Optically Active Bithienyls II. Synthesis and Resolution of 2,2'-Dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl *

SALO GRONOWITZ and HARALD FROSTLING

Organic Department, Chemical Institute, University of Uppsala, Uppsala, Sweden

Submitted in honour of the sixtieth birthday of our teacher, Professor *Arne Fredga*

Atropisomerism has been demonstrated for the first time in the 3,3'-bithienyl series. 2,2'-Dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl (V) was prepared by first coupling 5-methyl-3-thienyllithium to produce 5,5'-dimethyl-3,3'-bithienyl (III) using $CuCl_2$. Metalation of III with excess butyllithium yielded 2,2'-dicarboxy-5,5'-dimethyl-3,3'-bithienyl (IV) which upon bromination gave (V). This last compound was resolved into its antipodes by fractional crystallization of its cinchonine salt. V exhibits stable optical activity.

L argely owing to the work of Adams *et al.* (for review see Ref.[1]) many bi-phenyls with hindered rotation about the pivot bond either have been resolved into optical antipodes, or the axial asymmetry has been demonstrated by means of asymmetric transformations. Through these investigations it has been possible to obtain information regarding the relationship between the magnitude and character of the *ortho* substituents and rates of racemization.

During recent years the relative and absolute configurations of optically active biphenyls have attracted considerable interest. Mislow *et al.*[2-5] demonstrated the steric relationships existing between optically active biphenyls by means of chemical[2] and physico-chemical methods[3-5]. In particular the Fredga method of quasi-racemates[6] has proved very useful and convenient also when dealing with axially asymmetric compounds.

Attempts have been made to determine the absolute configuration by kinetic methods[7-11]. Thus Berson[7] has derived the absolute configuration of phenyl dehydrothebaine from a discussion of the stabilities of the possible transition states in the rearrangement which occurs when thebaine reacts with phenylmagnesium bromide. The absolute configurations of biphenyls

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have been determined by application of the Prelog method [12] to phenylglyoxy-lates of optically active hydroxybiphenyls [8,9,11], and use of the Meerwein-Ponndorf-Verley reduction of biaryl ketones in the presence of optically active alcohols [10]. Comparison of rotation dispersion curves has also been attempted in order to determine the absolute configurations of biphenyls [13].

Due to difficulties in synthesis very few investigations of restricted rotation in non-benzenoid aromatic systems have been undertaken. Adams et al. studied a few dipyridyls, phenylpyrroles and dipyrryls (for review see Ref.[1]). Some years ago Nord et al.[14,15] investigated two sterically hindered 2- and 3-phenylthiophenes which they synthesized from the appropriate halides by a crossed Ullmann synthesis. They also prepared some 3,3′-bithienyls by the Ullman reaction [16] but it is still difficult to prepare such compounds by this method.

A study of restricted rotation in the bithienyl series should give valuable information about the geometric and electronic properties of such compounds. It should also be possible to determine the configuration of optically active bithienyls relative to suitable biphenyls by the Fredga method. This has proved very useful for the correlation of central asymmetric thiophenes to the corresponding benzenes (for review see Ref.[6]). Desulphurization of such thiophenes with Raney-nickel was introduced by Fredga [17] as a convenient method for determining the configuration of phenylsubstituted optically active compounds relative to aliphatic compounds. It might therefore be possible to obtain information regarding the absolute configuration of bithienyls (and biphenyls) from the Raney-nickel disulphurization of optically active bithienyls.

The reaction of 3-thienyllithium derivatives, obtained by low-temperature halogen-metal interconversion of bromosubstituted thiophenes [18-20] with butyllithium, with cupric chloride, provides a very convenient route to 3,3′-bithienyls [21,22]. Sterically hindered 3,3′-bithienyls should then be easily available by metalation, halogen-metal interconversion, and other substitution reactions with these 3,3′-bithienyls. In this way a study of atropisomerism would be possible, and would entail even less preparative effort than that used in the biphenyl series.

