

## Stereochemistry of 3,3'-Bithienyls

## IV.\* On the Absolute Configuration of 2,2',4,4'-Tetrabromo-3,3'-bithienyl and 4,4'-Dibromo-2,2'-dicarboxy-3,3'-bithienyl

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By transforming optically active 4,4'-dibromo-2,2'-dicarboxy-3,3'-bithienyl (II) and 2,2',4,4'-tetrabromo-3,3'-bithienyl (III) to optically active hexabromo-3,3'-bithienyl (IV) it was found that (+)-II, (-)-III and (-)-IV had the same absolute configuration with respect to the bithienyl skeleton. Using the quasi-racemate method it was shown that (+)-II should be given the same chirality symbol as (+)-2,2'-dicarboxy-4,4'-dinitro-3,3'-bithienyl (VII), which is *R*.

Reacting (+)- and (-)-III with excess ethyllithium for 2 min at  $-70^{\circ}$  followed by carbonation gave completely racemic II. On using instead one equivalent of butyllithium, active 2,4,4'-tribromo-2'-carboxy-3,3'-bithienyl (V) was obtained.

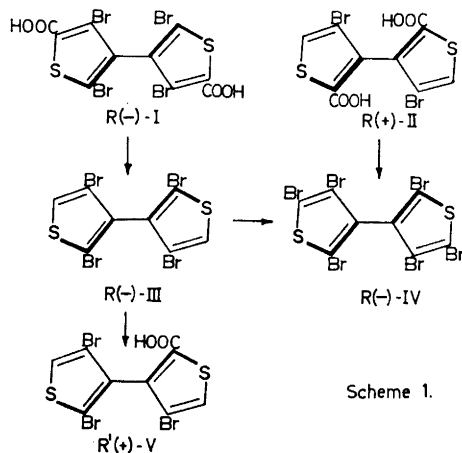
A simple rule for the specification of the abs. config. of 3,3'-bithienyls is given.

The CD curves of the enantiomers with the same abs. config. are compared.

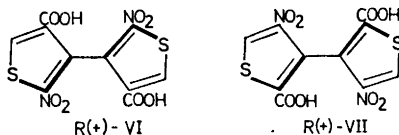
In connection with a general study of the stereochemistry of 3,3'-bithienyls, optically active 2,2',4,4'-tetrabromo-3,3'-bithienyl (III, Scheme 1) was prepared from the enantiomers of 2,2',4,4'-tetrabromo-5,5'-dicarboxy-3,3'-bithienyl (I).<sup>1</sup> The resolution of I through fractional crystallization of its brucine monosalt has now been simplified, and the preparation of optically active III from optically active I has been modified (Experimental).

The primary purpose of this paper is to report the determination of the absolute configuration of the enantiomers of tetrabromo compound III and related compounds. Gronowitz determined the abs. config. of optically active 4,4'-dicarboxy-2,2'-dinitro-3,3'-bithienyl (VI)<sup>2</sup> and 2,2'-dicarboxy-4,4'-dinitro-3,3'-bithienyl (VII)<sup>3</sup> by relating them to each other and to active

\* For Part III, see Ref. 8.



2,2'-dinitro-6,6'-diphenic acid, the abs. config. of which was known.<sup>4</sup> The method used was that of quasi-racemate formation between the corresponding dimethyl esters.<sup>5</sup> Mislow *et al.* had previously shown that this method could be adapted to optically active biphenyls.<sup>6</sup> The work of Gronowitz and Mislow indicated that it would be possible to obtain also a quasi-racemate from the enantiomers of two constitutionally similar 3,3'-bithienyls, for example the dimethyl esters of dibromo compound II and dinitro compound VII.



This was accordingly investigated, and the melting-point diagrams between the dimethyl esters of (+)- and (-)-II (VIII)<sup>7</sup> and the dimethyl ester of *R*(+)-VII (IX) are shown in Fig. 2. (Carboxylic acids are less suited because of their tendency to decarboxylate at elevated temperatures.) The phase diagram in Fig. 1 indicates that (+)-VIII and (-)-VIII form a true racemate, as do the active forms of IX.<sup>3</sup> The esters exhibit the same mode of rotation as the corresponding acids. (+)-VIII and (+)-IX gave a melting-point diagram of the eutectic type (Fig 2), while the forms with opposite mode of rotation gave a diagram exhibiting a weakly pronounced quasi-racemate. The diagrams indicate that the methyl esters with the same mode of rotation also have the same abs. config.

