The Ultraviolet Spectra of the Thiophene Derivatives.

The Ultraviolet Spectra of the Thiophene Derivatives.

Yozo SUGIMOTO,* Shoji NISHIMURA,** and Eiji IMOTO,***

The ultraviolet spectra of thirty-four thiophene derivatives are measured in hexane or in 95% ethanol. The λ_{max}'s of the first absorption bands of 2-monosubstituted thiophenes have a linear relationship to the λ_{max}'s of the first primary bands of the corresponding monosubstituted benzenes, while the λ_{max}'s of the first absorption bands of 3-monosubstituted thiophenes have no such a relationship to those of the corresponding benzenes. A 2-substituent of a thiophene derivative conjugates more strongly with the thiophene ring than the 3-substituent does. In di- and trisubstituted thiophenes, the substituents affect the spectra in various ways.

1. Introduction
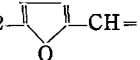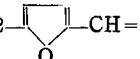
The ultraviolet spectra of thiophene and thiophene derivatives have been studied by many authors. The spectrum of thiophene was measured by Menzel,[1] Milazzo,[2] and Padhye and Desal.[3] The spectra of thiophene derivatives have been studied somewhat unsystematically. Earlier records of the spectra of thiophene derivatives was of alkyl and halogeno derivatives studied by Hartough,[4] of acyl derivatives by Campaigne,[5] of halogeno and nitro derivatives by Boig,[6] and of substituted thiophenecarboxylic acids by Sice,[7] and other data scattered in many individual papers. Abe,[8] and Ramart-Lucas, Grumez, Hoch, Klein, Martinoff, and Riff[9] measured the spectra of several thiophene derivatives together with the spectra of the other five-membered heterocyclic derivatives, and concluded that the electronic structure of a substituted heterocyclic compound does not so much depend upon the hetro-atom in the ring, but upon kinds and positions of the substituents.
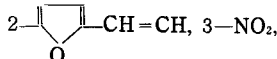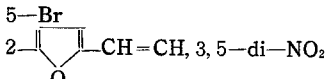
In this paper, the ultraviolet absorption spectra of thirty-four thiophene derivatives were measured, and the conjugation in the thiophene ring was discussed. Table 1 lists the spectrographic data in the order of their occurrence in the discussion, together with m.p.s or b.p.s, and references to the preparative methods adopted by us. The most intense band of a spectra of a thiophene derivatives is taken as the first absorption band, and the second intense band as the secondary absorption band.

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Table 1. The ultraviolet absorption of substituted thiophenes.

No.	Substituent	λ_{max}.	ε_{max}.	m. p.	Reference.
1	H	235	4,500	84**	(a)
2	2-CH₂COOH	235	3,900	76	(b)
3	3-CH₂COOH	234	3,400	80—81	(c)
4	2-COOH	{248 270	9,080 7,200	127—129	(d)
5	3-COOH	241	4,770	138—139	(e)
6	2-CHO	{257.5 279	8,540 6,030	78/3 mm**	(f)
7	2-COC₆H₅	{256 284	11,600 10,700	55—56	(g)
8	3-CN	{225 236	1,070 1,100	82/11 mm**	(h)
9	3-COCH₃	{221 227	1,100 1,070	57	(i)
10	3-Br	243	3,500	70/39 mm**	(j)
11	2-NHCOCH₃	264	10,300†	160	(k)
12	3-NHCOCH₃	257.5	5,950†	147—148	(k)
13	2-Cl, 5-COOH	{256 280	10,200 13,800	150—151	(l)
14	2-Br, 5-COOH	⌜251* 261* 276	~7,800 ~9,300 11,800	141—142	(m)
15	2-I, 5-COOH	{267 293	7,200 12,700	133—134	(n)
16	2-NO₂, 5-COOH	{250 312.5	2,550† 8,950	158—150	(o)
17	2-NO₂, 5-I	327	13,400	75	(p)
18	4-i-Pr., 2-COOH	{247 278	8,530† 6,170	91—92	(q)
19	4-Br, 2-COOH	{245 279	7,920† 4,170	113—114	(r)
20	4-NO₂, 2-COOH	{238 267	12,300† 4,800	154	(o)
21	4-NO₂, 2-COCH₃	{248 273	22,500 7,800	126—127	(s)
22	2-NO₂, 3-CN	{286 292	9,000 8,900	85—86	(k)
23	2-CN, 3-NO₂	{222 265	10,900 9,150	90—91	(k)
24	2-NO₂, 3-NHCOCH₃	{252 322	12,200 9,500	121—122	(r)
25	2-CH₃, 3-NO₂, 5-COOCH₃	{246 270	33,200 13,000	78—79	(s)
26	2-Br, 3-NO₂, 5-COOCH₃	{244 270	19,100 8,700	96—99	(t)
27	2-Cl, 3-NO₂, 5-COCH₃	{250 282	22,300 9,200	85—87	(u)
28	2-Br, 3-NO₂, 5-COCH₃	{253 282.5	21,600 9,500	104—106	(k)
29	2-CHO, 4-NO₂, 5-Cl	{251 283	26,800 11,500	101—102	(k)
30	2-CHO, 3,4-di-Br	{254 283	21,700 8,200	109—110	(k)
31	2—⟨O⟩—CH=CH, 5—NO₂	288	13,350	137—139	(k)
32	2—⟨O⟩—CH=CH, 3—NO₂	{248 287	16,850 9,800	47—47.5	(k)

