295. *The Infra-red Spectra and Chemical Structure of Some Aromatic Disulphides, Disulphones, and Thiolsulphonates.**

By J. Cymerman and J. B. Willis.

The infra-red spectra of a number of aromatic disulphides, disulphones, and thiolsulphonates are reported, and the characteristic absorption bands for the S–O, C–S, and S–S linkages are discussed. Our interpretation of the infra-red spectra confirms the chemical evidence that the compounds hitherto known as " disulphoxides " have the structure $R{\cdot}SO_2{\cdot}S{\cdot}R'$ rather than $R{\cdot}SO{\cdot}SO{\cdot}R'$ and should therefore be referred to as thiolsulphonates.

ALTHOUGH thiolsulphonates (" disulphoxides ") * have been known for over eighty years (cf. Marcker, *Annalen*, 1865, **136**, 83; Otto, *ibid.*, 1868, **145**, 13, 317) and their reactions have received considerable study, their structures have not yet been unequivocally established by physico-chemical evidence.

The symmetrical disulphoxide structure (I) was favoured by Fromm and Palma (*Ber.*, 1906, **39**, 3308), Hinsberg (*Ber.*, 1908, **41**, 2836, 4294; 1909, **42**, 1278), Gutmann (*ibid.*, 1908, **41**, 3351; cf. also Toennies and Lavine, *J. Biol. Chem.*, 1936, **113**, 571, 583). These compounds have also been considered as mixed anhydrides (II) (Gilman, " Organic Chemistry," p. 912, John Wiley & Sons, New York, 1943) and latterly as thiolsulphonates (III) (Smiles and Gibson, *J.*, 1924, 176; Gibson, Miller, and Smiles, *J.*, 1925, 1821; Miller and Smiles, *J.*, 1925, 224; Gilman, Smith, and Parker, *J. Amer. Chem. Soc.*, 1925, **47**, 851), while optical measurements (Hilditch, *J.*, 1910, 1091) appeared to show that either the disulphoxide or the thiolsulphonate structure could exist, according to the similar or dissimilar nature of R and R′.

$$\begin{array}{ccc} \mathrm{R{-}SO{-}SO{-}R'} & \mathrm{R{-}SO{-}O{-}S{-}R'} & \mathrm{R{-}SO_2{-}S{-}R'} \\ \text{(I.)} & \text{(II.)} & \text{(III.)} \end{array}$$

In this paper we consider the infra-red spectroscopic evidence obtained from the study of a series of these compounds. No previous measurements on infra-red absorption of thiolsulphonates have been found in the literature, and there is little information on the related disulphides and disulphones. A series of these compounds has therefore been prepared and their infra-red spectra have been examined.

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* In this paper the systematic name " thiolsulphonate " is used throughout, as our work shows this to be the correct structure of these compounds.

EXPERIMENTAL.

