

Substituent Chemical Shifts of (*E*)-1-Aryl-3-thienylpropen-1-onesIn-Sook Han Lee,<sup>†</sup> Hyun Ju Jeon, Ji Sook Yu, and Chang Kiu Lee\*

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Substituent chemical shifts were examined for the 2- and 3-thiophene derivatives of chalcone and compared to the thiophene series of derivatives with the phenyl series. The chemical shift values for the  $\alpha$ -carbons of the enones showed and inverse correlation with the Hammett  $\sigma$  values, but the correlation coefficients were moderate ( $r = 0.836 - 0.878$ ). On the other hand, the  $\beta$ -carbons showed a normal correlation with excellent correlation coefficients ( $r = 0.994$ ). The absolute magnitude of the  $\rho$  values for the  $\alpha$ -carbon are about half of those of the  $\beta$ -carbon. The observation may be the result of a through-space transition of the electronic effect of the substituents in addition to the through bond transition.

**Key Words:** Thiophene, Propenone, Hammett equation, Substituent effect

## Introduction

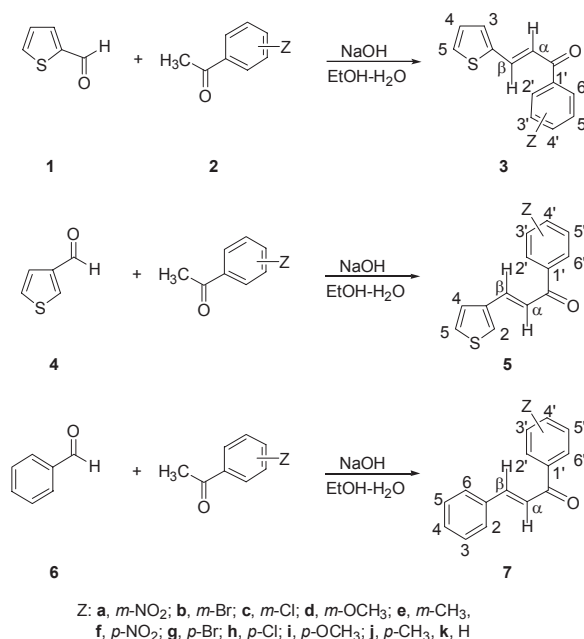
The positional isomers of five-membered monoheterocyclic aromatic compounds show quite contrasting physical and chemical properties. For example, 2-thiophenecarboxylic acid is more acidic ( $pK_a$  3.53) than its positional isomer, 3-thiophenecarboxylic acid ( $pK_a$  4.10).<sup>1</sup> The <sup>13</sup>C NMR signal of the carbonyl carbon of 2-thiophenecarboxylic acid (163.04 ppm) appears slightly upfield than that of the 3-isomer (163.63 ppm).<sup>2</sup> A similar trend is also observed for the aldehydes: 2-thiophenecarboxaldehyde (182.93 ppm) appears in the upfield than its 3-isomer (184.88 ppm).<sup>3</sup>

Unlike furan and pyrrole which show the  $\alpha$ -C signals more down field than those of the  $\beta$ -C, thiophene shows opposite chemical shift values for the  $\alpha$ -C (124.9 ppm) and the  $\beta$ -C (126.4 ppm).<sup>4</sup> It seems also worthy to note that the chemical shifts of the  $\beta$ -C of furan (109.9 ppm) and that of pyrrole (107.7 ppm) are close each other, but the  $\beta$ -C of thiophene has the value (126.4 ppm) which is closer to the chemical shift value of benzene (128.5 ppm) than those of the  $\beta$ -C's of furan or pyrrole.<sup>5</sup> Apparently, the electronic effect of the S atom is quite different from those of the O and N atoms. There are ample reports on the effect of the S atom in thiophene on the chemical shift values of the proton and carbon in the ring.<sup>6</sup>

In the course of our extensive studies on the difference in the physico-chemical behaviors of the positional isomers of five-membered monoheterocyclic aromatic compounds we have found that (*E*)-1-aryl-3-thienyl-2-propenones (**3** and **5**) show quite interesting NMR spectroscopic behaviors. Furthermore, comparison with the spectra of the phenyl series of similar type provides useful information on the aromaticity of thiophene.<sup>7</sup> We report here the substituent chemical shifts correlations with the 2- and 3-thienyl compounds **3** and **5** as well as the corresponding phenyl compounds **7**.

