352. *The Ultraviolet Absorption Spectra of some Arylthio-compounds, and of their Acetyl Derivatives.*

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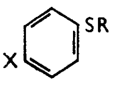
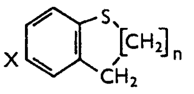
The ultraviolet absorption spectra of the organic sulphides PhSR (where R is Me, Et, Pr^i, and Bu^t) and o-$C_6H_4{\cdot}S{\cdot}[CH_2]_n$ (where $n = 2$—4), of their acetyl derivatives (Ac *para* to sulphur), and of methyl o-tolyl sulphide in hexane have been determined. The trends in the extinction coefficients reveal steric effects upon conjugation between the sulphur atom and the benzene ring. Parallel trends are observed in the (bathochromic) displacements of the absorption maxima of the acyclic sulphides and their acetyl derivatives, whereas for the cyclic compounds opposing trends are noted. The former are attributed to stabilisation of the photo-excited state by inductive electron-release from R to the sulphur atom.

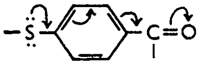
It has been shown [1] that, in aromatic ethers, the extent of mesomeric release of electrons from oxygen depends upon the angle (θ) between the plane of the oxygen atom's bonds and the plane of the benzene ring. The results now reported pertain to the ultraviolet absorption spectra of sulphides (Ia and IIa), and of the corresponding p-acetyl derivatives (Ib and IIb), and form part of a study of the effect on physical and chemical properties of varying the electron-release from a sulphur atom towards an aromatic nucleus.



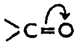
(I) a : X = H
b : X = Ac



(II) a : X = H
b : X = Ac



(III)



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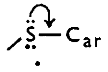

(V)

In hexane, the sulphides (Ia and IIa) (see Table) show only one ultraviolet absorption maximum in the region 2200—3200 Å, but the p-acetyl derivatives (Ib and IIb) show two (see Figure and Table). The values of $\lambda_{max.}$ for (Ia; R = Me, Et, Pr^i, and Bu^t) are in good agreement with those obtained by Fehnel and Carmack.[2] These bands are identified (cf. Burawoy [3]) as K-bands, and they show the usual trend in the value of ε (as R increases in bulk) that is expected for progressive inhibition of mesomeric release of electrons from sulphur towards the benzene ring. Ring closure from methyl o-tolyl sulphide to the dihydrobenzothiophen (IIa; $n = 1$) is accompanied by a small hypsochromic effect, but as n increases from 1 to 3, a bathochromic shift ensues. The corresponding changes in ε are in the sequence, (IIa; $n = 2$) > (IIa; $n = 1$) > o-$Me{\cdot}C_6H_4{\cdot}SMe$ > (IIa; $n = 3$).

Each absorption maximum of the ketones (Ib and IIb) is resolved into two peaks, separated by a shallow trough (cf. Braude and Sondheimer [4]). Both groups of bands are designated as K-bands; those lying near 2400 Å are probably due to absorption by the $\cdot CO\cdot C_6H_4\cdot$ partial chromophore (cf. ref. 4), while those in the vicinity of 3000 Å probably arise from interactions which encompass the whole conjugated system and which may be represented by (III). It is known [3] that extension of the length of a conjugated (absorbing) system produces a bathochromic displacement (with simultaneous increase in extinction) in the associated K-band; the latter assignment is made on this basis (compare curves A and B in the Figure). For compounds (Ib and IIb), variations in R and in n do

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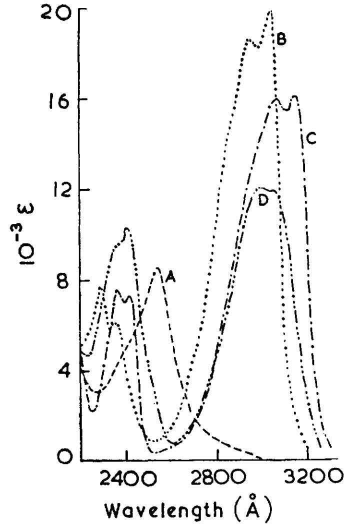
[1] Baddeley, Smith, and Vickars, *J.*, 1956, 2455.
[2] Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, (*a*) 84, (*b*) 2889.
[3] Burawoy, *J.*, 1939, 1177; *Tetrahedron*, 1958, **2**, 122.
[4] Braude and Sondheimer, *J.*, 1955, 3754.

not cause parallel variations in λ and ε for the two groups of bands. Greater significance is attached to the trends in the values of λ and of ε for the 3000 Å band.

