The Substituent Effects in Thiophene Compounds. III.[1] ^{1}H NMR and IR Studies in Methyl [*trans*-β-(Substituted 2-thienyl)acrylate]s

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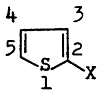
The ^{1}H NMR spectra and IR C=O stretching frequencies of methyl [*trans*-β-(3-, 4-, and 5-substituted 2-thienyl)acrylate]s are reported. The chemical shifts of the ring protons in methyl [*trans*-β-(4- and 5-substituted 2-thienyl)acrylate]s are correlated linearly with those of the corresponding protons in substituted thiophenes and methyl (substituted 2-thiophenecarboxylate)s. The substituent effects on the chemical shifts of α-protons in methyl [*trans*-β-(3- and 5-substituted 2-thienyl)acrylate]s have been interpreted by the mesomeric effect of the substituentes. The plots of the coupling constants in methyl [*trans*-β-(substituted 2-thienyl)acrylate]s against those in substituted thiophenes and methyl (substituted 2-thiophenecarboxylate)s gave good linear correlations. The IR C=O stretching wave numbers showed a narrow range of variation. The coupling constants in methyl [*trans*-β-(substituted 2-thienyl)acrylate]s were found to vary linearly with the electronegativity of the substituents.

In previous investigations,[1,2] the ^{1}H NMR spectra of 2- and 3-substituted thiophenes (**1** and **2**), and methyl (3-, 4-, and 5-substituted 2-thiophenecarboxylate)s (**3**—**5**), and methyl (2-, 4-, and 5-substituted 3-thiophenecarboxylate)s (**6**—**8**) were measured, and the effects of the substituents were discussed.



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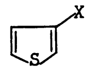

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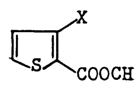

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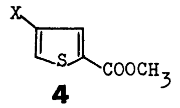

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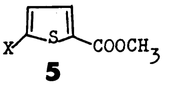

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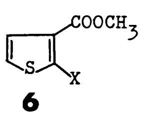

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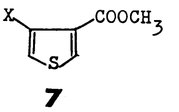

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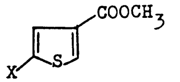

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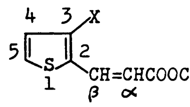
The investigation has been extended to the substituent effects in methyl [*trans*-β-(3-, 4-, and 5-substituted 2-thienyl)acrylate]s (**9**—**11**). The characteristics of the ^{1}H NMR spectra of methyl [*trans*-β-(substituted 2-thienyl)acrylate]s, and the correlations of the chemical shifts and of the coupling constants between these compounds and substituted thiophenes and methyl (substituted 2-thiophenecarboxylate)s have been discussed in this paper. The coupling constants of methyl [*trans*-β-(substituted 2-thienyl)acrylate]s are correlated with the electronegativities of the substituents. The IR C=O stretching frequencies of methyl [*trans*-β-(substituted 2-thienyl)acrylate]s were measured and compared with those of methyl (substituted 2-thiophenecarboxylate)s.



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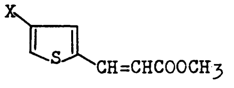

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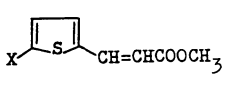

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Results and Discussion

The ^{1}H NMR spectra of methyl [*trans*-β-(3-, 4-, and 5-substituted 2-thienyl)acrylate]s were measured in deuteriochloroform at 25 °C. For convenience, the author used the notations H(2), H(3), H(4), H(5), H(α), and H(β) for the 2-, 3-, 4-, 5-, α-, and β-protons of methyl [*trans*-β-(substituted 2-thienyl)acrylate]s, and *cc*, *p*, *i*, and *s* for the correlation coefficient, slope, intercept, and standard deviation in the least-squares analysis. The ^{1}H NMR spectrum of methyl *trans*-β-(3-chloro-2-thienyl)acrylate (**9**, X=Cl) showed signals of (*ortho*-coupling) ring protons at δ 6.96 and 7.33, of (*trans*-coupling) olefinic protons at δ 7.86 and 6.27, and of methyl protons at δ 3.80. From the detailed analysis of the spectrum, the long-range couplings have been observed between H(5) and H(β) or H(α). It is noteworthy that the long-range coupling is observed between H(5) and H(α), because the interacting

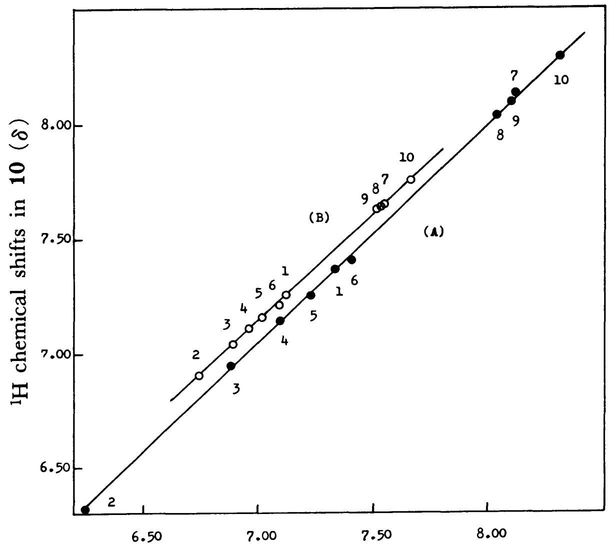


Fig. 1. Correlation between ^{1}H chemical shifts in **10** and **2**; numbering as in Table 2. A, δ_5(**10**) *vs.* δ_2(**2**). B, δ_3(**10**) *vs.* δ_4(**2**).

