

514. *Valence Vibration Frequencies and Hydrogen Bond Formation of Sulphoxide and Sulphone Groups. (Absorption Spectra and Structure of Organic Sulphur Compounds. Part V.)*

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The existence of characteristic infra-red frequencies in molecules incorporating the sulphone, sulphoxide, or selenoxide groups is established, and the observed frequencies are compared with the known bond-stretching vibration frequencies of sulphur monoxide, sulphur dioxide, and their halogen derivatives. Molecular-aggregation effects in the liquid and crystalline states are described. Hydrogen-bond formation with methyl alcohol or chloroform decreases the characteristic S-O bond-stretching frequencies; sulphoxides form stronger hydrogen bonds than do sulphones. It is unambiguously demonstrated that the sulphur-oxygen link is nearly a covalent double bond and contains a minor proportion of the polar co-ordinate single-bond structure which is relatively more important in sulphoxides than in sulphones. Substitution of electronegative halogen groups on the sulphur atom diminishes the fractional negative charge on the oxygen and increases the strength of the S-O bond. Infra-red measurements fail to reveal the existence of conjugation in the ground states of aromatic sulphoxides and sulphones.

In connection with a current investigation of the course of oxidation of certain types of organic sulphide, it became necessary to search for a sensitive and specific method of detection and determination of organic sulphoxides and sulphones. Infra-red spectroscopy obviously suggested itself as a promising diagnostic and analytical tool, but, surprisingly enough, no previous infra-red absorption measurements on sulphoxides or sulphones could be found in the literature. A thorough exploration of this field therefore appeared desirable, not only because of its potential value in chemical analysis, but more fundamentally because of the probable important bearing of a systematic study of S-O bond-stretching vibration frequencies on the vexed problem of the electronic nature of this linkage. Two alternative points of view have been persuasively argued in the past, mainly by Sutton and his school (*J.*, 1945, 146; cf. also Fehnel and Carmack,



J. Amer. Chem. Soc., 1949, **71**, 231, and Koch, this vol., p. 408) who regard the S-O link as essentially a covalent double bond involving expansion of the sulphur valency octet (Ia) and (IIa), and by Arndt and Eistert (*Ber.*, 1941, **74**, 451; cf. also Vogel, *J.*, 1948, 1833, and Wells, *ibid.*, 1949, 55) who formulate a polar co-ordinate single bond in all such compounds (Ib) and (IIb). This controversy may now be resolved as the result of considerations involving the hitherto unknown vibration frequencies and relative hydrogen-bonding effects of sulphoxides and sulphones which are described in the present paper.

EXPERIMENTAL.

Spectroscopic Technique.—The infra-red absorption spectra from 2.5—15 μ . were measured by means of a Grubb-Parsons single-beam automatic-recording Littrow-type spectrometer equipped with a Nernst filament source, 60° sodium chloride prism set for minimum deviation at 10 μ ., and thermistor bolometer detector. The radiation was interrupted at a frequency of 16½ cycles, the bolometer output being fed into an A.C. amplifier sharply tuned to this frequency. The rectified and smoothed amplifier output was applied to an Evershed pen recorder on which provision was made for the independent registration of wave-length calibration marks corresponding to regular angle increments of the Littrow mirror drive. A bilateral slit mechanism operated entrance and exit slits jointly, an effective slit width of 2—4 cm^{-1} being used in the characteristic spectral region of 7.5—10 μ . Over this wave-length range, the true position of absorption bands could be determined with an accuracy of 2—3 cm^{-1} by reference to a calibration curve which was set up by observation of the known frequencies of water vapour and ammonia, care being exercised to operate the spectrometer under sensibly constant temperature conditions. Relative frequency shifts arising from hydrogen-bond formation or other causes could be established as significant down to almost the same small wave-number interval through the simple expedient of superposing spectral records of the two samples under comparison, run consecutively without alteration of any of the spectrometer controls.

In the region of 2.5—4.3 μ ., where the dispersion of the sodium chloride prism is very poor, approximate wave-length calibration was obtained by reference to the known frequencies of liquid benzene (~3.25 μ .), liquid chloroform (3.31 μ .), and liquid methyl alcohol (3.52 μ .), as well as water vapour, carbon dioxide, and ammonia. Owing to the quite large frequency shifts incurred by the characteristic hydrogenic stretching frequencies on hydrogen-bond formation, significant qualitative and comparative spectral data on hydrogen-bonding effects could be obtained in this wave-length region, although quantitative precision was precluded by the low optical resolution.

Samples were first examined over the entire infra-red spectrum in their normal physical state as thin films of liquid, solid, or Nujol suspension held between sodium chloride flats, and, once the region of characteristic absorption had been ascertained, the relevant absorption bands were re-investigated in solvents in a special fixed cell. This cell consisted of two sodium chloride plates separated by metal washers 0.1 mm. thick, both top and bottom of the cell being provided with threaded brass caps for easy filling and cleaning. The whole assembly was cemented together with "Araldite" bonding resin obtained from Aero Research, Ltd., and the top and bottom could be conveniently sealed by brass screws carrying polythene washers. The thickness of this cell was not accurately determined, but the constancy of its path-length throughout the present series of measurements was confirmed by reference to the constant extinction values of a standard sample. A path-length value of $l = 0.0105$ cm. was employed in the calculations of the molecular extinction coefficients $\epsilon = [\log_{10} I_0/I]/lc$, where the concentration c is expressed in g.-mol./l. In view of the slight uncertainty in the true value of l , the absolute extinction coefficients may be in error by as much as 10%, but the relative extinction values given in Table I are certainly significant since the same cell was used throughout. Three or four different concentrations of solute (ranging from 0.02 to 0.2M.) were measured in all quantitative determinations, the final extinction coefficients being obtained from the slope of the resulting Beer's law curves which invariably formed a straight line passing through the origin of the plot $\log_{10} I_0/I$ against c . The AnalaR-grade solvents were not specially purified, except that chloroform was freed from alcohol and water.

Source of Materials.—The sulphoxides and sulphones were obtained by oxidation of the requisite sulphides. Diphenyl and diallyl sulphides were commercial samples purified by fractionation, the middle cuts boiling within 1° being used.

cycloHexyl methyl sulphide. Pure cyclohexene (110 g.) and methanethiol (50 g.), with acetone (6 c.c.) as photosensitizer, were sealed in a Pyrex tube and irradiated for 5.5 hours with light from a quartz mercury-vapour arc lamp. After careful fractionation in an atmosphere of nitrogen through an efficient column packed with glass helices, the yield of pure product, b. p. 68.0—68.5°/18 mm., n_D^{20} 1.4945, was 104 g. (Found: C, 64.3; H, 10.9; S, 24.6. Calc. for $C_7H_{14}S$: C, 64.6; H, 10.8; S, 24.6%).

