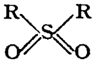
93. *Absorption Spectra and Structure of Organic Sulphur Compounds. Part IV. Unsaturated Sulphones.*

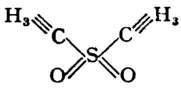
By H. P. Koch.

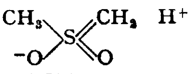
Existing physical and chemical data support the view that conjugation occurs with a sulphonyl group adjacent to double bonds, lone-pair electrons, or C–H bonds. This phenomenon affords a consistent interpretation of the recorded ultraviolet-absorption curves of phenyl alkyl, diphenyl, and *pp'*-dibromodiphenyl sulphones, but the evidence regarding the intramolecular geometrical conditions required by such conjugation appears ambiguous. Spectrographic measurements on dibenzyl sulphone and the α- and β-isoprene sulphones are also reported. The bond-length data of Cox and Jeffrey on β-isoprene sulphone are reinterpreted in terms of hyperconjugation.

The nature of the valency bonds in sulphones has recently been in dispute (cf. Phillips, Hunter, and Sutton, *J.*, 1945, 146), mainly as a result of Lister and Sutton's unexpected discovery that the S–O bond distances are extremely short in dimethyl sulphone (*Trans. Faraday Soc.*, 1939, **35**, 495; cf. also Cox and Jeffrey, *ibid.*, 1942, **38**, 214; Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360). The measured bond-length value of 1·44 A. appeared incompatible with the generally accepted co-ordinate single-bond formulation (I*a*), which was based on Lewis's octet theory and seemingly supported by the observed approximately tetrahedral distribution of the four sulphur valencies (Lister and Sutton; Cox and Jeffrey; Palmer; *locc. cit.*; Toussaint, *Bull. Soc. chim. Belg.*, 1945, **54**, 319). According to Phillips, Hunter, and Sutton, the alternative double-bond formulation (I*b*) affords a more satisfactory representation of the constitution of sulphones. The latter view has now been reconciled with the modern theory of valency (Kimball, *J. Chem. Physics*, 1940, **8**, 188). The primary four σ-bonds undoubtedly arise from tetrahedral sp^3 hybridisation in the ($3s$, $3p^3$) shell of doubly ionised sulphur (cf. Gurjanova, *J. Physical Chem. Russia*, 1943, **17**, 65), but two $3d$ orbitals are said to be additionally available for the formation of two strong π-bonds (valency shell " expansion "), and weaker π-bonds can apparently also be formed with two further $3d$ orbitals. These ideas readily account for the tetrahedral sexacovalent valency state of sulphur in the sulphones. The observed shortening of the S–O bonds may be attributed to double-bond formation (I*b*) arising through donation of electron pairs from the negative oxygen atoms in the primary structure (I*a*) to the unfilled $3d$ orbitals of the positive sulphur atom.


(I*a*.)


(I*b*.)


(II*a*.)

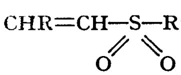

(II*b*.)

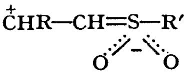
The following observations are chiefly concerned with conjugation phenomena occurring in unsaturated sulphones, and it will be shown that the electronic interaction between sulphonyl and organic functional groups can be consistently described in terms of the double-bonded ground-structure (I*b*). Nevertheless, the possible existence of minor resonance contributions from the single-bond form (I*a*) may be tacitly understood in every case.

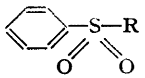
It is to be noted that the sulphur–oxygen bonds in saturated dialkyl sulphones differ from the double bonds of carbonyl, carboxyl, nitro-, and nitroso-groups, all of which give rise to weak ultraviolet absorption, in being completely transparent to wave-lengths greater than 1800 A. (Ley and König, *Z. physikal. Chem.*, 1938, *B*, **41**, 365, and observations by the author on dimethyl sulphone). Evidently, no suitable excited levels exist in the sulphone grouping.

