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THE SYNTHESIS OF CYCLOPENTADITHIOPHENES[1,2]

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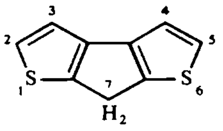
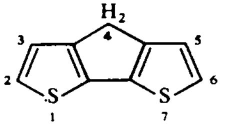
Abstract—The cyclopentadithiophenes (II–VI) in connection with studies of the charge transfer properties of dithienyls and related rigid analogs[3] have been synthesized. The last step in the synthetic schemes is a ring closure reaction, namely oxidation of the appropriate dilithio intermediates. This appears to be a useful general method.

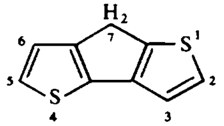
ALTHOUGH fluorene chemistry has been the subject of many investigations in the widest sense,[4,5] the heterocyclic analogues have attracted relatively little attention. The synthesis of three diazafluorenes[6] was reported in 1950 and recently the preparation of a thiophene analogue of a substituted fluorenone, obtained in 1% yield, was mentioned.[7] Of the six possible cyclopentadithiophenes, outlined below, we have already described the synthesis of 7*H*-cyclopenta[1.2-*b*: 4.3-*b*′]dithiophene (I) in an earlier publication.[8]



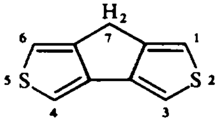
I



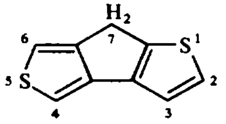
II



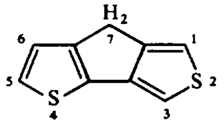
III



IV



V



VI

This paper deals with the synthesis of all of the remaining isomers. Compounds II through VI were prepared using the same synthetic "key-step" which proved successful in the case of I. This last step in the various reaction sequences leading to the desired cyclopentadithiophenes, involves an intramolecular oxidative ring closure of the appropriate dilithio derivatives with $CuCl_2$ in dilute ethereal solution at 0°. The dilithio intermediates could be obtained by halogen-metal interconversion[9] of the dibromo dithienylmethane precursors and n-butyllithium at −70°.

An improved method for the preparation of 3,3′-dibromo-2,2′-dithienylmethane (VII), an intermediate in the preparation of I,[8] was developed. Instead of the low yield reaction between 3-bromo-2-thenylchloride and 3-bromo-2-thienyllithium in

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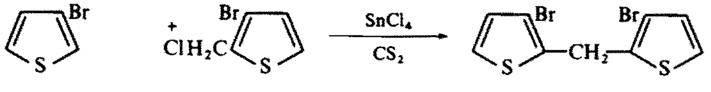
ether, we used a Friedel–Crafts alkylation of 3-bromothiophene[10] with 3-bromo-2-thenylchloride and $SnCl_4$. The yield amounted to 48%.

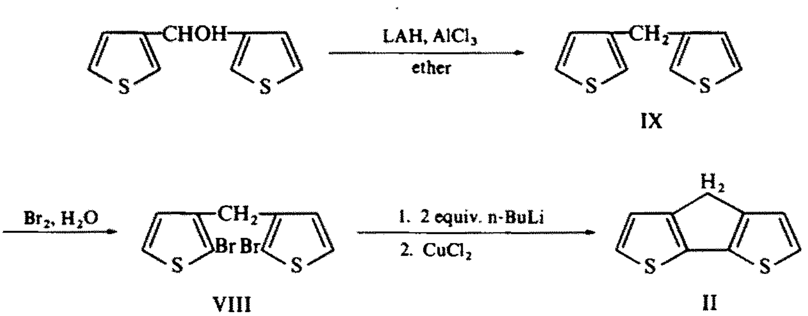


VII

On closer examination, the NMR spectrum of I reveals a broadened singlet at τ 6·41 for the methylene protons, clearly pointing to coupling with ring protons. In addition the spectrum shows the expected two triplets centered about τ 2·92 (aromatic protons at 2- and 5-positions) with $J_{2(5),CH_2} = 0{\cdot}6$ c/s and a broadened doublet at τ 3·07 ($J = 5{\cdot}0$ c/s).

The synthesis of 4*H*-cyclopenta[2.1-*b*: 3.4-*b*′]dithiophene (II) is summarized in Scheme 1.

Scheme 1



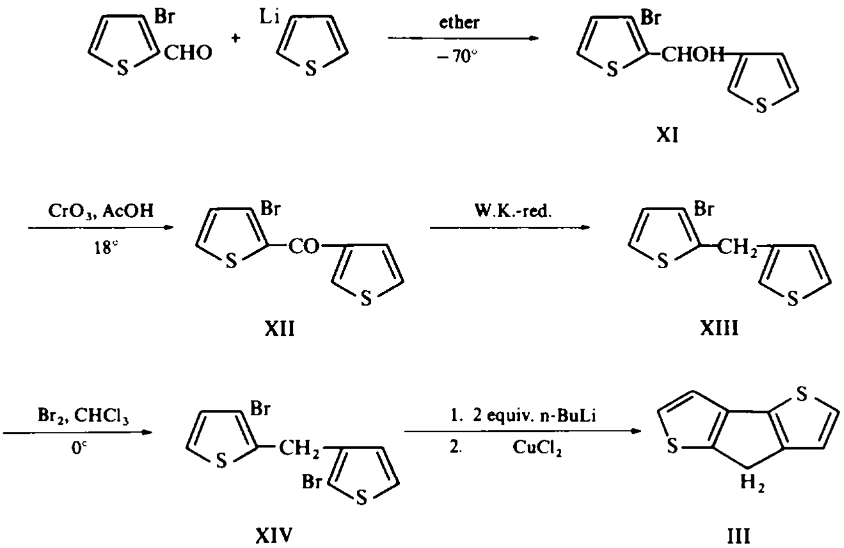
The starting material for the preparation of 2,2′-dibromo-3,3′-dithienylmethane (VIII) was the known 3,3′-dithienylcarbinol.[11] Reduction of this compound with an equimolar mixture of LAH and $AlCl_3$ in dry ether[12] furnished an 88% yield of the unknown 3,3′-dithienylmethane (IX), m.p. 31·5–32°. Addition of a CCl_4 solution of IX to aqueous bromine at 15°, caused rapid decoloration and gave the 2,2′-dibromo substituted derivative (VIII) in 50% yield.

The structure of VIII, m.p. 43°, was supported by elementary analysis and its NMR spectrum, which shows a characteristic coupling constant for the aromatic protons of a 2,3-disubstituted thiophene ring.[13]

The dibromo product VIII could be converted by metal-halogen interchange followed by intramolecular oxidative coupling into 4*H*-cyclopenta-[2.1-*b*: 3.4-*b*′]dithiophene (II), m.p. 74–75°, in 35% yield. The elementary analysis, NMR and UV spectra of this colorless solid are in accord with the structure assigned. The NMR spectrum shows a broadened singlet for the methylene protons and in consequence broadened peaks for the aromatic protons, again demonstrating mutual coupling. On carbonation of the dilithio intermediate of VIII, the expected 2,2′-dicarboxy-3,3′-dithienylmethane (X), a white solid, m.p. 240–241°, was obtained in good yield (61%).

The success of the oxidative cyclization reaction prompted its use in the preparation of the third analog via 2′,3-dibromo-2,3′-dithienylmethane (XIV), the precursor of 7*H*-cyclopenta[1.2-*b*: 3.4-*b*′]dithiophene (III). The synthesis is outlined in Scheme 2.

SCHEME 2

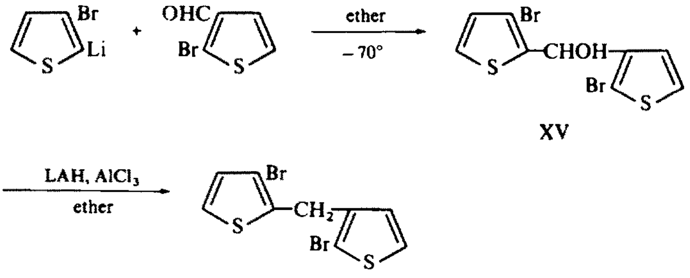


In an early attempt at the synthesis of III, we allowed 3-bromo-2-thiophenealdehyde[14] to react with 3-thienyllithium,[15] furnishing 3-bromo-2,3'-dithienylcarbinol (XI) as an impure orange viscous oil in approximately 90% yield. All attempts to purify this alcohol failed. Oxidation of the compound with CrO_3 in an acetic acid–water mixture at room temperature gave 3-bromo-2,3'-dithienylketone (XII), b.p. 150–160°/0·15 mm. The yield based on impure starting material was 53%. The structure of XII was established by elementary analysis and was supported by its IR and NMR spectra. Moreover a 2,4-dinitrophenylhydrazone, m.p. 243–244°, could be obtained. The ketone was subjected to a Wolff-Kishner reduction, without loss of the bromine atom[16] resulting in the formation of 3-bromo-2,3'-dithienylmethane (XIII), a colorless liquid with b.p. 102–106°/0·20 mm, in 62% yield. The assignment of the structure of XIII follows from the synthesis as well as from the IR and NMR spectra. Bromination of 3-bromo-2,3'-dithienylmethane (XIII) with bromine in dilute $CHCl_3$ solution at 0° yielded 70% of 2',3-dibromo-2,3'-dithienylmethane (XIV), b.p. 118–122°/0·20 mm, as an almost colorless liquid. The purified product analysed correctly for $C_9H_6Br_2S_2$. The by-products, presumably isomers, have remained unidentified. The structure of XIV is based chiefly on the NMR spectrum (Experimental).