Phenyl methyl sulphide. Sodium metal (23 g.) was dissolved in anhydrous ethanol (500 c.c.), and purified thiophenol (110 g.) slowly added to the hot solution. Methyl iodide (142 g.) was then run in with stirring at a rate sufficient to keep the mixture warm but not refluxing. After a further 12 hours, the solution was poured into water (3 l.), and the yellow oil separated. The fractionated product had b. p. 80.0/16.5 mm., n_D^{20} 1.5870 (yield, 110 g.) (Found: C, 67.7; H, 6.5; S, 25.8. Calc. for C_7H_8S : C, 67.7; H, 6.4; S, 25.8%).

Methyl 2-methylallyl sulphide. Sodium metal (20 g.) was dissolved in anhydrous ethanol (500 c.c.), and methanethiol (50 g.) distilled into the solution. 2-Methylallyl chloride (90 g.) was slowly added to the stirred hot solution at a rate such that gentle refluxing occurred. The solution after cooling and filtering was poured into water (3 l.), and the resulting oil was separated and dried ($MgSO_4$). After fractionation through an efficient packed column in an atmosphere of nitrogen, the product had b. p. 113.0—113.2°/758 mm., n_D^{20} 1.4712 (yield, 56 g.) (Found: C, 58.3; H, 9.8; S, 31.3. $C_8H_{10}S$ requires C, 58.8; H, 9.9; S, 31.3).

General Method of Preparation of Sulphoxides.—The appropriate pure sulphide was dissolved in purified acetone (25% solution w/w), and a slight excess of 30% hydrogen peroxide added slowly to the ice-cold stirred solution. After a further 24 hours at room temperature, the acetone was removed under reduced pressure and replaced by an equal volume of chloroform. The separated aqueous layer was removed and the chloroform solution dried over freshly calcined magnesium sulphate. Removal of the chloroform and careful fractionation of the residue, or, in the case of diphenyl sulphoxide, repeated crystallization from light petroleum (b. p. 60—80°) containing 5% of chloroform, yielded a pure product. The following data were recorded.

Diphenyl sulphoxide, m. p. 70.0—70.3° (Found: C, 71.1; H, 5.1; S, 16.2. Calc. for $C_{12}H_{10}OS$: C, 71.2; H, 5.0; S, 15.9%).

Phenyl methyl sulphoxide, b. p. 75°/0.01 mm., m. p. (if perfectly dry) 30.0—30.5°, n_D^{20} (supercooled liquid) 1.5885 (Found: C, 59.9; H, 5.95; S, 23.2. Calc. for C_7H_8OS : C, 60.0; H, 5.7; S, 22.9%).

cycloHexyl methyl sulphoxide, b. p. 88°/0.05 mm., n_D^{20} 1.5119 (Found: C, 57.6; H, 9.6; S, 22.0. $C_7H_{14}OS$ requires C, 57.5; H, 9.65; S, 21.9%).

Diallyl sulphoxide, b. p. 60—61°/0.05 mm., m. p. (if perfectly dry) 23.0—23.5° (Found: C, 55.1; H, 7.9; S, 24.8. Calc. for $C_6H_{10}OS$: C, 55.3; H, 7.75; S, 24.6%).

Methyl 2-methylallyl sulphoxide, b. p. 99—99.5°/13 mm., n_D^{20} 1.4996 (Found: C, 50.5; H, 8.45; S, 27.3. $C_5H_{10}OS$ requires C, 50.8; H, 8.55; S, 27.1%).

Diethyl and dibutyl sulphoxide were slightly impure samples prepared by oxidation of the appropriate sulphides with hydrogen peroxide in glacial acetic acid. The former had b. p. 88—90°/12 mm. and n_D^{20} 1.4570, and the latter b. p. 85—90°/0.1 mm. (solid at room temperature).

Hygroscopic Nature of Sulphoxides.—All the sulphoxides prepared, except the diphenyl derivative, proved to be very hygroscopic, absorbing approximately 1 mol. of water on exposure to the atmosphere. Spectroscopically pure samples (free from OH absorption at 3 μ . in a 0.1-mm. thickness) were difficult to obtain without special precautions in their drying and handling. Storing the liquid sulphoxides over phosphoric oxide at 0° (temperatures above 40° caused violent decomposition), followed by fractionation in a specially dried apparatus, proved satisfactory when no double bonds were present in the molecule. With the unsaturated sulphoxides, however, phosphoric oxide caused very violent decomposition even at 0° (with spontaneous ignition in the case of the methyl 2-methylallyl derivative), and the final drying had to be accomplished by long storage over freshly calcined magnesium sulphate, followed by careful fractionation as before.

General Method of Preparation of Sulphones.—The pure sulphide (10 g.) was dissolved in chloroform (100 c.c.), and 3*N*-sulphuric acid (250 c.c.) was added. The mixture was cooled to 0° and a slight excess of powdered potassium permanganate added slowly with vigorous stirring. The mixture was decolorised with sodium metabisulphite and made alkaline, and the chloroform layer separated, washed with water, and dried ($MgSO_4$). The solvent was then removed and the residue fractionated or recrystallized. The sulphones were not hygroscopic. The following data were obtained.

Phenyl methyl sulphone, m. p. 86.5—86.8° (Found: C, 53.9; H, 5.25; S, 20.5. Calc. for $C_7H_8O_2S$: C, 53.8; H, 5.1; S, 20.5%).

cycloHexyl methyl sulphone, b. p. 94.5—95°/0.05 mm., n_D^{20} 1.4918 (Found: C, 51.8; H, 8.8; S, 19.7. $C_7H_{14}O_2S$ requires C, 51.8; H, 8.7; S, 19.7%).

The source and physical constants of the dimethyl, diphenyl, and dibenzyl sulphones have been given in a previous paper (this vol., p. 413). "Butadiene sulphone" was a commercial recrystallised sample, m. p. 64°. Dicyclohexyl sulphone was kindly supplied by Dr. G. F. Bloomfield in the form of the pure crystallised sample, m. p. 131.5°.

Diphenyl selenoxide was prepared by the method of Edwards, Gaythwaite, Kenyon, and Phillips (*J.*, 1928, 2293) and, after repeated crystallisation from light petroleum (b. p. 60—80°) containing 5% of chloroform, had m. p. 111.0—111.5° (Found: C, 57.6; H, 4.2. Calc. for $C_{12}H_{10}OSe$: C, 57.8; H, 4.0%).

(Micro-analytical data were furnished by Dr. W. T. Chambers).

RESULTS AND DISCUSSION.

