

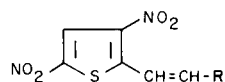
Synthesis and Spectral Properties of Some 1,2-Dithienylethenes and 1-Thienyl-4-phenylbutadienes

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A total of seven thiophene derivatives not previously reported have been prepared *via* the Knoevenagel condensation of an activated methylthiophene and a heterocyclic or aromatic aldehyde. The principal peaks in the ultraviolet and visible absorption spectra as well as some nuclear magnetic resonance data are reported for these compounds.

Polythienyl compounds are known to be active nematocides (2), and plant growth regulators (3). Certain stilbene derivatives have shown antifungal activity (4). We therefore prepared several 3-nitro-5-substituted-2-vinylthiophenes related to stilbene (structures I and II) where R was thienyl, furyl, phenyl or β -styryl.



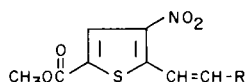
Ia) R = 3-C₄H₃S

b) R = 2-C₄H₃S

c) R = 2-C₄H₃O

d) R = -CH=CHC₆H₅

e) R = C₆H₅



IIa) R = 3-C₄H₃S

b) R = 2-C₄H₃S

c) R = 5-Cl-2-C₄H₂S

d) R = -CH=CHC₆H₅

Very few papers have appeared in the literature dealing with dithienylethenes. Y. K. Yur'ev and D. Eckhardt reported the synthesis of *trans*-1,2-di(2-thienyl)-ethene in 1961 (5) and Kellogg, Groen, and Wynberg reported the synthesis of some unsubstituted and methyl substituted dithienylethenes and their photolysis products in 1967 (6); in both laboratories the syntheses were accomplished *via* Wittig reactions. A convenient synthesis of the desired compounds would involve a Knoevenagel condensation of aromatic aldehydes with an activated methyl group on thiophene. Two electron withdrawing substituents *ortho* and *para* on a benzene ring are usually sufficient to activate a methyl group for the desired condensation (7,8). Condensation of 3,5-dinitro-2-methylthiophene and methyl 5-methyl-4-nitro-2-thenoate with benzaldehyde has been reported to occur in good yield (9).

The compounds, described in Table I, were all prepared by direct condensation of 3,5-dinitro-2-methylthiophene

or methyl 5-methyl-4-nitro-2-thenoate with 3-thenaldehyde, 2-thenaldehyde, 2-furfural, 5-chloro-2-thenaldehyde, or cinnamaldehyde under usual Knoevenagel conditions. The yields with cinnamaldehyde were exceptionally poor, and these reactions were accompanied by much tar formation.

Although the dinitro compounds (I) were too insoluble for satisfactory n.m.r. spectra, the data for the carbomethoxy derivatives (II) have been summarized in Table II. It was hoped that these 1,2-dithienylethenes might be clearly shown to be in the *trans*-configuration. The n.m.r. spectra of compounds IIa, b and d were too complex in the aromatic regions to extract coupling constants. However, the addition of a chlorine atom in IIc produced essentially two independent AB patterns from which coupling constants of 4 Hz and 16 Hz could be obtained. The AB pattern with J = 4 Hz was assigned to the protons on the thiophene ring since the coupling constant for 2,5-disubstituted thiophenes is reported to be about 4 Hz (10). The coupling constant of 16 Hz for the ethene protons is consistent with a *trans* configuration about the double bond (11).

Ultraviolet Absorption Spectra.

All of these brightly colored compounds exhibit relatively intense ($\epsilon > 10,000$) absorption spectra in the range of 200-450 $m\mu$ (See Table III). There are four distinct regions of absorption characteristic of these 2-vinyl-5-negatively substituted thiophenes. The first two (identified as the K and B bands in Table I) correspond closely to similar bands found in the simple bithienyls (12). These authors observed two characteristic moderately intense bands ($\epsilon = 5,000-16,000$) in the range of 204-210 $m\mu$ and 240-260 $m\mu$ for a series of thirty 5-substituted and 5,5'-disubstituted-2,2'-bithienyls. These bands correspond to the K and B bands of thiophene itself (13). All of the

