

1,3,12,14-Tetramethyldibenzo[*a,i*]dithieno[3,4-*e*;3',4'-*m*]cyclohexadecene. Reactions of the Bis-ylide from 2,5-Dimethylthiophen-3,4-diylbis(methylenetriphenylphosphonium chloride) with 2,5-Dimethylthiophen-3,4-dicarbaldehyde and with *o*-Phthalaldehyde

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Reaction of the bis-ylide derived from 2,5-dimethylthiophen-3,4-diylbis(methylenetriphenylphosphonium chloride) with 2,5-dimethylthiophen-3,4-dicarbaldehyde gave *cis,cis*-, *cis,trans*- and *trans,trans*-2,5-dimethyl-3,4-bis-[2-(2,4,5-trimethyl-3-thienyl)vinyl]thiophen [as (IV)]. With *o*-phthalaldehyde a similar mixture of isomers was formed, but in addition the macrocycle 1,3,12,14-tetramethyldibenzo[*a,i*]dithieno[3,4-*e*:3',4'-*m*]cyclohexadecene [as (V)] was obtained as a mixture of geometrical isomers. The n.m.r. spectrum of this substance gave no evidence of a ring current.

IN continuation of our studies in the thia-annulene series,¹ we have treated the bis-ylide derived from 2,5-dimethylthiophen-3,4-diylbis(methylenetriphenylphosphonium chloride) with 2,5-dimethylthiophen-3,4-dicarbaldehyde and with *o*-phthalaldehyde in dimethylformamide at 90 °C² in an attempt to prepare the 16 π -electron systems (I)³ and (II). In the event the reactions took a different course.

From the reaction with the thiophen dialdehyde four crystalline products were isolated. One was the aldehyde (III) formed by incomplete reaction. Its n.m.r. spectrum indicated that it was a mixture of the *cis*- and *trans*-isomers but the individual components could not be isolated. The three other products had almost identical mass spectra; all showed an abundant molecular ion at *m/e* 412. High resolution mass spectrometry of one of the isomers established the molecular formula C₂₄H₂₈S₃, and this and other spectroscopic evidence (see later) in conjunction with the method of preparation suggests that the compounds are *cis,cis*-, *cis,trans*-, and *trans,trans*-2,5-dimethyl-3,4-bis-[2-(2,4,5-trimethyl-3-thienyl)vinyl]thiophen [as (IV)], the two

methyl substituents at C-4 of the terminal thiophen nuclei arising by hydrolysis of unchanged ylide during isolation. Structures were assigned to the individual isomers on the basis of their i.r. spectra (see Experimental section). The electronic spectra of the three isomers were similar but showed small bathochromic and hypsochromic shifts in passing from the *cis,cis*- to the *trans,trans*-compound, presumably because,⁴ as models suggest, the *trans,trans*-isomer can more readily adopt a planar conformation than the *cis,trans*-isomer, which can do so more readily than the *cis,cis*-form. The n.m.r. spectrum of the *trans,trans*-isomer contained a singlet at τ 3.40 assigned to the magnetically equivalent olefinic protons, and four singlets in the region τ 7.53–7.94, each corresponding to two methyl groups. Assignments were made as illustrated in (IV) on the assumption that the C-4 and C-5 methyl substituents in the terminal rings of (IV) would have chemical shifts similar to those of the analogous methyl groups in 2,3,4,5-tetramethylthiophen (τ 8.17 and 7.87), and that the signal due to the C-2 and C-5 methyl substituents of the central ring, which has two unsaturated substituents, would