Characteristic Absorption Frequencies.—On recording the infra-red transmission curves of the seven different liquid or crystalline sulphoxides detailed in the experimental section, the characteristic group frequency could immediately be recognized in an extremely strong absorption region at 9.5—10 μ . Dilute solutions of the five specially purified sulphoxides in carbon tetrachloride all displayed a sharp high-intensity band at a remarkably constant mean frequency of 1055 cm^{-1} (Table I). Comparison with the fundamental vibration frequency, $\nu = 1124 cm^{-1}$, of the sulphur monoxide molecule (Herzberg, "Diatomic Molecules," Prentice-Hall, New York, 1939) leaves no doubt that we are here dealing with the expected bond-stretching vibration of

TABLE I.
Characteristic infra-red group frequencies (cm^{-1}).

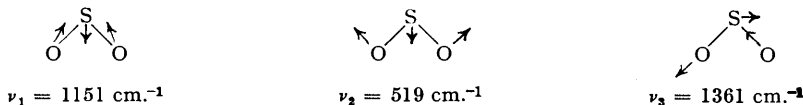
Substituents.	Sulphoxides,				Sulphones, ¹							
	ν_{SO}				ν_1				ν_3			
	CCl_4 soln.	(ϵ). ² (295)	liq. 1040	cryst. —	CCl_4 soln.	(ϵ). (495)	liq. 1138	cryst. —	CCl_4 soln.	(ϵ). (550)	liq. 1309	cryst. —
cycloHexyl methyl ...	1055	(295)	1040	—	1144	(495)	1138	—	1321	(550)	1309	—
Dicyclohexyl	—	—	—	—	1130	(495)	—	1124	1312	(410)	—	1299
Phenyl methyl	1055	(320)	1044	1035	1160	(870)	1155	1150	1334	(580)	1318	1293
Diphenyl	1055	(355)	1042	1035	1164	(680)	—	1151	1336	(250)	—	1313
Methyl 2-methylallyl	1061	(310)	1047	—	—	—	—	—	—	—	—	—
Diallyl	1047	(270)	1030	—	—	—	—	—	—	—	—	—

¹ Thompson (*J.*, 1948, 328) and Williams (*Rev. Sci. Inst.*, 1948, **19**, 135, and *Anal. Chem.*, 1948, **20**, 402) have published a correlation chart of organic group frequencies in which a single characteristic region extending from 1250 to 1350 cm^{-1} is assigned to sulphones. The ν_3 frequency has evidently been overlooked in this assignment which is reported to be based on unpublished work by Thompson.

² Molecular extinction coefficient (for definition, see Experimental).

the S-O link. The remarkable constancy of this group frequency in differently substituted organic derivatives is presumably related to the fact that the adjoining C-S links must be expected to have considerably lower vibration frequencies (near or below 600 cm^{-1}), so that no appreciable coupling of the two oscillators can take place in the compound molecule.

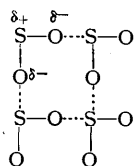
The seven sulphones were similarly examined and revealed the presence of *two* characteristic intense absorption regions in every case, occurring near 9 μ . and at 7.5—8 μ . in the crystalline or liquid samples. Four of the sulphones were also studied in dilute solution in carbon tetrachloride, and two sharp high-intensity bands were observed at frequencies of 1130—1164 cm^{-1} and 1312—1336 cm^{-1} , respectively (Table I). The related molecule of sulphur dioxide is known to give rise to a total of *three* strong fundamental absorption bands which have been assigned to the three normal modes of vibration as follows (Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, 1945):



In broad terms, these may be classified as symmetrical (ν_1) and non-symmetrical (ν_3) stretching, and symmetrical (ν_2) deformation frequencies, the emergence of *two* S-O bond-stretching frequencies in this molecule being due to the symmetrical or antisymmetrical coupling interaction of the two S-O bond vibrations. More strictly (Herzberg, *loc. cit.*), only ν_3 is a pure bond-stretching vibration, whereas in ν_1 the oxygen atoms do not move exactly along the line of the bonds. In the sulphones, the observed two strong characteristic frequencies obviously correspond to ν_1 and ν_3 in sulphur dioxide, their approximate constancy in the different compounds again being attributable at least in part to the necessarily very much lower vibration frequencies of the adjoining C-S bonds which preclude any effective coupling. On the other hand, although we have examined the same substances for the presence of a characteristic deformation, vibration ν_2 near 500 cm^{-1} (20 μ .) (unpublished work), no simple regularity could here be recognized, a feature which may well arise from the presence of other deformation as well as low frequency C-S stretching vibrations of the compound molecules in this spectral region.

Molecular Aggregation Effects.—It will be seen from the foregoing and from Table I that in both sulphoxides and sulphones molecular aggregation in the liquid and crystalline states leads to progressive decreases of the characteristic group frequencies as determined in dilute carbon tetrachloride (or carbon disulphide) solution. We may assume that the position of the bands approximates most closely to that of the isolated molecules when measured in these non-polar solvents, and the aggregation band shifts are therefore quite analogous to those commonly observed with simple polar molecules on passing from the gas to the liquid and the solid state. Thus, the fundamental vibration frequency of hydrogen chloride is lowered from 2886 cm^{-1} in the gas to 2785 cm^{-1} (liquid) and 2768 cm^{-1} (solid), and in sulphur dioxide itself the two stretching frequencies are shifted from 1151 cm^{-1} and 1361 cm^{-1} in the gas to 1144 cm^{-1} and 1336 cm^{-1} , respectively, in the liquid (Herzberg, *loc. cit.*). Similar phenomena have recently been described in the field of organic carbonyl compounds where the magnitude of the low-frequency displacement in a series of related molecules has been shown to increase with increasing polarity of the carbonyl linkage (Hartwell, Richards, and Thompson, *J.*, 1948, 1436). Rather strong intermolecular dipole interaction is clearly indicated in all these cases. In liquid sulphur dioxide, a transient cluster of molecules may be imagined (see inset), and it is instructive to note in connection with such a model that the asymmetric vibration frequency ν_3 which is of a more purely bond-stretching type than the symmetric ν_1 has undergone a much greater relative decrease from its true position in the gas. At the same time, the bond *deformation* vibration ν_2 of the molecule has actually *increased* from 519 to 524.5 cm^{-1} (Herzberg, *loc. cit.*). In a similar way, the ν_3 vibration in the sulphones is always more strongly affected than ν_1 by passing from the solution in non-polar solvents to the pure liquid or crystalline state (Table I).

