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STUDIES ON THE CHEMISTRY OF HETEROCYCLICS. XXX.[1] BIAROMATICS IN THE THIOPHENE SERIES. III. THE ULTRAVIOLET ABSORPTION SPECTRA OF BIPHENYL TYPE COMPOUNDS CONTAINING THE THIOPHENE RING

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The absorption spectra of biaromatics known to possess restricted rotation due to bulky *ortho* substituents have been determined by several investigators (1–7), wherein it was found that non-coplanar biphenyls possess an absorption spectrum very similar to the uncoupled parts. Similar results have been obtained on extension into the heterocyclic series (8). In a continuation of our earlier studies (9), this investigation is concerned with the study of biphenyl type stereoisomerism in the β-phenylthiophene and bithienyl series. In view of the latter, it was thought to be of interest to ascertain the effect of the thiophene ring on the ultraviolet absorption spectra of the biaromatics as well as the effect of the substituents attached to the heterocyclic moiety. In the preceding communication (10) the preparation of these compounds was presented.

The ultraviolet spectra of all the thiophene biaromatics were determined in absolute ethanol in an endeavor to ascertain the steric effects present in these compounds. In addition, it was also necessary to obtain the spectra of some of the uncoupled fragments, *viz.*, 2,5-dimethyl-3-thenoic acid, methyl 2,5-dimethyl-3-thenoate and 2,5-dimethyl-3-thenamide as well as that of the benzene moiety, *m*-nitrotoluene; although the spectra of the latter had already been determined in isoöctane (11) as well as in a solvent presumed to be ethanol (6), it was decided to redetermine it in absolute ethanol in order to best facilitate a comparison of this type. The compounds studied were 2,5-dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoic acid, its methyl ester and its amide, 2,2′,5,5′-tetramethyl-3,3′-bithienyl-4,4′-dicarboxylic acid, 2,2′,4,4′-tetranitro-5,5′-dimethyl-3,3′-bithienyl, 3,3′,5,5′-tetranitro-2,2′-bithienyl, 3,3′-dinitro-5,5′-diacetyl-2,2′-bithienyl and 3,3′-dinitro-2,2′-bithenyl-5,5′-dicarboxylic acid (dimethyl ester). The purpose of these measurements was to establish whether a correlation between the intensity of absorption and the approach to coplanarity could be observed.

EXPERIMENTAL

Materials. The preparation of all these compounds has been described elsewhere (10, 12). Further purification of the compounds to be studied has been carried out in the following manner:

2,5-Dimethyl-3-thenoic acid (m.p. 120–120.5°), 2,5-dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoic acid (m.p. 212–212.5°), 2,2′,4,4′-tetranitro-5,5′-dimethyl-2,2′-bithienyl (m.p. 185–186°), methyl 2,5-dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoate (m.p. 58.5°), and the corresponding amide (m.p. 177.5°) were all recrystallized from ethanol.

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[1] For paper XXIX of this series see ref. No. 10.

3,3′-Dinitro-5,5′-dicarbomethoxy-2,2′-bithienyl (m.p. 169–169.5°) and 3,3′-dinitro-5,5′-diacetyl-2,2′-bithienyl (m.p. 128.5°) were both recrystallized from glacial acetic acid.

3,3′,5,5′-Tetranitro-2,2′-bithienyl (m.p. 195–196°) was recrystallized from glacial acetic acid and then from alcohol.

m-Nitrotoluene (Eastman Kodak) was distilled *in vacuo*, the fraction boiling at 121°/22 mm. being collected. Methyl 2,5-dimethyl-3-thenoate (b.p. 97°/4 mm.) was redistilled *in vacuo.*

2,2′,5,5′-Tetramethyl-3,3′-bithienyl-4,4′-dicarboxylic acid was sublimed *in vacuo* at 230–240°/3 mm.

