Spectrochimica Acta, Vol. 27A, pp. 1467 to 1479. Pergamon Press 1971. Printed in Northern Ireland

The ultraviolet absorption spectra of alkyl *o*-methoxyphenyl sulphides, and oxa-thiaheterocycles, and of their sulphones

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(*Received* 25 *June* 1970)

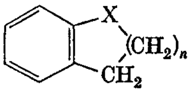
Abstract—Evidence is presented which shows that in the series of compounds (II) and (IV), conjugation between the benzene ring and sulphur atom is more affected by steric interactions than is that between the benzene ring and oxygen atom. Steric interactions appear to have little influence upon the u.v. spectra of the sulphones (III) and (V).

The spectra of the sulphides (IV) appear to provide evidence for the expansion of the sulphur atom's octet.

THE U.V. spectroscopic properties of the aromatic cyclic ethers (I; $X = \mathrm{O}$) [1] and thioethers (I; $X = \mathrm{S}$) [2] show that conjugation between the oxygen (or sulphur) atom and the benzene ring is affected by the steric requirements of the hetero-ring. In particular, it has been shown that conjugation is maximal in the five-membered ring compounds ($n = 1$), and it diminishes as n increases to 2 and to 3.

The positions [3] of the K-bands for anisole and for thioanisole show that the polarizability of sulphur is greater than that of oxygen.

It was therefore of interest to ascertain what effect the steric requirements of the hetero-ring would have upon conjugation between the benzene ring and the oxygen and sulphur atoms in "mixed" ethers of the type (II). The acyclic analogues (IV; $R = \mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^i$ and Bu^t) have also been included in this study to provide additional information concerning the effect upon u.v. light absorption of steric interactions between the alkylthio group, the *o*-methoxyl group and the *o*′-hydrogen atom.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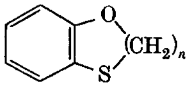
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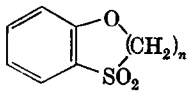
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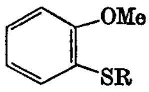
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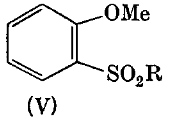
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The figures reproduce the spectra of anisole, thioanisole, and the alkyl *o*-methoxyphenyl sulphides (IV; $R = \mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^i$ and Bu^t) (Fig. 1), of the related sulphones (V; $R = \mathrm{Me}, \mathrm{Et}, \mathrm{Pr}^i$ and Bu^t) and methyl phenyl sulphone (Fig. 2), and of the heterocycles (II; $n = 1$, 2 and 3) and their related sulphones (III; $n = 1$ and 2)

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* To whom enquiries regarding this paper should be sent.

[1] G. BADDELEY, N. H. P. SMITH and M. A. VICKARS, *J. Chem. Soc.* 2455 (1956).

[2] M. J. Y. FOLEY and N. H. P. SMITH, *J. Chem. Soc.* 1899 (1963).

[3] A. BURAWOY, J. P. CRITCHLEY and A. R. THOMPSON, *Tetrahedron* **4**, 403 (1958).

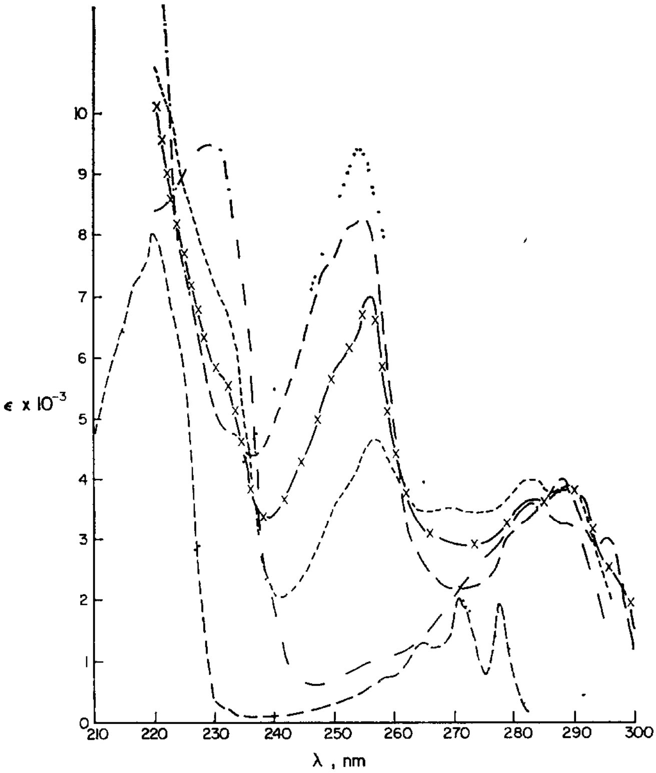

Fig. 1. U.v. spectra of alkyl *o*-methoxyphenyl sulphides (IV), anisole, and thioanisole.

