Tetrahedron. Vol. 34, pp. 587 to 590. Pergamon Press 1978. Printed in Great Britain

HETEROCYCLIC-FUSED TROPYLIUM IONS—VI

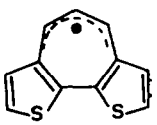
SYNTHESES AND STABILITY OF 4H-DITHIENO[2,1-b; 3,4-b']TROPYLIUM FLUOBORATE AND 7H-DITHIENO[1,2-b; 4,3-b']TROPYLIUM FLUOBORATE

S. GRONOWITZ* and P. PEDAJA
Division of Organic Chemistry 1, Chemical Center, University of Lund, Lund, Sweden

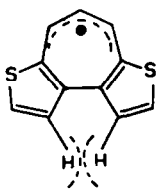
(*Received in the UK 24 July 1977; Accepted for publication 9 September 1977*)

Abstract—The synthesis of the two novel dithienotropylium ions 4H - dithieno[2,1-b; 3,4-b']tropyliumfluoborate 1 and 7H - dithieno[1,2 - b; 4,3 - b']tropyliumfluoborate 2 is described. The key reaction in achieving the tricyclic ring system was the reaction of 3,3' - bis - bromomethyl - 2,2' - bithienyl and 2,2' - bisbromomethyl - 3,3' - bithienyl, respectively, with sodium ethyl malonate. The pK_{R^+} values of 1 and 2 were determined by potentiometric titration and found to be 5.6 and 6.0, respectively.

The effects of the mode of fusion of different aromatic rings onto the b- and c-side of thiophene and other 5-membered heterocycles on spectroscopic and chemical properties have been studied in this laboratory for some time. Among systems previously investigated may be mentioned thienopyridines,[1] thiophene analogues of fluorene,[2] and some 1,2; 4,5 - dithieno- and furothieno-fused tropylium ions.[3-5] This investigation of heterocyclic-fused tropylium ions has now been extended to 1,2; 3,4 - dithieno-fused systems, and 4H - dithieno[2,1 - b; 3,4 - b']tropyliumfluoborate 1 and 7H - dithieno[1,2 - b; 4,3 - b']tropyliumfluoborate 2 were synthesized. We were interested in determining whether a peri effect caused by the hydrogen atoms in 2, leading to a nonplanar structure, would make 2 less stable than 1. Furthermore, the effect of a possible interaction of the free electron-pairs on sulphur in 1 was also of interest.

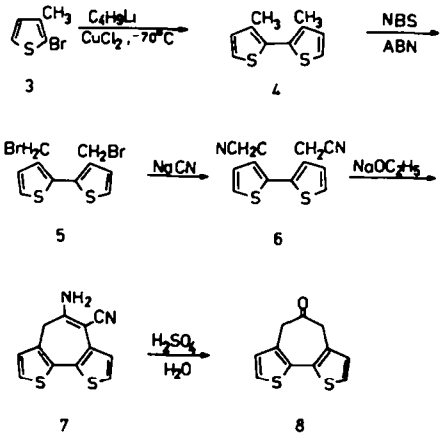


1



2

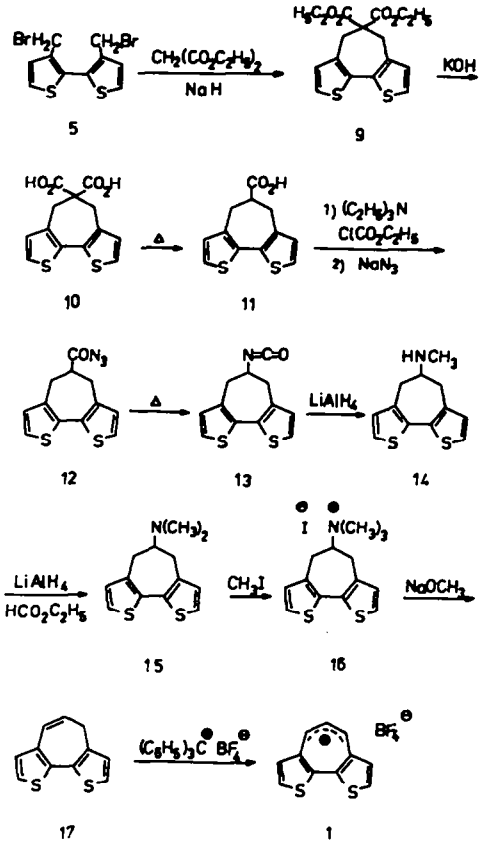
Various tricyclic compounds containing a seven-membered ring have been synthesized using the Thorpe-Ziegler cyclization of nitriles,[6] and therefore the synthetic route outlined in Scheme 1 was considered a possible approach to the tropylium ion 1. 3 - Methyl - 2 - bromothiophene 3 was coupled to 3,3' - dimethyl - 2,2' - bithienyl 4 by treatment with butyllithium and copper chloride. Radical bromination of 4 with N-bromosuccinimide in carbon tetrachloride using azo-bisisobutyronitrile as initiator then gave 3,3'-bisbromomethyl-2,2'-bithienyl 5 in 45% yield, together with ring-brominated products. 5 was then converted to 3,3' - biscyanomethyl - 2,2' - bithienyl 6 by treatment with sodium cyanide in dimethylsulphoxide. The cyclization reaction was then carried out in ethanol with sodium ethoxide as catalyst, giving 68% of 4H - 5 - amino - 6 - cyano-cyclohepta[2,1 - b; 3,4 - b']dithiophene 7. The structure of 7 was