Figures 1 and 2 illustrate the actual transmission curves of diphenyl sulphoxide and phenyl methyl sulphone over the characteristic band regions. In addition to the S-O stretching frequencies which are clearly the most strongly affected by aggregation, either compound also displays a lesser frequency decrease of the characteristic phenyl band near 1090 cm^{-1} . The broad and complex nature of the ν_1 and ν_3 absorptions in the "solid" curve of Fig. 2 represents a typical feature of the sulphone spectra in the crystalline state, only the main band



positions having been listed in Table I. It should perhaps be pointed out in conclusion that the molecular aggregation effects definitely cannot arise from hydrogen-bond formation, at least in the case of the diphenyl compounds where no potentially active α -methylene hydrogen atoms are available, and the same is almost certainly true of the other compounds.

FIG. 1.

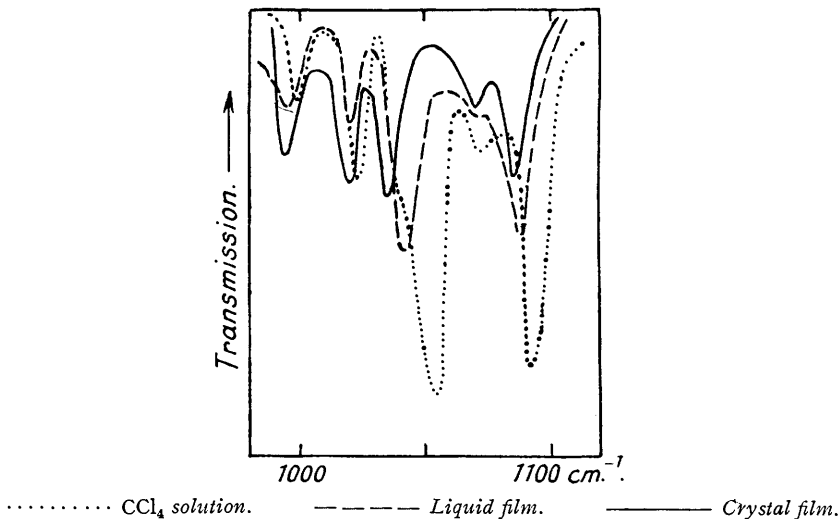
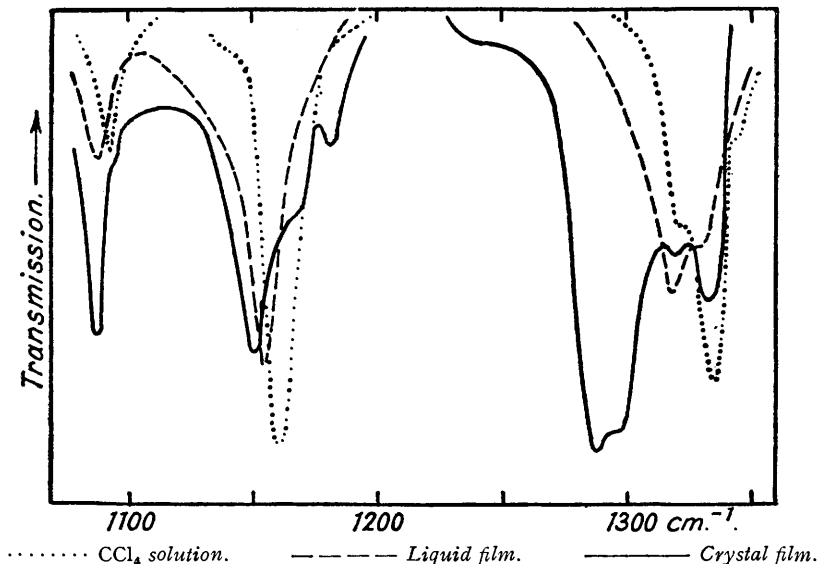
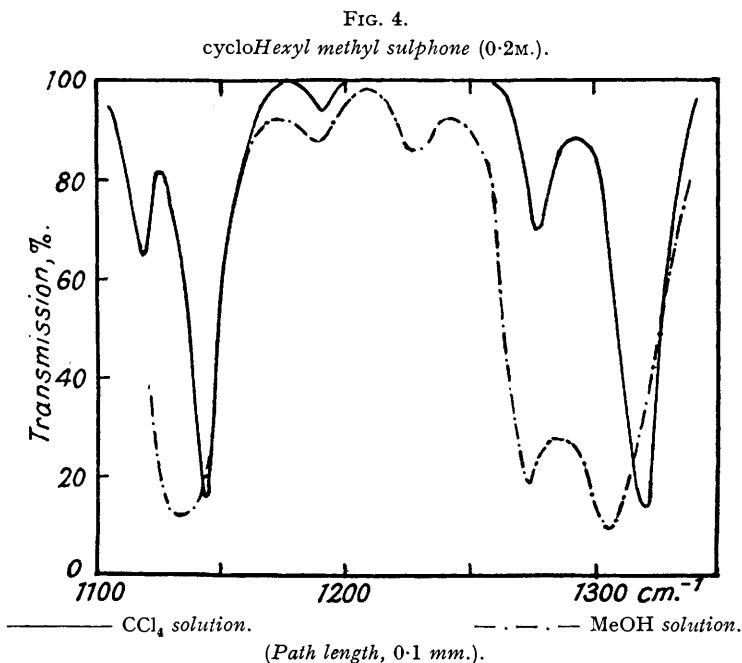
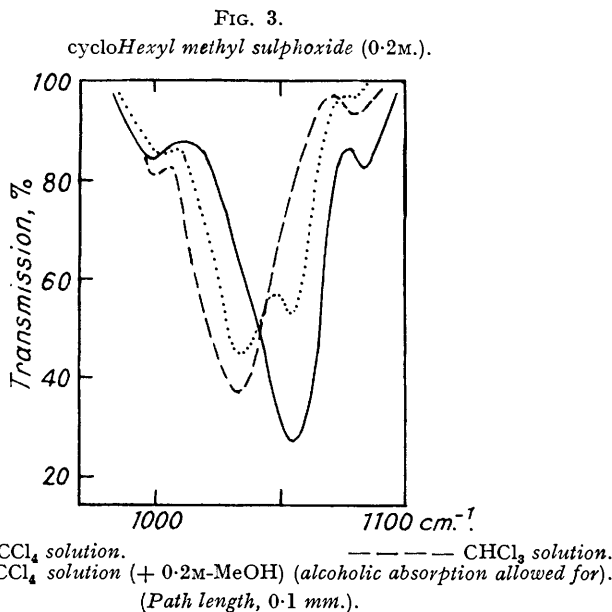
Diphenyl sulphoxide.

FIG. 2.

Phenyl methyl sulphone.