As a first example we have prepared and resolved into its optical antipodes the compound 2,2′-dicarboxy-4,4′-dibromo-5,5′-dimethyl-3,3′-bithienyl (V). 4-Bromo-2-thiophenealdehyde (I) was prepared as described earlier from 4-bromo-2-thienyllithium, obtained through halogen-metal interconversion between 2,4-dibromothiophene and butyllithium at −70°, and N,N-dimethyl formamide [19]. It was found that the yield could be increased to 86 % by increasing the scale twentyfold. Wolff-Kishner reduction of I according to the general description given by King and Nord[23] yields 4-bromo-2-methylthiophene (II) in 84 % yield. Thus in contrast to α-bound bromine, β-bromine is not removed during Wolff-Kishner reduction. Attempts to prepare II in one step by the reaction of 4-bromo-2-thienyllithium with methyl p-toluenesulphonate or dimethyl sulphate results in a mixture of isomeric bromo-2-methylthiophenes.

Treatment of II with butyllithium and anhydrous cupric chloride gave 5,5′-dimethyl-3,3′-bithienyl (III), m.p. 135—136° in 27 % yield. This yield

I

II

III

IV

V
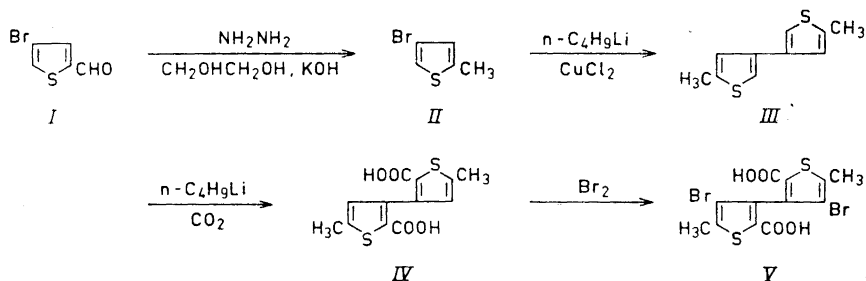
could not be increased although several variations of this preparation was attempted. Normally 50—60 % yields are obtained in this reaction [21,22]. The structure of III follows from the mode of its formation and reactions (see below). Its physical properties also differ from those of 5,5'-dimethyl-2,2'-bithienyl (m.p. 67° [24]), which would be the product if during the coupling with cupric chloride, 2-methyl-4-thienyllithium rearranged to the thermo-dynamically more stable lithium derivative [20]. The NMR-spectrum of III confirms this structure assignment. The ring hydrogen part of the NMR-spectrum of III in dimethyl sulphoxide consists of two rather broad bands at 4.85 ppm and 4.62 ppm relative to the solvent. The broadening is caused by unresolved splittings due to mutual couplings between the ring hydrogens and also between the ring hydrogens and the methyl groups. However, the width of the bands ($\approx$ 3 c/s) excludes the presence of any larger ring-coupling constant than J_{24} (1.5 c/s) [25].

Metalation of thiophenes with n-butyllithium is known to occur very selectively at the free α-positions (for review see Ref.[18]). Accordingly the product obtained by metalation of III with excess n-butyllithium followed by carbonation with dry ice was 2,2'-dicarboxy-5,5'-dimethyl-3,3'-bithienyl (IV), m.p. 254—257° (decomp.), obtained in 45 % yield.

The structure of IV is also evident from its NMR-spectrum in dimethyl sulphoxide solution. In this instance the remaining equivalent ring hydrogens at 4.20 ppm relative to the solvent show the coupling of about 1 c/s *, characteristic of a methyl group in the 2-position and a hydrogen in the 3-position of thiophenes [25].

Treatment of IV with excess bromine gave V, m.p. 311—313° (decomp.) in 80 % yield. The occurrence of nuclear bromination as opposed to side-chain bromination was evident from its NMR-spectrum which showed no absorption in the region characteristic of thiophenic hydrogens [25].

