564. *Absorption Spectra and Structure of Organic Sulphur Compounds. Part VII. Sulphoxides.*

By H. P. Koch.

Ultra-violet absorption curves of saturated, $\beta\gamma$-unsaturated, and aromatic sulphoxides in both hydrocarbon and hydroxylic solvents are presented and briefly discussed with reference to electronic interaction of groups. Certain experimental data suggest the possibility of enolization in the $\beta\gamma$-unsaturated compounds.

In continuation of previous measurements in this series (Parts I—IV, *J.*, 1949, 387 *et seq.*), the ultra-violet absorption spectra in solution of a representative group of organic sulphoxides have now been determined. Contrary to the behaviour of saturated organic sulphones which are transparent throughout the quartz ultra-violet region, the corresponding sulphoxides display considerable absorption as exemplified by the curve for the *cyclo*hexyl methyl compound shown in Fig. 1. This absorption is markedly enhanced in the $\beta\gamma$-unsaturated sulphoxides such as the methyl β-methylallyl (I) and the diallyl derivatives, which may be compared in Fig. 1 not only with the above saturated sulphoxide but also with a typical olefin, *cyclo*hexene; the comparison shows that electronic interaction occurs between the sulphoxide grouping and the allylic substituent. Further similar shifts of absorption occur in the " conjugated " methyl phenyl and diphenyl sulphoxides. The latter compound has been measured above 2400 A. by Chaix (*Bull. Soc. chim.*, 1933, **53**, 700), in excellent agreement with the present results. There is also remarkable similarity between the spectra of diphenyl sulphoxide and the corresponding selenoxide which is included in Fig. 1. As might be expected, the curves for the phenyl compounds display characteristic shoulders near 2750 A. attributable to the perturbed benzenoid chromophore; the very flat maximum for methyl phenyl sulphoxide near 2350 A. seems to correspond to the weakly selective absorption of saturated sulphoxides near 2100 A., and the more intense bands of the diphenyl derivatives to the well-known strong benzene absorption (log $\varepsilon \sim 4$) near 2000 A.

The sulphoxide spectrum is subject to considerable solvent effects, consistently with the known tendency of these compounds to form strong hydrogen bonds (cf. Part V, Barnard, Fabian, and Koch, *J.*, 1949, 2442). The greatest absorption occurs in *cyclo*hexane, and successive hypsochromic shifts result from replacing the non-hydroxylic solvent by alcohol and then by water, the additional shift between alcohol and water being relatively less marked. These features are illustrated by the high-intensity region of the methyl 2-methylallyl sulphoxide spectrum shown in Fig. 2. The 2300 A. shoulder of the curve measured in *cyclo*hexane presumably corresponds to the 2100 A. shoulder of *cyclo*hexyl methyl sulphoxide in alcohol (Fig. 1), the displacement being due to the combined effects of allylic substitution and the change in the nature of the solvent. A similar shoulder was observed in an $\alpha\beta$-unsaturated naturally occurring sulphoxide determined in aqueous solution by Schmid and Karrer (*Helv. Chim. Acta*, 1948, **31**, 1017, 1087), whose curve (Fig. 2) is seen to be displaced by some 250—300 A. from that referring to the $\beta\gamma$-unsaturated sulphoxide in the same solvent.

At low intensities (log $\varepsilon \sim 1$), a second band unexpectedly appears in the spectrum of methyl

2-methylallyl sulphoxide (I) near 2900 A., with solvent effects opposite to those recorded for the main absorption (cf. Fig. 2). As this band was present in several independently prepared and carefully purified samples, it is thought to be characteristic of the allylic compound itself rather than some impurity. A similar band is suggested by the broad tail of the diallyl sulphoxide curve in the same region (Fig. 1). The interesting possibility therefore arises that the long-wave absorption may be due to a trace (of the order of 0·1%) of a conjugated enol form such as (I*a*), which might be expected to absorb in this region and be present in low equilibrium concentration. We have not attempted to obtain more positive identification of this chromophore, chiefly because the most obvious approach by way of infra-red detection of a hydroxyl frequency would have doubtful value in such low concentration on account of the extreme tenacity with which bound water is held by the sulphoxide (Barnard, Fabian, and Koch, *loc. cit.*). It may nevertheless be significant that Barnard (*loc. cit.*) observed the occurrence of a violent reaction between phosphoric oxide and $\beta\gamma$-unsaturated, but not saturated, sulphoxides.

FIG. 1.

Absorption spectra, in ethanol.

