206. *Investigations of Aromatic Sulphides and Sulphones. Ultra-violet Absorption Spectra of Some Diaryl Sulphides.*

By A. Mangini and R. Passerini.

The ultra-violet absorption spectra of a considerable number of mono- and di-substituted derivatives of diphenyl sulphide have been investigated. The substituents were CH_3, Cl, Br, I, NH_2, NHAc, and NO_2; and the spectra of some of the amino-compounds have been measured also in aqueous hydrochloric acid solution. The spectra are analysed in terms of chromophores; and the polar influence of substituents, and the steric effect of *ortho*-substituents, are discussed. The two bands of diphenyl sulphide are assigned to different upper electronic states, arising essentially from the excitation of different chromophores, which it is allowable to consider separately, because the non-planar nature of the molecule permits sulphur to be strongly conjugated only with one ring at a time, and does not allow an effective through-conjugation including both rings. The spectra of the derivatives receive a consistent interpretation of this basis. Methyl and halogen substituents make only minor spectral modifications, but NX_2 and NO_2 have large spectral effects, which can be understood on the basis that functional conjugation, originating in NX_2, extends through the directly attached benzene ring only, while conjugation arising from NO_2 extends at least as far as this, though from a *p*-nitro-group it can also include the sulphur atom. The steric inhibition of conjugation of *o*-NO_2 and -NHAc groups with the aromatic ring can be seen in the spectra of a number of the examples.

Our work on conjugation and hyperconjugation (Mangini, *Atti Accad. Lincei*, 1949, **7**, 321) has been concerned with the electronic absorption spectra of aryl sulphides, sulphoxides, and sulphones, and with the effect thereon of substituents. The mode of involvement of sulphur in the aromatic chromophores is of special interest, since the rings of diphenyl sulphide are not coplanar (Toussaint, *Bull. Soc. chim. Belg.*, 1948, **54**, 319). This paper deals particularly with the ultra-violet absorption spectra of diphenyl sulphide, and of its derivatives having CH_3, Hal, NX_2, and NO_2 as substituents.

Experimental.—Carefully purified materials, prepared as indicated in the tables, were spectrally examined with the Beckman quartz instrument D.U., and occasionally with a Zeiss spectrograph, hydrogen and tungsten lamps being employed as light sources. Spectra were taken in solution, of concentration 1 in 10^5, in 95% ethanol or 2N-aqueous hydrochloric acid, readings being normally 1—2 mμ apart. In the tables, spectral positions and intensities of characteristic points are expressed in mμ and log ε/mole, respectively. The relatively lower accuracy of flat maxima and shoulders is indicated by parentheses and asterisks, respectively.

Discussion

(1) *Diphenyl Sulphide* (Table 1, No. 1, Fig. 1).—This spectrum has been recorded by Fox and Pope (*J.*, 1913, **103**, 1264) and by Chaix (*Bull. Soc. chim.*, 1933, **53**, 700), and during the course of our work, by the other authors quoted below [Robertson and Matsen (*J. Amer. Chem. Soc.*, 1950, **72**, 5250) give curves but not numerical data for band maxima]:

	mμ	log ε	mμ	log ε
Fehnel and Carmack [1]	250	4·08	277 [3]	3·76
Koch [2]	250	4·08	274	3·76
Present authors	250	4·08	274	3·75

[1] *J. Amer. Chem. Soc.*, 1949, **71**, 84.

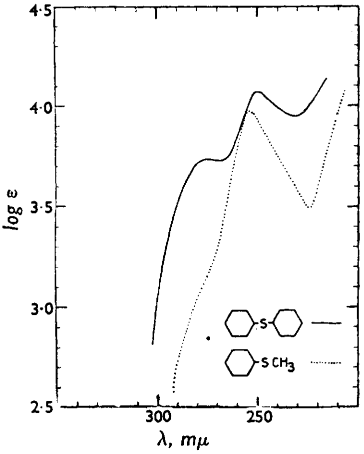
[2] *J.*, 1949, 387.

[3] The present authors obtained 277 mμ for this band with partly purified material, but the value shifted to and remained at 274 mμ after continued purification.