The oxidative ring closure of the intermediate 2',3-dilithio-2,3'-dithienylmethane to 7*H*-cyclopenta[1.2-*b*: 3.4-*b*']dithiophene (III), m.p. 46·5–47·2°, proceeded in 34% yield. The structure of III, a colorless solid, was supported by elementary analysis and its NMR and UV spectra. The NMR spectrum reveals marked coupling between the aromatic protons and the methylene protons. Indications for the positions of the different maxima in the NMR spectrum of III were obtained by comparison with the corresponding spectra of I and II.

Further evidence for the correctness of the structure attributed to XIV was obtained by an independent synthesis of this material, avoiding a direct bromination. Although this alternative preparation gave no unambiguous structure proof, it provides important support for the structure XIV in addition to furnishing a shorter route. Scheme 3 gives a survey of the reaction sequence:

SCHEME 3



XV

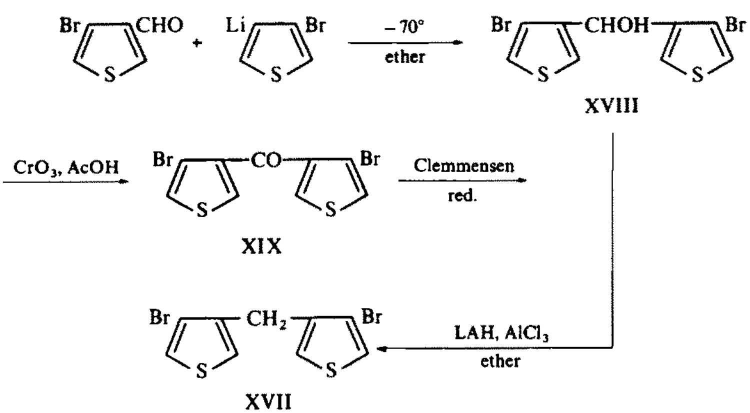
XIV

2-Bromo-3-thiophenealdehyde[14] was allowed to react with 3-bromo-2-thienyllithium.[15] This furnished 2′,3-dibromo-2,3′-dithienylcarbinol (XV), m.p. 56–58°, as a colorless crystalline material in 61% yield. Its structure followed from the synthesis and was confirmed by the IR and NMR spectra. The carbinol XV was reduced, using an equimolar mixture of LAH and $AlCl_3$ in dry ether.[12] This treatment resulted in an 88% yield of 2′,3-dibromo-2,3′-dithienylmethane (XIV) as a liquid with an elementary analysis in agreement with calculations. The IR and NMR spectra were completely identical with those recorded for compound XIV prepared *via* the bromination if XIII. GLC analysis showed a purity of 80%, possible indicating some isomerization.

The organometallic intermediate derived from XIV could be converted into 2′,3-dicarboxy-2,3′-dithienylmethane (XVI), a white solid, m.p. 241–242°, by reaction with CO_2 (yield 48 %).

In connection with the synthesis of the fourth isomer 7*H*-cyclopenta-[1.2-*c*:3.4-*c*′]dithiophene (IV), we were prompted to prepare 4,4′-dibromo-3,3′-dithienylmethane (XVII) (Scheme 4).

SCHEME 4



XVIII

XIX

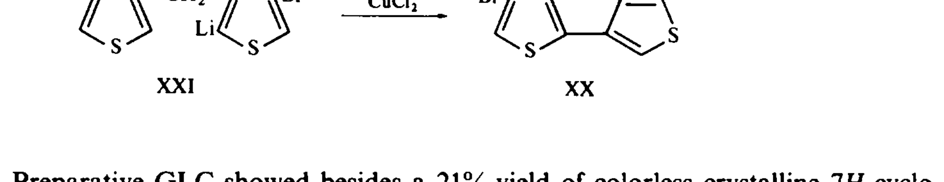
XVII

For this purpose a reaction of 4-bromo-3-thiophenealdehyde[14] with 3-bromo-4-thienyllithium[15] was carried out, furnishing a 60% yield of colorless crystalline 4,4′-dibromo-3,3′-dithienylcarbinol (XVIII), m.p. 80·5–81°. The structure of this compound was based on the synthesis and was supported by the IR and NMR spectra. In addition to a direct reduction with LAH and $AlCl_3$ in dry ether,[12] leading to an excellent yield (86%) of the desired dibromo compound XVII, the carbinol XVIII was oxidized to the dibromo ketone XIX. Lead tetraacetate in pyridine[17] as solvent appeared to be a suitable agent for this conversion (yield 80%). Nevertheless we preferred an oxidation with CrO_3 in an acetic acid–water mixture (yield 65%) owing to the simpler procedure. From the colorless crystalline product XIX, m.p. 85·5–86°, a 2,4-dinitrophenylhydrazone, m.p. 248–248·5°, could be obtained.

Wolff–Kishner reduction of XIX proceeded poorly. More satisfactory results were obtained with the aid of a Clemmensen reduction in dioxan solution. This solvent was used instead of ethanol to prevent ether formation with the reactant. 4,4′-Dibromo-3,3′-dithienylmethane (XVII) resulted from the reaction as a colorless crystalline material in 25% yield, m.p. 38–38·5°. The structure of XVII was based on the two synthetic procedures which gave completely identical products and was supported by the IR and NMR spectra.

The ring closure reaction of the dilithio derivative of XVII gave rise to the formation of a number of different products indicating a rather complicated course for the lithium-bromine interconversion reaction with the molecules under consideration. A possible interpretation for the formation of the major products IV and XX is given in Scheme 5.

SCHEME 5



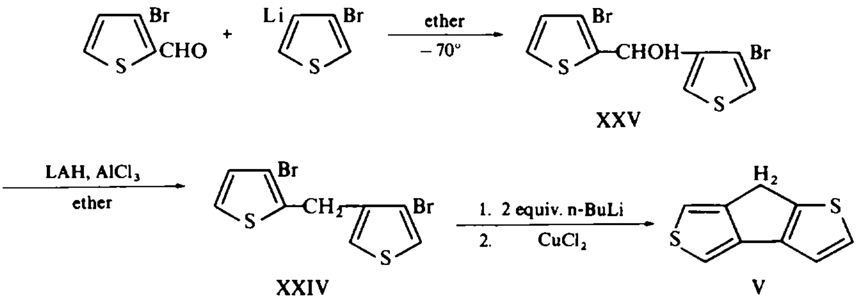
Preparative GLC showed besides a 21% yield of colorless crystalline 7*H*-cyclopenta[1.2-*c*: 3.4-*c*′]dithiophene (IV), m.p. 114–115°, small quantities of the starting material XVII, 3,3′-dithienylmethane (IX), and 4-bromo-3,3′-dithienylmethane, as was determined by GLC, NMR and UV spectroscopy and elementary analysis. The NMR spectrum of IV reveals a triplet for the methylene protons. Furthermore a white solid, m.p. 98·5–99°, with a correct elementary analysis for $C_9H_5S_2Br$ was isolated in 23% yield. That the latter compound was 6-bromo-7*H*-cyclopenta[2.1-*b*: 3.4-*c*′]dithiophene (XX) was supported by the NMR and UV spectra (Experimental). The β-position assigned to the bromine atom is based on the fact that debromination with zinc dust in acetic acid[18] proved to be unsuccessful, whereas treatment of XX with n-butyllithium, followed by hydrolysis, furnished in 21% yield 7*H*-cyclopenta[2.1-*b*: 3.4-*c*′]dithiophene (VI).

Whether 4-bromo-2,4′-dilithio-3,3′-dithienylmethane (XXI) is formed as the result of a direct metalation of the initially formed 4-bromo-4′-lithiodithienylmethane (XXII) with n-butyllithium, or as the intermediate product of a transmetalation[15] of XXII by 4,4′-dilithio-3,3′-dithienylmethane (XXIII) c.q. compound XXII itself, remains unknown. It is worthwhile noting that as opposed to the data in the literature,[15, 19] the metalation assumed here did not take place at the most acidic hydrogen atom.

In order to investigate the course of this rather unexpected reaction in detail, we treated the mixture obtained after halogen-lithium interconversion of XVII with methyl *p*-toluenesulfonate. The different products formed,[20] could be isolated and partly identified by preparative GLC. The reaction mixture appeared to contain 2% of 3,3′-dithienylmethane (IX), 4% of a monomethyl-3,3′-dithienylmethane (Me group probably in β-position), 18% of 4,4′-dimethyl-3,3′-dithienylmethane and 76% of 4-bromo-2,4′-dimethyl-3,3′-dithienylmethane, as was established by elementary analyses and their NMR spectra. This distribution clearly demonstrated the appearance of direct metalation in the 2-position to a large extent and is in agreement with the formation of a considerable amount of XX during the ring closure reaction of XVII (Scheme 5).

Logically, for the synthesis of 7*H*-cyclopenta[1.2-*b*: 3.4-*c*′]dithiophene (V), our interest was directed to the preparation of 3,4′-dibromo-2,3′-dithienylmethane (XXIV). The synthesis is outlined in Scheme 6.

