[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

# Ultraviolet Absorption Spectra and Acidic Strengths of Certain Dihydroxythiophene-1-oxides and 1-Dioxides[1,2]

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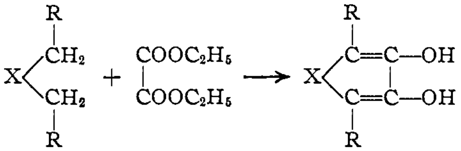
## Introduction

As part of a program devised to evaluate the electrical effect of the sulfur atom in various states of oxidation on contiguous groups in organic molecules we have prepared 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I),[4] 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-oxide (II), 2,5-dicarbethoxy - 3,4 - dihydroxyethiophene - 1 - dioxide (III), 3,4-dihydroxy-2,5-diphenylthiophene-1-dioxide (IV), 2,5-dicarbethoxy-3,4-dihydroxyfuran (V),[5] 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI)[6], and N-ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole (VII)[7] by the oxalic ester condensations as indicated schematically:



I $R = COOCH_3$; $X = S$
II $R = COOC_2H_5$; $X = SO$
III $R = COOC_2H_5$; $X = SO_2$
IV $R = C_6H_5$; $X = SO_2$
V $R = COOC_2H_5$; $X = O$
VI $R = COOC_2H_5$; $X = CH_2$
VII $R = COOC_2H_5$; $X = C_2H_5N$

The electrical effect of the sulfur atom in various states of oxidation (Compounds I, II, III, IV) and that of other hetero-atoms (Compounds V, VII) on the properties of the ester condensation products has been assessed by measurement of acidic strengths and ultraviolet absorption spectra.

## Experimental[8]

**A. Preparation of Compounds. 2,5-Dicarbomethoxy-3,4-dihydroxythiophene** (I).—The compound was prepared according to the directions given by Hinsberg.[4] Our material had m. p. 177° (reported 177°) and gave a green color with ferric chloride in alcohol.

**2,5-Dicarbethoxy-3,4-dihydroxythiophene-1-oxide** (II).—To fifteen grams of ethyl thiodiacetate dissolved in 20 ml. of acetone was added 7.5 ml. of 30% hydrogen peroxide solution. After four days acetone was removed at reduced pressure, benzene was added and the mixture was distilled until the distillate was clear. The residue on distillation yielded 9.0 g. of **ethyl sulfinyldiacetate**, an oil of b. p. 140–146° (4 mm.).

Eight grams of ethyl sulfinyldiacetate and 5.3 g. of ethyl oxalate were added to a solution of 1.7 g. of sodium dissolved in 30 ml. of absolute methanol. The reaction mixture was heated under reflux for one hour, allowed to stand twelve hours, and then decomposed by addition to three times its volume of water which contained 2.2 ml. of concentrated hydrochloric acid. The precipitate which appeared was separated by filtration, washed with methanol and crystallized from methanol four times to yield 1.2 g. of white needles, of m. p. 121–122°. The compound gave a green color with ferric chloride in alcohol and analyzed for 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-oxide (II). The equivalent weight was determined as described below under C.

*Anal.* Calcd. for $C_{10}H_{12}O_7S$: C, 43.5; H, 4.38; neut. equiv. (two acidic groups), 138. Found: C, 43.8; H, 4.55; neut. equiv., 137.

**2,5-Dicarbethoxy-3,4-dihydroxythiophene-1-dioxide** (III).—**Sulfonyldiacetic acid**[9] was prepared in 85% yield by hydrogen peroxide oxidation of thiodiacetic acid in glacial acetic acid. Our material had m. p. 184–185° (reported[7] 182°) after crystallization from concentrated hydrochloric acid.

A mixture of 98.0 g. of sulfonyldiacetic acid, 135 ml. of 95% ethanol, 2.0 g. of toluenesulfonic acid, and 500 ml. of benzene was refluxed with an attached water separator until no water appeared in the condensate. The reaction mixture was washed thoroughly with water, the benzene was removed by distillation, and the residue was distilled at reduced pressure to yield 118 g. of **ethyl sulfonyldiacetate**,[10] a colorless oil of b. p. 178–181° (5 mm.), $d^{27}$ 1.258, $n^{25}_{D}$ 1.4652.

