262. *Absorption Spectra of Some Sulphoxides in the Near Ultraviolet Region.*

By G. Leandri, A. Mangini, and R. Passerini.

Apart from any modification that conjugation may impose, the sulphoxide group itself is a chromophore producing moderately strong absorption near 220 mμ. It is suggested that the transition is one of an electron of the unshared $3sp^3$ pair of the sulphur atom into an appropriately oriented $3d$ sulphur orbital, *i.e.*, a transition between molecular orbitals of which these atomic orbitals are the main components. In a phenyl sulphoxide this transition would couple strongly with a B_{2u}-like transition of the benzene ring because the local transition moments would be parallel; and in a *para*-substituted phenyl sulphoxide it would couple strongly with the B_{2u}-derived transition of the corresponding monosubstituted benzene for the same reason. In *ortho*- and *meta*-substituted phenyl sulphoxides this coupling is expected to be considerably weaker, because the local transition moments are no longer parallel, and for steric reasons. The absorption spectra of a large number of aryl, diaryl, aralkyl, diaralkyl, and aralkyl aryl sulphoxides are recorded, and can be reasonably interpreted on the basis of the electronic assignment mentioned.

We have extended our study of ultraviolet spectra of organic sulphur compounds (sulphides,[1] sulphones,[2] and thiosulphones [3]) to sulphoxides. Sulphoxides R_2SO, unlike the other classes of sulphur compounds mentioned, even when both radicals R are fully saturated, possess a moderately strong absorption band in the quartz ultraviolet region.[4]

[1] Mangini and Passerini, *J.*, 1952, 1168; *J. Phys. Radium*, 1954, **15**, 625; *Experientia*, 1956, **12**, 49; *J.*, 1956, 4954; Mangini *et al.*, *Gazzetta*, 1954, **84**, 3, 36, 47, 606.
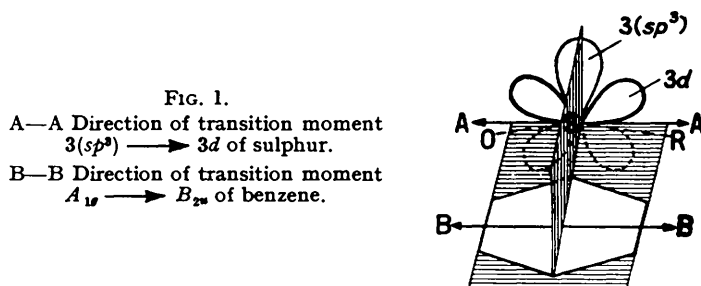[2] *Idem, ibid.*, p. 73.
[3] Leandri, Mangini, and Tundo, *J.*, 1957, 52.
[4] Koch, *J.*, 1950, 2892.

In non-polar solvents such as *cyclo*hexane the absorption maximum is near 220 mμ (log ε, *ca.* 3·30); in hydroxylic solvents this band is often at appreciably shorter wavelengths.[4, 5]

We have studied the spectra of methyl phenyl, benzyl phenyl, dibenzyl, and diphenyl sulphoxides and many of their substitution products. To simplify discussion we consider first the nature of the fundamental sulphoxide transition. We cannot deduce this from the spectra, but we can make a plausible suggestion, and then show that this enables many features of the spectra to be understood.

Bond lengths, bond angles, and dipole moments of sulphoxides, and the fact that sulphoxides can be optically resolved, indicate, as a first approximation, that the ground state of the valency shell of the sulphur aton can be described as an octet with $3sp^3$ hybridisation in the bonds and also in the unshared electron pair. To improve this description two further interactions may be taken into account. The first, conjugation of the unshared $3sp^3$ electron pair of sulphur with 2π electron shell of the unsaturated group, applies only when at least one of the groups R is unsaturated at the point of its attachment to sulphur, but it may then be quite important. The other effect, conjugation between one pair of unshared $2p$ electrons of oxygen with a vacant $3d$ orbital of sulphur, is universal, but is weak in sulphoxides (considerably weaker than in sulphones) or in sulphur groups containing still more oxygen, the extreme case being the sulphate ion. This could be restated by saying that two pairs of electrons which we started by calling unshared are really weakly π-bonding, one pair between S and C, and the other between O and S.

FIG. 1.
A—A Direction of transition moment
$3(sp^3)$ ——▶ $3d$ of sulphur.
B—B Direction of transition moment
A_{1g} ——▶ B_{2u} of benzene.