33	2—[thiophene]—CH=CH, 3—NO$_2$,	286	12, 800	114. 5—116. 5	(k)
34	5—Br 2—[thiophene]—CH=CH, 3, 5—di—NO$_2$	264	14, 900	186—187	(k)

* ; shoulder.   ** ; b.p.   † ; measured in 95% ethanol

References to Table 1

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2. Results and Discussion

1) Monosubstituted thiophenes.

2- and 3-Thienylacetic acid (Table 1, Nos. 2 and 3).   These spectra are closely similar to those of thiophene, 2- and 3-alkyl thiophenes. Their first absorption band appears as a vibrational structure near 235 $m\mu$, with a slight decrease of the intensity relative to the band of the thiophene at 235 $m\mu$. This would be resulted by a lack of the conjugation between the carboxyl group and the thiophene ring.

2- and 3-Thiophenecarboxylic acid (Table 1, Nos. 4 and 5). The latter has the first absorption band at 241 $m\mu$. The slight bathochromic shift and the intensification of the first absorption band (241 $m\mu$) of the thiophenecarboxylic acid relative to that of the thiophene at 235 $m\mu$ would be a normal result of the weak conjugation of the carboxyl group with the thiophene ring. The first absorption band of the 2-isomer appears as a considerably strong, structureless band near 250 $m\mu$. The effect of the 2-carboxyl group on the spectra is considerably greater than that of the 3-isomer. The second absorption band at 270 $m\mu$ of 2-thiophenecarboxylic acid has a little weaker intensity than the first absorption band. The second absorption band would be caused by some interaction between a heteroatom and a carboxyl group.

2-Formyl- and 2-benzoylthiophene (Table 1, Nos. 6 and 7). These spectra are almost similar. The first absorption band appears near 260 $m\mu$. The moderate bathochromic shift and the intensification relative to the band of thiophene are caused by the conju-

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gation of the carbonyl group with the ring. The first absorption bands of 2-formyl-
and 2-benzoylthiophene are stronger than that of 2-carboxylic acid. The second absorption
band appears near 280 $m\mu$, as in the case of 2-carboxylic acid.

3-Cyano- and 3-acetylthiophene (Table 1, Nos. 8 and 9). The first and second
absorption bands of 3-cyano- and 3-acetylthiophene appear in the shorter wave-length
than those of 2-isomers.[6][4]

3-Bromothiophene (Table 1, No. 10). The first absorption band appears at 243 $m\mu$,
which wave-length is longer than that of the 2-isomer, and which intensity is decreased
to a half of the 2-isomer.

2- and 3-Acetylaminothiophene (Table 1, Nos. 11 and 12). The first absorption
bands appear near 260 $m\mu$. The spectra of the 2-isomer is in a little longer wave-length
and has the nearly double intensity refered to that of the 3-isomer. Each spectra shows
a moderate bathochromic shift and a intensification relative to that of thiophene.

It may concluded from the results, the conjugation between a substituent at the 2-
position and the thiophene ring is stronger than that between a substituent at the 3-
position and the thiophene ring.