Both IV and V melt with decomposition (carbon dioxide evolution) and are best characterized by means of IR-spectra, although relatively reproducible decomposition points can be obtained if their determination is carried out in a specified manner described in the experimental part.

The dimethyl ester of V prepared by esterification with diazomethane, melts at 154—156°.

III was chosen as an intermediate instead of the more easily obtained 3,3'-bithienyl since the metalation of the latter with excess butyllithium gives on

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* Only the inner high intensity peaks of the quartet could be resolved.

carbonation a mixture of about equal amounts of 2,2'-dicarboxy-3,3'-bithienyl and 5,5'-dicarboxy-3,3'-bithienyl and these compounds are separated only with difficulty [26].

Resolution of V could be achieved by fractional crystallisation of its cinchonine salts from aqueous ethanol. All other optically active bases tested gave either oils or crystalline salts showing no resolution. Since both the cinchonine salts gave acids with the same maximum activity, it is assumed that complete resolution was obtained. This conclusion, however, is not as valid as if the same maximum activity had been obtained with different bases. The cinchonine salt of the antipode, which was dextrorotatory in acetone or alcohol, was least soluble and was apparently pure after one recrystallization. This antipode is strongly levorotatory in chloroform and in alkaline solution.

In dioxane solution this antipode shows a rotation-dispersion curve with a positive Cotton effect; the peak occurs at 334 mμ. The intense absorption permitted measurements only just beyond the peak.

The optical forms of V are very stable towards racemization. No racemization was observed when optically active V was heated in alkaline solution at 95° for 6 h.

The conjugation band at 249 mμ in the UV-spectrum of biphenyl is very sensitive to the presence of *ortho* substituents. Even a single fluorine substituent in one of the *ortho* positions of biphenyl results in a shift of this band towards shorter wave-lengths accompanied by a reduction of its intensity and in the appearance of a long wave-length band [27], regarded as originating in a benzene type transition. With very bulky *ortho* substituents the conjugation band disappears completely and the composition of the absorption spectrum is almost that provided by adding the spectra of the uncoupled parts [28]. Many attempts have been made to estimate the conformation of biphenyls from their UV-spectra (both from changes in absorption intensities and from wavelengths displacements), since it is obvious that the amount of conjugation between the rings depends on the mean interplanar angle. However, the effect of *ortho*-substituents is difficult to estimate; more over the functional relation between interplanar angle and resonance energy is not known precisely [29]. From the UV-spectra of 2,2'-ring closed and resolvable biphenyls in which the interplanar angle is practically constant it is evident, however, that the conjugation band is insensitive to small deviations from coplanarity [30,31].

The UV-spectra of bithienyls have been studied very litte. Bantjes [32] investigated the spectra of 2,2'-bithienyl and 2,3'-bithienyl and some of their derivatives and also the spectrum of 3,3'-bithienyl. It seems probable that the high intensity bands at 301 mμ in 2,2'-bithienyl, at 284 mμ in 2,3'-bithienyl and at 260 mμ in 3,3'-bithienyl correspond to the conjugation band at 249 mμ in biphenyl. In III the peak is at 264 mμ. The absorption at the lowest wave-length for 3,3'-bithienyl is in accordance with the smaller degree of conjugation which is known to be present in 3-substituted thiophenes [18].

Carboxyl groups and other carbonyl derivatives, acting as *ortho* substituents, complicate the study of the UV-spectra, however, since not only the conjugation between the rings may be changed but also the more or less coplanar arrangement between the ring and the substituent may be affected considerably [33]. It is therefore evident that considerably more data than is at
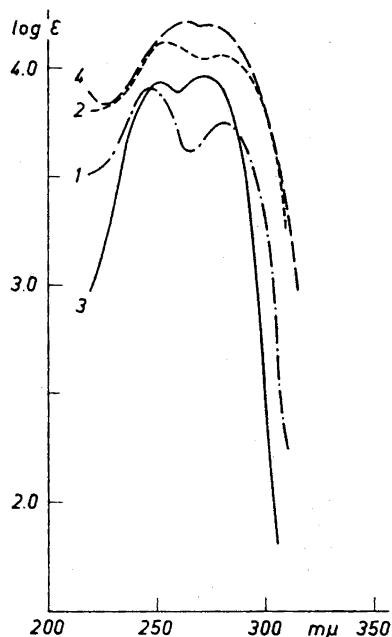
Fig. 1. UV-spectra of 4-bromo-5-methyl-2-thiophenecarboxylic acid (1), 2,2'-dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl (2), 5-methyl-2-thiophenecarboxylic acid (3), 2,2'-dicarboxy-5,5'-dimethyl-3,3'-bithienyl (4).