2,5-Dimethyl-3-thenamide was prepared from the corresponding acid in 68% yield by first converting it to the acid chloride *via* thionyl chloride and then treatment of this intermediate with ammonia. The melting point obtained was 136.5–137°, slightly higher than the 133–134° reported by Kitt (13), who prepared this compound *via* the Gattermann reaction involving the acid, aluminum chloride, and carbamyl chloride. A further recrystallization from alcohol was effected for the spectral studies.

Absorption spectra. A Beckman model DU spectrophotometer equipped with equally matched fused quartz cells was the instrument employed in all the determinations. U.S.P. absolute ethanol was the solvent used in every case. The solutions prepared were all of the order of $10^{-5}M$, necessitating the use of the volume dilution method. Readings were taken over a range of 220–310 mμ at every 5 mμ and at every one mμ in the region of maxima and minima. The curves were obtained by plotting the molar extinction coefficient $\times 10^{-3}$ as the ordinate *vs.* the wave length in mμ as the abscissa. The molar extinction coefficient is defined as $e = E/cl$, where E is the optical density, c is the concentration of the light absorbing species in moles per liter, and l is the length in cm. of the light path in the absorbing solution.

DISCUSSION

Graphs have been constructed to illustrate all of the curves. Two of the graphs offer a comparison among the β-phenylthiophenes and between the various 2,2′-bithienyls and 3,3′-bithienyls respectively, while all of the other graphs afford a comparison of each biaromatic with its respective moieties as well as the additive curve resulting from them.

Before proceeding with the discussion of these results, it is necessary to remember the basic assumptions upon which the selection of the *ortho* substituents is made (9). On the basis of these steric considerations the interference values for the β-phenylthiophene and 3,3′-bithienyl *ortho* substituted molecules were calculated and found to be sufficiently large to restrict rotation and hence enable isolation of optical antipodes in the cases where applicable. That ample interference is exhibited here to prevent coplanarity is further attested to by the use of models, or can be seen from drawings made to scale. However, similar considerations for the *ortho* substituted 2,2′-bithienyls would seem to indicate that they can achieve coplanarity.

In Fig. 1 the curve of 2,2′,5,5′-tetramethyl-3,3′-bithienyl-4,4′-dicarboxylic acid resembles that of 2,5-dimethyl-3-thenoic acid, thus pointing to the existence of non-coplanarity due to steric hinderance on the part of the *ortho* substituted groups. The mono acid possesses an absorption maximum of $e = 8.33 \times 10^3$ at 244mμ, while the bithienyl possesses a maximum of $e = 11.75 \times 10^3$, somewhat less than the expected two-fold effect. However, this might be explained by the fact that steric hinderance not only prevents coplanarity of the two rings