hydrogen nuclei in this compound are more separated than those in Zig-Zag[3–6] and W-letter couplings.[7,8] The spectra of other methyl [*trans*-β-(substituted 2-thienyl)acrylate]s are similar to this spectrum. In the series of compounds **10** and **11**, the long-range couplings were also found between hydrogens in thiophene ring and those in the side chain. In the series of **10**, both H(3) and H(5) couple with H(α) and H(β), but in the series of **11**, only H(3) with H(α) and H(β). It is found that H(4) in **9** does not couple with any hydrogen in the side chain, whereas H(4) in **11** couples with H(β) in methoxycarbonyl and nitro derivatives (J=0.20 Hz, in both cases). The spectra were assigned on the basis of chemical shifts and characteristic ring and long-range coupling constants. The refined chemical shifts and coupling constants were obtained

TABLE 1. ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF METHYL [*trans*-β-(3-SUBSTITUTED 2-THIENYL)ACRYLATE]S (SERIES **9**)

		Chemical shifts (δ)						Coupling constants/Hz					
No.	X	H(4)	H(5)	H(β)	H(α)	$COOCH_3$	Others	J_{45}	$J_{5\beta}$	$J_{5\alpha}$	$J_{\beta\alpha}$	Others	
1	H	7.05	7.37	7.79	6.24	3.79	7.29[H(3)]	5.05	0.75	0.40	15.60	3.65(J_{34}) 0.65($J_{3\beta}$)	1.15(J_{35}) 0.45($J_{3\alpha}$)
2	OCH_3	6.82	7.27	7.83	6.15	3.77	3.91(OCH_3)	5.50	0.65	0.35	15.75		
3	CH_3	6.85	7.24	7.85	6.17	3.79	2.34(CH_3)	5.10	0.85	—	15.50	0.40($J_{CH_3\text{-}4}$)	0.40($J_{CH_3\text{-}5}$)
4	Cl	6.96	7.33	7.86	6.27	3.80		5.35	0.85	0.30	15.80		
5	Br	7.03	7.33	7.83	6.30	3.81		5.35	0.90	0.30	15.80		
6	I	7.12	7.32	7.76	6.32	3.81		5.15	1.00	0.30	15.65		
7	CHO	7.49	7.34	8.38	6.44	3.83	10.20(CHO)	5.30	0.75	0.25	15.65	0.30($J_{CHO\text{-}4}$) 0.30($J_{CHO\text{-}\beta}$)	0.55($J_{CHO\text{-}5}$)
8	$COCH_3$	7.41	7.29	8.53	6.35	3.80	2.55($COCH_3$)	5.30	0.75	0.30	15.90		
9	$COOCH_3$	7.48	7.26	8.61	6.36	3.81	3.91($COOCH_3$)	5.30	0.80	0.30	15.95		

TABLE 2. ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF METHYL [*trans*-β-(4-SUBSTITUTED 2-THIENYL)ACRYLATE]S (SERIES **10**)

		Chemical shifts (δ)						Coupling constants/Hz						
No.	X	H(3)	H(5)	H(β)	H(α)	$COOCH_3$	Others	J_{35}	$J_{3\beta}$	$J_{3\alpha}$	$J_{5\beta}$	$J_{5\alpha}$	$J_{\beta\alpha}$	Others
1	H	7.25	7.37	7.79	6.24	3.79	7.05[H(4)]	1.15	0.65	0.45	0.75	0.40	15.60	3.65(J_{34}) 5.05(J_{45})
2	OCH_3	6.90	6.31	7.64	6.21	3.78	3.80(OCH_3)	1.70	0.60	0.40	0.60	0.40	15.60	
3	CH_3	7.04	6.94	7.71	6.19	3.78	2.24(CH_3)	1.35	0.65	0.40	0.65	0.35	15.60	0.40($J_{CH_3\text{-}3}$) 1.10($J_{CH_3\text{-}5}$)
4	Cl	7.11	7.14	7.66	6.24	3.80		1.50	0.55	0.45	0.60	0.35	15.70	
5	Br	7.15	7.25	7.67	6.24	3.79		1.40	0.65	0.40	0.65	0.35	15.65	
6	I	7.21	7.41	7.69	6.24	3.79		1.30	0.70	0.40	0.70	0.40	15.65	
7	CHO	7.64	8.12	7.74	6.30	3.81	9.87(CHO)	1.35	0.70	0.45	0.75	0.30	15.70	0.35($J_{CHO\text{-}3}$)
8	$COCH_3$	7.64	8.03	7.73	6.27	3.80	2.52($COCH_3$)	1.35	0.65	0.40	0.75	0.30	15.60	
9	$COOCH_3$	7.63	8.09	7.73	6.26	3.80	3.87($COOCH_3$)	1.30	0.70	0.45	0.85	0.35	15.70	
10	NO_2	7.75	8.29	7.69	6.34	3.82		1.50	0.70	0.40	0.75	0.30	15.70	

TABLE 3. ^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF METHYL [*trans*-β-(5-SUBSTITUTED 2-THIENYL)ACRYLATE]S (SERIES **11**)