Scheme 1.

confirmed by ^{1}H NMR and IR spectroscopy as being the enamino- and not the imino-form. The ^{1}H NMR spectra showed, in addition to the thiophene protons, a singlet with two protons at δ 3.5 ($-CH_2-$) and a broad singlet with two protons at δ 6.5 ($-NH_2$). IR spectra showed absorption bands at 1576 cm^{-1} (double bond) and at 2190 cm^{-1} (cyano group), values which are in agreement with similar compounds reported in the literature.[7] Attempted hydrolysis of the enamino nitrile 7, however, gave only trace amounts of a compound whose mass spectra were consistent with the expected ketone 4H - cyclohepta[2,1 - b; 3,4 - b']dithiophene - 5 - on 8. However, no useful method for the hydrolysis of 7 could be found, and consequently another synthetic route, outlined in Scheme 2, was used.

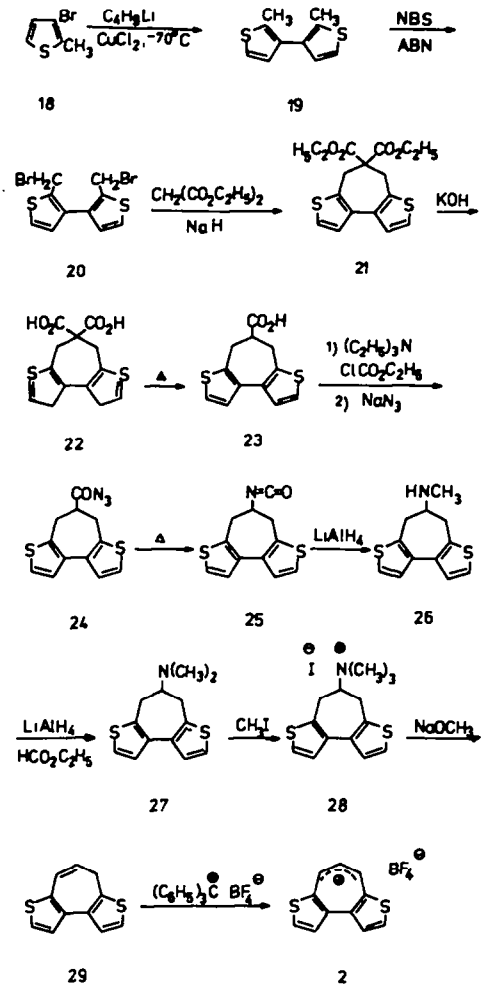
Alkylation of malonic ester with 5 gave 4H - 6 - hydrocyclohepta[2,1 - b; 3,4 - b']dithiophene - 5,5 - diethyldicarboxylate 9 in 76% yield. Hydrolysis of 9 with potassium hydroxide in ethanol gave the acid 4H - 6 - hydro-cyclohepta[2,1 - b; 3,4 - b']dithiophene - 5,5 - dicarboxylic acid 10, which was then decarboxylated by heating in quinoline to give 4H - 5,6 - dihydro-cyclohepta[2,1 - b; 3,4 - b']dithiophene - 5 - carboxylic acid 11. The overall yield from ester 9 to monocarboxylic acid 11 was 78% after recrystallization from toluene.



Scheme 2.

