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Benzophenones, 2-benzoylthiophenes, 2-benzoylpyrroles, and 2-benzoylfurans, which have substituents at *m*- and *p*-positions of the benzoyl ring were prepared and their ir and nmr spectra were obtained in 0.1 *M* chloroform-*d* solution. The chemical shift values of each series were plotted against the Hammett substituent parameters to give good correlation, with the exception of the *ortho*-Hs and -Cs. The slopes as well as the differences in chemical shift gave sets of meaningful values for the indices of aromaticity.

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There are a variety of methods for estimating the aromaticity of five-membered monoheterocyclic compounds, namely thiophene, furan, and pyrrole. The degree of aromaticity is typically compared to that of benzene whose aromaticity index is set as 1 [1]. A set of aromaticity indices of 1.00, 0.75, 0.59, and 0.46 were reported for benzene, thiophene, pyrrole, and furan, respectively, by comparison of the ring currents measured by the chemical shifts of the protons [2]. Consideration of bond length and the number of  $\pi$  electrons in the ring gives a different set of the indices: benzene 1, thiophene 0.93, pyrrole 0.91, and furan 0.87 [3]. There are a number of sets of the indices reported in the literature [1-3].

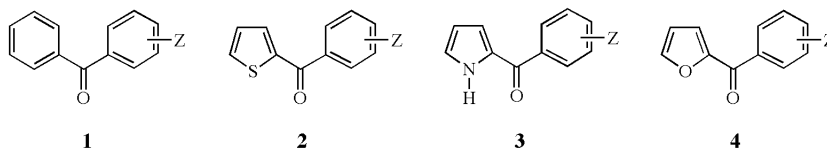
We have reported a method of estimating the aromaticity index by comparing the chemical shifts of the carbonyl carbon atoms of *m*- and *p*-substituted phenyl esters of the five-membered heterocyclic carboxylic acids to those of benzoic acids [4]. The results were: benzene 1.00, thiophene 0.85, and furan 0.75 in dimethyl sulfoxide-*d*<sub>6</sub>; and benzene 1.00, thiophene 0.90, and furan 0.78 in chloroform-*d*. A similar approach with *m*- and *p*-substituted anilides gave a slightly different set of the indices: benzene 1.00, thiophene 0.79, and furan 0.52 in dimethyl sulfoxide-*d*<sub>6</sub> [5]. The poor solubilities of the anilides in chloroform-*d* did not allow determination of a set of indices in that solvent. Our effort to estimate the index of aromaticity of pyrrole by similar method was not successful because of the difficulty of preparing the ester, *m*- and *p*-substituted phenyl 2-pyrrolicarboxylates and the 2-pyrrolylanilides. These esters and amides were very difficult to purify because they hydrolyze readily.

In order to complete the estimation of the aromaticity indices of the five-membered monoheterocyclic compounds under the same conditions we needed to have sets of substituted phenyl derivatives of the heterocycles for thiophene, pyrrole and furan. Therefore, we prepared the benzoyl derivatives of the heterocycles and obtained their NMR spectra. This paper reports the results of our attempts to obtain the indices of aromaticity.

#### Results and Discussions.

The *m*- and *p*-substituted benzoyl compounds **1-4** were prepared by Friedel-Crafts benzylation of benzene, thiophene, pyrrole, and furan in 30-85% yields. The ketones were purified by either recrystallization or column chromatography. Their ir, nmr, and mass spectra were consistent with the desired structures. Positions 3-, 4-, and 5- of the 2-substituted heterocycles can be considered as *ortho*, *meta*, and *para*, respectively, and such notation has been used throughout the present report.

In order to have a good correlation of the chemical shifts and the Hammett values, it is essential to observe the nmr spectra at the same concentration (0.1 *M*). Therefore, the purity of the compound was found to be critical [4,5]. Signals of <sup>1</sup>H and <sup>13</sup>C shift linearly upfield as the concentration increases. The plots (not shown) of <sup>1</sup>H against concentration show slopes of -9.3, -15.0, and -15.8 Hz/*M* for *o*-, *m*-, and *p*-H, respectively, of **1k**. The correlation coefficients are better than 0.999 for all cases. Similar plots of <sup>13</sup>C show slopes: CO -24.5; *i*-C 16.9; *o*-C -16.9; *m*-C -13.7; *p*-C -13.9 Hz/*M*. The <sup>1</sup>H and <sup>13</sup>C nmr chemical shift values of **1-4** are listed in Tables 1 and 2, respectively.



- 1-5** Z: **a**, *m*-NO<sub>2</sub>; **b**, *m*-Br; **c**, *m*-Cl; **d**, *m*-OCH<sub>3</sub>; **e**, *m*-CH<sub>3</sub>;  
**f**, *p*-NO<sub>2</sub>; **g**, *p*-Br; **h**, *p*-Cl; **i**, *p*-OCH<sub>3</sub>; **j**, *p*-CH<sub>3</sub>; **k**, H  
**1** Z: **l**, *p*-C<sub>2</sub>H<sub>5</sub>; **m**, *p*-*tert*-C<sub>4</sub>H<sub>9</sub>; **n**, *p*-NH<sub>2</sub>; **o**, *m*-NH<sub>2</sub>; **p**, *p*-N(CH<sub>3</sub>)<sub>2</sub>;  
**q**, *p*-OH; **r**, *p*-OCOCH<sub>3</sub>

Table 1

<sup>1</sup>H Chemical Shift Values of Substituted Phenyl Ketones **1-4** in Chloroform-*d* (0.1 M)

	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	2'-H	3'-H	4'-H	5'-H	6'-H	CH <sub>3</sub>
<b>1a</b>	7.81	7.54	7.66	8.62		8.45	7.71	8.14	
<b>1b</b>	7.79	7.50	7.62	7.94		7.72	7.37	7.71	
<b>1c</b>	7.79	7.50	7.61	7.78		7.56	7.43	7.67	
<b>1d</b>	7.81	7.48	7.59	7.36		7.14	7.38	7.34	3.86
<b>1e</b>	7.80	7.48	7.58	7.63		7.40	7.36	7.58	2.42
<b>1f</b>	7.80	7.53	7.66	7.94	8.34				
<b>1g</b>	7.77	7.49	7.60	7.68	7.63				
<b>1h</b>	7.77	7.49	7.60	7.76	7.46				
<b>1i</b>	7.75	7.47	7.56	7.83	6.96				3.89
<b>1j</b>	7.78	7.47	7.57	7.74	7.28				2.44
<b>1k</b>	7.81	7.48	7.59						
<b>2a</b>	7.66	7.23	7.82	8.71		8.46	7.73	8.20	
<b>2b</b>	7.64	7.19	7.76	7.99		7.72	7.38	7.78	
<b>2c</b>	7.64	7.18	7.76	7.83		7.57	7.44	7.74	
<b>2d</b>	7.68	7.16	7.72	7.38		7.13	7.41	7.45	
<b>2e</b>	7.68	7.12	7.61	7.66		7.34	7.36	7.63	
<b>2f</b>	7.63	7.22	7.83	8.02	8.36				
<b>2g</b>	7.62	7.18	7.74	7.74	7.65				
<b>2h</b>	7.63	7.18	7.74	7.82	7.48				
<b>2i</b>	7.64	7.16	7.69	7.91	6.99				
<b>2j</b>	7.65	7.16	7.70	7.79	7.30				

