90. *Absorption Spectra and Structure of Organic Sulphur Compounds. Part I. Unsaturated Sulphides.*

By H. P. Koch.

Ultraviolet absorption curves of various allyl, benzyl, acetyl, benzoyl, salicyl, phenyl, and nitrophenyl sulphides are presented and interpreted in terms of the most plausible polar excited structures deduced from the valency-bond resonance hypothesis. Hyperconjugation between C–S and C═C bonds is recognised in $\beta\gamma$-unsaturated sulphides, and first-order conjugation of lone-pair $3p^2$ sulphur electrons in $\alpha\beta$-unsaturated systems. The spectroscopic effect of crossed conjugation of a carbonyl group directly attached to both sulphur and an aromatic nucleus is exemplified by benzoyl and salicyl sulphides. A marked spectral variation which differentiates the isomeric 1- and 2-methyl*cyclo*hexyl phenyl sulphides is attributed to steric interference in the former molecule forbidding the geometrical conditions required for effective conjugation between sulphur and the benzene ring. Quasi-conjugation of the two aromatic rings appears to take place in diphenyl sulphide. Both steric and electronic interaction effects between non-bonded groups are invoked to account for the unusual chromophoric properties of phenyl *o*-nitrophenyl sulphide and related compounds.

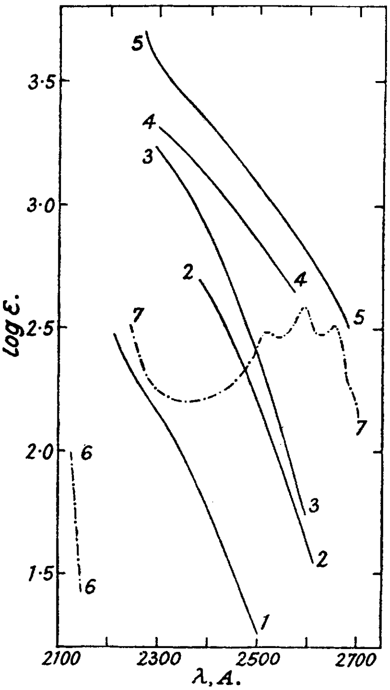
Although considerable progress has recently been made in the chemistry of organic sulphur compounds, mainly in relation to substances exhibiting anti-bacterial activity and in connection with the study of rubber vulcanisation, the reactivity of such molecules is still very imperfectly understood. The nature of electronic interaction between sulphur atoms and other functional groups requires much further elucidation. At the same time, the molecular structure of some important types of compound such as the polysulphides has not so far been established with any certainty.

Clearly, the final solution of such problems must await the application of rigorous wave-mechanical treatment on one hand and of *X*-ray structure analysis on the other, but in view of the rather intractable nature of these methods when applied to complex systems of a low degree of symmetry, it was thought worth while to explore the field by means of a more empirical approach. The ultraviolet absorption spectra in solution of a considerable variety of sulphur-containing molecules have therefore been examined, and the present series of papers is largely concerned with an attempt at correlation over a very extensive field. Although some of the results must necessarily be regarded as tentative, they will nevertheless suggest a number of useful points of attack for future work, and definitive conclusions about organic structure can often be deduced from the ultraviolet data. Further justification of the semi-empirical study of absorption spectra may be derived from the intrinsic value of the new experimental material which is thereby placed on record, be it for purposes of characterisation and chemical analysis or with regard to current theories of light absorption.

In absorbing ultraviolet rays of wave-lengths greater than 2000 A., a molecule passes from the ground state to an upper excited electronic level, and the frequency of the radiation absorbed is characteristic of the energy difference involved. Much of the subsequent discussion will be presented in terms of the commonly accepted working hypothesis that the excited state resulting from high-intensity absorption of light contains a significant proportion of polar structures in the resonance hybrid, and that the direction of polarisation in the excited structure is more or less parallel to the direction of the electric vector of the light absorbed. The postulated excited polar canonical structures will be chosen in accordance with the general rules that they should be energetically plausible, self-consistent over the entire field of sulphur compounds under investigation, compatible with the geometrical arrangement of the atoms in the molecule, and also as far as possible in agreement with the nature of the bonds as inferred from independent physical and chemical evidence. In the latter connection, reference will be made to *X*-ray and electron-diffraction data, vibrational spectra, and reactivity behaviour, wherever such information is available.