To approach the description of the transition, and of the upper state, from our first approximation to the ground state, we suggest that, since the highest occupied orbital of the latter will be the non-bonding $3sp^3$ sulphur orbital and the lowest unoccupied orbital will be one of the $3d$ sulphur orbitals, the transition in this approximation is $(3sp^3)^2 \rightarrow (3sp^3)(3d)$. As the transition is strong we assume that it is an allowed singlet–singlet transition; the upper orbital should be antisymmetric to a plane of symmetry of the lower, which, from what we have said, is the plane shown as vertical in Fig. 1. Thus the transition moment is perpendicular to this plane, and therefore, in a phenyl sulphoxide, parallel to the transition moment of the B_{2u}-like first singlet–singlet transition of the benzene ring. This is an expected symmetry relation to which reference will be made in discussing the spectra. Of course, the upper state ought to be described more accurately. The orbital which the optical electron enters is, from a spectroscopic viewpoint, a weakly antibonding molecular orbital, centred mainly on sulphur; but that makes no difference to the symmetry relation mentioned.

Data for the measurable critical points of the spectra are shown in Tables 1—4. In these nearly structureless band-systems small inflexions or changes of slope that can be seen but not measured have to be examined. Some curves are shown in Figs. 2—5. For comparison, data for some corresponding sulphones have also been included to show the different solvent effect occurring between the two series of compounds.

Unsubstituted Aromatic Sulphoxides.—The simplest situation arises in dibenzyl sulphoxide; as the benzene rings and the sulphoxide group are isolated, its spectrum

* McConnell, *J. Chem. Phys.*, 1952, **20**, 700.

(Table 1, Fig. 2) is essentially that of an aliphatic sulphoxide with the superposed, relatively weak, B_{2u}-like benzene transition appearing at its long-wave length end. There is no indication of interaction between the sulphoxide and benzenoid excitations.

In methyl phenyl and benzyl phenyl sulphoxide conjugation between a benzene ring

TABLE 1.   *Alkyl aryl sulphoxides and sulphones.*

			*cyclo*Hexane		Ethanol	
No.		M. p. or b. p.	λ (mμ)	log ε	λ (mμ)	log ε
(1)	Dibenzyl sulphoxide	m. p. 133°	(<210)	—	(215	4·25)
			222	4·26	222	4·29
					(257	2·58)
			265	2·90 •	260	2·68
					265	2·55 ᵇ
(2)	Methyl phenyl sulphoxide •	b. p. 144°/15 mm.	(232	3·29)	(226	3·51)
			253	3·60	238	3·61
					256	3·45 ᵇ
(3)	Benzyl phenyl sulphoxide	m. p. 124°	(246	3·54)	(237	3·66)
			261	3·71	248	3·76
			280	3·50 ᵇ		
(4)	Diphenyl methylene disulphoxide ...	m. p. 194°	—	—	(235	3·83)
					249	3·94
(5)	Benzyl phenyl sulphone †	m. p. 148°	(<212)	—	(<215)	—
			217	4·18	219	4·12
			(250	2·73)	(250	2·45)
			255	2·80 •	255	2·60 •
			259	2·93	259	2·85
			(262	2·88)	(263	2·80)
			265	3·06	265	3·03
			(269	2·74)	(270	2·73)
			272	2·94	272	2·90
(6)	Diphenyl methylene disulphone ‡ ...	m. p. 119—120°	—	—	222	4·29
					(240	2·13)
					260	3·19 ᶜ
					(262	3·16)
					267	3·36
					(270	3·16)
					274	3·29

• Inflexion.   ᵇ Shoulder.   ᶜ Small pronounced max. preceded by inflexions at 250 and 256 mμ.
• For spectrum in ethanol, see also Koch, *J.*, 1950, 2892; in ethanol and NaOEt the spectra are practically identical.
† Spectrum in ethanol, see also Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 236.
‡ In ethanol and NaOEt, single band, $\lambda_{max.}$ 267 (log ε = 3·80); $\lambda_{min.}$ 241 mμ (log ε = 3·56). For spectrum in ethanol see also Fehnel and Carmack, *loc. cit.*
Preparations.   (1) Hinsberg, *Ber.*, 1908, **41**, 2838.   (2) See Experimental.   (3) Pummerer, *Ber.*, 1910, **43**, 1401.   (4) Hinsberg, *J. prakt. Chem.*, 1912, **85**, 337.   (5) R. Otto and W. Otto, *Ber.*, 1888, **21**, 1695.   (6) *Idem, ibid.*, p. 346.

and the sulphoxide group is structurally possible.   The spectra (Table 1, Fig. 2) show evidence of strong interaction between the local excitations, in the form of a great transfer of intensity from the stronger (in our interpretation allowed) sulphoxide region to the weaker (in benzene forbidden) benzene region.   This transfer amounts to a merging of the two bands to give one with its maximum well towards the benzene region.   The strong coupling implies marked non-orthogonality between the parent sulphoxide and benzene transitions; in fact, we made this a maximum by making the moments parallel in our preliminary description of their nature in the absence of interaction.