Table 1 (continued)

	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	2'-H	3'-H	4'-H	5'-H	6'-H	CH <sub>3</sub>
<b>2k</b>	7.65	7.17	7.73	7.87	7.50	7.60			
<b>3a</b>	6.92	6.41	7.25	8.75		8.43	7.70	8.23	
<b>3b</b>	6.89	6.36	7.18	8.03		7.69	7.36	7.82	
<b>3c</b>	6.89	6.36	7.18	7.87		7.54	7.42	7.78	
<b>3d</b>	6.92	6.34	7.15	7.42		7.11	7.39	7.48	3.87
<b>3e</b>	6.89	6.34	7.15	7.70		7.39	7.37	7.70	2.43
<b>3f</b>	6.87	6.39	7.24	8.03	8.35				
<b>3g</b>	6.86	6.35	7.17	7.78	7.63				
<b>3h</b>	6.87	6.35	7.17	7.86	7.46				
<b>3i</b>	6.89	6.34	7.13	7.94	6.99				3.89
<b>3j</b>	6.89	6.33	7.14	7.83	7.29				2.44
<b>3k</b>	6.90	6.34	7.16	7.91	7.49	7.57			
<b>4a</b>	7.38	6.68	7.77	8.88		8.48	7.72	8.35	
<b>4b</b>	7.27	6.62	7.73	8.11		7.72	7.38	7.91	
<b>4c</b>	7.27	6.61	7.72	7.95		7.55	7.43	7.86	
<b>4d</b>	7.24	6.60	7.71	7.48		7.13	7.40	7.56	3.87
<b>4e</b>	7.21	6.58	7.70	7.75		7.40	7.37	7.70	2.43
<b>4f</b>	7.34	6.67	7.76	8.31	8.36				
<b>4g</b>	7.26	6.61	7.71	7.87	7.64				
<b>4h</b>	7.25	6.60	7.70	7.94	7.46				
<b>4i</b>	7.23	6.59	7.69	8.03	6.99				
<b>4j</b>	7.21	6.57	7.68	7.88	7.28				
<b>4k</b>	7.24	6.60	7.71	7.97	7.50	7.60			

Table 2

<sup>13</sup>C Chemical Shift Values of Substituted Phenyl Ketones **1-4** in Chloroform-*d* (0.1 M)

	C=O	<i>i</i> -C	<i>o</i> -C	<i>m</i> -C	<i>p</i> -C	1'-C	2'-C	3'-C	4'-C	5'-C	6'-C	CH <sub>3</sub>
<b>1a</b>	194.15	136.23	129.99	128.72	133.35	139.04	124.70	148.07	126.70	129.62	135.42	
<b>1b</b>	195.15	136.88	130.00	128.45	132.83	139.45	132.77	122.55	135.25	129.86	128.53	
<b>1c</b>	195.24	136.93	130.00	128.44	132.82	139.24	129.88	134.55	132.33	129.61	128.08	
<b>1d</b>	196.53	137.58	130.02	128.24	132.41	138.86	114.28	159.54	118.85	129.19	122.86	55.45
<b>1e</b>	196.96	137.73	130.02	128.21	132.31	138.13	130.43	137.60	133.17	128.06	127.35	21.34
<b>1f</b>	194.77	136.26	130.67	128.66	133.45	142.86	130.07	123.52	149.81			
<b>1g</b>	195.61	137.25	129.92	128.39	132.66	136.28	131.60	131.54	127.49			
<b>1h</b>	195.46	137.23	128.90	128.38	132.62	135.82	131.44	128.62	138.87			
<b>1i</b>	195.54	138.26	129.70	128.16	131.86	130.14	132.54	113.52	163.19			55.47
<b>1j</b>	196.49	137.93	130.29	128.18	132.13	134.86	129.91	128.95	143.22			21.64
<b>1k</b>	196.77	137.56	130.04	128.25	132.40	137.56	130.04	128.25	132.40			
<b>2a</b>	185.59	142.36	135.54	128.43	135.29	139.41	123.95	148.04	126.61	129.80	134.69	
<b>2b</b>	186.58	142.96	135.12	128.14	134.82	139.88	131.98	122.60	135.09	130.00	127.64	
<b>2c</b>	186.70	142.99	135.07	128.13	134.80	139.67	129.11	134.61	132.21	129.04	127.21	
<b>2d</b>	187.95	143.53	134.86	127.94	134.24	139.37	113.71	159.56	118.59	129.37	121.72	55.44
<b>2e</b>	188.03	143.34	133.90	127.73	134.59	138.62	129.93	137.75	132.97	127.94	126.06	21.66
<b>2f</b>	186.28	142.60	135.71	128.40	135.48	143.30	129.91	123.68	149.77			
<b>2g</b>	187.05	143.03	134.79	128.06	134.57	136.80	131.71	130.68	127.24			
<b>2h</b>	186.90	143.17	134.75	128.04	134.52	136.37	130.56	128.74	138.68			
<b>2i</b>	186.86	143.81	133.99	127.74	133.40	130.65	131.59	113.66	163.07			55.47
<b>2j</b>	187.93	143.76	134.47	127.84	133.82	135.38	129.37	129.07	143.03			25.61
<b>2k</b>	188.24	143.60	134.84	127.94	134.20	138.11	129.15	128.39	132.25			
<b>3a</b>	181.94	130.30	120.28	111.74	126.69	139.65	123.84	148.08	126.23	129.59	134.56	
<b>3b</b>	183.06	130.66	119.84	111.31	125.89	140.12	131.82	122.49	134.69	129.90	127.46	
<b>3c</b>	183.19	130.70	119.82	111.29	125.89	139.92	129.65	134.48	131.78	128.94	127.02	
<b>3d</b>	184.54	131.08	119.48	111.03	125.29	139.59	113.51	159.51	118.17	129.30	121.50	55.40
<b>3e</b>	185.05	131.20	119.41	110.93	125.16	138.31	129.43	138.13	132.59	128.13	126.16	21.38
<b>3f</b>	182.53	130.56	120.37	111.70	126.68	143.61	129.76	123.57	149.59			
<b>3g</b>	183.56	130.77	119.52	111.22	125.68	137.04	131.59	130.47	126.69			
<b>3h</b>	183.44	130.80	119.46	111.20	125.62	136.61	130.33	128.63	138.15			
<b>3i</b>	183.62	131.15	118.55	110.80	124.65	130.91	131.15	113.59	162.72			55.42
<b>3j</b>	184.58	131.20	119.04	110.88	124.95	135.61	129.09	128.99	142.46			21.57
<b>3k</b>	184.85	131.11	119.52	111.02	125.30	138.32	128.94	128.30	131.82			
<b>4a</b>	179.60	151.84	121.24	112.80	147.77	138.27	124.36	148.13	126.93	129.71	135.02	
<b>4b</b>	180.76	151.90	120.92	112.42	147.43	138.88	132.18	122.58	135.42	129.99	127.82	
<b>4c</b>	180.84	151.90	120.90	112.40	147.41	138.64	129.73	134.57	132.49	129.27	127.37	
<b>4d</b>	182.29	152.17	120.69	112.18	147.16	138.48	113.79	159.59	118.93	129.39	121.82	55.45
<b>4e</b>	182.77	152.25	120.49	112.10	147.02	138.25	129.64	137.25	133.31	128.19	126.43	21.31