The spectrum is dominated by two bands, the stronger at 250 mμ and the weaker at 274 mμ, and different descriptions have been offered of their electronic origin. Fehnel and Carmack deduce conjugation between the sulphur atom and the rings. Koch regards the bands as arising from transitions of the whole molecule, distinguished by the directions of the oscillating electric vectors. Robertson and Matsen think of the molecule essentially as a monosubstituted benzene, the PhS substituent perturbing the benzene system.

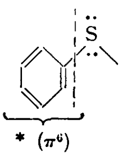
Apart from the circumstance that the bands obviously do not represent either a vibrational structure in, or a resonance doubling of, a single electronic transition, we have had in mind the analogy of the spectrum with those of diaryl and alkyl aryl ethers (Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2716; Robertson, Sceriff, and Matsen, *ibid.*, 1950, **72**, 1545), and specially with those of alkyl phenyl sulphides. The latter show two similar bands, though with the longer-wave one weakened, as in methyl phenyl sulphide (Fig. 1), or reduced to a shoulder, as in *cyclo*hexyl phenyl sulphide (Koch, *loc. cit.*).

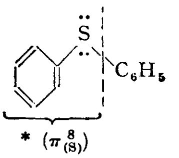
FIG. 1.*



* In the formulæ used in the Figures all rings are aromatic.

We infer that the bands represent distinct transitions of π electron states, and that neither necessitates any radical extension of conjugation to cover both phenyl rings. From its intensity and position, the shorter-wave band is identified as a perturbed form of the $\mathbf{B}_{2u}$ transition of the π^6 chromophore of benzene. The longer-wave band is ascribed to a similarly perturbed form of the transition of the 8-electron chromophore labelled $\pi^{8}_{(S)}$ ideally consisting of one unshared pair of sulphur electrons conjugated with the benzene π-shell. The assumption that the sulphur is conjugated essentially with one ring at a time (though, of course, with interchange) is the consistent basis on which we have attempted to interpret the spectra of substitution products, as is indicated below. This is reasonable in view of the non-planarity of diphenyl sulphide, which is expected greatly to reduce the significance of conjugative interaction between the benzene rings by way of sulphur :





(The asterisks locate the chromophores, *i.e.*, the groups of electrons which together accept most of the disturbance of excitation.)

(2) *Methyl and Halogeno-derivatives of Diphenyl Sulphide* (Table 1, Nos. 2—9, Figs. 2—4).—Just as nuclear methyl substituents produce no considerable change in the absorption spectra of thiophenol and methyl phenyl sulphide so neither methyl nor chlorine substituents bring about any radical change of spectrum in diphenyl sulphide. It is inferred that the interaction of these substituents with either the π^6 or the $\pi^{8}_{(S)}$ chromophore is small enough to be considered a perturbation, which does not change the essential character of either upper electronic state.

(3) *Amino-derivatives of Diphenyl Sulphide* (Table 1, Nos. 10—17, Figs. 5—7).—In contrast to the above, the spectral effect of an amino-substituent is very marked, as is illustrated by the *p*-amino-derivative (Fig. 6); the two original bands of diphenyl sulphide become enveloped by the contour of a single stronger band, having its maximum at 256 mμ. A *p*′-methyl substituent makes no difference to this result, and even a *p*′-amino-group only displaces the single band slightly towards longer wave-lengths, making it a little stronger. But with any of these amino- or diamino-compounds in hydrochloric acid, the single strong band breaks into two and weakens to give a spectrum almost identical with that of diphenyl sulphide. If the amino-groups are acetylated, one observes an

incipient splitting of the single strong band; but still the spectrum retains the general character of those of aminodiphenyl sulphides, rather than that of non-aminated diphenyl sulphide. Exceptions arise when the acetamido-groups are *ortho*-situated with respect to the sulphide bond; the spectrum then becomes practically identical with that of free diphenyl sulphide.

