# CCXXXV.—cis-trans-*Isomerism of Disulphoxides.*

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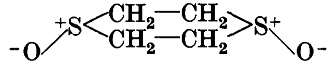
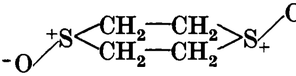
THE isolation of optically active ethyl *p*-toluenesulphinate (Phillips, J., 1925, **127**, 2552) and optically active sulphoxides of the type RR′SO (Harrison, Kenyon, and Phillips, J., 1926, 2079) proves that the three groups attached to the sulphur atom in these compounds do not lie in one plane with it. It follows that, if two sulphoxyl groups are present in a molecule, two isomerides should arise having the *cis*- and the *trans*-configuration, respectively. No such isomerism has hitherto been observed, although suitable disulphoxides have been known for half a century. We have therefore subjected two such cases to a closer investigation and have in each case isolated a pair of isomeric disulphoxides.

The so-called disulphoxides derived from the disulphides R•S•S•R′ are not in question, for it has become clear that they do not actually possess the disulphoxide structure R•SO•SO•R′, but are of the type R•S•$SO_2$•R′ (Smiles and Gibson, J., 1924, **125**, 176; Miller and Smiles, J., 1925, **127**, 224).

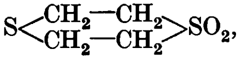
The simplest case is presented by the disulphoxides (I) and (II) of diethylene disulphide (1 : 4-dithian).

(I.)

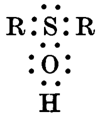




(II.)

Here the plane of symmetry present in the molecule of each isomeride excludes the possibility of enantiomorphism. A disulphoxide of 1 : 4-dithian was isolated by Crafts (*Annalen*, 1862, **124**, 110; 1863, **125**, 123), which was soluble in water and separated from it in rhomb-shaped crystals. An examination of the mother-liquor from the crystallisation of this substance has now revealed the presence of an isomeride. The two disulphoxides decompose without melting, and their characterisation has depended on their differences in solubility and in crystallographic properties. The α-isomeride is monoclinic and its solubility in 90% ethyl alcohol is less than one-fifth of that of the β-form, which is anorthic. The alternative formula  $S<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>SO_2$, which might represent one of the isomerides as structurally isomeric, is inadmissible, for both the α- and the β-isomeride are readily reduced to the parent disulphide, a reaction characteristic of sulphoxides, but never shown by sulphones.

The configurations of these disulphoxides cannot be determined with certainty, but it may be tentatively assumed that the α-isomeride, being the less soluble, is the *trans*-form (II). Attempts to convert one isomeride into the other by heating in aqueous solution alone, or with acetic or hydrochloric acid of various concentrations, were unsuccessful. When heated with 5—20% hydrochloric acid, both disulphoxides behaved as peroxides, yielding dithian itself. The fact that it was not possible to bring about the interconversion of these isomeric disulphoxides is surprising, yet it is in agreement with the stability of the optically active sulphoxides, which showed no marked tendency to racemisation.

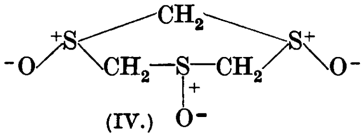
There is reason to suppose that the dissolution of an aldehyde or ketone in water involves the formation of a compound of the type $R\cdot C(OH)_2\cdot R'$, and with the older formulation of sulphoxides their ready solubility in water would by analogy have been attributed to the formation of a corresponding compound $R\cdot S(OH)_2\cdot R'$. If this were so, it would involve the rapid racemisation of active sulphoxides and the easy interconversion of *cis-trans*-isomerides in aqueous solution. On the other hand, from a consideration of the electronic formulæ it is clear that a compound $R\cdot S(OH)_2\cdot R'$ cannot exist as such, but only as the two ions :  $\begin{array}{c}R:\ddot{S}:R'\\ :\ddot{\underset{..}{O}}:\\ H\end{array}$ and $:\underset{..}{\dot{O}}:H$. Yet solutions of sulphoxides are not markedly alkaline, so that a complex, if it exists, must occur largely in some non-dissociated form. These considerations point to the following formula as a probable one : $\begin{matrix}R\\R'\end{matrix}:\ddot{\underset{.}{S}}:\ddot{\underset{..}{O}}:H:\ddot{\underset{..}{O}}:H$ (compare formulæ suggested for weak nitrogen bases by Moore and Winmill, J., 1912, **101**, 1635; Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1419).