Table 2(continued)  
<sup>13</sup>C Chemical Shift Values of Substituted Phenyl Ketones **1-4** in Chloroform-*d* (0.1 M)

	C=O	<i>i</i> -C	<i>o</i> -C	<i>m</i> -C	<i>p</i> -C	1'-C	2'-C	3'-C	4'-C	5'-C	6'-C	CH <sub>3</sub>
<b>4f</b>	180.35	151.86	121.43	112.80	147.89	142.10	130.28	123.60	149.96			
<b>4g</b>	181.24	152.12	120.59	112.38	147.22	135.85	131.73	130.87	127.68			
<b>4h</b>	180.99	152.09	120.51	112.32	147.15	135.36	130.70	128.68	138.96			
<b>4i</b>	181.14	152.60	119.64	112.03	146.51	129.80	131.70	113.68	163.26			55.46
<b>4j</b>	182.18	152.34	120.09	112.04	146.78	134.49	129.37	129.04	143.32			21.55
<b>4k</b>	182.54	152.24	120.55	112.17	147.08	137.22	129.24	128.38	132.54			

The assignments of each peak were made by analysis of <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>13</sup>C HETCOR spectra. In addition, the correlations of the values of the heterocycles against those of the corresponding benzene derivatives make the assignment unambiguous. Such plots for the protons and carbons in the substituted phenyl group (like Figure 4) show slopes of near unity with correlation coefficients of 0.999-1.000. This could also be used to make accurate assignments.

The average values of <sup>1</sup>H and <sup>13</sup>C chemical shifts for each series of 11 derivatives (**a-k**) are listed in Table 3. For the purpose of comparison the chemical shift values of benzene, thiophene, pyrrole, and furan in chloroform-*d* at 0.1 M concentration are also listed in the Table.

Table 3  
 Averaged Chemical Shift Values of the Benzoylketones **1-4** in Chloroform-*d* (0.1 M) and Their Differences

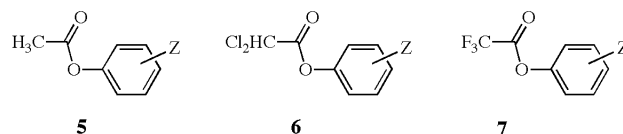
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
2,5(α)-H[a]	7.36	7.35	6.85	7.45
3,4(β)-H[a]	7.36	7.13	6.26	6.39
δ(α-β)	0.00	0.22	0.59	1.06
<i>Ortho</i> -H	7.79 ± 0.02	7.65 ± 0.03	6.89 ± 0.03	7.26 ± 0.12
<i>Meta</i> -H	7.49 ± 0.05	7.18 ± 0.05	6.36 ± 0.05	6.61 ± 0.07
<i>Para</i> -H	7.60 ± 0.06	7.74 ± 0.09	7.17 ± 0.08	7.72 ± 0.05
δ( <i>o</i> -β)	0.43	0.52	0.63	0.87
2,5(α)-C[a]	128.33	125.11	117.16	142.52
3,4(β)-C[a]	128.33	126.86	108.16	109.44
δ(α-β)	0	-1.75	9.00	33.08
C=O	195.70 ± 1.55	187.10 ± 1.51	183.67 ± 1.73	181.34 ± 1.74
<i>Ips</i> o-C	137.25 ± 1.01	143.19 ± 0.83	130.87 ± 0.33	152.12 ± 0.48
<i>Ortho</i> -C	129.96 ± 0.26	134.82 ± 0.92	119.57 ± 1.02	120.64 ± 1.00
<i>Meta</i> -C	128.37 ± 0.35	128.04 ± 0.39	119.19 ± 0.55	112.33 ± 0.47
<i>Para</i> -C	132.62 ± 0.83	134.52 ± 0.96	125.62 ± 1.07	147.22 ± 0.67
δ( <i>i</i> - <i>o</i> )	7.29	8.37	11.30	31.48

[a] Parent aromatic compounds.

The difference in chemical shifts of the *ortho*- and *meta*-Hs of the five-membered heterocycles are considered to be a measure of relative aromaticity [6]. The effect of the heterocycles on the chemical shift of protons and carbons in the unsubstituted benzoyl groups of **1k**, **2k**, **3k**, and **4k** is quite remarkable. For example, by

replacing the hydrogen of benzaldehyde with phenyl, 2-thienyl, 2-pyrrolyl, and 2-furyl rings the <sup>13</sup>C=O signals shift by +3.65, -5.05, -8.48, and -10.81 ppm, respectively, with the minus sign indicating upfield shift. Unlike the benzene ring, which causes a downfield shift, the heterocyclic rings induce shielding of the carbonyl carbon atom with oxygen, the most electronegative oxygen atom, causing the most upfield shift. This also seems consistent with the observation of the upfield shift of the <sup>13</sup>C=O in various benzoyl derivatives having electron-withdrawing substituents at *m*- and *p*-positions [7].

Recently, Neuvonen, *et al.* reported inverse correlation of the <sup>13</sup>C=O shift of *m*- and *p*-substituted phenyl esters of acetic acid (**5**), dichloroacetic acid (**6**), and trifluoroacetic acid (**7**) with the Hammett parameters, and proposed a novel concept to explain the reversed effect of the electron-withdrawing substituents [8].



