Ultraviolet Absorption Spectra of Arenethiols and Alkyl Aryl Sulphides

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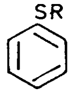
The u.v. absorption spectra of benzene-, toluene-, and mesitylene-thiols and the derived alkyl aryl sulphides have been determined and compared in polar and non-polar solvents. The effect of steric inhibition of resonance between the sulphur atom and aryl ring has been studied by varying the non-aryl sulphur substituent in the order H (thiols), Me, Et, Pr^i, and Bu^t, and also by introducing methyl groups on the aryl ring. Both the short wavelength (205—230 nm) and medium wavelength (235—270 nm) bands show a marked bathochromic shift when a t-butyl group or mesityl ring is introduced into the sulphides, whilst similar structural changes cause the long wavelength (275—300 nm) bands to undergo a hypsochromic shift. A rationalisation of the spectral changes has been examined using a free electron approach and assuming a predominantly conjugative interaction between the sulphur atom and the aryl group. An increase in the polarity of the solvent causes hypsochromic shifts which are increased by steric inhibition of resonance. The solvent shifts are attributed to hydrogen bonding to the sulphur atom.

In a previous paper[1] the u.v. spectra of 2,2'-bridged biphenyl derivatives with sulphide, sulphone, or ether groups at both ends of the bridge were investigated. Their spectra were complicated by the presence of conjugation of the phenyl ring with the sulphur or oxygen atom as well as the biphenyl conjugation. The interpretation of these spectra was assisted by making comparisons with the spectra of a series of alkyl phenyl sulphides (1) in which only phenyl–heteroatom conjugation is present. We now report an extension of this study which includes modification of the aryl ring in the form of *ortho-*, *meta-*, and *para-*tolyl derivatives (2)—(4) respectively and the mesityl derivatives (5).



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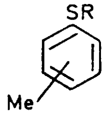

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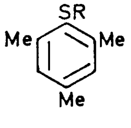

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The u.v. spectra of arenethiols and sulphides have been investigated by several workers[2-5] and the topic has

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[1] P. N. Braunton, I. T. Millar, and J. C. Tebby, *J.C.S. Perkin II*, 1972, 138.

[2] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84, 2889.

[3] H. P. Koch, *J. Chem. Soc.*, 1949, 387.

[4] A. Mangini and R. Passerini, *J. Chem. Soc.*, 1952, 1168.

[5] A. I. Kiss and B. R. Muth, *Acta Chim. Acad. Sci. Hung.* (*a*) 1960, **24**, 231; (*b*) 1960, **22**, 397.

been reviewed.[6,7a] Steric inhibition of lone-pair conjugation with the aryl ring together with large bathochromic and hyperchromic effects when *para*-orientated electron-withdrawing groups are attached to the aryl ring have shown that the sulphide group has a tendency to act as a lone-pair donor. The spectral changes which occur in a series of alkyl aryl sulphides have been interpreted in terms of the orientation of oscillating electric vectors.[2] Assignments of the bands have been made with the aid of molecular orbital and valence bond calculations[4] and also by comparison with the spectra of benzenethiol, phenol, and aniline.[5b] The conclusions have not been consistent.

RESULTS

The spectra of the benzene-, *o*-, *m*-, and *p*-toluene-, and mesitylene-thiols and the derived sulphides are recorded in Tables 1—3. In each series the non-aryl group varies in the order H (thiol), Me, Et, Pr^{i}, and Bu^{t}. The spectra contained three main bands, an intense band (log ε 4·0—4·5) at short wavelengths (205—230 nm), a moderately intense band (log ε 3·2—3·9) at medium wavelengths (235—270 nm), and a weak band (log ε 2·5—3·1) at long wavelengths (275—300 nm). The tendency of the bands to have shoulders or inflections differed. The vibrational structure of the weak band was the most persistent whereas the intense band possessed shoulders which were most pronounced in the less crowded alkyl sulphides. The central

TABLE 1

$\lambda_{max.}$/nm (log ε) Values of the main bands in the electronic absorption spectra of benzenethiol and alkyl phenyl sulphides (1)