Saturated Dialkyl Sulphides.—The ultraviolet absorption spectra of dialkyl sulphides have hitherto been investigated mainly by Ley and Arends (*Z. physikal. Chem.*, 1932, *B*, **15**, 311) and by Sjöberg (*ibid.*, 1942, **52**, 209), who reported the occurrence of a characteristic maximum at 1960 A., preceded by a low-intensity inflection near 2300 A. The former absorption region falls outside the range of the conventional quartz spectrophotometer employed in the present work, but the inflection is indicated in the absorption curve of di-*n*-butyl sulphide which is reproduced in Fig. 1.

FIG. 1.



1. *Di-*n*-butyl sulphide.*
2. *Propyl allyl sulphide.*
3. *Diallyl sulphide.*
4. *Di*cyclo*hex-2-enyl sulphide.*
5. *Dibenzyl sulphide.*
6. cyclo*Hexene* (*in* C_6H_{12}).
7. *Dibenzyl ether* (*in* C_6H_{12}).

No interpretation of this dialkyl sulphide spectrum has hitherto been advanced. In view of the relatively high intensity of the absorption peak at 1960 A. (log ε >3), it seems likely that charge-transfer rather than a purely intra-atomic valency shell transition is involved (cf. Mulliken, *J. Chem. Physics*, 1939, **7**, 135), so that the excited state may be considered to contain a significant proportion of the polar structures (I). Such excitation involves the polarisation of the p–sp^3 bond between sulphur and carbon, and the charge may presumably be transferred in either direction in view of the equivalence of these two atoms on the electronegativity scale given by Pauling (" The Nature of the Chemical Bond ", p. 60).

βγ-Unsaturated Sulphides.—The absorption properties of allyl and benzyl sulphides differ markedly from those of saturated dialkyl sulphides, but in a manner to be expected from the above hypothesis of polarisation of the sulphur–carbon bond in the excited structure (I). Curves 1, 2, and 6 of Fig. 1 demonstrate that propyl allyl sulphide (II) absorbs much more strongly and at longer waves than the sum of the separate absorptions of a saturated sulphide and a typical olefin, although sulphur and double bond are chromophorically insulated by the saturated methylene group in this molecule. Some kind of electronic interaction is evidently taking place, and the energy of the excited state has become lowered relative to that of the ground state. This phenomenon may be readily accounted for by a combination of the previously postulated structure (I) with the well-known principle of allylic resonance. In propyl allyl sulphide the first excited state would be expected to become stabilised by additional resonance contributions from the structures (III), resulting in the observed red shift of the ultraviolet absorption spectrum. Similar and yet more marked effects occur in diallyl sulphide (curve 3) and in the secondary βγ-unsaturated di*cyclo*hexenyl derivative (curve 4). Again, the absorption properties of dibenzyl sulphide (V; curve 5) may be contrasted with those of the homologous oxide (VI; curve 7) which has been examined by Mayer-Pitsch (*Z. Elektrochem.*, 1943, **49**, 368). The dibenzyl ether spectrum is " normal " in its close resemblance to the absorption of two chromophorically insulated alkylbenzene systems, but dibenzyl sulphide absorbs much more strongly with complete masking of the aromatic fine-structure bands. It is suggested that canonical structures of the polar (*o*- or *p*-) quinonoid type (VII) make a significant contribution to the optically excited state.

$CH_2R{-}\overset{\pm}{S}\ \overset{\mp}{C}H_2R$ (I.)

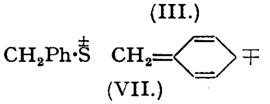
$CH_2Et\cdot S\cdot CH_2\cdot CH{:}CH_2$ (II.)

$CH_2Et\cdot\overset{\pm}{S}\ CH_2{:}CH\cdot\overset{\mp}{C}H_2$ (III.)

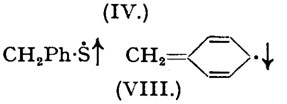
$CH_2Et\cdot\dot{S}\uparrow\ CH_2{:}CH\cdot\dot{C}H_2\downarrow$ (IV.)

$CH_2Ph\cdot S\cdot CH_2Ph$ (V.)

$CH_2Ph\cdot O\cdot CH_2Ph$ (VI.)



(VII.)



(VIII.)