Oxidative decarboxylation of secondary acids with lead tetraacetate has been used for the synthesis of unsaturated cyclic hydrocarbons,[8] so this method was tried on **11**. However, only trace amounts of the expected product, 4H - cyclohepta[2,1 - b; 3,4 - b']dithiophene **17**, could be detected by GLC analysis. Therefore, a longer synthetic route had to be used. **11** was treated with ethyl chlorocarbonate and triethylamine to give the mixed anhydride, which after addition of sodium azide gave 4H - 5,6 - dihydro-cyclohepta[2,1 - b; 3,4 - b']-dithiophene - 5 - carboxylic acid azide **12**. Without being purified, **12** was heated in toluene to give 4H - 5,6 - dihydro-cyclohepta[2,1 - b; 3,4 - b']dithiophene - 5 - isocyanate **13**. Reduction of **13** with lithium aluminium hydride then gave 4H - 5,6 - dihydro - 5 - methylamino-cyclohepta[2,1 - b; 3,4 - b']dithiophene **14**. Alkylation of **14** was carried out, in analogy with a method reported by Khanna *et al.*,[9] by treating the monomethyl amine with lithium aluminium hydride and ethyl formate to give the dimethyl amine 4H - 5,6 - dihydro - 5 - dimethylamino-cyclohepta[2,1 - b; 3,4 - b']dithiophene **15**. Treatment with methyl iodide now gave 4H - 5,6 - dihydro - 5 - trimethylamino-cyclohepta[2,1 - b; 3,4 - b']dithiophene iodide **16**, which was easily degraded to 4H - cyclohepta-[2,1 - b; 3,4 - b']dithiophene **17** by heating with sodium methoxide in dimethyl formamide. 4H - Dithieno[2,1 - b; 3,4 - b']tropyliumfluoborate **1** was then obtained after hydride ion abstraction with triphenylmethyl fluoborate.[10]

The isomeric tropylium ion 7H - dithieno[1,2 - b; 4,3 - b']tropyliumfluoborate **2** was prepared in analogy with **1**, starting with 3 - bromo - 2 - methylthiophene **18**. 2,2' - dimethyl - 3,3' - bithienyl **19**, 2,2' - bisbromomethyl - 3,3' - bithienyl **20**, diethyl - 7H - 9 - hydro-cyclohepta[1,2 - b; 4,3 - b']dithiophene - 8,8 - dicarboxylate **21**, 7H - 8,9 - dihydro-cyclohepta[1,2 - b; 4,3 - b']dithiophene - 8 - carboxylic-acid **22**, 7H - 8,9 - dihydro - 8 - methylamino-cyclohepta[1,2 - b; 4,3 - b']dithiophene **23**, 7H - 8,9 - dihydro - 8 - dimethylamino-cyclohepta[1,2 - b; 4,3 - b']dithiophene **24** and 7H - cyclohepta[1,2 - b; 4,3 - b']dithiophene **25** being the intermediate products. 2,2' - Bisbromomethyl - 3,3' - bithienyl **20** showed a tendency to decompose, and thus it was not isolated but used as crude product.



Scheme 3.

The stability constants, pK_{R^+} values, for ions **1** and **2** were determined by potentiometric titration of water solutions with sodium hydroxide. **2** was found to be the more stable, with a pK_{R^+} value of 6.0 while **1** gave pK_{R^+} 5.6. A discussion of the pK_{R^+} values, together with the synthesis of some isomers of **1** and **2**, will be given in a subsequent paper.

EXPERIMENTAL

M.ps are uncorrected. Experiments using butyl-lithium were performed in an atmosphere of dry nitrogen at a temperature of −70°, and the ether was dried by distillation from solid sodium. ^{1}H NMR spectra were recorded on Varian A-60 and Jeol MH-100 instruments with tetramethylsilane as internal standard. The in-

frared spectra were obtained on a Perkin–Elmer 257 instrument. Elemental analyses were carried out by Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, West Germany. Mass spectra were recorded with an LKB 9000 instrument.

3,3'-Dimethyl-2,2'-bithienyl **4**

To a soln of 0.89 mol of butyllithium in hexane/ether (600/1000 ml) was added, dropwise with stirring, 153.0 g (0.86 mol) of 2 - bromo - 3 - methylthiophene **3**.[2] After 15 min 120 g (0.90 mol) of dry copper(II) chloride was added in one portion. Stirring was continued and the temperature allowed to rise overnight. The reaction mixture was filtered (suction) and the filtrate washed with dilute hydrochloric acid and water, dried (magnesium sulphate) and evaporated. Distillation gave 69.5 g (84%) of the bithienyl as a colourless liquid, b.p. 131.0°/11 mm. ^{1}H NMR (CCl_4): δ 7.1 (d, 2H, thiophene, J = 5.1 Hz), 6.8 (d, 2H, thiophene, J = 5.1 Hz), 2.1 (s, 6H, $-CH_3$). *m/e* (%): 194 (100) M^+. (Found: C, 62.00; H, 5.21; S, 33.08. $C_{10}H_{10}S_2$ requires: C, 61.81; H, 5.18; S, 33.00%).