Among ketones (Ib), change of R from Me to Et to Pr^i produces a progressive bathochromic shift and diminution in ε. These trends correspond to those for the parent sulphides (Ia). On the other hand, as *n* increases from 1 to 3, the absorption maxima for the acetyl compounds (IIb) suffer a hypsochromic displacement, while, however, changes in ε parallel those for the parents (IIa).

In general, for both acyclic and cyclic sulphides, the trends in ε (compare, *e.g.*, curves C and D in the Figure) indicate an increasing steric effect on the mesomeric interaction of the sulphur atom and the benzene ring. In the case of the five- and the six-membered ring systems (IIa and b; *n* = 1 and 2), the reversal of the usual trend in ε (compare the corresponding oxygen analogues,[1] although it is recognised that in these compounds the significant absorption corresponds to *B*-bands [3]) is possibly caused by the greater strain in the five-membered ring of 2,3-dihydrobenzo[*b*]thiophen (IIa; *n* = 1) than in that of coumaran (IIa; *n* = 1; O in place of S). This strain may be considered to arise from the distortion of the angle of the sulphur atom's bonds, a consequence of the smaller bond angle in sulphur than in oxygen. Fehnel and Carmack [2b] tentatively suggested that the



Ultraviolet absorption spectra of compounds: (A) Ia, R = Me; (B) Ib, R = Me; (C) IIb, *n* = 1; and (D) IIb, *n* = 3; all in hexane.

Ultraviolet absorption spectra (λ in Å) of aryl sulphides and their acetyl derivatives.

Sulphide	$\lambda_{max.}$	ε	Compound	$\lambda_{max.}$	ε
Ia; R = H	2355	8850	*o*-Me·C_6H_4·SMe	2505	8040
,, Me	2540	8520	IIa; *n* = 1	2500	8760
,, Et	2560	8150	,, 2	2600	10,700
,, Pr^i	2580	5600	,, 3	2620	6600
,, Bu^t	2680	1380			

Acetyl deriv.	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
Ib; R = H	2230	8000	2275 *	6150	2765	15,810	2870 *	13,150
,, Me	2290	7710	2360	6080	2950	18,600	3040	19,900
,, Et	2300	7000	2370	6440	2970	16,600	3050	17,280
,, Pr^i	2320	8050	2390	8900	3010	15,990	3080	16,750
IIb; *n* = 1	2370	7580	2420	7300	3070	16,070	3150	16,180
,, 2	2350	5850	2430	5120	3055	18,220	3130	17,840
,, 3	2380 *	9680	2410	10,310	3000	12,100	3060	11,990

* Inflexion.

bathochromic shifts in the spectra of compound (Ia) associated with the variation of R may be regarded as evidence for the expansion of the sulphur octet. Such a polarisation would be expected to act in opposition to that which is normal for the carbonyl group. The net electron-migration in the absorbing system would therefore be smaller than that which would result when the polarisations (IV) and (V) reinforce each other (see III). If the variation of R in the series Me, Et, Pr^i, and Bu^t gives rise to a progressively greater prominence of the expansion of the sulphur octet, then a decreasing bathochromic shift in the spectra of compounds (Ib) may be expected. The results now reported do not fulfil this expectation. On the contrary, the large bathochromic shift that accompanies the introduction into methyl phenyl sulphide (Ia; R = Me) of the *p*-acetyl group, and its further increase with change in R, show that the effective electron-migration increases with the size of R. We explain these trends as due to stabilisation of the excited state by inductive electron-release, which increases in the order $Me < Et < Pr^i < Bu^t$. The opposite trends in the absorption maxima produced by variation in ring size—bathochromic in (IIa), hypsochromic in (IIb)—probably indicate the greater importance of the steric effect of the ring upon the conjugation of the sulphur atom in the compounds (IIb; $n = 1$—3) than in the parent substances (IIa; $n = 1$—3, respectively). A more complete interpretation of these observations must await further work.