To a warm solution of 20 g. of sodium in 200 cc. of absolute ethanol was added, in portions with stirring, a mixture of 44 g. of ethyl oxalate and 69 g. of ethyl sulfonyldiacetate. When the mildly exothermic reaction had subsided, the reaction mixture was heated for one hour on the steam-bath. The mixture was centrifuged and the gummy solid obtained was spread on glass plates where it dried in twelve hours to a bright-yellow powder. Forty-three grams of the yellow powder was dissolved in 150 ml. of water and acidified to *p*H 1 with concentrated nitric acid, and to the solution was added, with stirring, a solution of 150 g. of mercurous nitrate in 150 ml. of dilute nitric acid. The precipitated mercurous salt was separated by filtration, washed with water, and suspended in 100 ml. of water. To the suspension was added an excess of concentrated hydrochloric acid. The calomel which precipitated was separated by filtration and the filtrate was concentrated to one-third its original volume by distillation at reduced pressure. The crystalline material which separated was collected, washed with concentrated hydrochloric acid, crystallized twice from small volumes of 20% hydrochloric acid, and twice from benzene after drying to yield 17 g. of 2,5-dicarboxy-3,4-dihydroxythiophene-1-dioxide (III) in the form of white cubes of m. p. 116–117.5°.

*Anal.* Calcd. for $C_{10}H_{12}O_8S$: C, 41.1; H, 4.14; neut. equiv., 146 (two acidic groups); C-methyl, 2 (two ethyl ester groups); active H, 2 per mol. wt., 292. Found: C, 41.4; H, 3.98; neut. equiv., 146; C-methyl, 1.88; active H, 1.97, 2.00.

The compound is very soluble in water to give a yellow

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(1) A portion of this work was reported at the meeting of The American Association for the Advancement of Science in Berkeley, California, in June, 1948.

(2) The work reported here is taken from the Doctoral Dissertation of Robert M. Wagner in the Department of Chemistry at Stanford University.

(3) Present address: General Electric Company, Richland, Washington.

(4) Hinsberg, *Ber.*, **43**, 901 (1910); **45**, 2413 (1912).

(5) Johnson and Johns, *Am. Chem. J.*, **31**, 290 (1906).

(6) Dieckmann, *Ber.*, **27**, 966 (1894).

(7) For a similar synthesis see Johnson and Bengis, THIS JOURNAL, **33**, 741 (1911).

(8) All melting points are uncorrected.

(9) Prepared originally by permanganate oxidation: Loven, *Ber.* **17**, 2818 (1884).

(10) Loven, *ibid.*, **17**, 2821 (1884).

solution, crystallizable from strongly acidic, aqueous solutions and benzene, is strongly acidic in reaction (*cf.* Discussion) and gives a wine-red coloration with ferric chloride in water or alcohol.

The solubility in water and the high acidity of 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide caused difficulty in the isolation of the compound. Thus, although the compound is soluble in ether, a strongly acidified solution of the above-described reaction mixture could be extracted continuously with ether without any of the free acid appearing in the ether phase. Isolation was achieved by formation of the barium salt which was insoluble in 1:1 ethyl alcohol–water, followed by reaction of it with the calculated amount of sulfuric acid, and by the use of a cation exchange resin in the hydrogen cycle; but both of these methods proved inferior to the above-described separation through the mercurous salt.

**3,4-Dihydroxy-2,5-diphenylthiophene-1-dioxide** (IV).—Five grams of dibenzyl sulfone, 3.0 g. of ethyl oxalate, and 3.0 g. of dry sodium methoxide were heated together for one hour during which time 2.9 ml. of low-boiling liquid distilled from the reaction mixture. The dark residue was dissolved in 100 ml. of water and the solution was acidified to *p*H 2 with concentrated hydrochloric acid. The solid which separated was collected and crystallized from 1:3 ethanol–benzene to give 3.5 g. of 3,4-dihydroxy-2,5-diphenylthiophene-1-dioxide, white crystals of m. p. 232–233°.

*Anal.* Calcd. for $C_{16}H_{12}O_4S$: C, 64.1; H, 4.06; S, 10.7; neut. equiv., 150 (two acidic groups). Found: C, 64.2; H, 4.12; S, 10.7; neut. equiv., 148.

The substance gave an orange color with ferric chloride in alcohol and dissolved in dilute sodium bicarbonate to give a deep yellow solution. Its neutral equivalent was determined by titration in an anhydrous medium as described below under C.