		Chemical shifts (δ)						Coupling constants/Hz					
No.	X	H(3)	H(4)	H(β)	H(α)	$COOCH_3$	Others	J_{34}	$J_{3\beta}$	$J_{3\alpha}$	$J_{\beta\alpha}$	Others	
1	H	7.25	7.05	7.79	6.24	3.79	7.37[H(5)]	3.65	0.65	0.45	15.60	1.15(J_{35}) 0.75($J_{5\beta}$)	5.05(J_{45}) 0.40($J_{5\alpha}$)
2	OCH_3	6.93	6.15	7.64	5.94	3.76	3.92(OCH_3)	4.05	0.65	0.55	15.60		
3	CH_3	7.04	6.70	7.70	6.10	3.77	2.49(CH_3)	3.60	0.65	0.50	15.60	0.55($J_{CH_3\text{-}3}$) 0.30($J_{CH_3\text{-}\beta}$)	1.00($J_{CH_3\text{-}4}$)
4	Cl	7.02	6.87	7.63	6.11	3.78		3.90	0.65	0.55	15.65		
5	Br	6.99	7.01	7.65	6.13	3.78		3.80	0.60	0.55	15.65		
6	I	6.89	7.20	7.69	6.15	3.78		3.80	0.60	0.50	15.70		
7	CHO	7.32	7.70	7.75	6.43	3.82	9.91(CHO)	3.95	0.60	0.40	15.75		
8	$COCH_3$	7.24	7.60	7.72	6.38	3.81	2.56($COCH_3$)	4.00	0.60	0.40	15.70		
9	$COOCH_3$	7.22	7.70	7.72	6.35	3.81	3.90($COOCH_3$)	3.95	0.60	0.40	15.70	0.20($J_{4\beta}$)	
10	NO_2	7.18	7.85	7.67	6.42	3.83		4.30	0.60	0.40	15.85	0.20($J_{4\beta}$)	

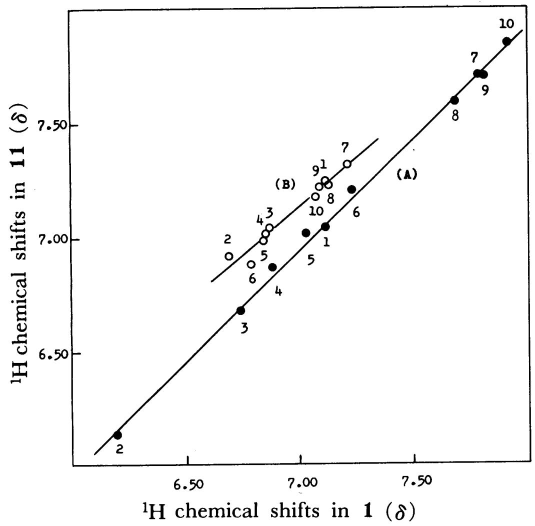
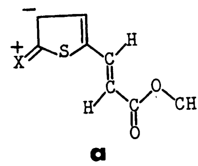


Fig. 2. Correlation between ^{1}H chemical shifts in **11** and **1**; numbering as in Table 3. A, δ_4(**11**) *vs.* δ_3(**1**). B, δ_3(**11**) *vs.* δ_4(**1**).

iteratively using LAOCN 3.[9] The results are given in Tables 1-3. The δ_5 (**10**)[10] *vs.* δ_2 (**2**), and δ_3 (**10**) *vs.* δ_4 (**2**) plots gave excellent correlations, as shown in Fig. 1 (A and B, respectively). Furthermore, the chemical shifts of ring protons in the series of compounds **10** were compared with those in the series of compounds **4**, and good correlations were observed between δ_5(**10**) and δ_5(**4**), and between δ_3(**10**) and δ_3(**4**). These data show that the ^{1}H chemical shifts of 5- and 3-positions in the thiophene ring have the same sensitivity for the substituent effects in both **10** and **4**, and suggest the possibility to estimate empirically with accuracy the ^{1}H chemical shifts of thiophene ring in other 2,4-disubstituted thiophene series. The chemical shifts of H(β) and H(α) in the series of compounds **10** show a narrow range of variation, as expected from those of H(5) in **2**. The effect of a substituent on the 4-position is considered to be transmitted mainly by the inductive effect to δ_β(**10**) and δ_α(**10**). The correlation between δ_α(**10**) and δ_5(**2**) gives a larger *cc* and a steeper *p* than that between δ_β(**10**) and δ_5(**2**).