3,3'-Bisbromomethyl-2,2'-bithienyl **5**

To a refluxing suspension of 50.0 g (0.28 mol) of N-bromosuccinimide in carbon tetrachloride (600 ml) was added 0.8 g of azo-bis-isobutyronitrile. After 2 min, 27.0 g (0.14 mol) of 3,3' - dimethyl - 2,2' - bithienyl **4** was added with stirring in one portion. Within 10 min, a vigorous reaction started, and the mixture was refluxed for another 30 min. Cooling, filtration and evaporation of the solvent gave a crystalline residue which was dissolved in ether and cooled overnight (0°), giving 22.0 g (45%) of white crystals, m.p. 87.5–88.0° (hexane). Concentration of the ether phase gave an oily product containing ring-brominated products. ^{1}H NMR (CCl_4): δ 7.4 (d, 2H, thiophene, J = 5.1 Hz), 7.2 (d, 2H, thiophene, J = 5.1 Hz), 4.4 (s, 4H, $-CH_2Br$). *m/e* (%): 352 (32) M^+, 271, 273 (100) M^+–Br. (Found: C, 33.94; H, 2.38; Br, 45.44. $C_{10}H_8Br_2S_2$ requires: C, 34.11; H, 2.29; Br, 45.38%).

3,3'-Biscyanomethyl-2,2'-bithienyl **6**

To a soln of 4.0 g (0.08 mol) of sodium cyanide in dimethylsulphoxide (50 ml), 14.0 g (0.04 mol) of 3,3' - bisbromomethyl - 2,2' - bithienyl **5** was added in small portions, with stirring and cooling, keeping the temperature below 30°. Stirring was continued for 15 hr, whereupon the mixture was poured into water and extracted with ether. The ether phase was dried (magnesium sulphate) and evaporated, giving 7.0 g (72%) of yellow crystals, m.p. 125.5° (isopropyl alcohol). ^{1}H NMR ($CDCl_3$): δ 7.5 (d, 2H, thiophene, J = 5.1 Hz), 7.2 (d, 2H, thiophene, J = 5.1 Hz), 3.6 (s, 4H, $-CH_2CN$). *m/e* (%): 244 (60) M^+. (Found: C, 58.99; H, 3.42; N, 11.34. $C_{12}H_8N_2S_2$ requires: C, 58.98; H, 3.30; N, 11.46%).

4H-5-Amino-6-cyano-cyclohepta[2,1-b; 3,4-b']*dithiophene* **7**

A soln of sodium ethoxide (prepared from 0.1 g (4 mmol) of sodium and 10 ml of ethanol) was added dropwise to a refluxing soln of 1.0 g (4 mmol) of 3,3' - biscyanomethyl - 2,2' - bithienyl **6** in ethanol (20 ml). Refluxing was continued 4 hr, the mixture cooled and dilute hydrochloric acid added. Extraction with ether, drying and evaporation gave 0.68 g (68%) of white needles, m.p. 158.5–160° (methanol). ^{1}H NMR ($(CD_3)_2CO$): δ 7.4 (d, 2H, thiophene, J = 5.1 Hz), 7.3 (d, 1H, thiophene, J = 5.1 Hz), 7.0 (d, 1H, thiophene, J = 5.1 Hz), 6.5 (s, broad, 2H, $-NH_2$), 3.5 (s, 2H, $-CH_2-$); MeOH: δ 3.3 (s, 3H), 2.9 (s, 1H). *m/e* (%): 244 (100) M^+. IR (KBr): ν_{NH_2} 3442, 3321, 3225, $\nu_{C\equiv N}$ 2190, $\nu_{C=C}$ 1576 cm^{-1}. (Found: C, 56.75; H, 3.87; N, 11.35. $C_{12}H_8N_2S_2 \cdot CH_3OH$ requires: C, 56.50; H, 4.38; N, 10.14%).

4H-Cyclohepta[2,1-b; 3,4-b']*dithiophen-5-one* **8**

4H - 5 - amino - 6 - cyano-cyclohepta[2,1 - b; 3,4 - b']dithiophene **7**, 1.5 g (6 mmol), was dissolved in sulphuric acid (14.0 ml of concentrated acid and 4.8 ml of water), the mixture heated to 90° for 10 min, and then poured into cold water (13.5 ml) and extracted with ether. Drying of the organic phase and evaporation gave one yellow crystal with m.p. 89.5–92.0° *m/e* (%): 220 (100) M^+.