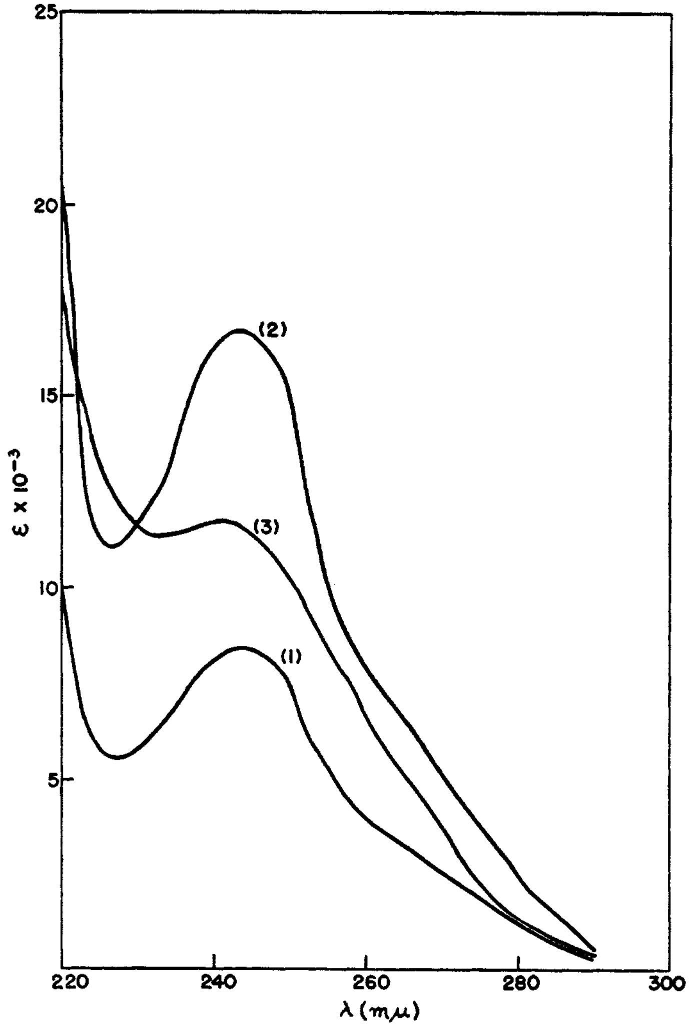

FIG. 1. ABSORPTION SPECTRA: (1) 2,5-Dimethyl-3-thenoic acid; (2) 2 × 2,5-Dimethyl-3-thenoic acid; (3) 2,2',5,5'-Tetramethyl-3,3'-bithienyl-4,4'-dicarboxylic acid.

but also blocks coplanarity of the carboxylic acid group with the ring to which it is attached.

In Fig. 2 the curve of 2,5-dimethyl-4-(6'-methyl-2'-nitrophenyl)-3-thenoic acid is similar to the theoretical curve calculated for it by adding the curves of the respective moieties (*m*-nitrotoluene has a maximum of $e = 6.82 \times 10^3$ at 264 mμ). It does not resemble the biphenyl type curve, thus negating the existence of resonance between the two rings due to the non-coplanarity of its structure as a result of the steric factor. The β-phenylthiophene possesses an absorption maximum of $e = 11.99 \times 10^3$ at 238 and 240 mμ, the curve exhibiting two peaks of equal intensity. Again it can be seen that the intensity is somewhat less