They concluded that electron-withdrawing substituents destabilize the carbonyl derivatives in ground-state by decreased resonance stabilization. Although the correlation was considered fair by the authors the correlation of <sup>13</sup>C=O with  $\nu_{C=O}$  was reported to have a negative slope (-0.07) with  $r^2 = 0.8142$  for *m*- and *p*-substituted phenyl acetate (**5**) [8]. The values of the carbonyl stretching frequencies seem to be consistent with the conventional thinking that the force constant of C=O bond increases by the presence of an electron-withdrawing group whereas the bond distances decrease [9].

However, reexamination of the values reported in the Supporting Information [8] and the values we obtained for the same series of **5** with 11 substituents [5] can hardly be considered a fair correlation of  $\nu_{C=O}$  with the Hammett  $\sigma$ . A plot of  $\nu_{C=O}$  vs.  $\sigma$  for the ester shows a slope of 4.73 cm<sup>-1</sup> with  $r = 0.428$ , while a plot of  $\nu_{C=O}$  vs.  $\sigma$  shows a slope of 1.35 ppm with  $r = 0.992$ . The observation strongly

suggests that the substituent should affect *differently* the chemical shift and the carbonyl stretching frequency.

The  $^{13}\text{C}=\text{O}$  signals of unsubstituted ( $Z = \text{H}$ ) **5**, **6**, and **7** appear at 169.49, 163.02, and 155.85 ppm, respectively, while their  $\nu_{\text{C}=\text{O}}$  signals are at 1765, 1777, and 1800  $\text{cm}^{-1}$ , respectively [8]. Plot of the values shows the reverse correlation in **5-7** with a slope of  $-0.379$  ( $r = 0.989$ ) as in Figure 1. Apparently, a strongly electron-withdrawing group bonded to the carbonyl carbon causes shielding of the carbon nucleus, but it makes the force constant of the  $\text{C}=\text{O}$  bond greater than an electron-donating group does.

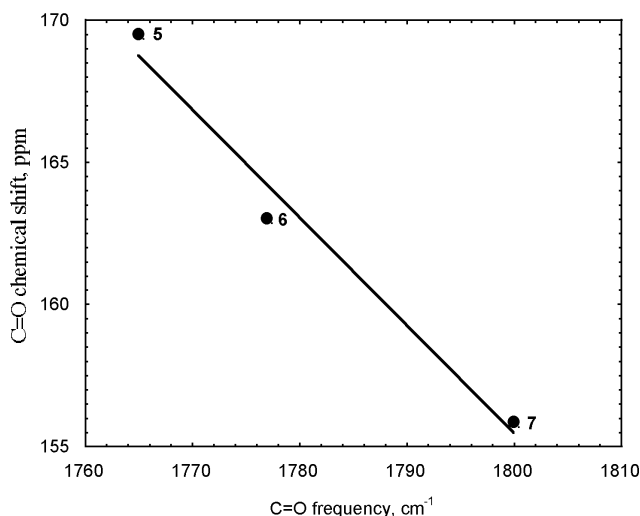


Figure 1. Correlation between the  $\text{C}=\text{O}$  frequency and the  $^{13}\text{C}$  chemical shift of the carbonyl carbon in **5-7**. The slope of the straight line is  $-0.379$  and  $r = 0.989$ .

In contrast, the aryl and heteroaryl rings show a mixed effect on the  $^{13}\text{C}=\text{O}$  and  $\nu_{\text{C}=\text{O}}$  signals of **1-4**. As mentioned earlier, the  $^{13}\text{C}=\text{O}$  signals shift to upfield going from **1** to **4**, but the  $\nu_{\text{C}=\text{O}}$  values shift to lower wave numbers: 1652  $\text{cm}^{-1}$  for **1k**, 1629  $\text{cm}^{-1}$  for **2k**, and 1614  $\text{cm}^{-1}$  for **3k**. However, **4k** is an exception, showing a value of 1647  $\text{cm}^{-1}$ , which is the largest among the heterocyclic ketones. A plot of the chemical shifts against the stretching frequencies for the carbonyl groups of **1k**, **2k**, and **3k** shows an excellent correlation ( $r = 0.998$ ) with a positive slope of 0.346, but the furan compound **4k** shows a clear exception as shown in Figure 2.

Table 4

Averaged Carbonyl Stretching Frequencies (in  $\text{cm}^{-1}$ ) of the Benzoyl Compounds **1-5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
All-(11)	$1653 \pm 8$	$1630 \pm 5$	$1614 \pm 10$	$1644 \pm 9$	$1765 \pm 6$
H	1652	1629	1614	1647	1764
Meta-(5)	$1657 \pm 4$	$1633 \pm 2$	$1614 \pm 14$	$1647 \pm 6$	$1768 \pm 3$
Para-(5)	$1650 \pm 2$	$1628 \pm 3$	$1611 \pm 13$	$1640 \pm 7$	$1762 \pm 2$

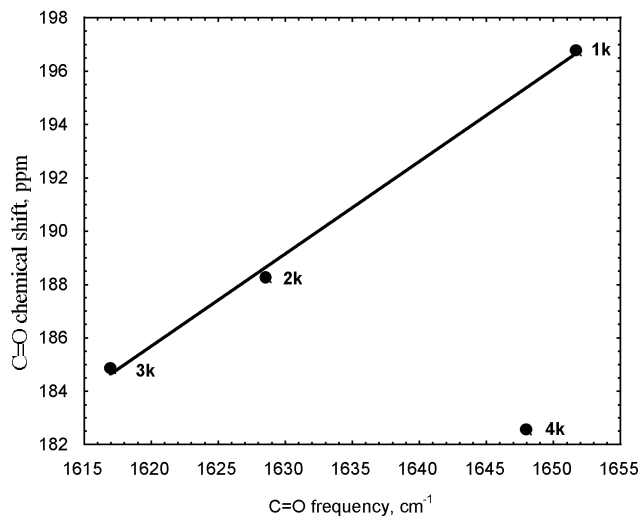


Figure 2. Correlation between the  $\text{C}=\text{O}$  frequency and the  $^{13}\text{C}$  chemical shift of the carbonyl carbon in **1k-4k**. The slope of the straight line is 0.346 and  $r = 0.998$ .