SCHEME 6

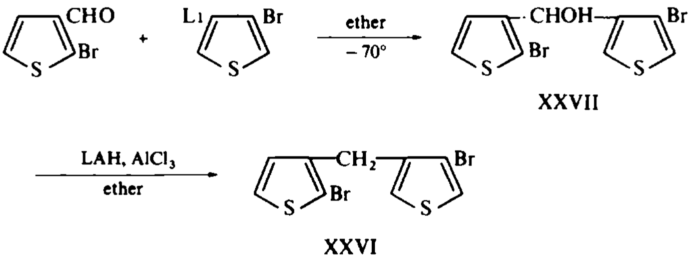


Reaction of 3-bromo-2-thiophenealdehyde[14] with 3-bromo-4-thienyllithium[15] at – 70° produced colorless crystals of 3,4′-dibromo-2,3′-dithienylcarbinol (XXV), m.p. 94·94·5°, in 70·5% yield. The structure of this coupling product followed from its formation and correct elementary analysis and was in accord with the NMR spectrum. Reduction of XXV using a mixture of LAH_4 and $AlCl_3$ in dry ether[12] furnished the dibromo dithienylmethane XXIV as a gaschromatographically pure colorless liquid, b.p. 145–150°/1·0 mm in 88% yield. Elementary analysis as well as the NMR spectrum supported the structure assigned.

Ring closure of XXIV *via* the dilithio derivative in the usual way gave 46% of 7*H*-cyclopenta[1.2-*b*: 3.4-*c*′]dithiophene (V) as a colorless crystalline material, m.p. 81–82°. Small amounts (<5%) of two by-products-one of which was 2,3′-dithienylmethane*—could be detected in the reaction mixture by GLC. The structure of V rest on the elementary analysis and was supported by the NMR and UV spectra (Experimental).

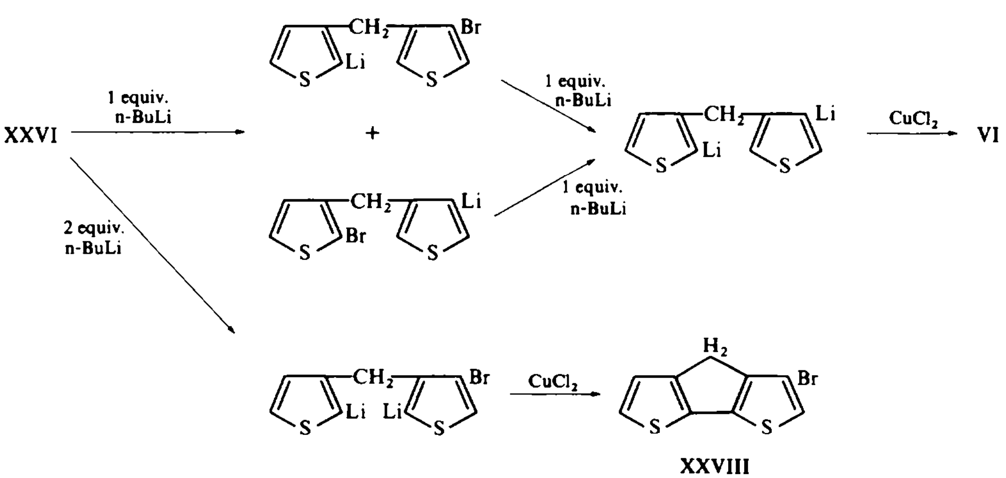
The formation of 7*H*-cyclopenta[2.1-*b*: 3.4-*c*′]dithiophene (VI), the last isomer in this series, was already mentioned during the discussion of the synthetic aspects of IV. A rational synthesis for VI *via* the familiar ring closure reaction was attempted by using the appropriate dibromo dithienylmethane XXVI (Scheme 8). The reactions resulting in the formation of XXVI are summarized in Scheme 7.

SCHEME 7



Reaction of 2-bromo-3-thiophenealdehyde[14] with 3-bromo-4-thienyllithium[15] at −70° gave in almost quantitative yield 2,3′-dibromo-3,4′-dithienylcarbinol (XXVII) as a very viscous light yellow oil. All attempts to purify the alcohol failed, mainly due to the fact that the material would not crystallize. The structure of XXVII

SCHEME 8



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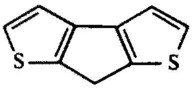
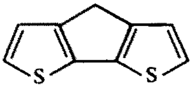
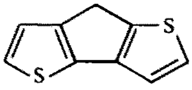
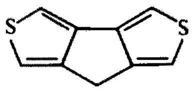
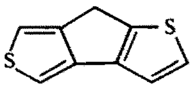
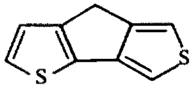
* Wolff-Kishner reduction of the known 2,3′-dithienylketone afforded this unknown compound, as a colourless liquid, b.p. 62–65°/0·1 mm, m.p. 16°.[21]

followed from the synthesis and was supported by the IR spectrum (hydroxyl frequency of 3400 cm^{-1}). Reduction of impure XXVII with a mixture of LAH and $AlCl_3$ in dry ether resulted in the formation of colorless crystalline 2,3′-dibromo-3,4′-dithienylmethane (XXVI), m.p. 31–31·5°, in approximately 75% yield. In addition to the correct elementary analysis, the NMR and IR spectra of this compound were consistent with the assigned structure (Experimental). The behavior of XXVI under ring closure conditions resembles the observations during the analogous reaction of XVII (Scheme 5) and is accounted for in Scheme 8.

Ring closure of XXVI after halogen–lithium interconversion with two equivalents of n-butyllithium at −70° afforded in a 10% yield colourless crystalline material with m.p. 91–91·5°. To this we assigned the structure 3-bromo-4*H*-cyclopenta[2.1-*b*: 3.4-*b*′]dithiophene (XXVIII) on the basis of the elementary analysis, spectral data and its unreactivity towards zinc dust in acetic acid (see above). Debromination *via* the lithio compound gave the expected cyclopentadithiophene (II), as could be detected qualitatively by NMR spectroscopy and GLC analysis.

TABLE 1. PHYSICAL AND SPECTRAL DATA OF THE CYCLOPENTADITHIOPHENES

		Yield of ring closure, %	M.p. °C	UV-spectrum[a] λ_{max}, mμ		NMR-spectrum[b] —CH_2—, τ
	I	38	66–67	220, 237 (sh)	268 298	6·41 (s)
	II	35	74–75	247,	312	6·66 (s)
	III	34	46·3–47·3	236,	287	6·52 (s)
	IV	21	114–114·5	230,	289	6·52 (t)
	V	46	81–82	217,	268	6·37 (s)
	VI	9	54–54·5	255,	297	6·58 (d)
Fluorene			116–117	207	263 297	6·36 (s)

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[a] Apart from fine structure.

[b] s = singlet, d = doublet, t = triplet.

Using preparative GLC we were able to isolate the desired 7*H*-cyclopenta[2.1-*b*: 3.4-*c*′]dithiophene (VI), m.p. 54–54·5°, as a second product in low yield (9%). The structure of this colorless crystalline analogue was supported by elementary analysis and its NMR and UV spectra. The NMR spectrum shows a doublet for the methylene protons (Experimental).

At this stage no reasonable explanation can be given for the fact that VI is formed in such a relatively low yield as compared with the other cyclopentadithiophenes. Table 1 gives a survey of the physical and spectral properties of the ring closed compounds.

Initial studies with these new condensed heterocyclic systems have been undertaken. Charge transfer spectra have been measured and will be reported on shortly.[3] Oxidation to fluorenone analogues also appear promising as does the study of the ions resulting from treatment of the cyclopentadithiophenes with n-butyllithium and lithium cyclohexylamide.[22]

UV Spectra

The UV spectra of the new cyclopentadithiophenes are reproduced along with the spectra of the corresponding dithienyls in Figs. 1–6.

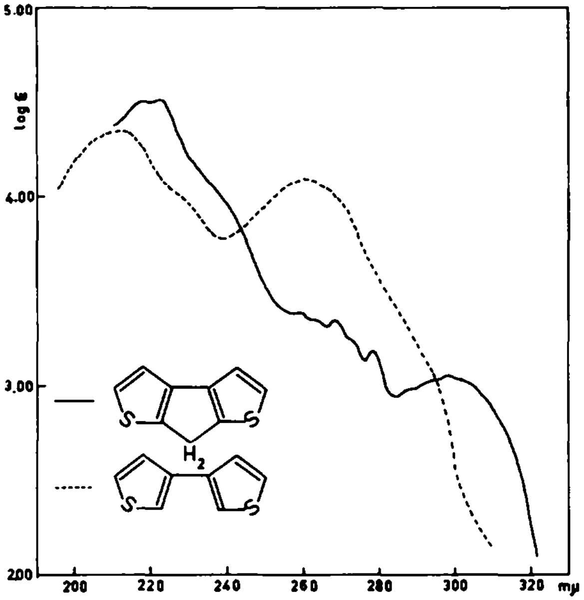

FIG. 1 UV spectra of 7*H*-cyclopenta[1.2-*b*: 4.3-*b*′]dithiophene (I) (———) and 3,3′-dithienyl (· · · · ·) in cyclohexane.