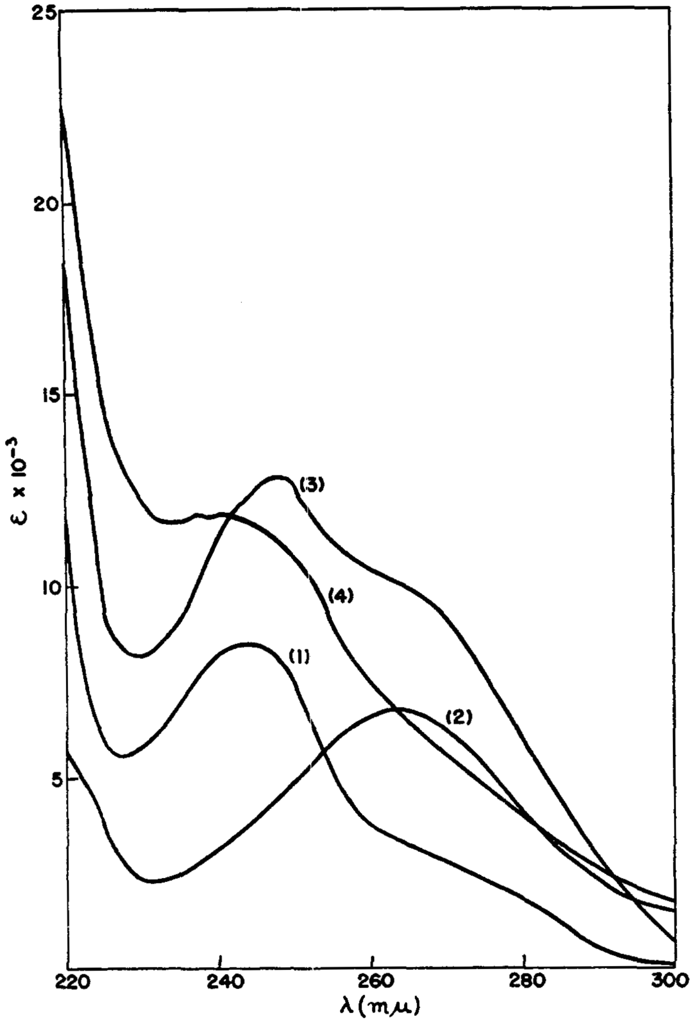

FIG. 2. ABSORPTION SPECTRA: (1) 2,5-Dimethyl-3-thenoic acid; (2) *m*-Nitrotoluene; (3) 2,5-Dimethyl-3-thenoic acid + *m*-nitrotoluene; (4) 2,5-Dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoic acid.

than expected theoretically, and this is most probably due to the fact that coplanarity of the nitro and carboxylic acid groups with their respective rings is also blocked. It is interesting to note that the intensity of this β-phenylthiophene is greater than that of its benzene analog, *i.e.*, 2,2′-dinitro-6,6′-bitolyl (1). This is, undoubtedly, due to the greater electron-releasing ability of the thiophene ring.

In Fig. 3 methyl 2,5-methyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoate exhibits a curve which is almost identical with that of the parent acid except for a slightly lower intensity. It possesses a maximum of e = 11.83 × 10^3 at 238 mμ and a maximum of e = 11.85 × 10^3 at 241 mμ. The lower intensity is probably due to

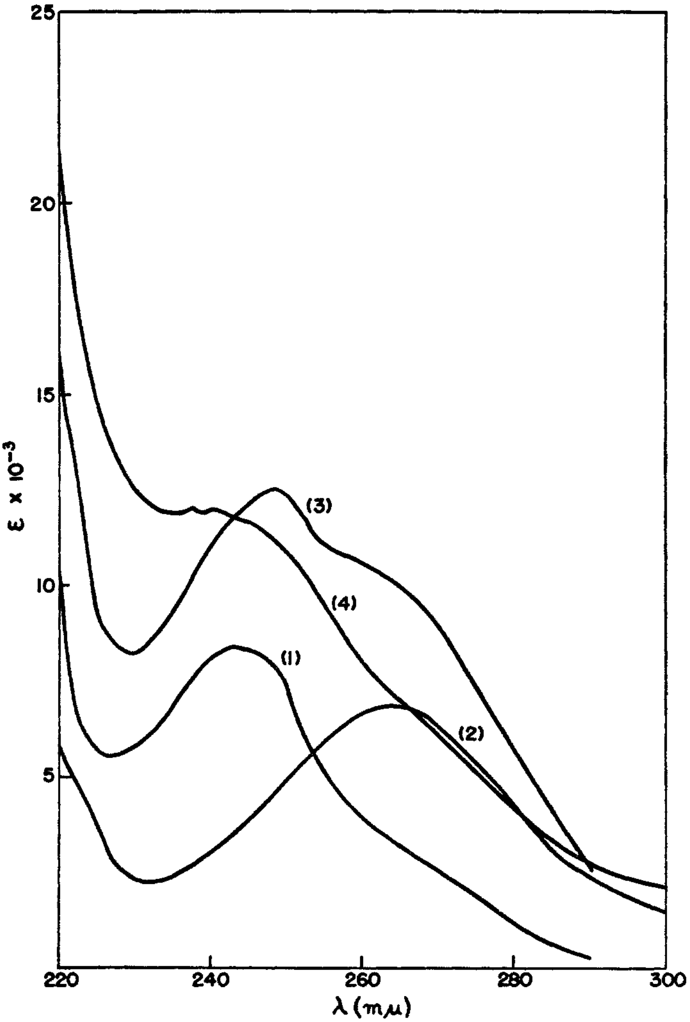

FIG. 3. ABSORPTION SPECTRA: (1) Methyl 2,5-dimethyl-3-thenoate; (2) *m*-Nitrotoluene; (3) Methyl 2,5-dimethyl-3-thenoate + *m*-nitrotoluene; (4) Methyl 2,5-dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoate.

the slightly greater steric factor in this compound. A comparison of this curve with the additive curve obtained from that of the respective moieties reveals the absence of conjugative effects in this molecule (methyl 2,5-dimethyl-3-thenoate exhibits a maximum of e = 8.53 × 10^3 at 244 mμ).

