10. *Absorption Spectra in the Near-ultraviolet of Some Thiolsulphonates.*

By G. Leandri, A. Mangini, and A. Tundo.

The spectra of methyl and phenyl benzenethiolsulphonate, and of various methyl-, chloro-, bromo-, methoxy-, and nitro-derivatives of the latter are recorded in *cyclo*hexane and in ethyl alcohol. The spectra are analyzed, by comparison among themselves and with the spectra of simple aromatic compounds, and the upper states to which the principal band systems are assigned are approximately described. The small modifying effects of methyl-, halogeno-, and methoxy-substituents, all groups which can hyperconjugatively or conjugatively supply electrons, are exerted notably from the *para*-position of the ring bound to the electron-attracting sulphone group, and the main effect is on bands with a transition moment in the line of the substituents. The larger modifying effect of the electron-attracting nitro-group is exerted chiefly from the *para*-position of the ring bound to thiol sulphur, which is able conjugatively to supply electrons. A much smaller effect is exerted from the *ortho*-position, presumably owing to steric twisting. There is evidence of specific interaction between ethyl alcohol and some of the nitrophenylthiol compounds.

As two of us have been investigating the chemical reactivity of aromatic thiolsulphonates [1] it seemed convenient to include this group of substances in the general investigation which is being made [2] into structural effects on the absorption spectra of aromatic sulphur compounds.

In the Table and in Figs. 1—3, we record the near-ultraviolet absorption spectra of two fundamental compounds of the series, methyl and phenyl benzenethiolsulphonate, (I) and (II), as well as those of a number of derivatives of (II) with a methyl, halogen, methoxyl, or nitro-substituent in either, or in each, ring, and also that of the polymethylated derivative, mesityl mesitylenethiolsulphonate (III). The solvents employed were *cyclo*hexane and ethyl alcohol, but the effect of solvent on the spectrum seems to be small in this series, except for certain nitro-derivatives.

(I) Ph·SO$_2$·SMe (II) Ph·SO$_2$·SPh (III) $C_6H_2Me_3$·SO$_2$·S·$C_6H_2Me_3$

Naturally, the simplest spectrum is that of compound (I): it has two absorption systems in the spectral range investigated. The weaker, at 260—280 mμ, displays some vibrational structure, with a band separation, 5—6 mμ, approximately agreeing with that expected for a breathing vibration of the benzene ring. The wavelength, the appearance of the vibrational progression, and the intensity (allowing that the apparent intensity of this system must be somewhat raised by overlapping) all suggest that the upper state involved is essentially the first singlet excited state of the aromatic π shell, the state of symmetry B_{2u} in benzene itself. The smallness of the modification which the transition to the state suffers on account of the MeS·SO$_2$ substituent might have been expected for two reasons. First, it has been shown in the example of aromatic sulphones [3] that conjugation between linked Ph and SO$_2$ groups is spectrally weak, unlike that between phenyl and sulphur in sulphoxides,[4] in thiosulphoxides,[5] and, still more, in sulphides.[6] Secondly, a weak perturbation by a single substituent will act particularly weakly on a transition to a B_{2u}-like upper state, since the transition will be much less affected than are the separate combining states.

The stronger system reaches its first maximum at 220 mμ, and runs smoothly to shorter wavelengths. This system has approximately the frequency and intensity expected for

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[1] Leandri and Tundo, *Ann. Chim. appl.*, 1954, **44**, 255, 264, 271.

[2] Mangini and Passerini, *J.*, 1952, 1168; Mangini *et al.*, *Gazzetta*, 1954, **84**, 3, 36, 47, 73, 606; Mangini and Passerini, *Experientia*, 1956, **12**, 49.

