

ULTRAVIOLET ABSORPTION SPECTRA IN THE THIOPHENE SERIES.
HALOGEN AND NITRO DERIVATIVES

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The ultraviolet absorption spectra of relatively few thiophene derivatives have been published in the literature, and these have usually been determined with 95% ethanol as solvent. The present study includes six thiophene compounds which have long been known but for which the ultraviolet absorption spectra have not previously been published. The results of this study have been summarized in Table I and the new ultraviolet absorption spectra curves are shown in Figures 1 and 2. All spectra were obtained using isoctane as solvent.

The information listed in Table I and shown in Figures 1 and 2 is self-explanatory. Data and curves for thiophene, 2-chlorothiophene, 2-bromothiophene, and 2,5-dibromothiophene have already been published but some of this information has been included here for purposes of comparison. A point of particular interest in the table and figures is the apparent hypsochromic effect of the second nitro group in 2,5-dichloro-3,4-dinitrothiophene as compared with 2-nitrothiophene and 2,5-dichlorothiophene.

EXPERIMENTAL

2-Cyanothiophene. This compound was prepared from 2-thiophenecarboxaldehyde by the formation and subsequent dehydration of the *syn*-oxime, using essentially the standard procedure. According to Putokhin and Egorova (1) the oxime has m.p. 130°. Our product melted sharply at 142.2° (corr.). However, dehydration of our oxime using the method of Putokhin and Egorova (2) gave the nitrile, b.p. 196°, corresponding to 196° as recorded by these same authors (2) and also by Hantzsch (3).

2-Iodothiophene. This compound was prepared by the method of Minnis (4) and also by the more convenient method of Lew and Noller (5). The freshly distilled product had b.p. 80–81° (20 mm.), and was a pale yellow liquid which darkened on standing. The boiling point of our sample was the same as the listed value (4, 5).

2-Nitrothiophene. This compound was prepared by the method of Babasinian (6) and gave white needles melting at 46.5° as listed in Hartough (7), page 228. Ten minutes in sunlight was sufficient to develop a light yellow to brown color. Before determination of the ultraviolet absorption spectra, the sample was recrystallized from pentane.

2,5-Diiodothiophene. The residue obtained from distillation of 2-iodothiophene as prepared by the method of Minnis (4), was recrystallized from alcohol, m.p. 41.5°, corresponding to the same value obtained by Minnis (4). The ultraviolet absorption spectra have not previously been published.

2,5-Dichloro-3,4-dinitrothiophene (VII). This compound has already been described in the literature (8, 9). The substance was found to be very soluble in chloroform, benzene, alcohol, and ether; it dissolved with difficulty in boiling pentane. The slightly yellow crystals gave m.p. 88°, compared with 88–91° as found in the literature (8).

Ultraviolet absorption spectra. All ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, model DU, using a 1-cm. quartz cell. A hydrogen discharge tube was used as the ultraviolet source and a tungsten lamp was employed in the visible range. Optical density measurements were made at intervals of 5 millimicrons

TABLE I
 SUMMARY OF ULTRAVIOLET ABSORPTION DATA

COMPOUND	B.P./M.P., °C.	MAXIMUM (m μ)	log ϵ	ϵ	INCREASE IN ϵ , %
Thiophene ^a (I)	84 ^b	231	3.85	7100	—
2-Bromothiophene	150-151 ^c	235-236	3.96	9100	28.8
2-Chlorothiophene	128 ^d	236	3.94 ^e	8700	23.0
2-Cyanothiophene (II)	196	243	3.97	9300	31.8
2-Iodothiophene (III)	80-81 ^f (20 mm)	243	3.97	9300	31.8
2-Nitrothiophene (IV)	46.5 (m.p.)	268-272 ^g 294-298 ^g	3.80 3.78	6300 6000	-10.9 ^h —
2,5-Dibromothiophene	210-212	252	3.96	9100	28.8
2,5-Dichlorothiophene (V)	163 ⁱ	252	3.87	7400	4.7
2,5-Diiodothiophene ^j (VI)	41.5 (m.p.)	266	4.15	14000	99.5
2,5-Dichloro-3,4-dinitrothiophene (VII)	88 ^k (m.p.)	315	2.43	270	—
		237	4.14	13800	95.0
		282-284 ^g	3.39	2450	—

^a American Petroleum Institute Research Project No. 44, Serial No. 136, and Hartough, *Thiophene and Its Derivatives*, pp. 101-102. ^b Literature value 84.12, Fawcett and Rasmussen, *J. Am. Chem. Soc.* **67**, 1705 (1945). ^c Hartough, p. 208, lists 149-151. ^d Literature value 128, Coonradt, *et al.*, *J. Am. Chem. Soc.*, **70**, 2564 (1948). ^e American Petroleum Institute Research Project No. 44, Serial No. 316 and Hartough, p. 104, give log ϵ 3.89. ^f Literature value is same as that given by Minnis, and also by Lew and Noller (see References 4, 5). ^g Plateau. ^h Decrease. ⁱ Literature value 162, same source as *d*. ^j Literature value 41.5, given by Minnis (Ref. 4). ^k Literature value 88-91, (Reference 8).

