Heterocyclic Fused Tropylium Ions VII. On the Synthesis of 9*H*-Dithieno-[2,1-*b*:4,5-c']tropylium Fluoborate and 4*H*-Dithieno[1,2-*b*:4,5-c']tropylium Fluoborate

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9*H*-Dithieno[2,1-*b*:4,5-c']tropylium ion (III) and 4*H*-dithieno[1,2-*b*:4,5-c']tropylium ion (IV) have been synthesized by ring-closure of 1-(4-carboxy-3-thienyl)-2-(3'-thienyl)ethane (IX) and 1-(4-carboxy-3-thienyl)-2-(2'-thienyl)ethane (XVI), respectively, followed by bromination-debromination to 9*H*-cyclohepta[2,1-*b*:4,5-c']dithiophen-9-one (XI) and 4*H*-cyclohepta[1,2-*b*:4,5-c']-dithiophen-4-one (XVIII), and finally by reduction and hydride transfer. The tropylium ions III and IV were less stable than the [*b*,*b*]-fused isomers previously studied.

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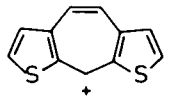
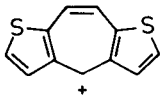
We have for some time studied the effect of annelation of heterocyclic aromatic rings onto the tropylium ion. 9*H*-Dithieno[2,1-*b*:4,5-*b*']tropylium perchlorate (I) and dithieno[1,2-*b*:5,4-*b*']tropylium perchlorate (II) have been synthesized (1,2). They were found to have very high pK_{R^+} values (+6.65 and +5.40, respectively), and they smoothly underwent deuterium exchange with concentrated deuteriosulphuric acid in the heterocyclic β-positions (3). X-Ray investigations show that the tricyclic system is coplanar (4) and explanations for the high stability of the dithieno-fused tropylium ions compared to the dibenzo analoques have been advanced (3). Ppp-calculated uv spectra of I and II were found to be in good agreement with the experimental ones (5).

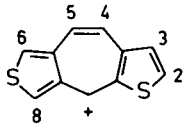
In both I and II the thiophene rings are fused with their *b*-sides and we were therefore interested in studying the effect of changing the mode of annelation on spectroscopic and chemical properties. In the present paper the synthesis and some properties of 9*H*-dithieno[2,1-*b*:4,5-c']tropylium fluoborate (III) and 4*H*-dithieno[1,2-*b*:4,5-c']tropylium fluoborate (IV) will be described.