Compound	Cyclohexane			95% Ethanol			5% Ethanol in water		
PhSH	205 (4·26)	236 (3·94)	280 * (2·82)	205 (4·20)	237 (3·92)	279 (2·92)	202 (4·20)	236 (3·81)	262 (3·30)
PhSMe	206 (4·19)	255 (4·02)	284 (3·00)	207 (4·11)	253 (3·99)	283 (2·93)	203 (4·23)	251 (3·99)	280 (2·97)
PhSEt	205 (4·08)	258 (3·88)	283 * (3·08)	205 (4·03)	255 (3·90)		203 (4·12)	250 (3·87)	
PhSPr^{i}	205 (4·32)	258 (3·78)	282i,† (3·11)	204 (4·04)	257 (3·75)		202 (4·18)	252 (3·77)	
PhSBu^{t}	220 (4·20)	268 (3·23)		219 (4·11)	265 (3·18)		218 (4·04)	257 (3·18)	

i = Inflection.

* Band bears several shoulders. † Band bears one shoulder. Units of ε, 1000 cm^{2} mol^{-1}.

TABLE 2

$\lambda_{max.}$/nm (log ε) Values of the main bands in the electronic absorption spectra of thiocresols and alkyl tolyl sulphides (2)—(4)

Compound	Cyclohexane			95% Ethanol			5% Ethanol in water		
				ortho-Compounds					
o-TolueneSH	208 (4·32)	235 (3·91)	277 * (2·89)	208 (4·36)	239 (3·85)	277 * (2·86)	205 (4·18)	237 (3·86)	277i (3·06)
o-TolylSMe	209 (4·26)	252 (3·89)	281i † (3·15)	209 (4·34)	250 (3·98)	278 (3·10)	206 (4·32)	247 (3·96)	276 (3·11)
o-TolylSEt	209 * (4·19)	254 (3·82)	281 (3·11)	209 (4·20)	251 (3·91)	279 (3·11)	205 (4·30)	247 (3·90)	275 (3·15)
o-TolylSPr^{i}	210 * (4·26)	253 (3·75)	281i † (3·20)	205 (4·20)	252 (3·71)	280 (3·15)	206 (4·18)	249 (3·72)	278 (3·11)
o-TolylSBu^{t}	224 (4·11)	271 (3·20)	277i (3·15)	223 (4·04)	271 (3·18)	277i (3·08)	218 (3·96)	263 (3·20)	277 (3·04)
				meta-Compounds					
m-TolueneSH	209 (4·32)	237 (3·84)	280i (2·86)	208 (4·36)	240 (3·86)	280i (2·92)	207 (4·30)	240 (3·84)	
m-TolylSMe	210i (4·20)	257 (3·93)	284i (2·97)	210 (4·28)	255 (3·97)	284i (2·98)	208 (4·23)	252 (3·92)	273i (3·06)
m-TolylSEt	210i * (4·12)	259 (3·86)	284i (3·04)	210 (4·20)	259 (3·90)		208 (4·23)	253 (3·85)	
m-TolylSPr^{i}	213i (4·23)	260 (3·82)	282i (3·15)	210 (4·11)	257 (3·78)		208 (4·18)	254 (3·73)	
m-TolylSBu^{t}	223 (4·04)	271 (3·23)	277i (3·15)	218 (4·08)	267 (3·23)	277i (3·08)	215 (4·08)	263 (3·20)	270 (3·18)
				para-Compounds					
p-TolueneSH	208 (4·30)	239 (3·99)	285i * (2·85)	206 (4·30)	239 (3·96)	284i * (2·92)	203 (4·32)	240 (3·91)	
p-TolylSMe	210 (4·08)	258 (3·96)	290i (2·93)	207 (4·18)	255 (4·08)	289i (2·92)	205 (4·32)	253 (4·01)	275 (3·07)
p-TolylSEt	210 [a] (4·11)	259 (3·84)	290i (2·86)	207 (4·11)	257 (3·97)		205 (4·15)	253 (3·91)	
p-TolylSPr^{i}	211 [a] (4·11)	261 (3·83)	290i (2·76)	222 (3·98)	257 (3·80)		220 (3·95)	254 (3·78)	
p-TolylSBu^{t}	225 (4·15)	267 (3·26)		224 (4·18)	263 (3·26)		223 (4·30)	258 (3·34)	

[a] This band appeared to be superimposed on a broader band which was centred at *ca*. 205 nm for the ethyl derivative and at 220 nm for the isopropyl derivative.