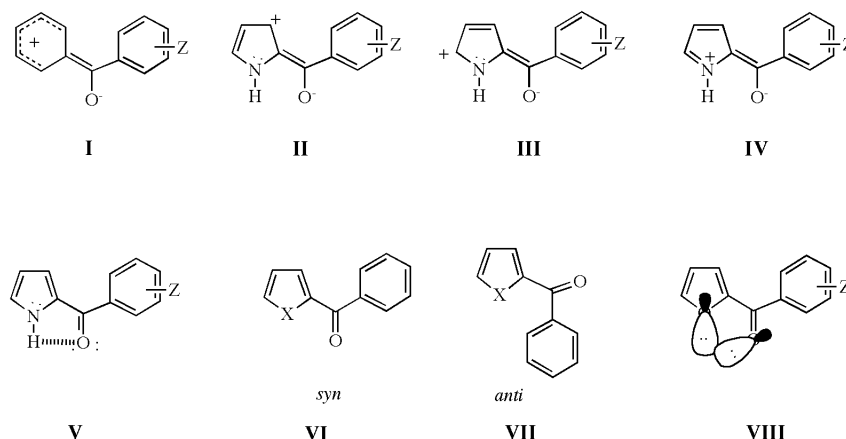
Because of the striking contrast between Figures 1 and 2, the  $\nu_{\text{C}=\text{O}}$  values of **1-5** were examined. The results are listed in Table 4.

As shown in Table 4 the average frequency of *meta*-substituted benzophenones **1a-e** is  $1657 \pm 4 \text{ cm}^{-1}$  whereas that of *para*-substituted compounds **1f-j** is  $1650 \pm 2 \text{ cm}^{-1}$ . Since the unsubstituted benzophenone **1k** shows a frequency of 1652  $\text{cm}^{-1}$ , it can be concluded that the presence of a substituent at the *para* position reduces the force constant of the  $\text{C}=\text{O}$  bond. A substituent at the *meta* position strengthens it regardless of the electron-withdrawing or -donating nature of the substituent. Similar trends are apparent with the series **2**, **3**, **4**, and **5** as shown in Table 4. The difference in the average values of  $\text{C}=\text{O}$  frequencies between *meta*- and *para*-substituted compounds are 5-7  $\text{cm}^{-1}$  for **1-5**. Therefore, the differences in the  $\nu_{\text{C}=\text{O}}$  values of **1k**, **2k**, **3k**, and **4k** should originate from the presence of the phenyl and the heteroaryl rings.

Aryl rings are generally known to have electron-donating ability through conjugation forms like **I**, and the frequency of carbonyl stretching decreases from acetophenone (1685  $\text{cm}^{-1}$ ) to benzophenone (1652  $\text{cm}^{-1}$ ). 2-Benzoylpyrrole (**3k**) shows the smallest  $\nu_{\text{C}=\text{O}}$  value (1614  $\text{cm}^{-1}$ ) among **1k-4k**, indicating that conjugation is most effective with the 2-pyrrolyl ketone like **II-IV**. This is not surprising if we consider the fact that the electronegativity of nitrogen atom is smaller than that of oxygen atom, and the sizes of carbon and nitrogen atoms are most compatible to form a  $\text{C}-\text{N}$  double bond to achieve **IV**. Also, the hydrogen bonding such as for **V** makes the  $\text{C}=\text{O}$  bond have single bond character and consequently, the frequency becomes the smallest.

As mentioned earlier the order of  $\nu_{\text{C}=\text{O}}$  values is **1** > **2** > **3** > **4**, but the order of  $\nu_{\text{C}=\text{O}}$  values is **1** > **4** > **2** > **3**. The

exceptional behavior of the furyl ketones **4** can be explained by the interaction between the oxygen atoms in the ring and the carbonyl group. It is well known that both oxygen atoms lie close together because the most favorable conformation of the carbonyl derivative of 5-membered heteroaromatic compounds is *syn* such as for **VI** [10]. The lone pair orbitals in both oxygen atoms lie in close proximity like **VIII** so that one of the lone pair electrons may move into C=O bond making its force constant greater. In this way the C=O stretching frequency becomes larger than those of **2** and **3**. It may be a similar phenomenon to that of  $\alpha$ -halogenated cyclic ketones in which the equatorial isomer absorbs at higher wave number ( $1745\text{ cm}^{-1}$ ) than the axial isomer ( $1725\text{ cm}^{-1}$ ) [11]. *Anti* conformation such as for **VII** should have no through-space interaction between the ring hetero atom and oxygen atom in the carbonyl group.



There are several factors that influence the chemical shift of a nucleus. Electronic shielding (or deshielding) originating from the inductive effect of neighboring groups is the most influential among them. In this regard the effect of a substituent on the chemical shift of benzene derivative can be correlated with a substituent parameter such as the Hammett values. The single substituent parameter (SSP)

and dual substituent parameter (DSP) approaches, which are represented in Equations 1 and 2, respectively, have been extensively studied for such practice [12].

$$= +_o \quad (1)$$

$$= I I^+ R R^+ o \quad (2)$$

The effects of *m*- and *p*-substituents in the benzoyl group on the chemical shift of  $^1\text{H}$  and  $^{13}\text{C}$  in benzene (**1**) and heterocyclic rings (**2-4**) were analyzed by the Hammett equation (Eq. 1). The results are listed in Table 5.

The plots of  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts against various substituent parameters show best correlation with the Hammett values [13]. Other values such as  $\sigma^+$  or  $\sigma^{\ominus}$  [14] do not show a reasonable correlation. Although DSP analysis shows good correlation the results are not listed because the major objective of the present report is to

determine the aromaticity indices of five-membered heterocyclic compounds.

The correlations show several interesting phenomena. First of all, *o*-Hs show no correlation while *m*- and *p*-Hs show fair correlations with  $\sigma$  values. The slopes of *p*-Hs are larger than those of *m*-Hs by 11.5, 26.2, 19.7 Hz for **1**, **2**, and **3**, respectively. But the opposite is the case with **4**.

Table 5  
Best Fit of the Single Substituent Parameter Equation for the  $^1\text{H}$  and  $^{13}\text{C}$  Chemical Shifts of **1-4** in Chloroform-*d* in Hz.

