hour. After being washed and dried, the solvent was evaporated. The solid obtained was recrystallized from ethanol. Compounds No. 20 and 23 were prepared by the method described above.

Unsymmetrical trisulfides. To a solution of 0.02 mole of alkyl hydrodisulfide (benzhydryl or benzyl hydrodisulfide) in 50 ml. of dry ether was added a solution of arenesulfenyl chloride (2-nitrobenzenesulfenyl, 2-nitro-4-chlorobenzenesulfenyl, or 2,4-dinitrobenzenesulfenyl chloride) in 50 ml. of dry ether at room temperature in a stream of inert gas under stirring. A very slight excess of the hydrosulfide was used, otherwise diaryl disulfide was formed from the arenesulfenyl chloride. This made it difficult to isolate the unsymmetrical from the symmetrical disulfide. The reaction system was protected against moisture by a calcium chloride tube. Stirring was continued for 2 hr., and the solution was washed, dried, and concentrated by evaporation. The solid obtained was recrystallized from ether.

For the synthesis of 2-naphthyl benzhydryl or benzyl trisulfide, 2-naphthalenesulfenyl thiocyanate was used in place of the sulfenyl chloride. The procedure was the same as for the above nitrophenyl alkyl trisulfides.

2,2'-Dinaphthyl mono-, di-, and trisulfides. These were also prepared as specimens for determining the spectra. The monosulfide was obtained by pyrolysis of lead 2-naphthalenethiolate[15] at 300–320° under 100 mm., and after several recrystallizations from a benzene-ethanol mixture, m.p. 148–149° (lit.,[15] m.p. 151°), the yield was 45%.

Anal. Calcd. for $C_{20}H_{14}S$: C, 83.88; H, 4.93; S, 11.20. Found: C, 84.04; H, 5.33; S, 11.0.

The disulfide was the oxidation product of 2-naphthalenethiol by iodine,[10] recrystallized from benzene, m.p. 139° (lit.,[10] m.p. 141.8–142.6°), yield 98%.

Anal. Calcd. for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43; S, 20.1. Found: C, 75.19; H, 4.33; S, 20.0.

The trisulfide was prepared by the ordinary method from the thiol and sulfur dichloride, recrystallized from benzene-ethanol mixture, m.p. 115–116° (Lit.,[16] m.p. 108–109°), yield 79%.

Anal. Calcd. for $C_{20}H_{14}S_3$: C, 68.53; H, 4.03; S, 27.45. Found: C, 68.75; H, 3.93; S, 26.8.

Determination of ultraviolet absorption spectra and molecular refraction. These were the same as those reported in Part I[8] of this series.

Acknowledgment. We wish to thank Dr. E. E. Campaigne of Indiana University for his kindness in revising the manuscript.

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(15) F. Krafft and R. Schönherr, *Chem. Ber.*, **22**, 825 (1889); N. A. Lange and H. S. Haupt, *J. Am. Chem. Soc.*, **51**, 2277 (1929).

(16) T. Hornung, *J. prakt. Chem.* [2], **60**, 137 (1899).

[CONTRIBUTION 984 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

The Ultraviolet Absorption Spectra of Some Unsymmetrical Disulfides[1]

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The ultraviolet absorption curves of certain unsymmetrical diaryl disulfides, Ar—S—S—Ar', were calculated as one-half the sum of the absorption curves of the two symmetrical disulfides, ArSSAr and Ar'SSAr'. Slight deviations from the calculated values in the observed curves were consistent with inductive effects of groups attached to sulfur in the two halves of the molecule, ArS— and Ar'S—. No transmission of electronic effects through the sulfur-sulfur bond could be detected in the ultraviolet spectra of the diaryl disulfides.

It is certain that disulfides undergo heterolytic cleavage in polar reactions. Nucleophilic cleavage of disulfide is evidenced by the reaction with organometallic reagents[3] and by Lewis-acid catalyzed electrophilic attack of disulfide on aromatic systems[4] and olefins.[5] Electrophilic cleavage may be illustrated by the reaction of disulfides with halides such as methyl iodide[6] or 2,4-dinitrochlorobenzene.[7] The whole question of heterolytic scission of the sulfur-sulfur bond in disulfides has recently been reviewed[8] with numerous examples of both types of cleavage. Such cleavage must be initiated by polarization of the disulfide bond.