2,2'-Dimethyl-3,3'-bithienyl **19**

Prepared in analogy with 3,3 - dimethyl - 2,2' - bithienyl **4**. From 115.0 g (0.65 mol) of 3-bromo-2-methylthiophene **18**,[11] 0.70 mol of butyllithium and 95.0 g of copper chloride, 26.1 g (41%) of the title compound was obtained, b.p. 135.5–137.5°/11 mm. Lit.[12]: yield 49% (from 3 - iodo - 2 - methylthiophene), b.p. 141–144°/17 mm.

2,2'-Bisbromomethyl-3,3'-bithienyl **20**

Prepared in analogy with 3,3 - bisbromomethyl - 2,2' - bithienyl **5** from 25.0 g (0.13 mol) of 2,2' - dimethyl - 3,3' - bithienyl, 46.0 g (0.26 mol) of N-bromosuccinimide and 1.0 g of azobisisobutyronitrile in 750 ml of carbon tetrachloride. The crude product was used in the ring-closure reaction without further purification.

Diethyl - 4H - 6 - hydro-cyclohepta[2,1 - b; 3,4 - b']*dithiophene - 5,5 - dicarboxylate* **9**

To a suspension of 5.0 g (0.11 mol) of sodium hydride (55% oil suspension) in toluene (400 ml) was added, dropwise with stirring, 16.5 g (0.10 mol) of ethyl malonate. Addition of dimethyl formamide (30 ml) and heating to 60° gave a clear solution of the anion. 35.8 g (0.10 mol) of 3,3' - bisbromomethyl - 2,2' - bithienyl **5** in toluene (100 ml) was added. After stirring and reflux for 2 hr, an additional 5.0 g (0.11 mol) of sodium hydride suspension was added. Refluxing overnight, filtration (suction) and evaporation gave an oil which was recrystallized from cold ethanol, yielding 27.0 g (76%) of yellow crystals, m.p. 88.5–89.0°. ^{1}H NMR (CS_2): δ 7.0 (d, 2H, thiophene, J = 5.0 Hz), 6.9 (d, 2H, thiophene, J = 5.0 Hz), 3.1 (s, 4H, $-CH_2-$), 4.0 (q, 4H, $-\underline{CH_2}CH_3$, J = 7.0 Hz), 1.1 (t, 6H, $-CH_2\underline{CH_3}$, J = 7.0 Hz). *m/e* (%): 350 (97) M^+. IR (KBr): $\nu_{C=O}$ 1740 cm^{-1}. (Found: C, 58.21; H, 4.80; S, 18.24. $C_{17}H_{18}O_4S_2$ requires: C, 58.26; H, 5.18; S, 18.30%).

Diethyl - 7H - 9 - hydro-cyclohepta[1,2 - b; 4,3 - b']*dithiophene - 8,8 - dicarboxylate* **21**

From 16.5 g (0.10 mol) of ethyl malonate, 10.0 g (0.22 mol) of sodium hydride and the crude product from radical bromination of 25.0 g (0.13 mol) 2,2' - dimethyl - 3,3' - bithienyl **19**, 14.1 g (31% overall yield) of white crystals, m.p. 104.0–104.5°, was obtained. ^{1}H NMR (CS_2): δ 7.0 (s, 4H, thiophene), 4.1 (q, 4H, $-\underline{CH_2}CH_3$, J = 7.0 Hz), 3.2 (s, 4H, $-CH_2-$), 1.2 (t, 6H, $-CH_2\underline{CH_3}$, J = 7.0 Hz). *m/e* (%): 350 (56) M^+. IR (KBr): $\nu_{C=O}$ 1732 cm^{-1}. (Found: C, 58.08; H, 5.01; S, 17.84. $C_{17}H_{18}O_4S_2$ requires: C, 58.26; H, 5.18; S, 18.30%).

4H - 5,6 - Dihydro-cyclohepta[2,1 - b; 3,4 - b']*dithiophene - 5 - carboxylic acid* **11**

11.0 g (0.031 mol) of the ester **9** was dissolved in ethanol (125 ml) and 3.7 g (0.066 mol) of solid potassium hydroxide added. Refluxing for 5 hr, followed by addition of acid to the dry precipitate, extraction with ether, drying of the ether phase (magnesium sulphate) nad evaporation gave the dicarboxylic acid as white crystals. Heating in quinoline to 160° caused decarboxylation, and the monocarboxylic acid was obtained after the addition of dilute hydrochloric acid and extraction with ether. Recrystallization from toluene gave 6.2 g (78%) of the title acid, m.p. 141.0–142.0°. ^{1}H NMR ($(CD_3)_2CO$): δ 7.1 (d, 2H, thiophene, J = 5.1 Hz), 6.8 (d, 2H, thiophene, J = 5.1 Hz), 3.1 (s, 5H), 9.8 (s, 1H, $-CO_2\underline{H}$). *m/e* (%): 250 (100) M^+. IR (KBr): $\nu_{C=O}$ 1700 cm^{-1}. (Found: C, 57.75; H, 4.03; S, 25.95. $C_{12}H_{10}O_2S_2$ requires: C, 57.59; H, 4.03; S, 25.62%).

