138. *The Configurations of the Disulphoxides of Thianthren.*

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BERGMANN and TSCHUDNOWSKY (*Ber.*, 1932, **65**, 457) measured the molecular electric moments of the geometrically isomeric disulphoxides of thianthren and found the values 1·7 *D* for the α-compound (m. p. 284°) and 4·2 *D* for the β-isomeride (m. p. 249°); and they deduced that the former is the *trans*-disulphoxide, with the oxygen atoms lying on the opposite sides of the heterocyclic ring, and the latter the *cis*-compound. The same conclusion has been reached by Baw, Bennett, and Dearns (J., 1934, 680) in the basis of the physical properties of the compounds. Consideration of the possible space arrangements of these compounds shows that this conclusion is probably erroneous, and that the configurations should be reversed.

Thianthren itself has a molecular electric moment of 1·5 *D* (Bennett and Glasstone, J., 1934, 128; Smyth and Walls, *J. Chem. Physics*, 1933, **1**, 337, give 1·41 *D*), which, as has been pointed out, must arise from the fact that the molecule has a folded structure, the folding taking place about a line passing through the sulphur atoms. It is very striking that the moment of the α-disulphoxide is only very slightly greater than that of the parent substance, in spite of the fact that the two oxygen atoms are united to the sulphur atoms by co-ordinate links (semipolar double bonds) each of which must possess a moment of about 2·5 *D* (Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147). It follows that the space arrangement of the two S→O links in this compound must be such that their electric moments almost cancel each other.

FIG. 1.

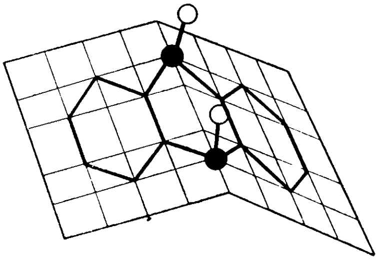


FIG. 2.

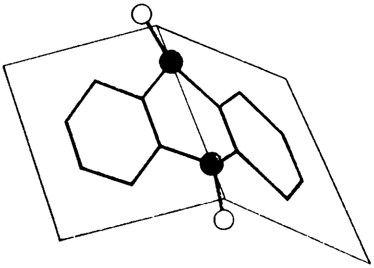
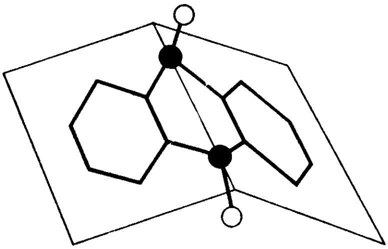


FIG. 3.



Because of the folded structure of the ring system, oxygen atoms can be attached to the two sulphur atoms in three different ways (Baw, Bennett, and Dearns, *loc. cit.*). These are shown in the figures, in which the black spheres represent sulphur atoms and the others are oxygen atoms; the angles between the three covalencies of sulphur are taken as 110° in accordance with the majority of the evidence (Bennett and Glasstone, *loc. cit.*). Figs. 1 and 2 are both *cis*-arrangements, since in each the two oxygen atoms are on one side of the heterocyclic ring; they are capable of interconversion by bending about the line joining the sulphur atoms. Fig. 3 is the only possible *trans*-arrangement. Only two disulphoxides are known. It would thus appear that the α-disulphoxide with the small moment is the *cis*-compound (Fig. 2), and the β-compound is the *trans*-arrangement (Fig. 3). The other possible *cis*-arrangement (Fig. 1) would be expected to have an electric moment of at least 6 *D*, since the component moments of the sulphoxide groups and the thianthren nucleus lie almost in the same direction. It is this configuration which is missing; the molecules appear to adopt the alternative *cis*-arrangement (Fig. 2).

This seems to be one of the few cases where, of two geometrical isomerides, the *cis*-compound has the greater symmetry, as is shown by its smaller electric moment and higher melting point.

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