Polarization of the disulfide bond may be considered to be stabilized by resonance involving a 10-electron sulfur shell, as in A ⟷ B. One might

A B

logically expect that placing a resonance system such as the two sulfur atoms of A ⟷ B between two chromophoric groups would be reflected in a bathochromic shift of the ultraviolet absorption of the simple chromophore. However, the opposite

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[2] Postdoctoral Research Associate 1959–1960, on leave from the University of Osaka Prefecture, Osaka, Japan.

(3) H. Burton and W. A. Davy, *J. Chem. Soc.*, 528 (1948).

(4) *Cf.* S. Archer and C. M. Suter, *J. Am. Chem. Soc.*, **74**, 4296 (1952); E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).

(5) *Cf.* B. Holmberg, *Arkiv Kemi, Mineral. Geol.*, **13B**, No. 14 (1939); A. Lein, D. McCauley, and A. Proell, U. S. Pat. **2,519,586**, Aug. 20, 1950 [*Chem. Abstr.*, **44**, 10728 (1950)].

(6) O. Haas and G. Dougherty, *J. Am. Chem. Soc.*, **62**, 1004 (1940).

(7) G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **45**, 832, 842 (1955).

(8) A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).

effect has been observed.[9] A sulfur atom attached to an aromatic system acts as an unsaturated atom, causing a bathochromic shift of the absorption of the parent aromatic system.[10] For example, benzene shows a characteristic absorption at 202 mμ ($\epsilon = 7000$) which is shifted to 236 mμ ($\epsilon = 10,000$) in thiophenol.[11] Conversion of —SH to —SCH_3 causes a further shift to longer wavelength (thioanisole absorbs at 254 mμ, $\epsilon = 9000$),[12] due to the inductive effect of the methyl group. However, oxidation to the disulfide causes a much smaller shift in absorption (diphenyl disulfide has an absorption maximum at 241 mμ, $\epsilon = 15,000$). The effect of conversion of a thiol to a symmetrical disulfide is approximately that of bonding two identical chromophores in the same molecule by an insulating group (*i.e.*, doubling the molar intensity without shifting the wavelength of absorption). Such effects were reported on thiol and disulfide groups attached to cinnamic acid systems.[9]

In the case of a symmetrical disulfide, the resonance represented by A ⟷ B is really the sum of two equivalent resonance structures of equal but opposite polarity, C ⟷ B:

$$\underset{\mathrm{C}}{\mathrm{Ar^a{-}\overset{-}{S}{=}\overset{+}{S}{-}Ar^b}} \longleftrightarrow \underset{\mathrm{A}}{\mathrm{Ar^a{-}S{-}S{-}Ar^b}} \longleftrightarrow \underset{\mathrm{B}}{\mathrm{Ar^a{-}\overset{+}{S}{=}\overset{-}{S}{-}Ar^b}}$$

The resonance contribution of the polar disulfide bond to the aromatic system might therefore be presumed to be neutralized, and the absorption of an aromatic disulfide, A, should be essentially that of two moles of the simple chromophore ArS-. On the other hand, an unsymmetrical diaryl disulfide, D, in which one aryl group carried electron releasing groups while the other carried strong electron attracting groups would be expected to polarize preferentially in one way, D ⟷ E. Such an

$$\underset{\mathrm{D}}{\mathrm{Ar{>}{-}\overset{-}{S}{-}\overset{+}{S}{>}{-}Ar'}} \longleftrightarrow \underset{\mathrm{E}}{\mathrm{Ar{>}{-}\overset{+}{S}{=}\overset{-}{S}{>}{-}Ar'}}$$

effect might be reflected in bathochromic shifts of the ultraviolet absorption. On the other hand, a lack of transmission of resonance through the disulfide bond should be characterized by an absorption spectrum which would be the sum of one-half of the spectra of the two corresponding symmetrical disulfides:

$$\epsilon_{\mathrm{arssar'}} = {}^1/_2(\epsilon_{\mathrm{arssar}} + \epsilon_{\mathrm{ar'ssar'}}) \;..$$

It is well known that the presence of an insulating group between two chromophores results in a spectrum in which the characteristic absorption of the two chromophores is generally additive.[13] The assumption is made that this relationship will not be valid if resonance is transmitted between the chromophores. This assumption is supported by the ultraviolet spectra of a series of stilbenes, where conjugation through the ethylenic linkage is well known.[14] The ultraviolet spectrum of *trans*-stilbene is characterized by a maximum at 295 mμ ($\epsilon = 29,000$)[15] and a shoulder at 324 mμ ($\epsilon = 17,000$)), while *trans*-4,4′-dinitrostilbene[16] has a peak at 333 mμ ($\epsilon = 29,000$). The hypothetical spectrum, one-half the sum of the spectra of these symmetrical stilbenes, exhibits a maximum at 295 mμ ($\epsilon = 25,000$) and a shoulder at 333 mμ ($\epsilon = 20,400$). The actual spectrum for *trans*-4-nitrostilbene shows only one peak at 355 mμ ($\epsilon = 27,000$).[15]