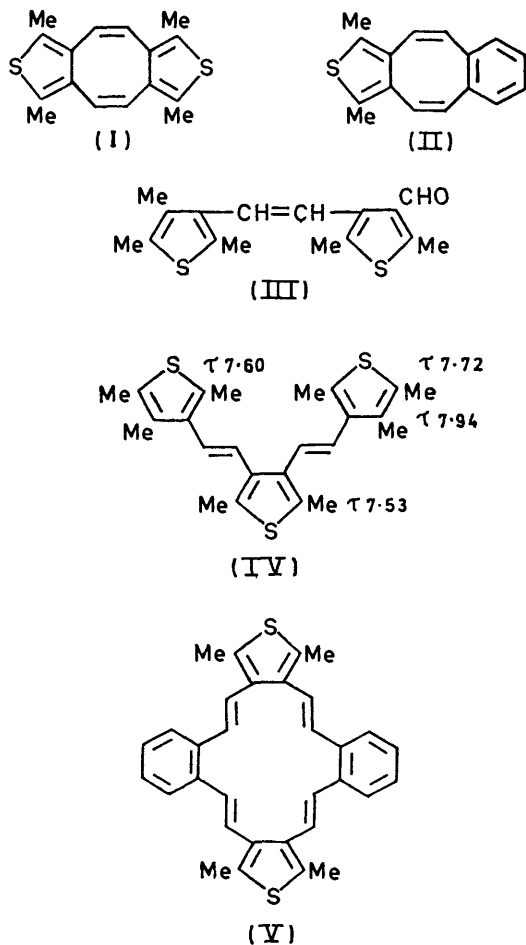
¹ W. Carruthers and M. G. Pellatt, *J. Chem. Soc. (C)*, 1971, 1485.

² Cf. A. P. Bindra, J. A. Elix, and M. V. Sargent, *Tetrahedron Letters*, 1968, 5573.

³ The tricyclic ring system of (I) has recently been prepared by P. J. Garratt and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 1972, **94**, 1022.

⁴ Cf. H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, London, 1962, p. 384.

appear at lower field than that due to the C-2 methyl groups of the terminal rings, in which there is only one unsaturated substituent.



Three analogous isomeric bis-olefins were obtained from the reaction with *o*-phthalaldehyde (see Experimental section). In addition this reaction gave a fourth product, shown by high resolution mass spectrometry to have the molecular formula $C_{32}H_{28}S_2$, for which a macrocyclic structure [as (V)] seems most likely. The i.r. spectrum shows bands due to both *cis*- (800) and *trans*- (963 cm^{-1}) double bonds, but the indefinite m.p., which could not be sharpened by recrystallisation or t.l.c., suggests that the substance is a mixture of geometrical isomers. The n.m.r. spectrum shows three groups of signals at τ 7.4–8.4 (4 \times Me), 5.0–6.1, and 2.4–3.8 in the approximate ratio 4 : 1 : 4. It appears that the signals due to the olefinic protons fall into two groups, some appearing among the aromatic proton signals at τ 2.4–3.8 and the others in the higher field group at τ 5.0–6.1. This is probably due to the influence of the ring currents associated with the individual benzene and thiophen nuclei and not to the presence of a ring current in the macrocycle. Molecular models show that the molecule cannot be planar in any configuration and suggest, further, that in some conformations some of the olefinic protons may lie in the

deshielding zone of the benzene and thiophen nuclei and others in the shielding zone.

EXPERIMENTAL

U.v. spectra, measured with a Unicam SP 800 spectrometer, refer to solutions in cyclohexane unless otherwise stated. Routine i.r. spectra were measured with a Perkin-Elmer Infracord, and high resolution spectra with a Hilger-Watts H 900 double-beam spectrometer. Mass spectra were recorded with a Hitachi RMU 60 instrument. 1H N.m.r. spectra were determined with a Perkin-Elmer 60 MHz instrument, for solutions in deuteriochloroform, with tetramethylsilane as internal standard.

Thin- (0.25 mm) and thick- (1.0 mm) layer chromatography plates were prepared from Kieselgel GF 254 (Merck). Light petroleum refers to the fraction b.p. 60–80 °C.

Reaction of 2,5-Dimethylthiophen-3,4-diylbis(methylene-triphenylphosphorane) with 2,5-Dimethylthiophen-3,4-dicarbaldehyde.—A solution of lithium ethoxide [from lithium (70 mg) and ethanol (17 ml)] was added during 5 h to a stirred solution of the appropriate phosphonium chloride (3.0 g) and the dialdehyde (625 mg) in dimethylformamide (120 ml) at 90 °C under nitrogen. The cooled solution was poured into water; the product was extracted with ether and chromatographed on a column of silicic acid (250 g). Elution with light petroleum-ether (49 : 1) gave first the mixture of geometrical isomers (IV) (135 mg) and then a mixture of the two geometrical isomers of 2,5-dimethyl-4-[2-(2,4,5-trimethyl-3-thienyl)vinyl]thiophen-3-carbaldehyde (II) (400 mg). Crystallisation from light petroleum gave yellow needles, m.p. 99–100 °C (Found: C, 66.4; H, 6.3; S, 22.2%; M^+ , 290. $C_{16}H_{18}OS_2$ requires C, 66.2; H, 6.3; S, 22.0%; M , 290), τ –0.1 and 0.2 (CHO of *trans*- and *cis*-compound, respectively) and 2.7–3.8 (two partially superimposed AB quartets of unequal intensity, CH:CH). The more abundant component was identified as the *trans*-olefin from its coupling constant 5 (J_{AB} 16.6 Hz); the other component had J_{AB} 3.6 Hz.

