Ultraviolet Absorption Spectra of Alkyl Benzyl Sulphides. Conformational Analysis of Alkyl Aryl Sulphides

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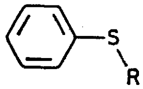
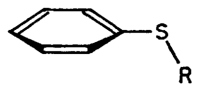
The u.v. spectra of a series of alkyl benzyl sulphides are consistent with the presence of a band which arises from mixed charge-transfer and locally excited states of very weakly π-conjugated sulphide and aryl groups. The u.v. spectra of alkyl aryl sulphides (including thioanisole) are consistent with the presence of one preferred conformation in which the alkylthio group is partially twisted out of plane of the aryl ring. *p*–π Overlap is sufficiently reduced to allow *d*-orbital participation to be detected.

THE u.v. spectra of alkyl aryl sulphides contain three bands in the region between 200 and 300 nm.[1,2] Although the central band near 255 nm is very sensitive to steric effects, the recent conformational analysis of these compounds utilised i.r. and photoelectron spectroscopy. The i.r. spectra indicate a steady decrease in conjugation between the phenyl ring and the sulphide group of alkyl phenyl sulphides (1) when the alkyl group is varied through the series methyl, ethyl, isopropyl, t-butyl.[3] On the other hand the photoelectron spectra indicate that there is a preference for two conformers, one with maximum *p*–π overlap (1a), the other with reduced overlap (1b), and that an increase in the bulk of the alkyl-thio group increases the proportion of the less conjugated conformer (1b).[4]


(1a)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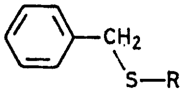
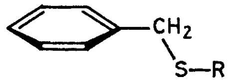

(2a)


(2b)

It has been established conclusively that the intensity of the u.v. absorption band in the central region decreases as the sulphide group is twisted out of plane of the aryl ring. However if the latest assignment of these bands is correct,[5] *i.e.* that the transition involves mixed charge-transfer and locally excited states, then the degree of *p*–π overlap required in the ground state to produce an intense absorption is uncertain.[6] Further information on these aspects were sought from the u.v. spectra of a series of alkyl benzyl sulphides (2).

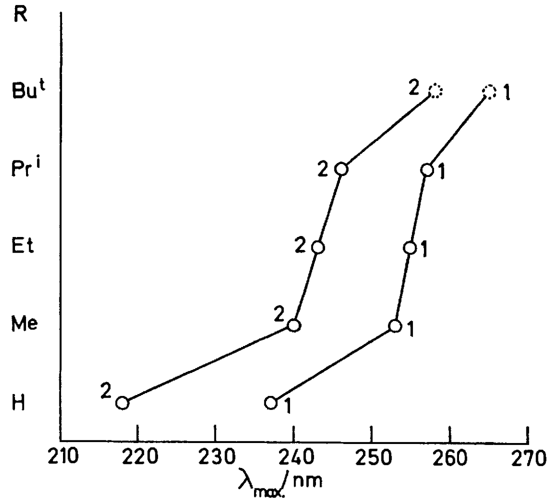
TABLE 1

Electronic spectra of alkyl benzyl sulphides in 95% ethanol

Compound	$\lambda_{max.}$/nm (log ε)		
BenzylSH	206 (4.04)	218 (3.86)	266 * (2.42)
BenzylSMe	207 (4.11)	240s (3.08)	266 * (2.57)
BenzylSEt	208 (4.11)	243s (3.04)	266 * (2.58)
BenzylSPr^i	208 (4.11)	246i (2.98)	266 * (2.57)
BenzylSBu^t	208 (4.11)		266 * (2.43)

* Structured band; s = shoulder, i = inflection.

The spectra of phenylmethanethiol and the sulphides (2) were determined on solutions in cyclohexane, 95% ethanol, and 5% ethanol in water. The change in solvent has little effect on the spectra and only the data for the 95% ethanol are presented in Table 1. The region above 200 nm contains three main bands: an intense band (log ε 4.04—4.11) at short wavelength (206—208 nm), a central band of variable intensity (log ε 3.86—2.98) and variable position (218—246 nm), and a weak band (log ε 2.42—2.58) at 266 nm. The latter band possesses well resolved vibrational fine structure when highly aqueous media are used. The short and long wavelength bands, which are little affected by modification of the alkylthio group, are attributed to the expected benzenoid transitions. Overlap of the long wavelength band accounts for the small variation of its extinction coefficient. The central band is influenced by the nature of the alkylthio group. It moves to longer wavelength and decreases in intensity as the R group is modified through the series H, Me, Et, Pr^i. The trend is the same as that for the central band of the aryl sulphides (see Figure). The absorption is so weak in the t-butyl compound that its position could not be accurately determined but its presence near 260 nm was apparent from the broadening of the long wavelength band. The much higher extinction coefficient (log ε 3.86) of the band at 218 nm of the thiol is probably due to overlap with the adjacent band because basification of the solution not only induced a 40 nm batho-



