Synthesis and properties of dithienodithiins
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1.1. THIANTHRENE

Ever since the synthesis of thianthrene in 1869 by Stenhouse\textsuperscript{1}, many chemists were fascinated by this molecule.

One of the basic questions concerning the structure of thianthrene was whether the molecule is planar or not.

Evidence for a non-planar structure in solution was first given by Bergman and Tschudnowsky\textsuperscript{2}, who measured a dipole moment of 1.68 D. Several values varying from 1.4-1.6 D were reported\textsuperscript{3-7}. This left little doubt that the molecule was folded along the S-S axis. A dihedral angle between the two benzene rings of 144° was deduced from the experimental dipole moment\textsuperscript{23}.

Thianthrene has a folded structure in the crystal state\textsuperscript{8,9} too, with a dihedral angle of 128° (the central ring has a boat conformation). The CSC angle is 100° and the folding can be explained as the result of the tendency of the sulfur atoms to retain a normal valence angle\textsuperscript{10}. The CS distance of 1.76 Å is less than the usually expected value of 1.81 Å for a single CS bond and about 25% double bond character was estimated for the CS bond\textsuperscript{14}. A folded structure (boat conformation) was found for the parent compound p-dithiin (synthesized in 1953\textsuperscript{13}) too\textsuperscript{31,12}.

Several publications have dealt with the interaction
of the π-systems of the two benzene rings in thianthrene.

While the dipole moment evidence indicates that the folded structure of thianthrene, found in the solid state, is maintained in solution, it is well recognized that the molecule oscillates rapidly through a planar position. This motion was compared with that of a butterfly or a bird.

Both experimental and theoretical evidence for a low inversion barrier is available. If thianthrene were a rigid, non-planar molecule, monosubstituted derivatives should be resolvable. However, attempts to resolve a carboxylic acid or an amine were unsuccessful. Further experimental evidence for a low barrier to inversion followed from dipole moment studies and more recently values of 3.58 and >4 kcal/mole were derived. Theoretically, energy barriers of 3-7 kcal/mole were deduced.

On oxidation of the sulfur atoms one monosulfoxide, two disulfoxides, one sulfoxide-sulfone and one disulfone are expected. All have been reported. Dipole moments, crystal structure data and pmr studies proved that the oxides of thianthrene have a non-planar structure and a low inversion barrier too. Other oxides are possible because of the non-planar structure of thianthrene itself, but in view of the low inversion barrier it is not surprising that they have not been isolated.

The cis-trans isomerism arising in the disulfoxides and the ability of 1,4-dithiin systems to form radical cations will be discussed in Chapters 3 and 5, respectively.

1.2. AIM AND SURVEY

Dithienodithiins can be regarded as thiophene analogues of thianthrene. The latter compound has been the
subject of a number of interesting studies (Section 1.1.). Dithienodithiins are of interest because many of the properties of thianthrene might be found again in a more or less modified way. Since four isomers of dithienodithiins are conceivable (1-4) the change in properties upon variation of the structure can be studied.

![Diagram](image)

The isomers 2 and 4 were known in the literature, but only for 4 a convenient synthesis was published\(^3\). The basic principle of this synthesis was the dimerization of 3-bromo-4-thiophene thiol with expulsion of two molecules of HBr.

A synthesis of 1 was developed along the same principle, but with 3-bromo-2-thiophene thiol as the starting material. Surprisingly the reaction of 3-bromo-2-thiophene thiol with KOH and Cu\(_2\)O in dimethylformamide gave a mixture of 1 and 2. In Chapter 4 the mechanism for this rearrangement is discussed, based on isolated intermediates and \(^{13}\)C-labeled starting material. Also the reactions of the other two \(\alpha\)-bromothiophene thiols are described in this chapter.

The synthesis of the isomers 1, 2 and 3 is described in Chapter 2. The properties of 1-4 (inversion barriers, dipole moments, ionization potentials, photo-electron spectra, X-ray structures) are discussed in terms of CNDO- and Hückel-calculations (Chapter 2).

In order to obtain information about the reactivity of the four sulfur atoms in each isomer, the dithienodithiins were oxidized with metachloroperbenzoic acid and dichlororiodobenzene. Only the \(p\)-dithiin-like sulfur atoms (central ring) are oxidized and of the oxidation products the mono- and disulfides and mono- and disulfones are
are characterized (Chapter 3). The disulfoxides all show **cis-trans** isomerism, the ratio **cis-trans** depending on the oxidizing agent.

The question which isomer is **cis** and which **trans** is solved by the use of uv and ir spectra and the ESR spectra of the radical anions prepared electrolytically at low temperatures (Chapter 3).

The different behaviour of 1-4 towards oxidation with two equivalents of MCPBA in dichloromethane led to a quantitative study of the oxidation rates (Chapter 3).

In Chapter 5 the radical cations of 1-4 (isolated as relatively stable antimonyhexachloride complexes) are studied. The ESR spectra are described and the proton hyperfine coupling constants assigned by means of selectively deuterated compounds. The hyperfine splittings from naturally occurring $^{33}$S and g-values are determined. The experimental values are compared with data obtained from Hückel-McLachlan calculations.

The ESR spectra of the radical anions of some planar ($\pi$-system) and non-planar sulfones are described. The proton hyperfine coupling constants of the radical anions, the reduction potentials and the uv spectra of a relatively large number of planar and non-planar sulfones is successfully correlated with data obtained from Hückel (McLachlan) calculations.