(IV; $R = \mathrm{Me}$) — · — · — ·
(IV; $R = \mathrm{Et}$) — × — × — ×
(IV; $R = \mathrm{Pr}^i$) - - - - - - - - - -
(IV; $R = \mathrm{Bu}^t$) — · · · — · · · — · · · —
PhOMe — — — — — —
PhSMe ······· ·· ······

(Fig. 3). The absorption maxima for these compounds, together with the band assignments are given in Tables 1, 4 and 5.

Alkyl o*-methoxyphenyl sulphides and sulphones*

There is very good agreement between the spectra already published for anisole [4] and thioanisole [5] and those recorded in Fig. 1. The spectra of the di-substituted compounds (IV) show three distinct areas of maximal absorption: 230–235, 254–258, and 280–290 nm; the first two regions are designated as *K*-bands ($B_{1u} \leftarrow A_{1g}$ transitions), and the latter as a *B*-band ($B_{2u} \leftarrow A_{1g}$ transitions).

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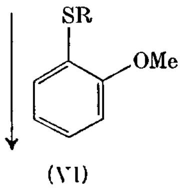
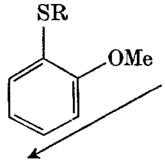
[4] J. C. Dearden, *J. Org. Chem.* **29**, 1821 (1964); J. C. Dearden and W. F. Forbes, *Can. J. Chem.* **37**, 1305 (1959).

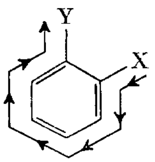
[5] A. Mangini, A. Trombetti and C. Zauli, *J. Chem. Soc.* (B), 153 (1967).



(VI)



(VII)



(VIII)

The *K*-bands are assigned to transitions which involve the effective charge migrations shown by the directions of the arrows in (VI) (for the bands at 254·5–258 nm) and in (VII) (for the bands at 230–235 nm). Variation of *R* in the series Me, Et, Pr^i and Bu^t is accompanied by divergent effects upon the positions and intensities of these *K*-bands. As *R* is changed progressively from Me to Bu^t, the inflection which corresponds to the transition (VII) undergoes a small blue-shift and progressively increases in intensity until (when $R = Bu^t$) it becomes a well-defined peak. Simultaneously, the peak which corresponds to the transition (VI) undergoes a small red-shift with progressive decrease in intensity. The behaviour of this latter peak upon varying *R* is exactly parallel to that which is found in the band for the

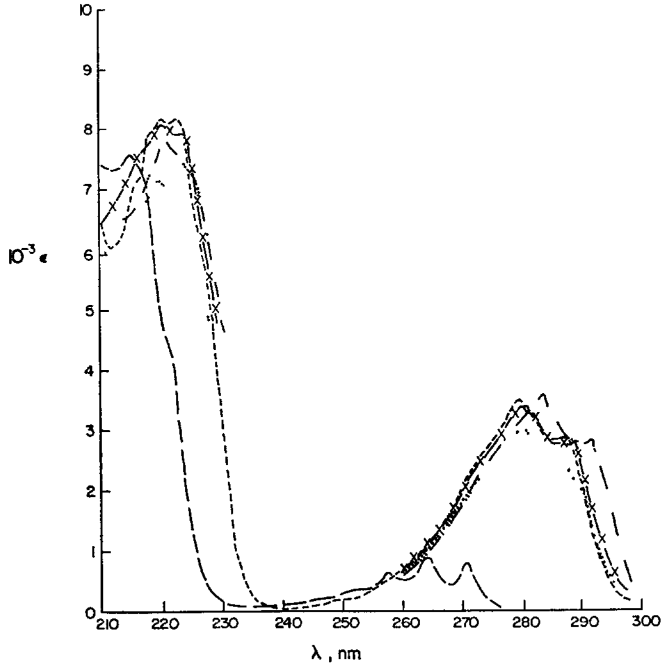


Fig. 2. U.v. spectra of alkyl *o*-methoxyphenyl sulphones (V), and methyl phenyl sulphone.