Some interesting support for the above ideas may be obtained from chemical and infra-red data which suggest that excited structures similar to (III) and (VII), possibly of the formal-bonded type (IV) and (VIII), may be of some importance in reactivity phenomena and even in the ground state of the molecule. Thus, Dr. Norman Sheppard (private communication) has observed that the S–C stretching vibration occurs at much lower frequencies in allyl that in saturated sulphides, and a similar effect is implicit in the data of Trotter and Thompson on benzyl and other disulphides (*J.*, 1946, 481; see following paper). These low-vibration frequencies are almost certainly indicative of a reduction in the physical strength of the sulphur–carbon bonds compared with those of the saturated analogues. Again, the relative chemical instability of the S–C linkage in βγ-unsaturated sulphides is apparent in the rather facile decomposition of dibenzyl sulphide on heating or in the presence of alkali (Hinsberg, *Ber.*, 1931, **64**, 2500), in the bond fission which occurs on reaction of diallyl sulphide with methyl iodide (Selker and Kemp, *Ind. Eng. Chem.*, 1944, **36**, 16), and in the equally characteristic reductive scission undergone by allylic but not by saturated sulphides in the presence of nascent hydrogen (Farmer and Shipley, *J. Polymer Sci.*, 1946, **1**, 300).

Clearly the ultraviolet, infra-red, and chemical evidence all seems to lead to the same general conclusion that a process akin to hyperconjugation takes place in the system $\mathrm{C{=}C{-}C{-}S}$. Similar hyperconjugation has long been recognised in α-methylenic olefins, $\mathrm{C{=}C{-}C{-}H}$ (cf. Deasy, *Chem. Reviews*, 1945, **36**, 145), and recently also in allylic halides, $\mathrm{C{=}C{-}C{-}Hal}$ (Baker, *Trans. Faraday Soc.*, 1941, **37**, 635; De la Mare, Hughes, and Ingold, *J.*, 1948, 17).

αβ-Unsaturated Sulphides.—It is well known that when an atom such as chlorine or nitrogen is directly attached to a carbon–carbon double bond, conjugation occurs between the unsaturated grouping and a lone pair of non-bonding *p*-electrons on the hetero-atom (cf. Walsh, *Trans. Faraday Soc.*, 1945, **41**, 35; Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45). The lone pair of $3p^2$ electrons in the outer valency shell of the sulphur atom displays analogous conjugating properties in αβ-unsaturated suphides, exemplified by such phenomena as the aromatic character of thiophen (Pauling, *op. cit.*, p. 226) or the low dipole moment of divinyl sulphide (IX) which is attributable to resonating polar structures of type (X) (Hannay and Smyth, *J. Amer. Chem. Soc.*, 1946, **68**, 1005). As would be expected from such first-order conjugation, αβ-unsaturated sulphides absorb much more strongly in the ultraviolet than either the saturated or the hyperconjugated βγ-unsaturated compounds. For instance, divinyl sulphide is reported to exhibit an absorption maximum of $\varepsilon = 5000$ near 2550 A. (Mohler, *Helv. Chim. Acta*, 1940, **23**, 1200), and 2-chloroethyl vinyl sulphide gives rise to a strong band at 2280 A. ($\varepsilon = 7000$) according to Bowden, Braude, and Jones (*J.*, 1946, 948). Vinyl sulphides, however, are not easily accessible in a state of high purity, and in the present paper a detailed account will be given of the spectra of phenyl and of α-carbonyl sulphides as interesting examples of this type of conjugation.

According to the views independently put forward by Kimball (*J. Chem. Physics*, 1940, **8**, 188) and by Rothstein (*J.*, 1940, 1550), an electron pair may be donated to one of the unfilled 3*d* orbitals of the sulphur atom. It is therefore possible that oppositely charged structures (X*a*) might also make some contribution to the excited states of vinyl and phenyl sulphides.

(IX.) $\mathrm{CH_2{:}CH{\cdot}\ddot{S}{-}CH{:}CH_2}$ (X.) $\mathrm{CH_2{:}CH{\cdot}\overset{+}{S}{:}CH{\cdot}C\overset{-}{H}_2}$ (X*a*.) $\mathrm{CH_2{:}CH{\cdot}\overset{-}{S}{:}CH{\cdot}C\overset{+}{H}_2}$

Acetyl Sulphides.—The ultraviolet absorption properties of a number of simple acetyl sulphides of the general formula (XI) have already been examined in alcoholic solution by Sjöberg (*loc. cit.*), who observed characteristic high-intensity maxima (log ε 3·56—3·60) near 2300 A. A similar band is also given by acetyl *cyclo*hexyl sulphide (XII; $\mathrm{R' = C_6H_{11}}$) in *cyclo*hexane solution ($\varepsilon = 4500$ at 2315 A.; curve 1 of Fig. 2), and this spectrum is undoubtedly associated with the sulphur–carbonyl conjugation involving contributions from the polar canonical structure (XIII) in the excited state.