## Results and Discussion

(*E*)-1-Aryl-3-thienyl-2-propenones (**3** and **5**) were prepared by the aldol condensations of 2- and 3-thiophenecarboxaldehyde (**1** and **4**), respectively, with *m*- and *p*-substituted acetophenones



**Table 1.** <sup>1</sup>H chemical shift values (Hz)<sup>a</sup> of **3** in 0.1 M-CDCl<sub>3</sub> obtained at 400 MHz

	3-H	4-H	5-H	$\alpha$ -H	$\beta$ -H
<b>a</b>	27.98	14.94	29.79	-7.33	33.48
<b>b</b>	8.50	3.87	10.56	-34.22	3.23
<b>c</b>	7.80	3.28	9.65	-31.81	3.63
<b>d</b> <sup>b</sup>	0.15	-1.01	-0.64	-10.21	-1.47
<b>e</b> <sup>b</sup>	-1.92	-1.88	-2.85	-5.33	-5.48
<b>f</b>	23.51	14.24	28.56	-23.76	17.18
<b>g</b>	3.86	2.13	6.23	-27.56	1.06
<b>h</b>	3.46	1.65	5.23	-23.50	0.95
<b>i</b> <sup>b</sup>	-6.80	-4.09	-8.81	3.62	-5.67
<b>j</b> <sup>b</sup>	-5.50	-3.90	-6.77	-1.15	-5.90
<b>k</b>	2945.95	2838.55	2970.49	2935.75	3179.73
Ave, $\delta$	7.37	7.10	7.44	7.30	7.95

<sup>a</sup>Positive value indicates downfield shift and the negative value indicates upfield shift from the chemical shift value of **3k**. <sup>b</sup>Methyl signal,  $\delta$ : **3d**, 3.88; **3e**, 2.44; **3i**, 3.89; **3j**, 2.43.

**Table 2.**  $^{13}\text{C}$  chemical shift values (Hz)<sup>a</sup> of **3** in 0.1 M- $\text{CDCl}_3$  obtained at 100 MHz

	2-C	3-C	4-C	5-C	C=O	$\alpha$ -C	$\beta$ -C	<i>ipso</i> -C
<b>a</b>	-55.9	103.7	23.9	126.8	-255.8	178.1	-161.2	131.6
<b>b</b>	-27.3	46.0	10.0	66.9	-155.8	78.8	-76.4	180.3
<b>c</b>	-28.1	46.1	10.5	65.5	-144.6	77.7	-74.1	157.5
<b>d</b> <sup>b</sup>	-1.7	0.7	-0.4	21.1	-31.9	0.7	1.0	138.4
<b>e</b> <sup>b</sup>	5.0	-4.7	-2.6	8.3	15.0	-20.4	19.1	34.3
<b>f</b>	-56.4	109.6	27.4	129.8	-163.5	180.6	-100.7	484.1
<b>g</b>	-21.0	35.2	8.3	51.2	-122.5	52.1	-72.0	-130.1
<b>h</b>	-19.5	30.8	7.1	30.5	-142.8	45.4	-66.9	-170.8
<b>i</b> <sup>b</sup>	16.9	-32.6	-7.0	-19.2	-182.5	-80.9	-17.2	-740.9
<b>j</b> <sup>b</sup>	11.1	-21.7	-4.9	-3.6	-55.9	-44.1	4.4	-257.7
<b>k</b>	14037.9	13206.3	12833.8	12879.1	18989.7	12078.0	13720.5	13810.1
Ave ppm	140.22	132.34	128.40	129.07	188.77	120.28	137.63	

<sup>a</sup>Positive value indicates downfield shift and the negative value indicates upfield shift from the chemical shift value of **3k**. <sup>b</sup>Methyl signal, ppm: **3d**, 55.46; **3e**, 21.39; **3i**, 55.19; **3j**, 21.43.