In the more complicated case of diphenyl sulphoxide, where the situation just described is duplicated, the resonance of the sulphoxide group with one benzene ring is exactly degenerate with its resonance with the other.   This should give the single resonance band already described with a doubled intensity (log ε larger by 0·3), but, as the sulphoxide group is common, the two resonance systems will interact and a new resonance will split the degenerate band into two.   The observed spectra (Table 2, Fig. 3) show the splitting.

TABLE 2. *Diaryl sulphoxides.*

No.	M. p. or b. p.	cycloHexane λ (mμ)	log ε	Ethanol λ (mμ)	log ε
(7) Diphenyl †	m. p. 71°	(219	4·10)	(220	4·05)
		226	4·13	233	4·15
		267	3·42 *ᵃ	265	3·32 ᵇ
(8) Phenyl o-tolyl	m. p. 42°	228	4·07 ᶜ	(223	4·04)
		280	3·17 ᵇ	235	4·16
				265	3·38 ᵈ
(9) Phenyl m-tolyl	m. p. 46—47°	230	4·11 ᵇ	(225	4·10)
		278	3·30 ᵇ	233	4·14
				270	3·29 ᵇ
(10) Phenyl p-tolyl	m. p. 72°	(223	3·97)	(222	4·01)
		233	4·05	237	4·20
		270	3·28 ᵃ	270	3·28 ᵃ
(11) Di-o-tolyl	m. p. 121°	227	4·05 ᵃ	(224	4·00)
		245	3·85 ᵃ	237	4·16
		270	3·38 ᵃ	(260	3·29)
		(277	3·27)	274	3·43
		280	3·28 ᶜ	282	3·30 ᵇ
(12) Di-m-tolyl	b. p. 215°/15 mm.	230	4·07 ᵇ	(228	4·28)
		(269	3·41)	235	4·21
		270	3·42 ᶜ	(268	3·59)
		(277	3·27)	270	3·61 ᶜ
		278	3·28 ᶜ	(278	3·48)
				280	3·49 ᶜ
(13) Di-p-tolyl	m. p. 96°	(221	4·11)	(224	4·10)
		237	4·20	240	4·27
		275	3·35 ᵇ	275	3·35 ᵇ
(14) o-Chlorophenyl phenyl	m. p. 61°	(226	4·12)	(225	4·10)
		230	4·13 ᶜ	235	4·17
		265	3·45 ᵃ	265	3·35 ᵇ
(15) m-Chlorophenyl phenyl	m. p. 39—40°	—	ᵉ	232	4·11 ᵇ
		273	3·35 ᶠ	268	3·30 ᵇ
		281	3·12 ᶠ		
(16) p-Chlorophenyl phenyl	m. p. 45—46°	(220	4·05)	(222	4·06)
		234	4·20	239	4·26
		280	3·16 ᵇ	275	3·20 ᵇ
(17) Di-p-chlorophenyl	m. p. 142°	221	4·18 ᶜ	(225	4·08)
		240	4·29	244	4·34
		280	3·40 ᵇ	260	3·78 ᶠ
(18) Di-p-bromophenyl	m. p. 151—152°	(219	4·15)	227	4·20 ᵃ
		226	4·19 ᶜ	248	4·42
		(231	4·18)	268	3·75 ᵃ
		248	4·34		
		268	3·75 ᶠ		
(19) p-Aminophenyl phenyl ●	m. p. 150°	(229	3·81)	(238	3·78)
		259	4·21	278	4·21
		290	3·57 ᵇ		
(20) Di-p-aminophenyl ●	m. p. 175°	—	—	(238	3·80)
				264	4·17
				(275	4·13)
				300	4·25
(21) p-Aminophenyl benzyl ●	m. p. 197—198°	(232	4·08)	(237	3·68)
		242	4·12	273	4·26
		(250	4·00)	300	3·80 ᵃ
		265	4·25		
		300	3·50 ᵈ		

ᵃ Inflexion. ᵇ Shoulder. ᶜ Slightly pronounced max. ᵈ Nearly flat shoulder at 269—279 mμ. ● 230 mμ band absent. ᶠ Nearly flat region. ● Weak shoulder.

● Arbitrary extinction values in cyclohexane solution.

† In H_2SO_4 (50% by vol.) : $\lambda_{infl.}$ 228 (log ε 4·08) ; $\lambda_{max.}$ 274 (log ε 3·49) ; for spectrum in ethanol, see Gibson *et al.*, *J.*, 1923, **123**, 874 ; Chaix, *Bull. Soc. chim. France*, 1933, **53**, 700 ; Koch, *J.*, 1950, 2892.

Preparations. (7) Colby and McLoughlin, *Ber.*, 1887, **20**, 198. (8—9) Courtot and Frenkiel, *Comp. rend.*, 1934, **199**, 557. (10) Chaix, *Bull. Soc. chim. France*, 1933, **53**, 700. (11—12, 14—17, 21) See Experimental. (13) Parker, *Ber.*, 1890, **23**, 1845. (18) Boeseken and Watermann, *Rec. Trav. chim.*, 1911, **30**, 130. (19) Hinsberg, *Ber.*, 1903, **36**, 113. (20) Gazdar and Smiles, *J.*, 1908, **93**, 1835.

