV; the latter, as a dibenzothiophene dioxide, should direct the next sulfonic acid group into the 2-position.

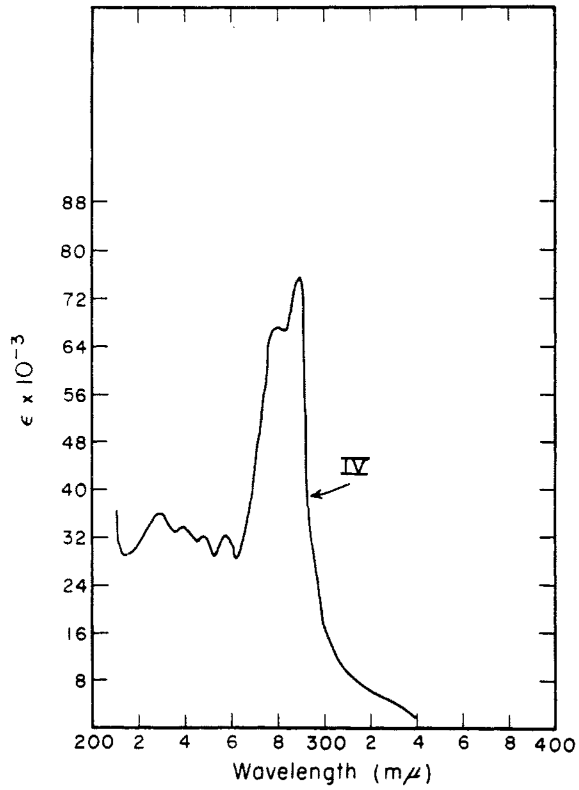
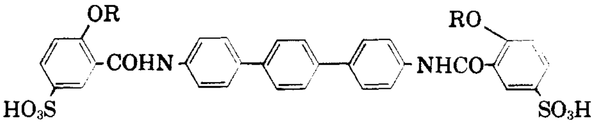


FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRUM OF THE DI-*o*-TOLUIDINE SALT OF IV IN METHANOL.

In contrast, certain derivatives of 4′,4″-diamino-*p*-terphenyl[4] can be sulfonated without sulfone formation. *o*-Ethoxy- and *o*-methoxy-benzoyl chloride react with this diamine in the presence of pyridine to give 4′,4″-bis(2-ethoxybenzamido)- and 4′,4″-bis(2-methoxybenzamido)-*p*-terphenyl, respectively, in quantitative yield. Sulfonation of these latter two substances with concentrated sulfuric acid at 100° gives 4′,4″-bis(2-ethoxy-5-sulfobenzamido)- (VII), and 4′,4″-bis(2-methoxy-5-sulfobenzamido)-*p*-terphenyl (VIII), which were isolated as their bistriethanolamine salts. Acid hydrolysis of VII and VIII results in the regeneration of 4′,4″-diamino-*p*-terphenyl indicating that the sulfo groups are in the benzoyl moiety. The sulfo groups are placed in position *para* to the alkoxy group by analogy with similarly constituted compounds.[5] These salts, as well as the free acids, are sensitive to calcium ion, forming insoluble precipitates in water containing these ions.



VII R = OC_2H_5
VIII R = OCH_3
IX R = OH

Phenyl salicylate reacts with 4′,4″-diamino-*p*-terphenyl in trichlorobenzene to give 4′,4″-bis(2-hydroxybenzamido)-*p*-terphenyl; this was sulfonated under the same conditions as were used with VII to give 4′,4″-bis(2-hydroxy-5-sulfobenzamido)-*p*-terphenyl (IX). The similarity of the ultraviolet absorption spectra of VII and VIII to that of their unsulfonated parent compounds demonstrates that the *p*-terphenyl residue is undisturbed during sulfonation (see Fig. 3).