As shown in Fig. 2, good correlations were obtained between δ_4(**11**) and δ_3(**1**) (A), and between δ_3(**11**) and δ_4(**1**) (B). The chemical shifts of **11** were compared with those of **5**, and better correlations were obtained between δ_4(**11**) and δ_4(**5**), and between δ_3(**11**) and δ_3(**5**). These results also suggest the possibility to estimate the ^{1}H chemical shifts of the thiophene ring in other 2,5-disubstituted thiophene series as in 2,4-disubstituted thiophene series. Quite similarly to the series of compounds **10**, the chemical shifts of H(β) is scarcely affected by the substituent at the 5-position, while that of H(α) considerably by the same substituent. The correlation between δ_α(**11**) and δ_5(**1**) also gives a larger correlation coefficient and a steeper slope than that between δ_β(**11**) and δ_5(**1**). The effect of the substituent on the 5-position is transmitted more strongly to H(α) than H(β) by a factor of about 5. This reason may be ascribed to the resonance effects as shown below. The shift of H(α) is presumed to be caused by a sizable contribution of the resonance structure **c**, which gives the charge delocalization on the α-carbon.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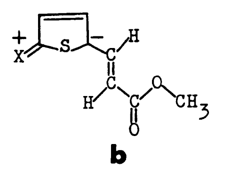
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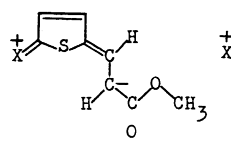
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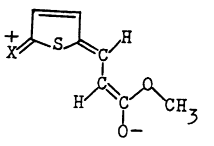
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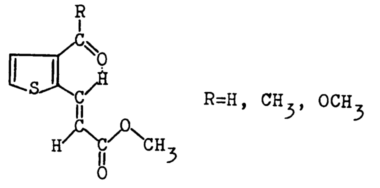
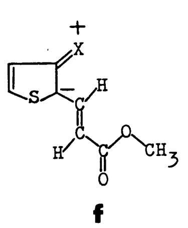
Figure 3 shows a close correlation between the effects of substituents on δ_4(**9**) and δ_4(**2**)(A), and a loose correlation between those on δ_5(**9**) and δ_5(**2**)(B). The chemical shifts of **9** were compared with those of **3**, and a good correlation was obtained between δ_4(**9**) and δ_4(**3**), and a fairly good correlation between δ_5(**9**) and δ_5(**3**). As shown in Table 1, formyl acetyl, and methoxycarbonyl groups cause significantly low field shifts of H(β) signal. These results may be interpreted by the preferred conformation **e**, in which the carbonyl group located very close to H(β) may form an intramolecular hydrogen bonding. This conformation may rationalize the facts that the chemical shift of the formyl proton in methyl *trans*-β-(3-formyl-2-thienyl)acrylate is shifted considerably towards a lower field than that of the 4-formyl derivative, and also that the former shows the carbonyl band at 1687 cm^{-1}, but the latter at 1701 and 1697 cm^{-1}. The large standard deviation of δ_β(**9**) *vs.* δ_2(**2**) plot may be caused by the complex influence due to neighboring anisotropy, intramolecular hydrogen bonding, inductive, mesomeric, and steric hindrance effects. The resonance contribution (**f**, **g**, **h**) similar to the case of 5-substituted derivatives is again expected with methyl [*trans*-β-(3-substituted 2-thienyl)acrylate]s.


R=H, CH_3, OCH_3

e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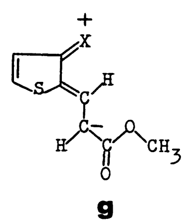
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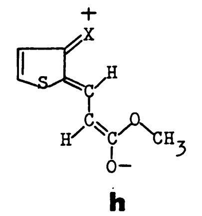
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The $\delta_\alpha(\mathbf{9})$ value is considered to show a narrower range of variation than that of $\delta_\alpha(\mathbf{11})$ due to the restricted contribution of mesomeric effect by steric hindrance of the 2-substituent. The correlation between $\delta_\alpha(\mathbf{9})$ and $\delta_2(\mathbf{2})$ gives a larger *cc* and a lesser *p*. For this reason the substituent effect on the chemical shift of H(α) by the 5-position is more sensitive than that by the 3-position by a factor of about 1.5.

Methyl proton chemical shifts of methyl [*trans*-β-(substituted-2-thienyl)acrylate]s are much less affected by the substituents on the ring, and the substituent effects on these chemical shifts are attenuated to approximately half of those of methyl (substituted 2-thiophenecarboxylate)s. Contrary to the correlation between $\delta_\alpha(\mathbf{9})$ and $\delta_\alpha(\mathbf{11})$, the $\delta_{COOCH_3}(\mathbf{9})$ *vs.* $\delta_{COOCH_3}(\mathbf{11})$ plot shows that the substituents on the 3-position affect the chemical shift of $COOCH_3$ more remarkably than those on the 5-position. The results of these comparisons are shown in Table 4.

The chemical shifts of the ring protons of methyl

TABLE 4. CORRELATIONS OF CHEMICAL SHIFTS OF SUBSTITUTED THIOPHENES, METHYL (SUBSTITUTED 2-THIOPHENECARBOXYLATE)S, AND METHYL [*trans*-β-(SUBSTITUTED 2-THIENYL)ACRYLATE]S

Series	Proton	Series	Proton	*cc*[a]	*p*[b]	*i*[c]	*s*[d]	*n*[e]
2	H(2)	**10**	H(5)	1.000	0.955	0.353	0.008	10
2	H(4)	**10**	H(3)	1.000	0.924	0.672	0.008	10
1	H(3)	**11**	H(4)	1.000	0.960	0.226	0.017	10
1	H(4)	**11**	H(3)	0.980	0.857	1.14	0.030	10
2	H(4)	**9**	H(4)	0.988	0.848	1.06	0.038	9[f]
2	H(5)	**9**	H(5)	0.538	0.326	4.91	0.044	9[f]
4	H(5)	**10**	H(5)	1.000	1.02	−0.317	0.007	10
4	H(3)	**10**	H(3)	0.999	1.02	−0.655	0.014	10
5	H(4)	**11**	H(4)	1.000	1.03	−0.241	0.004	10
5	H(3)	**11**	H(3)	0.989	1.13	−1.55	0.023	10
3	H(4)	**9**	H(4)	0.988	0.981	0.081	0.037	9[f]
3	H(5)	**9**	H(5)	0.642	0.229	5.59	0.038	9[f]
2	H(2)	**9**	H(β)	0.801	0.446	4.76	0.197	9[f]
2	H(2)	**9**	H(α)	0.915	0.136	5.29	0.035	9[f]
2	H(2)	**9**	$COOCH_3$	0.763	0.022	3.64	0.010	9[f]
2	H(5)	**10**	H(β)	0.604	0.357	5.10	0.035	10
2	H(5)	**10**	H(α)	0.818	0.473	2.81	0.024	10
2	H(5)	**10**	$COOCH_3$	0.801	0.151	2.70	0.007	10
1	H(5)	**11**	H(β)	0.578	0.083	7.09	0.039	10
1	H(5)	**11**	H(α)	0.950	0.433	3.06	0.049	10
1	H(5)	**11**	$COOCH_3$	0.868	0.057	3.38	0.010	10
9	H(β)	**11**	H(β)	0.365	0.056	7.25	0.047	9[f]
9	H(α)	**11**	H(α)	0.864	1.48	−3.09	0.076	9[f]
9	$COOCH_3$	**11**	$COOCH_3$	0.755	0.882	0.344	0.094	9[f]
3	$COOCH_3$	**9**	$COOCH_3$	0.927	0.416	2.15	0.028	9[f]
4	$COOCH_3$	**10**	$COOCH_3$	0.928	0.483	1.90	0.010	10
5	$COOCH_3$	**11**	$COOCH_3$	0.988	0.591	1.50	0.010	10