FIG. 2.*

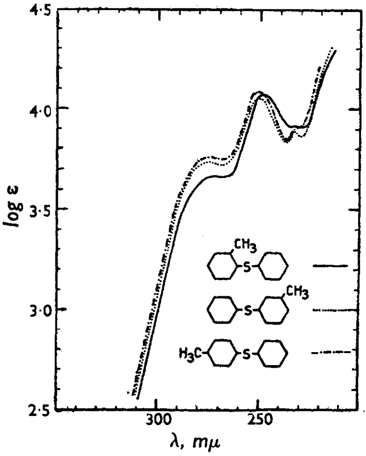


FIG. 3.*

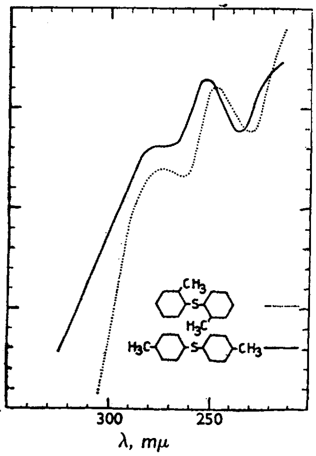
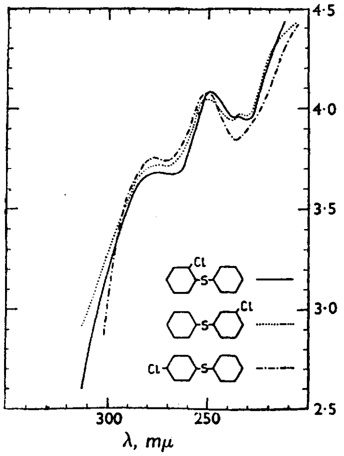
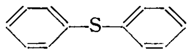


FIG. 4.*



* See footnote, Fig. 1.

TABLE 1.

	Substituents in 					Characteristic points:								
						up to 240 mμ		240—260 mμ		260—280 mμ				
No.	*o*	*m*	*p*	*o′*	*p′*	λ	log ε	λ	log ε	λ	log ε	Fig.	M. p. (uncorr.) or b. p.	Ref.
1	—	—	—	—	—	—	—	250	4·08	274	3·75	1	294°/ 760 mm.	(a)
2	CH_3	—	—	—	—	(232)	3·93	248	4·08	272	3·67	2	306·5°/ 760 mm.	(b)
3	—	CH_3	—	—	—	232	3·90	250	4·06	275	3·74	2	309·5°/ 760 mm.	(c)
4	—	—	CH_3	—	—	230 *	3·92	250	4·09	274	3·76	2	15·7°	(c)
5	CH_3	—	—	CH_3	—	—	—	248	4·11	274	3·70	3	64°	(d)
6	—	—	CH_3	—	CH_3	—	—	252	4·16	276	3·83	3	56—57°	(d)
7	Cl	—	—	—	—	(234)	3·96	249	4·09	275	3·69	4	186°/40 mm.	(e)
8	—	Cl	—	—	—	(234)	3·98	250	4·05	273	3·73	4	186°/30 mm.	(e)
9	—	—	Cl	—	—	—	—	250·5	4·08	275	3·76	4	188°/35 mm.	(f)
10	NHAc	—	—	—	—	—	—	246	4·25	(276)	3·76	5	86°	(g)
11	NHAc	—	—	—	CH_3	—	—	248	4·27	275 *	3·82	5	108°	(h)
12	—	—	NH_2	—	—	—	—	256	4·28	—	—	6	93°	(i)
13	—	—	NHAc	—	—	—	—	258	4·30	280 *	4·17	6	146°	(i)
14	—	—	NH_2	—	CH_3	—	—	258	4·31	—	—	7	74°	(j)
15	—	—	NHAc	—	CH_3	—	—	259	4·32	280 *	4·14	7	108—109°	(k)
16	—	—	NH_2	—	NH_2	—	—	—	—	264	4·39	—	108°	(i)
17	—	—	NHAc	—	NHAc	—	—	250 *	4·32	271	4·43	—	223—224°	(l)

(a) Supplied by Fraenkel and Landau, Berlin; (b) Weedon and Doughty, *Amer. Chem. J.*, 1905, **33**, 417; (c) Bourgeois, *Ber.*, 1895, **28**, 2323; (d) Purgotti, *Gazzetta*, 1890, **20**, 30; (e) Passerini, *Boll. sci. Fac. Chim. Ind.* (*Bologna*), 1950, **8**, 122; (f) Michaelis and Godchaux, *Ber.*, 1891, **24**, 763; (g) Mauthner, *ibid.*, 1906, **39**, 3598; (h) By acetylation, with acetic anhydride in acetic acid solution, of the amino-derivative prepared as indicated by Gilman, Smith, and Broadbent, *J. Amer. Chem. Soc.*, 1947, **69**, 2053; (i) Kehrman and Bauer, *Ber.*, 1896, **29**, 2363; (j) Law and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 3623; (k) Meyer and Heiduschka, *J. pr. Chem.*, 1903, **68**, 267; (l) Nietzki and Bothof, *Ber.*, 1894, **27**, 3261.