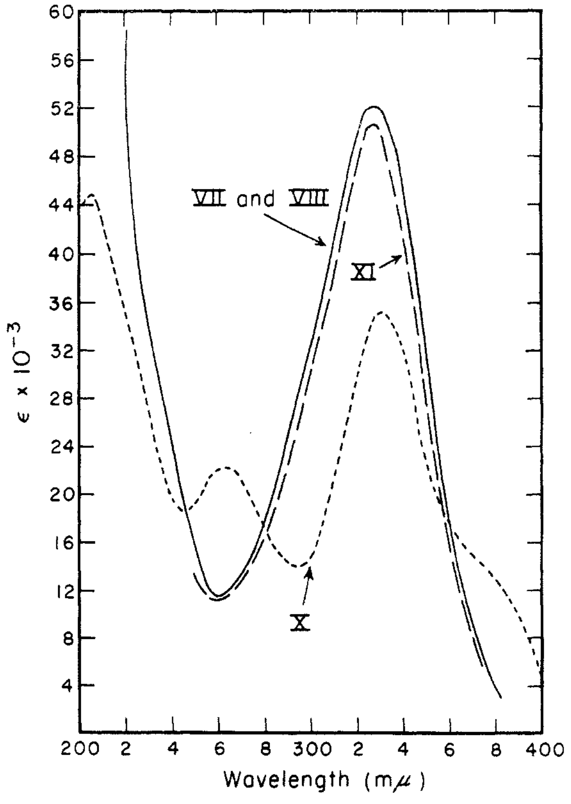


FIG. 3.—ULTRAVIOLET ABSORPTION SPECTRA OF THE SODIUM SALT OF VII, VIII, AND X IN WATER AND OF 4′,4″-BIS(2-ETHOXYBENZAMIDO)-*p*-TERPHENYL (XI) IN DIMETHYLFORMAMIDE.

4′,4″ - Bis(4 - methoxybenzamido) - *p* - terphenyl fails to react with concentrated sulfuric acid at 100°. More vigorous conditions (*e.g.*, oleum or chlorosul-

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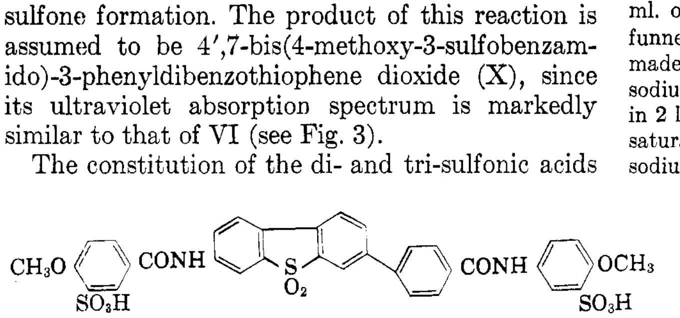
[4] C. C. Price and G. P. Mueller, *J. Am. Chem. Soc.*, **66**, 632 (1944).

[5] J. A. VanAllan, *J. Org. Chem.*, **19**, 56 (1954).

fonic acid) result in sulfonation accompanied by sulfone formation. The product of this reaction is assumed to be 4′,7-bis(4-methoxy-3-sulfobenzamido)-3-phenyldibenzothiophene dioxide (X), since its ultraviolet absorption spectrum is markedly similar to that of VI (see Fig. 3).

The constitution of the di- and tri-sulfonic acids of *o*-terphenyl has been well established.[2] The ultraviolet absorption spectra of these substances resemble closely the absorption spectrum of the parent *o*-terphenyl (see Fig. 4). There is no evidence of sulfone formation.