Hydrogen Bond Formation.—As the result of extensive investigation by Gillette and Daniels (*J. Amer. Chem. Soc.*, 1936, **58**, 1139), Gordy (*ibid.*, 1937, **59**, 817; 1938, **60**, 605; *J. Chem. Physics*, 1939, **7**, 93, 99; 1940, **8**, 170; 1941, **9**, 204), Davies and Sutherland (*ibid.*, 1938, **6**, 755), Buswell, Rodebush, and Roy (*J. Amer. Chem. Soc.*, 1938, **60**, 2528), and others, the infra-red spectroscopic effects of hydrogen-bond formation of the type $\text{X-O} \cdots \text{H-Y}$ are very well known. The stretching frequencies of both X-O and H-Y bonds shift towards lower values, the relative magnitude of the shifts in a series of related molecules affording a qualitative measure

of the relative strengths of the hydrogen bonds (cf. Davies, *Ann. Reports*, 1946, **43**, 5). Strong bonds are formed when HY is an alcohol, but weak hydrogen bonding also takes place with chloroform or bromoform, whereas extremely strong bonds are observed with hydrogen



chloride. The relative shift ($\Delta\nu/\nu$) in the H-Y frequency is generally much greater and more easily investigated than that for X-O, but characteristic decreases of the carbonyl stretching frequency resulting from hydrogen-bond formation have been noted by all the above authors. Gordy also studied the effect of a large variety of X-O compounds, including *n*-propyl sulphone, on the position of the D-OMe band of heavy methyl alcohol, and he found that the

relative magnitude of the frequency shifts could be correlated with the proton affinity or electron-donor ability of the oxygen atom in the X-O molecule (cf. also Briegleb, *Zeit. Elektrochem.*, 1944, 50, 35). Thus, the donor ability of the oxygen atoms of *n*-propyl sulphone was rated about equal to that of carboxylic esters.

Both for theoretical reasons and in order to determine its possible influence on the course of qualitative and quantitative infra-red analysis, we have made a systematic study of the spectral effects of hydrogen-bond formation by sulphoxides and sulphones. It was found that the characteristic sulphoxide frequency of the *cyclohexyl methyl* derivative in carbon tetrachloride solution remained unchanged in carbon disulphide, *cyclohexene*, or ethyl linolenate (containing activated α -methylene hydrogen atoms) but was lowered by 20 cm^{-1} when chloroform was employed as solvent. A pure alcoholic solution could not be measured on account of the strong C-O absorption in this spectral region, but a dilute equimolar (0.2M.) solution of methyl

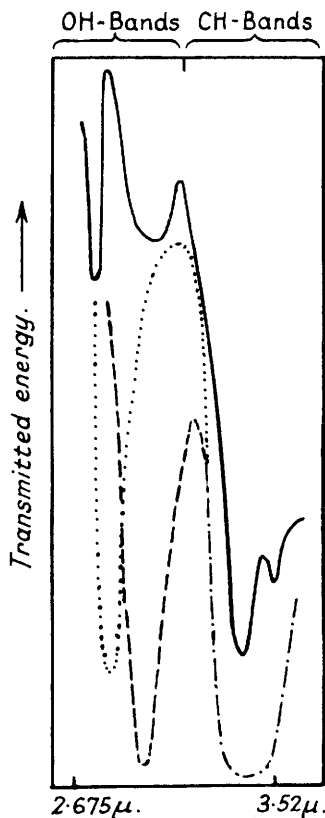
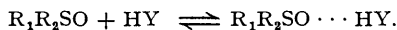


FIG. 5.
Methyl alcohol absorption (instrumental transmitted energy records).

— 0.1M-MeOH in CCl_4 (1-mm. path length).
- - - 1.1M-MeOH in *cyclohexyl methyl sulphoxide* (0.1-mm. path length).
..... 1.1M-MeOH in *cyclohexyl methyl sulphone* (0.1-mm. path length).

alcohol and sulphoxide in carbon tetrachloride gave *two* characteristic bands corresponding to bonded and unbonded sulphoxide groupings, respectively (Fig. 3). Two similar bands were also observed in the presence of 0.2M-*cyclohex-2-enyl* hydroperoxide (ROOH) in carbon tetrachloride solution, and in mixed chloroform-carbon tetrachloride, although chloroform concentrations as low as 0.2M. had no effect. These data correspond to the setting-up of an equilibrium in which either or both of the unassociated and the associated species are present :



As regards the solvent effects on the spectrum of *cyclohexyl methyl sulphone*, it was found that carbon disulphide or 0.2M. concentrations of either chloroform or methyl alcohol in carbon tetrachloride produced no change, but in pure chloroform the characteristic frequencies were lowered from 1144 and 1321 cm^{-1} to 1137 and 1310 cm^{-1} , respectively. In pure methyl alcohol the effect was relatively more marked and accompanied by a broadening of the bands now centred around 1134 and 1306 cm^{-1} , respectively (Fig. 4). Under these conditions, only the hydrogen-bonded species of solvated sulphone molecules appears to be present.

The formation of hydrogen bonds between *cyclohexyl* methyl sulphoxide or sulphone and methyl alcohol was confirmed by an examination of the OH band region of solutions of the alcohol in the *cyclohexyl* methyl compound as solvent (Fig. 5). Whereas a dilute solution of methyl alcohol in carbon tetrachloride gave two OH bands at ~ 3660 and ~ 3320 cm^{-1} , corresponding to unassociated and associated molecules respectively (cf. Fox and Martin, *Proc. Roy. Soc.*, 1937, A, **162**, 419; Gordy, *loc. cit.*), in the sulphoxide or sulphone as solvent only a single absorption frequency intermediate between those of associated and unassociated alcoholic OH groups was observed. Clearly, the characteristic OH frequency of the isolated methyl alcohol molecule near 3660 cm^{-1} undergoes typical hydrogen bonding shifts towards lower values when dissolved in either sulphoxide (~ 3350 cm^{-1}) or sulphone (~ 3515 cm^{-1}). The greatest displacement actually occurs when intermolecular hydrogen-bond formation takes place between the alcohol molecules themselves in the non-bonding carbon tetrachloride solvent, in accord with the well-known strength of the hydrogen bonds involved in the association of hydroxylic compounds.