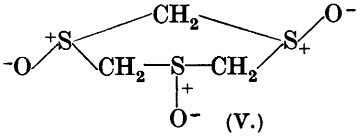
The disulphoxide derived from diethyldithiolethane,

$CH_2(SEt)\cdot CH_2\cdot SEt$,

was described by Beckmann in 1878 (*J. pr. Chem.*, 1878, **17**, 409). We have examined the oxidation of the closely related dimethyldithiolethane. The product of the reaction is a mixture of two isomeric disulphoxides, $Me{\cdot}SO{\cdot}C_2H_4{\cdot}SOMe$, the α-form, m. p. 163—164°, being less soluble in various solvents than the β-form, m. p. 128—130°. Both are readily reduced to the disulphide. One of these isomerides must be an inactive mixture (or compound) of two enantiomorphs, but it is not possible to discriminate between them. This pair of isomerides is closely analogous to the two diethiodides of the same disulphide which were recently described by Wedekind (*Ber.*, 1925, **58**, 2510).

It follows from the results now described that a cyclic trisulphoxide also should occur in two forms, and it is possible that the two isomeric trisulphoxides of trimethylene trisulphide obtained by Hinsberg (*J. pr. Chem.*, 1912, **85**, 1912; 1914, **89**, 547) are, in fact, the two substances (IV) and (V).


(IV.)


(V.)

The criticisms of Fromm and Schultis (*Ber.*, 1923, **56**, 937), however, suggest the advisability of a reinvestigation of this case.

We are indebted to Professor S. Smiles, F.R.S., for drawing our attention to the isomeric disulphoxides of thianthren (Fries and Vogt, *Ber.*, 1911, **44**, 756). The isomerism in this case is well established, but it has hitherto remained unexplained. It is evidently another example of the phenomenon under discussion.

## EXPERIMENTAL.

*Oxidation of* 1 : 4-*Dithian by Hydrogen Peroxide.*—To a solution of dithian (10 g.) in glacial acetic acid (200 c.c.) at 0°, hydrogen peroxide (2 mols. of 30% aqueous solution), dissolved in an equal volume of acetic acid, was added, and the mixture kept for 24 hours. Most of the acetic acid and any trace of unchanged sulphide were then removed in a current of steam and the solution was evaporated to dryness three times to remove acetic acid (yield, 12·5 g. of crude disulphoxides). The product consisted mainly of the α-disulphoxide, which is undoubtedly that described by Crafts. Crystallisation of the crude mixture from 90% ethyl alcohol (400 c.c.) yielded this compound, and one further crystallisation from 50% ethyl alcohol (50 c.c.) gave the pure substance (7·8 g.) in rhomb- or hexagonal-shaped plates, decomp. 263° (uncorr.) (Found : C, 31·3; H, 5·4; *M*, cryoscopic in water, 142, 149. Calc. : C, 31·55; H, 5·3%; *M*, 152).

The substance is readily soluble in cold water and practically insoluble in absolute ethyl alcohol and other organic solvents. It crystallises in the monoclinic system, having $a : b : c = 1{\cdot}267 : 1 : 0{\cdot}979$; $\beta = 104° 3'$. Crystals of the habit shown in Fig. 1 were obtained by slow evaporation of an aqueous solution. The following is a list of the forms and the angular measurements observed with three crystals :

| | *a* (100). | *m* (110). | *r* (101). | *R* ($\bar{1}01$). | *q* (011). |
|---|---|---|---|---|---|
| $\phi$ ...................... | 0° 0′ | *50° 52′ | 0° 0′ | 180° 0′ | *75° 40′ |
| $\rho$ ...................... | 90° 0′ | 90° 0′ | 46° 18′ | 28° 32′ | *45° 19′ |

The simpler rhomb-shaped crystals are developed on *R* bounded by *q* and *m*. The angle of the rhomb was observed under the microscope to be about 71° (calc., 71° 6′). The extinction on the face *R* is oblique. The position of the optic axes was not observed. The crystals had $d_{4^\circ}^{20^\circ}$ (vac.) 1·570.

By fractional crystallisation of the material retained in the mother-liquor of this sulphoxide a small amount of another, more soluble substance was obtained, which crystallised in needles from absolute ethyl alcohol. The separation was facilitated by the fact that the two substances, although not very different in microscopic appearance in ordinary light, were sharply differentiated when seen between crossed Nicols. The second isomeride was best obtained thus : The crude mixture of disulphoxides (6·2 g.) was warmed with aqueous alcohol (90%, 200 c.c.), and then cooled in ice, and the solution was filtered. The solid residue (4·3 g.) was almost pure α-disulphoxide. The solution on evaporation left a residue (1·9 g.), which was boiled with enough absolute ethyl alcohol to dissolve about half of it. The solution was filtered and, on cooling, it deposited the β-*isomeride* (0·8 g.), which was pure after one further crystallisation (Found : C, 31·55; H, 5·2; *M*, 132, 144. $C_4H_8O_2S_2$ requires C, 31·55; H, 5·3%; *M*, 152).