(V; R = Me)	— — — — — — — — — —
(V; R = Et)	··· ············
(V; R = Pr^i)	— × — × — × —
(V; R = Bu^t)	— · · · · — · · · · —
$PhSO_2{\cdot}Me$	—— —— —— —— ——

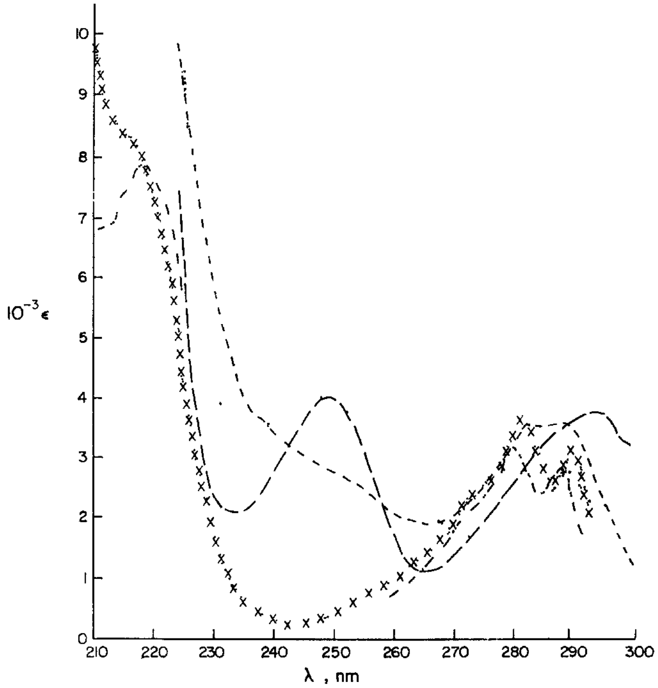


Fig. 3. U.v. spectra of cyclic sulphides (II; n 1–3), and sulphones (III; n 1 and 2).

(II; $n = 1$) — — — — — —
(II; $n = 2$) · · · · · · ·
(II; $n = 3$) —·—·—·—
(III; $n = 1$) × · · · × · · · ×
(III; $n = 2$) — ··—···—

same transition in the parent alkyl phenyl sulphides (IV; H in place of OMe) [2, 6]. This trend in ε may therefore with confidence be ascribed to a progressive inhibition of the mesomeric interaction between the sulphur atom and the aromatic ring, this being occasioned by the increasing steric interactions of the alkyl group attached to sulphur with the *o*-hydrogen atom and with the *o*′-methoxyl group. The bathochromic shift noted above can be ascribed, as in the previous case [2], to the increase in the stabilisation of the excited state by inductive electron-release from the alkyl group which increases in the order: $\mathrm{Me} < \mathrm{Et} < \mathrm{Pr}^i < \mathrm{Bu}^t$.

Braude and Sondheimer [7] used the relationship $\varepsilon/\varepsilon_0 = \cos^2 \theta$ to calculate θ, the angle of deviation from planarity in the ground state of two spectroscopically interacting (conjugated) chromophores; ε_0 is the molecular extinction coefficient when the chromophores are coplanar, and ε the molecular extinction coefficient when the angle of inclination of the planes of the chromophores is θ. This relationship has recently been used by Clark and Williams [8] to calculate the dihedral angle

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[6] E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.* **71**, 2890 (1949).

[7] E. A. Braude and F. Sondheimer, (a) *J. Chem. Soc.* 3754 (1955); (b) *J. Chem. Soc* 3773 (1955).

[8] E. R. Clark and S. G. Williams, *J. Chem. Soc.* (B) 859 (1967).

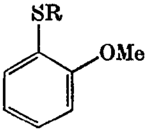
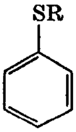
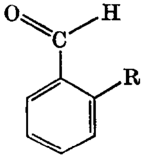
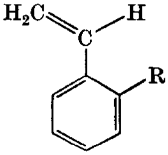
Table 1. Maxima in the u.v. spectra of alkyl *o*-methoxyphenyl sulphides, in hexane

	λ_{max} (nm)	ε	Band designation*
IV; R = Me	(233)	(4750)	K
	254·5	8270	K
	(281)	(3260)	B
	288	4000	
	295·5	3050	
IV; R = Et	(230)	(5810)	K
	256	7000	K
	283·5	3690	B
	288	3840	
	(296)	(2550)	
IV; R = Pr^i	(230·5)	(7000)	K
	257	4670	K
	283	4000	B
	289	3900	
IV; R = Bu^t	229·5	9500	K
	(258)	(1045)	K
	283	3610	B
	289	3280	
PhOMe	219·5	8050	K
	(258)	(710)	B
	265	1300	
	271	2045	
	277·5	1960	
PhSMe	254	9445	K
	(270)	(2475)	B
	(282)	(1010)	
	(290)	(468)	

( ) Denotes inflection.

* The Burawoy nomenclature is retained for convenience; see the text for the identification of the transitions.