**Table 3.**  $^1\text{H}$  chemical shift values (Hz)<sup>a</sup> of **5** in 0.1 M- $\text{CDCl}_3$  obtained at 400 MHz

	2-H	4-H	5-H	$\alpha$ -H	$\beta$ -H
<b>a</b>	23.46	6.78	6.08	-10.29	22.94
<b>b</b>	10.84	1.72	4.42	-30.66	2.86
<b>c</b>	10.98	1.50	4.50	-28.14	3.54
<b>d</b> <sup>b</sup>	-0.06	-2.67	-0.70	-10.05	-1.08
<b>e</b> <sup>b</sup>	-2.03	1.45	-1.37	-4.10	-4.59
<b>f</b>	27.24	4.67	13.11	-22.30	12.31
<b>g</b>	4.65	-3.44	1.90	-25.47	-0.17
<b>h</b>	5.44	-3.22	1.96	-21.55	-0.06
<b>i</b> <sup>b</sup>	-8.43	-2.56	-3.72	5.15	-4.42
<b>j</b> <sup>b</sup>	-6.08	2.26	-3.16	-0.32	-4.76
<b>k</b>	3044.22	2971.74	2951.82	2940.15	3122.24
Ave, $\delta$	7.62	7.43	7.38	7.31	7.81

<sup>a</sup>Positive value indicates downfield shift and the negative value indicates upfield shift from the chemical shift value of **5k**. <sup>b</sup>Methyl signal,  $\delta$ : **5d**, 3.88; **5e**, 2.40; **5i**, 3.89; **5j**, 2.43.

(**2**) in the presence of NaOH in ethanol-water solution.<sup>8</sup> Similarly, 3-phenyl derivatives **7** were prepared. The yields were generally good (60 - 90%).

All the products were purified by recrystallization from ethanol to analytical purity, which is essential for spectroscopic analysis. The NMR spectra of **3**, **5** and **7** were obtained in 0.1 M  $\text{CDCl}_3$  solutions. Assignments were made with the aid of  $^1\text{H}$ - $^1\text{H}$  COSY and  $^1\text{H}$ - $^{13}\text{C}$  HETCOR spectroscopy. The chemical shift values are listed in Tables 1-6.

The effect of a substituent on the chemical shift of  $^1\text{H}$  and  $^{13}\text{C}$  has been extensively investigated. Comprehensive references on the topic have been published.<sup>9</sup> One of the areas of such a study is to tabulate the statistical values so that the prediction of the chemical shift values for a new compound is possible by using the additivity rule.<sup>10</sup> The other approach is to correlate the substituent chemical shifts with the known substituent parameters such as the Hammett  $\sigma$ , the Taft  $\sigma_1$  and  $\sigma_R$ , or Swain-Loften  $F$  and  $R$  values.<sup>11</sup> The substituent effect on the chemical shift is typically analyzed by the single substituent parameter

**Table 4.**  $^{13}\text{C}$  chemical shift values (Hz)<sup>a</sup> of **5** in 0.1 M- $\text{CDCl}_3$  obtained at 100 MHz

	2-C	3-C	4-C	5-C	C=O	$\alpha$ -C	$\beta$ -C	<i>ipso</i> -C
<b>a</b>	71.2	-44.9	35.0	-1.4	-258.8	-150.9	174.8	129.8
<b>b</b>	58.0	-22.2	14.4	-1.0	-154.4	-70.4	78.4	180.0
<b>c</b>	54.4	-21.2	14.3	-0.9	-141.6	-63.5	77.5	160.3
<b>d</b> <sup>b</sup>	-1.1	1.7	-0.5	3.1	-31.1	5.4	0.6	142.1
<b>e</b> <sup>b</sup>	-10.8	4.5	-4.6	3.5	17.5	17.3	-18.5	3.4
<b>f</b>	125.9	-46.1	38.2	-8.5	-155.5	-80.1	179.6	488.5
<b>g</b>	39.9	-17.3	11.6	-4.8	-122.0	-65.4	50.5	-129.5
<b>h</b>	34.2	-15.2	10.6	-3.0	-137.5	-58.8	50.3	-169.7
<b>i</b> <sup>b</sup>	-44.0	15.6	-11.7	2.2	-188.8	-22.3	-84.9	-711.9
<b>j</b> <sup>b</sup>	-27.8	11.3	-7.7	4.4	-55.2	4.3	-43.7	-255.7
<b>k</b>	12915.9	13814.3	12518.0	12703.7	19077.6	12179.9	13824.8	13821.2
Ave ppm	129.43	138.02	125.17	127.13	189.66	121.36	138.69	

<sup>a</sup>Positive value indicates downfield shift and the negative value indicates upfield shift from the chemical shift value of **5k**. <sup>b</sup>Methyl signal, ppm: **5d**, 55.47; **5e**, 21.38; **5i**, 55.46; **5j**, 21.65.