a) Correlation coefficient. b) Slope. c) Intercept. d) Standard deviation. e) Number of compounds used in correlation. f) NO_2 is excluded.

TABLE 5. FREQUENCIES OF C=O STRETCHINC VIBRATIONS OF METHYL [*trans*-β-(SUBSTITUTED2-THIENYL)ACRYLATE]S

		$\nu_{C=O}$/cm^{-1}								
		Series **9**			Series **10**			Series **11**		
		Ester		Others	Ester		Others	Ester		Others
No.	X	*anti*[a]	*syn*[b]		*anti*	*syn*		*anti*	*syn*	
1	H	1715*	1725		1715*	1725		1715*	1725	
2	OCH_3	1706*	1720		1712*	1725		1708*	1721	
3	CH_3	1707*	1722		1711*	1725		1708*	1723	
4	Cl	1712*	1726		1715*	1728		1708*	1725	
5	Br	1712*	1726		1718*	1728		1710*	1725	
6	I	1712*	1727		1718*	1727		1709*	1725	
7	CHO	1717*	1728	1687	1719*	1727	1697 1701*	1718*	1729	1683
8	$COCH_3$	1715*	1725	1684	1719*	1728	1689	1718*	1728	1672
9	$COOCH_3$		1724			1728		1720*	1726	
10	NO_2				1714*	1729		1720*	1731	

a) *anti-s-trans* form. b) *syn-s-trans* form. * Shoulder.

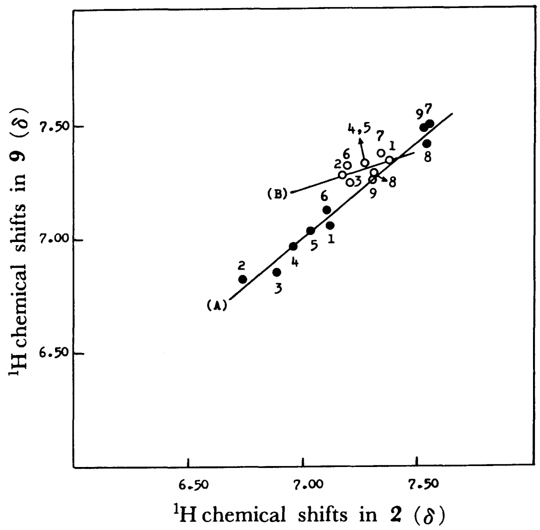

Fig. 3. Correlation between ^{1}H chemical shifts in **9** and **2**; numbering as in Table 1. A, δ_4(**9**) *vs.* δ_4(**2**). B, δ_5(**9**) *vs.* δ_5(**2**).

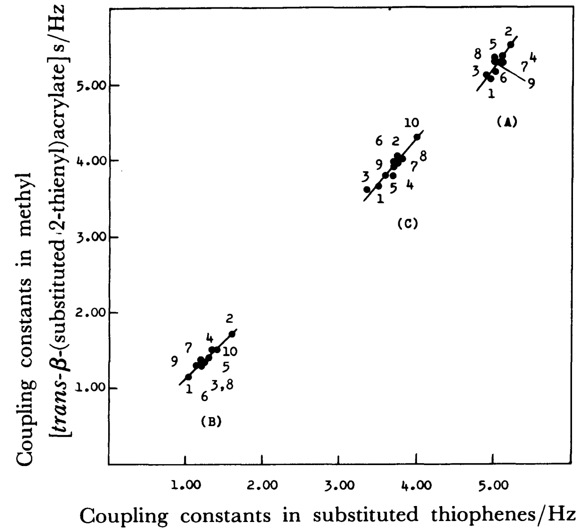

Fig. 4. Correlation between coupling constants in methyl [*trans*-β-(substituted 2-thienyl)acrylate]s and substituted thiophenes; numbering as in Table 1. A, J_{45}(**9**) *vs.* J_{45}(**2**). B, J_{35}(**10**) *vs.* J_{24}(**2**). C, J_{34}(**11**) *vs.* J_{34}(**1**).