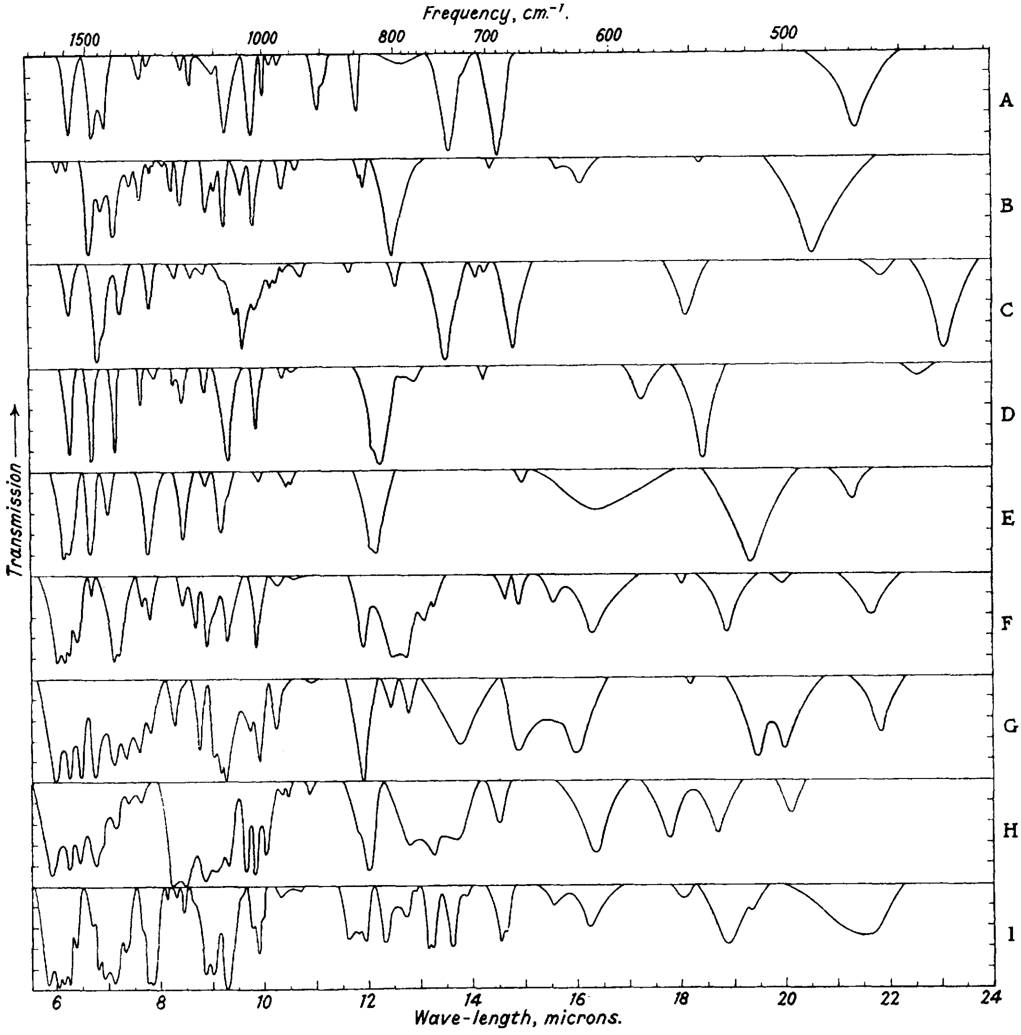
Source of Materials.—Diphenyl sulphoxide was prepared according to Hinsberg (*Ber.*, 1910, **43**, 289) and had m. p. 69·5—70°, b. p. 114—116°/0·02 mm.

Diphenyl sulphone (Beckurts and Otto, *Ber.*, 1878, **11**, 2066) had m. p. 123—124°.

Diphenyl, di-*p*-tolyl, and di-*o*-tolyl disulphide had m. p. 61°, 47—48°, and 38° respectively.

Di-*p*-cyanophenyl and di-*p*-aminophenyl disulphide were pure samples prepared by Bauer and Cymerman (*J.*, 1949, 3434). The preparation and physical constants of di-*p*-carbamylphenyl disulphide, diphenyl disulphide 4 : 4′-di(carboxyimino ethyl ether) dihydrochloride, and di-*p*-amidinophenyl disulphide dihydrochloride and dibenzenesulphonate have been given in a previous publication (Bauer and Cymerman, *J.*, 1950, 109).

FIG. 1.