TABLE 3

$\lambda_{max.}$/nm (log ε) Values of the main bands in the electronic absorption spectra of mesitylenethiol and alkyl mesityl sulphides (5)

	Cyclohexane				95% Ethanol				5% Ethanol in water			
MesityleneSH		209 (4·47)	240 (3·89)	280i (2·86)		209 (4·45)	239 (3·84)	279i (2·96)		208 (4·47)	240 (3·92)	270i (3·04)
MesitylSMe	207 (4·46)	224 (4·01)	268 (3·34)		206 (4·43)	220 (4·04)	265 (3·34)		203 (4·58)	220 (4·00)	261 (3·36)	
MesitylSEt	206 (4·64)	225i (4·12)	267 (3·38)		205 (4·60)	220 (4·05)	265 (3·33)		205 (4·65)	220 (4·08)	262 (3·34)	
MesitylSPri	207 (4·67)	225i (4·18)	268 (3·46)		206 (4·61)	222 (4·11)	266 (3·40)		203 (4·62)	220 (4·09)	262 (3·43)	
MesitylSBu^{t}	210 (4·69)	230 (4·06)	274 (3·01)		207 (4·70)	231 (4·08)	275 (3·05)		207 (4·72)	235 (4·04)	280 (3·04)	

Footnotes as in Table 1.

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[6] D. Cagniant and P. Cagniant, *Bull. Soc. chim. France*, 1966, 228; R. C. Passerini, 'Organic Sulphur Compounds,' ed. N. Kharasch, Pergamon, London, 1961, vol. 1, p. 57.

[7] H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, (*a*) p. 466; (*b*) p. 266; (*c*) p. 242.

band (at medium wavelength) had the least tendency to show vibrational structure.

Figure 1 summarises the shifts of the positions of the bands for the thiols and sulphides in cyclohexane. All the bands showed a bathochromic shift when the hydrogen atom was replaced by a methyl group, the central band being the most strongly affected. There was little change in the position and intensity of the bands of the methyl, ethyl, and isopropyl derivatives. However there was a marked and very interesting change upon introducing the bulky t-butyl group. The short and medium wavelength bands showed a marked bathochromic shift whereas the long wavelength band underwent a hypsochromic shift; all the bands decreased in intensity. These shifts were confirmed by the spectra of the mesityl compounds (5). The mesityl methyl groups introduced severe steric inhibitions of resonance between the sulphur atom and the aryl ring as soon as the SH group was replaced by SMe. Thus the short and medium wavelength bands of the mesityl sulphides showed a very large bathochromic shift which immediately placed them close to the position of the bands of the t-butyl phenyl and tolyl sulphides. The position of the weak band became more difficult to ascertain as steric hindrance weakened it further and in order to determine the relative position of this band for the more hindered sulphides it was necessary to measure the wavelengths of absorption at log ε 2·3 (see Figure 1). Since the shifts of the wavelengths at log ε 2·3 parallel the shifts of $\lambda_{max.}$ for the less hindered sulphides, we consider this approach gives a reliable estimate of the relative positions of the secondary bands. The marked hypsochromic shift which occurs upon the introduction of a t-butyl group in the phenyl and tolyl sulphides was also confirmed by the spectra of the mesityl compounds, *i.e.* a large hypsochromic shift was observed for all the alkyl mesityl sulphides. The spectra of the thiols were also determined in basic solution. An intense and very broad band (log ε 3·99—4·14) occurred in the 261—269 nm region (see Table 4).