Table 6. Correlations of C=O stretching vibration frequencies of methyl [*trans*-β-(substituted 2-thienyl)-acrylate]s against methyl (substituted 2-thiophenecarboxylate)s

Series	Series	$cc^{a)}$	$p^{b)}$	$i^{c)}$	$s^{d)}$	$n^{e)}$
3	**9**	0.784	3.71	1107.7	85.1	$6^{f)}$
4	**10**	0.544	1.48	1422.2	48.7	$9^{g)}$
5	**11**	0.905	5.45	698.2	86.5	$9^{g)}$

a), d), and e) as in Table 4. f) CHO, $COCH_3$, $COOCH_3$, and NO_2 are excluded. g) $COOCH_3$ is excluded.

[*trans*-β-(substituted 2-thienyl)acrylate]s were calculated by making use of those of 2- and 3-substituted thiophenes. Excluding the chemical shift of H(4) of methyl *trans*-β-(3-methoxy-2-thienyl)acrylate, the observed chemical shifts agree with the calculated values within 0.1 ppm in three cases. These results seem to suggest that the additivity rule which is based on substituted thiophenes, is also applicable to the chemical shifts of the ring protons in methyl [*trans*-β-(substituted 2-thienyl)acrylate]s. It is noteworthy that the chemical shifts of the ring protons in the carbonyl derivatives of **9** are in good agreement with the calculated values, although those of **3** differ from the calculated values, which have been stated in the preceding paper.[2] Since the predominant conformations of carbonyl groups are thought to be the *syn* form in **2**, and the *anti* form in **9**, the chemical shifts of the ring protons in the latter are expected to disagree with the calculated values. Nevertheless, the observed values are in good agreement with the calculated. The unexpected agreement is probably due to the accidental compensation caused by the additional effect of the carbonyl group interacting with the CH group in its proximity.

The wave numbers of the C=O stretching vibrations of the series of methyl [*trans*-β-(substituted 2-thienyl)-acrylate]s were measured in CCl_4. The results are given in Table 5. Although two separated C=O stretching bands of the ester group have been observed in some of methyl (substituted 2-thiophenecarboxylate)s,[2] a peak with a shoulder is usually observed in the series of compounds **9**, **10**, and **11**. The main peak at the higher frequency is assignable to the *syn-s-trans* form, and the shoulder to the *anti-s-trans* form. The C=O stretching wave numbers of *syn-s-trans* form show narrow ranges of variation, being 8 cm^{-1} for **9**, 4 cm^{-1} for **10**, and 10 cm^{-1} for **11**. These ranges are about half as wide as those for methyl (substituted 2-thiophenecarboxylate)s. The correlations between the C=O streching frequencies of methyl [*trans*-β-(substituted 2-thienyl)acrylate]s and those of methyl (substituted 2-thiophenecarboxylate)s are shown in Table 6. A good correlation was observed between $\nu_{C=O}$(**11**)[11] and $\nu_{C=O}$(**5**), and fair correlations between $\nu_{C=O}$(**9**) and $\nu_{C=O}$(**3**), and between $\nu_{C=O}$(**10**) and $\nu_{C=O}$(**4**). The substituent effects to the C=O band by positions 5, 3, and 4 of methyl [*trans*-β-(substituted 2-thienyl)acrylate]s and of methyl (substituted 2-thiophenecarboxylate)s show a considerably similar trend. It is interesting that the substituent effect in **4** is transmitted strongly to the C=O stretching frequency of methoxycarbonyl group, but the effect in **10** very weakly.

Plots of the proton-proton coupling constants in methyl [*trans*-β-(substituted 2-thienyl)acrylate]s against the corresponding coupling constants in substituted thiophenes gave good correlations as shown in Fig. 4. Moreover, good linear correlations were observed between the coupling constants for methyl [*trans*-*β*-(substituted 2-thienyl)acrylate]s and methyl (substituted 2-thiophenecarboxylate)s.

For methyl [*trans*-*β*-(substituted 2-thienyl)acrylate]s as well as for methyl (substituted 2-thiophenecarboxylate)s,[2] relationships were examined between the coupling constants and the sum of the electronegativities of substituents including 2-(methoxycarbonyl)vinyl group. Good correlations were found for J_{35}(**10**)[12] and J_{45}(**9**), but not for other coupling constants.

Experimental

The ^{1}H NMR spectra of the compounds were obtained at 100 MHz on a JEOL PS-100 spectrometer. The chemical shifts were determined with an accuracy of ±0.005 ppm relative to TMS as an internal standard, and the coupling constants were determined with an accuracy of ±0.02 Hz. The concentrations of the substrates were adjusted approximately to 0.3 mol dm^{-3}. The IR spectra were recorded on a Perkin-Elmer 257 spectrometer.

Methyl *trans*-*β*-(2-thienyl)acrylate and methyl [*trans*-*β*-(5-bromo-, 5-formyl-, and 5-nitro-2-thienyl)acrylate]s were prepared according to the reported procedures.[13—16]

Methyl trans-β-(4-Nitro-2-thienyl)acrylate. This material was prepared by esterification of the corresponding acid,[17] mp 142 °C. Found: C, 45.27; H, 3.20; N, 6.70; S, 15.00%. Calcd for $C_8H_7NO_4S$: C, 45.07; H, 3.31; N, 6.57; S, 15.04%. IR(KBr, cm^{-1}): 3100(=C–H); 1718(C=O); 1634(C=C); 967(*trans* CH=CH); 1535, 1433, 723(thiophene ring).