Tetrabromo compounds I and III are structurally much too different from the dinitro compounds VI and VII, and also from diacid II, to be expected to form a quasi-racemate with anyone of them. Therefore, efforts were made to secure a relation between II and III concerning the chirality by chemical methods. Two possible paths were investigated, one with active III as starting material, and the other starting with active II.<sup>7</sup>

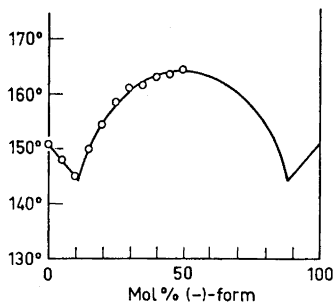


Fig. 1. (+)- and (-)-4,4'-Dibromo-2,2'-dicarbomethoxy-3,3'-bithienyl.

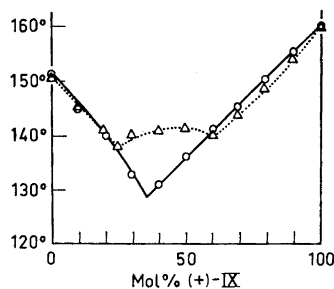


Fig. 2. (+)-4,4'-Dibromo-2,2'-dicarbomethoxy-3,3'-bithienyl (VIII) and *R*(+)-2,2'-dicarbomethoxy-4,4'-dinitro-3,3'-bithienyl (IX) (circles). (-)-4,4'-Dibromo-2,2'-dicarbomethoxy-3,3'-bithienyl (VIII) and *R*(+)-2,2'-dicarbomethoxy-4,4'-dinitro-3,3'-bithienyl (IX) (triangles).

The simplest way seemed to be to treat optically active III with alkyllithium at  $-70^{\circ}$  followed by carbonation, which should give diacid II. This reaction easily took place with racemic III.<sup>1</sup> If activity could be detected in the product, even if some racemization occurred, the relations between the two compounds would be clear. It was also of great theoretical interest to determine whether reactions of this type could be performed with retained activity in the product. However, when optically active III was reacted with ethyllithium or butyllithium for 2 min at  $-70^{\circ}$ , and the mixture thereafter was carbonated, only racemic diacid II was obtained. When shorter reaction times and less than two equivalents of alkyllithium were used, the product exhibited activity, but this was shown to originate from 2,4,4'-tribromo-2'-carboxy-3,3'-bithienyl (V), which was separated from the diacid II by TLC. As a by-product, 4,4'-dibromo-2-carboxy-3,3'-bithienyl was obtained, which could not be separated from monoacid V. This by-product was probably formed by partial hydrolysis of the intermediate 2,2'-dilithium derivative and was thus certainly inactive, since the diacid derived from the latter was inactive. By using gaseous carbon dioxide instead of dry ice, the formation of the by-product could be avoided.<sup>8</sup>

Since optically active II is stable at room temperature,<sup>7</sup> the racemization probably occurred in the intermediate 4,4'-dibromo-2,2'-dilithium-3,3'-bithienyl. Two mechanisms are possible, either *via* a *trans* coplanar conformation in which the small lithium atoms pass the bromines, or *via* a *cis* coplanar conformation. In the latter, the bulky 4,4'-bromines must pass each other, and this implies that the molecule must be bent, bringing the lithium atoms closer to each other. This might be possible if it were assumed that an intramolecular dimeric aggregate is formed. Colligative measurements indicate that *sp*<sup>2</sup>-hybridized organolithium compounds such as phenyllithium may be dimeric.<sup>9</sup> It is remarkable that the racemization was complete, despite the short reaction times and the low temperature. Reactions of this type will be further investigated.

Pure optically active V,  $[\alpha]_D^{25} = +15.6^\circ$  (EtOH), was prepared by reacting optically active III with less than one equivalent of butyllithium at  $-70^\circ$  followed by carbonation. In this case, probably no racemization occurred during the reaction, since the bulky 4'-bromine would then be forced to pass either the 2- or 4-bromine. The product therefore may be considered to be of high optical purity. The mode of rotation was different in the starting material, and the product, *i.e.* levorotatory III, gave dextrorotatory V. The rotations were measured in different solvent, benzene and ethanol, respectively.