X

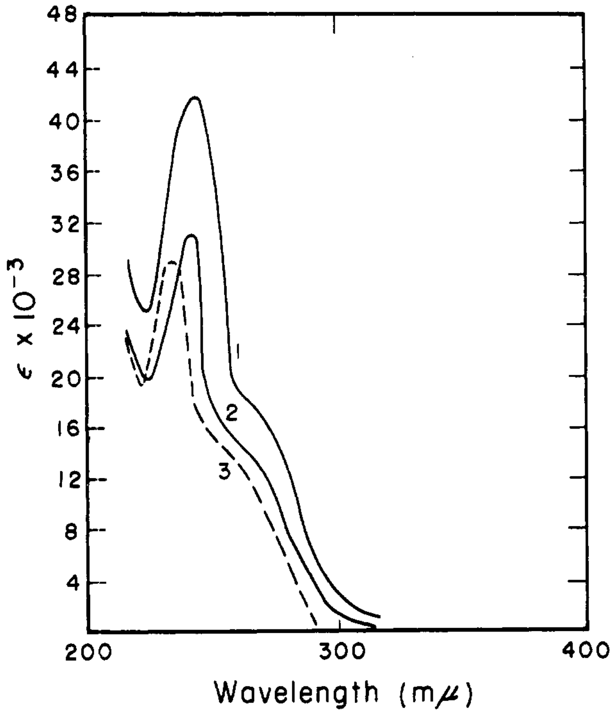


FIG. 4.—CURVE 1. POTASSIUM *o*-TERPHENYL-4,4″-X-TRISULFONATE IN WATER. CURVE 2. POTASSIUM *o*-TERPHENYL-4,4″-DISULFONATE IN WATER. CURVE 3. *o*-TERPHENYL IN CHLOROFORM.

The thiophene dioxide derivatives show a strong, pure blue fluorescence, while the *p*-terphenyl derivatives exhibit a greenish-blue fluorescence. The disulfone (IV) and the *o*-terphenyl derivatives show no fluorescence.

EXPERIMENTAL

4′,7-Disulfo-3-phenyldibenzothiophene dioxide (III). (*a*). First, 200 ml. of 20 percent oleum was added to 40 g. of *p*-terphenyl all at once. The temperature rose to 100°. Stirring and heating on the water bath at 95 to 100° was continued for 3 hours, after which time the reaction mixture had solidified. After cooling, the mixture was added to 200 ml. of water, cooled, and filtered through a sintered glass funnel. The filter cake was dissolved in 1.2 l. of hot water, made alkaline with sodium hydroxide, and the precipitated sodium salt was collected. The sodium salt was redissolved in 2 l. of hot water and salted out with an equal volume of saturated salt solution, giving 26 g. (29% yield) of the disodium salt of III.

(*b*). Alternately, 40 g. of *p*-terphenyl was added to 200 ml. of chlorosulfonic acid. The addition was conducted slowly because of the vigorous evolution of hydrogen chloride. When the addition was complete, the mixture was heated on the steam-bath for 1 hour. Complete solution ensued. The mixture was cooled and poured onto ice to precipitate the acid chloride. This was collected and dissolved in dilute sodium hydroxide. A little insoluble material was removed by filtration. The clear blue fluorescent filtrate then was treated with an equal volume (about 1200 ml.) of a hot, saturated salt solution and cooled to give 41 g. (46% yield) of the disodium salt of III. The analysis and physical properties of this and the following substances are collected in Table I.

Di-o-tolylguanidine salt of III. To a solution containing 10 g. of III as the disodium salt in 150 ml. of water was added 10 g. of 1,3-di-*o*-tolylguanidine hydrochloride in 150 ml. of water containing 3 ml. of concentrated hydrochloric acid. An immediate precipitate of the new salt was formed. The yield was 11.0 g. (81%).

The di-o-toluidine salt was made in a similar fashion in 89% yield.

X,X′-Disulfo-10,12-dithiaindeno[2,1b]fluorene 10,12-bis-dioxide (IV) was obtained in 53% yield by the sulfonation of *m*-terphenyl with 20% oleum, as described for the preparation of III. The di-*o*-toluidine salt and the di-*o*-tolylguanidine salt of IV were prepared in 83% yield and 89% yields, respectively.

3-(4-Sulfobiphenylyl)-7-sulfodibenzothiophene dioxide (V) was obtained in 47% yield by the sulfonation of *p*-quaterphenyl with 20% oleum as described for the preparation of III. It was analyzed as its disodium salt.

4′4″-Dinitro-p-terphenyl.[6] *p*-Terphenyl (40 g.) in 160 ml. of nitrobenzene was treated with 48 ml. of fuming nitric acid (*d.* 1.50) all at once. The temperature rose to 90° and all the starting material went into solution. On cooling, the product separated in a pure condition. One crystallization from nitrobenzene gave 33 g. (59%) of the dinitro-*p*-terphenyl, m.p. 270–271°.