The band of thiophene at 235 $m\mu$ was assigned to B-band,[12] but in some cases of
substituted thiophene derivatives, the assignment of the first absorption bands is unob-
vious. In Fig. 1, the λ_{max}'s of the first absorption bands of monosubstituted thiophenes
are plotted against the λ_{max}'s of the first primary bands of corresponding substituted

⟶ λ_{max} of the first primary absorption band of benzene derivative.
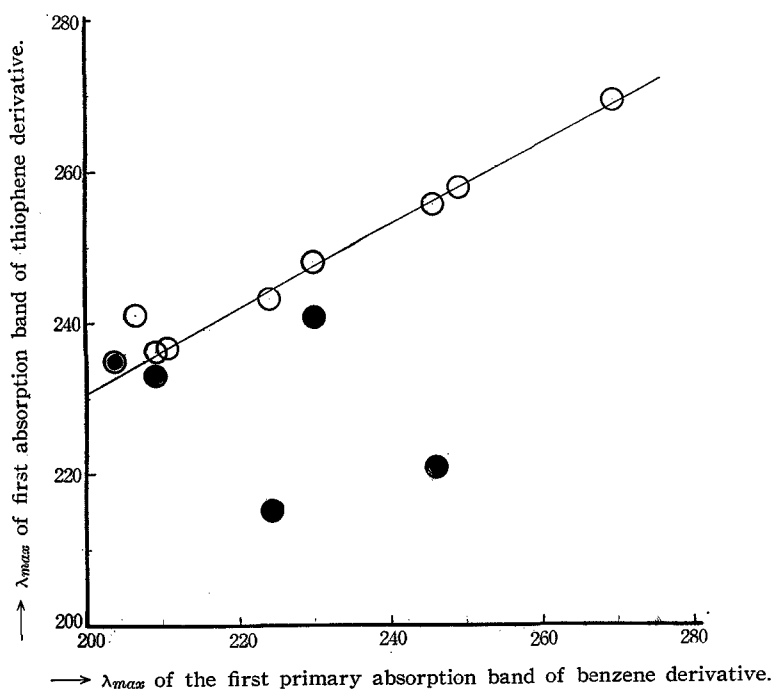
Fig. 1. Wave length maxima of the first absorption bands of 2-(○)
and 3-substituted thiophenes (●) vs. wave length maxima of the
first primary absorption bands of corresponding monosubstituted
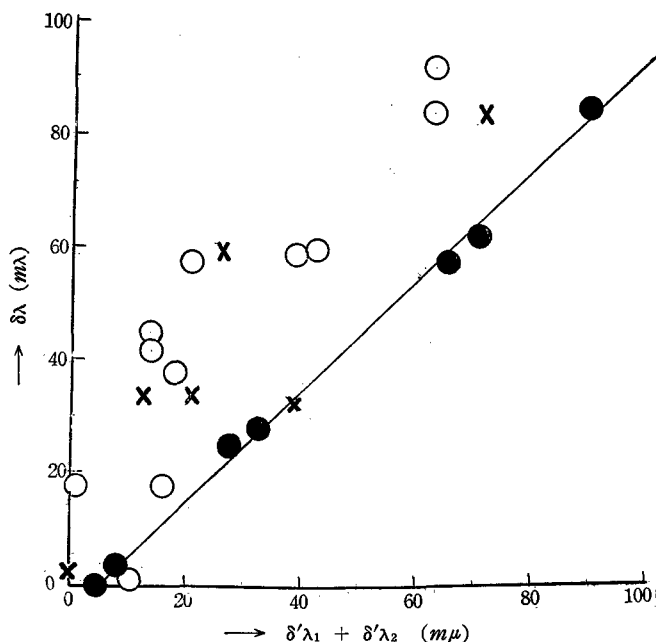benzenes.

Fig. 2. Wave length shifts of the first absorption bands of 2,5—(○),
2,4—(×) and 2,3-disubstituted thiophenes (●) plotted against the
sum of the $\delta'\lambda$ values of the two groups. $\delta'\lambda$ values are calculated
from the shifts of monosubstituted thiophenes relative to thiopene.

benzenes measured by Doub and Vandenbelt.[13] λ_{max}'s of the first absorption bands of 2-
substituted thiophenes have a linear relationship to the λ_{max}'s of the first primary bands
of corresponding benzene derivatives, and the relationship is given by the following
equation,

$$\lambda_{max\ (thiophenes)} = 0.55\ \lambda_{max\ (benzenes)} + 232$$

when λ_{max} is given in $m\mu$.

