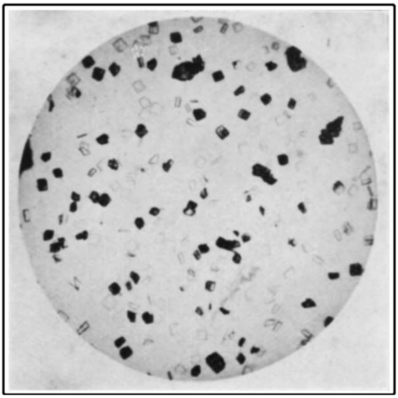
III.—*Stereoisomerism of Disulphoxides and Related Substances. Part IV. Di- and Tri-sulphoxides of Trimethylene Trisulphide.*

By Ernest Vere Bell and George Macdonald Bennett.

Stereochemical theory indicates the possibility of two disulphoxides and two trisulphoxides derived from the cyclic trimethylene trisulphide. A crystalline trisulphoxide was prepared by Hinsberg (*J. pr. Chem.*, 1912, **85**, 337), who subsequently announced that the small, almost insoluble residue rejected in its purification was an isomeric trioxide (*ibid.*, 1914, **89**, 547). On the other hand, Fromm and Schultis (*Ber.*, 1923, **56**, 937) contended that the latter substance is not a true sulphoxide of trimethylene trisulphide but a compound of high molecular weight. A single crystalline disulphoxide was also isolated by Hinsberg (*J. pr. Chem.*, 1913, **88**, 49). We have reinvestigated the oxidation of pure trimethylene trisulphide and have isolated a monoxide, two dioxides and two trioxides, and the relationships which exist between them lead to an exact determination of their configurations.

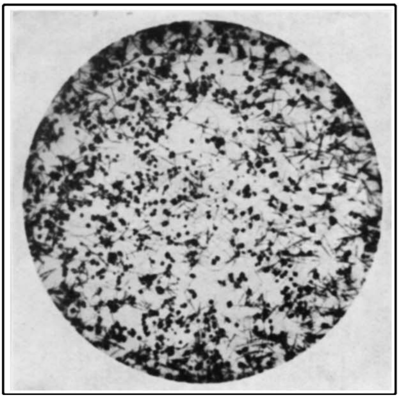
The practical problem involved was solved by the method of oxidation described in Part II (J., 1928, 86). Fromm and Ungar (*Ber.*, 1923, **56**, 2286) had reported that the oxidation of dithian with one molecular proportion of hydrogen peroxide yielded its dioxide, some of the sulphide being unchanged. It appeared to us, nevertheless, that a monoxide should be capable of existence and must occur as an intermediate in this oxidation. The carefully controlled oxidation of dithian did, in fact, yield the monoxide. When trimethylene trisulphide was oxidised by this method, it also furnished a *monoxide*. This was subjected to further cautious oxidation, and by fractional crystallisation of the product from water three distinct crystalline substances were isolated all having the composition and molecular weight of a dioxide of the parent sulphide. There had, however, been indications that two of these substances were polymorphic forms of one chemical individual. This polymorphism was confirmed by the direct interconversion of the two forms. Sidgwick's test (J., 1915, **107**, 672) was applied and the results indicate that the three substances are a pair of polymorphic forms of an α-*disulphoxide* and an entirely distinct β-disulphoxide. Crystals of these substances suitable for goniometry have not been obtained, but their character is illustrated by photomicrographs of the α-dioxide (Fig. 1, labile form; Fig. 2, labile form partly converted into the stable form; Fig. 3, stable form) and the β-dioxide (Fig. 4).

FIG. 1.



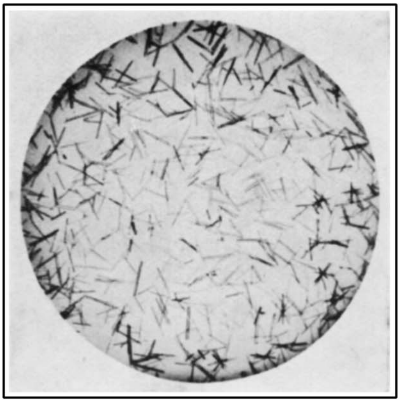
a-Dioxide (*labile*) (× 12).

FIG. 2.



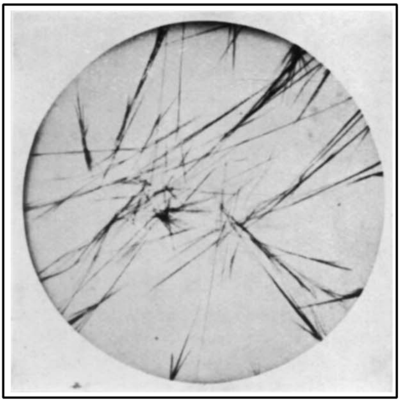
a-Dioxide (*labile and stable*) (× 12).

FIG. 3.



a-Dioxide (*stable*) (× 12).

FIG. 4.



β-Dioxide (× 12).

[*To face p.* 15.]