7H - 8,9 - Dihydro-cyclohepta[1,2 - b; 4,3 - b']*dithiophene - 8 - carboxylic acid* **22**

From 16.2 g (0.046 mol) of the ester **21**, 5.5 g (0.097 mol) of potassium hydroxide, 7.6 g (65%) of the title acid, m.p. 164.0–166.0 (toluene) was obtained, following the same procedure as described above. ^{1}H NMR ($(CD_3)_2CO$): δ 7.2 (s, 4H, thiophene), 3.2 (s, 5H). *m/e* (%): 250 (100) M^+. IR (KBr): $\nu_{C=O}$ 1676 cm^{-1}. (Found: C, 58.04; H, 4.14; S, 25.31. $C_{12}H_{10}O_2S_2$ requires: C, 57.59; H, 4.03; S, 25.62%).

4H - 5,6 - Dihydro - 5 - methylamino-cyclohepta[2,1 - b; 3,4 - b']*dithiophene* **14**

5.0 g (20 mmol) of 4H - 5,6 - dihydro-cyclohepta[2,1 - b; 3,4 -

b']dithiophene - 5 - carboxylic acid 11 was dissolved in acetone/water (60/8 ml). At 0°, 3.1 ml (22 mmol) of triethylamine in acetone (40 ml) was added, followed by 2.5 ml (22 mmol) of ethyl chlorocarbonate. After stirring for 30 min at 0°, 1.6 g (24 mmol) of sodium azide in water (5 ml) was added, followed by stirring for 60 min. Addition of ice water, extraction with ether, drying of the ether phase (magnesium sulphate) and evaporation gave an oily product, 4H - 5,6 - dihydro-cyclohepta-[2,1 - b; 3,4 - b']dithiophene - 5 - carboxylic acid azide 12. The crude product was immediately dissolved in toluene and heated to 100°. This caused rapid gas evolution, and after evaporation of the solvent, 4H - 5,6 - dihydro - 5 - isocyanate-cyclohepta[2,1 - b; 3,4 - b']dithiophene 13 was obtained as an oil. The structure was confirmed by ^{1}H NMR and IR spectroscopy. ^{1}H NMR (CCl_4): δ 6.9 (d, 2H, thiophene, J = 5.1 Hz), 6.6 (d, 2H, thiophene, J = 5.1 Hz), 3.9 (p, 1H, 5, J = 5.7 Hz), 3.0 (d, 4H, 4, 6, J = 5.7 Hz). IR (film): $\nu_{N=C=O}$ 2250 cm^{-1}.

The crude isocyanate 13 was dissolved in ether and added dropwise to a suspension of 0.75 g (20 mmol) of lithium aluminium hydride in ether. Refluxing for 90 min was followed by addition of aqueous sodium hydroxide (100 ml, 30%), evaporation of the ether and reflux for another 30 min, subsequent by extraction with ether, drying (magnesium sulphate) and evaporation gave 3.0 g (63%) of the title compound 14 as a yellow oil. Treatment with hydrogen chloride in ether gave 4H - 5,6 - dihydro - 5 - methylamino-cyclohepta[2,1 - b; 3,4 - b']-dithiophene-hydrochloride as white crystals, m.p. 145.0–147.5° (ethanol). ^{1}H NMR (CCl_4): δ 6.9 (d, 2H, thiophene, J = 5.0 Hz), 6.6 (d, 2H, thiophene, J = 5.0 Hz), 2.9 (s, 5H), 2.3 (s, 3H, –NC<u>H</u>$_3$), 1.1 (s, 1H, –N<u>H</u>). *m/e* (%): 235 (100) M$^+$. (Found: C, 53.00; H, 5.09; Cl, 13.08; N, 5.11. $C_{12}H_{14}ClNS_2$ requires: C, 53.02; H, 5.19; Cl, 13.04; N, 5.15%).