In order to examine the ultraviolet spectra of some unsymmetrical diaryl disulfides, a series of 4-nitrophenyl and 2,4-dinitrophenyl disulfides were prepared, in which the second aryl group was of the electron-rich class, phenyl, 4-tolyl, 4-anisyl, and β-naphthyl. These were chosen because they were all solids which could be purified by recrystallization. Unsymmetrical disulfides disproportionate on heating[17] or in acidic or basic solution[8] and are therefore difficult to obtain in the pure state. The compounds most commonly prepared in this class are those which are formed from treatment of the relatively stable nitrosulfenyl halides with thiols. These products are usually solids which can be purified by crystallization from cold solvents of low dielectric constant. They also contain a strong electron-attracting group, and hence are ideally suited to this study. The preparative detail and constants of these compounds are listed in Table I, parts A and B, and the syntheses described in the experimental part. Of these, the 4-methoxyphenyl and β-naphthyl derivatives are new.

As model compounds for spectral studies, the various symmetrical disulfides and corresponding methyl sulfides were prepared. Their properties are listed in Table I, parts C and D.

Discussion of the absorption spectra. The principal absorption maxima of all compounds investigated are tabulated in Table II. (All of the compounds absorb strongly in the far ultraviolet (below 220 mμ).) However, each simple methyl sulfide exhibits

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(9) E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 32 (1956).

(10) K. Bowden, E. A. Braude, and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(11) *Cf. An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd Ed., by A. E. Gillam and E. S. Stern, E. Arnold, London, 1957, p. 140.

(12) E. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(13) A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, 2nd Ed., E. Arnold Ltd., London, 1957, p. 134.

(14) M. Calvin and R. E. Buckles, *J. Am. Chem. Soc.*, **62**, 3324 (1940).

(15) M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 765 (1951).

(16) Prepared according to the procedure of Walden and Kernbaum, *Ber.*, **23**, 1959 (1890). The spectrum was determined on a Carey Model 14 spectrophotometer. Absolute ethanol was used as a solvent in order to obtain data comparable to that of Calvin and Alter.

(17) G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **44**, 63 (1954).

TABLE I

PHYSICAL CONSTANTS OF DIARYL DISULFIDES AND ARYL METHYL SULFIDES

Ar	M.P.		Formula	Sulfur, %		Nitrogen, %	
	Found	Reported		Calcd.	Found	Calcd.	Found
			A. 4-NITROPHENYL ARYL DISULFIDES				
C_6H_5-	59–59.5	58–58.5[a]	$C_{12}H_9O_2NS_2$	24.35	24.26	5.23	5.41
4-$CH_3C_6H_4$-	63–63.5	62–62.5[a]	$C_{13}H_{11}O_2NS_2$	23.12	23.09	5.05	5.17
4-$CH_3OC_6H_4$-	72.5–73		$C_{13}H_{11}O_3NS_2$	21.86	21.86	4.77	4.89
β-$C_{10}H_7$-	85–85.5		$C_{16}H_{11}O_2NS_2$	20.46	20.47	4.47	4.59
			B. 2,4-DINITROPHENYL ARYL DISULFIDES				
C_6H_5-	87.5–88	86–87[a]	$C_{12}H_8O_4N_2S_2$	20.80	20.49	9.09	9.20
4-$CH_3C_6H_4$-	114–115	114–115[a]	$C_{13}H_{10}O_4N_2S_2$	19.89	19.76	8.69	8.65
4-$CH_3OC_6H_4$-	98		$C_{13}H_{10}O_5N_2S_2$	18.91	18.92	8.28	8.38
β-$C_{10}H_7$-	181		$C_{16}H_{10}O_4N_2S_2$	17.89	17.65	7.82	7.89
			C. SYMMETRICAL DISULFIDES				
C_6H_5-	62.5–63.5	61[b]	$C_{12}H_{10}S_2$				
4-$CH_3C_6H_4$-	48–49	46[b]	$C_{14}H_{14}S_2$				
4-$CH_3OC_6H_4$-	44–45	44–45[c]	$C_{14}H_{14}O_2S_2$				
β-$C_{10}H_7$-	143–143.5	139[d]	$C_{20}H_{14}S_2$				
4-$NO_2C_6H_4$	183–184	181[a]	$C_{12}H_8N_2O_4S_2$				
	M.P.			n_D^{25}		B.P.	
			D. ARYL METHYL SULFIDES				
C_6H_5-				1.5839 (1.5832)[e]		84/18 mm. (82/18 mm.)[f]	
4-$CH_3C_6H_4$-				1.5707 (1.5730-20/D)[g]		104/20 mm. (104–105/20 mm.)[h]	
4-$CH_3OC_6H_4$-	25–26	26[i]					
β-$C_{10}H_7$	59.5–60.5	60[j]					
4-$NO_2C_6H_4$-	71–72	72[g]					
2,4-$(NO_2)_2C_6H_3$-	128–129	128[k]					