(SSP) and dual substituent parameter (DSP) approach, which are represented by Equations 1 and 2, respectively.<sup>12</sup>

$$\delta = \rho\sigma + \delta_0 \quad (1)$$

$$\delta = \rho_I\sigma_I + \rho_R\sigma_R + \delta_0 \quad (2)$$

Applying Eq. 1, Musumarra and Ballistreri reported the correlation of <sup>13</sup>C chemical shifts of C=O,  $\alpha$ -C,  $\beta$ -C, 2-C, 5-C, and *ipso*-C in **3** with the Hammett  $\sigma$  values.<sup>13</sup> But they examined seven compounds having substituents (OCH<sub>3</sub>, CH<sub>3</sub>, H, F, Cl, CN, and NO<sub>2</sub>) only at the *para* position. Furthermore, the measurement was made with the solution of 200 mg of the compound in 1.5 mL of CDCl<sub>3</sub>. The spectra were obtained at 25.05 MHz. There are discrepancies in the assignments between the literature values and our values which were obtained with 0.1 M solutions at 100 MHz. For example, they assigned the 4-C signal to be down-field to that of 5-C. But our assignments based on <sup>1</sup>H-<sup>13</sup>C HETCOR spectroscopy and HMBC show the opposite. The  $\rho$  values were reported only for the *ipso*-,  $\beta$ -, 2-, and 5-Cs.

**Table 5.** <sup>1</sup>H chemical shift values (Hz)<sup>a</sup> of **7** in 0.1 M-CDCl<sub>3</sub> obtained at 400 MHz

	2-H	3-H	4-H	$\alpha$ -H	$\beta$ -H
<b>a</b>	12.96	13.64	5.39	-2.04	30.18
<b>b</b>	0.91	3.84	4.16	-31.21	1.85
<b>c</b>	-0.08	7.25	-1.25	-28.20	3.15
<b>d</b> <sup>b</sup>	-2.30	-1.45	-1.51	-5.49	-1.88
<b>e</b> <sup>b</sup>	0.02	-1.15	-0.86	-3.62	-4.08
<b>f</b>	4.71	12.21	3.11	-22.82	10.14
<b>g</b>	0.11	1.84	0.90	-25.88	-1.08
<b>h</b>	-3.13	-1.31	-2.21	-21.43	-0.62
<b>i</b> <sup>b</sup>	-3.49	-5.12	-4.09	-3.69	-1.69
<b>j</b> <sup>b</sup>	-2.51	-3.21	-2.58	0.27	-4.16
<b>k</b>	3059.01	2965.86	2969.95	3013.16	3125.01
Ave. $\delta$	7.65	7.42	7.42	7.50	7.82

<sup>a</sup>Positive value indicates downfield shift and the negative value indicates upfield shift from the chemical shift value of **7k**. <sup>b</sup>Methyl signal,  $\delta$ : **7d**, 3.87; **7e**, 2.44; **7i**, 3.88; **7j**, 2.43.

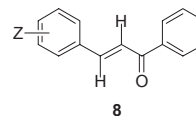
**Table 6.** <sup>13</sup>C chemical shift values (Hz)<sup>a</sup> of **7** in 0.1 M-CDCl<sub>3</sub> obtained at 100 MHz

	1-C	2-C	3-C	4-C	C=O	$\alpha$ -C	$\beta$ -C	<i>ipso</i> -C
<b>a</b>	-57.9	29.8	14.4	-62.7	-255.8	-146.2	193.4	128.0
<b>b</b>	-26.9	13.5	6.2	-32.7	-152.3	-68.1	87.7	179.5
<b>c</b>	-27.3	12.3	5.6	-58.8	-143.9	-65.4	84.0	157.8
<b>d</b> <sup>b</sup>	-1.8	0.7	-0.8	-98.2	-28.7	0.5	2.2	136.8
<b>e</b> <sup>b</sup>	5.6	-1.2	-1.6	-5.9	16.2	16.4	-20.5	3.6
<b>f</b>	-60.9	25.7	44.6	69.6	-154.5	-81.6	197.1	482.2
<b>g</b>	-21.3	6.8	106.0	21.4	-119.8	-64.4	56.0	-130.3
<b>h</b>	-19.3	6.0	4.4	19.6	-139.0	-60.7	49.8	-171.7
<b>i</b> <sup>b</sup>	19.0	-9.6	-4.7	-22.7	-186.0	-22.6	-89.6	-712.9
<b>j</b> <sup>b</sup>	11.4	-5.1	36.9	-13.3	-55.2	-0.1	-46.4	-258.8
<b>k</b>	13485.1	12843.0	12894.2	13053.2	190548	12205.9	14483.1	13818.1
Ave ppm	134.68	128.50	128.98	130.71	189.44	121.61	145.30	138.01