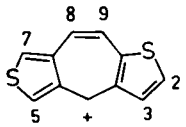
I



II

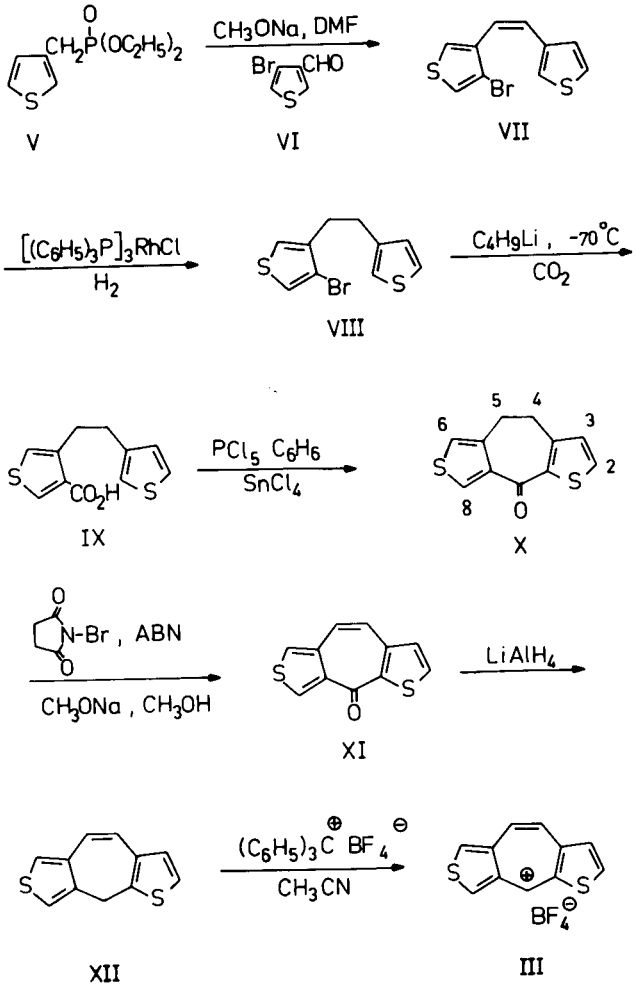


III



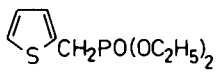
IV

Starting from diethyl 3-thenylphosphonate (V) and 4-bromo-3-thiophene aldehyde (VI), 1-(3-bromo-4-thienyl)-2-(3'-thienyl)ethane VII was obtained through the Wadworth-Emmons modification of the Wittig reaction. As observed previously (2), unusually high amounts of the *cis* isomer (*cis*/*trans* ratio 25/75) are formed with *ortho*-bromothiophene aldehydes. The *trans* isomer could easily be obtained pure by recrystallization. Homogeneous catalytic hydrogenation of the *cis*/*trans* mixture of VII using tris triphenylphosphine chlororhodium gave a 95% yield of 1-(3-bromo-4-thienyl)-2-(3'-thienyl)ethane (VIII) with no debromination. Halogen-metal interconversion of VIII with butyllithium followed by reaction with carbon dioxide gave 1-(4-carboxy-3-thienyl)-2-(3'-thienyl)ethane (IX) in 80% yield. Treatment of IX with phosphorus pentachloride in benzene gave the acid chloride, which without isolation was ring-closed to 4,5-dihydro-9*H*-cyclohepta[2,1-*b*:4,5-c']dithiophen-9-one (X). Side-chain bromination of X with *N*-bromosuccinimide using azobisisobutyronitrile as

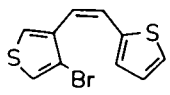


initiator followed by dehydrobromination with sodium methoxide in methanol gave 9*H*-cyclohepta[2,1-*b*:4,5-*c*']-dithiophen-9-one (XI) in 80% yield. Reduction of XI with lithium aluminium hydride led directly to 9*H*-cyclohepta-[2,1-*b*:4,5-*c*']dithiophene (XII). Hydride exchange between XII and trityl fluoborate according to the method of Dauben (6) led to dark violet crystals of 9*H*-dithieno[2,1-*b*:4,5-*c*']tropylium fluoborate (III) (Scheme 1). Further purification of XII by recrystallization was unsuccessful due to instability in solution at higher temperatures. Attempts to prepare the perchlorate by exchange with trityl perchlorate failed. However, the pmr spectrum in trifluoroacetic acid clearly showed that the desired tropylium ion had been obtained and all seven hydrogen resonances could be assigned.

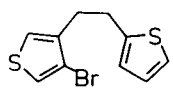
4*H*-Cyclohepta[1,2-*b*:4,5-*c*']dithiophen-4-one (XVIII) was prepared quite analogously to XI. Reaction of diethyl 2-thenylphosphonate (XIII) with VI gave 1-(3-bromo-4-thienyl)-2-(2'-thienyl)ethene (XIV) (*cis/trans* ratio 34/66). *Via* 1-(3-bromo-4-thienyl)-2-(2'-thienyl)ethane (XV), 1-(3-carboxy-4-thienyl)-2-(2'-thienyl)ethane (XVI), and 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:4,5-*c*']dithiophen-4-one (XVII), XVIII was thus obtained. Direct reduction of XVIII with lithium aluminium hydride failed, as the reaction stopped at the carbinol stage. However, the use of lithium aluminium hydride/aluminium chloride gave 4*H*-cyclohepta[1,2-*b*:4,5-*c*']dithiophene (XIX). Hydride exchange with trityl fluoborate then gave the intense violet IV. This could be kept at -15° for at least 15 hours with no notable change. However, at room temperature it decomposed giving off acidic fumes and also in solution it decomposed after some time with colour change from violet to blue and could therefore not be purified by recrystallization, nor could it be transformed to the perchlorate. The pmr spectrum of the crude product however also in this case clearly proved the structure.