	<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>	
	$\sigma$	r	$\sigma$	r	$\sigma$	r	$\sigma$	r
<i>Ortho</i> -H	9.9	0.478	-2.8	0.150	-2.8	0.132	56.0	0.906
<i>Meta</i> -H	25.2	0.965	26.3	0.939	25.9	0.934	36.4	0.931
<i>Para</i> -H	36.7	0.983	52.5	0.984	45.6	0.968	31.7	0.935
C=O	-207.4	0.787	-178.7	0.739	-241.0	0.819	-228.0	0.774
<i>Ipsso</i> -C	-190.5	0.992	-138.9	0.969	-83.7	0.937	-65.6	0.933
<i>Ortho</i> -C	17.2	0.564	138.2	0.957	145.1	0.951	139.5	0.941
<i>Meta</i> -C	54.2	0.976	64.1	0.990	90.8	0.988	78.7	0.982
<i>Para</i> -C	141.5	0.993	183.5	0.990	191.3	0.992	116.2	0.981
<i>Ipsso</i> -C'	757.4	0.785	825.6	0.833	761.8	0.789	724.5	0.779

The difference in the magnitude is only 4.7 Hz. Again, the electronic effect of oxygen atom is so significant that the effect of the substituents do not seem to make much difference. Even the correlation coefficient ( $r$ ) for the *para* series (0.967-0.984) is better than those of the *meta* series (0.934-0.965) in **1-3**. Contrastingly, they are virtually the same in **4** ( $r_m = 0.931$  vs.  $r_p = 0.935$ ).

The  $^{13}\text{C}=\text{O}$  shows a trend of a negative slope with poor, but similar, correlation coefficients ( $r = 0.739$ - $0.819$ ) for **1-4**. The inverse correlation of  $^{13}\text{C}=\text{O}$  vs  $\sigma$  has been reported for various benzoyl series,  $\text{Z}-\text{C}_6\text{H}_4-\text{C}(=\text{O})\text{X}$  ( $\text{X} = \text{NH}_2, \text{F}, \text{OEt}, \text{OH}, \text{Me}, \text{H}$ ) [7], *m*- and *p*-substituted phenyl esters  $\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{Z}$  [4], *m*- and *p*-substituted anilides  $\text{R}-\text{C}(=\text{O})-\text{NH}-\text{C}_6\text{H}_4-\text{Z}$  [5,15], and ethyl *m*- and *p*-substituted cinnamates,  $\text{Z}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{O}-\text{C}_2\text{H}_5$  [16]. The correlations were much better for the series of esters ( $r = 0.989$ ) [4]. Therefore, the rather poor correlation seems to warrant a further investigation. In order to examine the effect of the electron-donating and -withdrawing groups additional *m*- and *p*-substituted benzophenones ( $\text{Z} = p\text{-C}_2\text{H}_5$ , **1l**; *p*-*tert*- $\text{C}_4\text{H}_9$ , **1m**; *p*- $\text{NH}_2$ , **1n**; *m*- $\text{NH}_2$ , **1o**; *p*- $\text{NMe}_2$ , **1p**; *p*- $\text{OH}$ , **1q**; *p*- $\text{OCOCH}_3$ , **1r**) were prepared.

With total eighteen benzophenones (**1**), the slope is  $-102.1$  Hz with no apparent correlation pattern ( $r = 0.481$ ). However, there is a clear trend that shows a change in the signs of the slopes as shown in Figure 3.

With ten substituents that have negative  $\sigma$  values including H ( $\sigma = 0$ ), the slope is positive (270.9 Hz) with  $r = 0.843$ . On the other hand, a negative slope ( $-287.9$  Hz) with  $r = 0.914$  is observed with eight electron-withdrawing substituents (*i.e.*, +  $\sigma$  values). The correlation would have been much better ( $\sigma = 300.3$  Hz,  $r = 0.931$ ) if the point corresponding to *p*-OH were excluded. The exceptional

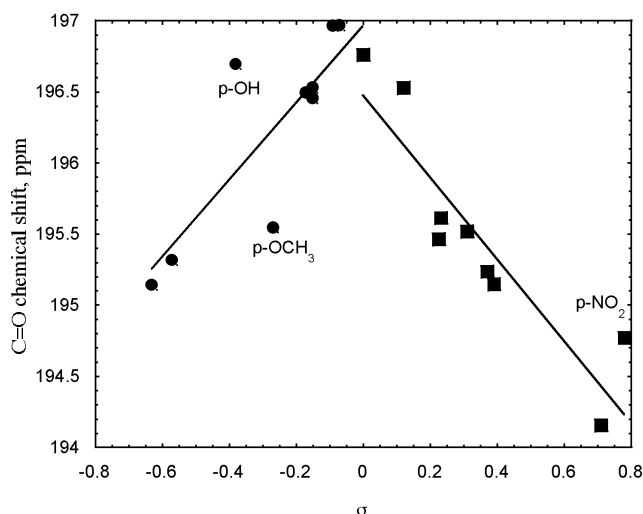
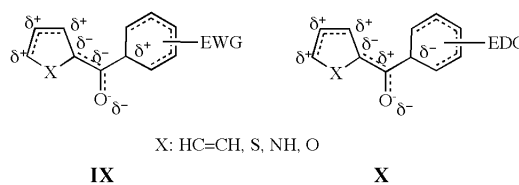


Figure 3. Correlation between  $\sigma$  and  $^{13}\text{C}=\text{O}$  in **1**. The slope of the circle data line is 2.71 ppm ( $r = 0.843$ ) and the slope of the rectangle data line is  $-2.88$  ppm ( $r = 0.914$ ).

behavior of the *p*-OH group may be due to favorable hydrogen bonding between the carbonyl oxygen atom and *p*-OH group [17].

It should be noted that the absolute values of the slopes are very close (*i.e.*, 270.9 vs. 287.9 Hz). This indicates that the magnitude of the upfield shift is about the same regardless of the sign of  $\sigma$  as long as their absolute values are same. This observation together with the very close  $^{13}\text{C}=\text{O}$  values for *p*-substituted **1** would be better explained by the polarization with opposite partial charges such as **IX** and **X**.



In contrast to  $^{13}\text{C}=\text{O}$ , the *i*-Cs of **1** show an excellent correlation with  $\sigma$  ( $r = 0.992$ ) with a negative slope ( $\sigma = -190.5$  Hz). The *i*-Cs of the heterocycles also show good correlations ( $r = 0.933$ - $0.969$ ), but the magnitudes of the slopes decrease in the order of **1** > **2** > **3** > **4**. The magnitude of the slope is the measure of the sensitivity of the chemical shift to the electronic effect of the substituent. *i*-C is the very first carbon bonded to the substituted benzoyl group. Therefore, the substituent effect should be most profound if the transmission of the effect takes place through bonds. The  $\sigma$  values listed in Table 5, however, are not consistent with such an expectation. If only the absolute values are considered,  $\sigma_i$  of **1** is the largest among all  $\sigma$  values of **1-4**. But  $\sigma_{ps}$  are the largest in **2** and **3** while  $\sigma_o$  is the largest in **4**. In **4**,  $\sigma_i$  is the smallest. The inductive effect of the oxygen atom is so great that the 2- and 5-Cs of the furan ring in **4** are not affected as much as in **1-3** by the electronic effect of the substituent. All  $\sigma_m$  values are smallest among each series of **1-3**, except **1**. The latter case cannot be compared because there is no apparent correlation in the chemical shift of *o*-C with  $\sigma$  ( $r = 0.564$ ). This is the only case which does not show a meaningful correlation of  $\sigma$  and  $\delta$ . It is known that both rings of **1** do not lie in the same plane [18]. Instead, they are skewed a little due to the interaction between *o*- and *o'*-Hs. Therefore, the *o*-C and *o*-H of **1** is under the influence of the field effect of the carbonyl group quite differently, and such effect should be greater than the effect of substituent transmitted through bonds or through space.