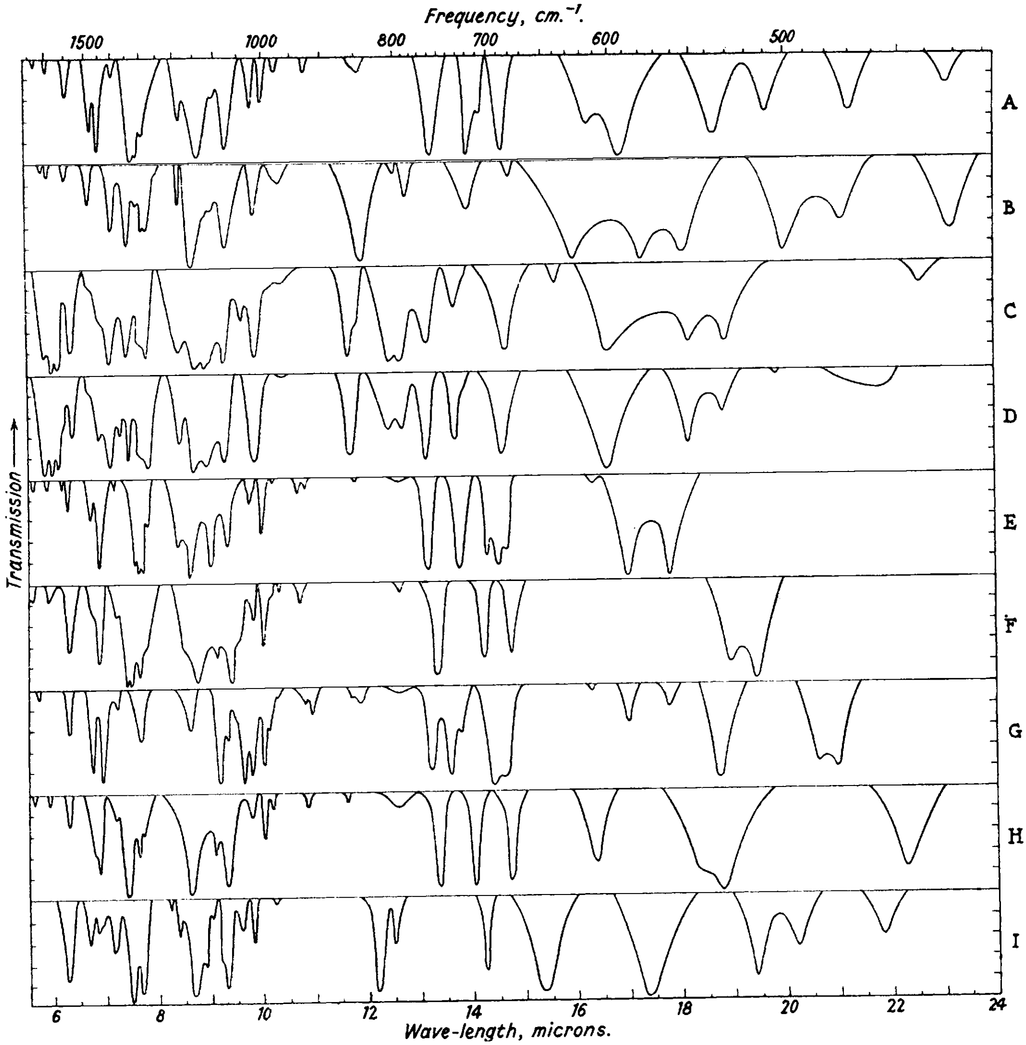


*A, Diphenyl disulphide. B, Di-*p*-tolyl disulphide. C, Di-*o*-tolyl disulphide. D, Di-*p*-cyanophenyl disulphide. E, Di-*p*-aminophenyl disulphide. F, Di-*p*-carbamylphenyl disulphide. Di-*p*-amidinophenyl disulphide (G) dihydrochloride, (H) dibenzenesulphonate. I, Diphenyl disulphide* 4 : 4′*-di-(carboxyimino ethyl ether) dihydrochloride.*

Phenyl benzenethiolsulphonate (Hinsberg, *Ber.*, 1908, **41**, 2838) had constant m. p. 45°.

p-Cyanophenyl *p*-cyanobenzenethiolsulphonate (Cymerman, Koebner, and Short, *J.*, 1948, 381). *p*-carbamylphenyl *p*-carbamylbenzenethiolsulphonate, and phenyl benzenethiolsulphonate 4 : 4′-di-(carboxyimino ethyl ether) dihydrochloride (Bauer and Cymerman, *loc. cit.*) were the pure samples described.