TABLE I

Properties of 3-Nitro-2-Vinyl Thiophene Derivatives

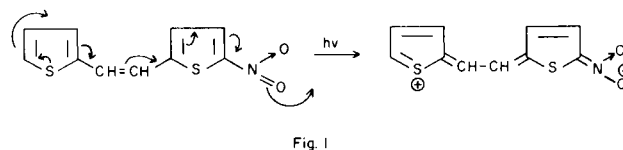
Compound	Purified Yield % (a)	°C MP	Formula	Nitrogen, % (g)		Sulfur, %		Color
				Calcd.	Found	Calcd.	Found	
Ia	48.5 (A)	204-205	C ₁₀ H ₆ N ₂ O ₄ S ₂ (b)	9.93	9.89	22.71	22.65	orange
Ib	70.0 (A)	235-237	C ₁₀ H ₆ N ₂ O ₄ S ₂ (c)	9.93	9.87	22.71	23.15	shiny red (h)
Ic	43.5 (B)	186-187	C ₁₀ H ₆ N ₂ O ₅ S	10.52	10.67	12.04	11.91	dk. red (h, i)
Id	1.2 (B)	241-242	C ₁₄ H ₁₀ N ₂ O ₄ S	9.26	9.28	10.60	10.55	red
IIa	74.0 (B)	139-140	C ₁₂ H ₉ NO ₄ S ₂ (d)	4.74	4.98	21.70	21.33	bronze
IIb	59.0 (B)	139-140	C ₁₂ H ₉ NO ₄ S ₂ (e)	4.74	4.91	21.70	21.47	orange
IIc	91.0 (C)	177-178	C ₁₂ H ₈ NO ₄ S ₂ Cl (f)	4.25	4.39	19.42	19.54	dk. orange
IId	9.0 (B)	156-157	C ₁₆ H ₁₃ NO ₄ S	4.44	4.65	10.17	10.15	orange

(a) Recrystallizing Solvents: A, xylene; B, ethanol; C, *t*-butyl alcohol. (b) Calcd: C, 42.54; H, 2.14. Found: C, 42.66; H, 2.40. (c) Calcd: C, 42.54; H, 2.14. Found: C, 42.24; H, 2.32. (d) Calcd: C, 48.80; H, 3.07. Found: C, 48.67; H, 3.09. (e) Calcd: C, 48.80; H, 3.07. Found: C, 48.87; H, 3.14. (f) Calcd: C, 43.70; H, 2.43. Found: C, 43.75; H, 2.60. (g) All analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. (h) These compounds crystallized as plates. All others were needles. (i) This compound has been reported by Y. Sugimoto, S. Nishimura and E. Imoto, *Bull. Univ. Osaka Prefecture, Ser. A*, 8, No. 1, 71 (1960). No preparation or analytical data were given. A m.p. of 186-187° was reported.

vinylthiophenes reported here show an intense peak ($\epsilon = 11,400-17,900$) at $206 \pm 2 \text{ m}\mu$ (K band) and a second band in the range of $247-268 \text{ m}\mu$ (B band). This second band reflects the influence of the 5-substituent on the parent chromophore, since the three 5-nitro-2-vinylthiophenes (Class I) absorb rather intensely ($\epsilon = 14,000-16,000$) at $264 \pm 4 \text{ m}\mu$, while the four 5-carbomethoxy-2-vinylthiophenes (Class II) absorb sharply at $248 \pm 1 \text{ m}\mu$ ($\epsilon = 10,000-20,000$). The more polar nitro group clearly causes a bathochromic shift of 15-20 $\text{m}\mu$ over that of the carbomethoxy group.

A third peak of less intensity, usually observed as a shoulder on the long wave-length side of the B-band, was also observed in the spectra of these vinylthiophenes. We have labeled this a B'-band, as it correlates closely with the B-band, appearing about $35 \pm 5 \text{ m}\mu$ further out in the spectrum in each case. This may be due to a $\pi-\pi^*$ local excitation of the vinylthiophene system, correlating with the $\pi-\pi^*$ B band. Curtis and Phillips (12) also observed an intense peak at $330-360 \text{ m}\mu$ ($\epsilon \cong 20,000$) in the absorption spectra of their bithienyls, characteristic of an electron transfer transition.

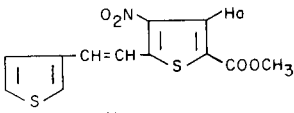
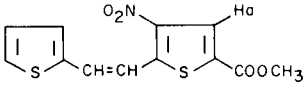
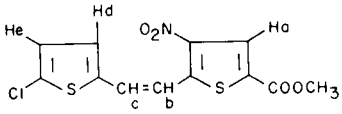
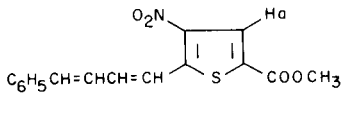
A similar peak, labeled the C band in Table III, is found in the long wavelength region ($382-445 \text{ m}\mu$) of the u.v. spectrum for all of these vinylthiophenes. It may be attributed to electronic transitions of the type shown in fig. I. Evidence that this band results from total



conjugation in the molecule is found in comparing related compounds. Note that the C band for compound Ia, in which a 3-substituted thiophene provides crossed conjugation (14) is hypsochromically shifted from that of compound Ib, in which a 2-substituted thiophene provides full conjugation. Similarly, compound IIc exhibits a bathochromic shift and great intensification of this long wave-length band over that of IIb, characteristic of conjugation of an additional auxochromic chlorine atom (fig. II). The spectrum of IId, with an additional vinyl group, is also characteristic of this extended conjugated system. Also consistent with the mechanism shown in fig. I, is that compound Ic shows a bathochromic shift of the C band relative to Ib. Since furan is less aromatic (15) than thiophene we would expect the disruption of aromaticity in Ic to occur at a lower energy, or higher wavelength value than that in Ib. Similarly, the hypsochromic shift of the C band in Ie, previously prepared by Rinke (9), is consistent with the higher energy required to disrupt the aromaticity of the benzene ring.

