

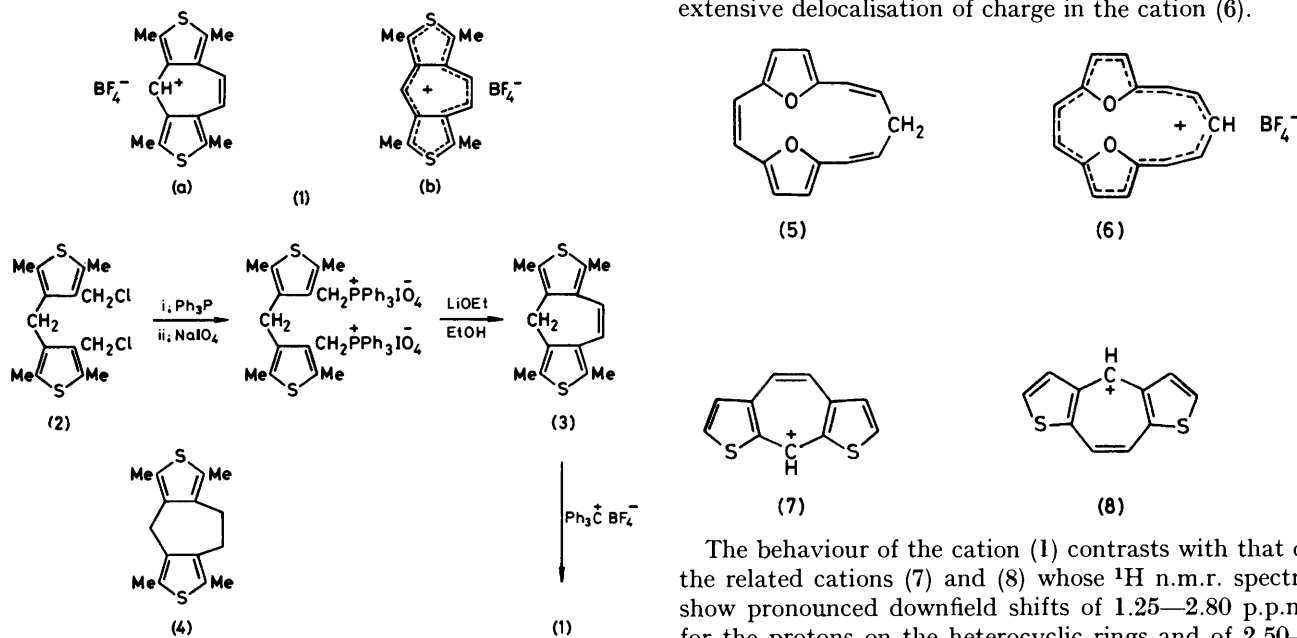
1,3,5,7-Tetramethylcyclohepta[1,2-*c*][4,5-*c'*]dithiophen-4-ylum Cation ; a Potential 14 π -Electron Aromatic System

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In the cation of 1,3,5,7-tetramethylcyclohepta[1,2-*c*][4,5-*c'*]dithiophen-4-ylum fluoroborate the charge is largely localised on the carbon atom flanked by the two thiophen rings.

THE cation of the salt (1), with 14 out-of-plane π electrons, might exist as the delocalised bridged dithia[13]annulene cation (1b) if the resulting delocalisation energy were greater than that of (1a). To test this we have prepared compound (1) from 3,3'-methylenebis-(2,5-dimethyl-4-chloromethylthiophen) by the route shown in the Scheme. Cyclisation to compound (3) was effected by an intra-

atom flanked by the two thiophen rings. Comparison with the n.m.r. spectra of the oxygen-bridged cyclopentadecaheptaene (5) and the derived fluoroborate (6) supports this conclusion. In the spectrum of the latter all the signals lie between δ 9.6 and 9.8 and show a pronounced downfield shift compared with their position in the spectrum of (5).² Here there is clear evidence of extensive delocalisation of charge in the cation (6).



SCHEME

molecular Wittig reaction from the bisphosphonium periodate¹ and abstraction of hydride ion from (3) with trityl fluoroborate then afforded the purple crystalline fluoroborate (1). The ^1H n.m.r. spectra of the two compounds consisted of four singlets with the chemical shifts shown in the Table.

^1H N.m.r. spectra of compounds (1) and (3) (δ)

	(1)	(3)
CH_2 of (3)		3.58
CH of (1)	9.25	
olefinic H	7.15	6.50
CH_3	3.25, 2.82	2.39, 2.34

Although all the signals move downfield in passing from the spectrum of (3) to that of (1), the very large shift of the signal due to the protons of the CH_2 group in (3) from δ 3.58 to δ 9.25 in (1) is particularly noticeable. This would seem to indicate that the positive charge in (1) is not extensively delocalised over the macrocyclic ring but is concentrated to a large extent on the carbon

The behaviour of the cation (1) contrasts with that of the related cations (7) and (8) whose ^1H n.m.r. spectra show pronounced downfield shifts of 1.25–2.80 p.p.m. for the protons on the heterocyclic rings and of 2.50–3.13 p.p.m. for the olefinic protons relative to the corresponding signals in their neutral methylene precursors.³ In these cations also delocalisation of charge is clearly more extensive than it is in (1).

The olefin (3) was smoothly reduced to the dihydro-compound (4) with diborane. This compound did not react with trityl fluoroborate emphasizing that, although there is little delocalisation in (1), the double bond in (3) nevertheless plays some part in the formation of the salt (1).