The inference drawn from these observations is that the band at about 256 mμ represents the unresolved envelope of bands of several upper electronic states, among them those already considered, and also an upper state of the $\pi^{S}_{(N)}$ chromophore, $\cdot C_6H_4\cdot\ddot{N}H_2$, the internal coupling in which, like that in $C_6H_5\cdot S\cdot$, is strong enough to require its distinctive recognition, and is too strong to admit of convenient classification of its upper state as a perturbed form of the absorption-forbidden benzene state. In acid, the last-mentioned chromophore has no effect for obvious reasons. Acetylation reduces its role for equally well understood causes. And, in its dependence on an *o*-acetamido-group, it again has no role, because of the steric inhibition of acetamido-to-aryl conjugation.

(4) *Nitrodiphenyl Sulphides* (Table 2, Nos. 18, 32, 35; Fig. 8).—It is convenient to compare the spectra of the three methyl nitrophenyl sulphides with those of the nitrodiphenyl sulphides : methyl *o*- and *p*-nitrophenyl sulphide have been examined by Fehnel and Carmack (*J. Amer. Chem. Soc.*, 1949, **71**, 2889), and *o*- and *p*-nitrodiphenyl sulphides by Koch (*loc. cit.*), with results which agree with ours : the latter are included in the more complete series of Fig. 8. This shows that the salient features of the spectra of the methyl nitrophenyl sulphides recur slightly modified in the spectra of the corresponding nitrodiphenyl sulphides. A strong suggestion is thereby conveyed that the same chromophores are in action in both cases, independently of the presence of a second aromatic ring in the nitrodiphenyl sulphides.

FIG. 5.*

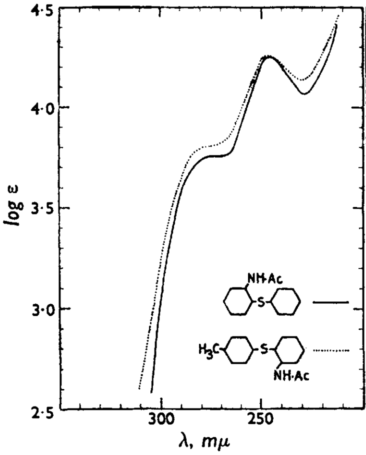


FIG. 6.*

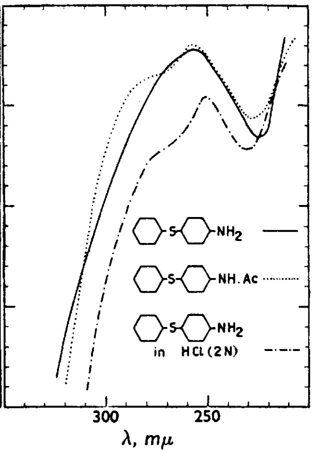
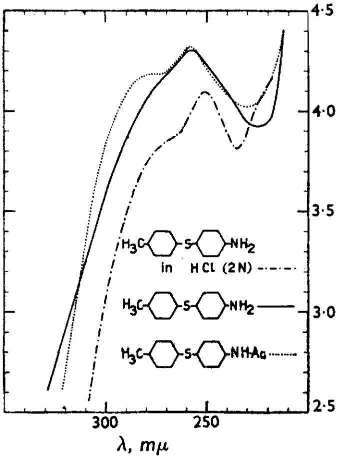


FIG. 7.*



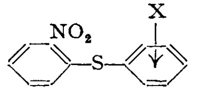
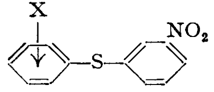
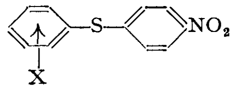
* See footnote, Fig. 1.