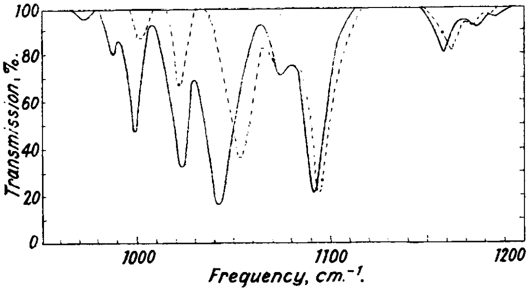
FIG. 2.



A, *Phenyl benzenethiolsulphonate, and its* (*B*) p-*cyano-*, (*C*) p-*carbamyl, and* (*D*) p-(*carboxyimino ethyl ether hydrochloride*) *derivatives. E, Diphenyl sulphone. F, Diphenyl disulphone. G, Diphenyl sulphoxide. H, Bisbenzenesulphonyl sulphide. I, Bistoluene*-p-*sulphonyl trisulphide.*

FIG. 3.

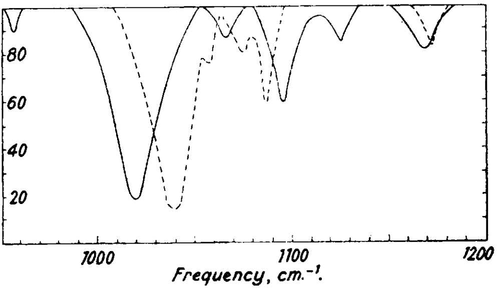
Diphenyl sulphoxide.



———, *Solid in " Nujol."*
– – – –, *Solution in* CCl_4.

FIG. 4.

Diisobutyl sulphoxide.



———, *Solid in " Nujol."*
– – – –, *Solution in* CCl_4.

Specimens of diphenyl disulphone, bisbenzenesulphonyl sulphide, and bistoluene-*p*-sulphonyl trisulphide were kindly supplied by Dr. A. McL. Mathieson, and di*iso*butyl sulphoxide by Professor W. Davies.

Spectroscopic Technique.—The infra-red spectra from 2·5 to 25 μ. (4000—400 cm.$^{-1}$) were measured with a Perkin–Elmer Spectrometer, Model 12B, using rock-salt optics for the region 4000—670 cm.$^{-1}$ and potassium bromide for the region 670—400 cm.$^{-1}$.

The specimens were measured in suspension in " Nujol " or methylene iodide–sulphur. In the 400—700-cm.$^{-1}$ range " Nujol " has practically no absorption in the thickness required for work with suspensions, while methylene iodide has an intense band at 570 cm.$^{-1}$ and a weaker one at about 490 cm.$^{-1}$. Methylene iodide, however, is transparent in the 1350 and 1450 cm.$^{-1}$ regions where " Nujol " absorbs heavily.

Some work on monosulphoxides was carried out with solutions in " AnalaR " carbon tetrachloride in a rock-salt cell of fixed path-length (about 0·5 mm.).

Figs. 1 and 2 show the spectra of disulphides and oxygen-containing compounds respectively over the range 1800—420 cm.$^{-1}$; the sample thickness used for the long-wave-length region, however, was not always the same as that used for the 4000—670-cm.$^{-1}$ region.

Figs. 3 and 4 show the spectra, in " Nujol " suspension and in carbon tetrachloride solution, of diphenyl sulphoxide and di*iso*butyl sulphoxide respectively. The absorption of the carbon tetrachloride has been subtracted for the spectra in solution.

RESULTS AND DISCUSSION.