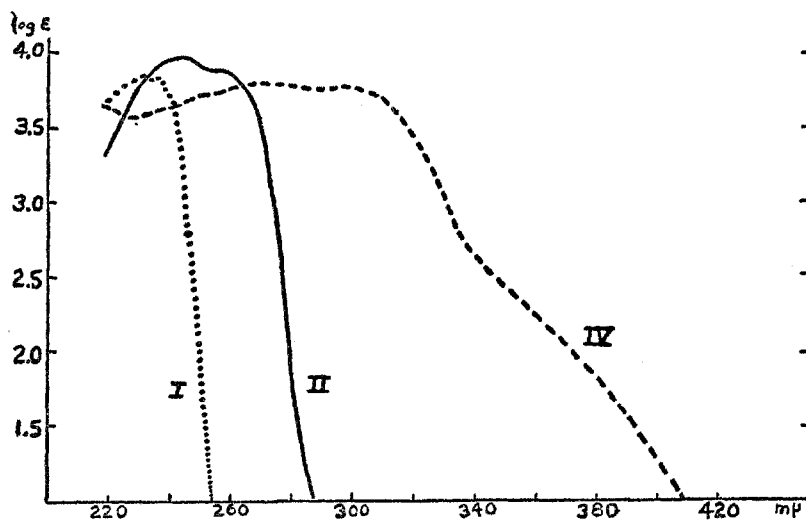


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA (in iso-octane): (I) Thiophene, (II) 2-Cyanothiophene, (IV) 2-Nitrothiophene

above 300 millimicrons, and at intervals of 2 millimicrons below 300, except in the vicinity of maxima and minima, where readings were taken at intervals of 1 millimicron. Figures 1 and 2 show the logarithm of the molar extinction coefficients plotted against wave length in millimicrons. Spectrophotometric grade isooctane was used as solvent in all cases. Substances were freshly recrystallized or distilled before the sample was taken and samples

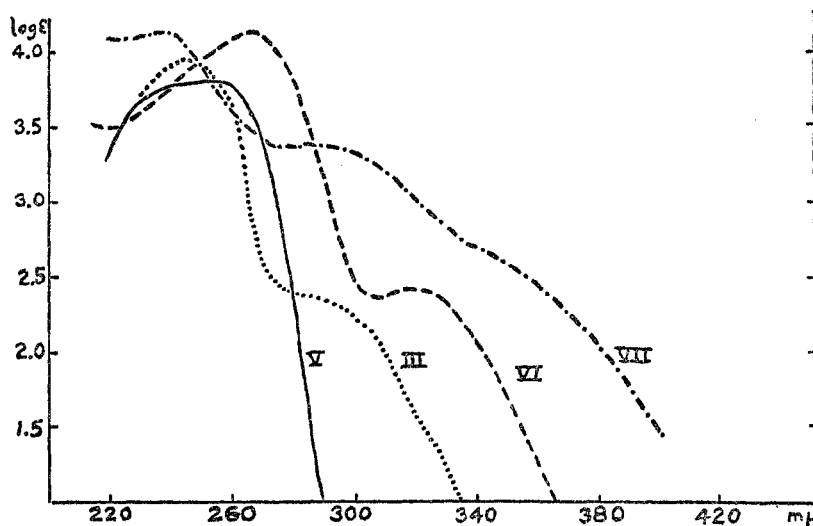


FIG. 2. ULTRAVIOLET ABSORPTION SPECTRA (in isooctane): (III) 2-Iodothiophene, (V) 2,5-Dichlorothiophene, (VI) 2,5-Diiodothiophene, and (VII) 2,5-Dichloro-3,4-dinitrothiophene

were kept in a closed, light-proof container to prevent any possible deterioration by the action of light.

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SUMMARY

Six derivatives of thiophene for which the ultraviolet absorption spectra in isooctane have been determined include 2-cyanothiophene, 2-iodothiophene, 2,5-diiodothiophene, 2-nitrothiophene, 2,5-dichlorothiophene, and 2,5-dichloro-3,4-dinitrothiophene. The ultraviolet absorption spectra data for thiophene, 2-bromo-, 2-chloro-, and 2,5-dibromo-thiophene have been included in Table I for purposes of comparison.

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