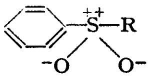
Hyperconjugation in Saturated Sulphones.—Rothstein (*J.*, 1937, 309) has shown that the marked activation of C–H bonds by adjacent sulphonyl groups cannot be accounted for purely in terms of the inductive effects associated with the formal positive charges in the structure (I*a*) (cf. Hochberg and Bonhoeffer, *Z. physikal. Chem.*, 1940, *A*, **184**, 419). Additional mesomeric effects were postulated, causing the C–H bond electrons to become partly donated to the neighbouring C–S linkage. Such hyperconjugation can be described in terms of alternative extreme canonical structures such as (II*a* and *b*).

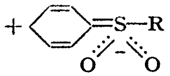
αβ-*Unsaturated Sulphones.*—" Expansion " of the sulphur valency octet has been invoked by a number of authors in order to explain the marked resemblance in chemical properties between αβ-unsaturated aliphatic sulphones and the analogous conjugated carbonyl compounds (cf. Kohler and Potter, *J. Amer. Chem. Soc.*, 1935, **57**, 1316). On the basis of the double-bonded ground-structure (I*b*), the resonance formulation (III and III*a*) provides a satisfactory description of the conjugation characteristics.


(III.)


(III*a*.)

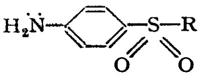

(IV.)

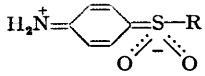

(IV*a*.)

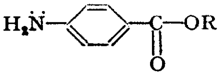

(IV*b*.)

Aromatic Sulphonyl Compounds.—The well-known *m*-directing properties of aromatic sulphonyl groups (IV) might be attributed to either inductive or mesomeric electron-attractive effects, arising respectively from the formal positive charge (IV*a*) or from *d*π-bond formation and conjugation (IV*b*). The special significance of mesomerism is, however, revealed in the marked bathochromic influence on the ultraviolet spectrum of benzene which is exerted by sulphonic substituents (Böhme and Wagner, *Ber.*, 1942, **75**, 606; Kumler and Strait, *J. Amer. Chem. Soc.*, 1943, **65**, 2349; Doub and Vandenbelt, *ibid.*, 1947, **69**, 2714) : no corresponding effect is produced by substituted ammonium groups in anilinium cations which equally carry a positive pole but are incapable of double-bond mesomerism because of the non-availability of stable *d*-orbitals in the nitrogen atom.

The aromatic conjugation of sulphonyl groups becomes enhanced when a basic amino-group is placed in the *p*-position of the ring. Thus, Kumler and Halverstadt (*ibid.*, 1941, **63**, 2182) concluded from dipole-moment measurements that the polar excited form (V*a*; R = NH_2) of sulphanilamide makes up some 3% of the ground state of the molecule, comparable with the 2·5% provided by the analogous polar form (VI*a*; R = OMe) in the ground state of methyl *p*-aminobenzoate. The characteristic ultraviolet-absorption spectra of sulphanilamide and *p*-aminobenzoic acid likewise present a striking resemblance (Kumler and Strait, *loc. cit.*; Havinga and Veldstra, *Rec. Trav. chim.*, 1947, **66**, 257), and the obvious correspondence between these two molecules is of considerable interest in connection with their significant relationship in bacterial metabolism.


(V.)


(V*a*.)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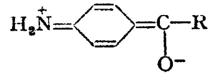
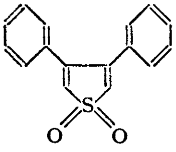

(VI*a*.)

In the dye field, sulphonic substitution in the aromatic nucleus *para* to the nitrogen atom of azo- or azoxy-derivatives similarly produces well-known auxochromic effects which may be attributed to charge-separated polar canonical resonance structures analogous to (V*a*) (cf. Fierz-David *et al.*, *Helv. Chim. Acta*, 1946, **29**, 1718).