<sup>a</sup>Positive value indicates downfield shift and the negative value indicates upfield shift from the chemical shift value of **7k**. <sup>b</sup>Methyl signal, ppm: **7d**, 55.46; **7e**, 21.39; **7i**, 55.47; **7j**, 20.66.

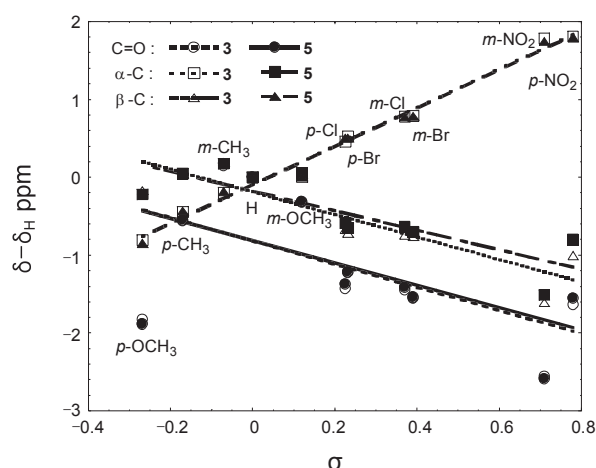
It was not mentioned as to why the  $\rho$  values for the other carbon signals such as C=O and  $\alpha$ -C were not reported.

Solaniova, *et al.*<sup>14</sup> investigated the correlation of <sup>13</sup>C chemical shifts of chalcones **7** and **8** with the Hammett  $\sigma$  parameters and  $\pi$  charge densities.



With the compounds **7**, which are very close to our work, they reported  $\rho$  values of -0.944 ppm ( $r = 0.935$ ) for nine substituents (*m*-Cl, *m*-Br, *m*-NO<sub>2</sub>, *p*-OCH<sub>3</sub>, *p*-CH<sub>3</sub>, *p*-F, *p*-Cl, *p*-Br, *p*-CN) and 2.863 ppm ( $r = 0.991$ ) for ten substituents (*p*-NO<sub>2</sub> included) for  $\alpha$ -C and  $\beta$ -C, respectively. However, they did not report a  $\rho$  value for the carbonyl carbon atom. Instead, the correlation for C=O was found, using an equation  $\Delta\delta = \delta_0 + f^*F + r^*R$ , with the six compounds having the *para* substituents. Values of  $f^*$  (-0.914) and  $r^*$  (2.152) were reported.

Applying the Eqn. 2 to the data of Solaniova, *et al.*, Brownlee,



**Figure 1.** Correlation between  $\sigma$  and <sup>13</sup>C chemical shifts of carbonyl- (circle),  $\alpha$ - (rectangle), and  $\beta$ -carbons (triangle) in **3** (light) and **5** (dark) in 0.1 M-chloroform-*d*.

**Table 7.** Best fit of the single substituent parameter equation for the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of **3**, **5** and **7** in  $\text{CDCl}_3$  in Hz