Table 2. Angles of deviation from coplanarity, θ°

				
R = Me	21[a]	—	21[b]	28[b]
Et	31[a]	12[a]		
Pr^i	45[a]	36[a]		
Bu^t	71[a]	66[a]		

[a] Using PhSMe as datum.

[b] Ref. [7].

between the planes of the benzene ring and of the oxygen atom's bonds in the heterocycles (I; X = O; n = 1, 2 and 3). Using the data for the transition (VI), the value of θ was derived from the above expression for the compounds (IV; R = Me, Et, Pr^i, and Bu^t); furthermore, a similar calculation was performed on Foley's data [2] for the corresponding alkyl phenyl sulphides, RSPh. The results are collected in Table 2, and comparison is made with Braude and Sondheimer's values of θ for *o*-methyl-benzaldehyde and -styrene [7].

There is a close similarity between the values of θ obtained by the introduction of the *o*-MeO group into thioanisole and those values obtained from the introduction of the *o*-methyl group into benzaldehyde and styrene, respectively; it may therefore be concluded that the magnitude of the steric effect is very similar in these cases. For the thioethers (IV) and for their analogues PhSR, variation in R produces parallel trends in θ. That, for a given R, the value of θ for each of the compounds (IV) should be greater than that of the parent thioether, PhSR, is not surprising when scale drawings of the molecules (Fig. 4) are considered. For (IV; R = Me) in conformation *a*, there is perceptible interaction between the oxygen atom and the hydrogen atoms of the SMe group, which tends to force the latter out of coplanarity with the benzene ring by rotation about the S—$C_{ar.}$ bond.[*] In the thioethers PhSR, scale drawings (e.g. Fig. 4, conformations *d* and *e*) show that only when R = Pr^i or Bu^t do similar steric interactions occur between the *o*-hydrogen atom and the hydrogen atoms of the SR group.

The effects of changes in the structure of R upon the K-band near 230 nm are now considered. As R is varied from Me to Bu^t, the absorption band which is characteristic of the transition (VII) is located within only a small range of wavelength (*ca.* 3 nm). However, the same structural changes produce a more significant change in ε which consists of a progressive increase in its value. Braude and Sondheimer [7] have stated that the smallest shifts in wavelength which can be considered significant are of the order of *ca.* 5 nm. It is therefore considered that in the compounds (IV), steric interactions which curtail the conjugation of the oxygen atom with the benzene ring are unimportant. Moreover, the increased probability of the transition (VII) (increase in ε) appears to be a direct consequence of the reduction in the probability of the transition (VI) through steric interaction. Support for this view is afforded by the Fig. 4a.

The B-bands of the *o*-di-substituted compounds (IV; R = Me — Bu^t) all lie at longer wavelengths than those for both anisole [4] and thioanisole [5]. These B-bands are remarkable for their insensitivity to change in R; only when R = Bu^t is there a perceptible shift (hypsochromic, 5 nm), and change (*ca.* 10 per cent diminution) in ε. Burawoy [9] has shown that *o*-substituents behave as the terminal

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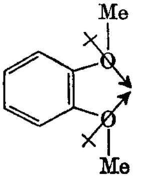
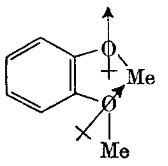
[*] Conformation *b* would require rotation about the O—C_{ar} bond in order to relieve the steric interaction between the sulphur atom and the hydrogen atoms of the OMe group; there is no spectroscopic evidence for this interaction. Conformation c is not favoured because of probable dipole interactions; cf. the dipole moment of veratrole (IV; SR = OMe), 1·23D, and the calculated moments [8a] of the conformations:



0·5D



2·1D

[8a] B. C. Curran, *J. Am. Chem. Soc.* **67**, 1835 (1945).

[9] A. Burawoy, *Hydrogen Bonding*, p. 267. Pergamon (1957); A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge and A. R. Thompson, *J. Chem. Soc.* 3721 (1955).

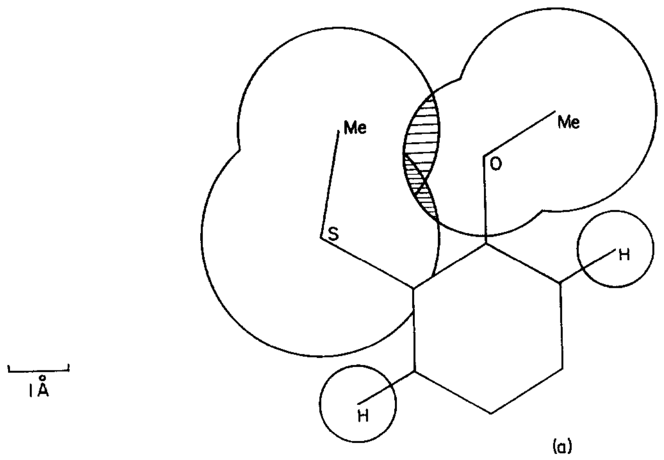


Fig. 4a.