[a] I. Danielsson, J. E. Christian, and G. L. Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **36**, 261 (1947). [b] K. W. Rosenmund and H. Harms, *Ber.*, **53B**, 2226 (1920). [c] A. J. Costanza, R. J. Coleman, R. M. Pierson, C. S. Marvel, and C. King, *J. Polymer Sci.*, **17**, 319 (1955). [d] S. S. Bhatnagar and B. Singh, *J. Indian Chem. Soc.*, **7**, 663 (1930). [e] C. M. Suter and H. L. Hansen, *J. Am. Chem. Soc.*, **54**, 4100 (1932). [f] M. P. Balfe, R. E. Darby, and J. Kenyon, *J. Chem. Soc.*, 382 (1951). [g] K. Brand and K. W. Kranz, *J. prakt. Chem.*, (2) **115**, 143 (1927). [h] H. Gilman and N. J. Beaber, *J. Am. Chem. Soc.*, **47**, 1449 (1925). [i] F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957). [j] H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, **4**, 342 (1921). [k] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

a characteristic peak; those of the electron-rich aromatic series in the vicinity of 255 mμ (280 mμ for the naphthyl compound), and those of the nitroaromatic series at about 335 mμ (Table II, part A). The symmetrical disulfides exhibit similar peaks of approximately twice the molar intensity, but shifted hypsochromically. This hypsochromic shift is consistent ($\Delta\lambda = -13 \pm 1$) when the aryl group has electron-releasing groups, but is nearly twice as great when the aryl group is *p*-nitrophenyl. Since the absorption maximum in this case is above 300 mμ, the magnitude of the shift would be expected to be greater. The β-naphthyl derivatives show a much more intense absorption in the 250 mμ range, but the effect of varying the sulfur function is decreased. In the case of the 2,4-dinitrophenyl derivatives, the disulfide was too insoluble in 95% ethanol to obtain a reliable absorption spectrum. The absorption of the methyl sulfide would, however, lead to a prediction of a peak at 310 mμ ($\epsilon = 18{,}000$) by analogy with the 4-nitro analogs.[18]

One-half the absorption of the symmetrical disulfide was taken as the normal absorption of the radical Ar-S-. Assuming no transmission of resonance effects by the disulfide link, as was previously indicated,[9] the absorption spectrum of the unsymmetrical disulfide was calculated as one-half the sum of the two symmetrical disulfides. The results of such calculation are shown in Figs. 1, 2, and 3, on which such a calculated curve is plotted, along with the observed absorption curves of the unsymmetrical and corresponding pair of symmetrical disulfides.

There is very close congruity of the calculated and observed curves in each of the three examples. The significant deviations are a small bathochromic shift of the *p*-nitrophenyl sulfur peak, and a larger hypsochromic shift in absorption of the electron-releasing arylsulfur moiety. These shifts are readily accounted for as inductive effects of functions attached to a sulfur atom which is in turn attached to an aromatic nucleus. For example the observed *p*-nitrophenyl sulfur peaks for the unsymmetrical

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(18) G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **45**, 180 (1955) report λ_{max} 332 mμ, log ϵ 4.03 for bis-2,4-dinitrophenyl disulfide in ethanol.