Other indications of the conjugating power of the sulphonyl group in more complex aromatic systems may be obtained from the literature. Resonance hybridisation and low-energy polar forms (VII*a*) are presumably associated with the marked stability and visible-light absorption of 3 : 4-diphenylthiophen sulphones (VII) (Hinsberg, *Ber.*, 1915, **48**, 1611); and the intense yellow colour displayed by the anion of 4-hydroxy-3-methylthiophen sulphone (VIII) (Backer and Strating, *Rec. Trav. chim.*, 1935, **54**, 170) appears to find a plausible explanation in the charge-resonance formulation (VIII and VIII*a*). Again, Bell (quoted by Ashley, Buchanan, and Easson, *J.*, 1947, 64) has suggested that the chief contributory canonical structure stabilising the molecule of *N*-(*p*-acetamidobenzenesulphonimido)pyridine (IX) should be formulated as (IX*a*), arising from conjugation of a lone electron pair on the nitrogen atom with the double-bonded sulphone group.



(VII.)

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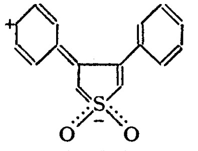
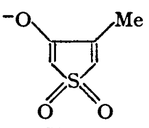
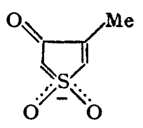


(VII*a*.)

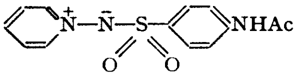


(VIII.)



(VIII*a*.)

(IX.)



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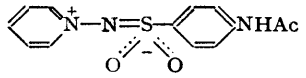
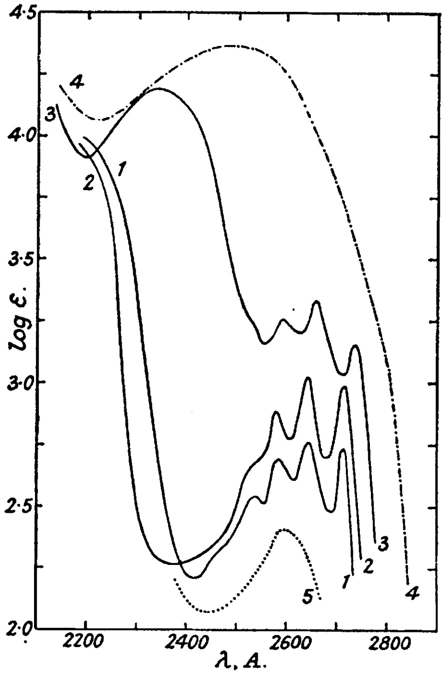


(IX*a*.)

FIG. 1.

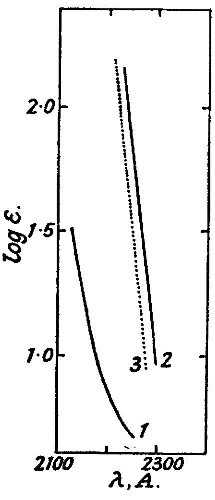
Phenyl sulphones (*in* EtOH).



1. *Benzenesulphonamide.*
2. cyclo*Hexyl phenyl sulphone.*
3. *Diphenyl sulphone.*
4. pp′-*Dibromodiphenyl sulphone.*
5. *Dibenzyl sulphone* (ε *per mol. wt.* × ½).

FIG. 2.

Isoprene sulphones (*in* EtOH).

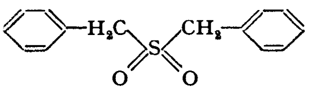


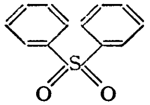
1. *β-Isoprene sulphone.*
2. *α-Isoprene sulphone.*
3. *Methyl*cyclo*hexene* (*in* C_6H_{12}).

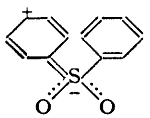
Absorption Spectra of cyclo*Hexyl Phenyl and Diphenyl Sulphones.*—Some new ultraviolet-absorption data presented in Fig. 1 may now be described against the background given above. No previous spectral measurements appear to have been made on phenyl alkyl sulphones, and only the fine-structure region of the spectrum of diphenyl sulphone was recorded by Chaix (*Bull. Soc. chim.*, 1933, **53**, 700). Fig. 1 includes a fresh determination of the benzenesulphonamide absorption for purposes of comparison (cf. Böhme and Wagner; Kumler and Strait; *locc. cit.*), as well as the spectra of *pp'*-dibromodiphenyl and dibenzyl sulphones.