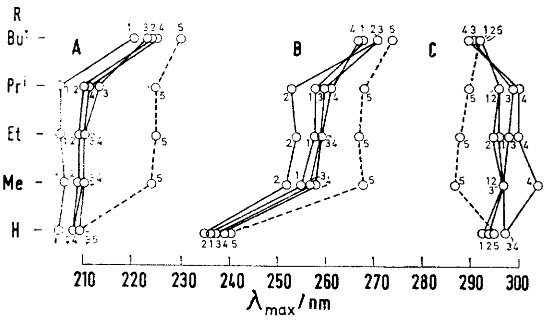


FIGURE 1 Change in $\lambda_{max.}$ of the primary bands and change in λ at log ε 2·3 in the u.v. spectra (cyclohexane solutions) of compounds (1)—(5) with the bulk of the R group: A, $\lambda_{max.}$ of primary β bands (log ε 4·0—4·5); B, $\lambda_{max.}$ of primary *p* bands (log ε 3·0—3·9); C, λ at log ε 2·3

An increase in the polarity of the solvent produced a small hypsochromic shift of *ca.* 5 nm for most bands. This tended to be larger for the central band of the alkyl sulphides and increased with the bulk of the *S*-alkyl group but not with the bulk of the aryl group, *i.e.* the mesityl sulphides (5). Aniline, *N*-methylaniline, *NN*-dimethylaniline, phenol, and the alkyl phenyl ethers also showed hypsochromic shifts in polar solvents, and the shifts increased with the bulk of the aryl group (see Table 5). In contrast the central band of the thiols showed a small bathochromic shift.

TABLE 4

$\lambda_{max.}$/nm (log ε) Values of the main bands in the electronic spectra of arenethiols in basic media

	Basified 95% ethanol		Basified 5% ethanol in water	
PhSH		269 (4·08)	216 (3·99)	264 (4·03)
o-TolueneSH		266 (3·99)	216 (4·14)	262 (4·08)
m-TolueneSH		269 (3·99)		263 (4·00)
p-TolueneSH		268 (4·10)		265 (4·07)
MesityleneSH	215 (4·42)	267 (4·06)	214 (4·33)	261 (4·14)

TABLE 5

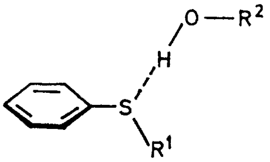
$\lambda_{max.}$/nm Values of the main bands in the electronic spectra of aniline and its *N*-methylated derivatives, and phenol and some of its alkyl ethers

	Cyclohexane			5% Ethanol in water	
$PhNH_2$	200 [a]	235 [b]	288 [c]	230	279
PhNHMe	203 [a]	245 [b]	295 [c]	236	284
$PhNMe_2$	209 [a]	252 [b]	298 [c]	244	288
PhOH		212 [d]	272 [c]	211	269
PhOMe		220 [d]	271 [c]	217	269
PhOEt		221 [d]	272 [c]	217	269
PhOPr^i		223 [d]	273 [c]	218	270
PhOBu^t		218	266	207	262

[a] log ε 4·3—4·5. [b] log ε 4·0—4·15. [c] log ε 3·0—3·4. [d] log ε *ca.* 3·8.

DISCUSSION

A change to more polar solvents generally causes bathochromic shifts for bands arising from $\pi \longrightarrow \pi^*$ transitions and a hypsochromic shift for bands arising from $n \longrightarrow \pi^*$ transitions. This generalisation arises mainly from studies of chromophores such as the carbonyl group. Bathochromic shifts for $\pi \longrightarrow \pi^*$ bands also applies to benzenoid compounds which bear electron-withdrawing groups but it has been stated [7b] to be negligible for benzenoid compounds bearing electron-donating substituents. Our results indicate that this is not true. Hypsochromic shifts were observed which were small for phenol and anisole (*ca.* 3 nm), but the shifts were larger (4—11 nm) for the sulphides and anilines; also the solvent shifts increased for the phenyl ethers and sulphides as the bulk of the R group increased. We suggest that hydrogen bonding between the hydroxylic solvents and the heteroatom [see (6)] increases with an increase of electron density on the heteroatom, *i.e.* as the inductive effect of R increases and as conjugation with the aryl ring decreases.* The bathochromic shifts of the central band of the thiols may be related to the