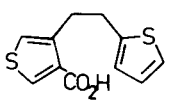
XIII



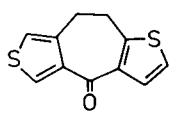
XIV



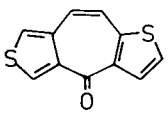
XV



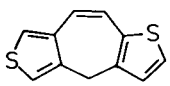
XVI



XVII



XVIII



XIX

Due to the instability of III and IV it has hitherto not been possible to determine their pK_{R^+} values, but they appear to be much lower than those of I and II. It is also evident from the behaviour of XI and XVIII towards lithium aluminium hydride that III has a higher pK_{R^+} value than IV, since only when relatively stable carbonium ions are intermediates are ketones reduced directly to methylene derivatives by lithium aluminium hydride alone (3).

As mentioned previously (3), additional evidence for the stability of the tropylium ions and the delocalization of the positive charge in the tricyclic systems was obtained from a study of the C=O stretching regions of the ketones. Due to the high contribution of dipolar resonance forms having C-O single bonds, low frequencies for the C=O stretch are expected. Thus, for instance, the two [*b*,*b*]-fused tropones showed C=O stretching frequencies at 50 cm^{-1} lower values than their corresponding dihydro derivatives, while no difference in C=O stretching frequency could be observed between the [*c*,*c*]-fused tropone and its dihydro derivative (3). A C=O stretch at 1590 cm^{-1} was observed for XI and at 1605 cm^{-1} for XVII. In the [*b*,*c*]-fused systems, the differences are thus 15 and 22 cm^{-1}, respectively, which provides additional evidence for the lower pK_{R^+} values of III and IV.

EXPERIMENTAL

General.

Gas chromatographic analyses were performed with a Perkin-Elmer 900 apparatus equipped with a flame ionization detector and connected to a Varian 480 digital integrator. Pmr spectra were recorded on a Varian A-60 instrument. Tetramethylsilane was used as an internal standard. A Perkin-Elmer 257 ir spectrometer was used for ir spectra. The elemental analyses were performed by the Department of Analytical Chemistry at the University of Lund.

1-(4-Bromo-3-thienyl-2-(3'-thienyl)ethene (VII).

A mixture of 18.6 g (0.08 mole) of diethyl 3-thenylphosphonate (7) and 15.3 g. (0.08 mole) of 4-bromo-3-thiophene aldehyde (8) dissolved in 80 ml. of anhydrous *N,N*-dimethylformamide was added drop-wise to a cold (0-5°) suspension of 6.5 g. (0.12 mole) of sodium methoxide in 50 ml. of *N,N*-dimethylformamide. The reaction mixture was stirred an additional 10-15 minutes and the cooling bath was removed. Stirring was continued at room temperature for 1.5 hours and then poured into cold water. The mixture was extracted with ether and the combined ethereal extracts were washed with 1 *N* aqueous solution of bisulphite and with water and dried over calcium chloride. After evaporation of the ether, purification was achieved by a fast and simple procedure by passing the product over a column of silica gel (120-230 mesh, 8-10 cm. high) and eluting with pentane. Elution was hastened by gentle suction. The colourless pentane solutions were evaporated yielding 20.4 g. (94%) of the title compound, free from traces of starting material; *cis-trans* ratio: 25/75 (vpc, BDS 10% on Chromosorb W, 210-215°. Recrystallization from ethanol gave the *trans* isomer, m.p. 62°; pmr (acetone): δ 7.02 (dd, 1, J_{12} = 16.6 Hz, $J_{5\text{-}CH_1}$ = 0.6 Hz, H(=CH-1) 7.24 (d, 1, J = 16.6 Hz, H(=CH-2) 7.3-7.6 (m, 3, H-2', H-4', H-5') 7.52 (d, 1, J_{25} = 3.6 Hz, H-2) 7.67 (dd, 1, J_{25} = 3.6 Hz, $J_{5\text{-}CH\text{-}1}$ = 0.6 Hz, H-5).