It is notable that  $\sigma_o$  and  $\sigma_p$  of **3** are the largest among  $\sigma_o$  and  $\sigma_{ps}$  of **1-4**. As mentioned earlier, conjugation such as **II-IV** is very feasible in **3**. Therefore, the *o*- and *p*-Cs of the pyrrole ring are likely to have a partial positive charge. The charge density is most likely to be influenced by the electronic effect of the substituent.

As in the case with  $^1\text{H}$   $\rho$  of **4** is larger than  $\rho$  in  $^{13}\text{C}$  correlation. The inductive effect of oxygen atom directly bonded to *p*-C should have profound effect. The excellent correlation of  $\rho$  with  $\rho$  may be explained better by a modified polarization mechanism for the transmission of the substituent effect [7,19]. The electronic effect of the substituent seems to travel as if it is a vector representing a dipole like **XI** and **XII**. Those atoms along the vector should be more sensitive to the effect. If the polarization determines the sign of the  $\rho$ , the vector should determine the magnitude of the  $\rho$ . The vector seems to pass through the *i*- and *p*-C atoms of **1-4**. The significant sensitivity of  $\rho$  of **2-4**, though smaller than  $\rho$ , should be due to the *s-trans* conformation of the carbonyl and C2-C3 double bond which makes C3 positive like **II**.

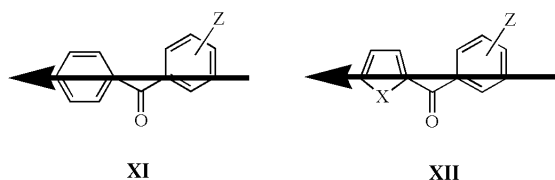


Figure 4 is an illustration of the correlation of  $\rho$ 's of **2-4** against  $\rho$ 's of **1**. Table 6 lists the slopes and correlation coefficients of such plots.

Except for *o*-H and *o*-C the correlations are excellent. As expected the slope of near unity with  $r = 0.999$  for *i*-C's indicates that the assignments are accurate for all *ipso* carbons of the substituted benzoyl group. No correlation with the *o*-H is due to the fact that there is no correlation of these shifts with the Hammett  $\rho$ . Because the chemical shifts of the *o*-C's of **1** do not correlate with  $\rho$  the correlation coefficients reflect merely a trend in the case of *o*-C's of **2-4** ( $r = 0.780-0.827$ ).

One of the striking features of such plots is that the slope of  $^{13}\text{C}=\text{O}$  is 1.00 ( $r = 0.998$ ) for **2**. This is a clear indication that the thiophene ring as a whole responds most similarly as benzene ring to the effect of the substituents.

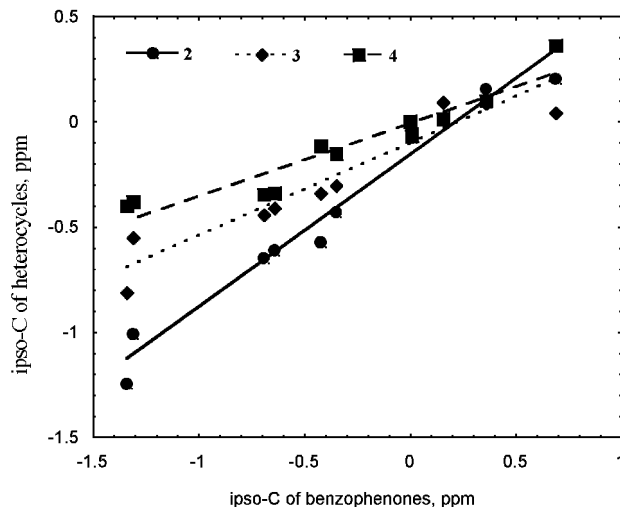


Figure 4. Correlations between  $\rho$  of **1** and  $\rho$  of **2-4**.

Pyrrole and furan rings are about 11% and 12% more sensitive than benzene ring. The *i*-C's are apparently less sensitive to the effect of the substituents. The values of the slopes 0.72, 0.44, and 0.35 may be a reflection of the aromaticity indices for thiophene, pyrrole, and furan, respectively, if the index of benzene is set to 1.00.

As listed in Table 3,  $\rho$ 's of the heterocycles appear downfield and the difference between  $\rho$  and  $\rho$  are 0.22, 0.59, and 1.06 ppm for thiophene, pyrrole, and furan, respectively. If an assumption is made that the difference of  $\rho$  and  $\rho$  of benzene is zero because it is fully aromatic and it corresponds to the index of aromaticity of 1.00, then the relative indices of aromaticity may be related to the difference between  $\rho$  and  $\rho$ . A set of indices may be proposed for thiophene 0.89 ( $= 1.00 - 0.22/2$ ), pyrrole 0.71 ( $= 1.00 - 0.59/2$ ), and furan 0.47 ( $= 1.00 - 1.06/2$ ). This seems quite reasonable not only because the difference in chemical shift of  $\rho$  and  $\rho$  is likely to originate from the presence of the heteroatom but

Table 6

Slopes and Correlation Coefficients of the Plots of  $^1\text{H}$  and  $^{13}\text{C}$  Chemical Shift Values of the 2-Benzoylthiophenes (**2**), 2-Benzoylpyrroles (**3**), and 2-Benzoylfurans (**4**) vs. Those of the Benzophenones (**1**) in Chloroform-*d*

	2		3		4	
		r		r		r
Ortho-H	0.46	0.517	0.49	0.457	1.22	0.410
Meta-H	1.04	0.995	1.06	0.993	1.47	0.981
Para-H	1.41	0.999	1.26	0.997	0.88	0.967
C=O	1.00	0.998	1.11	0.998	1.12	0.999
Ipsso-C	0.72	0.979	0.44	0.946	0.35	0.947
Ortho-C	3.84	0.827	3.91	0.780	3.92	0.806
Meta-C	1.16	0.991	1.65	0.996	1.44	0.994
Para-C	1.27	0.994	1.35	0.998	0.82	0.989
Ipsso-C'	0.99	0.999	0.99	0.999	0.96	0.999