2,5-Dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenamide gave a curve lacking a maximum (Fig. 4). However, it parallels the curves of the corresponding acid and ester except for the fact that a minimum is absent in the region below 240 mμ. The intensity is somewhat lower than its two analogs, but this can be attributed to the greater steric hinderance of the amide group. This is further attested to by comparison with the additive curve obtained from the corre-

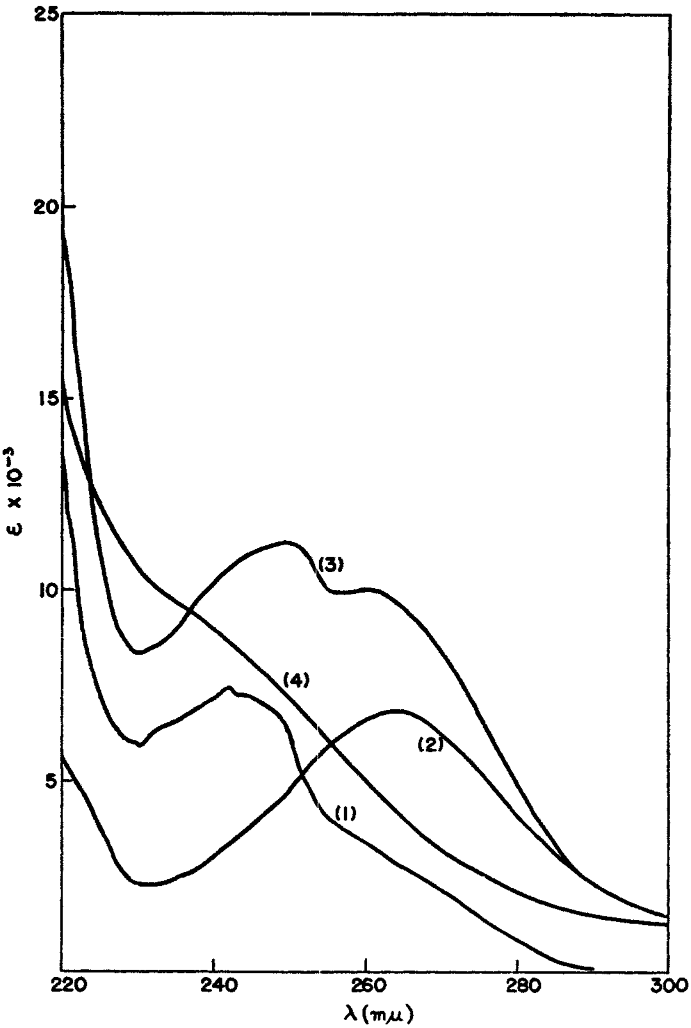

FIG. 4. ABSORPTION SPECTRA: (1) 2,5-Dimethyl-3-thenamide; (2) *m*-Nitrotoluene; (3) 2,5-Dimethyl-3-thenamide + *m*-nitrotoluene; (4) 2,5-Dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenamide.

sponding moieties (2,5-dimethyl-3-thenamide exhibited a spectral maximum of e = 7.52 × 10^3 at 242 mμ); the intensity is lower than that of the synthetic curve.

In Fig. 5 the curves of the β-phenylthiophenes are grouped together for comparison purposes. It can be clearly seen that they do not differ essentially but vary only in such details as fine structure and intensity.

In Fig. 6 the curves for the various symmetrically substituted 2,2′- and 3,3′-bithienyls containing nitro groups in the *ortho* position are shown.

3,3′-Dinitro-5,5′-dicarbomethoxy-2,2′-bithienyl exhibited a maximum at 248 mμ, where e is 26.90 × 10^3, thus indicating a biphenyl type spectral curve.