TABLE 3. *Aryl benzyl sulphoxides.*

No.		M. p.	cycloHexane		Ethanol	
			λ (mμ)	log ε	λ (mμ)	log ε
(22)	Methyl p-nitrophenyl	151—152°	(223	3·78)	(225	3·75)
			244	3·94	248	3·88
			(271	3·42)	(270	3·73)
			296	3·75	284	3·78
(23)	Benzyl p-nitrophenyl	168—169	(225	4·10)	226	4·13 b
			232	4·13 a	246	3·94 b
			251	3·96 c	—	—
			(277	3·53)	(270	3·75)
			305	3·74	293	3·85
(24)	p-Nitrobenzyl phenyl	161—162	(237	3·86)	(233	3·81)
			259	3·99	278	4·02
			(280	3·92)	330	3·15 c
			290	3·96		
(25)	p-Nitrobenzyl p-nitrophenyl *	181—182	(228	4·03)	(232	3·98)
			251	4·18	254—270	4·14 e
			(272	4·05)	285	4·18
			280	4·08 d		
(26)	p-Nitrobenzyl p-nitrophenyl ‡	161—162	(245	3·90)	(240	3·67)
			266	4·05	272.	4·05
			290	3·90 e		
(27)	Di-p-nitrobenzyl	216—217	absolutely insoluble		(232	3·30)
					277	4·03
(28)	o-Nitrophenyl phenyl	—	(238	4·03)	225	4·23 c
			244	4·05 a	270	3·80 c
			300	3·40 f	315	3·34 c
(29)	Di-o-nitrophenyl	188—189	(234	4·09)	230	4·20 e
			248	4·14		
			295	3·45 h		
(30)	m-Nitrophenyl phenyl	76—77	<(215)	—	229	4·30 e
			225	4·29 a	250	4·03 e
			245	4·12 b	262	3·96 e
			258	4·00 c	295	3·15 b
			295	3·02 b		
(31)	p-Nitrophenyl phenyl †	107—108	(235	3·83)	(238	3·87)
			260	4·08	265	4·06
			295	3·65 c	290	3·86 c
					330	2·95 b
(32)	Di-p-nitrophenyl ‡	179—180	(224	4·07)	(230	4·00)
			257	4·28 i	271	4·27
			273	4·20 i	345	2·90 b

a Slightly pronounced max. b Inflexion. c Shoulder. d Broad max., flat region 275—295 mμ (log ε = 4·05). e Flat region with broad max. at 256 mμ. f Very weak inflexion. g Flat region and irregular feature with hint of max. at 330 mμ. h Shoulder, with irregular feature towards the red. i Broad max. Nearly flat region at 273—281 mμ.

* In aqueous 0·1N-NaOH : only one max. at 285 mμ (log ε = 4·19).
† In conc. H_2SO_4 : $\lambda_{max.}$ 270° (log ε 4·36).
‡ Saturated *cyclo*hexane solution, arbitrary extinction values.

Preparations. (22—28, 30) See Experimental. (29) Leandri and Pallotti, *Boll. sci. Fac. chim. ind. Bologna,* 1955, **13**, 48. (31—32) Szmant and McIntosh, *J. Amer. Chem. Soc.,* 1951, **73**, 4356.

[The general banking of intensity towards shorter wavelengths is probably due to inter-action between the two equivalent systems.] The spectrum therefore ought to be approximately the same as for methyl phenyl sulphoxide (Table 1, Fig. 2), except that the intensity should be doubled, *i.e.*, log ε should be 0·3 unit greater than for the simpler molecule. This is, in fact, a fairly accurate description of the observed spectrum.

The coupling of the unshared electrons of sulphur with the benzene ring is also supported by some chemical evidence such as the *para*-orienting effect of the sulphoxide group in nitration in the phenyl series (in nitric acid solution).[5a]

5a Leandri and Pallotti, *Boll. sci. Fac. chim. ind. Bologna,* 1955, **13**, 48.