Progressive red shifts are displayed on stepwise replacement of the three hydrogen atoms of the acetyl group by chlorine. Thus, chloroacetyl *cyclo*hexyl sulphide absorbs maximally at 2380 A., the dichloroacetyl derivative at 2495 A., and the trichloro-compound at 2545 A., although no corresponding increases are noted in the intensity of the absorption (cf. Fig. 3). It seems likely that the explanation of these halogenation red shifts is to be sought in a raising of the ground state relative to the excited state, rather than in any change in the latter. Similar inductive or charge-transfer effects of chlorine transmitted through one saturated carbon atom are well known to affect the ground state of the related chloroacetic acids (XIV).

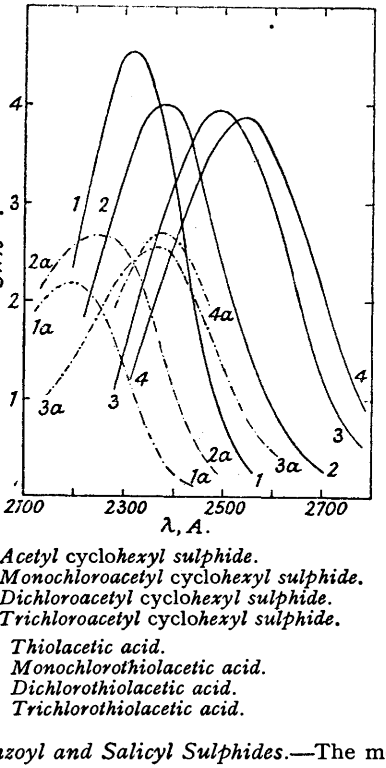
$\mathrm{CH_2R{-}\ddot{S}{-}CO{\cdot}CH_3}$ (XI.) $\mathrm{R'{-}\ddot{S}{-}CO{\cdot}CH_3}$ (XII.) $\mathrm{R'{-}\overset{+}{S}{=}C\overset{-}{O}{-}CH_3}$ (XIII.) $\mathrm{H{-}O{-}CO{-}CH_2Cl}$ (XIV.)

The broken curves of Fig. 2 illustrate the spectra of the acetyl hydrogen sulphides (thiolacetic acids; XII, R′ = H) corresponding to the above *cyclo*hexyl-substituted compounds. Infra-red absorption and other physical data confirm the acetyl–thiol structure of thiolacetic acid itself, and the curves show that the ultraviolet spectra of all four acids are of the same general type as those of their alkyl derivatives, although both wave-length and intensity of the bands have become considerably reduced. Electron-diffraction bond-length measurements due to Gordy (*J. Chem. Physics*, 1946, **14**, 560) suggest that the polar structure (XIII; R′ = H) makes only a very slight contribution to the ground state of thiolacetic acid.

It has previously been reported from these laboratories (Cunneen, *J.*, 1947, 137) that variation of the nature of the alkyl substituent has no influence on the acetyl sulphide spectrum, *cyclo*hexyl, 2-methyl*cyclo*hexyl, dihydromyrcene, and rubber acetyl sulphides being virtually identical in this respect.

FIG. 2.

Acetyl sulphides (in C_6H_{12}*).*

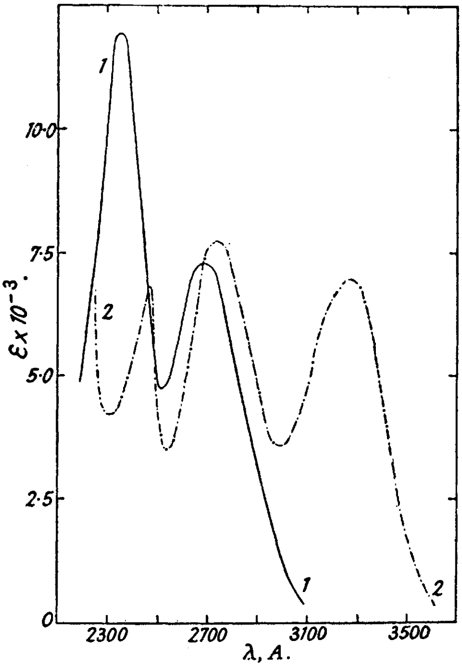


1. *Acetyl* cyclo*hexyl sulphide.*
2. *Monochloroacetyl* cyclo*hexyl sulphide.*
3. *Dichloroacetyl* cyclo*hexyl sulphide.*
4. *Trichloroacetyl* cyclo*hexyl sulphide.*

1*a*. *Thiolacetic acid.*
2*a*. *Monochlorothiolacetic acid.*
3*a*. *Dichlorothiolacetic acid.*
4*a*. *Trichlorothiolacetic acid.*

FIG. 3.

