An Analogue of 6a-Thiathiophthene Based on the Isothiazole System

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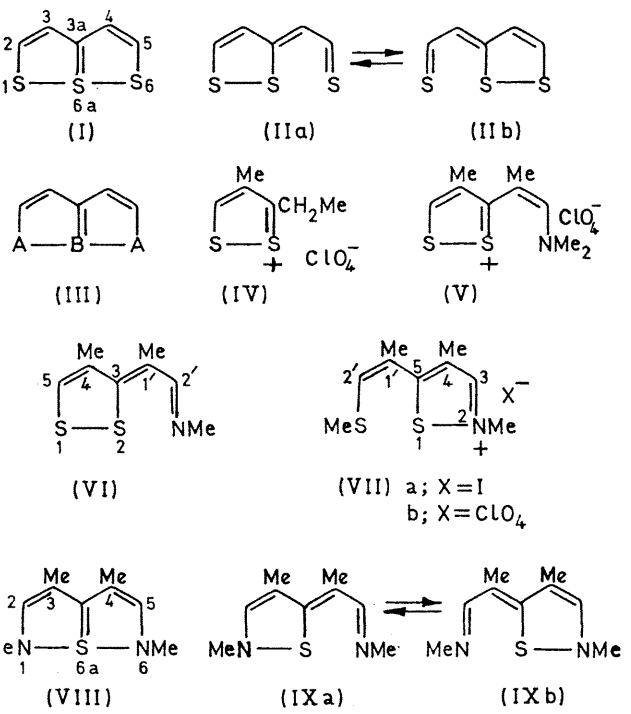
Summary An analogue of 6a-thiathiophthene has been synthesised and shown to be 1,3,4,6-tetramethylisothiazolo[5,1-*e*]isothiazole or a related system of rapidly interconverting valence isomers.

PROTON MAGNETIC RESONANCE spectra of 6a-thiathiophthenes in a variety of solvents show magnetic equivalence of ring protons or identical substituents at the pairs of sites C-2, C-5 and C-3, C-4. This demonstrates that these compounds *in solution* possess real or time-averaged C_{2v} symmetry, depending on the unresolved problem of whether 6a-thiathiophthene is a bicyclic structure (I)[1–3] or a system of rapidly interconverting monocyclic valence isomers (II).[4] Theoretical models† for the bicyclic formulation, employing four-electron three-centre bonding of the three sulphur atoms,[1] *pd*-hybridisation of the central sulphur atom,[2] or no-bond resonance structures,[3] prefer a collinear arrangement of the sulphur atoms. In this context it was of interest to synthesise and examine the properties of analogues (III) of 6a-thiathiophthene containing other heteroatoms of Groups V and VI, in which the different sizes of the heteroatoms A and B may have implications for bonding and structure (B is an element theoretically capable of valence shell expansion). We report here the synthesis of a derivative of (III; A = NMe, B = S).



3-Ethyl-4-methyl-1,2-dithiolium perchlorate (IV), colourless plates (from AcOH), m.p. 97—98°, was prepared (70%) and converted into the Vilsmeier salt (V) (80%), orange plates (from MeCN), m.p. 146—149°, according to established procedures.[5] Addition of 25—30% aqueous methylamine to a solution of the Vilsmeier salt in dimethylformamide at room temperature afforded the methylimine (VI) (92%), deep yellow needles (from MeCN), m.p. 132—133°, n.m.r.‡ δ ($CDCl_3$) 2·53 (1′-Me), 2·68 (4-Me), 3·56 (NMe), 7·70 (2′-H), and 8·46 (5-H). Heating the methylimine briefly with methyl iodide in acetonitrile gave the *S*-methylation

† One of these, (I),[2] is employed in this paper for convenience, without thereby implying a preference among the several possibilities.

‡ Chemical shifts (δ) are given in p.p.m. downfield from Me_4Si as internal reference.

product (VIIa) (98%), yellow needles (from MeCN), m.p. 175—177° (decomp.), which with 70% perchloric acid in acetonitrile afforded the corresponding perchlorate (VIIb) (83%), yellow needles (from EtOH), m.p. 115—120°, δ[$(CD_3)_2SO$] 2·10 (1′-Me), 2·39 (SMe), 2·56 (4-Me), 4·16 (NMe), 7·21 (2′-H), and 8·96 (3-H). On stirring a solution of the iodide (VIIa) in ethanol with 25—30% methylamine at room temp. the isothiazole (VIII) (44%) was formed, lemon yellow needles (from MeCN), m.p. 133—135°, M^+ at *m/e* 182 (100%). The ^1H n.m.r. spectrum ($CDCl_3$) showed only three sharp singlets at δ 2·49, 3·40, and 7·48, with relative intensities 3 : 3 : 1, which we assign to (3+4)-Me, (1+6)-Me, and (2+5)-H, respectively. The pattern was unchanged for solutions in CS_2 and $(CD_3)_2SO$. A "frozen" monocyclic structure (IX; a *or* b) is thus excluded. Crystallographic and theoretical studies may enable a decision to be made between a bicyclic formulation, such as (VIII), and a system of rapidly interconverting identical valence isomers (IX). Meanwhile, it is noteworthy that the pattern of the ^1H n.m.r. spectrum taken in CS_2 remained unchanged down to −70°.

Satisfactory elemental analyses and n.m.r. spectral data were obtained for all compounds cited.

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