Methyl- and Halogen-substituted Aromatic Sulphoxides.—Spectra are recorded in Table 2 and Fig. 3. The main points about them are as follows :

Methyl and halogen substituents in *para*-positions, even when there are two of them, make only very minor differences to the spectra, which are essentially those of the parent compounds. One and, still more, two *ortho*-substituents cause the long-wavelength benzene band-system to be less intense in the phenyl sulphoxide resonance system. This could be understood on the basis of *ortho*-substituents' twisting the aryl groups sufficiently partly to uncouple the local excitations of the phenyl and sulphoxide groups. However, the fact that one, and still more two, *meta*-substituents act in the same way, and almost as efficiently as *ortho*-substituents, is more difficult to explain on stereochemical grounds,

TABLE 4. *Aryl benzyl sulphones.*

No.		M. p.	cycloHexane		Ethanol	
			λ (mμ)	log ε	λ (mμ)	log ε
(33)	Methyl *p*-nitrophenyl	104°	(218	3·57)	255	3·83
			248	4·05		
			279	3·25 *		
			(285	3·18)		
			287	3·20		
			298	2·90 ♭		
(34)	Benzyl *p*-nitrophenyl •	172—173	(229	4·10)	(228	3·97)
			247	4·25	250	4·25
			280	3·65 •	286	3·67 •
(35)	*p*-Nitrobenzyl phenyl •	209	(232	3·58)	(234	3·47)
			264	4·09	269	4·09 •
			285	3·78 ♭	(270	4·07)
					272	4·09 •
(36)	*p*-Nitrobenzyl *p*-nitrophenyl •	195	(224	3·90)	(225	3·83)
			253	4·28	260	4·27
			278	3·86 ♭		

* Broad inflexion preceded by shoulder at 330 mμ (log ε = 4·10), and followed by inflex. at 360 mμ (log ε, 3·20) etc. ♭ Very weak inflexion. • Inflexion. ♃ Nearly flat region followed by weak max. at 287 mμ. • Small pronounced maximum.
• Saturated *cyclo*hexane solution, arbitrary extinction values.
Preparations. (33) Gaber and Crünberg, *J. Appl. Chem. U.S.S.R.*, 1939, **12**, 1481. (34) Zincke and Lehnardt, *Annalen*, 1913, **400**, 16; For spectrum in ethanol see Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84. (35—36) See Experimental.

unless we can assume that the repulsion of the sulphoxide oxygen atom, as an anionic (electron-swollen) atom, extends considerably beyond the usually accepted van der Waals radius.

However, the above facts are open to an electronic interpretation based on the consideration that the B_{2u}-derived local benzenoid excitation would, in an *ortho*- or *meta*-substituted phenyl sulphoxide, no longer have a transition moment parallel to that of the local sulphoxide transition : for the former will deviate towards perpendicularity with the line of bonding of the *ortho*- or *meta*-substituent. Coupling between the local transition moments must therefore be considerably weakened. If we adopt this interpretation, we must assume that the uncoupling, resulting from the diminished non-orthogonality, is quantitatively sufficient to allow the weaker local transition to reproduce itself more or less recognisably and separately in the spectra.

Nitro-substituted Aromatic Sulphoxides.—In compounds containing a *p*-nitrobenzyl group (Table 3, Fig. 4) the nitro-group has no continuous connexion through a π-electron shell with the sulphoxide group. Accordingly, the spectra are much as one would suppose from the preceding discussion, given that the long-wavelength local chromophore is that of nitrobenzene, rather than that of benzene, and is thus the source of a longer-wavelength (near 290 mμ) and more intense absorption than that due to the unsubstituted benzene ring.

In *p*-nitrophenyl phenyl sulphoxides where there is the possibility of through-conjugation between the nitro- and the sulphoxide group (Table 3, Figs. 4, 5), the spectra

suggest that such through-conjugation functions, though only moderately strongly : we see sometimes one very broad band, sometimes two merged and unresolved bands, extending, with a continuously maintained high intensity, over the phenyl sulphoxide and nitrobenzene regions of the spectrum.

ortho-Nitrophenyl phenyl sulphoxides (Table 3, Fig. 5) show a remarkable reduction in the intensity of absorption in the longer wavelength spectral region of the nitrobenzene
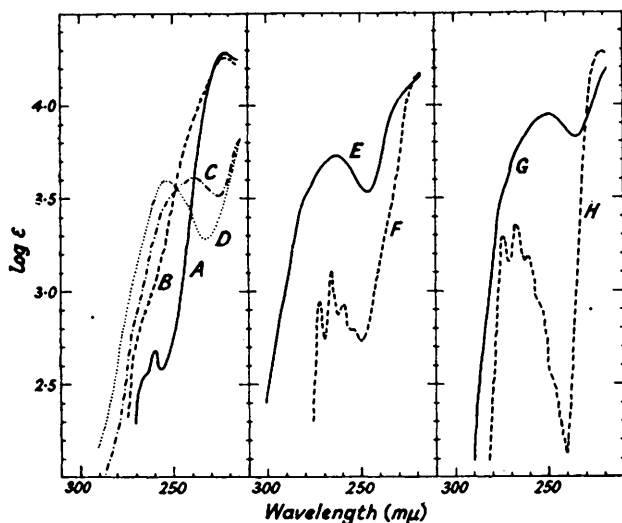

FIG. 2.
A, (Ph·CH₂·)₂SO in ethanol.
B, (Ph·CH₂·)₂SO in *cyclo*hexane.
C, Ph·SO·Me in ethanol.
D, Ph·SO·Me in *cyclo*hexane.
E, Ph·SO·CH₂Ph in *cyclo*hexane.
F, Ph·SO₂·CH₂Ph in *cyclo*hexane.
G, Ph·SO·CH₂·SO·Ph in ethanol.
H, Ph·SO₂·CH₂·SO₂·Ph in ethanol.