The following esters were prepared by the condensation of methyl acetate with the corresponding aldehydes[18—31] according to the procedure by Gilman and coworkers.[32]

Methyl trans-β-(3-Methoxy-2-thienyl)acrylate. Mp 52 °C. Found: C, 54.72; H, 4.95; S, 15.98%. Calcd for $C_9H_{10}O_3S$: C, 54.53; H, 5.08; S, 16.17%. IR (KBr, cm^{-1}): 3090 (=C–H); 1706 (C=O); 1618 (C=C); 970 (*trans* CH=CH); 1537, 1428, 727 (thiophene ring).

Methyl trans-β-(3-Methyl-2-thienyl)acrylate. Bp 113—113.5 °C/2 mmHg (1 mmHg≈133.322 Pa). Found: C, 59.20; H, 5.66; S, 17.49%. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53; S, 17.59%. IR (neat, cm^{-1}): 3100 (=C–H); 1715 (C=O); 1622 (C=C); 968 (*trans* CH=CH); 1532, 1438, 713 (thiophene ring).

Methyl trans-β-(3-Chloro-2-thienyl)acrylate. Mp 69 °C. Found: C, 47.55; H, 3.40; Cl, 17.31; S, 15.63%. Calcd for $C_8H_7ClO_2S$: C, 47.41; H, 3.48; Cl, 17.49; S, 15.82%. IR (KBr, cm^{-1}): 3130 (=C–H); 1721 (C=O); 1630 (C=C); 962 (*trans* CH=CH); 1508, 1422, 708 (thiophene ring).

Methyl trans-β-(3-Bromo-2-thienyl)acrylate. Mp 76 °C. Found: C, 38.75; H, 2.95; Br, 32.50; S, 13.11%. Calcd for $C_8H_7BrO_2S$: C, 38.88; H, 2.86; Br, 32.33; S, 12.98%. IR (KBr, cm^{-1}): 3130 (=C–H); 1720 (C=O); 1628 (C=C); 962 (*trans* CH=CH); 1503, 1422, 707 (thiophene ring).

Methyl trans-β-(3-Iodo-2-thienyl)acrylate. Mp 78 °C. Found: C, 32.58; H, 2.60; I, 43.07; S, 10.78%. Calcd for $C_8H_7IO_2S$: C, 32.67; H, 2.40; I, 43.15; S, 10.90%. IR (KBr, cm^{-1}): 3090 (=C–H); 1695 (C=O); 1622 (C=C); 960 (*trans* CH=CH); 1488, 1419, 709 (thiophene ring).

Methyl trans-β-(3-Formyl-2-thienyl)acrylate. Mp 112 °C. Found: C, 55.17; H, 4.00; S, 16.56%. Calcd for $C_8H_8O_3S$: C, 55.09; H, 4.11; S, 16.34%. IR (KBr, cm^{-1}): 3110, 3090 (=C–H); 1719, 1673 (C=O); 1633 (C=C); 961 (*trans* CH=CH); 1520, 1437, 718 (thiophene ring).

Methyl trans-β-(3-Acetyl-2-thienyl)acrylate. Mp 82 °C. Found: C, 57.15; H, 4.88; S, 15.38%. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79; S, 15.25%. IR (KBr, cm^{-1}): 3120, 3080 (=C–H); 1698, 1678 (C=O); 1615 (C=C); 978 (*trans* CH=CH); 1503, 1438, 1423, 722 (thiophene ring).

Methyl trans-β-(4-Methoxy-2-thienyl)acrylate. Mp 73 °C. Found: C, 54.70; H, 5.02; S, 16.29%. Calcd for $C_9H_{10}O_3S$: C, 54.53; H, 5.08; S, 16.17%. IR (KBr, cm^{-1}): 3090 (=C–H); 1706 (C=O); 1629 (C=C); 967 (*trans* CH=CH); 1551, 1430, 720 (thiophene ring).

Methyl trans-β-(4-Methyl-2-thienyl)acrylate. Bp 122—124 °C/3 mmHg. Found: C, 59.55; H, 5.80; S, 17.65%. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53; S, 17.59%. IR (neat, cm^{-1}): 3100 (=C–H); 1717 (C=O); 1616 (C=C); 967 (*trans* CH=CH); 1542, 1438, 1427, 721 (thiophene ring).

Methyl trans-β-(4-Chloro-2-thienyl)acrylate. Mp 80 °C. Found: C, 47.64; H, 3.52; Cl, 17.33; S, 15.65%. Calcd for $C_8H_7ClO_2S$: C, 47.41; H, 3.48; Cl, 17.49; S, 15.82%. IR (KBr, cm^{-1}): 3110 (=C–H); 1710 (C=O); 1633 (C=C); 959 (*trans* CH=CH); 1519, 1438, 1421, 719 (thiophene ring).

Methyl trans-β-(4-Bromo-2-thienyl)acrylate. Mp 75 °C. Found: C, 38.92; H, 2.80; Br, 32.58; S, 12.91%. Calcd for $C_8H_7BrO_2S$: C, 38.89; H, 2.86; Br, 32.33; S, 12.98%. IR (KBr, cm^{-1}): 3110 (=C–H); 1710 (C=O); 1633 (C=C); 959 (*trans* CH=CH); 1511, 1434, 1418, 718 (thiophene ring).

Methyl trans-β-(4-Iodo-2-thienyl)acrylate. Mp 44 °C. Found: C, 32.44; H, 2.35; I, 43.36, S, 11.02%. Calcd for $C_8H_7IO_2S$: C, 32.67; H, 2.40; I, 43.15; S, 10.90%. IR (KBr, cm^{-1}): 3080 (=C–H); 1703 (C=O); 1627 (C=C); 964 (*trans* CH=CH); 1500, 1438, 718 (thiophene ring).