**2,5-Dicarbethoxy-3,4-dihydroxyfuran** (V).—The compound was prepared according to the directions given by Johnson and Johns.[5] Our material had m. p. 190° (reported[5] 189–190°) and gave a purple color with ferric chloride solution in alcohol.

**2,5-Dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4** (VI).—The compound was prepared according to the method of Dieckmann.[6] Our sample had m. p. 118° (reported[6] 118°) and gave a wine-red color with ferric chloride in alcohol.

**N-Ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole** (VII).—**Ethylimino-bis-acetonitrile** was prepared by the method of Knoevenagel and Mercklin,[11] characterized as its hydrochloride of m. p. 112–113° (reported[11] 112–113°) and converted to diethyl **N-ethyliminodiacetate** by alcoholysis according to Curtius.[12] Our sample of the latter compound had b. p. 210–225° (11 mm.).

Five grams of diethyl N-ethyliminodiacetate and 3.5 g. of ethyl oxalate were added to a solution of 1.5 g. of sodium in 60 ml. of absolute ethanol. The reaction mixture was heated gently for one hour, distilled nearly to dryness in a stream of nitrogen, and the residue was dissolved in 50 ml. of water. Acidification of the solution with 5.3 ml. of concentrated hydrochloric acid threw down a white precipitate which was collected, washed with water, and crystallized from 50% alcohol to yield 0.7 g. of N-ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole, white crystals of m. p. 83–83.5°.

*Anal.* Calcd. for $C_{12}H_{17}O_6N$: C, 53.1; H, 6.33; N, 5.17. Found: C, 53.4; H, 6.38; N, 5.13.

The compound was insoluble in water, gave a green ferric reaction in alcohol, and was decomposed by alkali as evidenced by the appearance of a transient yellow coloration when the substance was dissolved in dilute sodium hydroxide.

B. **Determination of Ultraviolet Absorption Spectra.**—The absorption characteristics of the compounds were studied in a variety of media using a Beckman Quartz Spectrophotometer, Model DU. The instrument was balanced by varying the slit width with the sensitivity knob kept three and one-half turns from the extreme clockwise position giving a maximum nominal band width of 2 mμ, and measurements were made at 5 mμ intervals.

The absorption characteristics of the compounds in the various media did not change during the time required for the observations, and, with the single exception of the study of N-ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole which decomposed in alkaline media, there was no evidence, spectrophotometric or other, for decomposition of the compounds under the conditions employed. Thus, compounds I, VI and VII were recovered unchanged by dilution after one hour of solution in concentrated sulfuric acid. The spectra are reported in Figs. 1–4.

C. **Determination of Acidic Strengths.**—Titration curves for the compounds were obtained in water and in an anhydrous medium composed of isopropyl alcohol and propylene glycol according to the method of Palit[13] using a Beckman *p*H meter. When the *p*H meter was used in the anhydrous medium, it was found necessary to equilibrate the glass electrode for several hours with the medium before use.

The $pK$ values are taken as equal to the *p*H value at the half-neutralization points for the corresponding acidic hydrogens where the shape of the titration curve shows typical weak acid behavior.

The $pK'$ values are similarly derived from titrations carried out in the anhydrous medium and are considered to be of value in establishing relative acidic strengths only. The similar calculation of the $pK_2'$ values for the second enolic hydrogens of compounds I, II, III and IV is of little significance since in the titrations of these compounds the precipitation of a sodium or potassium salt commenced shortly after the equivalence point for the first hydrogen was reached. On the basis of the equilibria involved, this precipitation of the anion as a salt causes the acid to appear stronger than it actually is. Such values for $pK_2'$ are bracketed in Table I.

The titration curves are plotted in Figs. 5 and 6, and the corresponding $pK$ and $pK'$ values are summarized in Table I. Some reference compounds are included to establish the validity of the method.