Anal. Calcd. for $C_{10}H_7BrS_2$: C, 44.28; H, 2.60; S, 23.65. Found: C, 44.05; H, 2.70; S, 23.40.

1-(4-Bromo-3-thienyl)-2-(3′-thienyl)ethane (VIII).

A solution of 17.9 g. (0.066 mole) of the *cis-trans* mixture of 1-(3-bromo-4-thienyl)-2-(3′-thienyl)ethene in 200 ml. of ethanol was degassed for five minutes by a rapid stream of dry nitrogen. Then 0.8 g. of tris(triphenyl)phosphine chlororhodium(I) (9) was added to the solution, which was degassed again for another 3 minute period. The mixture was then hydrogenated in a Parr apparatus at 60-70° at a hydrogen pressure which varied between 60 and 30 psi. Hydrogenation was complete after 40-50 hours. After evaporation of the solvent, the product was purified by passing it through silica gel and eluting with pentane as described for VII, whereby 17.2 g. (95%) of the title compound, b.p. 120-121°/.03 mm., was obtained upon distillation *in vacuo*; pmr (perdeuterioacetone): δ 2.87 (s, 4, (CH_2-CH_2), 6.8-7.4 (m, 5, thioph.).

Anal. Calcd. for $C_{10}H_9BrS_2$: C, 43.96; H, 3.32; S, 23.47. Found: C, 44.20; H, 3.37; S, 23.50.

1-(4-Carboxy-3-thienyl-2-(3′-thienyl)ethane (IX).

To a solution of 13.6 g. (0.05 mole) of 1-(4-bromo-3-thienyl)-2-(3′-thienyl)ethane in 100 ml. of anhydrous ether cooled to -70°, 36 ml. of 1.42 *N* butyllithium in hexane was added dropwise at a rapid rate. After all of the butyllithium had been added, the reaction mixture was stirred an additional 10-15 minutes at -70° and then poured quickly onto crushed solid carbon dioxide covered with anhydrous ether. The mixture was allowed to warm up to 2-3°, water and ether were added, and it was shaken in a separatory funnel until all solid material was dissolved. The aqueous layer was separated and the ethereal layer was extracted with small portions of 1 *N* alkali solution. The combined aqueous phases were acidified with cold 5 *N* hydrochloric acid. The precipitate was filtered off and washed with water, yielding 9.5 g. (80%) of the title compound, m.p. 164° after recrystallization from ethanol; pmr (DMSO-d_6): δ 2.6-3.4 (m, 4, (-CH_2-CH_2)), 6.6-7.6 (m, 4, (thioph.)), 8.23 (d, 1, J_{25} = 3.4 Hz, H-5).

Anal. Calcd. for $C_{11}H_{10}O_2S_2$: C, 55.44; H, 4.23; S, 26.91. Found: C, 55.20; H, 4.21; S, 26.50.

4,5-Dihydro-9*H*-cyclohepta[2,1-*b*:4,5-*c*′]dithiophen-9-one (X).

To a solution of 8.1 g. (0.034 mole) of 1-(4-carboxy-3-thienyl)-2-(3′-thienyl)ethane in 200 ml. of benzene, 8.5 g. of phosphorus pentachloride was added. The mixture was warmed for a few minutes on a hot bath until all solids were in solution, and then refluxed for another 10 minutes. After cooling, the solution was degassed by a stream of nitrogen for 15-20 minutes. The solution was cooled again to 5-6° and 9.0 g. of tin tetrachloride in 50 ml. of benzene was quickly added. The dark colour of the resulting complex intensified with stirring. Efficient stirring was continued until the mixture reached room temperature. It was then heated on a water bath at about 90° for 10-12 minutes. The mixture was cooled and ether was added until a homogeneous solution was obtained. The mixture was cooled in an ice-bath and 200 ml. of 5 *N* hydrochloric acid followed by 200 ml. of water was added through the condenser with vigourous stirring. The aqueous phase was diluted with water and extracted with ether. The combined organic phases were washed consecutively with 5 *N* hydrochloric acid, 3 *N* hydrochloric acid, *N* hydrochloric acid, water, *N* sodium hydroxide and water and dried over calcium chloride. The solvent was evaporated and after recrystallization from acetonitrile, 6.05 g. of the title compound was obtained in yellow crystals, m.p. 110-111°; ir (deuteriochloroform): 1605 cm^{-1} (CO); pmr (perdeuterioacetone): δ 3.10 (s, 4, (CH_2-CH_2)), 7.05 (d, 1, J_{23} = 5.0 Hz, H-3), 7.27 (d, 1, J_{68} = 3.6 Hz, H-6), 7.77 (d, 1, J_{23} = 5.0 Hz, H-2), 8.28 (d, 1, J_{68} = 3.6 Hz, H-8). Shift assignments are based on the known effects of C=O groups on chemical shifts (10).