	<b>3</b>		<b>5</b>		<b>7</b>	
	$\rho$	$r$	$\rho$	$r$	$\rho$	$r$
$\alpha\text{-H}$	-24.78	0.607	-25.44	0.677	-22.26	0.562
$\beta\text{-H}$	30.18	0.864	21.85	0.881	22.29	0.761
2-H			33.43	0.989	10.63	0.764
3-H	31.77	0.963			17.45	0.963
4-H	18.39	0.959	7.37	0.731	7.20	0.845
5-H	37.31	0.979	13.63	0.950		
C=O	-148.60	0.597	-143.46	0.571	-142.66	0.573
C=O <sub>EDG</sub>	705.20	0.919	729.60	0.914	718.10	0.916
C=O <sub>EWG</sub>	-246.50	0.844	-243.60	0.833	-241.90	0.831
$\alpha\text{-C}$	-144.80	0.878	-125.04	0.836	-121.42	0.844
$\beta\text{-C}$	247.23	0.994	246.32	0.994	268.96	0.994
1-C					-77.66	0.993
2-C	-73.58	0.992	142.80	0.970	35.99	0.995
3-C	138.96	0.991	-61.37	0.989	19.42	0.986
4-C	32.62	0.984	-8.79	0.765	89.04	0.993
5-C	144.01	0.993	47.79	0.988		
1'-C	724.61	0.777	702.85	0.789	718.27	0.789

**Table 8.** Slopes and correlation coefficients of the plots of  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift values of the thiophene series (**3** and **5**) vs. those of the benzene series (**7**)

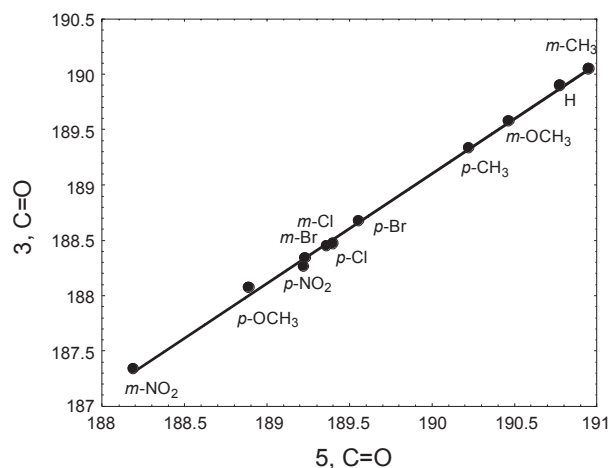
	<b>3/5</b>		<b>3/7</b>		<b>5/7</b>	
	slope	$r$	slope	$r$	slope	$r$
$\alpha\text{-H}$	1.079	0.994	1.024	0.992	0.929	0.977
$\beta\text{-H}$	1.406	0.997	1.168	0.980	0.824	0.974
C=O	0.993	0.999	1.000	0.999	1.009	0.999
$\alpha\text{-C}$	1.099	0.996	1.143	0.997	1.039	0.999
$\beta\text{-C}$	1.003	0.999	0.919	0.999	0.916	0.993
1'-C	1.020	0.999	1.023	0.999	1.003	0.999

*et al.* calculated the substituent chemical shifts, and reported values of  $\rho_{\text{I}}$  (-2.2) and  $\rho_{\text{R}}$  (1.3) for the C=O.<sup>15</sup> They also reported the negative  $\rho_{\text{I}}$  values for  $\beta\text{-C}$  (-1.1) and 1-C (-0.8) and the positive  $\rho_{\text{I}}$  values for  $\alpha\text{-C}$  (2.7) and 4-C (0.3). Although the signs of the values may be unchanged, the calculations were done with different sets of four resonance scales ( $\sigma_{\text{R}^-}$ ,  $\sigma_{\text{R}^0}$ ,  $\sigma_{\text{R}^{\text{BA}}}$ , and  $\sigma_{\text{R}^+}$ ) so that the best fit could be obtained. Therefore, the comparison of the magnitude of  $\rho_{\text{I}}$  and  $\rho_{\text{R}}$  values may not be justified.

We found that the SSP approach (Eqn. 1) is useful when the structurally related substrates are compared. For example, correlations of  $^{13}\text{C}=\text{O}$  of *m*- and *p*-substituted benzoyl derivatives of furan, pyrrole, thiophene, and benzene show good linearities when one series is plotted to other series.<sup>16</sup>

Figure 1 shows the correlations of the chemical shift values of the C=O,  $\alpha\text{-C}$ , and  $\beta\text{-C}$ s of **3** and **5** with the Hammett  $\sigma$  values.