TABLE I

ACID STRENGTHS

| Compound | In water $pK_1$ | $pK_2$ | In anhydrous medium[a] $pK_1'$ | $pK_2'$ |
|---|---|---|---|---|
| Picric acid | Strong | | Strong | |
| III | Strong | Strong[b] | Strong | (4.1) |
| Malonic acid | 2.9 | 6.1 | 4.5 | 7.8 |
| IV | *ca.* 4.3 | ... | 5.0 | (10.0) |
| Benzoic acid | 4.2 | | 6.2 | |
| II | ... | ... | 6.8 | (9.5) |
| Acetic acid | 4.8 | | 7.2 | |
| I | ... | ... | 7.7 | (9.9) |
| VI | ... | ... | 7.9 | 10.4 |

[a] The $pK'$ values are considered to be of value in determining relative acidic strengths only (*cf.* discussion under part C in Experimental Section). [b] While this article was in process of publication, Professor F. O. Koenig and Lorraine Mildred Winslow of the Department of Chemistry at Stanford University made an accurate determination of $pK_2$ for 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III) by the methods of Hamer [THIS JOURNAL, **56**, 860 (1934)] and Harned and Ehlers [*ibid.*, **54**, 1350 (1932)]. The value for $pK_2$ so obtained was 2.59 which may be compared with the value 1.92 obtained by Hamer for the bisulfate ion.

Although the titration data are plotted in terms of per cent. neutralized in Figs. 5 and 6, the determinations were

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[11] Knoevenagel and Mercklin, *Ber.*, **37**, 4093 (1904).

[12] Curtius, *J. prakt. Chem.*, **96**, 285 (1917).

[13] Palit, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 246 (1946).

carried out on weighed samples and, thus, served to determine the equivalent weights of the substances studied.

The insolubility of 3,4-dihydroxy-2,5-diphenylthiophene-1-dioxide in water precluded determinations of its acidity by titration in water. However, a saturated solution of the substance in water had a concentration by weight analysis of 4.7 × $10^{-4}$ mole per liter and showed $p$H 3.9. These data indicate an approximate $pK_1$, neglecting the second hydrogen, of 4.3.

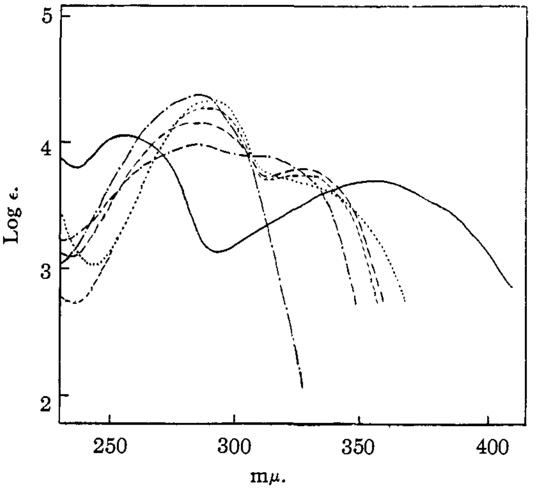

Fig. 1.—Ultraviolet absorption spectra in 1 *M* alcoholic hydrogen chloride: —, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III); ----, 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I); — —, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-oxide (II); —·—, 2,5-dicarbethoxy-3,4-dihydroxyfuran (V); —·—·, 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI); ......, N-ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole (VII).

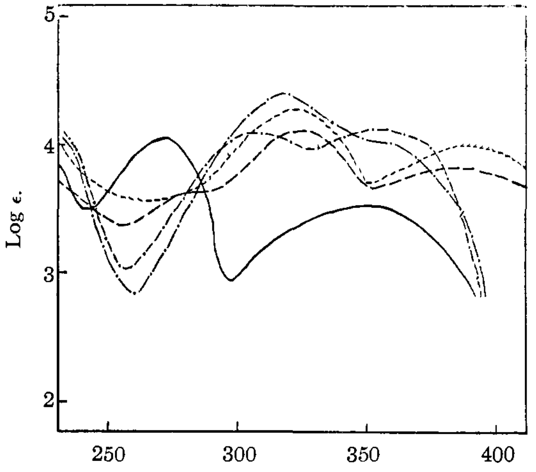

Fig. 2.—Ultraviolet absorption spectra in 5% potassium hydroxide: —, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III); - - - -, 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I); — — —, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-oxide (II); —·—, 2,5-dicarbethoxy-3,4-dihydroxyfuran (V); — —·, 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI).