With regard to the low-frequency shifts of the S-O frequencies observed in chloroform solution, independent spectroscopic support for the hydrogen-bonding hypothesis could again be obtained, although the evidence is here perhaps less complete. The expected change in the C-H stretching frequency of the chloroform can be analysed only in a few special cases (*e.g.*, mixtures with quinoline) when there is no interference from the presence of strongly absorbing aliphatic C-H groups. On the other hand, Buswell, Rodebush, and Roy (*loc. cit.*) as well as Gordy (*J. Chem. Physics*, 1939, **7**, 163) noticed that hydrogen-bonding mixtures of chloroform or bromoform with donor solvents frequently gave rise to moderately strong bands near 4.1 μ ., which were not displayed by either of the pure components. Gordy's suggestion that these were the characteristic frequencies of the weak O \cdots H bands formed in the associated complex appears to us quite untenable from several points of view and has already been adversely criticized by Sutherland (*Trans. Faraday Soc.*, 1940, **36**, 889) who favoured the band assignment put forward by Rodebush and his collaborators. According to these authors, the new frequency near 4.1 μ . represents the second harmonic of the C-H deformation vibration (ν_4) of chloroform (or bromoform), the intensity of this band quite plausibly becoming enhanced through complex formation. We have observed the emergence of a similar new association band in equimolar mixtures of chloroform with several of our S-O compounds. The exact position and strength of the band in the range 2440 — 2490 cm^{-1} varies somewhat from compound to compound, being at relatively high frequencies and strong in the mixtures containing sulphoxide (*cyclohexyl* methyl, phenyl methyl, methyl 2-methylallyl, or diphenyl), and at lower frequencies and weak in the sulphone complexes (*cyclohexyl* methyl or phenyl methyl). The general location of the band is in agreement with Rodebush's interpretation in that the frequency of a second harmonic normally appears at a value equal to, or slightly lower than, twice the frequency value of the first harmonic, whereas in the present case the new frequencies are observed to be higher than twice the value of the corresponding first harmonic in pure chloroform ($\nu_4 = 1205$ cm^{-1}). This is just as would be expected on the hydrogen-bonding hypothesis, since an increase in the force constant of the C-H deformation vibration of chloroform would be expected to occur on hydrogen-bond formation.

Relative Bonding Power of Chloroform and Methyl Alcohol.—Inspection of the above data as well as those given in Table II bears out the well-known fact that methyl alcohol forms stronger hydrogen bonds than chloroform. Although approximately equal displacements of the sulphoxide frequency are observed for solutions in either chloroform or carbon tetrachloride containing alcohol (Fig. 3 and the first column of Table II), the significant fact that the alcohol-complex persists at dilutions higher than those tolerated by the chloroform-complex has already been referred to above. The characteristic sulphone frequencies generally suffer a greater displacement in pure methyl alcohol than in pure chloroform; the same is also true of diphenyl selenoxide (see below) and of dimethyl sulphone for which the origin of the band could not be measured owing to insolubility in non-polar solvents. It might be remarked in this connection that the other crystalline sulphones were all poorly soluble in carbon tetrachloride, but highly so in chloroform. Whether or not this marked increase in solubility and the interaction energy involved is entirely due to the hydrogen bond, or caused in part by the existence of other more general polarization phenomena, seems to be still undecided (cf. Briegleb, *loc. cit.*).

Relative Bonding Power of Sulphoxides and Sulphones.—There is ample spectroscopic evidence that sulphoxides form stronger hydrogen bonds than do sulphones. Fig. 5 illustrates the increased capacity of *cyclohexyl* methyl sulphoxide over the corresponding sulphone to displace the OH band of methyl alcohol towards lower frequencies. Again, whereas the alcohol-

TABLE II.
Percentage S-O frequency decreases due to hydrogen bonding.

Substituents.	Sulphoxides,		Sulphones,			
	ν_{SO} .		ν_1 .		ν_2 .	
	CHCl ₃ or 0.2M-MeOH/CCl ₄ .	—	CHCl ₃ .	MeOH.	CHCl ₃ .	MeOH.
cycloHexyl methyl	2	—	0.6	0.9	0.8	1.2
Dicyclohexyl	—	—	0.4	—	0.8	0.8
Phenyl methyl	1.9	—	0.3	0.4	1.2	1.6
Diphenyl	1.6	—	0.3	—	1.3	—
Methyl 2-methylallyl	2.3	—	—	—	—	—
Dimethyl	—	—	—	—	—	—
			(1150 cm. ⁻¹)	(1145 cm. ⁻¹)	(1317 cm. ⁻¹)	(1305 cm. ⁻¹)

sulphoxide complex largely persists in dilute solution in carbon tetrachloride (Fig. 3), the same dilution ratio is sufficient to suppress entirely the appearance of the characteristic hydrogen-bonded sulphone bands in the spectrum. It has been shown that, in the mixtures with chloroform the presumed second harmonic of the C-H deformation vibration appears with much greater intensity and at relatively higher frequencies in the presence of sulphoxides than it does with sulphones. Finally, a comparison of the percentage S-O frequency shifts given in Table II indicates that the sulphoxide stretching frequency is more markedly affected by hydrogen-bonding solvents than either of the sulphone frequencies. In connection with the latter, we may also note that ν_2 is always decreased further than ν_1 , just as was observed in the molecular-aggregation phenomena described above. This significant difference between the behaviour of a strictly bond-stretching and a partly bond-bending vibration is exactly what would be expected if the hydrogen bonds were formed along the lines of the S-O bonds.

Certain chemical phenomena are probably similarly related to the increased capacity of sulphoxides, compared with sulphones, for the formation of strong hydrogen bonds. Thus, simple sulphoxides are extremely hygroscopic, absorbing one mole of water with great ease, and they are also known to form salts in the presence of mineral acids (Gilman, "Organic Chemistry," Wiley and Sons, New York, 1944, Vol. I, p. 872), whereas sulphones are inert in both these respects. Clearly, no reasonable doubt can be entertained that the donor properties of the sulphoxide-oxygen atom are distinctly superior to those of the oxygen atoms combined in sulphones.

Estimation of S-O Bond-stretching Force Constants.—As shown above, the infra-red examination of a representative variety of differently substituted sulphoxides and sulphones has revealed the existence of sensibly constant characteristic S-O stretching frequencies in this type of molecule. Moreover, the sulphoxide frequency is comparable to that of the simple sulphur monoxide molecule, and the two sulphone frequencies resemble even more closely those found in sulphur dioxide. We may therefore state with considerable confidence that the observed characteristic frequencies roughly correspond to vibrational motions confined to the SO groups of the molecules only (cf. Herzberg, *loc. cit.*, p. 199). Taking the simpler case of sulphur monoxide and the sulphoxides first, and neglecting the anharmonicity of the actual atomic vibration, we can approximately relate the observed frequency to the bond-stretching force constant k and the masses m_1 and m_2 of the vibrating atoms by the Hooke's law expression

$$\nu = \frac{1}{2\pi c} \sqrt{k \left(\frac{1}{m_1} + \frac{1}{m_2} \right)} \text{ cm.}^{-1}$$

Although identical masses are involved, direct comparison of this single frequency and its related bond force constant with the twin stretching frequencies observed in sulphur dioxide and the sulphones is clearly not possible unless the resonance-splitting of the vibration frequency of the two coupled bonds in the SO₂ group is allowed for. To a first approximation, one may make the assumption that the resonance-splitting is roughly symmetrical, and take the mean frequency $(\nu_1 + \nu_2)/2$ to be the desired vibration frequency which either S-O bond in the SO₂ group would have in the absence of coupling interaction with the other. Provided the quantitative limitations of such approximative treatment are clearly understood, its relative justification in this particular case may be illustrated by the example of sulphur dioxide itself. Putting

$$(\nu_1 + \nu_2)/2 = \frac{1}{2\pi c} \sqrt{k \left(\frac{1}{m_1} + \frac{1}{m_2} \right)},$$

where $\nu_1 = 1151$, $\nu_2 = 1361$, $m_1 = 32$, and $m_2 = 16$, we obtain a value for the bond force constant

$k = 9.86 \times 10^5$ dynes/cm, which is only about 1% lower than the accurate value of 9.97 obtained by rigorous methods (Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156**, 654; Herzberg, *loc. cit.*).