7H - 8,9 - *Dihydro* - 8 - *methylamino-cyclohepta*[1,2 - b; 4,3 - b']*dithiophene* 23

This compound was prepared as described above. From 5.0 g of 7H - 8,9 - dihydro-cyclohepta[1,2 - b; 4,3 - b']-dithiophenecarboxylic acid 22, 2.6 g (55%) of the methylamine 23 was obtained. The hydrochloride had m.p. 219.0–220.5°. ^{1}H NMR (CCl_4): δ 7.0 (m, 4H, thiophene), 3.0 (s, 5H), 2.3 (s, 3H, –CH_3), 1.6 (s, 1H, –N<u>H</u>). *m/e* (%): 235 (100) M$^+$. (Found: C, 52.90; H, 5.31; N, 5.58; S, 23.49. $C_{12}H_{14}ClNS_2$ requires: C, 53.02; H, 5.19; N, 5.15; S, 23.59%). For the isocyanate: PMR (CCl_4): δ 7.0 (s, 4H, thiophene), 4.1 (p, 1H, 8, J = 5.2 Hz), 3.1 (d, 4H, 7.9, J = 5.2 Hz). IR (film): $\nu_{N=C=O}$ 2260 cm^{-1}.

4H - 5,6 - *Dihydro* - 5 - *dimethylamino-cyclohepta*[2,1 - b; 3,4 - b']*dithiophene* 15

4H - 5,6 - Dihydro 5 methylamino-cyclohepta[2,1 - b; 3,4 - b']dithiophene 14, 1.0 g (4 mmol), dissolved in ether (10 ml), was added dropwise with stirring to a suspension of lithium aluminium hydride, 0.65 g (17 mmol), in ether (20 ml). After stirring for 20 min, the mixture was cooled (0°) and 1.5 ml (19 mmol) of ethyl formate was added dropwise. Stirring was continued for another 20 min, aqueous sodium hydroxide (50 ml, 3 N) was then added, the organic phase separated, dried (magnesium sulphate) and evaporated, giving 0.7 g (66%) of the dimethyl amine as a yellow oil. 4H - 5,6 - Dihydro - 5 - dimethylamino-cyclohepta[2,1 - b; 3,4 - b']dithiophene hydrochloride was prepared as above, m.p. 239.0–241.0° (isopropanol/ethanol). ^{1}H NMR (CCl_4): δ 6.9 (d, 2H, thiophene, J = 5.0 Hz), 6.7 (d, 2H, thiophene, J = 5.0 Hz), 2.7 (s, 5H, 4, 5, 6), 2.2 (s, 6H, –NC<u>H</u>$_3$).

7H - 8,9 - *Dihydro* - 8 - *dimethylamino-cyclohepta*[1,2 - b; 4,3 - b']*dithiophene* 24

From 1.5 g (6.3 mmol) of 7H - 8,9 - dihydro - 8 - methylamino-cyclohepta[1,2 - b; 4,3 - b']dithiophene, 1.0 g (26 mmol) of lithium aluminium hydride and 2.3 ml (29 mmol) of ethyl formate, using the same procedure as above, 1.0 g (63%) of 7H - 8,9 - dihydro - 8 - dimethylamino-cyclohepta[1,2 - b; 4,3 - b']dithiophene 24 was obtained. The hydrochloride was prepared as above, m.p. 250° (decomp.). ^{1}H NMR (CCl_4): δ 7.0 (m, 4H, thiophene, J = 5.0 Hz), 3.0 (m, 5H, 7, 8, 9), 2.2 (s, 6H, –CH_3). (Found: C, 54.23; H, 5.81; S, 22.39. $C_{13}H_{16}ClNS_2$ requires: C, 54.62; H, 5.64; S, 22.43%).

4H - *Cyclohepta*[2,1 - b; 3,4 - b']*dithiophene* 17

4H - 5,6 - Dihydro - 5 - dimethylamino-cyclohepta[2,1 - b; 3,4 - b']dithiophene 15, 0.5 g (2 mmol), was dissolved in ether and methyl iodide, 0.43 g (0.57 ml, 3 mmol), was added. After stirring for 24 hr, the precipitate was filtered off and washed with ether. The salt was then dissolved in dimethyl formamide, sodium methoxide, 0.5 g (10 mmol), was added and the mixture heated to reflux (open flame), then kept at 90° for 60 min. Addition of water, extraction with ether, washing, drying and evaporation gave 4H - cyclohepta[2,1 - b; 3,4 - b']dithiophene 17 as a brown oil, 0.25 g (61%). The analytical sample was purified by chromatography (silica-chloroform) and obtained as a colourless oil, n_D^{20} = 1.7038. ^{1}H NMR (CCl_4): δ 6.9 (four doublets, 4H, J = 5.0 Hz), 6.4 (d, 1H, J = 10.0 Hz), 5.6 (two triplets, 1H, J = 10.0 Hz and J = 6.6 Hz), 3.0 (d, 2H, J = 6.6 Hz). *m/e* (%): 204 (79) M$^+$, 203 (100) tropylium ion. (Found: C, 65.01; H, 3.87; S, 31.15. $C_{11}H_8S_2$ requires: C, 64.67; H, 3.95; S, 31.39%).

