The Structures of the 'Trimer' and 'Pentamer' obtained on Polymerization of Thiophen by Phosphoric Acid

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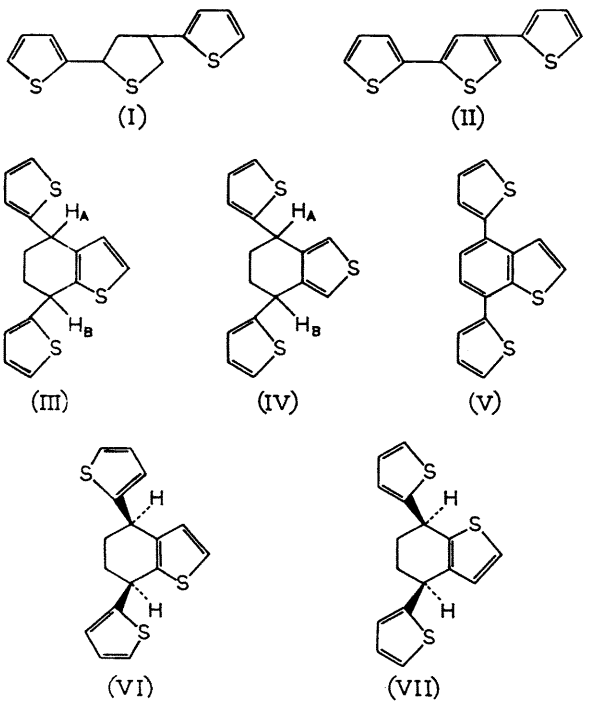
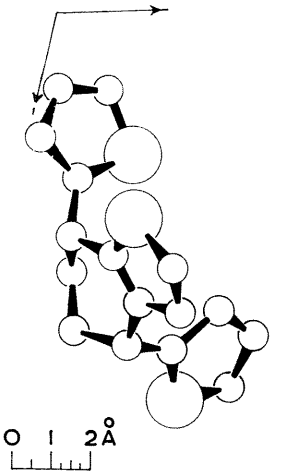
THE polymerisation of thiophen by acid catalysts has been investigated;[1,2] with 100%-orthophosphoric acid a liquid trimer (I) and a "pentamer" of unknown constitution are formed.[2]

Structure (I) for the trimer was deduced[2] from spectral data and destructive hydrogenation–desulphurisation of the compound to a hydrocarbon mixture, though Wynberg *et al.*[3] suggested that this liquid trimer is a source of 2,2′;4′,2″-terthienyl. However, the correctness of structure (I) has been questioned.[4]

We have re-examined the acid-catalysed polymerisation of thiophen described by Meisel *et al.*[2] as a potential source of 2,2′-bithienyl derivatives.[5] The crude product contained the "trimer" and the "pentamer" as the two principal components (*ca.* 4 : 1). Distillation and repeated chromatography gave the trimer as colourless needles, $C_{12}H_{12}S_3$ (analysis and mass spectrum), m.p. 37°. Spectral data were consistent with the structure (I); dehydrogenation with chloranil in xylene gave 2,2′ : 4′,2″-terthienyl (II) in high yield.



The "pentamer" fraction gave colourless plates, $C_{16}H_{14}S_3$ (analysis and mass spectrum), m.p. 112° (*i.e. three* sulphur atoms apparently derived from *four* molecules of thiophen). Spectroscopic evidence [λ_{max} 238 (log ϵ 4·36)] showed three unconjugated thiophen nuclei, probably as 2-thienyl units (bands at 850, 825 and 685 cm.$^{-1}$).[6] N.m.r. (100 Mc./sec.; CS_2): τ 2·94—3·45 [complex m, 8H (thiophen)], 5·70 (complex, m, 2H), and 7·92 (asymm. t, 4H).



FIGURE

The conformation of the major component of the disordered structure.

The benzothiophen structures (III) and (IV) appeared consistent with this evidence and with the mass spectrum which showed the loss of 28 mass units, attributed to the $-CH_2-CH_2-$ system. Protons H_A and H_B are non-equivalent in (III) as distinct from (IV); spin-decoupling with irradiation at τ 7·90 reduced the complex signal at τ 5·70 to two distinct singlets at τ 5·6 and 5·74, favouring the unsymmetrical structure (III). However, the above evidence does not differentiate between the possible *cis*- and *trans*-isomers of (III).

Dehydrogenation with tetrachloro-*p*-benzoquinone in xylene gave a compound, $C_{16}H_{10}S_3$, m.p. 73°, the spectral properties of which were consistent with 4,7-di-(2-thienyl)-benzo[*b*]thiophen (V) rather than the corresponding benzo[*c*]thiophen structure, which would be derived from (IV). However, attempted proof by synthesis of (V) was unsuccessful.

The structure of (III) is however unambiguously established by *X*-ray analysis as (VI), with the thienyl groups *cis*.

The crystals are monoclinic; $C_{12}H_{16}S_3$; space group

$P2_1/c$, $Z = 4$; $a = 14{\cdot}13$, $b = 7{\cdot}68$, $c = 13{\cdot}78$ Å, $\beta = 104{\cdot}1°$.[7] About 2000 independent structure amplitudes were obtained by visual estimation of equi-inclination Weissenberg films. Patterson methods were frustrated by an unexpected plethora of vector peaks of approximately equal height in the Patterson distribution; the structure was eventually solved by a "direct methods" approach which gave the signs of 250 of the largest unitary structure factors (E_0's) and the resulting E-map revealed the entire structure. Subsequent structure-factor and electron-density calculations confirmed this but also revealed considerable disorder (*ca.* 2 : 1) was associated with two of the sulphur atoms, of the type (VI) ⟷ (VII). The disordered structure has been successfully refined by least-squares calculations (R 0·16). The six-membered ring adopts a half-chair conformation; a view of the major component of the disordered structure is given in the Figure. The trimer (I) does not appear to be an intermediate in the production of (VI).

We acknowledge the awards of an Anderson Fellowship (D.M.H.) and an S.R.C. postgraduate studentship (D.M.J.). We thank Professor H. Wynberg for a sample of (II).

(*Received, December 18th*, 1968; *Com.* 1738.)

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