The mean sulphone stretching frequency $(\nu_1 + \nu_3)/2$ was derived from the four sets of solution values given in Table I, and the resulting average value of 1238 cm^{-1} may be compared with the average sulphoxide frequency of 1055 cm^{-1} . It represents a considerable increase (more than 17%) over the latter, corresponding to an increase of 35—40% in the force constant of the S—O bond. Such large differences cannot be due to the approximate nature of the method of estimation employed but must arise from a real and important difference in the relative physical strengths of the oxy-bonds in sulphoxides and sulphones. A chemical corollary may be found in the fact that sulphoxides, but not sulphones, are readily reducible to the corresponding sulphides under a variety of conditions (Gilman, *loc. cit.*).

Electronic Nature of the S—O Linkage.—Some valuable new insight into the electronic nature of the S—O bond can be gained by a consideration of the relative stretching frequencies and force constants of sulphoxides and sulphones in conjunction with those of certain closely related compounds and such data as are available on the relative bond lengths and bond polarities. Table III gives a list of different types of sulphoxide or sulphone derivatives whose vibration frequencies are known, the compounds being arranged together in their order of increasing frequency values. The first column gives the molecular formulæ, in which all S—O bonds have been conventionally and arbitrarily depicted as double; R denotes an organic residue. The second column lists the observed S—O bond frequencies, only the mean stretching frequency $(\nu_1 + \nu_3)/2$ being given for the sulphones. The corresponding approximate force constants are given in the third column, and bond-length data in the last. Before considering the theoretical significance of the Table, we will briefly indicate the source of the frequency data other than those already described.

Diphenyl selenoxide was examined in the course of the present work for purposes of comparison. A very strong infra-red frequency appeared at 821 cm^{-1} in the crystal and at 838 cm^{-1} in carbon disulphide, the suspected nature of this frequency being confirmed by the typical shifts observed in hydrogen-bonding solvents. Chloroform gave rise to a frequency decrease of 1.8% as well as a new complex band near 2480 cm^{-1} considerably stronger than the corresponding band with diphenyl sulphoxide, and pure methyl alcohol markedly broadened and shifted the 838- cm^{-1} band by more than 2%. This behaviour, together with the approximate location and high intensity of the frequency, establishes its correct assignment to the Se—O bond-stretching vibration. The frequency values, approximate force constants, and bond-length data for methyl alcohol and formaldehyde have been taken from the literature (Barnes *et al.*, *Ind. Eng. Chem., Anal.*, 1933, **15**, 659) and are similarly included here for purposes of rough comparison of the C—O with the S—O bond. The characteristic frequencies of dichloro- and difluoro-sulphoxides (thionyl chloride and fluoride, respectively) and dichloro-sulphone (sulphuryl chloride) are the published values observed in the Raman spectra (Hibben, "The Raman Effect and its Chemical Applications," Reinhold, New York, 1939).

In a series of related molecules, the length of a particular bond generally decreases as the bond becomes stronger, and a number of semi-empirical equations have in fact been proposed from time to time to express the correlation between bond length and force constant in quantitative terms. The occurrence of such correlation in sulphur-oxygen compounds seems implied by the data of Table III which suggest a slight decrease in bond lengths as the frequencies and force constants of related molecules increase. In particular, the reported increase in physical bond strength on passing from sulphur monoxide and the sulphoxides to sulphur dioxide and the sulphones is reflected in a significant shortening of the S—O bond which is certainly beyond the limits of possible experimental error. The apparently anomalous internuclear separation in sulphur monoxide is presumably due to a somewhat different type of potential function for this bond which differs from all the others by virtue of the triplet character of its ground state.

Exponents of the covalent double bond theory of the sulphur-oxygen link have drawn attention to the surprisingly short oxy-bonds in sulphur dioxide and the sulphones, shorter than in sulphur monoxide, and they have equally pointed out that the strength of these bonds determined from data on the heats of formation appears to be rather greater than that found in the diatomic molecule (~ 100 kcal.), where it is presumably double (Phillips, Hunter, and Sutton, *J.*, 1945, 146). The observed vibration frequencies in Table III fall in line with these two arguments. Since the nature of the sulphur monoxide bond as essentially double rather than single would hardly seem open to serious question, the even *higher* vibration frequencies of

TABLE III.

Some bond characteristics of the sulphur-oxygen link.

Molecule.	ν_{SO} or $(\nu_1 + \nu_3)/2$ (cm.^{-1}).	$k \times 10^{-5}$ (app.) (dynes/cm.).	$r \times 10^8$ (cm.).
Ph \begin{array}{l} \diagup \text{Se=O} \\ \diagdown \end{array}	(838)	(5.5)	—
H ₃ C—OH	(1034)	(5.77)	(1.43)
R \begin{array}{l} \diagup \text{S=O} \\ \diagdown \end{array}	1055	6.95	1.47 ³
S=O	1124	7.9	1.4935 ⁴
Cl \begin{array}{l} \diagup \text{S=O} \\ \diagdown \end{array}	1229	9.4	1.45 ± 0.02 ⁵
R \begin{array}{l} \diagup \text{S} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \\ \diagdown \end{array}	1238	9.6	1.44 ± 0.02 ⁶
S \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}	1256	9.97 ²	1.43 ± 0.01 ⁷
Cl \begin{array}{l} \diagup \text{S} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \\ \diagdown \end{array}	1303 ¹	10.6	1.43 ± 0.02 ⁵
F \begin{array}{l} \diagup \text{S=O} \\ \diagdown \end{array}	1312	10.8	—
H ₂ C=O	(1744)	(12.1)	(1.21)