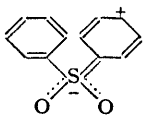
The marked conjugating effect of a sulphone group directly attached to the benzene ring is apparent from the relative aromatic absorptions of *cyclo*hexyl phenyl (IV; R = C_6H_{11}) and dibenzyl (X) sulphones (curves 2 and 5). The latter spectrum resembles the weak absorption of a simple alkylbenzene, but *cyclo*hexyl phenyl sulphone absorbs somewhat more strongly even than benzenesulphonamide (IV; R = NH_2), with fine-structure maxima at identical wave-lengths in the two conjugated sulphonyl compounds (2715, 2645, and 2580 A.; curves 2 and 1). The light-absorption properties of both 1- and 2-methyl*cyclo*hexyl phenyl sulphones were completely identical with those of the unsubstituted *cyclo*hexyl derivative.

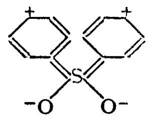
Further modification arises in the spectrum of diphenyl sulphone (XI; curve 3). The fine-structure region has now become displaced by 250 cm.$^{-1}$ to the red (max. at 2735, 2660, and 2595 A.), and intense absorption also occurs at 2350 A. (log ε = 4·2). The new band may represent a shift of the 2150 A. region of the monophenyl sulphonyl compounds (cf. Doub and Vandenbelt, *loc. cit.*), or it may be due to a novel type of conjugation in the structure, similar to that invoked for diphenyl sulphide (this vol., p. 392). From the latter point of view, the two benzene rings would be quasi-conjugated *via* one of the 3*d* orbitals of the sulphur atom, and charge-resonance involving the two equivalent structures (XI*a* and *b*) would occur. This state of affairs seems unlikely, however, owing to the proven non-coplanarity of the two benzene rings in the molecular structure (see below). More probably, the possibility of additional polarisation, depicted by the extreme excited structure (XI*c*), plays a part in shifting the spectrum from that observed for the monophenyl sulphonyl compounds.


(X.)

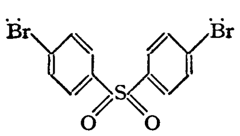

(XI.)

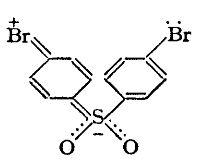

(XI*a*.)

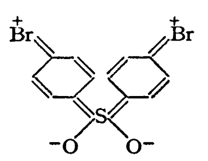

(XI*b*.)


(XI*c*.)

The spectrum of the *pp'*-dibromo-derivative (XII) is of particular interest in view of a recent *X*-ray analysis of its crystal structure and molecular geometry by Toussaint (*loc. cit.*). The characteristic high-intensity transition of diphenyl sulphone appears to be facilitated by *pp'*-dibromination, since an even stronger broad maximum is now observed around 2500 A. (log ε = 4·37), while the fine-structure region has become entirely masked except for the " kink " reproduced in curve 4 of the figure. The bathochromic influence of the bromine substituent may be compared with the corresponding effect of *p*-amination on the spectrum of benzenesulphonamide (see above), being presumably associated with stabilisation of the positive charge in the polar excited forms (XI*a* and *b*) through donation of lone electron pairs from the halogen atoms [structures (XII*a* and *b*)]. It may be noted that the frequency shift resulting from *pp'*-bromination is about twice as large in diphenyl sulphone as it is in diphenyl sulphide (this vol., p. 392), mesomeric and inductive effects respectively being invoked in the two cases.

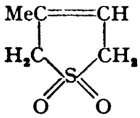

(XII.)

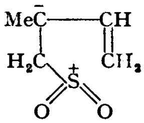

(XII*a*.)

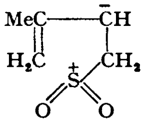

(XII*b*.)