Fig. 4. Scale drawings of "in-plane" conformations of methyl *o*-methoxyphenyl sulphide (IV; R = Me), and *t*-butyl phenyl sulphide. [Dimensions—bond lengths and interaction radii—see Refs. [7a, 8]; the interaction radius of sulphur was taken to be twice its covalent radius (cf. Ref. [7a]).]

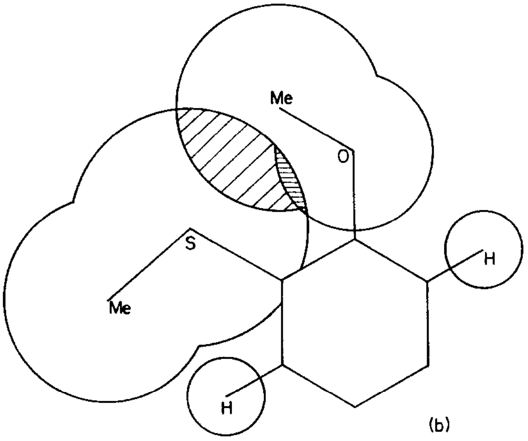


Fig. 4b.

groups of a conjugated system which extends round a benzene ring. B-bands are thus believed to arise from electronic transitions which may be represented by (VIII). The extension in the length of such an absorbing system over that in the monosubstituted analogue has the effect of shifting the B-band to longer wavelength and increasing the value of ε. Curtailment of such interactions may be expected to reverse these effects. This expectation is realised only in the case of (IV; $R = \mathrm{Bu}^t$). Comparing the trends in the K-bands for the transition (VI) with those in the B-bands, it would appear that the latter are much less sensitive to steric effects than the former. Despite the operation of a pronounced steric effect in (IV; $R = \mathrm{Bu}^t$), there is still a marked similarity between its spectrum and the spectra of the

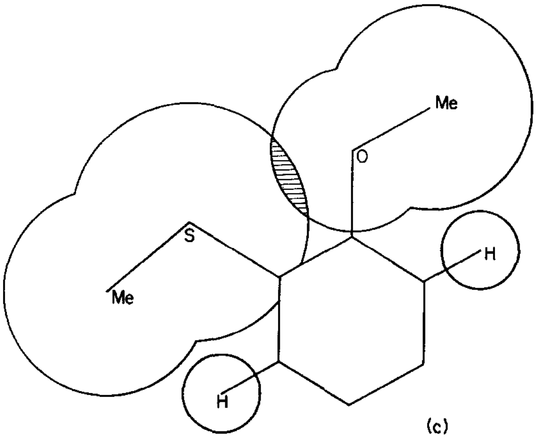


Fig. 4c

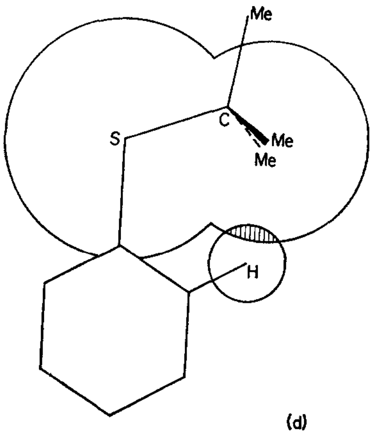


Fig. 4d

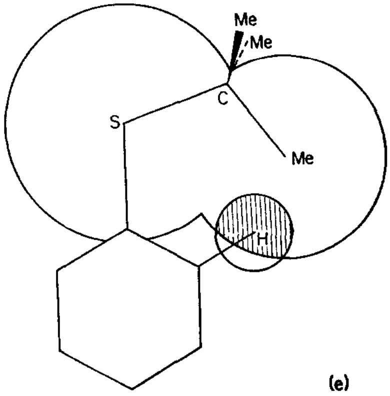


Fig. 4e

analogues (IV; R = Me — Pr^i). This suggests that the transition responsible for the B-band in these compounds is that depicted by (VIII; X = OMe, Y = SR). During this transition the sulphur atom would be expected to expand its octet, utilising its 3d orbitals. As the overlap of the 3d orbitals of the sulphur atom with the π-orbitals of the benzene ring is less angularly dependent than that of 3p orbitals, the smaller effect of the steric interactions when R = Bu^t is not surprising.