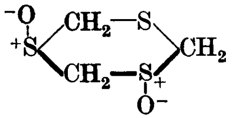
When these dioxides were subjected to further oxidation, each yielded the α-trioxide, but oxidation of the β-dioxide gave in addition a second (β)-*trioxide* more than ten times as soluble in water as its isomeride. A careful search showed that none of this substance was present in the product of oxidation of the α-dioxide.

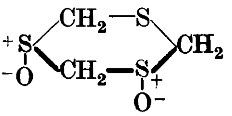
It is clear that Hinsberg's dioxide is identical with our β-dioxide and that his crystalline trioxide is identical with our α-trioxide. The sparingly soluble " trioxide " is entirely different from our β-trioxide and therefore our results confirm the criticism of Fromm and Schultis.

Gentle reduction of any of the five oxidation products we describe yields the parent trisulphide.

A consideration of the results of oxidising the two dioxides shows that the α-dioxide must have the *trans*-configuration (I) and the β-dioxide the *cis*-configuration (II).

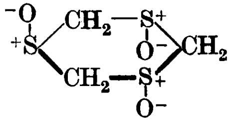
(I.)

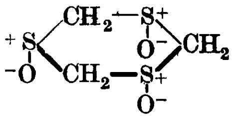




(II.)

(III.)





(IV.)

For the addition of an oxygen atom to (I) must yield a single trioxide (III) whether the added atom be above or below the plane of the ring. But, on the other hand, the *cis*-configuration (II) must on oxidation produce a mixture of isomerides having the *cis-trans*-(III) and the *cis-cis*-configuration (IV). It also follows that the α-trioxide, being the common oxidation product of both dioxides, is represented by (III), and the β-trioxide has the *cis-cis*-configuration (IV).

The genetic relationships between these substances thus lead to an absolute proof of their stereochemical structures. This is of great interest at a time when the possibility of the closure of a ring between groups in the *trans*-position, the new conception of the Beckmann transformation, and complications of the type of the Walden inversion introduce an uncertainty into many similar stereochemical problems. It is reassuring to notice that the configurations deduced above are in agreement with those which might have been tentatively assumed from the solubility relations of the isomerides : the *cis* (β)-dioxide is more soluble in water than its *trans* (α)-isomeride and the *cis-cis* (β)-trioxide much more so than the *cis-trans* (α)-isomeride. This lends considerable support to the allocation of formulæ to the two dioxides of dithian which we made in Part I (J., 1927, 1799).

The configurative relationships between the di- and tri-sulphoxides described above are closely analogous to those involved in the work of Perkin and Robinson (J., 1921, **119**, 1392) on ethyl dibromoadipate and still more in that of Ing and Perkin (J., 1925, **127**, 2387) on the dibromoglutaric esters. The latter authors found that two stereoisomeric methyl $\alpha\alpha'$-dibromoglutarates, each by a malonic ester condensation, yielded two isomeric *cyclo*butane-1 : 2 : 2 : 3-tetracarboxylic esters. One of these esters by hydrolysis and loss of carbon dioxide gave a single *trans*-*cyclo*butane-1 : 2 : 3-tricarboxylic acid, whereas the other yielded a mixture of this acid with its *cis*-isomeride. The principle of Ing and Perkin which we have utilised should have led to a determination of the configuration of the original dibromo-esters, but the results point to a partial interconversion of stereoisomerides and are therefore inconclusive. No configurative changes of this type can have occurred in our experiments, for the trimethylene trisulphide ring remained intact throughout and the reactions involved are practically quantitative at laboratory temperature.

The large number of analyses used to control the fractional crystallisations involved in this investigation would have been almost impossible from the point of view of either time or cost but for the macro-modification of Pregl's determination of sulphur which we have recently described (J., 1928, 3192).

EXPERIMENTAL.

Oxidation of Trimethylene Trisulphide to a Monoxide.—Carefully purified acetone (4 l.) and trimethylene trisulphide (recrystallised successively from glacial acetic acid and xylene; 39·2 g.) were stirred together at 40° while a solution of hydrogen peroxide (35·8 g. of 27% strength in 400 c.c. of acetone) was run in drop by drop during 6 hours. After 12 hours, the solvent was evaporated and the solid residue was extracted with hot water, 7 g. of trimethylene trisulphide remaining undissolved. The material recovered from the water by evaporation was further freed from dioxide by extraction of the monoxide with absolute ethyl alcohol. This substance (14 g.) was finally recrystallised several times from water. *Trimethylene trisulphide monoxide* forms colourless needles with a straight extinction and a high double refraction, m. p. 187° (Found : S, 62·3. $C_3H_6OS_3$ requires S, 62·3%). It is easily soluble in warm but less soluble in cold water or acetic acid, and moderately easily soluble in ethyl alcohol or acetone.

Oxidation of the Monoxide to the Isomeric Dioxides.—The monoxide (30·7 g. collected from three of the above-described oxidations), dissolved in glacial acetic acid (750 c.c.), was kept stirred at room temperature during the addition, over a period of 6 hours, of the calculated amount of hydrogen peroxide (25·2 g. of 27% strength in 375 c.c. of acetic acid). After 12 hours, the acetic acid was distilled under reduced pressure below 50°. The crude oxidation product was separated by a long process of fractional crystallisation from water into the labile and stable forms of the α-dioxide and the β-dioxide.