Table 7 lists the slopes ( $\rho$ ) and the correlation coefficients ( $r$ ) obtained from the similar plotting. As shown in Table 7, the chemical shift values for the  $\alpha\text{-H}$ s and  $\beta\text{-H}$ s of **3**, **5**, and **7** do not show fair correlations with  $\sigma$ . But the plots of the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for a series of **3** vs. those of the corresponding series of **5** show excellent correlation. For example, the plot of the  $^{13}\text{C}$  chemical shifts of the carbonyl carbon in **3** against those

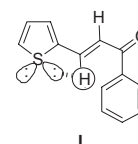
**Figure 2.** Plot of  $^{13}\text{C}$  chemical shifts of carbonyl carbons in **3** against those in **5**.

in **5** shows a slope of 0.993 with a correlation coefficient value of 0.999, as shown in Figure 2.

Similar plotting among the series resulted in the values for the slopes and the correlation coefficients as listed in Table 8.

It is interesting to note that the value of the slope for the  $\beta\text{-H}$  is 1.406 whereas that for the  $\beta\text{-C}$  is 1.003 for the plot of **3** against **5**, as shown in Table 8.

The  $\beta\text{-C}$  in **3** and **5** are the atoms that are directly bonded to the 2- and 3- positions of the thiophene ring, respectively. Therefore, the slope of near unity for the  $\beta\text{-C}$  may imply that the electronic effect of S atom in thiophene is quite uniform throughout the ring. On the other hand, the larger value of the slope for the  $\beta\text{-H}$  may be a result of the through-space interaction of the lone pair electrons on S atom with the electrons on the  $\beta\text{-H}$  due to the conformation like **I**.



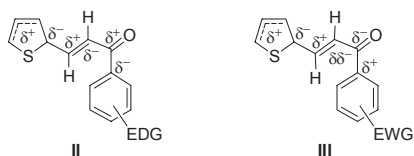
Although the  $\alpha\text{-H}$ s and  $\beta\text{-H}$ s do not show good correlations with  $\sigma$ , as shown in Table 7, it should be pointed out that the  $\alpha\text{-H}$ s show an inverse trend while the  $\beta\text{-H}$ s show a normal trend with the better correlation coefficients. The correlation of  $^{13}\text{C}$  chemical shifts with the Hammett  $\sigma$  values show a similar phenomena. The  $\alpha\text{-C}$ s show an inverse correlation with fair  $r$  values (0.878 for **3**, 0.836 for **5**, and 0.844 for **7**) while the  $\beta\text{-C}$ s show a normal correlation with excellent  $r$  values (0.994 for **3**, **5**, and **7**).

One of the striking phenomena that appears in the correlation of the carbon chemical shifts with  $\sigma$  is the apparent lack of correlation of the carbonyl carbon ( $r=0.571\sim 0.597$ ). As shown in Tables 2, 4, and 6, both electron-donating (e. g., *p*-OCH<sub>3</sub>) and electron-withdrawing (e. g., *p*-NO<sub>2</sub>) groups cause an up-field shift of the  $^{13}\text{C}=\text{O}$  signals. When the correlations were attempted separately for the electron-donating and -withdrawing groups, positive and negative  $\rho$  values were obtained, respectively, with fair correlation coefficient values. But the slopes for the former

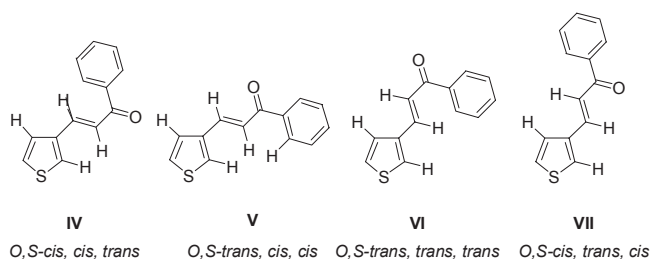


( $\rho = 705.2 \sim 729.6$  Hz) are about three-times larger than those of the latter ( $\rho = -241.9 \sim -246.5$  Hz).