Fehnel and Carmack [10], and Baliah and his co-workers [11] have studied the effects of structure upon the u.v. spectra of methyl aryl sulphones; Table 3 contains some of their results.

Two areas of absorption are recognisable: an intense band near 220 nm, and a band of lower intensity near 270 nm. From Table 3, the effects of electron-releasing

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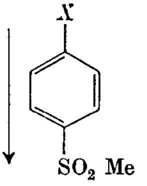
[10] E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.* **71**, 231 (1949); **72**, 1292 (1950).

[11] (a) V. Baliah and S. Shanmuganathan, *J. Indian Chem. Soc.* **35**, 31 (1958); (b) V. Baliah and V. Ramakrishnan, *J. Indian. Chem. Soc.* **35**, 151 (1958); (c) V. Baliah and T. Rangarajan, *J. Indian. Chem. Soc.* **38**, 33 (1961).

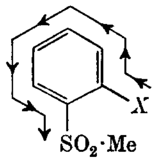
Table 3. U.v. absorption of methyl aryl sulphones [10, 11]

$R{\cdot}C_6H_4{\cdot}SO_2Me$	Wavelength, nm (ε)	
	K-band	B-band
R = *H*	217(7100)	264(900)
p-Me	225(11,750)	267(540)
o-Me	219(7200)	270(1700)
o-Bu^t	222(7200)	272(1700)
p-MeO	240(16,500)	—
o-MeO	224(8000)	283(4200)

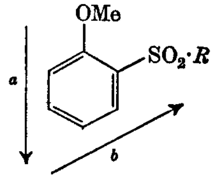
substituents situated *o*- or *p*- to the $SO_2{\cdot}Me$ group upon these bands can be seen. Two significant features are revealed: (i) a *p*-substituent produces a greater bathochromic shift (and increase in ε) upon the 220 nm band than does an *o*-substituent; (ii) an *o*-substituent produces a greater bathochromic shift (and increase in ε) upon the 270 nm band than does a *p*-substituent. This behaviour of the absorption bands characterises them as a *K*-band (220 nm band) and a *B*-band (270 nm band); the corresponding transitions are as shown in (IX) and (X), respectively. Table 4 records the wavelengths and extinction coefficients for the sulphones (V; *R* = Me — Bu^t), and for methyl phenyl sulphone. The data for the latter and for (V; *R* = Me) are in good agreement with those previously published [10, 11a, 11c].



(IX)



(X)



(XI)

In accordance with the conclusions drawn from the evidence in Table 3, the high intensity bands near 220 nm and the medium intensity bands near 270 nm in Table 4 are designated as *K*-, and *B*-bands, respectively. For compounds (V), the *K*-band consists of two peaks (or, as when *R* = Bu^t, one peak and an inflection); one peak remains constant at 220 ± 0·5 nm, whilst the other is found at 223–226 nm. (This fine structure was not reported by BALIAH and SHANMUGANATHAN, presumably on account of their having used ethanol as solvent.) Since the *K*-band of anisole occurs at 219·5 nm and that of methyl phenyl sulphone at 215 nm, these two peaks correspond to the transitions *a* and *b* in (XI). Now, BURAWOY has shown [9] that when a methoxyl group is present as a branch in an absorbing system, it produces only a *small* bathochromic effect upon the *K*-band of the parent compound. In the light of these precedents the peaks in the range 223–226 nm for the compounds (V; R = Me — Bu^t) are considered to arise from the transition *b* in (XI). The peak at *ca.* 220 nm corresponds therefore to the transition *a*; the lack of effect of the sulphone group upon the energy of the transition which involves the MeO group and the benzene ring is noteworthy, and may be related to its electron-attractive polarity. The comparative insensitivity of both the *K* (transition *b*)- and *B*-bands to change in *R* provides further evidence of the unimportance of steric effects upon conjugation

Table 4. Maxima in the u.v. spectra of alkyl *o*-methoxyphenyl sulphones, in hexane

	λ_{max} (nm)	ε	Band designation
V; R = Me	(216·5)	(7175)	K
	(218·5)	(7950)	
	220	8150	
	222·5	8180	
	(275)	(2750)	B
	279·5	3430	
	287·5	2850	
V; R = Et	219·5	7160	K
	223	7115	
	(275)	2375	B
	280	2985	
	287	2490	
V; R = Pr^i	220·5	8090	K
	223·5	7940	
	280	3350	B
	287	2760	
	288·5	2780	
V; R = Bu^t	220·5	7865	K
	(226)	(7085)	
	284	3550	B
	291·5	2790	
$PhSO_2{\cdot}Me$	215	7575	K
	(220·5)	(4600)	
	(252·5)	(325)	B
	257·5	625	
	264	850	
	270·5	750	

which involves the interaction of 2p and 3d orbitals [*cf.* 10, 11b, 11c]. The similarity between the B-bands of the sulphides (IV; R = Me – Bu^t) and of the corresponding sulphones (V) with regard to position, and to relative insensitivity to variation in R would appear to provide support for the view expressed above that the transition (VIII; X = OMe, Y = SR) is largely responsible for the B-band of the sulphides.