α-Trimethylene trisulphide dioxide (yield, 6 g.) decomposes at 220—280° and is dimorphous. The *labile* form crystallises from water in almost square plates with a high double refraction and an extinction angle of 16° (Found : C, 21·0 ; H, 3·6 ; S, 56·35. $C_3H_6O_2S_3$ requires C, 21·2 ; H, 3·5 ; S, 56·5%). The *stable* form crystallises from water in stout monoclinic prisms with an extinction angle of 35° (Found : C, 20·8 ; H, 3·7 ; S, 56·6%. *M*, cryoscopic in water, 174, 206. $C_3H_6O_2S_3$ requires *M*, 170). When this form is recrystallised from water, it often, but not always, separates in the labile form. The latter, on standing in contact with the solution from which it has crystallised, changes more or less rapidly into the stable form.

The β-trimethylene trisulphide dioxide (yield, 4 g.) decomposes at 200—215° (Found : C, 21·2 ; H, 3·5 ; S, 56·4 ; *M*, 153, 174). It crystallises from water in bundles of pointed needles having an extinction angle of 32°. Both α- and β-dioxides are sparingly soluble in most organic solvents, but soluble in acetic acid.

Solubilities of the Isomerides and Proof of the Polymorphism.—The solubilities of the stable form of the α-dioxide and of the β-dioxide were determined by evaporation of a weighed sample of an aqueous solution which had been stirred with the solid for 3 hours in a thermostat at 25·0°. 100 G. of water at 25° dissolve 1·70 g. of the α-dioxide, and 4·53 g. of the β-dioxide.

The following results were obtained by Sidgwick's cryoscopic method with water as solvent :

Depression with α-dioxide (labile)	0·087°
,, ,, α-dioxide (stable)	0·073
,, ,, α-dioxide (labile and stable)	0·083
,, ,, β-dioxide	0·226
,, ,, β-dioxide and α-dioxide (stable)	0·270

These figures show that the two forms of α-dioxide are polymorphic and the β-dioxide is isomeric.

Oxidation of the Isomeric Dioxides.—The α-dioxide (2·45 g.), dissolved in acetic acid (100 c.c.), was stirred at laboratory temperature while, during 1 hour, 50 c.c. of a solution of hydrogen peroxide (38·6 g. of 25·4% strength in 1 l. of acetic acid) were added. After 12 hours, the acetic acid was distilled under diminished pressure. The residue (yield, nearly quantitative) consisted of the single substance α-trimethylene trisulphoxide and crystallised from water in bundles of radiating minute prisms with oblique extinction, decomp. 230—280° (Found: S, 51·2. Calc. for $C_3H_6O_3S_3$: S, 51·6%). It is insoluble in alcohol or acetone, and sparingly soluble in acetic acid or water.

The β-dioxide was oxidised in a precisely similar manner. The crude product (2·9 g.) was separated by fractional crystallisation from water into the α-trioxide described above (Found: S, 51·5%) and the β-*trimethylene trisulphoxide*, which crystallised from water in minute separate prisms with an extinction angle of 32°, decomp. 220—260° (Found: S, 52·0%). This substance is sparingly soluble in alcohol, acetone, and other organic solvents and moderately easily soluble in acetic acid or cold water.

Solubilities of the Isomeric Trioxides in Water.—The solubilities, determined as before, are: 100 g. of water at 25·0° dissolve 0·134 g. of the α-trioxide and 1·437 g. of the β-trioxide.

Reduction of the Sulphoxides.—The α- and β-dioxides and the α- and β-trioxides were each reduced by means of zinc dust and dilute hydrochloric acid to the parent trimethylene trisulphide, which was identified by its melting point and that of a mixture with the trisulphide.

Oxidation of Trimethylene Trisulphide to the Trioxide.—The finely powdered trisulphide was kept for a week with hydrogen peroxide (3 mols.) in acetic acid, and the solution filtered. The solid residue, recrystallised from water, yielded the pure α-trioxide (Found: S, 51·1%). The acetic acid was removed from the solution by distillation in steam and evaporation on the steam-bath. There remained a mixture of the disulphoxides (Found: S, 55·3%).

Examination of Hinsberg's Supposed Isomeric Form of Trimethylene Trisulphide.—Trimethylene trisulphide was heated with hydriodic acid (*d* 1·7) for 1½ hours at 100°. Water was added, and the product was filtered off and washed successively with water, thiosulphate, and again with water. It was a pale brown, crystalline substance, m. p. 247° (decomp.), and evolved a trace of hydrogen sulphide above its melting point. Recrystallisation converted it into the ordinary trisulphide of m. p. 216°. The determination of its molecular weight was therefore not feasible. The composition [Found: I, 0·9; C, 24·6, 24·7; H, 4·6, 4·4; S (as $BaSO_4$), 68·6. CH_2S requires C, 26·1; H, 4·35; S, 69·55%], after allowance has been made for the small amount of iodine present, is still different from that of a polymeride of CH_2S. There would appear to be some oxygen in the substance.

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