The second way in which an attempt was made to establish the relation between the chirality of optically active II and III involved decarboxylation of diacid II,  $[\alpha]_D = +44^\circ$  (EtOH), with mercuric acetate in boiling acetic acid for 15 min, and treating the resulting acetoxymercury derivative with an aqueous bromine-potassium bromide solution. In the latter stage, mercury is substituted for bromine,<sup>10</sup> and since also free positions in thiophenes may easily be mercurated under the conditions used,<sup>10</sup> hexabromo-3,3'-bithienyl, (IV)  $[\alpha]_D = -3.8^\circ$  (benzene) was obtained instead of tetrabromo compound II. Treatment of III,  $[\alpha]_D = -20^\circ$  (benzene), with excess bromine afforded hexabromo-3,3'-bithienyl,  $[\alpha]_D = -12^\circ$  (benzene). Obviously some racemization took place in the decarboxylation reaction. From IR and CD spectra, it was evident that the activity in both preparations originated from hexabromo-3,3'-bithienyl. It was thus shown that (-)-I, (-)-III, (-)-IV, (+)-II, and (+)-V must have the same absolute configuration of the bithienyl skeleton. This cannot be altered in the above reactions unless the molecule assumes conformations in which the aromatic rings lie in the same plane, and this would only result in racemization. The chirality of I relative to III follows from the preparation of optically active III.<sup>1</sup>

(+)- and (-)-II have previously been prepared by oxidation of (+)- and (-)-4,4'-dibromo-2-carboxy-2'-hydroxymethyl-3,3'-bithienyl, respectively,<sup>7</sup> and therefore the chirality of the latter compounds can be deduced from that of optically active II. To check the optical purity, racemic II was resolved through fractional crystallization of its brucine salt. The salt of the dextrorotatory form was purified by repeated crystallization to yield (+)-II with the same magnitude of rotation as obtained previously.

Before the optically active compounds mentioned above are assigned chirality symbols, the application of existing rules to 3,3'-bithienyls should be made clear. The new rules proposed in 1966 by Cahn *et al.*<sup>11</sup> for the specification of axial chirality do not alter the symbols given by Gronowitz to the enantiomers of VI and VII<sup>3</sup> using the rules from 1956.<sup>12</sup> In 3,3'-bithienyls, the axis of chirality is the pivot bond, and only C-3 and C-3' are situated on that axis. According to the new rules, the two pairs of carbon atoms C-2, C-4 and C-2', C-4' should be investigated first, since they are bound directly to atoms on the axis of chirality. To see which carbon atom in each pair takes precedence over the other, not only the substituents should be considered, but also the atoms in the bithienyl skeleton. Thus in both 2,2'-dicarboxy-4,4'-dinitro-3,3'-bithienyl and 4,4'-dicarboxy-2,2'-dinitro-3,3'-bithienyl, C-2 takes precedence over C-4, and C-2' over C-4', since the path to higher order of precedence in both cases leads from C-2 and C-2' to the ring sulphur atoms, but from C-4 and C-4' to carbon or nitrogen atoms. This gives the same symbols

for the enantiomers of VI and VII as the old rules. The two enantiomers with, for example, *R*-chirality have also the same abs. config. of the bithienyl skeleton.

In the same way, the chirality symbol for the enantiomers I, III and IV shown in Scheme 1 is found to be *R*. In all three compounds, the 2,2'- and 4,4'-substituents are equal, and the ring sulphur atoms give precedence to C-2 and C-2'. In II, the bromine atoms give precedence to C-4 and C-4', and since the order is altered in both rings, the chirality symbol is still *R* for the form in Scheme 1. It can be shown that all 3,3'-bithienyls having  $C_2$  symmetry with or without eventual 5- or 5'-substituents will always be assigned the chirality symbol *R*, if the bithienyl skeleton has the absolute twist (*R*-chirality), shown by the formulas in Scheme 1, and *vice versa*. Since the 1- and 5-positions of each ring are always different, it will never be necessary to consider a 5-substituent to determine the order of precedence of C-2 and C-4.