Preparative layer chromatography (eluant light petroleum) of the first fraction from the column gave the individual isomers of 2,5-dimethyl-3,4-bis-[2-(2,4,5-trimethyl-3-thienyl)vinyl]thiophen [as (IV)]. The *cis,cis*-isomer (R_F 0.37) formed needles (1 mg) (from light petroleum), m.p. 185–188 °C (Found: m/e , 412.1359. $^{12}C_{24}^{1}H_{28}^{32}S_2$ requires M , 412.1353); ν_{max} (KBr) 830 cm^{-1} ; λ_{max} , 229, 244, 269 μm , and 304 nm (ϵ 17,600, 18,200, 13,500, and 6000). The *cis,trans*-isomer (R_F 0.34) gave pale yellow needles (4 mg) (from light petroleum), m.p. 138 °C (Found: m/e 412); ν_{max} (KBr) 960 and 800 cm^{-1} ; λ_{max} , 244, 278, 231 μm , and 310 nm (ϵ 25,600, 22,200, 24,800, and 14,600), and the *trans,trans*-compound (R_F 0.25) gave prisms (8 mg), m.p. 159 °C, m/e 412; ν_{max} (KBr) 975 cm^{-1} ; λ_{max} , 248, 282, 233 μm , and 330 nm (ϵ 25,400, 26,700, 21,800, and 14,700).

1,3,12,14-Tetramethyldibenzo[*a,i*]dithieno[3,4-*e*;3',4'-*m*]-cyclohexadecene (V).—Reaction of *o*-phthalaldehyde (550 mg) with the bis-ylide [from the phosphonium chloride (3.0 g)] was carried out as in the foregoing experiment. The crude product (443 mg) gave four pure substances on preparative layer chromatography. Three of these were the geometrical isomers of *o*-bis-[2-(2,4,5-trimethyl-3-thienyl)vinyl]benzene; the *trans,trans*-isomer formed crystals (from ethanol), m.p. 137 °C (Found: C, 76.1; H, 6.3; S, 17.4%;

⁵ L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1959, p. 85.

m/e 378·1482. $^{12}\text{C}_{24}^{1}\text{H}_{26}^{32}\text{S}_2$ requires C, 76·2; H, 6·9; S, 16·9%; *M*, 378·1482; ν_{max} (KBr) 965 cm^{-1} ; λ_{max} 244, 288, and 315 nm (ϵ 26,400, 24,600, and 21,800); τ 2·4—3·6 (8H, m), and 7·56, 7·72, 7·83, 7·89, 8·16, and 8·22 (3H each, 6 \times Me). The *cis,cis*-compound formed rhombs, m.p. 135—138 °C (from ethanol), mass spectrum identical with that of the *trans,trans*-compound; ν_{max} (KBr) 800s cm^{-1} ; λ_{max} 227 nm (ϵ 32,400, 28,900, and 6150). The *cis,trans*-isomer (needles from ethanol) had m.p. 103—106 °C, ν_{max} (KBr) 810m and 965s cm^{-1} ; λ_{max} 242 and 294 nm (ϵ 22,200 and 21,300), mass spectrum identical with those of the other two isomers.

The slowest-running band on the preparative plates afforded an unstable yellow oil (32 mg) which crystallised in ethanol to give the *macrocycle* as colourless needles which rapidly turned yellow in the presence of oxygen; m.p. 235—240 °C (decomp.) (Found: *M*⁺, 476·1633. $^{12}\text{C}_{32}^{1}\text{H}_{28}^{32}\text{S}_2$ requires *M*, 476·1633); ν_{max} (KBr) 963s and 800m cm^{-1} ; λ_{max} (EtOH) 249 nm (ϵ 16,800, 15,200, and 2640).

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