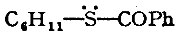
Benzoyl sulphides (in C_6H_{12}*).*



1. *Benzoyl* cyclo*hexyl sulphide.*
2. o-*Hydroxybenzoyl* cyclo*hexyl sulphide.*

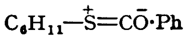
Benzoyl and Salicyl Sulphides.—The molecule of benzoyl *cyclo*hexyl sulphide (XV) contains a system of crossed conjugation. Two alternative polar excited structures are reasonable, in which the oxygen acquires negative charge either from the sulphur atom (XVI) or from the benzene ring (XVII; *p*- or *o*-quinonoid). The observed ultraviolet spectral characteristics strongly suggest that both types of excitation take place independently of each other on absorption of light (curve 1 of Fig. 3). The first band at 2680 A. (ε = 7300) greatly resembles the analogous maxima of the series of acetyl sulphides, except for a further red shift which may be attributed to the ground-state effect of phenyl substitution. On the other hand, the more intense maximum at 2350 A. (ε = 12,000) coincides with the absorption displayed by an isolated benzoyl group in such molecules as acetophenone or dibenzoyl peroxide. Thus, the two absorption regions of benzoyl *cyclo*hexyl sulphide appear to correspond to two distinct modes of electronic transition, one (at 2680 A.) proceeding to an excited state containing a high proportion of the polar form (XVI), and the other (at 2350 A.) to an upper level involving the quinonoid structures (XVII). These two types of excitation occurring in the same molecule preserve their independent identity presumably because they are associated with electric moments approximately at right angles to each other in the plane of the conjugated system. For a given molecule (XVIII) at any given instant, the main absorption may be visualised as taking place *either* at 2680 A. *or* at 2350 A., depending on the orientation of the molecule relative to the electric vector of the incident light. Other analogous systems of crossed conjugation will be discussed in Part III.

When a hydroxyl group is substituted in the *o*-position of the benzoyl sulphide molecule, further interesting spectral changes occur (curve 2, Fig. 3). The 2680 A. sulphur conjugation band is only slightly changed (maximum at 2745 A., ε = 7700), but the integrated area of the benzoyl absorption has been greatly reduced (ε = 6700 at 2475 A.) while there emerges a new long-wave band at 3275 A. (ε = 7000). The latter wave-length position is characteristic of the salicyl group (Morton and Stubbs, *J.*, 1940, 1354), and the new band is doubtless associated with the polar excited structure (XIX), utilising the electron-donor properties of the phenolic oxygen. The electric moment of this transition should be expected to be inclined at some 45° to that of the benzoyl type of excitation, and it seems to " steal " most of the intensity of the latter.



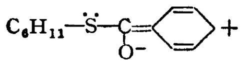
$C_6H_{11}-\overset{\bullet\bullet}{S}-COPh$

(XV.)



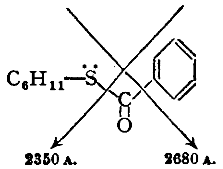
$C_6H_{11}-\overset{+}{S}=C\overset{-}{O}\cdot Ph$

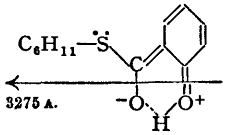
(XVI.)



(XVII.)

(XVIII.)





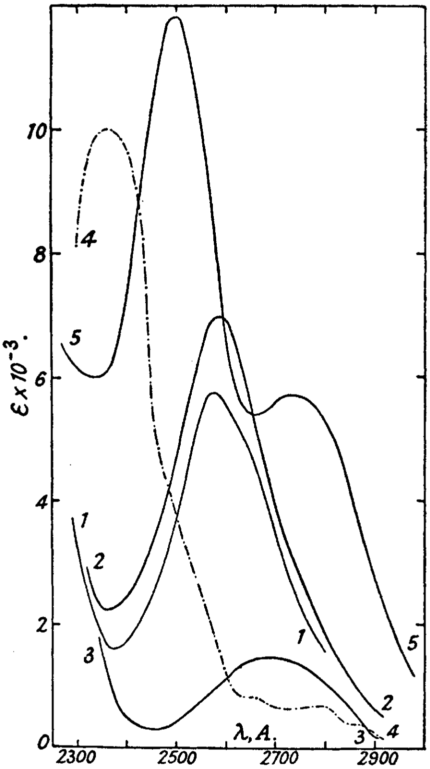
(XIX.)