4′,4″-Diamino-p-terphenyl.[4] By the use of dimethylformamide as a solvent, this amine may be readily prepared. Compare Ref. 6. A suspension of 40 g. of the dinitro compound in 250 ml. of dimethylformamide and about 6 g. of Raney nickel in a small Parr shaker was reduced at 90–95°. In about 3 hours, absorption of hydrogen gave a pressure drop of 58 lbs. (theory, 53). The colorless, blue fluorescent solution was filtered through Perlite and evaporated to dryness to give 32 g. (98%) of the diamine, m.p. 241–242°.

4′,4″-Bis(2-ethoxybenzamido)-p-terphenyl. o-Ethoxybenzoyl chloride (9.4 g.) was slowly added to 6.5 g. of the diamine, dissolved in 50 ml. of dry pyridine, and the mixture was heated on the steam-bath for 3 hours. After cooling, the product was filtered, washed well with water, and recrystallized from dimethyl sulfoxide; the yield was 10 g. (67%); m.p. 269° from dimethyl formamide.

Anal. Calc'd for $C_{36}H_{32}N_2O_4$: C, 77.8; H, 5.8. Found: C, 77.9; H, 5.5.

This substance had a U.V. spectrum of λ_{max} 327 mμ (ϵ, 50.4×10^{-3}) in dimethyl formamide.

The following two compounds were prepared in a similar fashion:

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(6) H. France, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 1364 (1938).

TABLE I

ANALYTICAL RESULTS AND SPECTRAL DATA

No.	Emp. Form.	Calc'd C	Calc'd H	Found C	Found H	M.p., °C.	λ_{max}, mμ	$\epsilon \times 10^{-3}$
I	$C_{18}H_{12}Na_2O_6S_2$	58.4	3.2	58.3	3.0	—	291	34.0[a]
Ia	$C_{32}H_{32}N_2O_6S_2$[b,c]	63.5	5.3	63.3	5.6	>270	—	—
III	$C_{18}H_{10}Na_2O_8S_3 \cdot H_2O$	42.0	2.0	42.0	2.0	—	257	30.2
							310	24.8[a]
IIIa	$C_{32}H_{30}N_2O_8S_3 \cdot 2H_2O$[b]	54.8[d]	4.3	54.8	4.8	>270	221	31.0
							256	35.0
							309	30.0
							335	12.7[e]
IIIb	$C_{48}H_{46}N_6O_8S_3 \cdot H_2O$[g,(c+e)]	60.9[f]	4.9	60.9	5.6	220–222	253	36.2
							309	31.2
							340	12.0[e]
IVa	$C_{32}H_{28}N_2O_{10}S_4 \cdot H_2O$[b]	51.4	3.8	50.8	4.3	>270	258	32.1
							278	67.3
							290	75.8[e]
Va	$C_{54}H_{42}N_6O_8S_3$[g,h]	65.0	4.2	64.8	4.6	195	208	88.0
							262	39.5
							318	43.0[e]
VI	$C_{30}H_{24}N_2NaO_{12}S_3$[l]	48.1	3.2	47.8	3.3	—	262	35.4
							329	35.4
							363	13.8
VIa	$C_{44}H_{44}N_4O_{12}S$[i,b,h]	57.5	4.8	57.1	5.0	258	260	36.7
							335	43.4
							363	15.7[e]
VII	$C_{48}H_{62}N_4O_{16}S_2$[j,(c+e)]	56.8	6.2	56.3	6.3	271	327	52.0[a]
VIII	$C_{46}H_{58}N_4O_{16}S_2$[j,(c+e)]	55.9	5.9	55.9	5.8	254	327	51.9[a]
IX	$C_{32}H_{22}N_2Na_2S_2O_{10}$	54.4	3.1	53.9	3.3	—	348	40.0
							317	38.0[k]
X	$C_{34}H_{28}N_2Na_2O_{12}S_3$	51.2	3.6	50.8	3.2	—	264	22.2
							330	35.1[a]

[a] In water. [b] Di-*o*-toluidine salt. [c] Crystallized from water. [d] Calc'd: N, 4.0; S, 13.6. Found: N, 4.1; S, 13.9. [e] Methanol. [f] Calc'd: N, 8.8; S, 10.2. Found: N, 8.7; S, 10.0. [g] *o*-Tolylguanidine salt. [h] From butanol. [i] Calc'd: N, 6.2; S, 10.5. Found: N, 6.5; S, 10.9. [j] Bistriethanolamine salt. [k] In dilute sodium hydroxide (see Ref. 5). [l] Calc'd: S, 12.9. Found: S, 12.6.