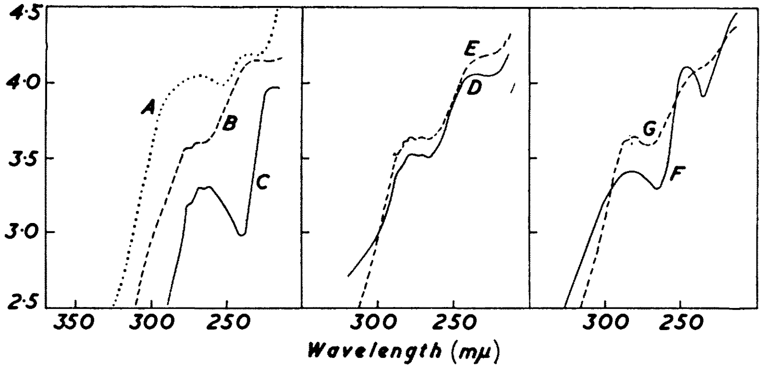
[3] Leandri, Mangini, and Passerini, *Gazzetta*, 1954, **84**, 73.

[4] Leandri *et al.*, unpublished.

[5] Baker and Kloosterziel, *Rec. Trav. chim.*, 1954, **73**, 129.

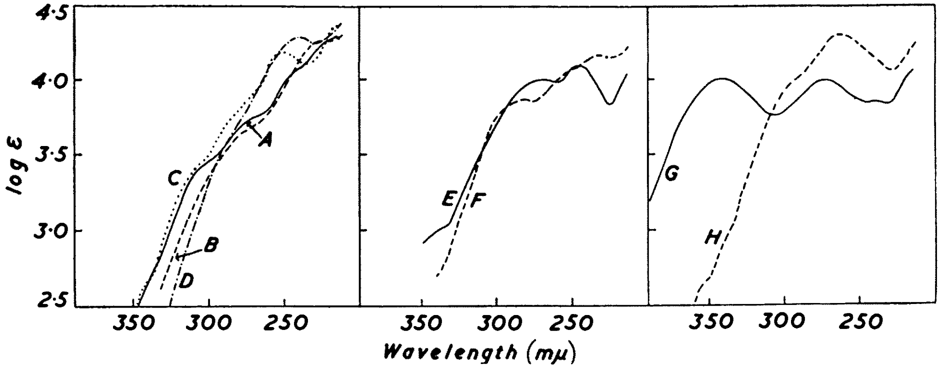
[6] Mangini and Passerini, ref. 2; Mangini *et al.*, *Gazzetta*, 1954, **84**, 3.

FIG. 1.



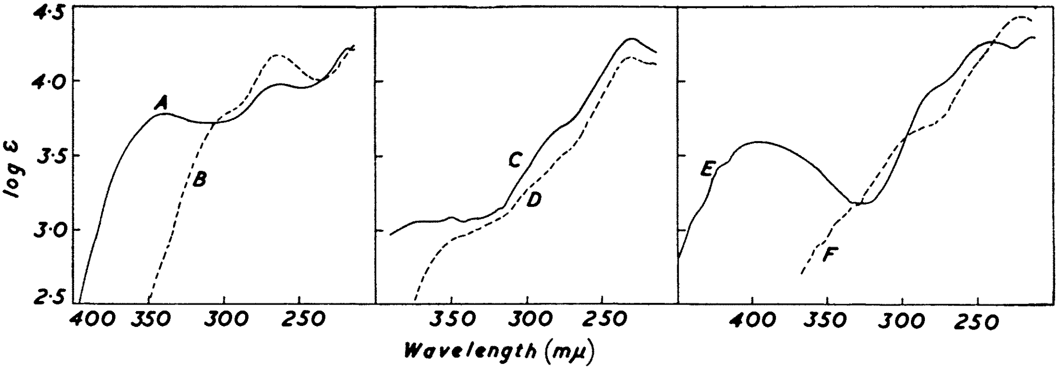
A, $2:4:6\text{-}(CH_3)_3C_6H_2{\cdot}S{\cdot}SO_2{\cdot}C_6H_2(CH_3)_3\text{-}2:4:6$ in *cyclo*hexane.
B, $Ph{\cdot}S{\cdot}SO_2{\cdot}Ph$ in *cyclo*hexane.
C, $CH_3{\cdot}S{\cdot}SO_2{\cdot}Ph$ in *cyclo*hexane.
D, $o\text{-}Cl{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}Ph$ in ethanol.
E, $o\text{-}Cl{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}Ph$ in *cyclo*hexane.
F, $o\text{-}Cl{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_6H_4Cl\text{-}o$ in ethanol.
G, $o\text{-}Cl{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_6H_4Cl\text{-}o$ in *cyclo*hexane.