7H - *Cyclohepta*[1,2 - b; 4,3 - b']*dithiophene* 25

From 0.5 g of 7H - 8,9 - dihydro - 8 - dimethylamino-cyclohepta[1,2 - b; 4,3 - b']dithiophene 24, 0.22 g (54%) of the title compound was obtained following the same procedure as described above. n_D^{20} = 1.6952. ^{1}H NMR (CCl_4): δ 7.0 (one singlet, 2H, and 2 doublets, 2H, J = 5.2 Hz), 6.5 (d, 1H, J = 10.0 Hz), 5.6 (two triplets, 1H, J = 10.0 Hz and J = 6.4 Hz), 3.2 (d, 2H, J = 6.4 Hz). *m/e* (%): 204 (83) M$^+$, 203 (100) tropylium ion. (Found: C, 65.07; H, 3.83; S, 30.95. $C_{11}H_8S_2$ requires: C, 64.67; H, 3.95; S, 31.39%).

4H - *Dithieno*[2,1 - b; 3,4 - b']*tropylium fluoborate* 1

To a soln of 0.10 g (0.5 mmol) of 4H - cyclohepta[2,1 - b; 3,4 - b']dithiophene 17 in 10 ml of dry ethyl acetate, 0.2 g (0.6 mmol) of triphenylmethyl fluoborate in 5 ml of acetonitrile was added dropwise. After stirring for 30 min, the mixture was cooled overnight, giving 0.12 g (83%) of the tropylium ion as yellow crystals. Recrystallization from acetonitrile–ethyl acetate gave m.p. 210° (decomp.). ^{1}H NMR (D_2SO_4): δ 8.8–9.8 (m, AB_2-system, ν_5 9.0, $\nu_{4,6}$ 9.7, J_{AB} = 10.2 Hz), 8.8 (d, 2H, thiophene, J = 5.7 Hz), 8.5 (d, 2H, thiophene, J = 5.7 Hz). (Found: C, 45.61; H, 2.33; S, 21.91. $C_{11}H_7S_2BF_4$ requires: C, 45.54; H, 2.43; S, 22.10%).

7H - *Dithieno*[1,2 - b; 4,3 - b']*tropylium fluoborate* 2

From 0.1 g of 7H - cyclohepta[1,2 - b; 4,3 - b']dithiophene 25, 0.11 g (76%) of the tropylium ion, m.p. 250° (decomp.), was obtained by the same procedure as above. ^{1}H NMR (D_2SO_4): δ 9.8 (d, 2H, 7 and 9, J = 10.0 Hz), 9.5 (d, 2H, thiophene, J = 5.6 Hz), 9.1 (d, 2H, thiophene, J = 5.6 Hz), 8.8 (t, 1H, 8, J = 10.0 Hz). (Found: C, 45.57; H, 2.37; S, 22.03. $C_{11}H_7S_2BF_4$ requires: C, 45.54; H, 2.43; S, 22.10%).

Acknowledgements—Grants from the Swedish Natural Science Research Council to S.G. and from the Royal Physiographic Society in Lund to P.P. are gratefully acknowledged.

REFERENCES

[1]S. Gronowitz and E. Sandberg, *Arkiv. Kemi.* 32, 249 (1970).
[2]A. Wiersema and S. Gronowitz, *Acta Chem. Scand.* 24, 2593 (1970).
[3]B. Yom-Tov and S. Gronowitz, *Chem. Scr.* 3, 165 (1973).
[4]S. Gronowitz, B. Yom-Tov and U. Michael, *Acta Chem. Scand.* 27, 2257 (1973).
[5]T. Liljefors, U. Michael, B. Yom-Tov and S. Gronowitz, *Acta Chem. Scand.* 27, 2485 (1973).
[6]E. C. Taylor and A. McKillop, *The Chemistry of Cyclic Enaminonitriles and o-Aminonitriles*. Wiley, New York (1970).
[7]Ref. 6, p. 4.
[8]J. D. Bacha and J. K. Kochi, *Tetrahedron* 24, 2215 (1968).
[9]J. M. Khanna, V. M. Dixit and N. Anand, *Synthesis* 607 (1975).
[10]H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.* 79, 4557 (1957).
[11]S. Gronowitz, P. Moses, A.-B. Hörnfeldt and R. Håkansson, *Arkiv Kemi* 17, 165 (1961).
[12]S. Gronowitz and S. Hagen, *Ibid.* 27, 153 (1963).