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* The bulk of the R group does not appear to hinder solvation presumably because it is orientated to one side of the plane of the aryl ring allowing formation of the solvent-hydrogen bond from the other side of the aryl ring.

opposite effect, *i.e.* the thiols are sufficiently acidic that the polar solvent assumes the role of a base. The effect is small and only sufficient to affect the more sensitive central band. Note that basification of the thiol solutions produced a 20—30 nm bathochromic shift for this band (see Table 4). Overall the solvent effects and the position of the bands show that there is considerable interaction of the sulphur atom with the aryl ring even when steric inhibition is at a maximum and indicate that there is a transfer of electron density towards the ring during excitation.

The short, medium, and long wavelength bands may be assigned to transitions originating from the second primary (β), first primary (*p*), and secondary (α) bands of benzene.[7c] The appearance of the β band above 200 nm at reduced intensity is in accordance with the strong conjugative effects of the sulphur atom. Thus the β band of benzene at $\lambda_{\text{max.}}$ 183 nm (log ε 4·7) appears at 197 (4·5) for aniline and at 205 nm (4·3) for thiophenol. The *p* and α bands are similarly shifted but with an increase in intensity. The shift of the *p* band from the thiophenols (thiophenol, $\lambda_{\text{max.}}$ 236 nm) to the sulphides (thioanisole, $\lambda_{\text{max.}}$ 255 nm) is quite marked. The shift is slightly larger than the shifts of the *p* bands in the anilines (aniline, $\lambda_{\text{max.}}$ 230; *N*-methylaniline, 243; and *NN*-dimethylaniline, 251 nm) (see Table 5). This is probably associated with the higher polarisability of sulphur.

Figure 1 shows that the introduction of a t-butyl group produces a marked bathochromic shift for the β and *p* bands but a hypsochromic shift for the α bands. An exception is the α band of the mesityl compounds. The position of the α bands in this series was confirmed by simple empirical curve analysis of absorbance plot spectra. The unusual effect of the t-butyl group on the α band of the mesityl compounds is attributed to some loss of planarity of the aryl ring. In support of this explanation the n.m.r. chemical shift of the aromatic protons of (5; R = Bu^{t}) was τ 3·06 compared with 3·20 for mesitylene and the other mesityl sulphides.

In a comparison of the effect of the different aryl groups (see Figure 1) notable is the shorter wavelength of the bands of most of the *o*-tolyl compounds (2) (it is especially noticeable for the central *p* band) and the longer wavelength of the bands of the *p*-tolyl compounds (4) (in this case it is particularly noticeable for the α band). The *ortho*-effect is not related to steric inhibition of resonance since the shift is in the opposite direction to that caused by the mesityl group. Therefore the *ortho*- and *para*-effects are probably of an electronic nature. The spectra of the mesityl sulphides (5) contain a fourth band, which appears in the short wavelength region (208 ± 2 nm) of the spectrum (see Table 3). It is very intense (log ε 4·5—4·7) and is attributed to the second part of the now non-degenerate β band, the other part appearing at *ca.* 225 nm (log ε 4·1).

The opposing shifts of the primary and secondary bands upon introducing steric inhibition of resonance is quite unusual. Twisting of an essentially single bond of a conjugated system normally produces a hypsochromic shift. The aryl ethers[8] are an example (see Table 5) and bulky substituents shift both primary and secondary bands to shorter wavelength with a corresponding reduction in intensity. Since sulphur is known to conjugate very strongly, it was of interest to examine conjugation effects on the energy of the molecular orbitals using the free electron model.

If the absorption bands are considered as arising from perturbed benzene transitions then the effect of conjugation *only* on the energies of the π orbitals of benzene * is to raise the energy levels of four of the six orbitals, as shown diagramatically in Figure 2. The two orbitals which possess nodes at a carbon atom are unaltered.