FIG. 2.



$o\text{-}NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}Ph$ in : *A*, ethanol; *B*, *cyclo*hexane.
$m\text{-}NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}Ph$ in : *C*, ethanol; *D*, *cyclo*hexane.
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}Ph$ in : *E*, ethanol; *F*, *cyclo*hexane.
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2\text{-}p$ in : *G*, ethanol; *H*, *cyclo*hexane.

FIG. 3.



$p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}Ph$ in : *A*, ethanol; *B*, *cyclo*hexane.
$o\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}Ph$ in : *C*, ethanol; *D*, *cyclo*hexane.
$o\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2\text{-}o$ in : *E*, ethanol; *F*, *cyclo*hexane.

No.	Thiosulphonates, $R{\cdot}S{\cdot}SO_2{\cdot}R'$			In C_6H_{12}		In EtOH	
	R	R′		λ (mμ)	log ε	λ (mμ)	log ε
(1)	Me	Ph	B. p. 173°/10 mm.	220	3·97 (*a*)	220	3·96 (*a*)
				(240	2·97)	(238	3·06)
				262	3·30	262	3·31
				(265	3·28)	(266	3·30)
				268	3·30	267—268	3·31
				276	3·17 (*b*)	275	3·19 (*b*)
(2)	Ph	Ph *	M. p. 45°	228	4·15 (*a*)	230	4·13 (*a*)
				(266	3·59)	270	3·60
				270	3·61	274	3·57 (*c*)
				275	3·56 (*c*)	(278	3·55)
(3)	o-C_6H_4Me	Ph	M. p. 57—58°	228	4·11 (*b*)	225	4·08
				269	3·70 (*b*)	259	3·78 (*b*)
				(274	3·65)	275	3·66 (*d*)
				276	3·66		
(4)	p-C_6H_4Me	Ph	M. p. 54°	222	4·16 (*d*)	228	4·15 (*a*)
				270—275	3·70 (*b*)	270—275	3·76 (*c*)
(5)	Ph	p-C_6H_4Me	M. p. 74—75°	236	4·28	237	4·22
				271	3·63	268	3·65 (*a*)
				266—272	3·63 (*a*)	276	3·60 (*b*)
				275	3·58 (*d*)		
(6)	o-C_6H_4Me	o-C_6H_4Me	M. p. 55—56°	233	4·12 (*a*)	220—229	4·16 (*d*)
				(270	3·69)	267—274	3·72 (*d*)
				276	3·72	276	3·76
				285	3·68 (*c*)	284	3·71 (*c*)
(7)	p-C_6H_4Me	p-C_6H_4Me	M. p. 76°	236	4·20	236	4·25
				267	3·72 (*e*)	267	3·84 (*e*)
				276	3·63 (*c*)	278	3·74 (*d*)
(8)	2 : 4 : 6-$C_6H_2Me_3$	2 : 4 : 6-$C_6H_2Me_3$	M. p. 132°	235	4·18 (*a*)	235	4·17
				(253	3·98)	(254	3·95)
				266	4·04 (*a*)	270	4·04
				290	3·88 (*c*)	280	4·01 (*f*)
						293	3·86 (*b*)
(9)	o-C_6H_4Cl	Ph	M. p. 63—64°	230	4·15 (*e*)	230	4·08 (*c*)
				268	3·59 (*b*)	268	3·57 (*e*)
				(274	3·56)	(276	3·55)
				278	3·58	278	3·56
				290	3·45 (*c*)	290	3·43 (*c*)
(10)	p-C_6H_4Cl	Ph	M. p. 71—72°	242	4·21	236	4·17 (*a*)
				270	3·80 (*b*)	270	3·75 (*b*)
(11)	Ph	o-C_6H_4Cl	M. p. 79°	235	4·17 (*f*)	236	4·06 (*a*)
				(267	3·62)	(266	3·50)
				272	3·64 (*a*)	272	3·52
				(275	3·62)	(273	3·51)
				278	3·65 (*a*)	278	3·53
				(282	3·61)	284	3·43 (*b*)
				285	3·54 (*b*)		
(12)	Ph	p-C_6H_4Cl	M. p. 81—82°	238	4·32	238	4·22
				270	3·70	270	3·61 (*d*)
						276	3·57 (*b*)
						280	3·55 (*b*)
(13)	o-C_6H_4Cl	o-C_6H_4Cl	M. p. 108°	242	4·08 (*c*)	247	4·11
				(270	3·58)	(266	3·28)
				280	3·65	283	3·41
				288	3·61 (*c*)		
(14)	p-C_6H_4Cl	p-C_6H_4Cl	M. p. 134—135°	241	4·37	230	4·25 (*a*)
				265	3·92 (*b*)	238	4·23 (*d*)
				280	3·75 (*c*)	270	3·71 (*b*)
						280	3·64 (*d*)
(15)	Ph	p-C_6H_4Br	M. p. 69°	243	4·35	235	4·24
				(270	3·75)	(268	3·65)
				271	3·76 (*b*)	271	3·66
						280	3·60 (*b*)
(16)	p-C_6H_4Br	p-C_6H_4Br	M. p. 158—159°	245	4·42	236	4·33 (*a*)
				270	3·95 (*b*)	270	3·88 (*e*)
				288	3·70 (*c*)	281	3·78 (*b*)
(17)	o-$C_6H_4{\cdot}OMe$	o-$C_6H_4{\cdot}OMe$	M. p. 110°	235	4·12 (*b*)	232	4·17 (*c*)
				(267	3·48)	(268	3·55)
				293	3·94	295	3·93
(18)	p-$C_6H_4{\cdot}OMe$	p-$C_6H_4{\cdot}OMe$	M. p. 89—90°	245	4·31	245	4·27
				260—267	4·18 (*d*)	262	4·18 (*a*)