In a 3,3'-bithienyl possessing  $C_1$  symmetry with *R*-chirality of the bithienyl skeleton, the chirality symbol will be *R* or *S*, depending on whether or not the corresponding carbon atoms in the two rings take precedence. In formula V, C-2 is of higher order than C-4 (left ring). Both are bound to bromine, and C-2 is further bound to sulphur, but C-4 to C-5. In the other ring, C-4 has higher precedence than C-2, since it is attached to bromine and carbon, while C-2 is bound to sulphur and carbon. The chirality symbol for the enantiomer V in Scheme 1 is *S*, despite the *R*-chirality of the ring system. It is of no importance from which side the molecule is viewed.

Since it will often be confusing to speak about "the same chirality" of compounds which have been designated by different chirality symbols, and in order to avoid tedious explanations which would be necessary in such cases, we suggest the following rule for the specification of the chirality of 3,3'-bithienyls:

*A 3,3'-bithienyl will be assigned the chirality symbol R (or S) if the unsubstituted compound with unchanged chirality of the bithienyl skeleton would be assigned the chirality symbol R (or S). If the symbol should be altered, using the general rules,<sup>11</sup> this is indicated with R' (or S').*

Using this rule, all enantiomers shown in Scheme 1 will be assigned the chirality symbol *R* (*R'* for compound V), as they all have the same twist\* of the bithienyl skeleton, and the similarities between compounds V, III and II are more pronounced.

From the melting-point diagrams in Fig. 2 it follows that (+)-II should be given the symbol *R*. By the transformation mentioned above, the symbols for the enantiomers of I and III - V can be deduced, as shown in Scheme 1 and in Experimental.

The CD curves of compounds I - V and dinitro compound VII, which have been assigned the same abs. config. (*R*) with respect to the bithienyl skeleton, are shown in Figs. 3 and 4. The absorption band near 250 m $\mu$  is in the CD spectra resolved into two bands of opposite sign. In the 5,5'-dicarboxy compound I, this absorption band and the corresponding CD bands are shifted

\* This is not necessarily the *trans-skew* conformation P(x) shown in Scheme 1, but may instead be the *cis-skew* conformation M(x),

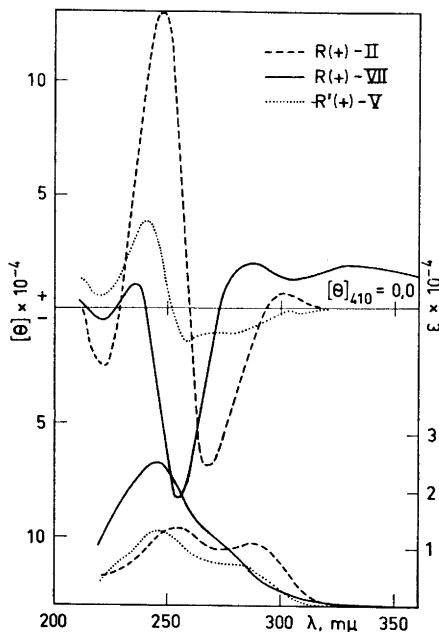


Fig. 3. CD and UV spectra (dioxane) of 2,2'-dicarboxy-4,4'-dinitro-3,3'-bithienyl (VII), 4,4'-dibromo-2,2'-dicarboxy-3,3'-bithienyl (II), and 2,4,4'-tribromo-2'-carboxy-3,3'-bithienyl (V).

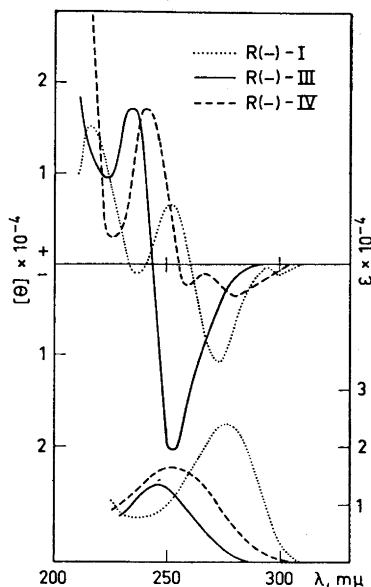


Fig. 4. CD and UV spectra (dioxane) of 2,2',4,4'-tetrabromo-3,3'-bithienyl (III), hexabromo-3,3'-bithienyl (IV), and 2,2',4,4'-tetrabromo-5,5'-dicarboxy-3,3'-bithienyl (I).