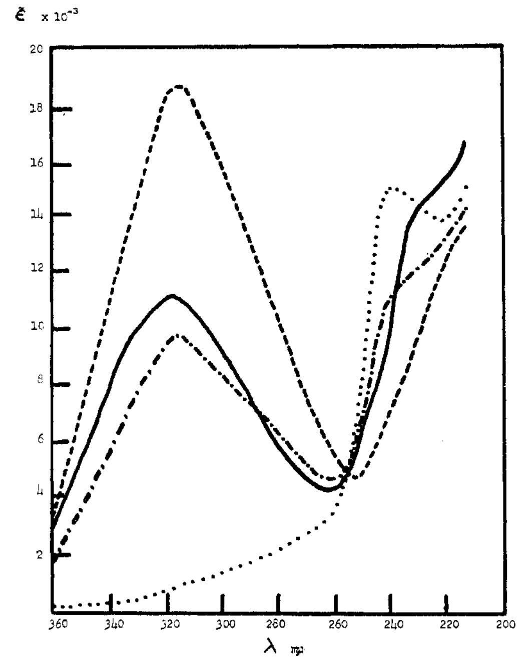

Fig. 1. ——— Absorption spectra of bis-4-nitrophenyl disulfide – – – –; diphenyl disulfide. . . . ; 4-nitrophenyl phenyl disulfide (observed) ———; 4-nitrophenyl phenyl disulfide (calculated) — · —

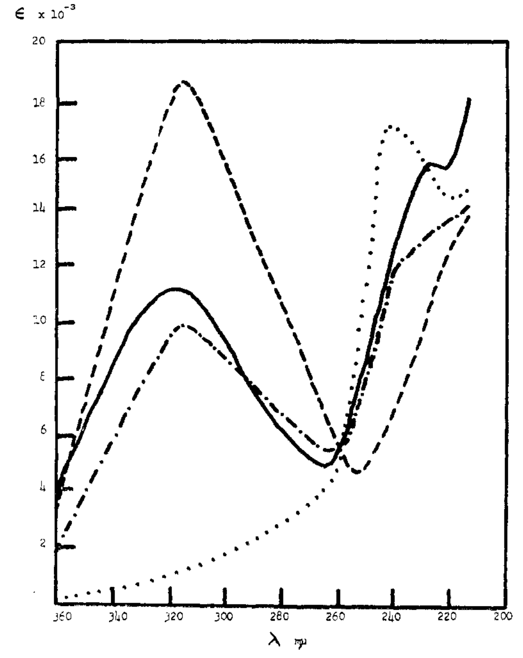

Fig. 2. ——— Absorption spectra of bis-4-nitrophenyl disulfide – – – –; bis-4-tolyl disulfide . . . . ; 4-nitrophenyl 4'-tolyl disulfide (observed) ———; 4-nitrophenyl 4'-tolyl disulfide (calculated) — · —

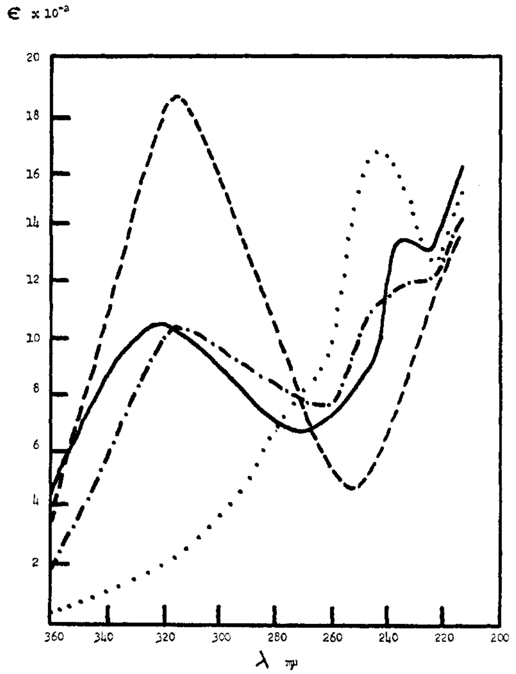

Fig. 3. ——— Absorption spectra of bis-4-nitrophenyl disulfide – – – –; bis-4-methoxyphenyl disulfide . . . . ; 4-nitrophenyl 4'-methoxyphenyl disulfide (observed) ———; 4-nitrophenyl 4'-methoxyphenyl disulfide (calculated) —. —

disulfide in Figs. 1, 2, and 3 are shifted bathochromically +2, +3, and +8 mμ, corresponding to the inductive effect of increasingly higher electron density of the substituent attached to sulfur. On the other hand, the observed peaks for the electron-releasing aryl sulfur chromophore in Figs. 1, 2, and 3 are shifted hypsochromically −13, −13, and −9 mμ, respectively, corresponding to the inductive effect of an electronegative group attached to the sulfur atom of the chromophore.