β-*Dithian dioxide* separates from aqueous or absolute alcohol in elongated plates or flat needles, decomp. 235—250°. It crystallises in the anorthic system, having the angular elements *ab*, 105° 0′; *d*, 56° 17′; *e*, 127° 14′; *f*, 61° 44′; and *g*, 120° 59′. Crystals of the habit shown in Fig. 2 were obtained by slow crystallisation of an aqueous solution. The following forms and mean angular values were observed with three crystals :

| | *a* (100). | *b* (010). | *c* (001). | *o* (111). |
|---|---|---|---|---|
| $\phi$ ........................ | 0° 0′ | *105° 0′ | *241° 11′ | *60° 28′ |
| $\rho$ ........................ | 90° 0′ | 90° 0′ | *40° 56′ | *37° 29′ |

The extinction on *a* is at about 4° to the edge *ab*. The biaxial optic picture is seen in convergent light on face *a*, the optic axial plane being nearly parallel to the edge *ab* and the acute bisectrix nearly normal to *a*. $d_{4^\circ}^{20^\circ}$ (vac.) 1·554.

*Determinations of Solubility and Proportion of the Isomerides present.*—100 C.c. of ethyl alcohol dissolve less than 1 g. of the α-isomeride at the boiling point, and approximately 0·1 g. at 20°; the β-isomeride is three times as soluble in cold alcohol. The solubilities of the two substances in 90·7% ethyl alcohol were determined accurately in a thermostat at 22·0°. 100 C.c. of solution contained 0·38 g. of α-isomeride and 2·26 g. of β-isomeride. Use being made of these values, the proportion of the two isomerides present in the oxidation product was determined. The mixture (0·4006 g. made by means of hydrogen peroxide) was stirred for several hours in a closed bottle at 22·0° with 90·7% alcohol (25·0 c.c.); 10 c.c. of the solution then contained 0·0557 g. of material (mean value). The influence of each on the solubility of the other being neglected, the two must be present in the proportion of 11·0% of the β- and 89·0% of the α-isomeride. A similar determination on the product of oxidation of dithian in ether by means of nitrous fumes showed the presence of 8·9% of the β-isomeride.

FIG. 1.

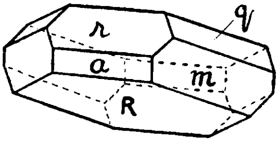
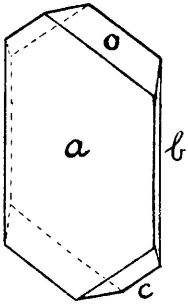


FIG. 2.



*Reduction of the Disulphoxides.*—A solution of the α-disulphoxide in acetic acid was boiled with addition of hydrochloric acid and zinc dust in excess. The solution when diluted and cooled deposited crystals of dithian (yield more than 50% of the theoretical), which was identified by direct comparison and the m. p. of a mixture with pure dithian. When the β-disulphoxide was reduced in the same way, dithian was again produced in quantity.

*Attempted Interconversion of the Isomerides.*—The α-disulphoxide was boiled for several hours in aqueous solution, and a known amount of ethyl alcohol then added. The weight of α-isomeride so recovered was exactly that expected, and therefore no conversion of α- into β-isomeride had occurred. The experiment was repeated with addition of acetic and dilute hydrochloric acids, but no positive evidence of interconversion was obtained. When either isomeride was heated under reflux or in a sealed tube with hydrochloric acid (5—35%), dithian was always produced; it was identified as before. The second isomeride was in no case detected.

*Oxidation of Dimethyldithiolethane.*—The dimethyldithiolethane required was obtained very conveniently by methylating dithioglycol with methyl sulphate and aqueous alkali. To the disulphide (10 g.), dissolved in glacial acetic acid (100 c.c.) and cooled, hydrogen peroxide (20 g. of 29·2% aqueous solution) was added, and the mixture kept for 24 hours. The solution was then evaporated twice with addition of water, and the residue (12·5 g.) of mixed disulphoxides fractionally crystallised from ethyl alcohol, a mixture of ethyl alcohol and ethyl acetate (1 : 1), and finally from toluene or xylene. Two disulphoxides were thus separated, of which the α-isomeride was obtained pure more easily, as it was present in the larger quantity.

α-*Dimethylethylenedisulphoxide* crystallises from ethyl alcohol in monoclinic needles, m. p. 163—164° (Found: C, 31·1; H, 6·5; *M*, cryoscopic in camphor, 159. $C_4H_{10}O_2S_2$ requires C, 31·2; H, 6·5%; *M*, 154). It is readily soluble in water and moderately easily soluble in cold ethyl acetate or hot xylene.

β-*Dimethylethylenedisulphoxide* crystallises from alcohol or ethyl acetate in monoclinic bipyramids, m. p. 128—130° (Found: C, 31·0; H, 6·7%; *M*, 145). It is readily soluble in water or ethyl alcohol and sparingly soluble in ethyl acetate or hot toluene. The solubilities of the two isomerides in ethyl acetate at laboratory temperature are: α-, 0·16 g./100 c.c. (of solution); β-, 0·42 g./100 c.c. The melting point of the β-compound is not depressed by the addition of a little of the α-compound, although such mixtures have a considerable melting interval instead of a sharp melting point.

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