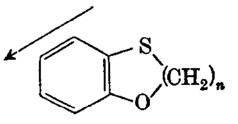
Cyclic sulphides (II) *and their sulphones* (III)

The sulphides (II) exhibit a K-band near 250 nm and a B-band near 290 nm (see Fig. 3 and Table 5). Change in the size of the hetero-ring from five ($n = 1$) to six ($n = 2$) members produces little change in the positions of both bands; a small reduction in the intensity of the B-band is observed. However, when $n = 3$, the K band undergoes a bathochromic shift and decrease in ε, whereas the B-band suffers a hypsochromic shift and the value of ε increases almost to that of the five-membered ring compound. It is therefore inferred that only in (II; $n = 3$) do the steric requirements for maximum conformational stability of the hetero-ring compete effectively with those for maximum conjugation between the benzene ring and the sulphur and/or oxygen atom; and that the transition (XII) is more affected by an unfavourable conformation of the hetero-ring than is the transition (XIII).

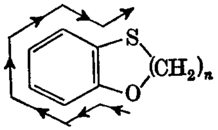
For the sulphones (III; $n = 1$ and 2), a K-band is recognisable near 220 nm, and a B-band (with some fine structure) in the region 280–290 nm. Expansion of the hetero-ring from five to six members is accompanied by a small bathochromic shift

Table 5. Maxima in the u.v. spectra of the cyclic sulphides (II) and their sulphones (III), in hexane

	λ_{max} (nm)	ε	Band designation
(II; $n = 1$)	249·5	3975	*K*
	293·5	3740	*B*
(II; $n = 2$)	244	4200	*K*
	252	3760	
	(282)	(2120)	*B*
	289	2760	
	297	2290	
(II; $n = 3$)	(254·5)	(2500)	*K*
	282	3530	*B*
	288	3580	
(III, $n = 1$)	(215)	(8350)	*K*
	281	3600	*B*
	290	3140	
(III, $n = 2$)	218	7860	*K*
	279 5	3130	*B*
	288	2810	



(XII)



(XIII)

of the *K*-band, and a small (*ca.* 2 nm) shift of the *B*-band. No useful conclusion can be drawn from this movement of the *K*-band because of its lack of fine structure. The small hypsochromic shift in the *B*-band *may*, however, be indicative of a small steric interaction arising from the six-membered ring's having to adopt an energetically unfavourable conformation.

EXPERIMENTAL

Materials

Anisole was purchased, and dried over sodium wire prior to distillation. Thioanisole was prepared from thiophenol, and the alkyl *o*-methoxyphenyl sulphides were prepared from *o*-methoxythiophenol by methods taken from the literature. The physical and (for new compounds) analytical data are given in Table 6. The alkyl aryl sulphones were prepared from the above sulphides by oxidation with hydrogen peroxide in acetic acid [13] Analytical data for the new compounds, and physical constants are given in Table 7.

Benz-1,3-oxathiole (II; $n = 1$). A solution of *o*-hydroxythiophenol (prepared from *o*-aminophenol by the xanthate method) (25 g) in ethyl methyl ketone (500 ml) was added during 14 hrs to a stirred, boiling mixture of dibromomethane (35 g) and anhydrous potassium carbonate (56 g) in ethyl methyl ketone (1 l.). After the addition, stirring and heating were continued for a further 6 hr. (A nitrogen

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[12] V. N. Ipatieff, H. Pines and B. S. Friedman, *J. Am. Chem. Soc.* **60,** 2731 (1938).

[13] F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.* **79,** 720 (1957).

Table 6. Alkyl aryl sulphides

Compound	Method of preparation	b.p. (°/mm)	n_D^{20}	Analysis Found (%) C	H	S	Required (%) C	H	S
PhSMe	(a)	84/20	1·5880	—	—	—	—	—	—
(IV; R = Me)	(a)	125/15	1·5939	—	—	—	—	—	—
(IV; R = Et)	(a)	130/15	1·5670	64·3	7·3	19·1	64·2	7·2	19·1
(IV; R = Pr^i)	(b)	129/14	1·5583	65·8	7·5	17·4	65·9	7·7	17·6
(IV; R = Bu^t)	(c)	133/15	1·5450	67·4	8·4	16·3	67·3	8·2	16·3

(a) ArSH and dialkyl sulphate in the presence of alkali.
(b) ArSH and Pr^{i}Br in the presence of alkali [12].
(c) ArSH and isobutene in sulphuric acid [12].