about 25  $m\mu$  towards higher wavelengths. In all CD spectra, the negative bands come at higher wavelengths than the positive ones. The two opposite CD effects are not equally pronounced in all curves. In compounds I, II and III, the negative curve and the positive are of comparable amplitude, in compounds IV and V the positive effect is greater, and in dinitro compound VII the negative one.

At higher wavelengths (260–310  $m\mu$ ), one or more CD bands of low amplitude appear. These bands are negative in compounds I, IV and V, but positive in diacids II and VII, which further underlines the similarities of the latter two compounds. The CD spectrum of VII has been discussed previously by Gronowitz.<sup>3</sup>

#### EXPERIMENTAL

*R(-)*- and *S(+)*-2,2',4,4'-Tetrabromo-5,5'-dicarboxy-3,3'-bithienyl (I). To 15.5 g (0.027 mol) of racemic I<sup>1</sup> in 200 ml of hot ethanol (96%), 5.5 g (0.014 mol) of anhydrous brucine in 100 ml of hot ethanol was added. The solution was refluxed for 2 h and allowed to cool overnight, yielding 10.8 g of salt. The carboxylic acid,  $[\alpha]_D^{25} = -7.1^\circ$ , was liberated from 0.2 g of the salt. The remainder was recrystallized from ethanol to yield 9.7 g, from which 5.4 g (31%) of *R(-)*-I,  $[\alpha]_D^{25} = -7.9^\circ$  (EtOH), was obtained as crystals containing carbon tetrachloride.<sup>1</sup>

To the hot mother liquor of the first crystallization, a further 5.4 g (0.014 mol) of anhydrous brucine was added. The solution was boiled for 15 min, during which time the salt crystallized. After cooling, 8.0 g of solid was filtered off, yielding 3.5 g (20 %) of *S*(+)-I,  $[\alpha]_D^{25} = +7.9^\circ$ . The acids were liberated from the salts as described previously.<sup>1</sup> CD of the *R*(-)-form (Fig 4):  $[\theta]_{299} - 1050$ ;  $[\theta]_{274} - 10\ 500$ ;  $[\theta]_{252} + 6700$ ;  $[\theta]_{237} - 1160$ ;  $[\theta]_{217} + 15\ 100$ . UV:  $\epsilon_{276} 24\ 200$ .

*R*(-)- and *S*(+)-2,2',4,4'-Tetrabromo-3,3'-bithienyl (III). A solution of 5.0 g (7.7 mmol) of *S*(+)-I and 10 g (31 mmol) of mercuric acetate in 100 ml of acetic acid was refluxed for 4 h. On cooling, 7.3 g of a solid crystallized. 1.0 g was recrystallized from acetic acid, yielding 0.7 g of *S*(+)-5,5'-diacetoxymercuri-2,2',4,4'-tetrabromo-3,3'-bithienyl, m.p.  $> 350^\circ$ ,  $[\alpha]_D^{25} = +23.8^\circ$  (dioxan).

The remaining 6.3 g of solid and the acetic acid solution were added to 130 g of sodium chloride in 500 ml of water. After stirring for 15 min at room temperature, 100 ml of conc. hydrochloric acid was added, after 10 min followed by 50 ml of ether and 25 ml of carbon disulphide. The mixture was stirred vigorously for 1 h, the layers were separated, and the aqueous phase was extracted with carbon disulphide. The combined organic phases were evaporated, yielding 2.9 g of a yellow solid,  $[\alpha]_D^{25} = +16^\circ$ , which was dissolved in carbon disulphide and chromatographed on an alumina column. Elution with carbon disulphide: petroleum ether (b.p.  $40-60^\circ$ ) 1:4 gave 2.2 g (67 %) of pure *S*(+)-2,2',4,4'-tetrabromo-3,3'-bithienyl, m.p.  $163-164^\circ$ ,  $[\alpha]_D^{25} = +20^\circ$  as white crystals.