A cursory survey shows a rough resemblance between the spectra of the ring compounds and the open compounds pointing clearly to structural relationships. Owing to the increased conjugation as a result of the fixed coplanar position of the thienyl rings, the cyclopentadithiophenes absorb at slightly longer wavelengths in

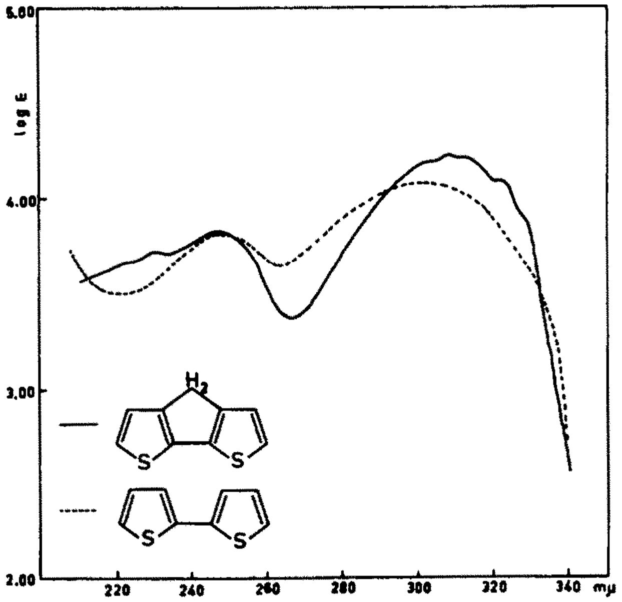

FIG. 2 UV spectra of 4*H*-cyclopenta[2.1-*b* : 3.4-*b*′]dithiophene (II) (———) and 2,2′-dithienyl (· · · · · ·) in cyclohexane.

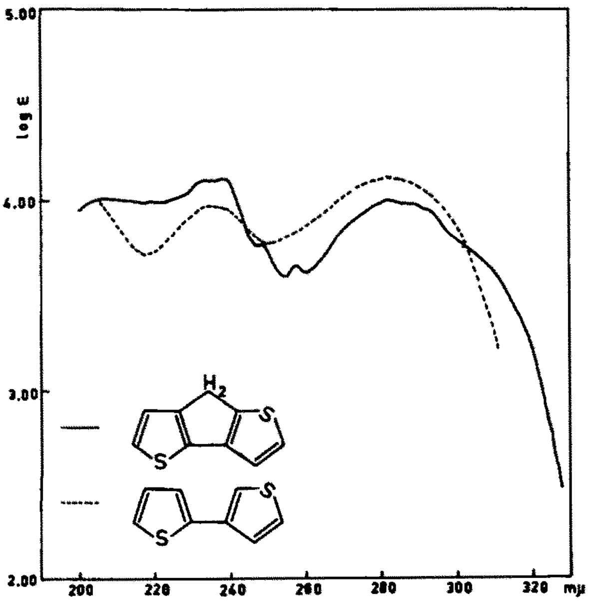

FIG. 3 UV spectra of 7*H*-cyclopenta[1.2-*b* : 3.4-*b*′]dithiophene (III) (———) and 2,3′-dithienyl (· · · · · ·) in cyclohexane.

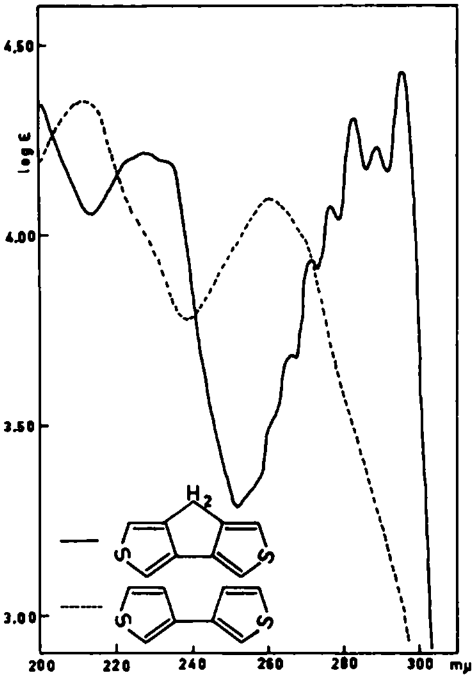

FIG. 4 UV spectra of 7H-cyclopenta[1.2-c: 3.4-c']dithiophene (IV) (———) and 3,3′-dithienyl (· · · · · ·) in cyclohexane.

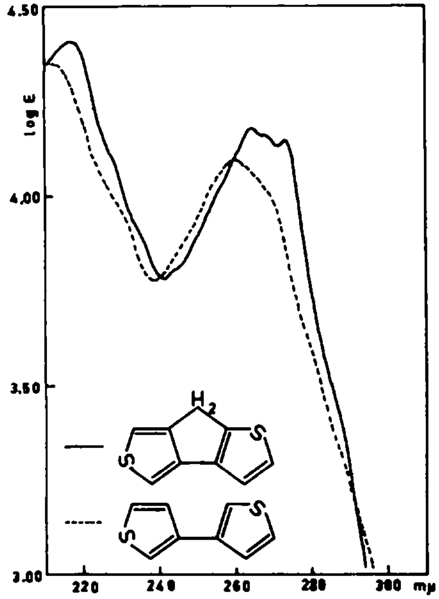

FIG. 5 UV spectra of 7H-cyclopenta[1.2-b: 3.4-c']dithiophene (V) (———) and 3,3′-dithienyl (· · · · · ·) in cyclohexane.

comparison with the dithienyls. All spectra of the "bridged" compounds reveal some fine structure, mainly in the long wavelength region, a feature which was already reported for the first isomer (I). This characteristic fine structure has been associated with a strained planar or nearly planar structure.[23]

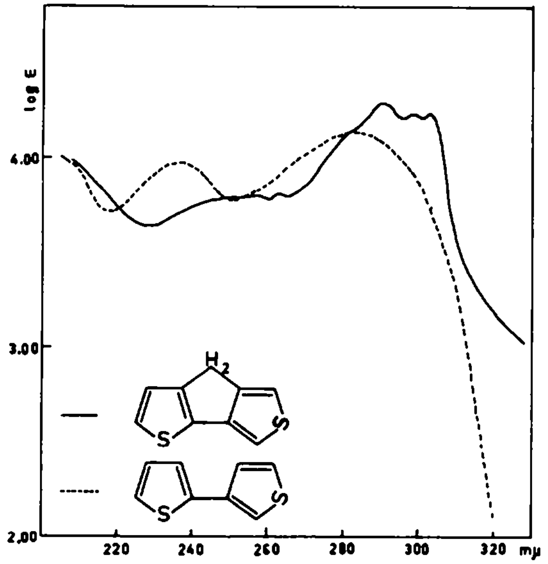

Fig. 6 UV spectra of 7*H*-cyclopenta[2.1-*b*: 3.4-*c*′]dithiophene (VI) (———) and 2,3′-dithienyl (· · · · ·) in cyclohexane.

EXPERIMENTAL

NMR spectra were obtained using a Varian A-60 spectrometer, in CCl_4 soln unless stated otherwise, with TMS (τ 10) as an internal standard. UV spectra were recorded in cyclohexane on a Zeiss PMQ II spectrophotometer. IR spectra were determined in CCl_4 soln in KBr plates or neat on a Perkin–Elmer Infracord Model 137. The alumina was made by E. Merck, A. G. Darmstadt, West Germany, no. 1077, activity I. All m.ps and b.ps are uncorrected. The micro analyses were carried out in the Analytical Section of our Department under the direction of Mr. W. M. Hazenberg.

3,3′-*Dibromo-2,2′-dithienylmethane* (VII).[9] To a stirred mixture of 15·0 g (0·092 mole) 3-bromothiophene[10] and 0·5 g (0·002 mole) $SnCl_4$ dissolved in 50 ml CS_2, a soln of 6·4 g (0·030 mole) 3-bromo-2-thenylchloride in 20 ml CS_2 was added dropwise in the course of 2 hr at room temp. After stirring for 5 hr the dark liquid was poured into a mixture of crushed ice and conc HCl. The organic layer was separated and the aqueous layer extracted with CS_2. The combined organic layers were washed with 10% $NaHCO_3$ aq and with water. After drying over $MgSO_4$ and removal of the CS_2, the excess of 3-bromothiophene was distilled off. The crude product was collected at 160–170°/3 mm and purified over an alumina column using n-hexane as the eluent. After removal of the solvent, two recrystallizations from MeOH with ice-salt cooling yielded 4·8 g (48%) of colorless VII, m.p. 37–38°.

3,3′-*Dithienylmethane* (IX). To a suspension of 5·82 g (0·153 mole) LAH in 50 ml abs ether was added a soln of 20·4 g (0·153 mole) $AlCl_3$ in 70 ml abs ether. A soln of 30·0 g (0·153 mole) 3,3′-dithienylcarbinol in 120 ml abs ether was added to this stirred reducing mixture at such a rate as to cause gentle refluxing (about 20 min). After boiling under reflux for 15 min the reaction mixture was cooled in an ice bath and treated with 120 ml EtOAc to decompose the excess reagent. The resulting suspension was poured into a mixture of 200 ml of ice–water and 40 ml of conc H_2SO_4. The layers were separated and the aqueous phase was extracted with ether. The combined organic layers were washed with $NaHCO_3$ aq and with water.

Steam distillation of the residue after removal of the solvents furnished 24·1 g (88 %) of colorless crystalline IX.