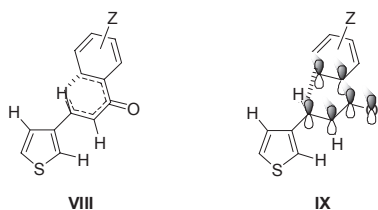
It is also noticeable that the negative  $\rho$  values were obtained for the  $\alpha$ -C and the carbons directly bonded to the  $\beta$ -C that may be called '*ipso*-C' (C-2 of **3**, C-3 of **5**, and C-1 of **7**) whereas the positive  $\rho$  values were obtained for the  $\beta$ -C. Furthermore, the absolute magnitudes of the  $\rho$  values of the  $\beta$ -C were about twice those of the  $\alpha$ -C and 3-4 times of the *ipso*-C. In addition, the correlation coefficients are not only the best but also the same ( $r = 0.994$ ) for the three series. The signs of the  $\rho$  values for the C=O,  $\alpha$ -,  $\beta$ -, and *ipso*-Cs may be explained by the induced  $\pi$  polarization mechanism as shown in **II** and **III** for **3** as an example.



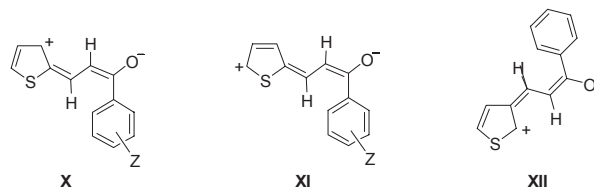
But the largest magnitude of the  $\rho$  value for the  $\beta$ -C for each series cannot be explained by the mechanism of the transmission of the substituent effect through bonds. If the distance from the substituent is the major factor in determining the magnitude of the  $\rho$  value, the order should be  $\text{CO} > \alpha\text{-C} > \beta\text{-C} > \textit{ipso}\text{-C}$ . However, the observed order is  $\beta\text{-C} > \text{CO} > \alpha\text{-C} > \textit{ipso}\text{-C}$ . Apparently, there should be another mechanism for transmitting the substituent effect. A plausible explanation may be derived from the consideration of the conformation of the enone system. There are four possible conformations for the enones **3**, **5**, and **7**, and they may be illustrated as **IV-VII**, drawn with **5** as an example.



Based on the  $^1\text{H}$ - $^1\text{H}$  COSY spectroscopy that shows a strong coupling between the *ortho*-H and  $\beta$ -H ( $^4J$ ) and no coupling between the *ortho*-H and  $\alpha$ -H, we were able to rule out **VI** and **VII**. With the conformation **IV**, it is feasible to form a pseudo six-membered ring that enables the substituent effect through a pseudo bond between the  $\beta$ -H and  $2'$ -C like **VIII**. Alternatively, a pseudo  $\pi$  orbital overlapping is feasible as in **IX**. Such pseudo-bonding should lead to effective transmission of the substituent effect to the  $\beta$ -C, explaining the largest  $\rho$  values.



It is also interesting to note that the  $\rho$  values for 3-C and 5-C of **3** are quite large with good correlation coefficients. On the other hand, only C-2 of **5** has a significantly large  $\rho$  value. This can be explained by the contribution of the resonance structures like **X** and **XI** for **3** and **XII** for **5**.



The magnitude of the  $\rho$  values and the correlation coefficients for  $1'$ -C of **3**, **5**, and **7** are close to those reported in the literature.<sup>16</sup>

## Experimental

**NMR spectra.** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$  and were referenced to tetramethylsilane. The solutions were 0.10 M in  $\text{CDCl}_3$ . Each solution was prepared in a 1 mL cylindrical volumetric flask by weighing the compound into the flask and filling with solvent containing 1%-TMS. A portion (0.6 mL) of the solution was transferred into a 5 mm NMR tube and the spectrum was obtained at 20  $^\circ\text{C}$ . The chemical shift values are listed in Tables 1-6.

**Compounds.** Starting materials **1**, **2**, **4**, and **6** are all commercial compounds and were used as delivered. The aldol condensation products **3**, **5**, and **7** were prepared by following literature procedures.<sup>8</sup>

**An illustrative procedure.** (*E*)-1-Phenyl-3-(2-thienyl)-2-propenone. Acetophenone (**2k**, 0.66 mL, 5.7 mmol) and 2-thiophenecarboxaldehyde (**1**, 0.50 mL, 5.7 mmol) were added to an ice-cold solution of 2.67 M-NaOH solution (4.3 mL) and ethanol (2.7 mL). The solution was gradually brought to room temperature and stirred for 4 h. Upon cooling in a freezer a pale yellow precipitate formed. The solid was collected by filtration and the residue was washed with 1 M-HCl solution (5 mL). The solid was recrystallized from ethanol-water to give **3k** (1.12 g, 92%).

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