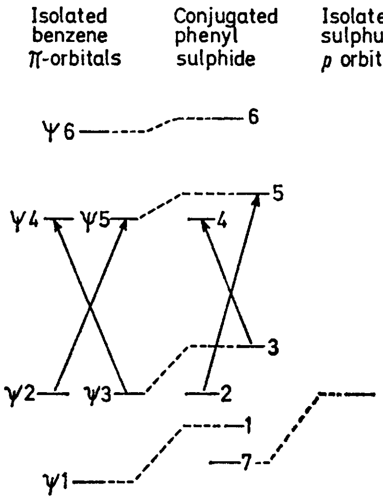

FIGURE 2 Representation of the conjugation effect of a sulphide group on the benzene π orbitals. Arrows indicate forbidden α and *p* transitions

The first primary and the secondary bands arise from the ' forbidden ' transitions, which are shown in Figure 2. It can be seen that conjugation with the sulphur atom increases the energy of the $\psi 2 \longrightarrow 5$ transition and decreases the energy of the $\psi 3 \longrightarrow 4$ transition. Thus a predominantly conjugative interaction could account for the opposing shifts of primary and secondary bands.

The ether group causes both benzenoid bands to undergo a bathochromic shift. A shift of the nodes of the $\psi 2$ and $\psi 4$ molecular orbitals away from C-1 would allow conjugation to raise the energies of all four orbitals ($\psi 2$ and $\psi 3$ more than $\psi 4$ and $\psi 5$). This would reduce the transition energies for both the $\psi 2 \longrightarrow 5$ and $\psi 3 \longrightarrow 4$ transitions in accordance with observation. Thus although *p* orbitals are probably involved in the interaction of the ether and sulphide groups with the aryl rings the opposite spectral shifts may be due to a

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* The orbital energy diagram ignores the interelectronic interactions which cause the secondary transition to be of lower energy than the primary one.[9] Therefore the changes indicated in Figure 2 are relative only.

[8] G. B. Baddely, N. H. P. Smith, and M. A. Vickers, *J. Chem. Soc.*, 1956, 2455.

[9] H. H. Jaffé, D. L. Beveridge, and M. Orchin, *J. Chem. Educ.*, 1967, **44**, 383.

difference in the nodal positions of the benzenoid molecular orbitals. The amount of charge transfer to the ring is probably different for the oxygen and sulphur atoms of these compounds but we are unable to decide if this is the cause of any orbital differences. A theoretical study of these interesting results would be desirable.

EXPERIMENTAL

Spectra were recorded on a Beckman DB–G grating spectrophotometer using matched silica 2 and 5 mm cells. Spurious maxima of lower wavelength than 208 nm can be produced by stray light when the solvent absorption is large.[10] Cyclohexane and 95% ethanol was purified by distillation and had 40% transmission in 2 mm cells at 202 nm and the stray light was $<1\%$ at 200 nm.

Solutions of suitable concentration were prepared by direct weighing (0·10—0·50 mg) on a Cahn balance. The loss of substance during weighing by evaporation was checked and found to be negligible. The accuracy of the volumetric flasks was determined by direct weighing, and the error estimated to be of the order of 1%. (The spectrum of each compound in a particular solvent was determined three times or until consistent results were obtained.) The spectra of the thiols in basic media were determined by adding a drop of 5N-sodium hydroxide in water to the cell solutions used to determine the spectra in neutral media; the addition of several more drops caused no change in the spectra.

The ethers, thiols, and sulphides were obtained by standard methods or were commercial samples, distilled until pure by b.p. and n.m.r. examination. The preparation and characterisation of these compounds will be reported separately.

We acknowledge the preliminary study carried out by Dr. P. N. Braunton on the phenyl sulphides and ethers and helpful discussions with Professor I. T. Millar.

[2/2465 *Received*, 31*st October*, 1972]

[10] Unicam SP 800 Instruction Manual, Section 11–4; G. H. Beavan, E. A. Johnson, R. G. J. Miller, and H. A. Willis, 'Molecular Spectroscopy,' Heywood, London, 1961, p. 65.