332. *The Stereochemistry of Thianthren.*

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Previous authors have attempted the optical resolution of monosubstituted thianthrens, since it is known from dipole measurements that the thianthren molecule is non-planar. If the folded structure persists in solution, any monosubstituted thianthren derivative should be capable of existing in optically isomeric forms. Attempts to resolve 2-thianthrenyltrimethylammonium salts have proved unsuccessful, and a value calculated for the energy required for the transformation of thianthren from the folded to the planar state indicates a small degree of configurational stability.

In view of the attempted optical resolution of thianthren derivatives (Bennett, Lesslie, and Turner, J., 1937, **444**), some relevant investigations carried out some time ago are recorded. 2-Aminothianthren was prepared, and its optical resolution attempted in order to see whether the folded structure of the thianthren molecule, deduced by studies of dipole moments, is sufficiently rigid to permit the existence of optical isomers.

By following Krishna's directions (J., 1923, **123**, 156) for the reduction of 2-nitrothianthren by zinc in 90% acetic acid, a product was obtained which had the same m. p. as that given for 2-aminothianthren; but this was actually the acetyl derivative, and hydrolysis afforded 2-aminothianthren, which proved to be so weak a base that salts with active acids could not be isolated (cf. Bennett, Lesslie, and Turner, *loc. cit.*, who obtained a coloured *d*-camphor-10-sulphonate). In view of these difficulties, 2-*thianthrenyltrimethylammonium iodide* was made, and thence its well-defined salts with *d*-camphor-10-sulphonic acid, α-bromo-*d*-camphor-π-sulphonic acid, and *d*-diacetyltartaric acid. These were all repeatedly crystallised, but no evidence of optical resolution could be obtained.

It is therefore concluded that in solution the thianthren molecule oscillates so rapidly through a mean planar position that it virtually possesses a plane of symmetry. Sutton and Hampson (*Trans. Faraday Soc.*, 1935, **31**, 945), from measurements of the dipole moments of diphenyl sulphide and of thianthren, conclude that in these compounds the sulphur valency angle is approximately 110°. When the thianthren molecule assumes a planar configuration, the valency angles of both sulphur atoms become distorted to 120°, and the energy needed to effect this change can be estimated.

From the spectroscopic data for hydrogen sulphide (Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **889**, 654), it is calculated that approximately 3600 cals. per mole are needed to increase the sulphur valency angle by 10°. If this value be taken to apply to the case of the sulphur bonds in thianthren, some 7000 cals. per mole would be required for the transformation of thianthren from the folded to the planar state. If this figure be accepted, it is clear that the facility with which the thianthren molecule may become planar is such that optical resolution would be impossible; for it is only when the heat of racemisation becomes more than some 20,000 cals. per mole that optical activity is observable.

Experimental.

2-*Acetamidothianthren*.—58 G. of 2-nitrothianthren were reduced by Krishna's method (*loc. cit.*). The product, after a preliminary crystallisation from xylene, crystallised from dilute alcohol in colourless plates, m. p. 186°; yield 36 g. (Found: C, 61·7; H, 4·3; N, 5·15. Calc. for $C_{14}H_{11}ONS_2$: C, 61·5; H, 4·0; N, 5·1%). The substance gives a deep purple solution in concentrated sulphuric acid.

2-*Aminothianthren*.—36 G. of the acetyl derivative were boiled under reflux with 700 c.c. of concentrated hydrochloric acid and 250 c.c. of alcohol for 8 hours. The product was cooled, and the resulting solid filtered off, digested with sodium hydroxide solution, collected, washed, and crystallised from dilute alcohol, from which it separated as colourless needles or plates, m. p. 160°; yield 29 g. (Found: C, 62·3; H, 4·0; N, 6·0. Calc. for $C_{12}H_9NS_2$: C, 62·4; H, 3·9; N, 6·0%). The base gives a red solution in concentrated sulphuric acid. It can be diazotised in hydrochloric acid, and the product couples with β-naphthol, giving a scarlet dye. Neither the hydrochloride nor the sulphate of 2-aminothianthren could be isolated from aqueous solutions.