Characteristic Frequency of the Sulphoxide Link.—Schreiber (*Analyt. Chem.*, 1949, **21**, 1168), from measurements on thionyl chloride, diphenyl sulphoxide, and di-*n*-butyl sulphoxide in carbon tetrachloride solution, suggested tentatively that an absorption band near 1190 cm.$^{-1}$ was characteristic of the $S{-}O$ linkage. For diphenyl sulphoxide he reported a strong band at 1183 cm.$^{-1}$ with a well-defined shoulder at 1166 cm.$^{-1}$. In a repetition of Schreiber's work we found no peak at 1183 cm.$^{-1}$ but a well-marked band at 1160 cm.$^{-1}$ in the solid (1163 cm.$^{-1}$ in carbon tetrachloride solution) with slight shoulders at 1173 and 1183 cm.$^{-1}$. It will be observed from Fig. 3 that the 1163-cm.$^{-1}$ band is much weaker than the band at 1053 cm.$^{-1}$ (1042 cm.$^{-1}$ in the solid), which we have reason to think is the $S{-}O$ frequency. Di*iso*butyl sulphoxide gave a strong band at 1019 cm.$^{-1}$ (solid) or 1039 cm.$^{-1}$ (solution) and only weak absorption in the region of 1190 cm.$^{-1}$ (see Fig. 4).

Our results on these two monosulphoxides are, however, in good agreement with those of Barnard, Fabian, and Koch (*J.*, 1949, 2442). These authors, from a study of a number of monosulphoxides, concluded that the $S{-}O$ band has a characteristic vibration frequency of 1055 cm.$^{-1}$, and that in accordance with theory (Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **200**, 409) and experiment (Amstutz, Chessick, and Hunsberger, *Science*, 1950, **111**, 305; Barnard, Fabian, and Koch, *loc. cit.*; Phillips, Hunter, and Sutton, *J.*, 1945, 146) the $S{-}O$ bond in sulphoxides has considerable double-bond character. The oxygen atom can take part in intermolecular bonding, which explains the shift of 11 cm.$^{-1}$ in the 1053-cm.$^{-1}$ band of diphenyl sulphoxide and of 20 cm.$^{-1}$ in the 1039-cm.$^{-1}$ band of di*iso*butyl sulphoxide on passage from solution to the solid state. The band at 1163 cm.$^{-1}$ in diphenyl sulphoxide does not undergo an appreciable frequency change on passage from solution to solid, which confirms that it is not due to a $S{-}O$ vibration.

The high frequency (1238 cm.$^{-1}$) found by Schreiber for the $S{-}O$ vibration in thionyl chloride (cf. 1229 cm.$^{-1}$ for the corresponding Raman frequency of the liquid: Cabannes and Rousset, *Ann. physique*, 1933, **19**, 229) is explained by Barnard, Fabian, and Koch (*loc. cit.*) by supposing that, on replacement of the organic substituents by halogen, the contribution of the structure $RR'S^{+}{-}O^{-}$ is lowered relative to that of $RR'S{=}O$. A similar argument has been used by Hartwell, Richards, and Thompson (*J.*, 1948, 1436) to explain the increased carbonyl frequency in halogen-substituted acids and ketones. Table I shows the $C{=}O$ and $S{=}O$ frequencies for some related carbonyl and sulphoxy-compounds.

TABLE I.

Molecule.	Frequency (cm.$^{-1}$).	Molecule.	Frequency (cm.$^{-1}$).
$(CH_3)_2C{:}O$ [1] (*l*)	1718	$R_1R_2S{:}O$ [4] (*s*)	1040
$(CH_3O)_2C{:}O$ [2] (*l*)	1747	$(CH_3O)_2S{:}O$ [5] (*l*)	1200
$(C_2H_5O)C{:}O$ [2] (*l*)	1744	$(C_2H_5O)_2S{:}O$ [5] (*l*)	1200
$Cl_2C{:}O$ [3] (*l*)	1807	$Cl_2S{:}O$ [6] (*l*)	1229

[1] Hartwell, Richards and Thompson, *loc. cit.* [2] Dadieu and Kohlrausch, *Wien. Ber.*, 1930, **139**, 77. [3] Ananthakrishnan, *Proc. Indian Acad. Sci.*, 1937, **5***A*, 285. [4] Barnard, Fabian, and Koch, *loc. cit.* [5] Matossi and Aderhold, *Z. Physik*, 1931, **68**, 683. [6] Cabannes and Rousset, *loc. cit.*