The Experimental section details the Friedel–Crafts acetylation of aromatic sulphides by Baddeley's procedure.[5]

EXPERIMENTAL

Materials.—Sulphides. Methyl phenyl sulphide (thioanisole), b. p. 75—76°/14 mm., n_D^{19} 1·5873, and ethyl phenyl sulphide, b. p. 87—88°/15 mm., n_D^{18} 1·5662, were prepared by alkylation of thiophenol with dimethyl sulphate and diethyl sulphate, respectively, in the presence of alkali. Isopropyl phenyl sulphide, b. p. 89—90°/15 mm., n_D^{18} 1·5470, and phenyl t-butyl sulphide, b. p. 100—103°/20 mm., n_D^{17} 1·5325, were obtained by the method of Pines *et al.*[6] Methyl *o*-tolyl sulphide, b. p. 98—100°/13 mm., n_D^{18} 1·5808, was prepared by methylation of *o*-thiocresol as above. *o*-Thiocresol, b. p. 83—87°/15 mm., was obtained from *o*-toluidine by the potassium ethyl xanthate method [7] (N.B.: the mixture of diazotised *o*-toluidine and potassium ethyl xanthate is liable to explode). 2,3-Dihydrobenzo[*b*]thiophen, b. p. 100—101°/11 mm., n_D^{18} 1·6188, was prepared from benzo[*b*]thiophen by way of the 1,1-dioxide, by the method of Bordwell and McKellin.[8] Thiochroman was obtained by reduction of chroman-4-thione with lithium aluminium hydride–aluminium chloride:[9] a solution of chroman-4-thione [10] (5·0 g.) and powdered anhydrous aluminium chloride (3·4 g.) in sodium-dried ether (100 ml.) was added with stirring to one of lithium aluminium hydride (2·6 g.) and powdered anhydrous aluminium chloride (10·0 g.) in sodium-dried ether (100 ml.) at such a rate as to maintain refluxing. Stirring was continued at room temperature for 30 min. after reaction had subsided, and then the excess of reducing agent was destroyed with ethyl acetate. The mixture was added to 6N-sulphuric acid, and thiochroman [11] (2·8 g., 60%), b. p. 128—130°/16 mm., n_D^{18} 1·6040 (Found: C, 72·0; H, 6·5. Calc. for $C_9H_{10}S$: C, 72·0; H, 6·6%), was isolated by conventional procedures. 2,3,4,5-Tetrahydro-1-benzothiepin (homothiochroman),[12] b. p. 142—144°/23 mm., n_D^{18} 1·5939 (Found: C, 73·0; H, 7·2. Calc. for $C_{10}H_{12}S$: C, 73·2; H, 7·3%), was obtained from the 5-ketone [12] by reduction in diethylene glycol with 90% hydrazine hydrate and potassium hydroxide.

Acetyl Derivatives.—The following method (cf. Baddeley [5]) was used to prepare the acetyl derivatives (Ib and IIb). To a solution of the complex of acetyl chloride (5·1 g.) and powdered anhydrous aluminium chloride (9·5 g.) in ethylene dichloride (50 ml.) was added a mixture of ethylene dichloride (15 ml.) and methyl phenyl sulphide (8·0 g.). The whole was left at room

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[5] Baddeley, *J.*, 1949, S99.
[6] Pines, Ipatieff, and Friedman, *J. Amer. Chem. Soc.*, 1938, **60**, 2731.
[7] Tarbell and Fukushima, *Org. Synth.*, Coll. Vol. III, 1955, p. 809.
[8] Bordwell and McKellin, *J. Amer. Chem. Soc.*, 1951, **73**, 2251.
[9] Nystrom and Rainier, *J. Amer. Chem. Soc.*, 1958, **80**, 2896.
[10] Krollpfeiffer and Schultze, *Ber.*, 1923, **56**, 1819.
[11] von Braun, *Ber.*, 1910, **43**, 3220.
[12] Cagniant and Deluzarche, *Compt. rend.*, 1946, **223**, 677.

temperature until the evolution of hydrogen chloride gas had ceased, then decomposed with ice and hydrochloric acid. The usual method of isolation gave *p*-(methylthio)acetophenone (6·4 g., 60%); extraction of this with hot light petroleum (b. p. 60—80°) and cooling gave needles, m. p. 79—80°;[13] the 2,4-dinitrophenylhydrazone separated from ethyl acetate as needles, m. p. 231—232°.[13]