Doub and Vandebelt found also that the ratios of the wave-length of the secondary
bands to the first primary bands of monosubstituted benzenes, $\lambda_{sec.}/\lambda_{prim.}$, were almost
constant. The ratios $\lambda_{sec.}/\lambda_{first.}$ in 2-formyl-, 2-acetyl-, 2-nitro-, 2-benzoyl-, and 3-cyano-
thiophene are 1.08, 1.07, 1.10, 1.11 and 1.12, respectively. These values are nearly
constant, and are a little smaller than the mean value obtained from the spectra of
monosubstituted benzenes in water, 1.25.

2) Disubstituted thiophenes.

2-Chloro-, 2-bromo-2-iodo-, and 2-nitro-5-thiophenecarboxylic acid (Table 1. Nos. 13,
14, 15 and 16). (Fig. 3) The spectra of these halogeno derivatives are similar, and
their first absorption bands appear in longer wave-length than the second absorption
band. The iodine atom exhibits a bathochromic shift relative to the other halogen
isomers. These spectra have a low intense, vibrational structure in the range of 220 $m\mu$
and 240 $m\mu$. The nitro compound shows the first absorption band at longer wave-length,
but decrease in intensity relative to the halogeno derivatives. Thus the substituents
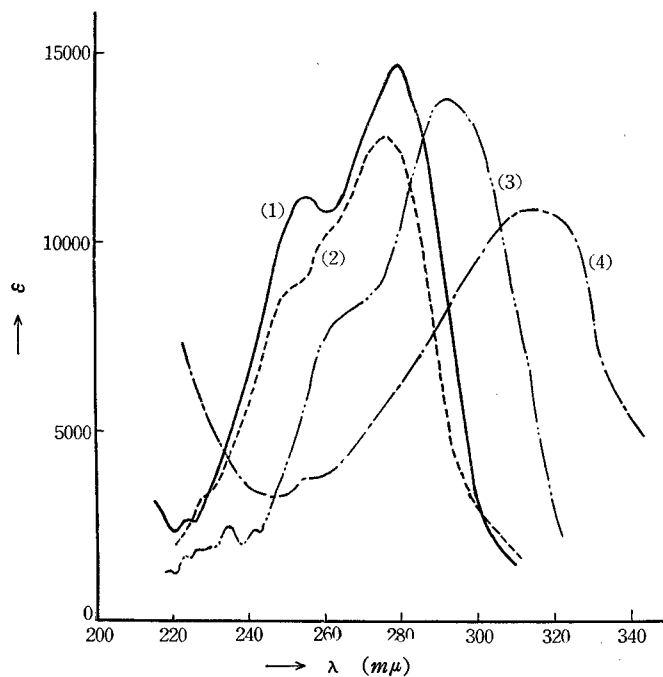
Fig. 3. Ultraviolet absorption of
   (1) 2-chloro-5-thiophenecarboxylic acid (in hexane),
   (2) 2-bromo-5-thiophenecarboxylic acid (in hexane),
   (3) 2-iodo-5-thiophenecarboxylic acid (in hexane),
   (4) 2-nitro-5-thiophenecarboxylic acid (in ethanol).
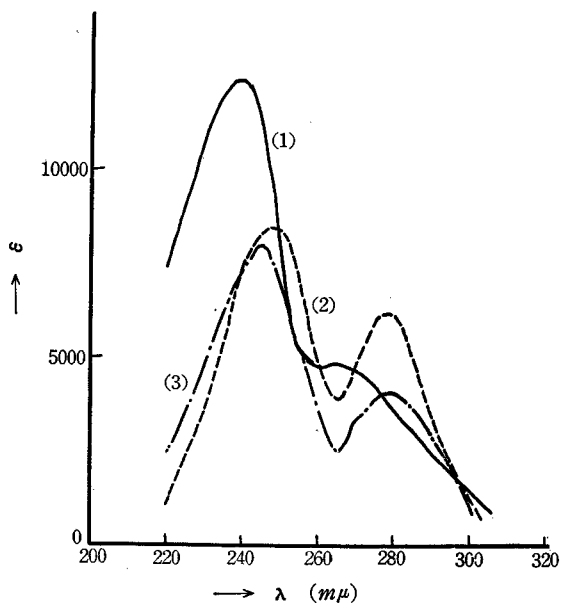

Fig. 4. Ultraviolet absorption (in 95% ethanol) of
 (1) 4-nitro-2-thiophenecarboxylic acid,
 (2) 4-iso-propyl-2-thiophenecarboxylic acid,
 (3) 4-bromo-2-thiophenecarboxylic acid.

in 2,5-disubstituted thiophenes affect the spectra rather in a wave-length than in a in-tensity.