As to absorption on the long-wave side of 300 mμ, doubtless the responsible system involves the nitro-group. For both sets of nitro-compounds the intensities of the band in this region are in the order *p*->*o*->*m*-. This is the expected order of ability of the NO_2 and SR groups to conjugate through the intervening ring : for *ortho*-conjugation is restricted by non-planarity, and *meta*-conjugation is not possible. The wave-lengths of these long-wave bands are in the order *o*-> *m*- > *p*-. The longer wave-length of the *o*- than of the *p*-bands can be understood, just as for quinones, or nitroanilines, or nitrophenols, because the longest path through the conjugated system is longer in *ortho*- than in *para*-conjugated systems. As a summary of these conclusions, the long-wave chromophores may be indicated as follows :

$$\underbrace{o\text{-}NO_2\cdot C_6H_4\cdot SR}_{*\ (\pi^{10})} \qquad \underbrace{m\text{-}NO_2\cdot C_6H_4\cdot SR}_{*\ (\pi^{8})} \qquad \underbrace{p\text{-}NO_2\cdot C_6H_4\cdot SR}_{*\ (\pi^{10})}$$

As to the shorter-wave side of 300 mμ, one has first to notice that the absorption of *o*-nitrodiphenyl sulphide is the same as that of diphenyl sulphide, just as that of methyl *o*-nitrophenyl sulphide is like that of methyl phenyl sulphide. Presumably the *o*-nitro-group, twisted, as it must be, from the ring-plane, does not impair the participation of the ring in the chromophores of the non-nitrated parents. The *m*-nitro-compounds show strongly diminished absorption in the 274-mμ region, but not in the 250-mμ region. This seems consistent since the *m*-nitro-groups will be functionally conjugated with their own rings, but not through those rings with sulphur; yet the conjugation between the nitro-groups and their benzene rings will interfere with the conjugation of the latter with sulphur, on which the $\pi_{(S)}^{8}$ chromophore depends. The *para*-compounds show further weakening of absorption in the 274-mμ region, and also weakening towards 250 mμ. This agrees with the idea that the nitro-group is now through-conjugated, so that it can seriously disturb the whole spectral behaviour of the molecule. Only *p*-nitrodiphenyl sulphide shows a vestigious band near 260 mμ, arising, one may presume, from excitation of the π^6 chromophore of the benzene ring remote from the nitro-group.

TABLE 2.

X in 		Characteristic points:								
		210—250 mμ		260—300 mμ		beyond 300 mμ			m. p.	
No.		λ	log ε	λ	log ε	λ	log ε	Fig.	(uncorr.)	Ref.
18	—	240	4·24	(268)	3·86	368	3·65	8	79°	(a)
19	CH$_3$-*o*	240	4·23	270	3·89	370	3·68	—	87—88	(b)
20	CH$_3$-*m*	241	4·23	270 *	3·86	369	3·63	—	86	(b)
21	CH$_3$-*p*	242	4·25	270	3·89	371	3·67	—	89—90	(b)
22	Cl-*o*	240	4·25	275	3·87	364·5	3·65	9	121—122	(c)
23	Cl-*m*	238	4·25	275	3·85	365	3·64	9	107—108	(c)
24	Cl-*p*	225	4·35	275	3·83	367	3·71	9	94	(c)
		(240)	4·27	—	—	—	—			
25	Br-*m*	238	4·28	273	3·83	363	3·64	9	107—108	(c)
26	Br-*p*	232	4·38	275·5	3·89	364	3·66	9	108—109	(c)
		(236)	4·37	—	—	—	—			
27	I-*m*	238	4·40	270	3·87	364	3·66	9	99—100	(c)
28	I-*p*	240	4·44	275	3·94	365·5	3·67	9	130—131	(c)
29	NH$_2$-*p*	242	4·36	265	4·29	373	3·67	10	102	(d)
30	NHAc-*p*	235	4·40	272	4·22	371	3·71	10	195	(e)
		245	4·44	—	—	—	—			
31	NMe$_2$-*p*	240	4·28	282	4·41	375	3·67	10	187—188	(f)
X in 										
32	—	250	4·28	—	—	336—346	3·02	8	42·5	(g)
33	CH$_3$-*p*	250	4·31	—	—	340—344	2·98		60·5—61	(c)
		—	—	—	—	346	3·02			
34	NMe$_2$-*p*	250	4·28	280	4·48	362	2·95	10	119—120	(c)
X in 										
35	—	—	—	260 *	3·70	337	4·13	8	55	(h)
36	CH$_3$-*o*	—	—	262 *	3·62	338	4·15	—	64	(b)
37	CH$_3$-*m*	—	—	262 *	3·69	338	4·12	—	47	(b)
38	CH$_3$-*p*	222	4·23	262 *	3·70	339	4·13	—	81·5	(i)
39	Cl-*o*	—	—	260 *	3·82	332	4·09	9	115	(b)
40	Cl-*m*	—	—	260 *	3·80	333	4·12	9	72	(b)
41	Cl-*p*	225	4·27	(262)	3·76	336	4·12	9	84—85	(b)
42	Br-*m*	—	—	260 *	3·77	330	4·11	9	71—72	(c)
43	Br-*p*	229·5	4·27	265	3·81	334	4·11	9	94	(j)
44	I-*m*	231	4·28	260 *	3·78	332	4·11	9	81—82	(c)
45	I-*p*	240	4·26	270	3·88	336	4·11	9	101—102	(j)
46	NH$_2$-*p*	245	4·12	265	4·21	345	4·12	10	144	(k)
47	NHAc-*p*	248	4·29	270	4·15	339	4·14	10	193	(k)
48	NMe$_2$-*p*	—	—	279	4·37	342	4·12	10	181	(l)