Ethyl phenyl sulphide (9·1 g.) was similarly treated in ethylene dichloride (60 ml.) with acetyl chloride (5·2 g.) and anhydrous aluminium chloride (9·7 g.) and gave *p*-(ethylthio)-acetophenone[14] (5·8 g., 49%), needles [from light petroleum (b. p. <40°)], m. p. 43°; the 2,4-*dinitrophenylhydrazone* separated from ethyl acetate in needles, m. p. 191—191·5° (Found: C, 53·7; H, 4·7; N, 15·2. $C_{16}H_{16}N_4O_4S$ requires C, 53·3; H, 4·4; N, 15·5%). For the following compounds, the mixture was heated under reflux; the duration of heating is given after the quantities of reactants.

p-(*Isopropylthio*)*acetophenone* (3·0 g., 39%), prisms [from light petroleum (b. p. <40°)], m. p. 27° (Found: C, 68·3; H, 7·3; S, 16·4. $C_{11}H_{14}OS$ requires C, 68·0; H, 7·2; S, 16·5%), from isopropyl phenyl sulphide (6·0 g.), acetyl chloride (3·1 g.), anhydrous aluminium chloride (5·8 g.), and ethylene dichloride (100 ml.); 1 hr. The 2,4-*dinitrophenylhydrazone* (needles from ethyl acetate) had m. p. 172—173° (Found: C, 54·6; H, 4·5; N, 15·0. $C_{17}H_{18}N_4O_4S$ requires C, 54·5; H, 4·8; N, 15·0%).

5-*Acetyl*-2,3-*dihydrobenzo*[b]*thiophen* (3·8 g., 33%), needles [from light petroleum (b. p. <40°)], m. p. 43° (Found: C, 67·5; H, 5·8; S, 18·1. $C_{10}H_{10}OS$ requires C, 67·4; H, 5·6; S, 18·0%), from 2,3-dihydrobenzo[*b*]thiophen (9·0 g.), acetyl chloride (5·2 g.), anhydrous aluminium chloride (10·0 g.), and ethylene dichloride (150 ml.); 1 hr. The 2,4-*dinitrophenylhydrazone* (needles from ethyl acetate) had m. p. 282° (Found: C, 53·4; H, 4·0; N, 15·5. $C_{16}H_{14}N_4O_4S$ requires C, 53·6; H, 3·9; N, 15·6%).

6-Acetyl(thiochroman)[15] (2·6 g., 29%), needles [from light petroleum (b. p. <40°)], m. p. 49° (Found: C, 68·6; H, 6·4; S, 16·6. Calc. for $C_{11}H_{12}OS$: C, 68·7; H, 6·2; S, 16·7%), from thiochroman (7·0 g.), acetyl chloride (3·7 g.), anhydrous aluminium chloride (7·0 g.), and ethylene dichloride (150 ml.); 1 hr. The 2,4-dinitrophenylhydrazone separated from ethyl acetate as needles, m. p. 244°[15] (Found: C, 54·7; H, 4·4; N, 14·9. Calc. for $C_{17}H_{16}N_4O_4S$: C, 54·8; H, 4·3; N, 15·0%).

7-Acetyl-2,3,4,5-tetrahydro-1-benzothiepin, b. p. 200—204°/20 mm., n_D^{17} 1·6121 (Found: C, 69·7; H, 6·7. Calc. for $C_{12}H_{14}OS$: C, 69·9; H, 6·9%) [2,4-*dinitrophenylhydrazone*, needles (from ethanol), m. p. 194° (Found: C, 56·1; H, 4·8; N, 14·7. $C_{18}H_{18}N_4O_4S$ requires C, 55·9; H, 4·6; N, 14·5%)], was prepared by the published method.[12] *p*-Acetyl(thiophenol),[16] b. p. 148—150°/15 mm., m. p. 27°, was prepared[7] from 4-aminoacetophenone.

Spectra.—These were determined for hexane solutions by using a Hilger Uvispek photoelectric spectrophotometer.

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[13] King, McWhirter, and Rowland, *J. Amer. Chem. Soc.*, 1948, **70**, 239.

[14] Auwers and Beger, *Ber.*, 1894, **27**, 1738.

[15] Cagniant and Cagniant, *Compt. rend.*, 1950, **231**, 1508.

[16] Schwarzenbach and Rudin, *Helv. Chim. Acta*, 1939, **22**, 360.