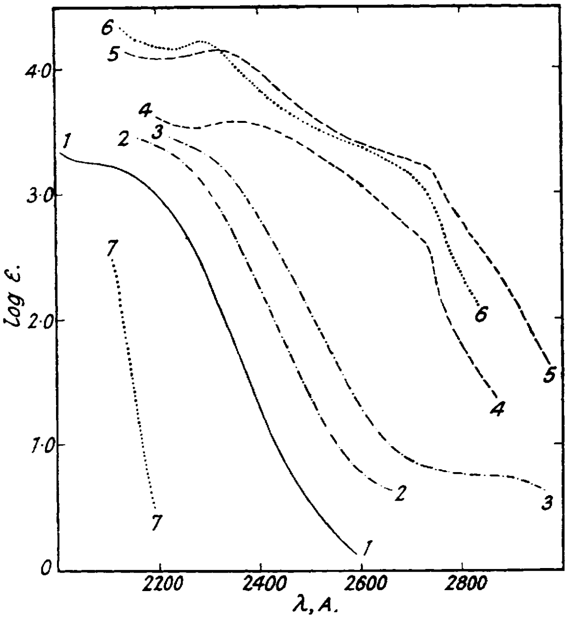

FIG. 2.

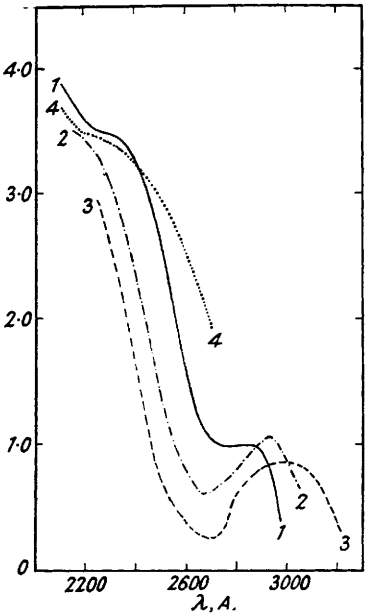

FIG. 1.—1, cyclo*Hexyl methyl sulphoxide.* 2, *Methyl 2-methylallyl sulphoxide.* 3, *Diallyl sulphoxide.* 4, *Methyl phenyl sulphoxide.* 5, *Diphenyl sulphoxide.* 6, *Diphenyl selenoxide.* 7, cyclo*Hexene.*

FIG. 2.—*Absorption of methyl 2-methylallyl sulphoxide in* (1) cyclo*hexane,* (2) *ethanol, and* (3) *water. Curve* 4 *is absorption of " sulphoraphene,"* $Me\cdot SO\cdot CH{:}CH\cdot[CH_2]_2\cdot NCS$, *in water* (*after Schmid and Karrer,* loc. cit.).

$CH_2{:}CMe\cdot CH_2\cdot SOMe$ (I.) $CH_2{:}CMe\cdot CH{:}S(OH)\cdot Me$ (I*a*.)

The nature of conjugation in $\alpha\beta$-unsaturated and phenyl sulphones has recently been discussed in Part VI of this series by Koch and Moffitt (*Trans. Faraday Soc.*, in the press). The theoretical conclusions obtained for the sulphones do not necessarily apply to the corresponding sulphoxides, however, without modification; in fact, it would seem likely from the lower degree of symmetry that the conjugating power of the sulphoxide grouping should be rather less. Some interesting experimental evidence on this point is available from the recent work of Eastman and Wagner (*J. Amer. Chem. Soc.*, 1949, **71**, 4089), who found that the 1-oxide (*i.e.*, sulphoxide) derived from certain 3 : 4-dihydroxythiophens was spectroscopically and chemically similar to the parent sulphide, whereas the 1 : 1-dioxide (*i.e.*, sulphone) was distinct and exhibited strong acidity attributable to conjugation of the S–O bonds. The present ultra-violet measurements support the view that some conjugation occurs in $\alpha\beta$-unsaturated and monophenyl sulphoxides, with additional conjugation in the symmetrical diphenyl compound; at the same time, the positive absorption of saturated sulphoxides and the marked chromophore interaction in βγ-unsaturated derivatives is reminiscent of the behaviour of the corresponding sulphides rather than sulphones. It seems that the sulphoxide grouping has electronic properties intermediate between those of sulphides and sulphones, quite in accordance with the presence of one lone pair of sulphur electrons and one sulphur–oxygen double bond, respectively. Although more fundamental theoretical and experimental investigation of these relationships is evidently required, it is not proposed to develop the subject further in these laboratories.

Added in Proof (*September* 11*th*, 1950).—Mr. J. P. Teegan and Dr. A. D. Walsh have kindly photographed the vacuum ultra-violet absorption spectrum of a highly purified sample of dimethyl sulphoxide (m. p. 16°) prepared by Dr. D. Barnard. A first absorption region at *ca.* 1900 A. was followed by a more intense region, 1750—1550 A., in which some discrete bands could be observed. A third intense region below 1350 A. apparently contained a series of Rydberg bands superimposed on a background of continuous absorption, but the discrete bands in this region may have been due to sulphur dioxide produced by photo-decomposition.

Experimental.—Pure sulphoxide specimens were supplied by Dr. D. Barnard (cf. Barnard, Fabian, and Koch, *loc. cit.*). The spectrographic technique was the conventional Spekker method, a Hilger small quartz spectrograph being employed, except below 2100 A. where the Spekker photometer absorbed rather strongly and a semi-quantitative single-beam Henri method of varying exposures on Ilford Q plates was applied (cf. Carr, *J. Amer. Chem. Soc.*, 1929, **51**, 3051).

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