The Structure of the So-called " Disulphoxides."—If these compounds had the formula (I) or (II), sulphur–oxygen vibrations in the neighbourhood of 1040 cm.$^{-1}$ would be expected. In (I) there would be an $S{-}O$ bond from each of the two adjacent sulphur atoms, and some slight vibrational interaction might be expected, as in the case of adjacent $\mathrm{C{:}O}$ bonds. The Raman spectra of 1 : 2-diketones recorded by Kohlrausch and Pongratz (*Ber.*, 1934, **67**, 976) show that a shift of only 5—15 cm.$^{-1}$ occurs in benzil (1683 cm.$^{-1}$, compared with 1678 cm.$^{-1}$ for dibenzoylmethane) and in diacetyl (1725 cm.$^{-1}$, compared with 1710 cm.$^{-1}$ for 3 : 3-dimethylpentane-2 : 4-dione); and Thompson (*Trans. Faraday Soc.*, 1940, **36**, 988) records 1730 cm.$^{-1}$ for glyoxal, compared with 1745 cm.$^{-1}$ for formaldehyde. Although, as pointed out by Barnard, Fabian, and Koch, the analogy between the sulphoxide group and the carbonyl group is not perfect on account of the different geometry of the sulphur and carbon valencies, it is unlikely that interaction would shift the S–O frequencies by more than about 10 cm.$^{-1}$ from the mean position. Now the thiolsulphonates have no characteristic bands in the neighbourhood of 1040 cm.$^{-1}$. The nearest bands to this frequency are those at 1020 and 1080 cm.$^{-1}$, which cannot be due to an S–O vibration as they occur with all the disulphides as well as with the thiolsulphonates. There are, however, *two* strong bands, at about 1150 and 1340 cm.$^{-1}$, at almost the same frequency as in sulphur dioxide (ν_1 = 1151 cm.$^{-1}$, ν_3 = 1361 cm.$^{-1}$) and the sulphones (Schreiber, *loc. cit.*). Table II shows these frequencies for the thiolsulphonates and disulphones studied in the present work. The inference is that the compounds hitherto known as " disulphoxides " have the structure $\mathrm{R{\cdot}SO_2{\cdot}S{\cdot}R'}$ rather than $\mathrm{R{\cdot}SO{\cdot}SO{\cdot}R'}$ and should therefore be referred to as thiolsulphonates.

TABLE II.

Thiolsulphonates, $\mathrm{R{\cdot}SO_2{\cdot}SR}$, R =	ν_1.	ν_3.	Sulphones,	ν_1.	ν_3.
Ph	1144	1331	$\mathrm{Ph_2SO_2}$	1158	1298, 1312, 1319
p-$\mathrm{C_6H_4{\cdot}CN}$	1154	1342	$\mathrm{(Ph{\cdot}SO_2)_2}$	1150	1339, 1354
p-$\mathrm{C_6H_4{\cdot}CO{\cdot}NH_2}$	1154	1342	$\mathrm{(Ph{\cdot}SO_2)_2S}$	1166	1345, 1361
p-$\mathrm{C_6H_4{\cdot}C(OEt){:}NH,HCl}$	1154	1341	$(p$-$\mathrm{C_6H_4{\cdot}SO_2{\cdot}S)_2S}$	1154	1338

TABLE III.