EXPERIMENTAL

U.v. spectra were recorded on a Unicam SP 800 spectrophotometer and ^1H n.m.r. spectra on a Jeol MH-100 instrument at 100 MHz.

3,3'-Methylenebis-(2,5-dimethyl-4-chloromethylthiophen) (2).—This compound was obtained as a by-product from the chloromethylation of 2,5-dimethylthiophen by the method of Dimroth, Pohl, and Follmann.⁴ On one occasion when the reaction was carried out on five times the published

scale the methylenebisthiophen was the major product (20%) of the reaction, possibly because of inefficient cooling of the reaction mixture. It was separated from 2,5-dimethyl-3,4-dichloromethylthiophen by fractional crystallisation from light petroleum (b.p. 60–80 °C), to form colourless needles, m.p. 175–176 °C (Found: C, 54.4; H, 5.4; Cl, 21.3; S, 18.9%; M^+ , 332. $C_{15}H_{18}Cl_2S_2$ requires C, 54.1; H, 5.4; Cl, 21.3; S, 19.2%; M , 332), δ ($CDCl_3$) 4.35 (s, 4 H, CH_2Cl), 3.90 (s, 2 H, $ArCH_2Ar$), 2.35 (s, 6 H, CH_3 adjacent to CH_2Cl), and 2.25 (s, 6 H, CH_3 adjacent to CH_2Ar).

3,3'-Methylenebis-[2,5-dimethyl-4-thienyl(triphenyl)phosphonium] Diperiodate.—A solution of the above bischloromethyl compound (2.0 g) and triphenylphosphine (3.2 g) in dimethylformamide (20 ml) was boiled for 3 h. The cooled solution was poured into anhydrous ether and the crystalline product filtered off and washed with ether to give the bisphosphonium chloride as a microcrystalline powder (5.1 g), m.p. 205–210 °C (decomp.). A solution of this material (2.2 g) in warm water (50 ml) was added to a solution of sodium periodate (1.1 g) in water (20 ml). The bisphosphonium periodate was precipitated immediately. It was collected, thoroughly washed with cold water and dried at 40 °C/0.05 mmHg overnight, to give a white powder (2.2 g); δ ($CDCl_3$) 8.0–7.1 (30 H, m, Ar), 4.3 (4 H, d, J 15 Hz, CH_2P), 2.3 (2 H, s, $ArCH_2Ar$), 1.8 (6 H, s, CH_3), and 1.7 (6 H, s, CH_3). On one occasion an attempt to dry the product at 60 °C *in vacuo* resulted in a violent explosion.

1,3,5,7-Tetramethylcyclohepta[1,2-c][4,5-c']dithiophen (3).—A solution of the bisphosphonium periodate (1.0 g) and lithium ethoxide (from 14 mg of lithium) in ethanol (20 ml) was boiled under nitrogen for 3 h. The cooled solution was filtered, ethanol removed under reduced pressure, and the residue taken up in ether. The recovered product was chromatographed on silica gel. Elution with light petroleum–ether (20 : 1) gave the *dithiophen* (110 mg, 40%) as colourless needles, m.p. 107–108 °C (from methanol) (Found: C, 69.3; H, 6.1; S, 24.5%; M^+ , 260. $C_{15}H_{16}S_2$ requires C, 69.2; H, 6.2; S, 24.6%; M , 260), δ ($CDCl_3$) 6.50 (2 H, s, $CH=CH$), 3.58 (2 H, s, CH_2), 2.39 (6 H, s, CH_3), 2.34

(6 H, s, CH_3). λ_{max} . (methanol), 235, 265infl., 270, and 299 nm (ϵ 8 140, 11 230, 11 560, and 16 110).

Treatment of this compound (100 mg) in anhydrous tetrahydrofuran (5 ml) with borane–tetrahydrofuran complex (1M; 2 ml) for 1 h at 25 °C and warming the resultant solution with acetic acid (10 ml) at 60 °C for 3 h gave the 8,9-dihydro-1,3,5,7-tetramethylcyclohepta[1,2-c][4,5-c']dithiophen (4) (64 mg, 63%) as colourless needles, m.p. 107–108 °C, after preparative layer chromatography and crystallisation from methanol, M^+ , 262. $C_{15}H_{18}S_2$ requires M , 262; δ ($CDCl_3$) 3.68 (2 H, s, $ArCH_2Ar$), 2.80 (4 H, s, CH_2CH_2), 2.36 (6 H, s, CH_3), 2.24 (6 H, s, CH_3).

1,3,5,7-Tetramethylcyclohepta[1,2-c][4,5-c']dithiophen-4-ylidene Fluoroborate (1).—Hydrofluoroboric acid (40%, 0.5 ml) dissolved in acetic anhydride (4 ml) was cautiously added, with cooling in an ice-bath, to a solution of triphenylmethanol (105 ml) in acetic anhydride (0.5 ml), followed by a solution of the dithiophen (3) (68 mg) in acetic anhydride (1 ml). After 5 min the dark green solution was diluted with ether (30 ml) and the purple precipitate was collected. Crystallisation from acetonitrile gave the *fluoroborate* as a purple microcrystalline powder (78 mg), m.p. >350 °C (Found: C, 51.8; H, 4.6. $C_{15}H_{16}S_2BF_4$ requires C, 52.0; H, 4.4%), λ_{max} . (CH_3CN) 300, 345infl., and 480 nm (ϵ 22 080, 2 300, and 5 480); δ (CF_3CO_2H) 9.25 (1 H, s, $ArCHAr$), 7.15 (2 H, s, $CH=CH$), 3.25 (6H, s, CH_3), and 2.82 (6 H, s, CH_3).

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