In the same way, except for the isolation of the mercury derivative, *R*(-)-III, 2.3 g (62 %),  $[\alpha]_D^{25} = -20^\circ$  was obtained from 5.0 g of *R*(-)-I.

The upper part of the alumina column grew black during the elution, indicating the presence of mercury compounds in the raw product. CD of the *R*(-)-form (Fig 4):  $[\theta]_{254} - 20\ 200$ ;  $[\theta]_{235} + 17\ 200$ . UV:  $\epsilon_{245} 13\ 200$ .

Reaction between optically active 2,2',4,4'-tetrabromo-3,3'-bithienyl and alkyllithium. To 1.0 g (2.1 mmol) of *S*(+)-III,  $[\alpha]_D = +20^\circ$ , in 20 ml of anhydrous ether cooled to  $-70^\circ$ , 10 ml of 0.85 M ethyllithium was added. After 2 min, the mixture was poured onto crushed dry ice. Work-up in the usual way gave 0.6 g (70 %) of racemic 4,4'-dibromo-2,2'-dicarboxy-3,3'-bithienyl (II) ( $[\alpha]_D < 0.1^\circ$ ,  $c = 2.6$ , EtOH).

In a subsequent experiment, using 2.1 mmol of *S*(+)-III and 3.5 mmol of ethyllithium, 0.5 g of a product was obtained,  $[\alpha]_D = -4.4^\circ$  (EtOH), which according to PMR consisted of about 70 % II, 20-25 % 2,4,4'-tribromo-2'-carboxy-3,3'-bithienyl (V), and 5-10 % 4,4'-dibromo-2-carboxy-3,3'-bithienyl. TLC (silica, 3 mm), using dioxan: benzene: acetic acid 25: 90: 2 as solvent, gave two bands. From the upper one, a mixture of the two monocarboxylic acids was obtained,  $[\alpha]_D = -12^\circ$ . The lower band gave inactive diacid II. In the IR spectrum between  $950\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$ , diacid II exhibited a peak at  $1008\text{ cm}^{-1}$ , 4,4'-dibromo-2'-carboxy-3,3'-bithienyl at  $997\text{ cm}^{-1}$ , and monoacid V peaks at  $975\text{ cm}^{-1}$  and  $1021\text{ cm}^{-1}$ . The CD spectrum of the active material was identical with that of pure active monoacid V.

*R*(+)-2,4,4'-Tribromo-2'-carboxy-3,3'-bithienyl (V). To 0.80 g (1.6 mmol) of *R*(-)-III in 20 ml of anhydrous ether cooled to  $-70^\circ$ , 1.4 ml of 1.0 M butyllithium<sup>8</sup> was added. After 2 min gaseous carbon dioxide was bubbled into the reaction mixture. Work-up gave 0.5 g of an acidic product,  $[\alpha]_D = +14.5^\circ$ . IR and PMR spectra<sup>8</sup> showed that the main product was monoacid V, containing 5-10 % diacid II as the only by-product. Recrystallization from ethanol-water gave 0.3 g of V, m.p.  $236-240^\circ$ ,  $[\alpha]_D^{25} = +15.6^\circ$ . [Found: C 24.64; H 0.70; S 14.84. Calc. for  $C_9H_3Br_3O_2S_2$  (447.0): C 24.18; H 0.68; S 14.35.] CD (Fig. 3):  $[\theta]_{311} - 1280$ ;  $[\theta]_{281} - 10\ 900$ ;  $[\theta]_{259} - 14\ 200$ ;  $[\theta]_{239} + 38\ 000$ . UV:  $\epsilon_{279} 7420$ ;  $\epsilon_{247} 13\ 600$ .

*R*(-)-Hexabromo-3,3'-bithienyl (IV). A. From *R*(-)-III. Excess bromine was poured onto 0.10 g of *R*(-)-III. After evaporation of the bromine, the residue was boiled with ethanol, the insoluble part was filtered off and recrystallized from ligroin, b.p.  $80-110^\circ$ . 50 mg of *R*(-)-IV was obtained, m.p.  $142-142.5^\circ$ ,  $[\alpha]_D^{25} = -12.2^\circ$ , with the same IR spectrum as the racemic compound, except for a singlet instead of a doublet at  $1250\text{ cm}^{-1}$ . CD (Fig. 4):  $[\theta]_{282} - 3380$ ;  $[\theta]_{260} - 2280$ ;  $[\theta]_{244} + 17\ 000$ . UV:  $\epsilon_{252} 16\ 700$ .