present available is necessary for a more detailed discussion of the UV-spectra of hindered and unhindered bithienyls.

It is apparent, however, from a comparison of the UV-spectrum of V with that of 2-methyl-3-bromo-5-thiophenecarboxylic acid (VI) (Fig. 1), that conjugation between the two rings in V is minimal. There is a close correspondence between the two spectra with V exhibiting doubled extinction. The primary band [34] in V shows a weak bathochromic shift. The spectrum of IV differs still further from that of 5-methyl-2-thiophenecarboxylic acid. In this instance the primary absorption band is shifted from 251 mμ to 262 mμ and partly obscures the secondary band at 276 mμ, which appears as an inflection.

It is evident however, that two such large groups as the carboxyl must have an appreciable influence on the conjugation band of 3,3'-bithienyl. It is therefore not permissible to regard the UV-spectrum of IV as characteristic of 3,3'-bithienyl derivatives with unhindered rotation.

EXPERIMENTAL

4-Bromo-2-thiophenealdehyde. 202 g (86 %) of 4-bromo-2-thiophenealdehyde, (b.p. 115—116°/10 mm Hg) was obtained from 1130 ml of 1.2 N butyllithium, 300 g (1.24 mole) of 2,4-dibromothiophene [25] in 400 ml of ether and 110 g (1.51 mole) of N,N-dimethyl formamide, as described in Ref.[19]

4-Bromo-2-methylthiophene. 202 g of 4-bromo-2-thiophenealdehyde, 200 ml of hydrazine hydrate (99 %) and 500 ml of ethylene glycol were placed in a 2-l three-necked flask arranged for distillation and equipped with a thermometer extending below the surface of the reaction mixture and a mechanical stirrer. The solution was heated to 130—140° and water and excess hydrazine were distilled off. After 30 min a small amount of water-

insoluble material separated from the distillate and was returned to the reaction flask. The solution was cooled to 40°, 200 g of potassium hydroxide was added and an efficient condenser was fitted to the flask. The flask was carefully heated with stirring, and at about 90° a vigorous reaction with evolution of nitrogen occurred. After the reaction had subsided the mixture was refluxed for an additional 15 min. The 4-bromo-2-methyl thiophene thus formed was steam distilled from the reaction mixture. The distillate was extracted with ether, and the ether extracts were washed with 6 N hydrochloric acid and water, dried and distilled. The yield of 4-bromo-2-methylthiophene was 167 g (88 %) b.p. 61—62°/11 mm Hg, $n_D^{20} = 1.5725$. (Found: C 34.13; H 2.93. Calc. for C_5H_5BrS (177.1): C 33.91; H 2.84).

5,5'-Dimethyl-3,3'-bithienyl. 160 g (0.91 mole) of 4-bromo-2-methylthiophene in 150 ml of anhydrous ether were added during 5 min under vigorous stirring to 1300 ml of 0.9 N butyllithium, cooled to −70° in the conventional nitrogen-swept four-necked flask. After 5 min 134 g (1 mole) of anhydrous $CuCl_2$ was added and the mixture was stirred for 3 h at −70°. After standing at room temperature for an additional 3h, 750 ml of 5 N hydrochloric acid was added with cooling and stirring. The ether phase was carefully extracted with 5 N hydrochloric acid in order to remove the cuprous chloride formed in the above reaction. After washing the ether phase with water, sodium carbonate solution and water again, followed by drying, ether and butyl bromide were removed *in vacuo*. The crystalline residue was twice recrystallised from ligroin, yielding 19 g (27 %) of 5,5'-dimethyl-3,3'-bithienyl, in the form of colourless flakes, m.p. 135—136°. (Found: C 62.01; H 5.23; S 32.90 Calc. for $C_{10}H_{10}S_2$ (194.3): C 61.81; H 5.19; S 33.00.)