Compound.	C–S band, cm.$^{-1}$.	Aromatic " non-para " band, cm.$^{-1}$.	S–S band, cm.$^{-1}$.
Disulphides, $\mathrm{R_2S_2}$, R =			
Ph	689	737 (?)	468
p-$\mathrm{C_6H_4Me}$	696	—	486
o-$\mathrm{C_6H_4Me}$	676	702 (w)	433
p-$\mathrm{C_6H_4{\cdot}CN}$	580 or 705 (w)	—	443
p-$\mathrm{C_6H_4{\cdot}NH_2}$	612 or 670 (w)	—	469
p-$\mathrm{C_6H_4{\cdot}CO{\cdot}NH_2}$	673 and/or 686	—	461
p-$\mathrm{C_6H_4{\cdot}C(NH_2){:}NH,HCl}$	674	—	457
p-$\mathrm{C_6H_4{\cdot}C(NH_2){:}NH}$ (dibenzenesulphonate)	690	—	497
p-$\mathrm{C_6H_4{\cdot}C(OEt){:}NH,HCl}$	685 and/or 690	—	465
Thiolsulphonates, $\mathrm{R{\cdot}SO_2{\cdot}SR}$, R=			
Ph	686	706	470
p-$\mathrm{C_6H_4{\cdot}CN}$	631 and/or 680	—	473
p-$\mathrm{C_6H_4{\cdot}CO{\cdot}NH_2}$	683	—	463
p-$\mathrm{C_6H_4{\cdot}C(OEt){:}NH,HCl}$	687	—	461
Miscellaneous Sulphur-containing Aromatic Compounds :			
Diphenyl sulphone	683, 690	699	—
Diphenyl disulphone	680	705	?
Diphenyl sulphoxide	686	695	—
Bis(benzenesulphonyl) sulphide	681	715	449
Bis(toluene-p-sulphonyl) trisulphide	653 and/or 702	—	458
Aliphatic Compounds :			
Methionine	688	—	—
Cysteine hydrochloride	651	—	—
Cystine	674	—	454
Glutathione	691	—	—

It will be seen that in the solid state, the higher frequency of the sulphones is often split.

No band characteristic of the $\mathrm{SO_2}$ deformation frequency (519 cm.$^{-1}$ in sulphur dioxide itself) was recognisable in the spectra.

Carbon–Sulphur Vibration Frequencies.—The assignment of characteristic vibration frequencies to the C–S bonds in molecules as complex as the present ones is rather uncertain. Trotter and Thompson (*J.*, 1946, 481) and also Sheppard (*Trans. Faraday Soc.*, 1950, **46**, 429) concluded from the study of a number of simple aliphatic sulphides and disulphides that the

C–S frequency was variable but usually lay between 600 and 700 cm.$^{-1}$. All the compounds studied in the present investigation showed bands in this region. An unambiguous assignment is not possible, however, as the ν_4 frequency of the benzene ring, which appears in benzene itself as a strong band at 671 cm.$^{-1}$, persists in a large number of monosubstituted, but not in *p*-disubstituted, benzene derivatives, as a band near 700 cm.$^{-1}$. This has been noted by other authors (Barnes *et al.*, *Analyt. Chem.*, 1948, **20**, 402). Table III shows a possible assignment, and includes also some aliphatic sulphur compounds for comparison. The S–S frequencies are discussed below.

Sulphur–Sulphur Vibration Frequencies.—All the disulphides, thiolsulphonates, and disulphones, with the exception of diphenyl disulphone, show a band in the region 430—490 cm.$^{-1}$ (see Table III). The band is frequently weak or badly defined, but may be due to an S–S vibration. Trotter and Thompson, and also Sheppard (*loc. cit.*), identified such bands in the 450—520-cm.$^{-1}$ region for several simple aliphatic disulphides; in general the bands were found to be weak in absorption but strong in Raman spectra.

It is possible that the failure of diphenyl disulphone to give a band in this region is caused by the molecule's possessing a centre of symmetry and existing in the *trans*-form only, so that the S–S vibration is inactive in absorption. In the solid state the selection rules would not be expected to apply rigorously, but the band due to the S–S vibration should be weak if the molecule has a centre of symmetry. It is known from the *X*-ray structure analysis of Dawson, Mathieson, and Robertson (*J.*, 1948, 322) that the space group is either $P1$ or $P\bar{1}$. In the latter case the molecule has a centre of symmetry.

The aliphatic disulphide, cystine, was found to have a band at 454 cm.$^{-1}$ which can be attributed to an S–S vibration.

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(J. C.) CHEMISTRY DEPARTMENT, UNIVERSITY OF SYDNEY.
(J. B. W.) DIVISION OF INDUSTRIAL CHEMISTRY,
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION,
MELBOURNE. [*Received, November 6th,* 1950.]