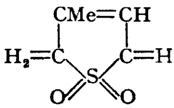
The proposed resonance contributions from (XII*a* and *b*) suggest that in *pp'*-dibromodiphenyl sulphone the S–C bonds should be short and the S–O bonds slightly lengthened relative to the corresponding bonds in the conventional formulation (XII). Toussaint (*loc. cit.*) derived apparently normal (1·84 ± 0·04 A.) S–C but unusually long (1·54 ± 0·05 A.) S–O bond distances from his *X*-ray measurements, comparison here being made with the electron-diffraction data on dimethyl sulphone as standard (Lister and Sutton, *loc. cit.*). The O–S–O bond angle of 131° also appears to be unexpectedly wide (cf. Jeffrey and Cox, *loc. cit.*). In view of the relatively large experimental errors inherent in the analytical method employed, the significance of these results may be doubtful, but if anything, they seem to support the postulated resonance. The observed geometrical configuration of the molecule is of more considerable interest. It is found that the two benzene rings as well as the plane of the sulphone group are arranged at right angles to the plane formed by the two sulphur–carbon links. In the corresponding sulphide and similar conjugated systems (cf. Toussaint, *loc. cit.*; and Part I), the benzene rings are always as nearly *coplanar* as is compatible with the steric requirements of the structure, the resulting near-planar arrangement affording the maximum possible resonance stabilisation. Since the two benzene rings lie in *perpendicular* planes in the observed structure of *pp'*-dibromodiphenyl sulphone, it must be concluded that mutual resonance interaction cannot occur. On the other hand, a maximum of conjugation between each phenyl group separately and the sulphone grouping may well result from the perpendicular configuration observed in the crystal, although definite knowledge regarding the relevant symmetry properties of the postulated π-bonding 3*d* orbitals of sulphur seems to be lacking. It should be noted, however, that resonance interaction between sulphonyl and unsaturated bonds apparently also takes place in the necessarily *planar* cyclic systems of the thiophen and isoprene sulphones (VIII and XIII). The experimental evidence concerning the geometrical conditions of sulphone conjugation is evidently ambiguous. It may perhaps be significant in this connection that Kimball (*loc. cit.*) predicted the possibility of two different types of π*d*-bonds with sulphur on theoretical grounds.

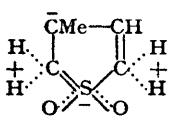
The Structure of β-*Isoprene Sulphone.*—Butadiene and many of its homologues combine with sulphur dioxide to form stable crystalline cyclic sulphones, the chemistry of which has been extensively studied by Backer, Zujdewijn, and others (cf. Suter, " The Organic Chemistry of Sulphur; Tetracovalent Sulphur Compounds ", Wiley, 1944, p. 729). Cox and Jeffrey (*loc. cit.*) carried out an accurate *X*-ray determination of the bond-parameters of β-isoprene sulphone (XIII), and they found that all the links forming part of the heterocyclic ring had hybrid character, being intermediate in length between single and double bonds. For instance, while " normal " bond-distances were observed for S–O (1·44 A.) and C–Me (1·54 A.), the three cyclic C–C bonds measured 1·41 A. and the C–S bonds 1·75 A. (all values ± 0·02 A.). In order to account for these unusual features, Cox and Jeffrey suggested resonance with the two virtually equivalent polar forms (XIII*a* and *b*), although no supporting evidence was adduced from the valency characteristics of other βγ-unsaturated sulphones. This formulation is not now regarded as a plausible interpretation of the experimental results. First, it does not account for the observed S–C bond-distances of 1·75 A. which are *very* short compared with the corresponding parameters in dimethyl sulphone (1·90 ± 0·03 A., according to Lister and Sutton, *loc. cit.*). Secondly, the proposed resonating structures (XIII) and (XIII*a* and *b*) involve divergent positions in space of the methylenic hydrogen atoms, if anything like the normal geometrical bond arrangement around saturated and unsaturated carbon atoms is to be preserved; moreover, the required planar trigonal distribution of the two hydrogens attached to the >C=C grouping in (XIII*a* and *b*) is precluded by the cyclic conformation of the structure. Thirdly, the described hypothesis entirely fails to account for the very pronounced α-methylenic reactivity of β-isoprene sulphone (C–H bonds unstable towards Grignard reagent, dilute alkali, or ultraviolet light).