2,2'-Dicarboxy-5,5'-dimethyl-3,3'-bithienyl (IV). 500 ml of 0.9 N butyllithium was added dropwise with stirring to a solution of 18.5 g (0.095 mole) of 5,5'-dimethyl-3,3'-bithienyl in 300 ml of dry ether in the conventional four-necked nitrogen-swept flask. The mixture was refluxed for 2 h and poured onto solid carbon dioxide in ether. After the temperature had risen to −10°, the mixture was hydrolysed with water. The ether phase was extracted with sodium carbonate solution and the combined aqueous phases were acidified with 2 N hydrochloric acid. The crude acid was filtered off, air-dried and then extracted twice with 30 ml of ether to remove some mono acid. The residue was recrystallized from acetic acid yielding 12 g (45 %) of 2,2'-dicarboxy-5,5'-dimethyl-3,3'-bithienyl as colourless crystals, m.p. 254—257° (decomp.). (Found: Equiv. wt 140; C 50.92; H 3.74. Calc. for $C_{12}H_{10}O_4S_2$ (282.3): Equiv. wt 141; C 51.05; H 3.57).

2,2'-Dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl (V). An excess of bromine was poured onto 7.0 g (0.025 mole) of 2,2'-dicarboxy-5,5'-dimethyl-3,3'-bithienyl. The bromine was evaporated over night and the residue heated with 200 ml of sodium carbonate solution, filtered and acidified with 2 N hydrochloric acid. The crude acid was filtered off, dried and washed with ether. Recrystallisation from acetic acid yielded 8.5 g (78 %) of 2,2'-dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl in the form of white crystals, m.p. 311—313° (decomp.). (Found: C 32.64; H 1.94; Br 36.53. Calc. for $C_{12}H_8Br_2O_4S_2$ (440.2): C 32.74; H 1.83; Br 36.32).

2,2'-Dicarbomethoxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl was prepared by methylation of the acid with diazomethane. M.p. 154—156° after recrystallisation from ethanol. (Found: C 36.21; H 2.62; Br 33.76. Calc. for $C_{14}H_{12}Br_2O_4S_2$ (468.3) C 35.91; H 2.58; Br 34.15.

5-Methyl-2-thiophenecarboxylic acid [36] was prepared by metalation of 2-methylthiophene with butyllithium followed by carbonation. M.p. 139—140°.

4-Bromo-5-methyl-2-thiophenecarboxylic acid was prepared by bromination of 5-methyl-2-thiophenecarboxylic acid in acetic acid solution. M.p. 197—199° after recrystallisation from aqueous ethanol. (Literature values [37] 197—198°).

Resolution of 2,2'-dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl

Preliminary tests on resolution. 0.001 mole of optically inactive acid and 0.002 mole of optically active base were dissolved together in various solvents, *e.g.* water, aqueous ethanol, ethanol, ethyl acetate and acetone. Oils were obtained with cinchonidine, strychnine and quinidine. Phenyl isopropyl amine, α-phenyl ethylamine, brucine and quinine gave crystalline salts of inactive acid. Only cinchonine gave resolution.

Table 1.