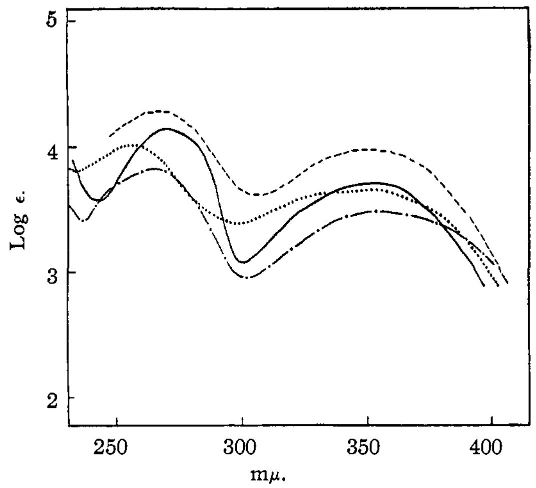

Fig. 3.—Ultraviolet absorption spectra of 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III) in various media: —, water; —·, 95% ethanol; ----, glacial acetic acid; ........, 9 *M* sulfuric acid.

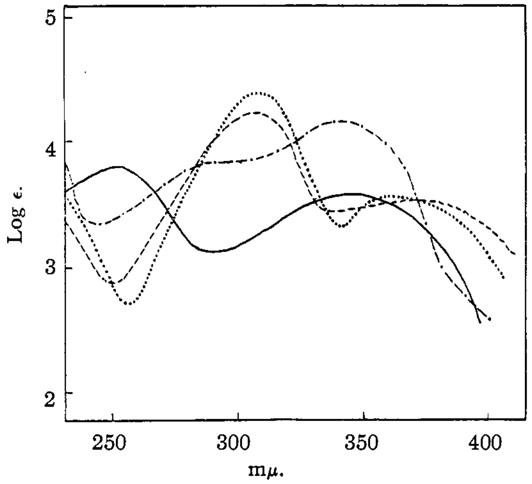

Fig. 4.—Ultraviolet absorption spectra in concentrated sulfuric acid: —, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III); -----, 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I); ......., N-ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole (VII); — —·, 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI).

## Discussion

Comparison of the $pK_1'$ values for the first enolic hydrogens of 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I) ($pK_1'$ = 7.7) and 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-oxide (II) ($pK_1'$ = 6.8) indicates that the sulfoxide group exerts only a slightly stronger proton-releasing effect on the enolic hydrogen than does a sulfide function in the same position. This observation is in accord with the reported[14] failure of bis-(phenylsulfinyl)-methane to show acidic properties. The near identity of the ultraviolet absorption spectra of the two compounds (I and

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(14) Shriner, Struck and Jorison, THIS JOURNAL, **52**, 2060 (1930).

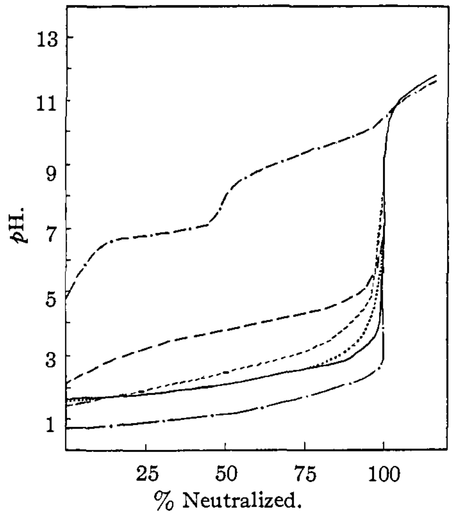

Fig. 5.—Titration curves in water: —, sulfuric acid; ........ and —·, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III), 0.02 and 0.25 $M$, respectively; — —·, 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI); — — —, thiodiacetic acid; - - - -, sulfonyldiacetic acid.

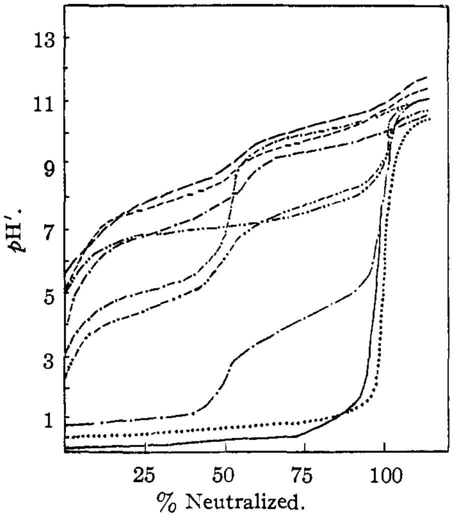

Fig. 6.—Titration curves in propylene glycol–isopropyl alcohol: —, sulfuric acid; —·, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III); ......, picric acid: - - - -, 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I); — — —, 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-oxide (II); — —·, 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI); —·—, 3,4-dihydroxy-2,5-diphenylthiophene-1-dioxide (IV); · · —, acetic acid; · · — —, malonic acid.