	Thiolsulphonates, $R{\cdot}S{\cdot}SO_2{\cdot}R'$			In C_6H_{12}		In EtOH	
No.	R	R′		λ (mμ)	log ε	λ (mμ)	log ε
(19)	*o*-$C_6H_4{\cdot}NO_2$	Ph	M. p. 83—84°	231	4·16	231	4·28
				335	2·99 (*b*)	275	3·70 (*b*)
				350	2·94 (*c*)	325—370	3·07 (*d*)
(20)	*p*-$C_6H_4{\cdot}NO_2$	Ph	M. p. 104—105°	264	4·17	262	3·98 (*a*)
				295	3·81 (*b*)	(310	3·72)
						340	3·78 (*a*)
(21)	Ph	*o*-$C_6H_4{\cdot}NO_2$	M. p. 79°	226	4·27 (*a*)	220	4·28 (*d*)
				270	3·70 (*b*)	270	3·76 (*f*)
						295	3·51 (*e*)
						309	3·40 (*c*)
(22)	Ph	*p*-$C_6H_4{\cdot}NO_2$	M. p. 105—106°	232	4·16 (*a*)	244	4·09
				(276	3·86)	(260	3·99)
				281	3·87 (*a*)	269	4·01 (*a*)
(23)	Ph	*m*-$C_6H_4{\cdot}NO_2$	M. p. 99°	239	4·29 (*a*)	250	4·18
				280	3·70 (*b*)	283	3·76 (*d*)
						300	3·49 (*d*)
						310	3·40 (*c*)
(24)	*o*-$C_6H_4{\cdot}NO_2$	*o*-$C_6H_4{\cdot}NO_2$	M. p. 191—192°	221	4·42 (*a*)	241	4·26 (*a*)
				280	3·71 (*b*)	270	4·00 (*b*)
						285	3·90 (*d*)
						(320—332	3·19)
						397	3·59 (*g*)
(25)	*p*-$C_6H_4{\cdot}NO_2$	*p*-$C_6H_4{\cdot}NO_2$	M. p. 182°	262	4·29	237	3·85 (*c*)
				290	4·00 (*b*)	271	3·99
						(305	3·76)
						342	4·00