Similar shifts occur in the spectra of the 2,4-dinitrophenyl disulfides as can be seen by comparison of the peaks shown in Table II. These are somewhat more complicated, probably due to *ortho*-effect. A similar result is also apparent in the two unsymmetrical disulfides derived from β-naphthalenethiol. Here again the picture is more complex due to the more intense absorption of the chromophore. In this case the hypsochromic shift of attaching an electronegative group to sulfur is magnified (−16 mμ for *p*-nitrophenylsulfur and −20 mμ for 2,4-dinitrophenylsulfur).

One must conclude from these results that no electronic effects are transmitted through a disulfide bond. Any stabilization of the polarized sulfur-sulfur bonds, as in D⟵⟶E, by expansion of the valence shell of sulfur, is not reflected in the ultraviolet absorption spectra. The ultraviolet spectra are more properly explained by a simple inductive polarization as in $\mathrm{Ar} \gg\!\!-\overset{\delta-}{\mathrm{S}}-\overset{\delta+}{\mathrm{S}}\gg\!\!-\mathrm{Ar'}$.[19]

The absorption curves of unsymmetrical disulfides then may be approximated as the sum of the absorptions of the two halves of the molecule, ArSX and Ar'SY. The absorption of each half may be calculated as one-half the absorption of the corresponding symmetrical disulfide, with suitable

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(19) For a discussion of the spectrum and properties of the elongated polarized disulfide bond, see H. P. Koch, *J. Chem. Soc.*, 394 (1949).

allowance for shifting of peaks due to the inductive effects of the groups X and Y attached to sulfur.

EXPERIMENTAL[20]

Ultraviolet absorption measurements. The ultraviolet absorption spectra were determined with a Beckman model DK-1 recording quartz spectrophotometer equipped with a hydrogen discharge tube and 1-cm. silica cells. All of the spectra were measured down to the wave-length vicinity of 215 mμ. The wave lengths and molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table II.

TABLE II

Ultraviolet Absorption Spectra of Diaryl Disulfides and Aryl Methyl Sulfides[a]

		Maxima[c]	
Compound	Source[b]	λ (mμ)	ε
A. Aryl Methyl Sulfides			
Phenyl methyl sulfide	1	254	8,700
4-Tolyl methyl sulfide	1	255	9,500
4-Methoxyphenyl methyl sulfide	2	256	8,200
β-Naphthyl methyl sulfide	1	280	7,600
		252	30,400
4-Nitrophenyl methyl sulfide	5	338	11,100
2,4-Dinitrophenyl methyl sulfide	3	331	11,100
		267	5,800
B. Symmetrical Disulfides			
Diphenyl disulfide	4	241	15,000
Bis-4-tolyl disulfide	4	242	17,000
Bis-4-methoxyphenyl disulfide	5	244	16,700
Bis-4-nitrophenyl disulfide	5	316	18,600
Bis-2,4-dinitrophenyl disulfide	6	332	10,700[d]
Di-β-naphthyl disulfide	4	248	44,300
C. Unsymmetrical Disulfides			
4-Nitrophenyl phenyl disulfide	7	318	11,200
		(228)	14,400
4-Nitrophenyl 4′-tolyl disulfide	7	319	11,200
		228	15,700
4-Nitrophenyl 4′-methoxyphenyl disulfide	5	322	10,600
		235	13,600
4-Nitrophenyl β-naphthyl disulfide	5	317	10,900
		232	36,400
2,4-Dinitrophenyl phenyl disulfide	7	311	7,200
		(265)	8,000
		(235)	12,700
2,4-Dinitrophenyl 4′-tolyl disulfide	7	310	9,300
		(265)	10,500
		(235)	17,300
2,4-Dinitrophenyl 4′-methoxyphenyl disulfide	5	311	10,000
		242	17,700
2,4-Dinitrophenyl β-naphthyl disulfide	5	(285)	26,000
		228	95,000

[a] All spectra were determined in 95% ethanol. [b] Source references: (1) prepared by methylating the corresponding thiol with dimethyl sulfate in alkali; (2) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79,** 717 (1957); (3) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54,** 1985 (1932); (4) prepared by oxidation of the appropriate thiol; (5) see section on "Preparation of Compounds"; (6) G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **45,** 180 (1955); (7) I. Danielsson, J. E. Christian, and G. L. Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **36,** 261 (1947); [c] The wave lengths in parentheses denote inflection points. [d] Data of Ref. b (6).