4-iso-Propyl-, 4-bromo-, and 4-nitro-2-thiophenecarboxylic acid (Table 1, Nos. 18, 19 and 20). (Fig. 4) These spectra are closely similar. The first absorption bands appear near 240 $m\mu$. which are in shorter wave-length than the second absorption bands near 280 $m\mu$. The nitro group affects the spectrum not in the wave-length, but in the intensity.

2-Cyano-3-nitro-, 2-nitro-3-cyano- and 2-nitro-3-acetylaminothiophene (Table 1, Nos. 22, 23 and 24). These spectra are specific to each substituent. The spectra are effected chiefly by a 2-substituent, but a little by a 3-substituent.

The main effect of substituents in the 2,5-disubstituted thiophenes appears in the wave-length shift of the band, but the main effect of substituents in the 2,4-disubstituted thiophenes appears in the intensity change of bands.

The algebraic sums of the shift of the first absorption band of a monosubstituted thiophene are compared with the shifts of the first absorption band of the correspond-ing disubstituted thiophene derivatives. Though the calculated values are slightly greater than the measured values, it is apparent from Fig. 2 that calculated values and measured values are related with a linear relationship in the case of 2,3-disubsti-tuted thiophenes. In the case of 2,5-disubstituted compounds, on the other hand, the calculated shifts are smaller than the measured shifts. This suggests that some degree of a conjugation exist between substituents.

According to the results studied of benzene derivatives, the intensities of rather weakly conjugated disubstituted benzene derivatives vary in proportion to vector sums of spectroscopic moments.[14] The intensities of the first absorption band of 2,5-disubsti-tuted thiophenes are calculated by the following equation,

$$I = I_0 + m_1^2 + m_2^2 + m_1 m_2 \cos 148°.$$

where m_1 and m_2 are the spectroscopic moments of substituents, 1 and 2 which are calculated from the first absorption bands of monosubstituted thiophenes and that of thiophene in the same solvent, and 148° is the bond angle between 2- and 5-substituent.

Table 2. Spectroscopic calculation of intensity of first absorption bands of 2,5-disubstituted thiophenes.

Compound	Calculated value	Measured value	Solvent
2, 5-Dimethylthiophene	8, 160	7, 590[4]	iso-Octane
2, 5-Dibromothiophene	7, 840	7, 120[4]	iso-Octane
2, 5-Diiodothiophene	8, 110	7, 400[4]	iso-Octane
2-Chloro-5-thiophene-carboxylic acid	11, 000	13, 800	Hexane
2-bromo-5-thiophene-carboxylic acid	13, 000	11, 700	Hexane
2-Iodo-5-thiophene-carboxylic acid	15, 500	12, 700	Hexane
2-Bromo-5-nitrothiophene	8, 700	10, 200	Hexane
2-Iodo-5-nitrothiophene	10, 400	13, 400	Hexane

Thiophene in hexane ($\lambda_{max} = 235$) $\varepsilon = 4,500$; in iso-octane ($\lambda_{max} = 231$) $\varepsilon = 7,600$, calculated spectroscopic moments of substituents, CH_3 ; 44, Cl ; 13, Br ; 28, NO_2 ; —39, COOH ; —68.

.The values are listed in Table 2 together with intensites of the first absorption bands. The calculated values are greater than the measured values in the case of symmetric compounds, but smaller in the case of compounds in which the conjugation between substituents could be expected. These facts suggest that there is a considerable conjugation between the substituents at 2- and 5-position. The spectroscopic moments of 3-substituents are not calculated.

3) Trisubstituted thiophenes.

Methyl 2-methyl- and 2-bromo-3-nitro-5-thiophenecarboxylate (Table 1, Nos. 25 and 26). These spectra are shown in Fig. 5. The influence of 2-substituent appears in the intensity of the first absorption band. The higher intensity of 2-methyl isomer over 2-bromo are also observed in the first absorption bands of 2-methyl[10] and 2-bromo-5-thiophenecarboxylic acid (Table 1, No. 14).