Phenyl Sulphides.—The broken curve 4 of Fig. 4 represents the spectrum of thoiphenol, in good accord with similar measurements by Chaix (*Bull. Soc. chim.*, 1933, **53**, 700), Böhme and Wagner (*Ber.*, 1942, **75**, 606), and Bowden, Braude, and Jones (*loc. cit.*). The relatively weak and discontinuous first absorption region from 2950 to 2600 A. is no doubt due to the partial benzenoid chromophore, while the intense band at 2360 A. must be assigned to first-order conjugation between the non-bonding ($3p^2$) electron pair of the sulphur atom and the π-electrons of the benzene ring. Curves 1 and 2 indicate that alkylation of the acidic hydrogen induces a marked red shift of this absorption, similar to that observed with thiolacetic acid, although the extinction coefficient is here reduced rather than intensified.

A remarkable variation arises between the spectral curves 2 and 3 which differentiate the isomeric 1-methyl- and 2-methyl-*cyclo*hexyl phenyl sulphides (cf. Cunneen, *J.*, 1947, 36). In accordance with normal expectation, the 2-methyl isomer (XX) resembles the non-methylated *cyclo*hexyl compound in displaying a strong band at 2590 A. (ε = 7000), attributable to excitation involving the plausible polar resonance structures (XXI; *p*- or *o*-quinonoid); but little more than the residual aromatic absorption occurs when the methyl substituent is placed in the 1-position (XXII). The explanation of this anomaly is to be sought in steric factors. The

Fig. 4.

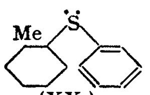
Phenyl sulphides.



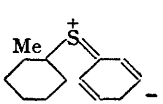
1. cyclo*Hexyl phenyl sulphide* (*in* C_6H_{12}).
2. 2-*Methyl*cyclo*hexyl phenyl sulphide* (*in* C_6H_{12}).
3. 1-*Methyl*cyclo*hexyl phenyl sulphide* (*in* C_6H_{12}).
4. *Thiophenol* (*in* C_6H_{12}).
5. *Diphenyl sulphide* (*in* EtOH).

symmetry properties of the sulphur *p*-orbitals require that in the polar excited form (XXI) the sulphur–*cyclo*hexyl single bond should lie in the same plane as the benzene ring, a condition which cannot be fulfilled in the molecule of 1-methyl*cyclo*hexyl phenyl sulphide (XXII) because of steric hindrance. Scale models of the latter isomer suggest that considerable spatial interference occurs between an aromatic *o*-hydrogen and one of the groups attached to the quaternary carbon atom as long as the sulphur–*cyclo*hexyl bond is kept coplanar with the benzene ring. The polar resonance form analogous to (XXI) would therefore be highly unstable in the 1-methyl compound (XXII), a circumstance which brings about the disappearance of the characteristic ultraviolet absorption.

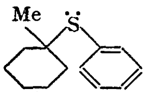
Diphenyl sulphide (XXIII; curve 5 of Fig. 4) gives rise to two high-intensity absorption bands, at 2740 A. ($\varepsilon = 5700$) and at 2500 A. ($\varepsilon = 11,800$), in agreement with those recorded by Chaix (*loc. cit.*). The 2740 A. absorption no doubt corresponds to the 2575 A. sulphur–benzene conjugation band of *cyclo*hexyl phenyl sulphide which is of similar intensity, the red shift being attributable at least in part to a change in the energy of the ground state. As regards the new and very strong maximum at 2500 A., comparison with the spectra of related molecules suggests that the associated upper electronic state may involve the resonance of charge between the two aromatic rings which are quasi-conjugated *via* the non-bonding $3p$ orbital of the intervening sulphur atom. Similarly intense ultraviolet absorption has been observed in the 2000—2500 A. region of diphenyl ether (XXIV) (Mayer-Pitsch, *loc. cit.*) and *as*-diphenylethylene (XXV) (Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1818). In terms of the conventional valency-bond formulæ, the postulated excited level contains important contributions from a resonance hybrid of the equivalent structures (XXVI, *a* and *b*).



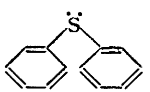
(XX.)



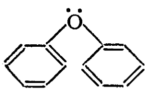
(XXI.)



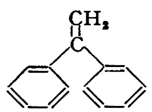
(XXII.)



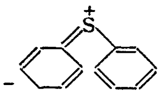
(XXIII.)



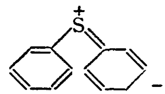
(XXIV.)



(XXV.)