Anal. Calcd. for $C_{11}H_8OS_2$: C, 59.96; H, 3.66; S, 29.10. Found: C, 60.00; H, 3.57; S, 28.90.

9*H*-Cyclohepta[2,1-*b*:4,5-*c*′]dithiophen-9-one (XI).

To a solution of 5.0 g. (0.023 mole) of 4,5-dihydro-9*H*-cyclohepta[2,1-*b*:4,5-*c*′]dithiophen-9-one in 100 ml. of anhydrous carbon tetrachloride, 4.05 g. (0.023 mole) of *N*-bromosuccinimide mixed with 0.5 g. of azobisisobutyronitrile was added with stirring and the mixture refluxed for 1.5 hours. The reaction mixture was cooled to room temperature and the succinimide filtered off. The filtrate was washed twice with water, dried over sodium sulphate and evaporated. The residue was dissolved in 150 ml. of methanol and 4 g. of sodium methoxide was added. The mixture was refluxed for 0.5 hour, then concentrated to one-half its volume and poured into water. The insoluble organic material was extracted with chloroform. The combined chloroform extract was washed with water, dried and evaporated, yielding 4.0 g. (80%) of the title compound, m.p. 155° after recrystallization from acetonitrile; ir (deuteriochloroform): 1590 cm^{-1}; pmr (deuteriochloroform): δ 6.83 (d, 1, J_{45} = 11.4 Hz, H-5), 7.16 (d, 1, J_{45} = 11.4 Hz, H-4), 7.20 (d, 1, J_{23} = 5.1 Hz, H-3), 7.67 (d, 1, J_{23} = 5.1 Hz, H-2), 7.67 (d, 1, J_{68} = 3.8 Hz, H-6), 8.68 (dd, 1, J_{68} = 3.8 Hz, J = 0.6 Hz, H-8).

Anal. Calcd. for $C_{11}H_6OS_2$: C, 60.52; H, 2.77; S, 29.39. Found: C, 60.40; H, 2.64; S, 29.20.

9*H*-Cyclohepta[2,1-*b*:4,5-*c*′]dithiophene (XII).

To 150 ml. of anhydrous ether, 2.0 g. (9.2 mmoles) of 9*H*-cyclohepta[2,1-*b*:4,5-*c*′]dithiophen-9-one and 0.6 g. of lithium aluminium hydride was added and the mixture stirred overnight at room temperature. The excess of metal hydride was decomposed by careful addition of an ethereal solution of ethyl acetate. The reaction mixture was then poured into 1 *N* hydrochloric acid stirred until all solids were dissolved. The layers were separated and the aqueous phase was extracted with ether. The combined ether phases were washed with water, dried over calcium chloride and evaporated, yielding 1.8 g. (96%) of the title compound, m.p. 109° after recrystallization from hexane; pmr (deuteriochloroform): δ 4.01 (s, 2, CH_2), 6.51 (d, 1, J_{45} = 11.5 Hz, H-5), 6.74 (d, 1, J_{45} = 11.5 Hz, H-4), 6.84 (d, 1, J_{23} = 5.4 Hz, H-3), 6.94 (d, 1, J_{23} = 5.4 Hz, H-2), 7.07 (s, 1, J_{68} = 3.9 Hz), 7.13 (s, 1, J_{68} = 3.9 Hz, H-6).

Anal. Calcd. for $C_{11}H_8S_2$: C, 64.66; H, 3.94; S, 31.39. Found: C, 64.30; H, 3.80; S, 31.70.