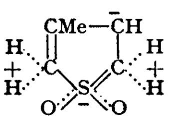

(XIII.)

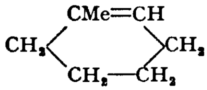

(XIII*a*.)

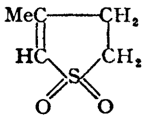

(XIII*b*.)


(XIV.)


(XIV*a*.)


(XIV*b*.)


(XV.)


(XVI.)

Cox and Jeffrey also suggested that hyperconjugation, the possibility of which is implicit in the formal structural representation (XIV), might be an additional cause of the abnormal cyclic bond lengths in β-isoprene sulphone. Since hyperconjugation phenomena must assume greatly enhanced significance when the $C{\equiv}H_2$ bonds are adjacent to *two* unsaturated groupings and furthermore attached to a cyclic system (cf. *cyclo*pentadiene, Hannay and Smyth, *J. Amer. Chem. Soc.*, 1946, **68**, 244), no serious inconsistency arises from the absence of any measurable shortening in the exocyclic carbon–methyl bond. Clearly, the existence of extensive hyperconjugation in β-isoprene sulphone accounts both for the partial double-bond character of all the cyclic bonds, and also for the marked α-methylenic reactivity of the molecule as previously pointed out by Rothstein (*loc. cit.*). Resonance between (XIV) and the two virtually equivalent forms (XIV*a* and *b*) is proposed, in place of the discarded set of resonating structures (XIII, XIII*a* and *b*). If all three forms (XIV, XIV*a* and *b*) are assumed to be equally important in the ground state, maximum resonance stabilisation would result and each of the bonds in the ring become endowed with 33% double-bond character, in conformity with the measured length (1·41 A.) of the three cyclic C–C bond distances. The strength of the methylenic C–H bonds would at the same time be reduced by 33% no-bond character. The S–O linkages should also become lengthened relatively to those found in dimethyl sulphone, but the latter effect could apparently not be observed experimentally.

β-Isoprene sulphone is highly transparent to ultraviolet light, absorbing considerably less than would be expected from the conventional formula (XIII). This phenomenon is illustrated in Fig. 2, where the absorption of the sulphone (curve 1) is compared with that of the tri-substituted cyclic ethylenic bond in methyl*cyclo*hexene (XV; curve 3). Low-energy excited absorbing states of the molecule evidently do not exist. On the other hand, the ultraviolet absorption of the αβ-unsaturated α-isoprene sulphone (XVI; curve 2) resembles that of the analogous simple double-bond compound (XV), with little spectrographic evidence of sulphonyl conjugation.

EXPERIMENTAL.

Dimethyl sulphone was prepared by the method of Lister and Sutton (*loc. cit.*) and recrystallised from water; m. p. 108°.

Fig. 1.—Commercial samples of benzenesulphonamide and of diphenyl sulphone were recrystallised from ethanol; m. p. 151—152° and 123—124° (cf. Mikeska, Farinacci, and Bogert, *J. Amer. Chem. Soc.*, 1936, **58**, 1869), respectively. Dibenzyl sulphone was prepared according to Shriner, Struck, and Jorison (*ibid.*, 1930, **52**, 2067) and obtained in needles, m. p. 149—150°, from ethanol. This substance was insoluble in 20% aqueous sodium hydroxide solution. *cyclo*Hexyl and 1- and 2-methyl*cyclo*hexyl phenyl sulphones were pure crystalline samples prepared by Dr. J. I. Cunneen (*J.*, 1947, 36). A specimen of *pp'*-dibromodiphenyl sulphone was kindly supplied by Dr. J. Toussaint.

Fig. 2.—The isoprene sulphones were recrystallised from water, the starting material being that also employed by Cox and Jeffrey for *X*-ray analysis. β-Isoprene sulphone melted at 63—63·5°, and α-isoprene sulphone (needles) at 78—79°. The methyl*cyclo*hexene curve is taken from Bateman and Koch (*J.*, 1944, 600).

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