II) in alcoholic hydrogen chloride (Fig. 1), in which medium the substances may be assumed to be present as undissociated molecules, further emphasizes the similarity of the electrical effect of the groups –S– and –SO– on attached groups. Both the sulfide and sulfoxide functions appear, however, to exert an electron-attracting influence relative to a methylene group in the same position as evidenced by comparison of the $pK_1'$ values for the thiophene derivatives (I and II) with that for 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI) ($pK_1' = 7.9$). The similarity in the absorption spectra of the three thiophene derivatives (I, II, III), the cyclopentadiene derivative (VI), and 2,5-dicarbethoxy-3,4-dihydroxypyrrole (VII) (Fig. 1) finds explanation in the observation that the systems –CO–C($CH_3$)═CH– and –CO–C(Br)═CH– have the same ultraviolet absorption spectra and that in general the concept of cross conjugation is without physical basis.[15]

The appearance of a single absorption maximum for 2,5-dicarbethoxy-3,4-dihydroxyfuran (V) (Fig. 1) in acidic solution taken with the appearance of the two characteristic bands in alkaline medium (Fig. 2) suggests that the furan derivative is present in the acidic solution in a different molecular form than that of the thiophene, pyrrole and cyclopentadiene derivatives (I, II, III, VI, VII) under the same conditions.

The ultraviolet absorption spectra of the 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III) (Figs. 1, 2, 3, 4) in various media are similar to those of the other compounds studied insofar as the two characteristic bands are present. In the case of the sulfone (III), however, the intensity of absorption is lower for both bands, the short wave length band is considerably shifted to shorter wave lengths, and the position of maximum absorption for the long wave length band is little altered by changes in the medium (*cf.* Figs. 1, 2, 3). The latter situation is not the case with the thiophene (I) and thiophene-1-oxide (II) derivatives in which the low intensity bands, as well as the high intensity bands, undergo marked bathochromic shifts in going from moderately acidic to alkaline media, *i. e.*, from neutral molecule to conjugate base. This observation that the presence of the enolic hydrogens in III has little to do with the ultraviolet absorption characteristics of the compound suggests that the electron distribution is not much dependent upon the presence of the enolic hydrogens, a situation tantamount to ascribing to the sulfone (III) a very high level of acidity.

Such is indeed the case. From the titration curve for the compound in the anhydrous medium (Fig. 6), in which acetic acid shows approximately a four hundred-fold decrease ($pK' = 7.2$) relative to its strength in water ($pK = 4.8$), it is evident that the first enolic group of the sulfone (III) still shows strong acid behavior. The basicity of the anhydrous medium, is, however, enough lower than that of water to bring out the weak acid nature of the second enolic hydrogen of III, which was not observed in the titration of the compound in water (*cf.* Fig. 5). Although the titration procedure was not extended to even less basic solvents in order to evaluate a relative acid-

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[15] Woodward, THIS JOURNAL, **63**, 1123 (1941).

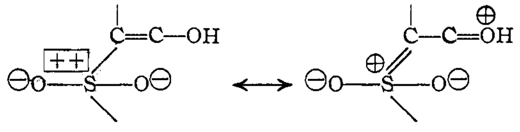
ity for the first hydrogen of the sulfone (III), it is apparent from the curve (Fig. 6) that the compound is at least as strong an acid as picric acid ($pK = 1$). It is probably stronger with regard to the first enolic hydrogen since even in 0.25 molar solution the second hydrogen of III showed strong acid behavior (Fig. 5) and the first and second dissociation constants of dibasic acids having proximate acidic groups usually differ by a factor of at least three powers of ten.