FIG. 3.
A, Ph₂SO in ethanol.
B, Ph₂SO in *cyclo*hexane.
C, (*p*-Me·C₆H₄·)₂SO in *cyclo*hexane.
D, (*o*-Me·C₆H₄·)₂SO in *cyclo*hexane.
E, *m*-Cl·C₆H₄·SO·Ph in *cyclo*-hexane.
F, Ph·CH₂·SO·C₆H₄·NH₂-*p* in ethanol.
G, Ph·CH₂·SO·C₆H₄·NH₂-*p* in *cyclo*hexane.
H, Ph·SO·C₆H₄·NH₂-*p* in ethanol.
J, Ph·SO·C₆H₄·NH₂-*p* in *cyclo*-hexane.
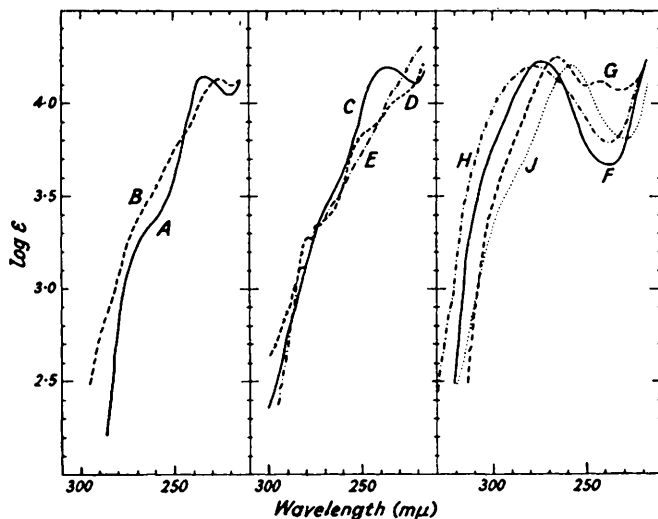
chromophore, obviously owing to steric twisting of the nitro-group, with partial break-down of its conjugation with the aromatic π-shell.

Amino-substituted Aromatic Sulphoxides.—Of those studied (Table 2, Fig. 3), all contain the *p*-aminophenyl sulphoxide system. Inasmuch as the sulphoxide group has unfilled sulphur 3*d* orbitals, as well as some double bonding between sulphur and oxygen, some degree of through-conjugation between the electron-donating amino-group and the *para*-sulphoxide group is possible. Even though the electron displacement is opposite in

direction to that due to a conjugated *para*-nitro-group, one might expect the *para*-amino-group to exert somewhat similar spectral effects. In fact we see a large red-shift of the main band, which covers with high intensity the normal long-wavelength region of the aniline chromophore. In the spectrum of di-*p*-aminophenyl sulphoxide there are two

FIG. 4.
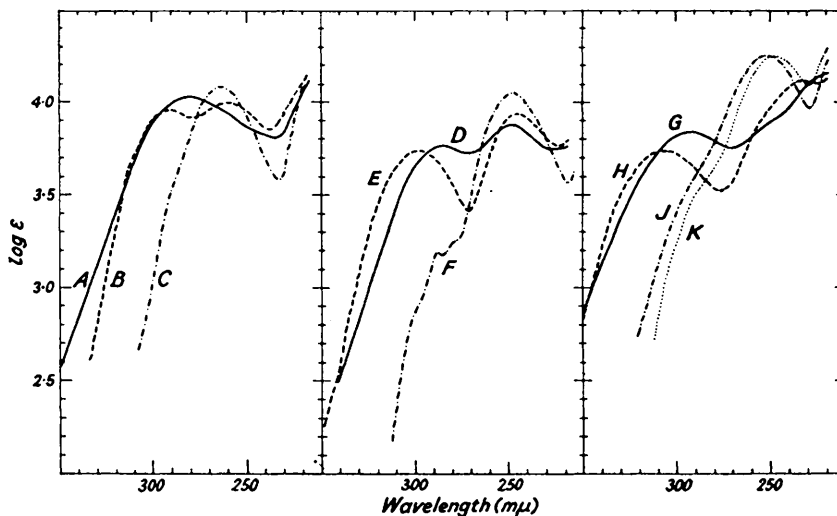
A, Ph·SO·CH$_2$·C$_6$H$_4$·NO$_2$-*p* in ethanol; *B*, Ph·SO·CH$_2$·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane; *C*, Ph·SO$_2$·CH$_2$·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane; *D*, Me·SO·C$_6$H$_4$·NO$_2$-*p* in ethanol; *E*, Me·SO·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane; *F*, Me·SO$_2$·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane; *G*, Ph·CH$_2$·SO·C$_6$H$_4$·NO$_2$-*p* in ethanol; *H*, Ph·CH$_2$·SO·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane; *J*, Ph·CH$_2$·SO$_2$·C$_6$H$_4$·NO$_2$-*p* in ethanol; *K*, Ph·CH$_2$·SO$_2$·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane.