¹ $\nu_1 = 1190$, $\nu_3 = 1415 \text{ cm.}^{-1}$. ² Accurate value calculated by Penney and Sutherland (*loc. cit.*). ³ Accurate electron diffraction sector method value by Bastiansen and Viervoll, *Acta Chim. Scand.*, 1948, **2**, 702. ⁴ From electronic spectra (Herzberg, "Diatomic Spectra"). ⁵ Electron-diffraction value by Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360. ⁶ Electron-diffraction value by Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495; X-ray crystal structure value by Cox and Jeffrey, *ibid.*, 1942, **38**, 214. ⁷ Accurate electron-diffraction value by Schomaker and Stevenson, *J. Amer. Chem. Soc.*, 1940, **62**, 1270.

sulphur dioxide, the sulphones, and the thionyl and sulphuryl halides signify that in these molecules, if anything, the bond order must be *greater* than it is in sulphur monoxide. Against this view, the adherents of the polar co-ordinate single bond theory would apparently argue that the increased shortness and physical strength of these oxy-bonds might equally well be due to their increased polarity rather than bond multiplicity (Arndt and Eistert, *loc. cit.*). Such arguments not only seem to lack any sound theoretical basis, but they can be shown to run counter to the available evidence on the relative polarities of the sulphur-oxygen bonds.

The greater the polarity of the S-O bond, the greater will be the fractional negative charge and proton-attracting power of the terminal oxygen atom (cf. Gordy, *loc. cit.*, 1941). We may therefore employ the relative proton affinities of a series of related sulphoxides as a sensitive criterion of relative bond polarities, in much the same way in which Walsh has employed the first ionization potential of the non-bonding electrons of the oxygen atom in the related case of the carbonyl bond (*Trans. Faraday Soc.*, 1946, **42**, 56). Now we have amply demonstrated above, first, that sulphoxides display distinctly greater proton-attracting power than do sulphones and, secondly, that the oxy-bond is distinctly *weaker* in sulphoxides than it is in sulphones. Clearly then, increased strength of the sulphur-oxygen bond is associated, not with an increase, but with a significant *decrease* of bond polarity. The same conclusion apparently follows from an examination of the effects of halogen substitution. Table III illustrates the increase in the physical strength of the oxy-bond resulting from replacement of the organic substituents of sulphoxides or sulphones by chlorine or, more markedly still, by fluorine; on the other hand, Audrieth and Steinmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2115) observed from the relative heats of mixing with chloroform that the donor properties and hence the polarity of the bond decreased on replacing the ethoxy-groups of diethoxy-sulphoxide or -sulphone (diethyl sulphite or sulphate, respectively) by chlorine atoms, just as occurred also in the case of diethoxy-carbonyl (diethyl carbonate). In fact, there exists a striking analogy between our series of sulphur compounds and similar tables of interrelated carbonyl derivatives in which the direct attachment of halogen also causes a

sharp increase in the vibration frequency of the oxy-bond (Hartwell, Richards, and Thompson, *loc. cit.*). Walsh (*loc. cit.*) has drawn up such a table and shown that, in general, bond length and bond polarity of the carbonyl group decrease as the bond force constant goes up. Both he and Hartwell, Richards, and Thompson pointed out that these relationships could be simply and satisfactorily summarized by a valence-bond representation in which a given carbonyl derivative is held to be somewhere intermediate in structure between IIIa and b, with the important proviso



that no resonance strengthening accrues to the hybrid bond (Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60). A similar interpretation in terms of varying proportions of the *a* and *b* structures of (I) and (II) would obviously account for the observed gradations of Table III in which, in general, the bond polarity decreases with increasing physical strength of the bond.

The new knowledge of relative bond polarities from the study of hydrogen-bond formation clearly affords an unambiguous demonstration that the high physical strength of the sulphur-oxygen bond is due, not to the polarity of a postulated co-ordinate single link, but to bond multiplicity. The bond is more nearly a covalent double bond if referred to the bond characteristics of sulphur monoxide as a rough standard. On the other hand, except by way of first approximation, the sulphur-oxygen link is not a definite and unchangeable entity as was suggested by Phillips, Hunter, and Sutton (*loc. cit.*). There is a variable contribution from the polar single bond structure (I or IIb) which is appreciable in the sulphoxides, less important in the sulphones, and probably rendered all but negligible by the presence of the electron-attracting halogens in sulphuryl chloride and thionyl fluoride. In the last-mentioned two molecules, the approximate force constant seems only little different from that of a typical carbonyl double bond, although the quantitative significance of a direct comparison of bond force constants involving different pairs of atoms must remain doubtful. The relative hydrogen-bonding effects suggest that the polar single bond structure may be slightly more important in diphenyl selenoxide than it is in the corresponding sulphoxide. We may finally add that the rather clumsy valence-bond picture of (*a*)-types of structure supplemented by relatively minor contributions from (*b*) without bond strengthening by "ionic-covalent resonance" can be advantageously replaced by the molecular orbital method of representation. Moffitt (work in course of publication elsewhere) has shown that molecular orbital treatment of the S-O bond yields results in complete and detailed agreement with those based on our experimental approach.

The Conjugation Problem.—The S-O bond being largely double, conjugation phenomena might be expected to occur in the presence of adjacent phenyl or ethylenic groups, just as they do in the corresponding carbonyl derivatives. The analogy is not necessarily valid, however, any more than the quite imperfect analogy between the (planar) geometry of the carbonyl group and the known pyramidal structure of sulphoxides. If conjugation does take place, it should be reflected in a lowered stretching force constant and vibration frequency of the oxy-bond; a frequency decrease of nearly 2% is observed in such molecules as benzaldehyde or acetophenone (Hartwell, Richards, and Thompson, *loc. cit.*; Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068).

According to Table I, phenyl methyl and diphenyl sulphoxide have precisely the same S-O bond vibration frequency as the saturated cyclohexyl methyl compound. The corresponding aromatic sulphone derivatives display an unexpected small frequency *increase* over the saturated analogues, the significance of which is perhaps doubtful. It could be envisaged that the inductive electron-attracting effect of the phenyl group in these molecules may serve to *reduce* the relative importance of contributing single-bond structures (I and IIb) and thereby offset, or more than offset, the expected contribution of the mesomeric (conjugated) forms of the type (*c*) or (*d*). In that case, the relative influence of the conjugative compared with the inductive



effect would appear to be greater in the sulphoxides than in the sulphones; at the same time, the complete invariance of the sulphoxide frequency suggests that even here conjugation is very slight. Since a rather different conclusion has been derived from near-ultra-violet

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absorption spectra (Fehnel and Carmack, *loc. cit.*; Koch, *loc. cit.*, and work in progress on sulphoxides; Schmid and Karrer, *Helv. Chim. Acta*, 1948, **31**, 1017, 1087), it must be presumed that conjugation is important in the *upper excited state*, and possibly in reactive transition states, but not in the ground level of the sulphoxide and sulphone molecules.

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