Recrystallization from EtOH gave the analytical sample m.p. 31·5–32°. The UV spectrum in cyclohexane showed a max at λ 237·5 mμ (log ε 4·04) and shoulders at λ 240 mμ (log ε 4·03) and λ 244 mμ (log ε 3·99). The NMR spectrum showed a multiplet at τ 2·80–3·22 and a singlet at τ 6·12, area ratio singlet, multiplet 1:3. (Found: C, 60·06, 60·01; H, 4·50, 4·53; S, 35·53, 35·82. $C_9H_8S_2$ requires: C, 59·94; H, 4·47; S, 35·56%).

2,2'-*Dibromo*-3,3'-*dithienylmethane* (VIII). To a vigorously stirred soln of 10·62 g (0·0664 mole) Br_2 in 318 ml water at 15° was added rapidly a soln of 6·0 g (0·033 mole) of IX in 24 ml CCl_4. After a few min the mixture turned colorless. Stirring was continued for 15 min, whereupon 125 ml ether was added and the organic layer was separated. The water layer was extracted with ether and the combined organic phases were washed with $NaHCO_3$ aq and with water. After drying over $MgSO_4$ and removal of the solvents, the residue (10·9 g) crystallized on cooling. The product was purified over an alumina column, using 500 ml n-hexane as the eluent. After evaporation of the solvent and washing of the crystalline product with 7 ml cold MeOH, one recrystallization from 40 ml MeOH with ice-salt cooling yielded 5·6 g (50%) pure colourless VIII, m.p. 43°. The UV spectrum revealed a max at λ 241 mμ (log ε 4·28). The NMR spectrum showed a singlet at τ 6·20 and two doublets centred on τ 3·34 and 2·92 (J = 6·0 c/s) respectively, area ratio singlet, two doublets 1:2. (Found: C, 31·82, 32·01; H, 1·89, 1·80; Br, 47·05, 46·91; S, 18·54, 18·94. $C_9H_6Br_2S_2$ requires: C, 31·97; H, 1·78; Br, 47·29; S, 18·96%).

4*H*-*Cyclopenta*[2,1-*b*:3,4-*b'*]*dithiophene* (II). A soln of 2,2'-dilithio-3,3'-dithienylmethane was prepared at −70° from 20·0 g (0·0592 mole) VIII in 300 ml abs ether and 95 ml 1·37N ethereal n-BuLi (0·130 mole) in a 1 litre 3-necked flask. The yellow soln was poured under N_2 in an externally cooled (−20°) dropping funnel, which was attached to a second 2 litre 3-necked flask containing 17·0 g (0·126 mole) anhyd $CuCl_2$ (dried at 130° for 0·5 hr) in 100 ml of abs ether, maintained under dry N_2. While stirring the ice-cooled suspension vigorously the dilithio compound was added dropwise in the course of 0·5 hr. After stirring at 0° for 6 hr, 200 ml 2N HCl was added and the reaction mixture filtered with suction in order to remove the greyish ppt of Cu_2Cl_2.

The ether layer was separated and the aqueous phase extracted with ether. The combined ethereal extracts were washed several times with 4N HCl, $NaHCO_3$ aq, and finally with water. After drying over $MgSO_4$ and removal of the solvent, the residue was extracted with 175 ml n-hexane and purified over an alumina column using 500 ml n-hexane as the eluent. After removal of the solvent the impure product was pressed on a buchner funnel and crystallized from a little EtOH. Sublimation *in vacuo* (0·05 mm) followed by a recrystallization from EtOH afforded 3·65 g (35%) of colourless II, m.p. 74–75°. The UV spectrum showed maxima at λ mμ, (log ε) 224 (sh) (3·67), 230 (3·72), 247 (3·83), 252 (sh) (3·79), 300 (sh) (4·15), 303 (4·19), 308 (4·23), 312 (4·22), 317 (sh) (4·16), 322·5 (4·09) and 328 (sh) (3·91). The NMR spectrum revealed a broadened singlet at τ 6·66 and two broadened doublets centred on τ 3·12 and 3·04 (J = 4·9 c/s) respectively, area ratio singlet, two doublets 1:2. (Found: C, 60·80, 60·66; H, 3·54, 3·59; S, 35·72, 35·67. $C_9H_6S_2$ requires: C, 60·61; H, 3·39; S, 35·96%).

2,2'-*Dicarboxy*-3,3'-*dithienylmethane* (X). A soln of 2,2-'-dilithio-3,3'-dithienylmethane was prepared at −70° from 4·59 g (0·0136 mole) of VIII in 45 ml abs ether and 22·0 ml 1·36N ethereal n-BuLi (0·0299 mole) and poured into solid CO_2 covered with ether. After standing for 2 hr the reaction mixture was hydrolysed with 100 ml water and the ether phase extracted with 10% $NaHCO_3$ aq. The combined aqueous layers gave on acidification with 4N HCl 3·1 g of crude product. Two recrystallizations from an 1:1 EtOH–water (Norit) yielded 2·2 g (61%) of XIII, m.p. 240–241° (dec). The UV spectrum (96% EtOH), λ_{max} 262·5 mμ (log ε 4·38). The NMR spectrum in dioxan showed a singlet at τ 5·18 and two doublets centred on τ 3·09 and 2·54 (J = 5·0 c/s) respectively. The IR spectrum (KBr) showed OH absorption at 2900 cm^{-1} and CO absorption at 1675 cm^{-1}. (Found: C, 48·93, 48·50; H, 3·15, 3·25; S, 23·50, 23·61. $C_{11}H_8O_4S_2$ requires: C, 49·23; H, 3·01; S, 23·90%).

3-*Bromo*-2,3'-*dithienylcarbinol* (XI). To a stirred suspension of 3-thienyllithium which was prepared at −70° from 119 g (0·73 mole) 3-bromothiophene[10] in 260 ml abs ether and 550 ml 1·43N ethereal n-BuLi (0·79 mole), a soln of 140 g (0·73 mole) 3-bromo-2-thiophenealdehyde[14] in 350 ml abs ether was added. After stirring overnight, the cooling bath was removed and 260 ml water was added at −10°. The ether layer was washed with water until neutral and dried over $MgSO_4$. Careful removal of the solvent furnished 182 g (90%) impure XI as an orange viscous liquid n_D^{20} 1·6463. Purification was tried in vain. The IR spectrum showed OH absorption at 3350 cm^{-1} whereas the CO absorption of the starting material (1670 cm^{-1}) had been disappeared. The UV spectrum revealed a max at λ 241 mμ (log ε ∼ 4·06).

3-*Bromo*-2,3'-*dithienylketone* (XII). An oxidizing soln of 50·0 g (0·500 mole) CrO_3 in 800 ml AcOH and

400 ml water was added to a stirred soln of 47·0 g (0·171 mole) impure XI in 250 ml AcOH, cooled to 8°, in the course of 2 hr. After stirring at room temp for 6 hr, the mixture was poured into 2 litres water. The acid layer was extracted with 1·5 litres ether and the combined organic layers were washed with conc $NaCO_3$ aq and with water until neutral. After drying over $MgSO_4$, removal of the ether and fractionation of the residue the fraction boiling between 150–160°/0·15 mm was redistilled and yielded 24·7 g (~54%) of pure XII as a light yellow viscous oil, b.p. 150°/0·1 mm, n_D^{20} 1·6922. The UV spectrum showed maxima at λ 222 mμ (log ε 4·00) and 265·5 mμ (log ε 4·12). The IR spectrum showed a CO absorption at 1640 cm^{-1}. The NMR spectrum revealed doublets centred on τ 2·97 and 2·54 (J = 5·1 c/s) and three quartets between τ 2·08–2·02, 2·56–2·46 and 2·79–2·65 ($J_{4'5'}$ = 5·0 c/s) respectively. Observed *splittings*: $J_{2'5'}$ = 2·8 c/s and $J_{2'4'}$ = 1·4 c/s. (Found: C, 39·44, 39·74; H, 1·84, 1·90; S, 23·47, 23·43. $C_9H_5BrOS_2$ requires: C, 39·56; H, 1·84; S, 23·46%).

The compound gave a 2,4-dinitrophenylhydrazone,[24] m.p. 243–244°. (Found: C, 39·91, 39·81; H, 2·29, 2·03; N, 12·25, 12·32; S, 13·84, 13·95. $C_{15}H_9BrN_4O_4S_2$ requires: C, 39·75; H, 2·00; N, 12·36; S, 14·15%).

3-*Bromo*-2,3'-*dithienylmethane* (XIII). A stirred mixture of 82 ml ethylene glycol, 22·0 g (0·0805 mole) of XII and 16·5 ml (0·340 mole) 99% hydrazine hydrate was heated at 140° for 45 min. After distilling of *in vacuo* 20 ml of turbid liquid, the mixture was cooled in an ice bath and 16·5 g (0·294 mole) powered KOH was added. The mixture was stirred and heated at 130° until the evolution of N_2 finished, whereupon 200 ml 2N HCl was added to the ice-cooled mass. Extraction with n-hexane and washing with $NaHCO_3$ aq and water were followed by drying over $MgSO_4$ and removal of the solvent. Fractionation of the residue gave 13·0 g (62·3%) of XIII as a colourless liquid, b.p. 102–106°/0·2 mm, n_D^{20} 1·6364. The UV spectrum showed a max at λ 237·5 mμ (log ε 4·03). The IR spectrum indicated no CO absorption. The NMR spectrum revealed in the multiplet between τ 3·29–2·86, two doublets centred on τ 3·23 and 3·09 (J = 5·3 c/s) respectively and a broadened singlet at τ 6·00. (Found: C, 41·55, 41·49; H, 2·68, 2·69; S, 24·29, 24·61. $C_9H_7BrS_2$ requires: C, 41·70; H, 2·72; S, 24·74%).