9*H*-Dithieno[2,1-*b*:4,5-*c*′]tropylium Fluoroborate (III).

To a solution of 0.30 g. (1.5 mmoles) of 9*H*-cyclohepta[2,1-*b*:-4,5-*c*′]dithiophene in 50 ml. of anhydrous ethyl acetate, cooled in an ice-salt mixture, 0.6 g. of trityl fluroborate dissolved in 6 ml. of anhydrous acetonitrile was added with stirring. After stirring for 0.5 hour, 0.30 g. of dark-violet crystals of the title compound were filtered off in a dry box, m.p. 244° dec. Attempts to purify the compound by recrystallization failed due to its instability; pmr (trifluoroacetic acid): δ 8.00 (d, 1, J_{23} = 5.2 Hz, H-3), 8.36 (d, 1, J_{45} = 11.2 Hz, H-4), 8.77 (d, 1, J_{45} = 11.2 Hz, H-5), 8.91 (d, 1, J_{68} = 3.6 Hz, H-6), 9.30 (d, 1, J_{23} = 5.2 Hz, H-2), 9.57 (d, 1, J_{68} = 3.6 Hz, H-8), 9.92 (s, 1, H-9).

1-(4-Bromo-3-thienyl)-2-(2′-thienyl)ethane (XIV).

From 17.14 g. (0.074 mole) of diethyl 2-thenylphosphonate (II) and 14.4 g. (0.074 mole) of 4-bromo-3-thiophene aldehyde, following the procedure given for the synthesis of the isomer VII, 19.3 g. (96%) of the title compound was obtained with a *cis-trans* ratio of 34:66. The pure *trans* isomer was obtained through recrystallization from ethanol, m.p. 52-53°; nmr (deuteriochloroform): δ

6.6-7.4 (m, thiophenic and olefinic protons).

Anal. Calcd. for $C_{10}H_7BrS_2$: C, 44.28; H, 2.60; S, 23.65. Found: C, 44.30; H, 2.83; S, 23.60.

1-(4-Bromo-3-thienyl)-2-(2′-thienyl)ethane (XV).

Homogeneous hydrogenation of 17.9 g. (0.066 mole) of a mixture of *cis* and *trans* 1-(4-bromo-3-thienyl)-2-(2′-thienyl)ethene over tris triphenylphosphine chlorohodium(I), following the procedure given above for VIII, gave 17.1 g. (94%) of the title compound, b.p. 118-119°/0.3 mm; pmr (perdeuterioacetone): δ 2.6-3.4 (m, 4, CH_2CH_2), 6.5-7.5 (m, 5, thioph.).

Anal. Calcd. for $C_{10}H_9BrS_2$: C, 43.96; H, 3.32; S, 23.47. Found: C, 43.90; H, 3.14; S, 23.90.

1-(4-Carboxy-3-thienyl)-2-(2′-thienyl)ethane (XVI).

From 15.5 g. (0.0568 mole) of 1-(4-bromo-3-thienyl)-2-(2′-thienyl)ethane, 41.0 ml. of 1.42 *N* butyllithium in hexane and carbon dioxide, the procedure given above for IX gave 11.1 g. (82%) of the title compound, m.p. 136° after recrystallization from ethanol; pmr (perdeuterioacetone): δ 3.15 (s, 4, CH_2-CH_2), 6.6-7.1 (m, 2, H-3′, H-4′), 7.27 (d, 1, J_{25} = 3.4 Hz, H-2), 7.29 (dd, 1, $J_{3'5'}$ = 1.6 Hz, $J_{4'5'}$ = 4.8 Hz, H-5′), 8.25 (d, 1, J_{25} = 3.4 Hz, 5-H).

Anal. Calcd. for $C_{11}H_{10}O_2S_2$: C, 55.44; H, 4.23; S, 26.91. Found: C, 55.80; H, 4.23; S, 26.60.

8,9-Dihydro-4*H*-cyclohepta[1,2-*b*:4,5-*c*′]dithiophen-4-one (XVII).