Crystallisation	1	2	3
ml 50 % ethanol	1000	300	75
g, salt	6	2	0.6
$[a]_D^{25}$ of acid	+ 42	+ 43	+ 43

7.0 g (0.017 mole) of 2,2'-dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl and 10.2 g (0.035 mole) of cinchonine were dissolved in 1 l of hot aqueous ethanol (50 %) and allowed to stand over-night. The precipitate was filtered off and dried. About 0.3 g of the salt was set apart, the acid isolated and the optical activity measured in acetone. The remaining salt was recrystallised from 50 % ethanol. It appears from Table 1 that complete resolution had already been obtained after one crystallisation. The mother-liquors from the second and third crystallisations were therefore evaporated to dryness *in vacuo* and the salt used for the preparation of the (+)-acid *.

Since no base was found which gave a more insoluble salt with the (—)-form, the mother liquor from the first crystallisation of the cinchonine salt was concentrated step-wise *in vacuo*. The salt which separated was filtered off and the activity of the acid measured. The course of resolution is seen in Table 2.

Table 2.

Evaporation	1	2	3	4	5	6
Remaining mother-liquor	500	250	125	75	30	0
g, salt	6	3	1	0.6	0.4	0.11
$[a]_D^{25}$	—10°	—35°	—39°	—41°	—43°	—43°

(+)-2,2'-Dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl was obtained almost quantitatively by treating the cinchonine salt with 2 N hydrochloric acid and extracting with ether. The ether was evaporated and the residue recrystallised from acetic acid, yielding white crystals, m.p. 302 — 305° (decomp.) which had the same IR-spectrum as that of the active acids. R.D. in dioxane (c 0.725), temp. 26°: $[M]_{589}$ + 240°, $[M]_{400}$ + 690°, $[M]_{350}$ + 1000°, $[M]_{334}$ + 1300°, $[M]_{327}$ + 810°.

The rotations in some other solvents are given in Table 3.

(—)-2,2'-Dicarboxy-4,4'-dibromo-5,5'-dimethyl-3,3'-bithienyl was obtained by treating the last two fractions of the more soluble cinchonine salt in the same way as described for the (+)-form. M.p. 301 — 304° (decomp.) ($[a]_D^{25}$ = —43°, c, 0.260, acetone).

Melting points of compounds which melted with decomposition were determined by placing the capillary tubes in the m.p. apparatus at a temperature of 10° below the melting point and heating with a rate of about 3°/min.

Racemization experiment. 0.0321 g of the (+)-acid was diluted to 5.00 ml with 0.100 N sodium hydroxide (a_D^{25} = — 1.22). After heating in a closed vessel to 95° for 6 h the same rotation was obtained.

Table 3.

Solvent	conc.g acid/dl	a_D^{25}	$[a]_D^{25}$	$[M]_D^{25}$
Acetone	0.836	+ 0.36°	+ 43°	+ 190°
Dimethyl sulphoxide	0.190	+ 0.10°	+ 53°	+ 230°
Ethanol	0.420	+ 0.23°	+ 55°	+ 240°
Chloroform	0.660	— 0.38°	— 57.5°	— 250°
0.1 N sodium hydroxide	0.642	— 1.22°	— 190°	— 840°

* The antipode which is dextrorotatory in acetone will be designated the (+)-acid.

Table 4. UV-data for some bithienyls and thiophenes.

Compound	Primary band		Secondary band	
	λ_{max} mμ	ε	λ_{max} mμ	ε
5-Methyl-2-thiophenecarboxylic acid	252	9 600	273	9 000
4-Bromo-5-methyl-2-thiophenecarboxylic acid	246	8 100	280	5 600
2,2′-Dicarboxy-5,5′-dimethyl-3,3′-bithienyl	262	17 200	(276)	15 500
2,2′-Dicarboxy-4,4′-dibromo-5,5′-dimethyl-3,3′-bithienyl	253	13 400	274	11 200

The UV-spectra were recorded on a Beckman quartz spectrophotometer using ethanol as the solvent. The data are given in Table 4.

The rotation dispersion curve was recorded on a Rudolph selfrecording spectropolarimeter. The *NMR-spectra* were obtained with a Varian Associates model V-4300-B high resolution spectrometer operating at 40 Mc/s in the same way as described earlier [25].

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