Methyl trans-β-(4-Formyl-2-thienyl)acrylate. Mp 96 °C. Found: C, 54.98; H, 4.15; S, 16.18%. Calcd for $C_9H_8O_3S$: C, 55.09; H, 4.11; S, 16.34%. IR (KBr, cm^{-1}): 3080 (=C–H); 1709, 1672 (C=O); 1633(C=C); 978 (*trans* CH=CH); 1528, 1435, 721 (thiophene ring).

Methyl trans-β-(4-Acetyl-2-thienyl)acrylate. Mp 86 °C. Found: C, 57.08; H, 4.83; S, 15.09%. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79; S, 15.25%. IR (KBr, cm^{-1}): 3080 (=C–H); 1708, 1668 (C=O); 1631 (C=C); 988 (*trans* CH=CH); 1527, 1408, 728 (thiophene ring).

Methyl trans-β-(5-Methoxy-2-thienyl)acrylate. Mp 56 °C. Found: C, 54.68; H, 4.82; S, 16.38%. Calcd for $C_9H_{10}O_3S$: C, 54.53; H, 5.08; S, 16.17%. IR (KBr, cm^{-1}): 3090 (=C–H); 1707 (C=O); 1616 (C=C); 973 (*trans* CH=CH); 1538, 1423, 703 (thiophene ring).

Methyl trans-β-(5-Methyl-2-thienyl)acrylate. Mp 55 °C. Found: C, 59.48; H, 5.31; S, 17.75%. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53; S, 17.59%. IR (KBr, cm^{-1}): 3080 (=C–H); 1708 (C=O); 1620 (C=C); 992 (*trans* CH=CH); 1536, 1435, 720 (thiophene ring).

Methyl trans-β-(5-Chloro-2-thienyl)acrylate. Mp 53 °C. Found: C, 47.62; H, 3.42; Cl, 17.23; S, 15.80%. Calcd for $C_8H_7ClO_2S$: C, 47.41; H, 3.48; Cl, 17.49; S, 15.82%. IR (KBr, cm^{-1}): 3060 (=C–H); 1719 (C=O); 1626 (C=C); 969 (*trans* CH=CH); 1524, 1422, 721 (thiophene ring).

Methyl trans-β-(5-Iodo-2-thienyl)acrylate. Mp 88 °C. Found: C, 32.81; H, 2.55; I, 43.02; S, 11.12%. Calcd for $C_8H_7IO_2S$: C, 32.67; H, 2.40; I, 43.15; S, 10.90%. IR (KBr, cm^{-1}): 3050 (=C–H); 1708 (C=O); 1623 (C=C); 9.71 (*trans* CH=CH); 1519, 1417, 717 (thiophene ring).

Methyl trans-β-(5-Acetyl-2-thienyl)acrylate. Mp 147 °C. Found: C, 57.48; H, 4.58; S, 15.23%. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79; S, 15.25%. IR (KBr, cm^{-1}): 3080 (=C–H); 1711, 1657 (C=O); 1627 (C=C); 987 (*trans* CH=CH); 1519, 1449, 731 (thiophene ring).

Methyl [*trans*-*β*-(3-, 4-, and 5-methoxycarbonyl-2-thienyl)-acrylate]s were prepared by the oxidation of the corresponding methyl [*trans*-*β*-(formyl-2-thienyl)acrylate]s followed by the esterification.

Methyl trans-β-(3-Methoxycarbonyl-2-thienyl)acrylate. Mp 82 °C. Found: C, 52.95; H, 4.58; S, 14.28%. Calcd for

$C_{10}H_{10}O_4S$: C, 53.09; H, 4.46; S, 14.17%. IR (KBr, cm^{-1}): 3110, 3080 (=C–H); 1719, 1708 (C=O); 1621 (C=C); 978 (*trans* CH=CH); 1518, 1438, 1429, 719 (thiophene ring).

Methyl trans-*β-(4-Methoxycarbonyl-2-thienyl)acrylate.* Mp 89 °C. Found: C, 52.98; H, 4.43; S,14.06%. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.46; S, 14.17%. IR (KBr, cm^{-1}): 3100 (=C–H); 1718, (C=O); 1630 (C=C); 982 (*trans* CH=CH); 1533, 1431, 722 (thiophene ring).

Methyl trans-*β-(5-Methoxycarbonyl-2-thienyl)acrylate.* Mp 97 °C. Found: C, 53.31; H, 4.25; S, 14.28%. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.46; S, 14.17%. IR (KBr, cm^{-1}): 3070, (=C–H); 1719 (C=O); 1633 (C=C); 963 (*trans* CH=CH); 1529, 1432, 731 (thiophene ring).

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10) The notation $\delta_r(\mathbf{N})$ is hereafter used for the chemical shift for the *r*th(position)-proton on thiophene ring of the series of compounds **N**.

11) The notation $\nu_{C=O}(\mathbf{N})$ is hereafter used for the carbonyl stretching frequency of the series of compounds **N**.

12) The notation $J_{rs}(\mathbf{N})$ is hereafter used for the spin-spin coupling constant between *r*th- and *s*th-protons of the series of compounds **N**.

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19) In the preparation of methyl [*trans-β*-(acetyl 2-thienyl)acrylate]s, [(2-methyl-1,3-dioxolan-2-yl)-2-thiophenecarbaldehyde]s were used.

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