2-*Thianthrenyltrimethylammonium Iodide*.—6 G. of 2-aminothianthren were shaken in 40 c.c. of water for 30 minutes with the addition of three successive 2-c.c. portions of methyl sulphate, the liquid being made alkaline before each addition. The mixture, containing a doughy lump of solid, was then heated on the water-bath for 15 minutes, made alkaline, and cooled. The oil which separated soon solidified, and was filtered off, washed, and dried. This crude material, consisting of partly and completely methylated amine, was not purified, but was heated with 30 c.c. of methyl iodide in a sealed tube at 100° for 24 hours. The methyl iodide was distilled from the dark product, and the residue refluxed with acetone. The mixture was cooled, and the solid filtered off and washed with acetone until it was only faintly cream-coloured. It crystallised from hot water in glistening, colourless plates, m. p. 190°; yield 6 g. (Found: C, 44·6; H, 4·2; N, 3·7; I, 31·4. $C_{15}H_{16}NIS_2$ requires C, 44·8; H, 4·0; N, 3·5; I, 31·6%).

The *iodide* is moderately soluble in hot ethyl and methyl alcohols, but practically insoluble in ether, chloroform, ethyl acetate, etc. On being shaken with silver chloride in water it is converted into the chloride, which is readily soluble in cold water, and crystallises from ethyl alcohol–ether in prisms, m. p. 181°. The nitrate, similarly prepared by means of silver nitrate, crystallises from water in prisms, m. p. 201°. Solutions of these salts in water give an immediate precipitation of the crystalline quaternary iodide on addition of a minute trace of alkali iodide.

Attempted Resolution of 2-*Thianthrenyltrimethylammonium Salts*.—(a) d-*Camphor*-10-*sulphonate*. 4·66 G. of *d*-camphor-10-sulphonic acid were treated in hot water with a slight excess of silver carbonate, and the filtered solution was heated for 1 hour on the water-bath with 8·04 g. of 2-thianthrenyltrimethylammonium iodide. The silver iodide was filtered off, and the aqueous solution on cooling deposited the *d*-camphor-10-sulphonate as colourless plates. It was crystallised from warm water. The molecular rotations of the successive crops of crystals (dried in a vacuum) remained steady at the value due to the *d*-camphor-10-sulphonate ion. The 1st, 3rd, 6th, and 7th crops had $[M]^{16^\circ}_{5461}$ + 60·5°, + 61·5°, + 60·0°, and + 60·0° respectively ($p = 0·8$), and m. p. 140°. For the *d*-camphor-10-sulphonate ion under the same conditions, $[M]^{16^\circ}_{5461} = + 57·5°$.

(b) α-*Bromo*-d-*camphor*-π-*sulphonate*. This was similarly prepared from 4·02 g. of the quaternary iodide and 4·18 g. of the silver salt of the active acid. Crystallised from ethyl alcohol–ether, it separated in colourless needles. Three successive crystallisations gave crops having $[M]^{16^\circ}_{5461}$ + 331° (0·1 g. in 23 c.c. H_2O + 2 c.c. EtOH), m. p. 224°. The α-bromo-*d*-camphor-π-sulphonate ion under the same conditions had $[M]^{16^\circ}_{5461}$ + 332°.

(c) *Hydrogen* d-*diacetyltartrate*. 4·02 G. of 2-thianthrenyltrimethylammonium iodide were shaken with excess silver carbonate in 60 c.c. of water. After 2 hours the product was filtered, and the filtrate treated with 2·16 g. of *d*-diacetyltartaric anhydride. Air was passed through the solution to expel carbon dioxide, and when left in a vacuum desiccator overnight, the solution deposited crystals. Recrystallisation from methyl alcohol–ether afforded colourless prisms, giving an acid solution in water (Found: N, 2·75. Calc. for the acid salt: N, 2·75%). The 1st, 2nd, and 3rd crops had $[M]^{16^\circ}_{5461}$ − 64·5°, − 65·5°, and − 65·5° respectively ($p = 0·60$), and m. p. 171° (decomp.). Under the same conditions, the hydrogen *d*-diacetyltartrate ion had $[M]^{16^\circ}_{5461}$ − 63·5°.

To aqueous solutions of the active salts described in (a), (b), and (c), potassium iodide was added to precipitate the quaternary iodide. This was converted into the chloride by shaking with an aqueous suspension of silver chloride, and in every case the product was found to be optically inactive.

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