2',3-*Dibromo*-2,3'-*dithienylmethane* (XIV). Bromination of 10·0 g (0·0386 mole) of XIII in 40 ml $CHCl_3$ with 6·20 g (0·0388 mole) Br_2 in 180 ml $CHCl_3$ at 0° was carried out as described above. The mixture was stirred for a total of 1 hr at 0° and washed with $NaHCO_3$ aq and with water. The organic phase was refluxed with a soln of 2·5 g (0·045 mole) KOH in 50 ml EtOH for 5 hr and the resulting liquid was poured into 300 ml water. The $CHCl_3$ layer was separated, washed with water and dried over $MgSO_4$. Removal of the solvent yielded crude liquid product. Purification was effected over an alumina column using n-hexane and finally by fractionating *in vacuo*. There was obtained 9·1 g (70%) of XIV as a colourless liquid, b.p. 118–122°/0·2 mm, n_D^{20} 1·6547. The UV spectrum revealed a max at λ 241 mμ (log ε 4·10). Analytical GLC on Apiezon L at 275° showed 80% of pure XIV to be present. The NMR spectrum showed four doublets centred on τ 3·27 and 2·95 (J = 5·6 c/s), 3·16 and 3·00 (J = 5·4 c/s) respectively and a singlet at τ 6·00. (Found: C, 32·08, 32·04; H, 1·76, 1·80; S, 18·66, 18·68. $C_9H_6Br_2S_2$ requires: C, 31·97; H, 1·78; S, 18·96%).

2',3-*Dibromo*-2,3'-*dithienylcarbinol* (XV). This carbinol was prepared at −70° as described above from 38·0 g (0·157 mole) 2,3-dibromothiophene[25] in 75 ml abs ether and 130 ml 1·31N ethereal n-BuLi (0·170 mole), after 15 min stirring followed by 30·0 g (0·157 mole) 2-bromo-3-thiophenealdehyde[14] in 90 ml abs ether. Stirring was continued at −70° for 2 hr before 75 ml water were added at −10°. The crude solid material was washed with cold n-hexane and recrystallized from 1·25 litre n-hexane (Norit), a treatment giving 33·8 g (61%) slightly coloured XV, m.p. 56–58°. Four recrystallizations gave the analytically pure sample, m.p. 59–60·5°. The UV spectrum showed a max at λ 243 mμ (log ε 4·20). The IR spectrum showed a OH peak at 3340 cm^{-1}. The NMR spectrum revealed four doublets centred on τ 3·15 and 2·86 (J = 5·2 c/s), 3·08 and 2·86 (J = 5·6 c/s) respectively and broadened singlets at τ 7·21 and 3·95. (Found: C, 30·57, 30·48; H, 1·74, 1·75; Br, 44·93, 45·04; S, 18·06, 18·11. $C_9H_6Br_2OS_2$ requires: C, 30·52; H, 1·70; Br, 45·14; S, 18·11%).

2',3-*Dibromo*-2,3'-*dithienylmethane* (XIV) (reduction of XV). The reduction was carried out as described above using 3·21 g (0·085 mole) LAH in 50 ml abs ether and 11·52 g (0·086 mole) $AlCl_3$ in 60 ml abs ether for 30·0 g (0·085 mole) of XV in 180 ml abs ether. After the addition, refluxing was continued for 5 min and the excess reagent was decomposed with 100 ml EtOAc.

Fractionation *in vacuo* furnished 25·0 g (88%) of XIV, b.p. 126–130°/0·25 mm, n_D^{20} 1·6568. The spectral data were identical with those recorded earlier. Analytical GLC on Apiezon L at 275° indicated 80% of pure XIV to be present. (Found: C, 31·96, 32·09; H, 1·78, 1·76; Br, 47·18, 47·60; S, 19·19, 19·38. $C_9H_6Br_2S_2$ requires: C, 31·97; H, 1·80; Br, 47·28; S, 18·96%).

7*H-cyclopenta*[1.2-*b*: 3.4-*b*']*dithiophene* (III). A soln of 2',3-dilithio-2,3'-dithienylmethane was prepared at −70° from 15·6 g (0·0461 mole) of XIV in 270 ml abs ether and 85 ml 1·24N ethereal n-BuLi (0·105 mole) in a 500 ml 3-necked flask. Ring closure was effected with 13·6 g (0·101 mole) anhyd $CuCl_2$ in 85 ml abs ether as described above. The crude product was distilled with steam, yielding 3·4 g of a crystalline solid. Washing with cold 4:1 EtOH–water followed by recrystallization under shaking from this solvent (Norit) afforded 2·8 g (34%) of colourless III, m.p. 46·3–47·3°. Sublimation *in vacuo* (40°/0·2 mm) gave the analytical sample m.p. 46·5–47·2°. The UV spectrum showed maxima at λ mμ (log ε) 207 (4·01), 219 (4·00), 226 (sh) (4·02), 233 (4·11), 238 (4·12), 248·5 (3·77), 257·5 (3·66), 282 (4·00), 288 (sh) (3·98) and 305 (sh) (3·72). The NMR spectrum revealed a broadened singlet at τ 6·52 and four doublets centred on τ 2·90 (split in two triplets by the methylene protons: J = 0·6 c/s) and 3·06 (J = 5·0 c/s), 3·13 (broadened) and 3·04 (J = 4·8 c/s) respectively. (Found: C, 60·42, 60·53; H, 3·26, 3·32; S, 35·79, 35·76. $C_9H_6S_2$ requires: C, 60·61; H, 3·39; S, 35·96%).

2′,3-Dicarboxy-2,3′-dithienylmethane (XVI). Prepared as described above, starting from 4·60 g (0·0136 mole of XIV in 75 ml abs ether and 22·5 ml 1·31N ethereal n-BuLi (0·0295 mole). Two recrystallizations of the 3·2 g crude product from AcOH yielded 1·75 g (48%) white crystalline XVI, m.p. 241–242° (dec.). The UV spectrum (96% EtOH) showed a max at λ 249 mμ (log ε 4·26) and a shoulder at λ 266 mμ (log ε 4·16). The IR spectrum (KBr) showed a OH peak at 2850 cm^{-1} and a CO absorption at 1675 cm^{-1}. The NMR spectrum in dioxan revealed a singlet at τ 5·03 and two doublets centred on τ 3·04 and 2·54 (J = 5·0 c/s), 2·90 and 2·64 (J = 5·2 c/s). (Found: C, 49·13, 49·41; H, 3·07, 2·98; S, 23·32, 23·47. $C_{11}H_8O_4S_2$ requires: C, 49·23; H, 3·01; S, 23·90%).

4,4′-Dibromo-3,3′-dithienylcarbinol (XVIII). The preparation of this carbinol was carried out as described above for the formation of XV. Reaction of 72·6 g (0·30 mole) 3,4-dibromothiophene[20] in 100 ml abs ether with 220 ml 1·36N ethereal n-BuLi (0·30 mole) at −70°, followed by 57·3 g (0·30 mole) 4-bromo-3-thiophenealdehyde[14] in 100 ml abs ether furnished a crude liquid product which solidified on standing. Recrystallization from petrol (b.p. 60–80°) yielded 63·3 g (60%) almost colourless XVIII, m.p. 80·5–81°. The UV spectrum showed a max at λ 246 mμ (log ε 4·04). The IR spectrum (CCl_4) showed a OH peak at 3300 cm^{-1}. The NMR spectrum revealed four doublets centred on τ 2·80 and 2·98 (J = 3·3 c/s), 4·28 and 6·71 (J = 4·0 c/s). (Found: C, 30·62, 30·65; H, 1·81, 1·78; S, 17·79, 17·85. $C_9H_6Br_2OS_2$ requires: C, 30·52; H, 1·70; S, 18·12%).

4,4′-Dibromo-3,3′-dithienylketone (XIX) (*by oxidation of* XVIII *with* CrO_3). The oxidation was carried out as described above for XI. From 20 g (0·057 mole) of XVIII in 80 ml AcOH and 17 g (0·17 mole) CrO_3 in 270 ml AcOH and 130 ml water, there was obtained without distillation 16·5 g solid crude product. Recrystallization from MeOH gave 13·0 g (65·5%) colourless crystalline XIX, m.p. 85·5–86°. The UV spectrum revealed maxima at λ 226 mμ (log ε 4·18) and λ 260 mμ (log ε 4·04). The IR spectrum (CCl_4) showed a CO absorption at 1670 cm^{-1}. The NMR spectrum showed two doublets centred on τ 2·65 and 2·24 (J = 3·4 c/s). (Found: C, 31·08, 30·87; H, 1·27, 1·18; S, 18·05, 18·15. $C_9H_4Br_2OS_2$ requires: C, 30·70; H, 1·15; S, 18·21%).