Table 7. Alkyl aryl sulphones

Compound	m p. (°C)	Analysis Found (%) C	H	S	Required (%) C	H	S
$PhSO_2Me$	86–87$^{(a)}$	—	—	—	—	—	—
(V; R = Me) [14]	92·5–93·5$^{(a)}$	—	—	—	—	—	—
(V; R = Et)	89·5–90·5$^{(a)}$	53·8	6·3	16·0	54·0	6·0	16·0
(V; R = Pr^i)	60–61$^{(b)}$	56·1	6·8	15·0	56·0	6·6	15·0
(V; R = Bu^t)	77–78$^{(b)}$	57·6	6·9	13·8	57·6	7·1	14·0

$^{(a)}$ From hot water.
$^{(b)}$ From aqueous methanol.

atmosphere was maintained throughout). The cooled mixture was filtered, the solvent recovered and the residue distilled to give *benz*-1,3-*oxathiole* (16·6 g, 59%), b.p. 96–97/9 mm, n_D^{20} 1·6124 (Found: C, 60·8; H, 4·3; S, 23·0. C_7H_6OS requires C, 60·9; H, 4·3; S, 23·2%). *Benz*-1,3-*oxathiole*-3-*dioxide* (III; $n = 1$) was obtained by heating a solution of (II; $n = 1$) (2·8 g) in glacial acetic acid (25 ml) with 30% hydrogen peroxide (12 ml) under reflux for one hour. When poured on to ice, the mixture gave a white solid (2·4 g, 70%), from which *benz*-1,3-*oxathiole*-3-*dioxide* was obtained as needles, m.p. 142–143°, on recrystallisation from methanol (Found: S, 19·0. $C_7H_6O_3S$ requires S, 18·8%).

Benz-1,4-oxathien (II; $n = 2$) was prepared from *o*-hydroxythiophenol and ethylene bromohydrin [15] according to the method of Greenwood and Stevenson [16]. It had b.p. 122–124°/15 mm, n_D^{20} 1·6025 (Found: C, 63·1; H, 5·4. Calc. for C_8H_8OS: C, 63·1; H, 5·3%). The sulphone (III; $n = 2$) [16], prepared by the same method as that described above, separated as needles (from aqueous methanol), m.p. 82–83° (Found: C, 52·1; H, 4·6. Calc. for $C_8H_8O_3S$: C, 52·2; H, 4·4%).

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[14] S. Smiles and M. E. Heppenstall, *J. Chem. Soc.* 903 (1938).

[15] J. Read and M. M. Williams, *J. Chem. Soc.* **111**, 240 (1917); **117**, 360, 1216 (1920); F. H. McDowall, *J. Chem. Soc.* 499 (1926).

[16] D. Greenwood and H. A. Stevenson, *J. Chem. Soc.* 1514 (1953).

Benz-1,5-oxathiepin (II; $n = 3$). A mixture of *o*-hydroxythiophenol (12·5 g) and allyl bromide (12·1 g) was stirred and irradiated for five hours with u.v. light (from a Hanovia 500 w mercury resonance lamp, 40 cm from the reaction mixture). The mixture, dissolved in ethyl methyl ketone (100 ml), was added during seven hours to a stirred suspension of anhydrous potassium carbonate (14 g) in boiling ethyl methyl ketone (1 l.). Heating and stirring were continued for a further four hours and, after cooling, the mixture was filtered. Concentration of the filtrate gave an oil, distillation of which gave *benz*-1,5-*oxathiepin* (14·5 g, 87%), b.p. 110–112°/11 mm, n_D^{20} 1·5765 (Found: C, 64·9; H, 5·7. $C_9H_{10}OS$ requires C, 65·0; H, 6·1%). Attempts to obtain the sulphone by the method described above were fruitless.

Light absorption measurements

The spectra were obtained using the following photoelectric spectrophotometers: a Hilger "Uvispek" [for (IV; R = Me – Bu^t) and (V; R = Me – Bu^t), PhOMe and PhSMe], and a Unicam SP 500 [for (II; $n = 1 - 3$), and (III; $n = 1, 2$)]. Hexane was used as solvent.

Acknowledgments—We thank Dr. A. R. THOMPSON for helpful discussions, and Mr. B. MANOHIN and his staff for the analyses.