Preparation of compounds. All of the pure compounds used in this study were recrystallized or redistilled immediately before the spectra were determined. The physical constants of all the previously known compounds checked closely with reported results. These physical constants are listed in Table I.

Bis-4-nitrophenyl disulfide was prepared by a modification of the procedure in *Organic Syntheses.*[21] Sodium disulfide solution[21] (0.375 mole) was added slowly to a solution of 0.5 mole of *p*-chloronitrobenzene (78.8 g., m.p. 84–86°) in 500 ml. of 95% ethanol. The mixture was then heated on a steam bath, gently at first, then at full heat for 2 hr. After cooling, the solid was filtered, stirred thoroughly with water, filtered, and washed with ethanol.

The product was purified by the method of Zincke.[22] The crude product (51 g., 33%) was placed in 200 ml. of ethanol and the solution brought to reflux. To this solution was added a concentrated aqueous solution of 20.4 g. of crystalline sodium sulfide and 10.2 g. of sodium hydroxide. The apparatus was shaken vigorously for about 20 min., whereupon the mixture was diluted with 8–10 volumes of water, and filtered. The filtrate was acidified with dilute hydrochloric acid and oxidized with aqueous ferric chloride solution. Upon cooling, the crystals were filtered and recrystallized from glacial acetic acid to give 18 g. (12%) of yellow needles melting at 183°.

4-Methoxybenzenethiol was prepared by the method reported for *m*-thiocresol in *Organic Syntheses.*[23] Eighteen grams (0.15 mole) of powdered *p*-anisidine (m.p. 62°) was diazotized, converted to *p*-methoxyphenyl ethyl xanthate, hydrolyzed with potassium hydroxide, and then acidified with sulfuric acid. The crude thiol was distilled with steam, and then distilled under vacuum, to yield 38 g. (24%) of colorless oil, 134°/5.4 mm.

General procedure for the preparation of 4-nitrophenyl aryl disulfides. The procedure used was a modification of that by Danielsson and co-workers.[24] According to this procedure a desired unsymmetrical disulfide can be prepared without isolating the sulfenyl chloride, due to the extreme sensitivity of the sulfenyl chloride to moisture. The finely powdered bis-4-nitrophenyl disulfide (3.08 g., 0.01 mole) was suspended in 40 ml. of chloroform in a three necked flask equipped with a thermometer, gas-inlet tube, and condenser, the top of which was protected with a calcium chloride drying tube, and carbon tetrachloride bubble trap.[25] As a slow stream of chlorine gas was passed into the mixture, the color of the solution turned dark yellow, and the suspended disulfide gradually disappeared. The current of chlorine was continued for 30 min. after the solution became homogeneous. The excess chlorine was then expelled with nitrogen gas. The passage of gases was regulated by maintaining an even flow through the carbon tetrachloride trap as the temperature changed in the reaction mixture. Through a funnel, which replaced the gas-inlet tube, 0.02 mole of the arenethiol in 20 ml. of chloroform was added dropwise to the sulfenyl chloride solution under reflux. After the thiol was added, the solution was refluxed for another hour, during which time small amounts of copper-bronze were added if the color of

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[20] Microanalyses were performed by Miss Joanna Dickey and Midwest Microlab, Inc. All melting points are uncorrected.

[21] M. T. Bogert and A. Stull, *Org. Syntheses,* **Coll. Vol. I,** 220 (1941).

[22] Th. Zincke and S. Leuhart, *Ann.*, **400,** 7 (1913).

[23] D. S. Tarbell and D. K. Fukushima, *Org. Syntheses,* **Coll. Vol. III,** 809 (1955).

[24] I. Danielsson, J. E. Christian, and G. L. Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **36,** 261 (1947).

[25] M. H. Hubacher, *Org. Syntheses,* **Coll. Vol. II,** 455 (1943).

the sulfenyl chloride had not disappeared. The mixture was then filtered, the solvent removed under vacuum, and the solid product recrystallized from *n*-hexane. During each recrystallization, some insoluble bis-4-nitrophenyl disulfide had to be removed before crystallization was allowed to proceed.