4,4′-Dibromo-3,3′-dithienylketone (XIX) (*by oxidation of* XVIII *with lead tetraacetate*). To a stirred soln of 42 g (0·12 mole) of XVIII in 600 ml pyridine, 100 g (0·23 mole) freshly prepared lead tetraacetate[26] was added slowly. After refluxing and stirring for 2 hr another 20 g (0·046 mole) lead tetraacetate was added to the reaction mixture. The reaction was continued for 24 hr followed by removal of most of the solvent by distillation. The residue was acidified with 2N HCl and extracted with ether. The organic layer was separated, washed with 10% $NaHCO_3$aq and water and dried over $MgSO_4$. Fractionation *in vacuo* after removal of the ether furnished 33·6 g (80%) of XIX, b.p. 174–195°/0·5–0·9 mm.

The compound gave a 2,4-dinitrophenylhydrazone,[24] m.p. 248–248·5°. (Found: C, 34·03; H, 1·66; N, 10·40. $C_{15}H_7Br_2N_4O_4S_2$ requires: C, 33·85; H, 1·52; N, 10·53%).

4,4′-Dibromo-3,3′-dithienylmethane (XVII) (*Clemmensen reduction of* XIX). Granulated Zn (50 g, 0·76 at) was amalgamated with 150 ml 5% $HgCl_2$aq for 1 hr.[27] The supernatant liquid was decanted and 10 g (0·028 mole) of XIX in 200 ml dioxan was added, followed by 125 ml conc HCl under vigorous stirring. While stirring was continued for 26 hr at room temp an additional amount of 10 ml conc HCl was added to the reaction mixture every 6 hr. The resulting liquid was poured into water and the whole extracted with ether. The ether phase was washed with water and dried over $MgSO_4$. Removal of the solvent gave 9·5 g oil, which was purified over an alumina column using n-hexane. Crystallization from MeOH yielded 2·4 g (25%) of XVII, m.p. 38–38·5°. The UV spectrum showed a max at λ246 mμ (log ε 4·07). The NMR spectrum revealed a broadened singlet at τ 6·14 and two doublets centred on τ 3·15 (split in two triplets by the methylene protons, J = 0·9 c/s) and 2·71 (J = 3·4 c/s). (Found: C, 31·92, 32·08; H, 1·84, 1·80; S, 18·83, 18·85. $C_9H_6Br_2S_2$ requires: C, 31·97; H, 1·77; S, 18·96%).

4,4′-Dibromo-3,3′-dithienylmethane (XVII) (*reduction of* XVIII). The reduction was carried out as described above using 5·6 g (0·15 mole) LAH in 8 ml abs ether and 37·6 g (0·28 mole) $AlCl_3$ in 80 ml abs ether for

28·0 g (0·0790 mole) of XVIII in 160 ml abs ether. After the addition, refluxing was continued for 30 min. Crystallization from MeOH furnished 23·3 g (86%) of XVII.

7H-Cyclopenta[1.2-*c*: 3.4-*c*′]*dithiophene* (IV). Compound XVII (10·1 g, 0·030 mole) in 150 ml abs ether was treated with 50 ml 1·31N ethereal n-BuLi (0·065 mole) at $-70°$ in the manner as described above. Ring closure was effected with 10 g (0·074 mole) anhyd $CuCl_2$ in 100 ml abs ether in the usual way. After a first purification of the crude product over an alumina column using n-hexane, there was obtained 4·5 g crystalline solid. Preparative GLC (using a 2 m-0·4 cm diameter-Silicon Rubber SE 30 column at 208°) yielded as major products:

(a) 1·1 g (21%) of IV, purified by sublimation *in vacuo*, m.p. 114–114·5°. The UV spectrum showed maxima at λ mμ, (log ε) 223 (sh) (4·20), 227·5 (4·22), 233 (sh) (4·20), 260 (sh) (3·49), 266 (3·69), 271 (3·94), 276 (4·08), 283 (4·31), 289 (4·24), 295 (4·43), 212 (4·35), 229 (sh) (3·98), 260 (4·09) and 293 (sh) (3·13). The NMR spectrum revealed a triplet centred on τ 6·52 and two doublets centred on τ 3·17 (split in two triplets by the methylene protons: $J = 1{\cdot}2$ c/s) and 3·02 ($J = 2{\cdot}2$ c/s) respectively. (Found: C, 60·71, 60·56; H, 3·42, 3·38; S, 36·36, 35·67. $C_9H_6S_2$ requires: C, 60·61; H, 3·39; S, 35·96%).

(b) 1·8 g (23%) of XX, purified on an alumina column using n-hexane as the eluent, m.p. 98·5–99°. The UV spectrum showed maxima at λ mμ (log ε) 247 (3·71), 291 (4·32), 301 (4·22) and 305 (sh) (4·20). The NMR spectrum gave a doublet centred on τ 6·60 ($J = 1{\cdot}2$ c/s), a singlet at τ 2·99 and a doublet centred on τ 3·14 ($J = 2{\cdot}2$ c/s) in a multiplet between τ 3·02–3·20. (Found: C, 41·80, 41·79; H, 1·87, 1·88; Br, 30·30, 30·70; S, 24·73, 24·76. $C_9H_5BrS_2$ requires: C, 42·03; H, 1·96; Br, 31·08; S, 24·93%).

As by-products, we detected small amounts of starting material XVII and IX, by comparison of the NMR spectra and GLC retention times with data of authentic samples. Finally a small amount of a liquid with n_D^{20} 1·6370 was isolated, which gave a correct elementary analysis for $C_9H_7BrS_2$. All facts indicated this to be 4-bromo-3,3-dithienylmethane. The NMR spectrum showed a broadened singlet at τ 6·17 and a multiplet at τ 2·80–3.40, area ratio singlet, multiplet 2:5. (Found: C, 41·66, 41·73; H, 2·75, 2·84; S, 24·68, 24·97. $C_9H_7BrS_2$ requires: C, 41·70; H, 2·72; S, 24·74%).

Methylation of 4,4′-*dilithio*-3,3′-*dithienylmethane*. The dilithio derivative was prepared from 10·1 g (0·030 mole) of XVII and 128 ml 1·44N ethereal n-BuLi (0·079 mole) at $-70°$. Reaction of this mixture with 12·1 g (0·064 mole) methyl-*p*-toluenesulphonate in 30 ml abs ether yielded 8·0 g crude product, partly solid. The product was filtered with suction and the remaining solid recrystallized from petrol (60–80°). There resulted 6·3 g (76%) 4-bromo-2,4′-dimethyl-3,3′-dithienyl-methane, m.p. 109·5–110·5°. The NMR spectrum ($CDCl_3$) revealed two singlets at τ 2·97 and 7·68, two multiplets centred on τ 3·58 and 3·13, two doublets centred on τ 6·27 and 7·77, respectively, area ratio 1:3:1:1:2:3. (Found: C, 45·71, 45·98; H, 3·82, 3·96; Br, 27·98, 28·06; S, 22·09, 22·17. $C_{11}H_{11}BrS_2$ requires: C, 45·99; H, 3·86; Br, 27·82; S, 22·33%).

The filtrate was analyzed with preparative GLC (using a 2 m-0·4 cm diameter-Silicon Rubber SE 30 column at 165°, with temp programming up to 300°–7.5° pro min). There were isolated additionally three products in the following order:

(a) 0·1 g (2%) of IX (yield from peak area).

(b) 0·2 g (4%) monomethyl-3,3′-dithienylmethane. The NMR spectrum revealed a multiplet at τ 2·77–3·29 and two singlets at τ 6·18 and 7·90, area ratio 5:2:3. (Found: C, 61·42; H, 5·14; S, 32·83, 33·04. $C_{10}H_{10}S_2$ requires: C, 61·80; H, 5·19; S, 33·01%).

(c) 1·1 g (18%) 4,4′-dimethyl-3,3′-dithienylmethane, m.p. 30·5°–31·5°. The NMR spectrum showed two broadened doublets centred on τ 7·40 and 7·25 ($J = 3{\cdot}0$ c/s) and two broadened singlets centred on τ 6·36 and 7·90 respectively, area ratio 1:1:1:3. (Found: C, 63·03, 63·04; H, 5·75, 5·77; S, 31·13, 31·26. $C_{11}H_{12}S_2$ requires, 63·41; H, 5·81; S, 30·78%).

3,4′-*Dibromo*-2,3′-*dithienylcarbinol* (XXV). Prepared at $-70°$ as described above from 218 g (0·90 mole) 3,4-dibromothiophene[20] in 300 ml abs ether and 620 ml 1·56N ethereal n-BuLi (0·95 mole), followed by 182 g (0·95 mole) 3-bromo-2-thiophenealdehyde[14] in 300 ml abs ether. Crystallization from n-hexane yielded 225 g (70·5%) of XXV, m.p. 92–93°. An analytically pure sample after recrystallization from the same solvent had m.p. 94–94·5°. The NMR spectrum revealed a multiplet at τ 2·65–3·15 and two doublets centred on τ 3·95 and 7·22 ($J = 3{\cdot}7$ c/s) respectively, area ratio 4:1:1. (Found: C, 30·61, 30·96; H, 1·38, 1·49; S, 18·01, 18·04. $C_9H_6Br_2OS_2$ requires: C, 30·52; H, 1·70; S, 18·12%).