(a) Roberts and Turner, *J.*, 1926, 1208; (b) Gilman, Smith, and Broadbent, *J. Amer. Chem. Soc.*, 1947, **69**, 2055; (c) Passerini, *Boll. sci. Fac. Chim. Ind.* (*Bologna*), 1950, **8**, 122; (d) Hodgson, Wolf, and Rosenberg, *J.*, 1930, 181; (e) By acetylation, with acetic anhydride in acetic acid solution, of the amino-derivative; (f) Zincke and Farr, *Annalen*, 1912, **391**, 93; (g) Hammick and Williams, *J.*, 1938, 211; cf. Passerini (c); (h) Hodgson, Reggie, and Smith, *J.*, 1937, 1636; (i) Law and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 1930, **52**, 3623; (j) Amstutz, Fehnel, and Woods, *ibid.*, 1947, **69**, 1923; (h) Raiziss, Clemence, Severac, and Moltzsch, *ibid.*, 1939, **61**, 2763; (l) Zincke and Lenhardt *Annalen*, 1924, **400**, 24.

(5) *Nitrophenyl Tolyl Sulphides and Halogenophenyl Nitrophenyl Sulphides* (Table 2, Nos. 21—28, 33, 36—45; Fig. 9).—The spectra of the nitrodiphenyl sulphides are modified only to a trifling extent by methyl substitution in the non-nitrated ring, and only in detail