TABLE II

N.M.R. Spectra of Methyl 5-Vinyl-4-Nitro-2-Thenoates (a)

Compound	Proton Ratio	δ -Value (b)	Assignment Coupling (Hz)
 IIa	3 5 1	3.85 (s) 6.7-7.9 (m) 8.1 (s)	$\text{CH}_3\text{OC}-\overset{\text{O}}{\parallel}$ Ha
 IIb	3 5 1	3.9 (s) 7.0-8.0 (m) 8.1 (s)	$\text{CH}_3\text{OC}-\overset{\text{O}}{\parallel}$ Ha
 IIc	3 1 1 1 1 1	3.9 (s) 6.9 (d) 7.02 (d) 7.20 (d) 7.80 (d) 8.17 (s)	$\text{CH}_3\text{OC}-\overset{\text{O}}{\parallel}$ Hd or He J = 4 Hd or He J = 4 Hb or Hc J = 16 Hb or Hc J = 16 Ha
 IIId	3 9 1	3.9 (s) 6.8-7.8 (m) 8.2 (s)	$\text{CH}_3\text{OC}-\overset{\text{O}}{\parallel}$ Ha

(a) All measurements were on a Varian A-60 spectrometer using tetramethylsilane as internal standard and deuteriochloroform as solvent. (b) s, singlet; d, doublet; m, multiplet.

TABLE III

Ultraviolet and Visible Absorption Maxima of Thiophene Derivatives

Compound, (a)	K band	B band	B' band	C band
	λ max, $m\mu$ (ϵ) (b)	λ max, $m\mu$ (ϵ)	λ max, $m\mu$ (ϵ)	λ max, $m\mu$ (ϵ)
Ia	208 (17,900)	262 (16,000)	(295) (7,400)	417 (22,000)
Ib	206 (12,700)	268 (14,300)	(300) (9,850)	435 (15,800)
Ic (c)	206 (13,800)	267 (19,300)	(306) (9,400)	443 (31,000)
Id	206 (15,100)	(261)(14,190)	291 (15,700)	445 (25,100)
Ie	206 (27,000)	258 (23,000)	290 (13,200)	382 (14,100)
IIa	206 (11,400)	247 (14,800)	(280) (8,800)	393 (6,320)
IIb	205 (12,000)	248 (19,100)	(278) (14,900)	403 (4,000)
IIc	207 (15,100)	248 (9,500)	289 (12,200)	415 (20,000)
IId	207 (13,700)	249 (12,600)	280 (14,800)	414 (19,700)

(a) Compounds of Class I are 5-NO₂ derivatives, Class II are 5-COOCH₃ derivatives. (b) All spectra were taken on a Bausch and Lomb Spectronic 505 from 200 $m\mu$ - 500 $m\mu$ in spectral-grade ethanol. Wavelengths in parentheses refer to inflection points. (c) The spectrum of this compound in hexane solution has been reported by Y. Sugimoto, S. Nishimura and E. Imoto, "Bull. Univ. Osaka Prefecture", Ser. A, 8, No. 1, 71 (1960), who include only the B and B' bands, 265 $m\mu$ (15,000), 305 $m\mu$ (5,500).

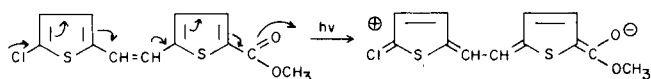


Fig. 11

EXPERIMENTAL (16)

Condensation Reactions.

General Procedure.

In a 300 ml. 3-necked round bottom flask, fitted with a mechanical stirrer, Dean and Stark water trap and condenser, was placed approximately 25 mmoles of the substituted methylthiophene and 40 mmoles of the freshly distilled aldehyde dissolved in 100 ml. of anhydrous xylene. About 7 drops of piperidine were added initially, and after 0.5 hour an additional 5 to 10 drops were added. The time of the reaction was ca 1 hour, the reaction being stopped when clear solvent distilled into the trap. Usually it was not necessary to recycle any of the liquid from the trap for the solvent to lose its cloudy appearance.

Some of the solvent was then evaporated and the compound recrystallized, after treatment with decolorizing carbon. The mother liquor was then further concentrated and an additional amount of product was obtained. A typical example is as follows.

1-(3-Nitro-5-carbomethoxy-2-thienyl)-2-(3-thienyl)ethene (IIa).

A solution of 5 g. (25 mmoles) of methyl 5-methyl-4-nitro-2-thenoate, prepared according to the procedure of Rinkes (9) from 5-methyl-4-nitro-2-thenoic acid (17), and 4.2 g. (37 mmoles) of 3-thenaldehyde (18) in 100 ml. of xylene with 7 drops of piperidine added, was refluxed for 90 minutes. After 40 minutes an additional 10 drops of piperidine were added. The solvent was concentrated to 1/2 volume, and the dark precipitate recrystallized from acetone after treatment with decolorizing carbon. Bronze needles, (4.4 g., 74%) melting from 139-140° were obtained.

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