FIG. 5.

A, Ph·SO·C$_6$H$_4$·NO$_2$-*p* in ethanol.
B, Ph·SO·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane.
C, Ph·SO·C$_6$H$_4$·NO$_2$-*o* in ethanol.
D, Ph·SO·C$_6$H$_4$·NO$_2$-*p* in *cyclo*hexane.
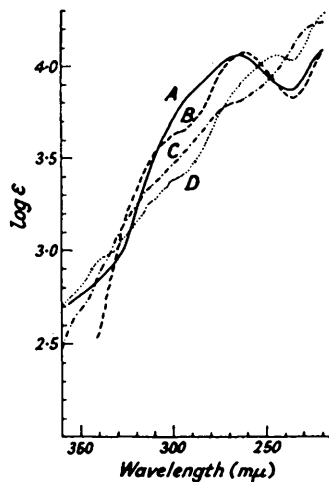
resolved bands of similar intensity, owing to the equivalence and overlapping of the constituent *p*-aminophenyl sulphoxide chromophores, as arose with the parent substance.

EXPERIMENTAL

Absorption spectra were recorded with a Hilger Uvispek photoelectric spectrophotometer in B.D.H. *cyclo*hexane and 95% ethanol, specially purified for spectroscopy. Concentrations were 10^{-2} g./l. except for compounds only slightly soluble in *cyclo*hexane, for which saturated solutions were used and arbitrary log values calculated.

In the Tables minima are in parentheses; shoulders or inflexions have been indicated.

Materials.—Methyl phenyl sulphoxide. Methyl phenyl sulphide (5 g.) was oxidised at 10—20° with peracetic acid [*i.e.*, hydrogen peroxide (4 c.c.; 32%) in glacial acetic acid (100 c.c.)] for a few hours. The solution was diluted to 500 c.c with water and extracted with ether. The ethereal solution was washed with aqueous sodium carbonate (10%) and with water, dried (Na_2SO_4), and the ether was removed, the residue being fractionated *in vacuo*. The colourless oil had b. p. 144°/15 mm. [Van Hove [6] (who used nitric acid) reports 263·5—264°/760 mm.]

Di-o-tolyl sulphoxide. Prepared as above by oxidation of the corresponding sulphides the white di-*ortho*-compound, crystallised from light petroleum, had m. p. 121° (the product obtained by action of thionyl chloride on *ortho*-tolylmagnesium halide [7] had the same m. p.) and the di-*meta*-compound was a colourless oil which was distilled under reduced pressure, b. p. 215°/15 mm. (as in lit.[7]).

o-Chlorophenyl phenyl sulphoxide. To *o*-chlorobenzenesulphinyl chloride (17 g.), prepared by heating *o*-chlorobenzenesulphinic acid with thionyl chloride on a water-bath for 15 min. (yellowish oil, b. p. 112—113°/3 mm.) in benzene (50 c.c.) were added small quantities of anhydrous aluminium chloride (30 g.). After being heated for 45 min. the mixture was dropped into iced-water, the excess of benzene steam-distilled off, and the oil suspension extracted with ether, the ether finally being evaporated off. The residue was distilled under reduced pressure and gave an oil, b. p. 199°/4 mm., which became a white *solid*. Crystallisation from light petroleum gave prisms, m. p. 61° (Found : S, 13·65. $C_{12}H_9OClS$ requires S, 13·6%).

m-Chlorophenyl phenyl sulphoxide, prepared as for the *o*-isomer, crystallised from light petroleum as prisms, m. p. 39—40° (Found : S, 13·7. $C_{12}H_9OClS$ requires S, 13·6%).

p-Chlorophenyl phenyl sulphoxide. *p*-Chlorobenzenesulphinic acid, when treated with thionyl chloride, gave *p*-chlorobenzenesulphinyl chloride as a yellowish oil, b. p. 134°/8 mm. On treatment with aluminium chloride in benzene this gave an oil, b. p. 228°/16 mm., which solidified. Recrystallisation from light petroleum gave prisms, m. p. 45—46° (Bergmann and Tschudnowsky [8] report b. p. 228°/21 mm.).