The ultraviolet absorption spectra for the compound (III) in 1 *M* alcoholic hydrogen chloride, 9 *M* sulfuric acid, and concentrated sulfuric acid (Figs. 1, 3, and 4) show little difference which suggests that, in contrast to the behavior of the much less strongly acidic I, VI, and VII under similar conditions (*cf.* Fig. 4 and the discussion below) the thiophene dioxide (III) is present, not as its conjugate acid, but rather in molecular form in concentrated sulfuric acid. Such behavior would be expected of only the most weakly basic substances, and hence of only the strongest acids when the molecule in question has ampholytic character.

In the anhydrous medium the first enolic hydrogen of 3,4-dihydroxy-2,5-diphenylthiophene-1-dioxide (IV) shows an acidic strength ($pK_1'$ 5.0) only 3-fold less than that of the first hydrogen of malonic acid ($pK_1'$ 4.5, $pK_1$ 2.9) in the same medium. Because of its low solubility in water the diphenylthiophene derivative (IV) could not be titrated in aqueous solution. However, it is apparent that the compound is as strong an acid as a typical carboxylic acid in water ($pK$ 5). An approximate determination of the acidic strength in water, as described under C in the Experimental Section, gave $pK_1$ 4.3.

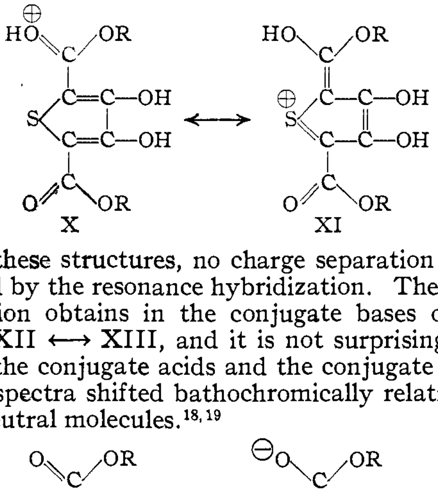
It is apparent from these considerations that the strong electron-attracting influence of the sulfonyl group is transmitted through the carbon–carbon double bond to the enolic hydroxyl groups in the compounds studied. Indeed, the effect is greater than that exerted by a carbethoxyl group in the same position as indicated by a comparison of the acidic strengths of 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I) ($pK_1'$ 7.7) and 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI) ($pK_1'$ 7.9) with those of the thiophene derivatives III and IV. This conclusion is in accord with the observation that bis-(phenylsulfonyl)-methane dissolves in aqueous sodium hydroxide and may be alkylated by treatment of the alkaline solution with alkyl halides[14] while malonic ester is unreactive in the same sense under the same conditions.

Since, in the compounds studied, the powerful electron-attracting influence of the sulfonyl group is transmitted through a double bond it is concluded that the effect is not one of simple induction but is better symbolized by the resonance hybridization VIII ⟷ IX.

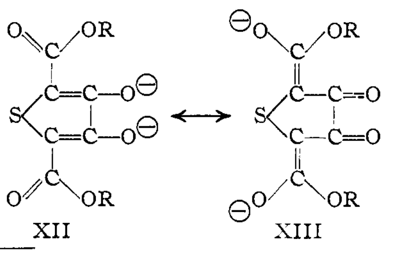

VIII IX

Structures VIII and IX involve a sulfur atom with a decet of electrons. Such an expansion of the octet, involving the unused *d* orbitals of the sulfur atom has been suggested by various investigators to explain the physical and chemical properties of organic and inorganic compounds of sulfur.[16] The work reported here thus provides additional experimental evidence in support of this hypothesis.

We turn now to a consideration of the marked bathochromic shifts observed in the spectra of 2,5-dicarbomethoxy-3,4-dihydroxythiophene (I) and N-ethyl-2,5-dicarbethoxy-3,4-dihydroxypyrrole (VII) in going from a 1 *M* alcoholic hydrogen chloride medium to a concentrated sulfuric acid medium (*cf.* Figs. 1 and 4). Both I and VII are weakly acidic, and unlike 2,5-dicarbethoxy-3,4-dihydroxythiophene-1-dioxide (III), might be expected to be converted to their conjugate acids in concentrated sulfuric acid. In view of the failure of thiophene and pyrrole to show basic properties attributable to their hetero atoms, and the reported[17] conversion of carboxylic esters to their conjugate acids by concentrated sulfuric acid we propose structures of the type X ⟷ XI for the conjugate acids of the thiophene derivative I and the pyrrole VII, present in solutions of the compounds in concentrated sulfuric acid.