2-Chloro- and 2-bromo-3-nitro-5-acetylthiophene (Table 1, Nos. 27 and 28).

These spectra are closely similar, as shown in Fig. 6. The difference between the effects of chlorine and bromine atom is closely resemble to that of o-chloro- and o-bromo nitrobenzene of which spectra were reported by Forbes.[15] The first absorption bands of 2-chloro- and 2-bromo-3-nitro-5-acetylthiophene are at a little shorter wavelength than that of 2-acetylthiophene[4], but the intensities are increased nearly a double.
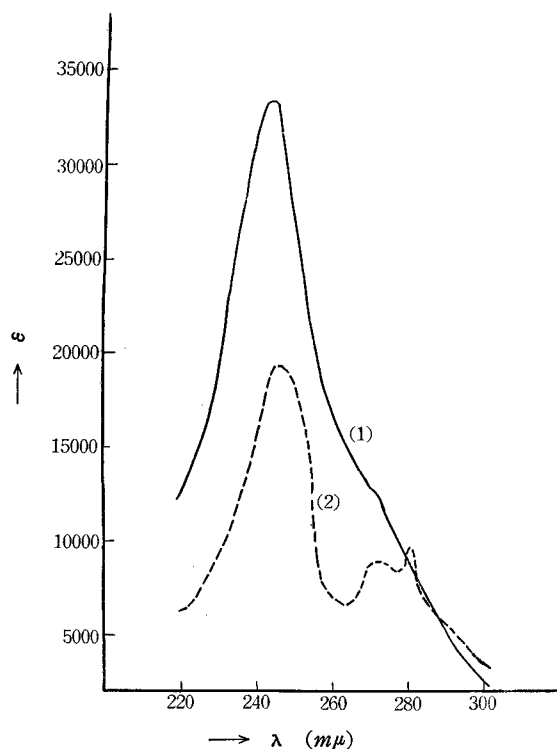

Fig. 5. Ultraviolt absorption (in hexane) of
    (1) 5-methyl-4-nitro-2-thiophenecarboxylic acid,
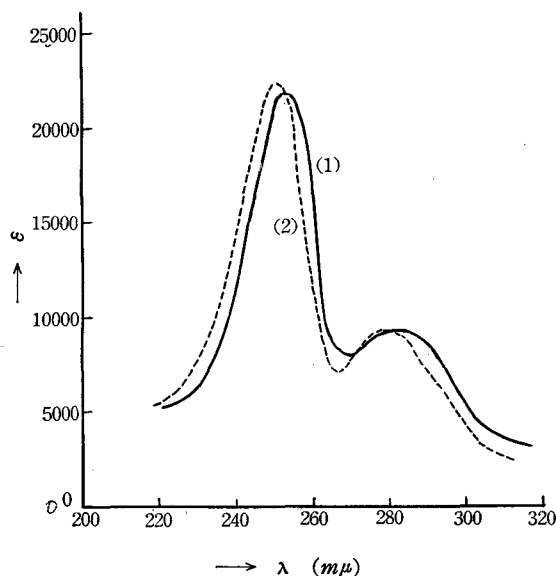   (2) 5-bromo-4-nitro-2-thiophenecarboxylic acid.

Fig. 6. Ultraviolet absorption (in hexane) of
(1) 5-bromo-4-nitro-2-acetylthiophene,
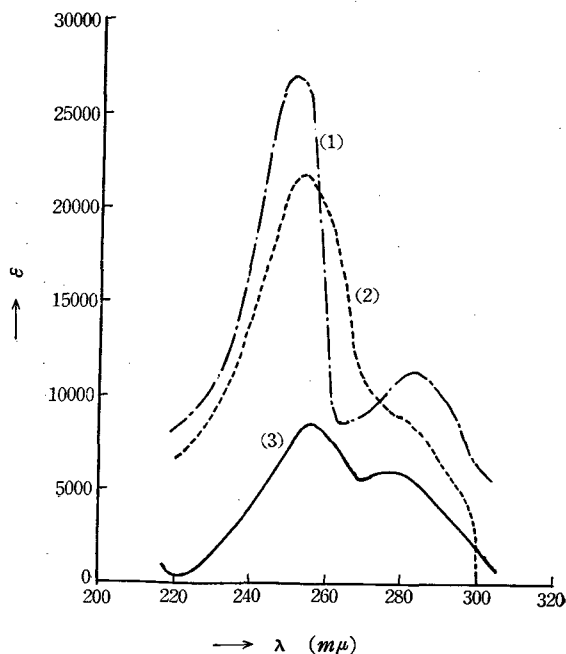(2) 5-chloro-4-nitro-2-acetylthiophene.