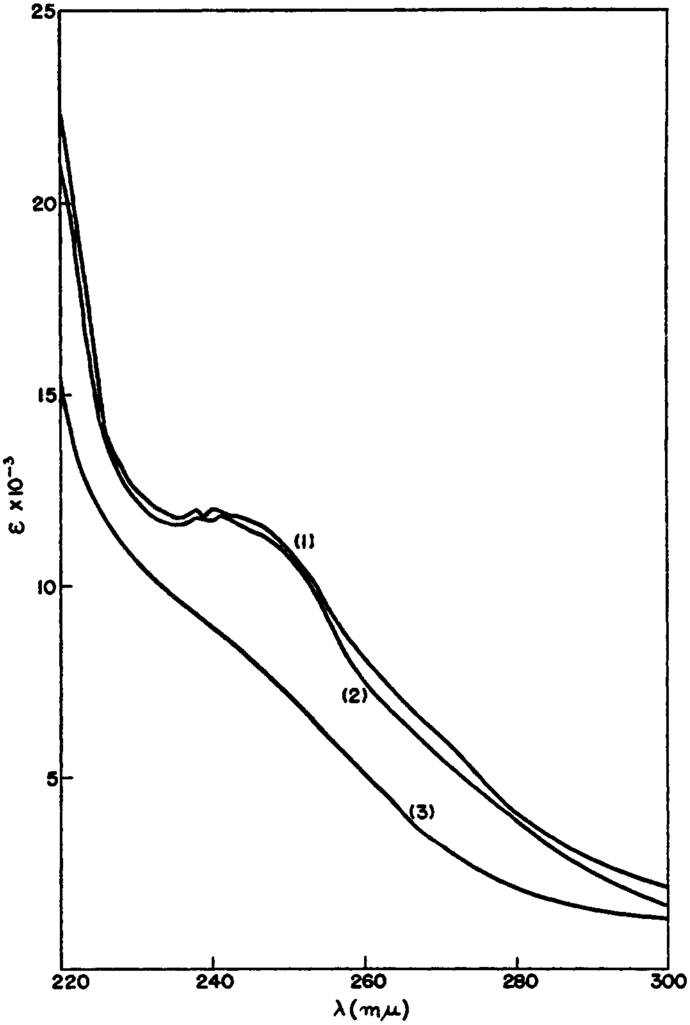

FIG. 5. ABSORPTION SPECTRA: (1) 2,5-Dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoic acid; (2) Methyl 2,5-dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenoate; (3) 2,5-Dimethyl-4-(6′-methyl-2′-nitrophenyl)-3-thenamide.

The increased intensity and the shift of absorption maxima to longer wave lengths are due to the effect of conjugation between the two rings, resulting in a large contribution of the ionic state to the ground state of the molecule. As coplanarity is necessary in order for this effect to operate, it can be concluded that steric hinderance cannot occur to any considerable extent here, a fact in accord with the molecular structure, as it possesses only two *ortho* substituted groups.

3,3′-Dinitro-5,5′-diacetyl-2,2′-bithienyl gave a maximum of e = 53.45 at 248 mμ. Although the maximum wave length is identical with that of 3,3′-dinitro-5,5′-dicarbomethoxy-2,2′-bithienyl, the intensity is almost double. This is probably due to the greater conjugation of the acetyl groups with the thio-