X XI

**In these structures,** no charge separation is required by the resonance hybridization. The same situation obtains in the conjugate bases of the type XII ⟷ XIII, and it is not surprising that both the conjugate acids and the conjugate bases have spectra shifted bathochromically relative to the neutral molecules.[18,19]


XII XIII

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[16] For discussions of earlier work on the expanded sulfur valence shell problem, *cf.* Fehnel and Carmack, THIS JOURNAL, **71**, 84, 231 (1949); Heymann, *ibid.*, 260 (1949); Fehnel, *ibid.*, 1063 (1949).

[17] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 45–47.

[18] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[19] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 61.

The bathochromic shift observed in the case of 2,5-dicarbethoxy-3,4-dihydroxycyclopentadiene-2,4 (VI) in going from alcoholic hydrogen chloride as solvent to concentrated sulfuric acid contrasts with the hypsochromic shift in the case of the sulfone (III) under the same conditions (Figs. 1, 3, 4), and is interpreted as involving conjugate acid formation at a carbethoxyl group in VI with consequent elimination of charge separation in the resonating chromophoric system.

## Summary

A study of the acidic strengths and ultraviolet absorption spectra of certain dihydroxythiophene-1-oxides and 1-dioxides has provided further evidence for an expanded valence shell for the sulfur atom in the sulfone configuration.

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# Inorganic Complex Compounds Containing Polydentate Groups. II. The Complexes Formed between Triethylenetetramine and the Nickel(II) Ion

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The stereochemical configuration of the quadricovalent complexes of the nickel(II) ion has been extensively investigated. This ion has been shown to be able to direct its valence bonds toward the corners of a tetrahedron[4,5,6,7] and of a plane.[6,7,8,9]

Various criteria have been used to obtain information about the configuration of these complex compounds. Lifschitz and co-workers[10] attempted to relate color and magnetic properties to bond direction. Yellow compounds were classed as planar because of diamagnetism; blue paramagnetic compounds indicated tetrahedral bond direction. This distinguishing characteristic, however, breaks down in many cases.

Mellor and co-workers[7] found that the electronegativity of the coördinating group influences the stereochemical configuration. The very electronegative donor atom, oxygen, imposes tetrahedral $sp^3$ bonds upon the nickel(II) ion. As the electronegativity decreases through nitrogen to sulfur, the bonds are directed toward the corners of a coplanar square. In the compounds containing four nitrogen donor atoms the statistical distribution is about half planar, half tetrahedral. Many complexes of this type can show both configurations.[10] Other factors such as steric hindrance due to coördinating groups and functional groups attached to donor atom also affect the configuration of these complexes.

In most of these complexes the coördinating group is a mono- or bidentate group. Very few quadridentate complexes containing the same donor atom have been investigated. In all of these cases[8,9,11] the configuration of the coördinating group imposes a planar configuration upon the complex.

This study was undertaken to determine the type of configuration of the complex or complexes formed between the nickel(II) ion and triethylenetetramine ($NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$) (abbreviated trien). This quadridentate base can orient itself with little difference in strain around a metal ion exhibiting tetrahedral or planar valence bond direction.

Since the configuration of the trien molecule does not impose a definite bond direction upon the central ion, this investigation may throw more light upon the factors which influence the direction of valence forces in the complexes containing the nickel(II) ion.

Since the nickel(II) ion also has a tendency to form octahedral complexes, the data obtained in this study may also indicate the ease of conversion of nickel(II) complex ions from tetra- to hexacoördination. This may lead to some information about the configuration of the tetracoordinated complexes since Dwyer and Mellor[12] found that planar diamagnetic nickel(II) complex ions show little tendency to assume sixfold coordination. Paramagnetic tetrahedral complex compounds, however, can easily be converted to an octahedral configuration by the uptake of two more donor groups.

## Experimental

**A. Spectrophotometric Studies. 1. Absorption Data.**—Standard solutions of 0.05 *M* nickel chloride and 0.05 *M* trien were used in the absorption studies. Fixed amounts of nickel chloride were mixed with varying amounts of trien to give solutions with the following ratios

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(1) Based upon the M.S. thesis of B. E. Douglas, Tulane University, 1947.

(2) Presented in part before Division of Physical and Inorganic Chemistry at the 112th American Chemical Society Meeting, New York, September, 1947.

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