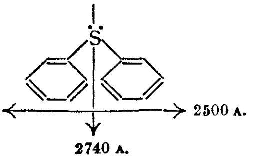


(XXVI*a*.)



(XXVI*b*.)

The apparently independent existence of two alternative modes of conjugation and electronic excitation in the diphenyl sulphide molecule may conceivably be ascribed to the fact that a considerable energy barrier arising from the steric interference of two *o*-hydrogen atoms must oppose the coplanar configuration demanded by the resonance (XXVI *a* and *b*) (cf. Coates and Sutton, *J.*, 1942, 567; Jones, *loc. cit.*). Rotation of one of the benzene rings out of the common plane would leave the sulphur conjugation of the other benzene ring unimpaired (absorption at 2740 A.), or, alternatively, a lesser degree of rotation and partial conjugation of *both* benzene rings might occur (absorption at 2500 A). In the crystal structure of the *pp'*-dibromo-derivative of diphenyl sulphide (Toussaint, *Bull. Soc. chim. Belg.*, 1945, **54**, 319) both benzene rings are symmetrically inclined at 36° to their hypothetical common plane, and a similar symmetrical structure would seem to be the most likely configuration of the ground state of diphenyl sulphide in solution. More probably, then, the real reason why the two closely interrelated types of conjugation can be recognised as separate entities absorbing at 2740 and 2500 A., respectively, arises from the circumstance that the two transitions are associated with electric moments approximately at right angles to each other in the near-planar structure (XXVII). For a given molecule, the relative absorption at the two alternative wave-length positions will then be a function of the molecular orientation relative to the electric vector of the incident light.



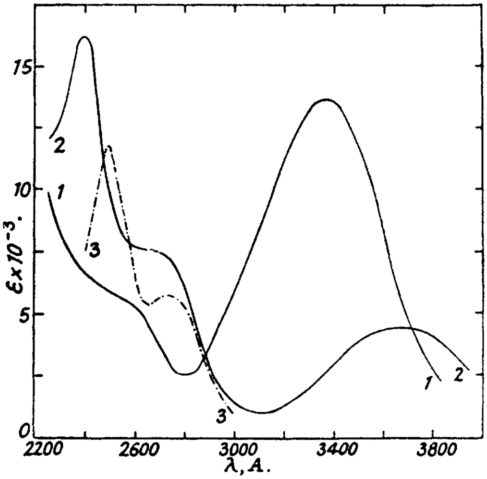
(XXVII.)

Bromo- and Nitro-phenyl Sulphides.—The *pp'*-dibromodiphenyl sulphide described crystallographically by Toussaint (*loc. cit.*) was also examined in the present spectroscopic survey. The absorption bands in solution are of the same general character as those displayed by the halogen-free parent compound, but the whole spectrum is displaced in the direction of longer wave-lengths and greater intensities. Thus, the 2500 A. ($\varepsilon = 12,000$) band of diphenyl sulphide is shifted to 2580 A. ($\varepsilon = 19,000$), and the 2740 A. ($\varepsilon = 6000$) band to 2820 A. ($\varepsilon = 9500$) on *pp'*-bromination. Both ground and excited states are probably affected by the inductive electronegative influence of halogen substitution, but the energy difference between the two levels has clearly been reduced and the transition moment enhanced. Analogous spectral displacement occurs on *p*-bromination of dimethylaniline (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838).

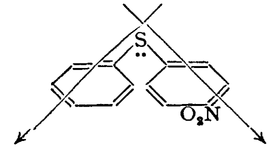
Some interesting effects are observed when a single nitro-group is introduced in the *p*- or *o*-position of diphenyl sulphide (XXVIII and XXXI). Toussaint (*Bull. Soc. roy. Sci. Liège*, 1943, 533) noted that the *o*- but not the *p*-isomer absorbed radiation at 4360 A. and was the more deeply coloured. Whereas the *o*-isomer exhibits high-intensity absorption resembling that of unsubstituted diphenyl sulphide, Fig. 5 shows that the total near-ultraviolet absorption of the *p*-compound is actually very much greater than that of the *o*-form, although at *shorter* wavelengths (below 2900 A.) the *p*-derivative is more transparent. Analogous relationships characterise the spectra of the *p*- and *o*-nitrodimethylanilines which afford the same type of lone-pair electron conjugation, with basic nitrogen substituted for sulphur (cf. Remington, *loc. cit.*). As regards the *p*-isomers, comparatively stable polar excited structures such as (XXIX) may be written, and nitro-group conjugation of this type is doubtless responsible for the intense absorption band of phenyl *p*-nitrophenyl sulphide at 3375 A. (ε = 13,500) (curve 1 of Fig. 5). The inflection near 2600 A. may be attributed to alternative polarisation by electric vectors oriented at right angles to the above, involving the sulphur conjugation of the unsubstituted aromatic ring (*o*- and *p*-quinonoid polar structures XXX). In the *o*-nitrated molecule (XXXI),

FIG. 5.