B. From *R*(+)-II. A solution of 0.2 g (0.5 mmol) of *R*(+)-II,  $[\alpha]_D = +44^\circ$ , and 1.6 g of mercuric acetate (5 mmol) in 10 ml of acetic acid was heated to reflux. After 10 min, a precipitate appeared, and after 15 min, 2.5 ml of a KBr<sub>3</sub> solution made from 16 g (0.1 mol) of bromine and 35.7 g (0.3 mol) of potassium bromide in 100 ml of water was added. The reaction was instantaneous, giving 0.15 g of a solid,  $[\alpha]_D = -3^\circ$ , which was im-

mediately filtered from the hot solution. Chromatography on alumina, as described for III, yielded 0.1 g of IV,  $[\alpha]_D^{25} = -3.8^\circ$  (31 % optical purity or less). The CD spectrum was identical with that of the product under A (calculated to the same optical purity). The IR spectrum was identical with that of racemic IV.

R(+)-4,4'-Dibromo-2,2'-dicarboxy-3,3'-bithienyl (II). 8.2 g (0.02 mol) of racemic II and 15.8 g (0.04 mol) of anhydrous brucine were dissolved in 500 ml of hot ethanol. After cooling overnight, the surface of the glass vessel was covered with a transparent film, containing a few collections of small crystals which slowly increased. After 7 days, the film had disappeared, and 9.5 g of salt was obtained, which was recrystallized without difficulties from ethanol. The progress of the resolution is given below. After each crystallization, the carboxylic acid was liberated from 0.2 g of salt, and the activity measured in ethanol.

Crystallization	1	2	3	4
ml ethanol	500	200	185	180
g salt	9.5	7.3	6.1	4.7
$[\alpha]_D^{25}$ of acid	+30°	+41°	+44°	+44°

The activity was also measured in dioxan;  $[\alpha]_D^{25} = +57^\circ$  and in 0.1 N NaOH;  $[\alpha]_D^{25} = +222^\circ$ . CD (Fig. 3):  $[\theta]_{300} + 7300$ ;  $[\theta]_{266} - 68\ 500$ ;  $[\theta]_{244} + 130\ 000$ ;  $[\theta]_{219} - 25\ 000$ . UV:  $\epsilon_{272} 9800$ ;  $\epsilon_{252} 13\ 700$ .

The mother liquors of the first two crystallizations were mixed and evaporated. From the residue, 4.1 g of II,  $[\alpha]_D^{25} = -18^\circ$  was obtained. The (-)-form was not further resolved, since this resolution was made to check the optical purity of previous preparations from optically active 4,4'-dibromo-2-carboxy-2'-hydroxymethyl-3,3'-bithienyl, giving II with  $[\alpha]_D^{25} = +44^\circ$  and  $-44^\circ$ .<sup>7</sup>

R(+)-2,2'-Dicarboxy-4,4'-dinitro-3,3'-bithienyl (VII).<sup>3</sup> CD (Fig. 3):  $[\theta]_{332} + 18\ 300$ ;  $[\theta]_{266} + 19\ 000$ ;  $[\theta]_{255} - 83\ 000$ ;  $[\theta]_{235} + 10\ 700$ ;  $[\theta]_{211} - 6100$ . UV:  $\epsilon_{245} 33\ 000$ .

*Melting point diagrams.* The mixtures of the carboxylic esters were obtained by mixing carefully measured volumes of acetone solutions of known concentration of each compound. After evaporation of the solvent at room temperature, the residue was powdered and dried, and the melting points determined using a hot-stage microscope.

The IR spectra were recorded on a Perkin-Elmer 257 grating infra-red spectrophotometer. The CD curves were obtained at 27° with a Cary 60 recording spectropolarimeter, equipped with a circular dichroism accessory, using dioxane solutions containing  $10^{-3}$  mmol of sample/10 ml in 1 mm cells. The UV spectra (dioxane) were recorded on a Unicam SP 800 spectrophotometer.

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