Fig. 7. Ultraviolet absorption (in hexane) of
(1) 5-chloro-4-nitro-2-thiophenealdehyde,
(2) 3,4-dibromo-2-thiophenealdehyde,
(3) 2-thiophenealdehyde.

4-Nitro-5-chloro- and 3,4-dibromo-2-thiophenealdehyde (Table 1, Nos. 29 and 30.) These spectra are shown in Fig. 7, together with that of 2-thiophene-aldehyde. As shown in Fig. 7, the effect of the second and the third substituents on spectra appears in the intensity.

5-Nitro-, 3-nitro-, 3-nitro-5-bromo- and 3,5-dinitro-2-(2-furfurydenemethyl)-thiophene. (Table 1, Nos. 31, 32, 33 and 34). Though the shapes of the spectra of these compounds are closely similar to each other as shown in Fig. 8., the spectrum of 3,5-dinitro-2-(2-furfurydenemethyl)-thiophene shows a striking hypsochromic shift relative to the mononitro drivatives. This hypsochromic effect of the second nitro group must not be caused by a steric hinderance between the thiophene ring and the furfurydenemethyl group, because the steric inhibition between those could not be expected. This expectation is confirmed from the fact that even the two thiophene rings in the 3,3',5,5'-tetranitro-2,2'-bithienyl are coplanner,[16] which must be suffered from the steric hinderance more largely than the furfurydenemethylthiophene.

The similar hypsochromic effect of a nitro group has been observed by Boig.[6]

3. Experimental

A Hitachi quartz spectrophotometer with a hydrogen discharge tube source are used for all measurements. Extinction coefficients are calculated by dividing the observed densities by the molar cell concentration.
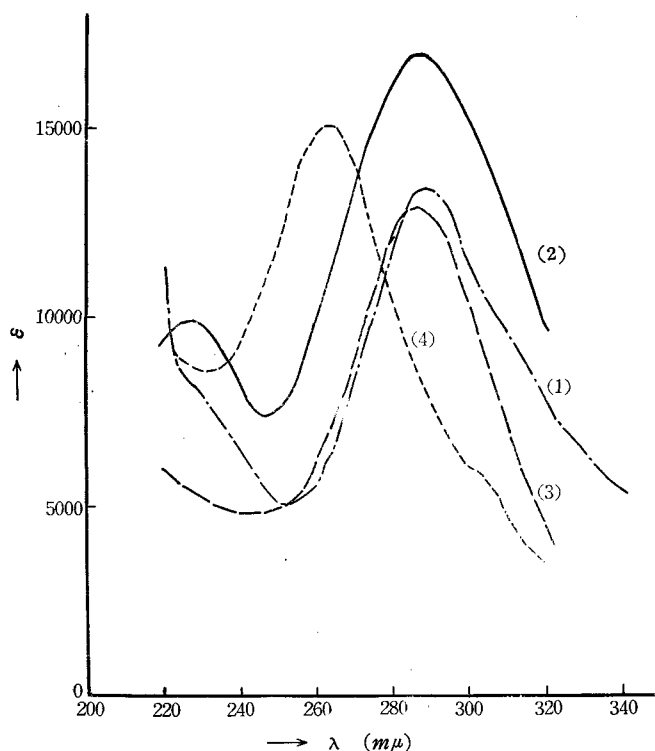
Fig. 8. Ultraviolet absorption (in hexane) of
　(1)　5-nitro-2-(2-furfurydenemethyl)-thiophene,
　(2)　3-nitro-2-(2-furfurydenemethyl)-thiophene,
　(3)　3-nitro-5-bromo-2-(2-furfurydenemethyl)-thiophene.
　(4)　3,5-dinitro-2-(2-furfurydenemethyl)-thiophene.

Concentrations are about 10^{-4} mole/liter in all measurements.

Liquid samples are redistilled before use and solid compounds are recrystallized from suitable solvents. Boiling and melting points are checked with the value cited in literatures to confirm the purities of samples.

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