* The absorption spectrum in ethanolic and *n*-hexane solution was recorded, during our work, by Baker and Kloosterziel; § Cymerman and Bauer (*Research*, 1950, **3**, 146) also described this spectrum: data are coincident with ours.

(*a*) Broad or ill-defined max. (*b*) Inflexion and shoulder. (*c*) Shoulder. (*d*) Flat or nearly flat region. (*e*) Convexity or concavity. (*f*) Constant values in absorption for broad region. (*g*) Flat maximum followed by inflexion.

(1), (3), (9), (11), (17) See Experimental. (2) Hinsberg, *Ber.*, 1908, **41**, 2838. (4), (5), (10), (12), (15), (21), (22), (23) Leandri and Tundo, *Ann. Chim. Appl.*, 1954, **44**, 264. (6), (8), (13), (18), (23) *Idem, ibid.*, p. 255. (7) Otto and Gruber, *Annalen*, 1868, **145**, 13; Pauly, *Ber.*, 1876, **9**, 1640. (14) Troger *et al.*, *Annalen*, 1868, **145**, 323. (16) Knoevenagel *et al.*, *Ber.*, 1908, **41**, 3328; Olivier, *Rec. Trav. chim.*, 1914, **33**, 105. (19), (20) Leandri and Tundo, *Ann. Chimica*, 1954, **44**, 74. (24) Zincke and Parr, *Annalen*, 1912, **391**, 72. (25) Miller and Smiles, *J.*, 1925, **127**, 224.

transition to the second singlet excited state of the aromatic π shell. Now the nature of the second singlet excited state of benzene itself has been a subject of controversy. It has been widely regarded, essentially on the basis of molecular-orbital calculations, as having the symmetry B_{1u}, even after Craig[7] had suggested, on the basis of configuration-interaction and valency-bond calculations, *i.e.*, resonance methods, that the symmetry was more probably E_{2g}; and a recent experimental study[8] has led to the conclusion that its symmetry cannot be B_{1u}, but might be E_{2g}. However, either of these assignments would require that, in a monosubstitution product of benzene, absorption to the corresponding upper state would involve electronic oscillation parallel to the line of bonding of the substituent: and because even a weak conjugation between the substituent and the π shell must increase the uncertainty of position of the electrons in this direction during transition, we should definitely expect such conjugation to produce a certain bathochromic shift. In benzene, the first maximum of the second band system occurs at 203 mμ, so that the shift, if our identification is correct, is 17 mμ.

The immediate parent of most of the substitution products we have studied is phenyl benzenethiolsulphonate (II). Its spectrum is generally similar to that of the methyl ester, and, like it, consists of a weaker and a stronger band-system. The weaker one is in its previous spectral position at 260—280 mμ, and it shows the same vibrational structure, but it is about twice as strong as before. Our interpretation is that the two benzene rings are excited almost independently, and that the weaker band-system really consists of two practically coincident and identical band-systems derived by excitation of either of the

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[7] Craig, *Proc. Roy. Soc.*, 1950, *A*, **200**, 410, 474.

[8] Dunn and Ingold, *Nature*, 1955, **176**, 65.

benzene π shells to its B_{2u}-like state. In either case, the transition moment in the shell will be almost perpendicular to the line of bonding of the substituent, and therefore the perturbations which these substituents produce in the transitions will be very small indeed, with the result that the band systems closely coincide to give a doubled intensity.