General procedure for the preparation of 2,4-dinitrophenyl aryl disulfides. One-hundredth mole of 2,4-dinitrobenzenesulfenyl chloride, freshly recrystallized from carbon tetrachloride (m.p. 98°) was dissolved in 100 ml. of hot, dry ether and placed in a three necked flask fitted with a thermometer, dropping funnel, and a reflux condenser, the top of which was protected with a calcium chloride drying tube. To this solution was added dropwise 0.01 mole of the arenethiol in 30 ml. of dry ether. In the case of β-naphthlenethiol, 140 ml. of dry ether was required because of the insolubility of this compound in ether. After the thiol addition was complete, the mixture was refluxed for an additional 2 hr. During this time evolution of hydrogen chloride was observed. The solution was then allowed to stand overnight without heating. The solvent was then removed and the product recrystallized from a mixture of ethanol and benzene.

4-Nitrophenyl methyl sulfide was prepared by reducing bis-4-nitrophenyl disulfide to the thiol according to the procedure of Zincke[22] as reported above. The thiol was then methylated with dimethyl sulfate in alkali. The product was recrystallized from 95% ethanol to give light yellow needles, m.p. 71–72°. The reported melting point[26] is 72.°

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[26] K. Brand and K. W. Kranz, *J. prakt. Chem.*, (2) **115**, 143 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Ultraviolet Spectra of Triptycene Derivatives

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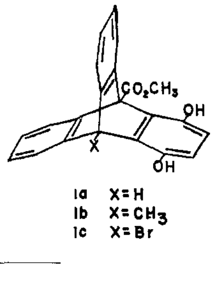
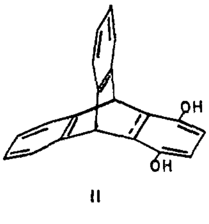
The preparation and ultraviolet spectra of several bridgehead derivatives of 2,5-dihydroxytriptycene are reported. It is shown that these spectra can be successfully interpreted by the model previously developed for triptycene. The bridgehead substituents have a negligible effect on the spectra.

Recently a model was developed for the interpretation of the ultraviolet spectrum of triptycene.[2] According to this model the triptycene spectrum is essentially that of an *o*-substituted benzene which, however, has been slightly displaced by interaction of the weak transition dipoles. An extension of this model to triptycenes which are substituted in one of the rings suggests that their ultraviolet spectra should be approximately the sum of the bands found in the three separate chromophores. This is only an approximation since weak interactions similar to those in triptycene should occur in such derivatives. The particular triptycene derivatives to be considered in this paper are methyl 2,5-dihydroxy-1-triptoate, Ia, methyl 6-methyl-2,5-dihydroxy-1-triptoate, Ib, methyl 6-bromo-2,5-dihydroxy-1-triptoate, Ic, as well as the simpler 2,5-dihydroxtriptyrene, II. With these molecules it should be possible to not only test the extension of the spectral model but also to determine what effect, if any, the isolated bridgehead substituents have on the spectra.

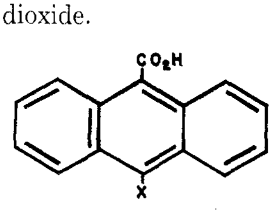


Ia X=H
Ib X=CH_3
Ic X=Br



II

Preparation of 6-bridgehead derivatives. The 6-bridgehead derivatives were prepared from the appropriately substituted anthroic acids by the same sequence employed by Bartlett and Greene[3] for Ia. Accordingly, 9-anthroic acid, IIIa, was synthesized in 80% yield by the metallation of 9-bromoanthracene with phenyllithium followed by reaction of the organometallic intermediate with carbon dioxide.



IIIa X=H
IIIb X=CH_3
IIIc X=Br

This method in our hands proved to be superior to that of the Latham, May, and Mosettig procedure[4] which gave 9-anthroic acid in 62% yield by reaction of oxaylyl chloride with anthracene. The substituted acids, IIIb and IIIc, were prepared by the procedure of Mikhaĭlov and Bronovitskaya.[5] This involved the preparation of the organo lithium

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[1] Based in part on the Ph.D. dissertation of A. C. Craig, Dept. of Chemistry, Cornell University, 1959.

[2] C. F. Wilcox, Jr., *J. Chem. Phys.*, in press; Dr. Edel Wasserman has informed us that he has carried out an excition treatment of triptycene (Ph.D. dissertation, Harvard, 1958). We would like to acknowledge an enlightening discussion of this treatment with Dr. Wasserman.

[3] P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

[4] H. G. Latham, Jr., E. L. May, and E. Mosettig, *J. Am. Chem. Soc.*, **70**, 1079 (1948).

[5] B. N. Mikhaĭlov and V. P. Bronovitskaya, *Zhur. Obshceĭ. Khim.*, **22**, 157 (1952).