From 9.5 g. (0.040 mole) of 1-(4-carboxy-3-thienyl-2-(2′-thienyl)ethane, 10 g. of phosphorus pentachloride and 10.4 g. of tin tetrachloride in 230 ml. of benzene, following the procedure described above for X, 7.3 g. (83%) of the title compound was obtained as yellow crystals, m.p. 87-88° after recrystallization from acetonitrile; ir (deuteriochloroform): 1618 cm^{-1} (C=O); pmr (perdeuterioacetone): δ 3.15 (s, 4, CH_2-CH_2), 7.15 (d, 1, J_{23} = 5.5 Hz, H-2), 7.23 (d, 1, J_{57} = 3.7 Hz, H-7), 7.61 (d, 1, J_{23} = 5.5 Hz, H-3), 8.31 (d, 1, J_{57} = 3.7 Hz, H-5).

Anal. Calcd. for $C_{11}H_8OS_2$: C, 59.96; H, 3.66; S, 29.10. Found: C, 60.10; H, 3.54; S, 28.90.

4*H*-Cyclohepta[1,2-*b*:4,5-*c*′]dithiophen-4-one (XVIII).

From 5.0 g. (0.023 mole) of 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:-4,5-*c*′]dithiophen-4-one, following the procedure given above for XI, 3.8 g. (76%) of the title compound, m.p. 136° after recrystallization from acetonitrile was obtained; ir (deuteriochloroform): 1595 cm^{-1} (C=O); pmr (deuteriochloroform): δ 6.82 (d, 1, J_{89} = 11.6 Hz, H-8), 7.09 (d, 1, J_{89} = 11.6 Hz, H-9), 7.32 (d, 1, J_{23} = 5.6 Hz, H-2), 7.66 (d, 1, J_{57} = 3.8 Hz, H-7), 8.00 (dd, 1, J_{23} = 5.6 Hz, J_{39} = 0.5 Hz, H-3), 8.62 (dd, 1, J_{57} = 3.8 Hz, J_{58} = 0.5 Hz, H-5).

Anal. Calcd. for $C_{11}H_6OS_2$: C, 60.52; H, 2.77; S, 29.39. Found: C, 60.37; H, 2.75; S, 29.10.

4*H*-Cyclohepta[1,2-*b*:4,5-*c*′]dithiophene (XIX).

To a 0.6 g. of lithium aluminium hydride and 2 g. of aluminium chloride in 100 ml. of anhydrous ether, 1.1 g. of 4*H*-cyclohepta[1,2-*b*:4,5-*c*′]dithiophen-4-one was added and the mixture refluxed for 4 hours. The work-up was carried out as described above for XII, yielding 0.96 g. (94%) of the title compound, m.p. 113°, after recrystallization from methanol; pmr (deuteriochloroform): δ 3.92 (s, 2, CH_2), 6.51 (d, 1, J_{89} = 11.6 Hz, H-8), 6.75 (s, 1, J_{89} = 11.6 Hz, H-9), 6.84 (d, 1, J_{23} = 5.0 Hz, H-3), 6.91 (d, 1, J_{57} = 3.2 Hz, H-5), 7.12 (d, 1, J_{57} = 3.2 Hz, H-7), 7.17 (d, 1, J_{23} = 5 Hz, H-2).

Anal. Calcd. for $C_{11}H_8S_2$: C, 64.66; H, 3.94; S, 31.39. Found: C, 64.40; H, 3.93; S, 31.30.

4*H*-Dithieno[1,2-*b*:4,5-*c*′]tropylium Fluoborate (IV).

From 0.20 g. of 4*H*-cyclohepta[1,2-*b*:4,5-*c*′]dithiophene and 0.30 g. of trityl fluoborate, following the procedure described above, 0.20 g. of the title compound was obtained in dark-violet crystals, which were too unstable to be purified by recrystallization; pmr (nitromethane/trifluoracetic acid): δ 8.00-8.33 (m, 2, H-8, H-9), 8.68 (d, 1, J = 4.6 Hz, thioph.), 8.94 (d, 1, J = 4.6 Hz, thioph.), 9.07 (d, 1, J_{57} = 3.4 Hz, H-7), 9.71 (d, 1, J_{57} = 3.4 Hz, H-5), 9.92 (s, 1, H-4).

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