What has been called the stronger band-system appears in this spectrum as two somewhat smooth maxima, one in the former position at 220 mμ and the other at 230 mμ: each band appears to be a little stronger than one band of the ester (I), but not nearly twice as strong. The two maxima are too far apart to be regarded as members of a vibrational progression in a single band-system, and we believe them to be the main bands of separate, overlapped, band-systems, formed by the raising of either benzene ring to its second excited state, probably E_{2g}-like. In either case, excitation will involve electronic oscillation parallel to the line of bonding of the substituent, so that any perturbation of which this substituent is capable will exert its maximum effect on the spectrum. Comparison with the spectrum of the methyl ester makes it natural to assign the maximum at 220 mμ to the excitation of the ring at the sulphone end of the molecule, and that at 230 mμ to excitation of the thiol-bound ring.

In the spectra of phenyl sulphides a band of moderate strength appears on the long-wave side of the B_{2u}-like band. This has been regarded as arising from the $(3p)^2(2\pi)^6$ combined chromophore of the $C_6H_5{\cdot}S{\cdot}$ group. It is so weakened as to be hardly visible in the spectrum of the phenyl ester (II). We can understand such a weakening on the grounds that the electron-attracting sulphone group must reduce the capacity of the unshared electrons of the thiol sulphur atom to conjugate with the aromatic π shell.

The most notable common feature of the effects of methyl and halogen substituents in the *ortho-* or *para*-position of either ring, and even of the effect of the methoxyl group, and of an accumulation of six methyl groups, is the smallness of the changes which they induce in the general character of the spectrum. The weaker long-wave and stronger short-wave band systems are still present, in roughly similar positions, and with more or less similar relative intensities; but, as would be expected, the systems are broadened, and vibrational structures are partly or wholly smoothed out. The spectral changes observed are greatest for methoxyl groups, and greater for halogen than for methyl substituents; on the whole, they are greater for *para-* than for *ortho*-substitution; they are undoubtedly greater for substitution in the SO_2-linked ring than in the other ring; and they are greater in their effect on the shorter-wave system, the first main band of which is often brought into the neighbourhood of 240 mμ. We can qualitatively understand some of these differences. By conjugation or hyperconjugation, the substituents named supply electrons to the benzene rings to which they are bound in the order MeO > Hal > Me. They will do this the better when the ring bears an electron-attracting sulphone group in an *ortho-* or *para*-position. Through-conjugation with the sulphone group from a *para*-substituent is likely to disturb the intervening aromatic π shell more than from an *ortho*-substituent. And the disturbance from *para*-groups will have its main spectral effect when the transition moment has a large component in the line of the substituents.

For all the compounds discussed so far the spectrum in ethyl alcohol is almost identical with that in *cyclo*hexane, except for phenyl *o*-chlorobenzenethiolsulphonate, and for the corresponding *oo'*-dichloro-derivative.

The effect of a nitro-substituent is different. We shall refer first to spectra measured in *cyclo*hexane. The nitro-group exerts its main spectral effect when in the *para*-position of the ring attached to the thiol sulphur atom. When a single nitro-group is thus placed, the main feature of the spectrum is a strong band at 264 mμ, having a shoulder on the long-wave side, and completely over-lying all normal longer-wave features of the spectra of thiolsulphonates of type (II).

We explain this, as we do the similar bands of other nitro-aromatic compounds, by assuming that nitro–aryl conjugation is so strong as to modify the separate nitro- and aryl chromophores out of recognition, the effective chromophore now being the 8-electron π system of the whole group $NO_2{\cdot}C_6H_5$. When the nitro-group is moved to the *ortho*-position of the thiol-bound ring, this band is so weakened as to be hardly visible even as a shoulder. We assume that this is because the nitro-group is twisted by steric effect, so that its conjugation is broken. Much the same happens when the nitro-group is placed in the other benzene ring, even when it is in the *para*-position, and still more when it is in the *ortho*- or *meta*-position. The nitro-group thus behaves oppositely from all the other substituents: they conjugatively supply electrons and therefore conjugate best with the ring from which the sulphone group can withdraw them; whilst the nitro-group withdraws electrons and hence conjugates best with the ring towards which the thiol sulphur atom can supply them. When *p*-nitro-groups are introduced into both rings, it is that in the thiol-bound ring which controls the spectrum.