4',4"-Bis(2-methoxybenzamido)-p-terphenyl, m.p. 279° from dimethyl sulfoxide; yield 76%.

Anal. Calc'd for $C_{34}H_{28}N_2O_4$: C, 77.3; H, 5.3. Found: C, 77.1; H, 5.2.

The U.V. spectrum had λ_{max} 327 mμ (ϵ, 50.0 × 10^{-3}) in dimethyl sulfoxide.

4',4"-Bis(4-methoxybenzamido)-p-terphenyl, m.p. 282° from dimethyl sulfoxide, yield 79%.

Anal. Calc'd for $C_{34}H_{28}N_2O_4$: C, 77.3; H, 5.3. Found: C, 77.1; H, 5.1.

4',4"-Bis(2-ethoxy-5-sulfobenzamido)-p-terphenyl (VII). A mixture of sulfuric acid (23 ml.) and 7 g. of 4',4"-bis(2-ethoxybenzamido)-*p*-terphenyl was heated on the steam-bath. The starting material quickly dissolved to give a deep brown solution. After about 0.5 hour, the product began to separate. Heating was continued for a further 2 hours; then the mixture was cooled and filtered through a sintered glass funnel. The solid was slurried with methanol and again was filtered. The product then was taken up in distilled water and brought to neutrality with triethanolamine. The triethanolamine salt was precipitated by the addition of an equal volume of methanol. The product separated as a beautifully crystalline, pure white material; yield, 9.0 g.

The acid was hydrolyzed by refluxing a solution of 3 g. in 35 ml. of 65% sulfuric acid for 3 hours. The precipitated sulfate was converted to 4',4"-diamino-*p*-terphenyl, m.p. 241°, by dilute sodium carbonate. In an analogous manner, 4',4"-bis(2-methoxybenzamido)-*p*-terphenyl was sulfonated to give *4',4"-bis(2-methoxy-5-sulfobenzamido)-p-terphenyl* (VIII); this was analyzed as the bistriethanolamine salt.

4',4"-Bis(2-hydroxybenzamido)-p-terphenyl. A mixture of 1.3 g. of 4',4"-diamino-*p*-terphenyl and 2.14 g. of phenyl salicylate in 15 ml. of α-methylnaphthalene was refluxed for 2 hours. The product began to separate from the reaction mixture soon after the heating began. After cooling the product, 2.45 g. was filtered off, washed with ligroin, and crystallized from 400 ml. of α-chloronaphthalene to give 2.1 g. of the bis-hydroxybenzamide, m.p. >280°.

Anal. Calc'd for $C_{32}H_{24}N_2O_4$: C, 76.8; H, 4.8. Found: C, 77.6; H, 5.3.

The U.V. spectra had λ_{max} 348, 317 mμ (ϵ, 43 and 41 × 10^{-3}) in dilute NaOH.

4',4"-Bis(2-hydroxy-5-sulfobenzamido)-p-terphenyl (IX) was prepared by sulfonation of the bisamide in a similar manner. In this case, the aqueous solution was brought to neutrality with dilute sodium carbonate and the product was salted out; yield, 82%.

4',7-Bis(4-methoxy-3-sulfobenzamido)-3-phenyldibenzothiophene dioxide (X). 4',4"-Bis(4-methoxybenzamido)-*p*-terphenyl (3 g.) was added to 15 ml. of chlorosulfonic acid. When solution was complete, the mixture was heated to 95–100° for 40 min., cooled, and decomposed by pouring upon ice. The precipitate was collected on a sintered glass funnel and was dissolved in dilute sodium hydroxide to give a yellow, strongly fluorescent solution. Addition of ethanol to this aqueous solution gave the disodium salt of X, in a yield of 3.3 g.

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