3,4′-*Dibromo*-2,3′-*dithienylmethane* (XXIV). Compound XXV (10·5 g, 0·0297 mole) in 40 ml abs ether was reduced as described above using 2·0 g (0·053 mole) LAH in 3 ml abs ether and 14·1 g (0·105 mole) $AlCl_3$ in 30 ml abs ether. After the addition, refluxing was continued for 0·5 hr. The crude product was purified over an alumina column using n-hexane as the eluent. Removal of the solvent yielded 8·9 g (88%) of liquid XXIV, n_D^{20} 1·6600, m.p. about 10°, b.p. 145–150°/1·0 mm. The UV spectrum showed a max at λ 245 mμ (log ε 4·03). The NMR spectrum revealed a doublet centred on τ 6·00 (J = 0·9 c/s) and a multiplet at τ 2·80–3·25, area ratio, multiplet, doublet 2:1. (Found: C, 31·82, 31·90; H, 1·79, 1·74; S, 19·07, 18·97. $C_9H_6Br_2S_2$ requires: C, 31·97; H, 1·77; S, 18·96%).

7H-Cyclopenta[1.2-*b*: 3.4-*c*′]*dithiophene* (V). Compound XXIV (9·7 g, 0·029 mole) in 150 ml abs ether was treated with 50 ml 1·30N ethereal n-BuLi (0·065 mole) at −70° in the manner described. Reaction of the mixture with 10 g (0·074 mole) anhyd $CuCl_2$ in 100 ml abs ether furnished 5·4 g crude solid which was purified over an alumina column using n-hexane. The resulting 3·4 g colourless material was subjected to analytical GLC incidating the presence of 1–3% 2,3′-dithienylmethane and 3–5% of an unknown compound. Sublimation *in vacuo*, followed by crystallization from EtOH afforded 2·4 g (46%) pure colourless crystalline V, m.p. 81–82°. The UV spectrum revealed maxima at λ mμ, (log ε) 217 (4·41), 228 (sh) (4·09), 236 (3·88), 244 (3·81), 256 (4·02), 264 (4·18), 267 (sh) (4·16), 273 (4·15) and 285 (sh) (3·51). The NMR spectrum showed a multiplet at τ 2·80–3·25 and a broad singlet at τ 6·37, area ratio multiplet, singlet 2:1. (Found: C, 60·33, 60·54; H, 3·43, 3·60; S, 35·48, 35·56. $C_9H_6S_2$ requires: C, 60·61; H, 3·39; S, 35·96%).

2,3′-*Dibromo*-3,4′-*dithienylcarbinol* (XXVII). This carbinol was prepared as described from 68·5 g (0·283 mole) 3,4-dibromothiophene[20] in 200 ml abs ether and 225 ml 1·27N ethereal n-BuLi (0·286 mole) at −70°, followed by 53·7 g (0·283 mole) 2-bromo-3-thiophenealdehyde[14] in 135 ml abs ether. The crude product, a light yellow very viscous oil, weighed 99·7 g (99%) and could not be crystallised and purified. The IR spectrum showed a OH absorption at 3400 cm^{-1} and no CO absorption of the starting material.

2,3′-*Dibromo*-3,4′-*dithienylmethane* (XXVI). Prepared as described by reduction of 14·0 g (0·039 mole) of XXVII in 100 ml abs ether with a mixture of 2·63 g (0·069 mole) LAH in 5 ml abs ether and 18·5 g (0·138 mole) $AlCl_3$ in 40 ml abs ether. After the addition, refluxing was continued for 5 min. The crude product was purified over an alumina column using n-hexane as the eluent. Crystallization from n-hexane at −40° gave 9·9 g (75%) of XXVI as white needles, m.p. 31–31·5°. The NMR spectrum revealed 5 doublets centred on τ 6·15 (J = 1·0 c/s), 3·27 and 2·86 (J = 5·6 c/s), 3·22 (split in two triplets by the methylene protons: J = 1·0 c/s) and 2·80 (J = 3·4 c/s) respectively, area ratio aromatic, aliphatic protons 2:1. The UV spectrum showed a max at λ 241 mμ (log ε 4·15). (Found: C, 31·99, 31·77; H, 1·82, 1·85; Br, 47·30, 47·17; S, 18·65, 18·63. $C_9H_6Br_2S_2$ requires: C, 31·97; H, 1·79; Br, 47·28; S, 18·96%).

7H-Cyclopenta[2.1-*b*: 3.4-*c*′]*dithiophene* (VI). Compound XXVI (9·0 g, 0·026 mole) in 160 ml abs ether was treated with 40 ml 1·29N ethereal n-BuLi at −70° in the manner described. Ring closure was carried out using 8·0 g (0·059 mole) anhyd $CuCl_2$ in 40 ml abs ether. The crude product was purified over an alumina column using n-hexane as the eluent. Removal of the solvent gave a light yellow oil, which partly solidified on standing. Addition of 10 ml n-hexane and cooling at −10° furnished crystalline material which was filtered off with suction. Recrystallization from EtOH gave 0·67 g (10%) of XXVIII m.p. 91–91·5°. The NMR spectrum showed two singlets at τ 6·65 and 3·08, two doublets centred on τ 2·92 and 3·07 (J = 5·0 c/s) respectively. Area ratio aromatic, aliphatic protons, 3:2. (Found: C, 42·10, 42·24; H, 1·96, 1·86; Br, 31·10, 30·89; S, 24·63, 24·57. $C_9H_5BrS_2$ requires: C, 42·03; H, 1·96; Br, 31·08; S, 24·93%).

The remaining filtrate was subjected to preparative GLC (using a 2 m-0·4 cm diameter-Silicon Rubber SE 30 column at 190°). Compound VI (0·42 g, 9%) could be isolated after sublimation *in vacuo*, as white needles, m.p. 54–54·5°. The UV spectrum showed maxima at λ mμ, (log ε) 245 (3·78), 255 (3·81), 263 (3·84), 281 (sh) (4·18), 287 (sh) (4·27), 291 (4·34), 299 (4·26) and 303 (4·26). The NMR spectrum revealed a doublet centred on τ 6·58 (J = 1·0 c/s), two doublets centred on τ 2·91 and 3·14 (J = 5·0 c/s) and a multiplet at τ 3·00–3·30. (Found: C, 60·34, 60·12; H, 3·45, 3·43; S, 35·31, 35·70. $C_9H_6S_2$ requires: C, 60·61; H, 3·39; S, 35·96%).

REFERENCES

[1] Part IV in the series *Steric effects in Heterocyclic Systems*. For part III, see D. J. Zwanenburg, H. de Haan and Hans Wynberg, *J. Org. Chem.* **31**, 3363 (1966).

[2] Partly taken from A. Kraak, Ph.D. Thesis, Groningen (1967).

[3] A. Kraak and Hans Wynberg, *Tetrahedron*, in press.

[4] G. Rieveschl and F. E. Ray, *Chem. Rev.* **23**, 287 (1938).

[5] G. M. Badger and J. W. Cook, *Chemistry of Carbon Compounds* (Edited by E. H. Rudd) Vol. IIIB; p. 1446. Elsevier, Amsterdam (1956).

[6] J. Druey and P. Schmidt, *Helv. Chim. Acta* **33**, 1080 (1950).

[7] Y. Poirier, L. Legrand and N. Lozac'h, *Bull. Soc. Chim. Fr.* 1054 (1966).

[8] Hans Wynberg and A. Kraak, *J. Org. Chem.* **29**, 2455 (1964).

[9] S. Gronowitz, *Advances in Heterocyclic Chemistry* (Edited by A. Katritzky) p. 75. Academic Press, New York, N.Y. (1964).

[10] S. Gronowitz and T. Raznikiewicz, *Organic Syntheses* Vol. 44; p. 9. Wiley, New York, N.Y. (1964).

[11] S. Gronowitz and Barbro Eriksson, *Arkiv. Kemi* **21**, 335 (1964).

[12] J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.* 1405 (1961).

[13] R. A. Hoffman and S. Gronowitz, *Arkiv. Kemi* **16**, 563 (1960).

[14] S. Gronowitz, P. Moses, A. B. Hörnfeldt and R. Håkansson, *Ibid.* **17**, 165 (1961).

[15] P. Moses and S. Gronowitz, *Ibid.* **18**, 119 (1961).

[16] S. Gronowitz and H. Frostling, *Acta Chem. Scand.* **16**, 1127 (1962).

[17] R. E. Partch, *Tetrahedron Letters* 3071 (1964).

[18] S. Gronowitz, *Acta Chem. Scand.* **13**, 1045 (1959).

[19] S. Gronowitz, *Arkiv. Kemi* **7**, 361 (1954).

[20] S. Gronowitz, P. Moses and R. Håkansson, *Ibid.* **16**, 267 (1960).

[21] E. Campaigne and H. L. Thomas, *J. Am. Chem. Soc.* **77**, 5365 (1955).

[22] M. J. Janssen and J. de Jong, *Rec. Trav. Chim.* **86**, 1246 (1967).

[23] H. Suzuki, *Bull. Chem. Soc. Japan* **32**, 1357 (1959).

[24] R. L. Shriner, R. C. Fuson and D. Y. Curtin, *The Systematic Identification of Organic Compounds* p. 219. Wiley, New York, N.Y. (1956).

[25] S. Gronowitz and K. Dahlgren, *Arkiv. Kemi* **21**, 201 (1964).

[26] A. I. Vogel, *A Textbook of Practical Organic Chemistry* (3rd Edition) p. 199. Longmans Green (1959).

[27] L. F. Fieser and R. G. Kennelly, *J. Am. Chem. Soc.* **57**, 1611 (1935).