For some of these nitro-compounds, as for all the thiolsulphonates discussed earlier, the spectrum in alcohol is similar to that in *cyclo*hexane, but for phenyl *p*-nitrobenzenethiolsulphonate, and particularly for some derivatives having a nitro-group in the *para*- or *ortho*-position of the thiol-bound ring, it may be markedly modified in ethyl alcohol: the main feature of these spectra is an additional band at about 340 and 400 mμ. This must signify some specific interaction between alcohol and the nitrobenzenethio-group, presumably the formation of an easily dissociable addition compound, since the original compound can always be recovered.

EXPERIMENTAL

Materials.—Known compounds were prepared according to the authors cited in the references in the Table. The preparation of new compounds is now described.

Methyl benzenethiolsulphonate. Potassium benzenethiolsulphonate (1 g.), dissolved in water (20 c.c.), was added, dropwise and with stirring, to methyl iodide (0·7 g.). After a few hours at 30—40°, a crude oil separated, which was fractionated *in vacuo*; b. p. 173°/10 mm. (Found: S, 34·0. $C_7H_8O_2S_2$ requires S, 34·0%).

o-*Tolyl benzenethiolsulphonate.* Silver benzenesulphinate (1·8 g.) was added, dropwise and with stirring, to a chloroform solution of *o*-tolylsulphur chloride [9] (1 g. in 50 c.c.). The silver chloride was filtered off and the solution concentrated under reduced pressure; the resulting white product was collected, and crystallized from ethanol, forming needles, m. p. 57—58° (Found: S, 24·4. $C_{13}H_{12}O_2S_2$ requires S, 24·2%).

2-*Chlorophenyl benzenethiolsulphonate.* By a similar method, *o*-chlorophenylsulphur chloride (1 g.) (Montanari,[9] b. p. 112—115°/18 mm.) and silver benzenesulphinate (1 g.) gave prisms, m. p. 63—64°, from ethanol (Found: S, 22·8. $C_{12}H_9OClS$ requires S, 22·5%).

Phenyl 2-*chlorobenzenethiolsulphonate.* Condensation of silver *o*-chlorobenzenesulphinate with phenylsulphur chloride (b. p. 86—87°/14 mm.) leads to plates, m. p. 75° (Found: S, 22·5. $C_{12}H_9O_2ClS$ requires S, 22·5%).

2-*Methoxyphenyl* 2-*methoxybenzenethiolsulphonate.* This *ester* was prepared by oxidation of the corresponding disulphide (1 g.) in chloroform solution (50 c.c.) with perbenzoic acid (20 c.c., 4·87%). The mixture was kept at room temperature for 2 days and then treated with a 5% aqueous solution of sodium hydrogen carbonate. From the dried (Na_2SO_4) chloroform solution, prisms were obtained. After crystallization from ethanol, they had m. p. 110° (Found: S, 20·8. $C_{14}H_{14}O_4S_4$ requires S, 20·6%).

Absorption Spectra.—The ultraviolet absorption spectra were measured with a Hilger photoelectric spectrophotometer (and Cary recording spectrophotometer 11 MS-50 in the case of 4-nitrophenyl benzenethiolsulphonate). Solvents were *cyclo*hexane (B.D.H. specially purified) and ethanol; concentrations were 0·01 g./l.

The authors thank Prof. C. K. Ingold, F.R.S., for helpful discussion and criticism, Dr. M. Pallotti for her co-operation in the experimental part, and the Italian " Consiglio Nazionale Ricerche " for a grant.

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[*Received, May 9th,* 1956.]

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[9] Montanari, *Gazzetta*, 1956, **86**, in the press.