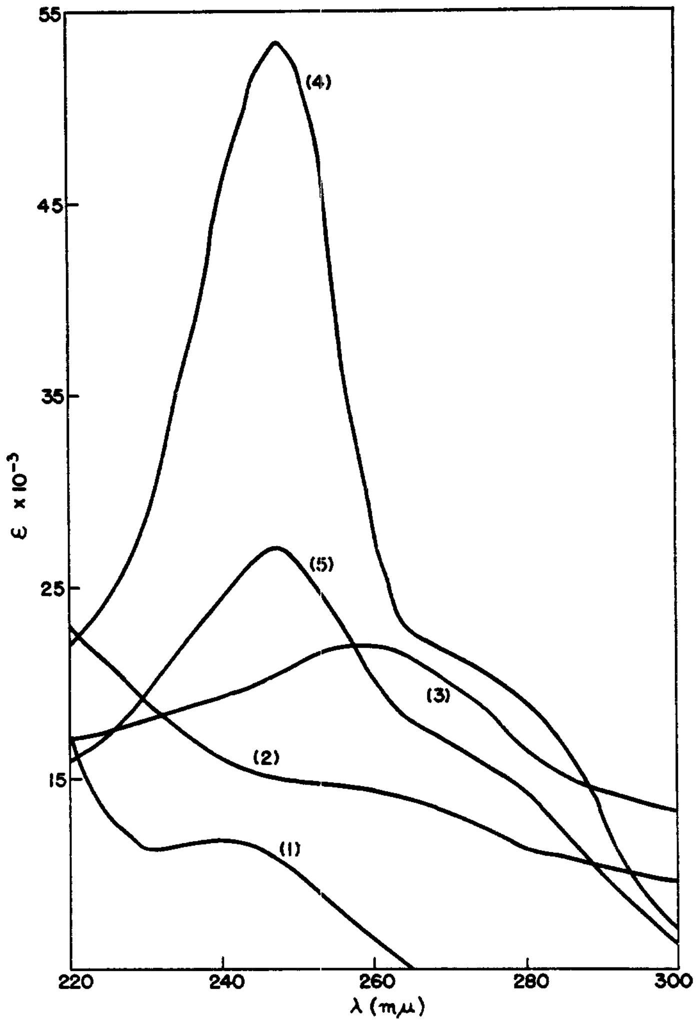

FIG. 6. ABSORPTION SPECTRA: (1) 2,2′,5,5′-Tetramethyl-3,3′-bithienyl-4,4′-dicarboxylic acid; (2) 2,2′,4,4′--Tetranitro-5,5′-dimethyl-3,3′-bithienyl; (3) 3,3′,5,5′-Tetranitro-2,2′-bithienyl; (4) 3,3′-Dinitro-5,5′-diacetyl-2,2′-bithienyl; (5) 3,3′-Dinitro-5,5′-dicarbomethoxy-2,2′-bithienyl.

phene ring, inasmuch as the phenomenon of crossed conjugation, present in the ester, is absent here. At any rate, the data clearly indicate that conjugation between the two rings takes place, *i.e.*, coplanarity must exist, thus negating steric hinderance.

3,3′,5,5′-Tetranitro-2,2′-bithienyl exhibited a maximum of e = 21.72 × 10^3 at 259 mμ, thus pointing to a coplanar structure. It agrees in this respect with the results obtained from the other 3,3′-dinitro-2,2′-bithienyls. The bathochromic shift of the wave length of maximum absorption is further proof of the presence of the conjugative effect.

2,2′,4,4′-Tetranitro-5,5′-dimethyl-3,3′-bithienyl failed to exhibit a maximum, and its intensity was below that of the 2,2′-bithienyl dinitro compounds; hence, it can be distinguished from them. This might be partially due to the steric factor which is undoubtedly operative here.

In conclusion, it can be stated that the β-phenylthiophenes and the 3,3′-bithienyls studied exist in a non-coplanar form and hence should be capable of resolution, while the 2,2′-bithienyls considered here can achieve coplanarity and so would not lend themselves to resolution very readily, if at all. However, it should also be stated that evidence of non-coplanarity does not necessarily lead to the conclusion that resolution is possible, but only that it is indicated inasmuch as other factors, such as the activation energy for racemization, are also involved (3).

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SUMMARY

The ultraviolet absorption spectra of several β-phenylthiophenes and 2,2′- and 3,3′-bithienyls containing *ortho* substituents have been determined and compared with the spectra of the uncoupled parts. Decreased intensities and hypsochromic shifts were the typical effects in the case of the non-coplanar molecules that were sterically hindered by the bulky groups. Due to the lack of conjugation between the rings, these compounds approximate the additive absorption of the superimposed moieties.

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