Di-p-chlorophenyl sulphoxide. Aluminium chloride (30 g.) was added, with constant cooling and in small quantities, to chlorobenzene (100 c.c.) and thionyl chloride (15 g.). After 2 hr. on a water-bath, followed by steam distillation, this gave a solid which gave prisms, m. p. 142° (from ligroin). (Cf. ref. 9. Prepared by oxidation of the sulphide with peracetic acid [10] or with nitric acid,[11] it had m. p. 139° and 143° respectively.)

p-Aminophenyl benzyl sulphoxide. *p*-Aminophenyl benzyl sulphide (3·5 g.) in acetone (50 c.c.) was oxidised with hydrogen peroxide (1·5 c.c.; 30%). After a week at room temperature, acetone was removed *in vacuo* leaving white prismatic *needles*. Recrystallised from ethanol, these had m. p. 197—198° (Found : N, 6·2. $C_{13}H_{13}ONS$ requires N, 6·05%).

Methyl p-nitrophenyl sulphoxide. Methyl 4-nitrophenyl sulphide (10 g.) was oxidised in glacial acetic acid (100 c.c.) with hydrogen peroxide (7 c.c.; 30%). The product, needles (from benzene), had m. p. 151—152° (Zincke and Lenhardt [12] give m. p. 149°; oxidation was with nitric acid).

Benzyl 4-nitrophenyl sulphoxide. Benzyl *p*-nitrophenyl sulphide (6 g.), glacial acetic acid (400 c.c.), and hydrogen peroxide (2·5 c.c.; 32%) were kept for a week at room temperature. After dilution with water (1 l.) a yellowish precipitate separated which gave *plates*, m. p. 168—169° (from ethanol) (Found : S, 5·55. $C_{13}H_{11}O_3NS$ requires S, 5·4%).

By oxidation of the parent sulphide with peracetic acid the following products have been obtained : p-*Nitrobenzyl phenyl sulphoxide*, plates, m. p. 161—162° (from ethanol) (Found : N, 5·5. $C_{13}H_{11}O_3NS$ requires N, 5·4%). *p-Nitrobenzyl p-nitrophenyl sulphoxide*, needles, m. p. 181—182° (from ethanol) (Found : N, 9·2. $C_{13}H_{10}O_5N_2S$ requires N, 9·15%). *Benzyl p-nitrobenzyl sulphoxide*, yellowish prisms, m. p. 161—162° (from ethanol) (Found : N, 5·5. $C_{14}H_{13}O_3NS$ requires N, 5·1%). *Di-p-nitrobenzyl sulphoxide*, needles, m. p. 216—217° (from ethanol) [previously prepared [13] by electrolytic oxidation of di-*p*-nitrobenzyl sulphide

[6] Van Hove, *Bull. Acad. roy. Belg., Cl. Sci.*, 1926, **12**, 929; *Chem. Zentr.*, 1927, **98**, 1821.
[7] Courtot and Frenkiel, *Compt. rend.*, 1934, **199**, 557.
[8] Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, B, 457.
[9] Parker, *ibid.*, 1890, **23**, 1845.
[10] Boeseken and Koning, *Rec. Trav. chim.*, 1911, **30**, 130.
[11] Fries and Vogt, *Annalen*, 1911, **381**, 343.
[12] Zincke and Lenhardt, *ibid.*, 1913, **400**, 14.
[13] Fichter and Wenk, *Ber.*, 1912, **45**, 1379.

or by oxidation with nitric acid, it had m. p. 208—210°].   *p*-Nitrobenzyl *p*-nitrophenyl sulphone, yellow needles, m. p. 195° (cf. ref. 15), from ethanol–dioxan (2 : 1).

o-*Nitrophenyl phenyl sulphoxide.* Chloroform solutions of perbenzoic acid (4·12% ; 144 c.c.) and *o*-nitrophenyl phenyl sulphide (10 g. in 150 c.c.) were mixed and cooled in ice. Next day, the mixture was washed with 5% aqueous sodium carbonate, dried, and evaporated. The *sulphoxide*, yellow needles, had m. p. 92—93° (from ligroin) (Found : N, 5·8. $C_{12}H_9O_3NS$ requires N, 5·7%).

m-*Nitrophenyl phenyl sulphoxide*, prepared as the *ortho*-isomer, gave needles, m. p. 76—77° (from benzene–ligroin) (Found : N, 5·7%).

p-Nitrophenyl phenyl sulphone was prepared by oxidation of the sulphide with peracetic acid at 100° as plates, m. p. 172—173° (Fromm and Wittmann,[14] by oxidation with chromic acid, obtained material m. p. 169° and 172°).

Benzyl *p*-nitrobenzyl sulphone was prepared as described above.   The crude product gives ivory-coloured plates, m. p. 209° (as in the literature [15]) from ethanol–dioxan (2 : 1).

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14 Fromm and Wittmann, *Ber.*, 1908, **41**, 2270.
15 Waldron and Reid, *J. Amer. Chem. Soc.*, 1923, **45**, 2399.