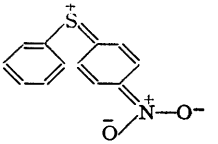
Nitrophenyl sulphides (in EtOH).



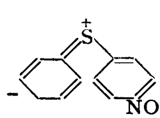
1. *Phenyl* p-*nitrophenyl sulphide.* 3. *Diphenyl sulphide.*
2. *Phenyl* o-*nitrophenyl sulphide.*



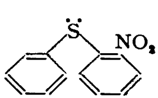
(XXVIII.)



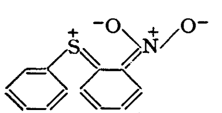
(XXIX.)



(XXX.)

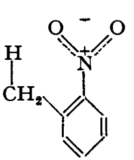


(XXXI.)

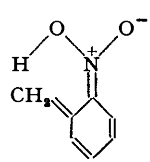


(XXXII.)

(XXXIII.)



(XXXIV.)



(XXV.)

the main axes of polarisation would be expected to be directed differently from those of the *p*-isomer, and curves 2 and 3 demonstrate that below 3000 A. the spectrum is remarkably like that of the unsubstituted diphenyl sulphide. In fact, the spectroscopic effect of the *o*-nitro-group is relatively slight, and the long-wave absorption attributable to nitro-group conjugation (XXXII) is greatly reduced in intensity. Steric hindrance may again be recognised. The postulated polar excited structure (XXXII) demands the nitro-group to be coplanar with the benzene ring, a condition which is improbable or energetically disfavoured because of the resulting interference between the van der Waals radii of one of the oxygens and the sulphur atom (cf. Hampson *et al.*, *J.*, 1937, 10; 1939, 98; Thomson, *J.*, 1944, 404; Remington, *loc. cit.*). Hence the reduced intensity of the characteristic maximum. Generally, short-wave displacement accompanies the intensity decrease of sterically hindered conjugation bands, and the observed *red* shift of the near-ultraviolet absorption relative to that of the *p*-isomer seems anomalous. Similar unusual red-shifts were also reported by Remington (*loc. cit.*) for the hindered *o*-nitroanilines which were more deeply coloured than the unhindered *p*-isomers, but no explanation was then offered. It is now suggested that these peculiarities may arise from some degree of electronic interaction across space between the two non-bonded interfering groups. In terms of extreme canonical resonance structures, the polar excited state of phenyl *o*-nitrophenyl sulphide is thought to be stabilised by minor contributions from the cyclic form (XXXIII), which seems both sterically and energetically reasonable. Rather similarly, the hindered conjugation between nitro-group and benzene ring in *o*-nitrotoluene (XXXIV; cf. Remington, *loc. cit.*) may well be somewhat stabilised by the hydrogen bonding and hyperconjugation phenomena implied in the hypothetical extreme structure (XXXV). These formulations offer at least a qualitative explanation of the unusual wave-length positions in the sterically hindered low-intensity absorption bands of *o*-nitro-substituted phenyl sulphides, anilines, and toluenes.

EXPERIMENTAL.

The absorption curves were recorded in the usual manner with a Hilger small quartz spectrograph and Spekker photometer.

Diphenyl sulphide and the alkyl and alkenyl sulphides were prepared and purified in these laboratories by Dr. F. W. Shipley. Dibenzyl sulphide was a commercial sample which melted at 48—49° after recrystallisation. The bromo- and nitro-phenyl sulphides were made available through the kindness of Dr. J. Toussaint of the University of Liége, and all other compounds described in this paper were furnished by Dr. J. I. Cunneen (cf. *loc. cit.*).

Beer's law was obeyed by the dilute spectrographic solutions of the thiolacetic acids in *cyclo*hexane.

Independently prepared duplicate solution were examined for each of the three phenyl alkyl sulphides described, and concordant results obtained in every case. The small difference observed between the absorption intensities of the *cyclo*hexyl and the 2-methyl*cyclo*hexyl phenyl sulphides therefore appears to be significant. On the other hand, the 2590 A. absorption maximum of the phenyl sulphide derived from dihydromyrcene (Cunneen, *loc. cit.*) coincides exactly with that of the analogously alkyl-substituted 2-methyl*cyclo*hexyl compound.

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