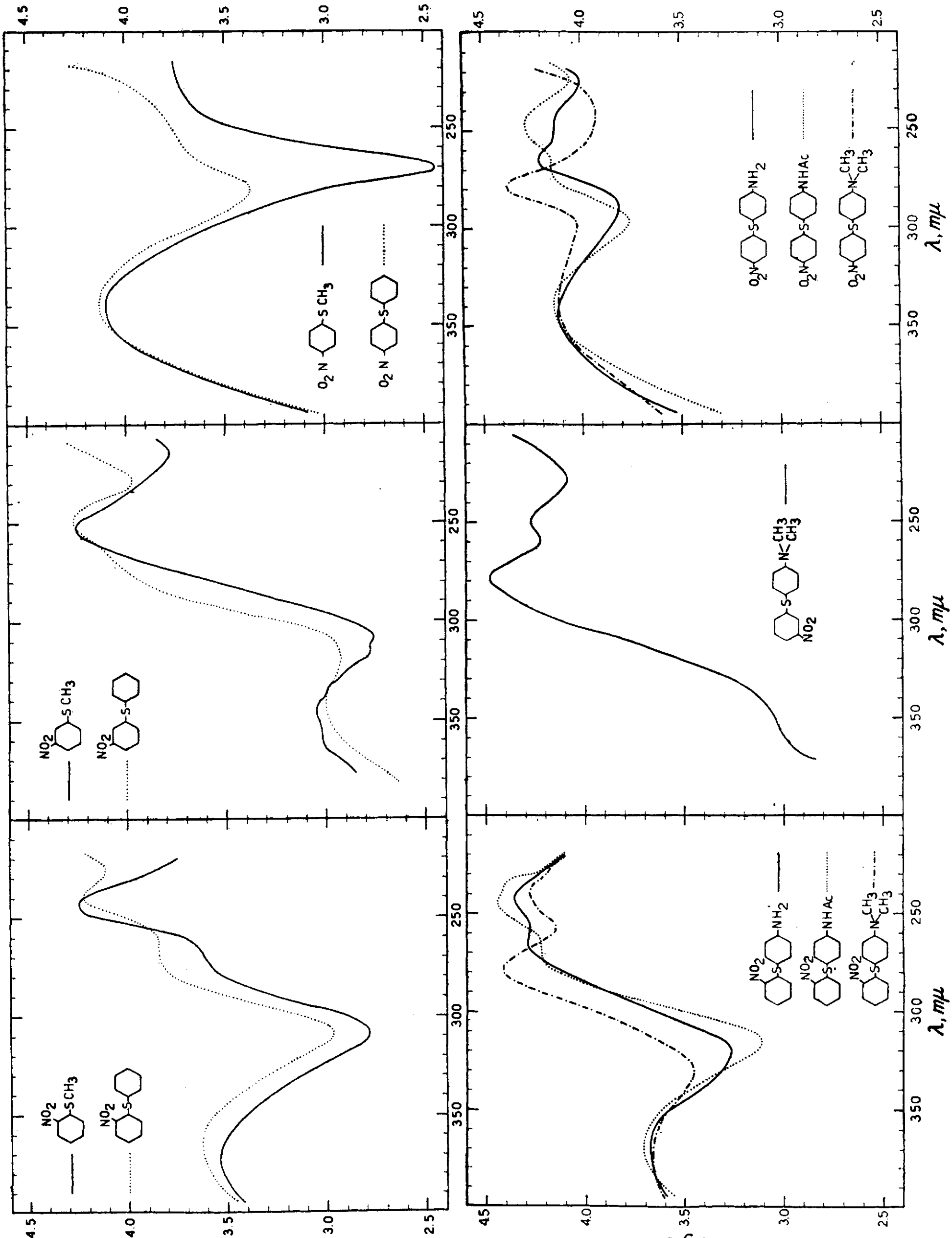


Fig. 8.*

* See footnote, Fig. 1.

by halogeno-substitution in that ring (Fig. 9). Accordingly, the broad features of all these spectra are covered by the discussion of the preceding section.

As to the detailed differences, one of the more general is that halogeno-substitution shifts the bands credited to the nitro-containing π^{10} chromophore slightly (1—7 mμ) towards shorter wave-lengths. This could be an electrostatic effect arising from the electronegativity of the halogen.

(6) *Amino-derivatives of Nitrodiphenyl Sulphides* (Table 2, Nos. 29—31, 34, 46—48; Fig. 8).—It is a striking feature of these spectra that, while the parts on the shorter-wave side of 300 mμ vary considerably from compound to compound, the longer-wave bands, ascribed to the π^{10} chromophore of *o*- and *p*-$NO_2 \cdot C_6H_4 \cdot S \cdot$, are practically unaltered by the various NX_2 substituents. From this we conclude that there is no functional through-conjugation between the NX_2 and the NO_2 groups, a result which should be expected in