Change in $\lambda_{max.}$ of the central bands in the u.v. spectra (95% ethanol solutions) of phenyl sulphides (1) and benzyl sulphides (2) with the bulk of the R group chromic shift but also decreased the extinction coefficient to log ε 3.58.

The spectra show that absorption in the central region can occur when the extent of p–π conjugation in the ground state is quite low. The steric effects do not support the presence of charge-transfer transitions involving *non-conjugated* components.[7] Thus an increase in the bulk of the alkyl group should favour conformation (2b) which would make the charge-transfer (non-conjugated phenyl and sulphide) transition more probable; however the reverse is observed. Thus the results support the assignment of the central bands, for both the aryl and benzyl sulphides, to a charge-transfer transition which has mixed with locally excited states in a partially conjugated system. The marked sensitivity of the intensity of this band to steric effects indicates that the charge-transfer character is mainly in the excited state.[6] The spectra also show that the bathochromic shifts induced by steric effects on this type of transition can be just as large as the hypsochromic shifts which occur upon the steric distortion of fully conjugated molecules.

The spectrum of thioanisole (1; R = Me) contains a shoulder on the central band which in the vapour is found as a separate maximum, whereas for other n-alkyl sulphides in solution the additional band is only just discernible.[8] The splitting of the central band indicates that the locally excited and charge-transfer states are nearly degenerate. Such bands interact to give two bands whose separation is directly related to the resonance integral between the phenyl ring and the sulphide group. Thus the merging of the bands with increase in the bulk of the alkyl group is in accordance with conformational changes which reduce p–π conjugation.

The lack of any change in the benzenoid bands of the benzyl sulphides and the modest changes in the corresponding bands of the aryl sulphides support their origins from locally excited states. We have examined the spectra of the aryl sulphides for evidence of sulphur d-orbital participation because such a participation would be dependent on reduced p–π conjugation. Previous investigations of this kind has utilised interference experiments on the intensities of the ^1L_b band.[9] This method showed there to be no d-orbital involvement for arenethiols.[10]

The data on alkyl aryl sulphides in our previous report[1] (the relevant parts are reproduced in Table 2) show that an increase in the size of the alkyl group steadily reduces the intensity of the ^1L_b band of the p-tolyl sulphides but increases the intensity of this band for the phenyl sulphides. The intensity of the ^1L_b band of the o- and m-tolyl sulphides also increases. Thus the differences shown in Table 2 appear to be genuine reflections of changes in intensity of the bands, and, as interference experiments, the data show that d-orbitals are influencing the transition states, and furthermore, that the influence increases with the bulk of the alkyl group. This experiment shows that in contrast to the aryl thiols the b_1 π-orbitals of the alkyl aryl sulphides have at least an equal amount of benzene π and sulphur lone-pair character, *i.e.* the resonance integral has fallen to at least half.

TABLE 2

Electronic spectra of benzene- and toluene-p-thiols and their alkylated derivatives in cyclohexane

Compound	$\lambda_{max.}$/nm	log ε	Compound	$\lambda_{max.}$/nm	log ε
PhSH	280	2.82	p-TolylSH	285	2.85
PhSMe	284	3.00	p-TolylSMe	290	2.93
PhSEt	283	3.08	p-TolylSEt	290	2.86
PhSPr^i	282	3.11	p-TolylSPr^i	290	2.76

In conclusion the results do not support the presence of two preferred conformers, one with maximum p–π overlap. The considerable reduction of the resonance integral in thioanisole indicates that there is a significant distortion away from the planar conformation even before the more bulky groups such as isopropyl are introduced. Furthermore the merging of the split central band in the n-alkyl phenyl sulphides indicates an actual change in the extent of conjugation in the most preferred conformation.

EXPERIMENTAL

The u.v. spectra were determined as before[1] on a Perkin-Elmer 402 instrument using matched 5 mm silica cells. The compounds were prepared by standard procedures and characterised by i.r. and n.m.r. spectroscopy and m.p. or b.p.

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