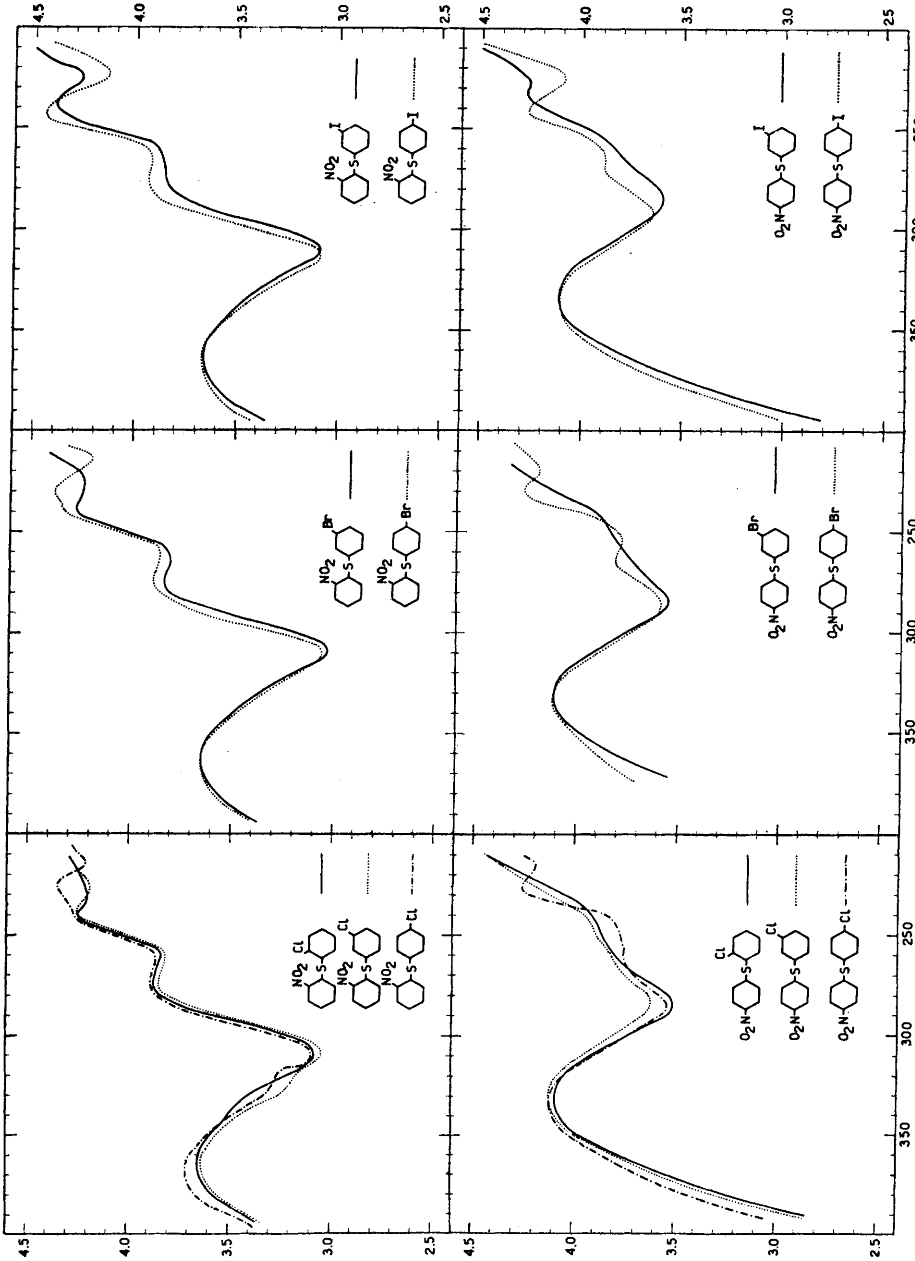


FIG. 9.*

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* See footnote, Fig. 1.

consequence of the non-coplanarity of the benzene rings. The band attributed to the chromophore π^8 of the group *m*-$NO_2\cdot C_6H_4\cdot$ is partly overlapped, but not necessarily otherwise altered in the dimethylamino-derivative (No. 34).

As to the region beyond 300 mμ, the intense bands of the dimethylamino-compounds at 280 mμ are ascribed to the $\pi_{(N)}^{8}$ chromophore $\cdot C_6H_4\cdot NMe_2$ of dimethylaniline (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838; Klevens and Platt, *ibid.*, 1949, **71**, 1714; Robertson and Matsen, *ibid.*, 1950, **72**, 1543). The bands at 265—272 mμ in the amino-compounds, and their acetyl derivatives, are similarly assigned (Doub and Vanderbelt, *loc. cit.*). The bands at 240—250 mμ in the *o*- and *m*-dimethylamino-compounds are assigned to the π^6 benzene chromophore, which is weakened to ineffectiveness in the *p*-nitro-compound, by nitro-to-sulphide through-conjugation; just as the same chromophore, though it is active in methyl *o*- and *m*-nitrophenyl sulphide, is greatly weakened in methyl *p*-nitrophenyl sulphide (cf. Fig. 8). The bands near 240 mμ of the nitroamino-compounds and their acetyl derivatives are tentatively attributed to the same π^6 chromophore of the nitrated ring. The apparent duplication of this band on acetylation of the *p*-amino-*o*-nitro-compound may be connected with the circumstances that acetanilide itself (Klingstedt, *Z. physikal. Chem.*, 1928, *B*, 1, 74) has a band in this region.

This work has benefitted by an exchange of views with Professor C. K. Ingold, F.R.S., and Dr. D. P. Craig.

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