Table 7  
Yields, Mp, Elemental Analysis, and  $\nu_{\text{C=O}}$  Data of Compounds **1-4**

Compd	Yield %	Mp °C	Calcd				Observed				$\nu_{\text{C=O}}$ $\text{cm}^{-1}$
			C, %	H, %	X, %	S, %	C, %	H, %	X, %	S, %	
<b>1a</b>	89	92-94	68.72	3.99	6.16[a]		68.55	4.03	6.41[a]		1655
<b>1b</b>	84	liquid	59.80	3.47	30.60[b]		60.05	3.55	30.45[b]		1661
<b>1c</b>		85-87	72.07	4.19	16.36[c]		72.33	4.48	16.12[c]		1653
<b>1d</b>	68	liquid	79.23	5.70			78.99	5.57			1659
<b>1e</b>		liquid	85.68	6.16			85.82	6.01			1656
<b>1f</b>	79	136-138	68.72	3.99	6.16[a]		68.66	4.05	6.33[a]		1652
<b>1g</b>		80-82	59.80	3.47	30.60[b]		59.96	3.43	30.57[b]		1649
<b>1h</b>		75-77	72.07	4.19	16.36[c]		72.15	4.33	16.31[c]		1651
<b>1i</b>		60-62	79.23	5.70			79.50	5.55			1650
<b>1j</b>		56-57	85.68	6.16			85.85	6.41			1649
<b>1k</b>		48-49	85.69	5.53			85.72	5.50			1652
<b>1l</b>	15	liquid	85.68	6.71			85.88	6.82			1649
<b>1m</b>	45	liquid	85.67	7.61			85.89	7.58			1649
<b>1n</b>	94	121-124	79.17	5.62	7.10[a]		78.99	5.68	7.35[a]		1588
<b>1o</b>	88	81-84	79.17	5.62	7.10[a]		79.02	6.75	7.39[a]		1648
<b>1p</b>	11	88-90	79.97	6.71	6.22[a]		79.78	6.52	6.45[a]		1599
<b>1q</b>		132-135	78.77	5.09		78.88	5.31			1562	
<b>1r</b>	95	69-70	74.99	5.03			75.08	5.22			1651
<b>2a</b>	51	107-110	56.65	3.03	6.01[a]	13.75	56.84	3.20	5.92[a]	13.80	1631
<b>2b</b>	53	60-62	49.46	2.64	29.91[b]	12.00	49.25	2.50	29.98[b]	11.78	1631
<b>2c</b>	11	56-58	59.33	3.17	15.92[c]	14.40	59.08	3.25	15.85[c]	14.58	1632
<b>2d</b>	39	liquid	66.03	4.62			14.69	66.32	4.66		1635
<b>2e</b>	35	liquid	71.26	4.98			15.85	71.33	5.01		1634
<b>2f</b>	8	173-175	56.65	3.03	6.01[a]	13.75	56.88	3.36	5.88[a]	13.48	1628
<b>2g</b>	77	97-100	49.46	2.64	29.91[b]	12.00	49.56	2.61	29.84[b]	11.81	1626
<b>2h</b>	87	95-97	59.33	3.17	15.92[c]	14.40	59.47	3.33	15.64[c]	14.25	1631
<b>2i</b>	64	69-72	66.03	4.62			14.69	66.21	4.38		1629
<b>2j</b>	66	69-71	71.26	4.98			15.85	71.44	5.12		1627
<b>2k</b>	77	48-50	70.19	4.28		17.03	70.35	4.40		16.86	1629
<b>3a</b>	28	82-83	61.11	3.73	12.96[a]		61.36	3.81	12.80[a]		1615
<b>3b</b>	29	76	52.83	3.22	5.60[a]	31.95[b]	52.65	3.44	5.85[a]	31.77[b]	1628
<b>3c</b>	57	86	64.25	3.92	6.81[a]	17.24[c]	64.40	4.03	6.59	17.01[c]	1610
<b>3d</b>	33	liquid	71.63	5.51	6.96[a]		71.55	5.56	6.74		1605
<b>3e</b>	44	66	77.81	5.99	7.56[a]		77.95	6.12	7.48		1612
<b>3f</b>	32	162	61.11	3.73	12.96[a]		61.25	3.82	12.77		1615
<b>3g</b>	43	123-124	52.83	3.22	5.60[a]	31.95[b]	52.74	3.32	5.40	31.80[b]	1624
<b>3h</b>	32	114	64.25	3.92	6.81[a]	17.24[c]	64.08	3.98	6.95	17.12[c]	1614
<b>3i</b>	40	109-110	71.63	5.51	6.96[a]		71.65	5.59	6.68[a]		1605
<b>3j</b>	25	115	77.81	5.99	7.56[a]		77.85	6.15	7.35[a]		1602
<b>3k</b>	36	71	77.17	5.30	8.18[a]		77.38	5.45	8.01[a]		1614
<b>4a</b>	6	107-110	60.83	3.25	6.45[a]		60.66	3.38	6.51[a]		1645
<b>4b</b>	13	52-54	52.62	2.81	31.83[b]		52.88	2.90	31.56[b]		1633
<b>4c</b>	15	liquid	63.94	3.41	17.16[c]		63.69	3.44	17.23[c]		1648
<b>4d</b>	10	liquid	71.28	4.98			71.54	5.25			1646
<b>4e</b>	35	liquid	77.40	5.41			77.45	5.56			1645
<b>4f</b>	2	165-171	60.83	3.25	6.45[a]		60.98	3.44	6.52[a]		1639
<b>4g</b>	10	63-65	52.62	2.81	31.83[b]		52.61	2.91	31.59[b]		1654
<b>4h</b>	18	59-61	63.94	3.41	17.16[c]		64.08	3.55	17.03[c]		1651
<b>4i</b>	10	59-60	71.28	4.98			71.35	5.00			1632
<b>4j</b>	36	liquid	77.40	5.41			77.59	5.54			1644
<b>4k</b>	22	liquid	76.73	4.68			76.80	5.01			1647

[a] Nitrogen; [b] Bromine; [c] Chlorine.

because the values are in the range of reported sets of aromaticity indices [1].

The *o*-H signals shift to downfield by the electronic effect of the carbonyl group. The magnitudes of the averaged shifts are 0.43, 0.52, 0.63, and 0.87 ppm for

**1**, **2**, **3**, and **4**, respectively. The difference may be related to the aromaticity and the set of values 1.00, 0.83, 0.68, and 0.49 can be calculated by dividing the difference of **1** with the differences of **2**, **3**, and **4**, respectively.



Unlike  $^1\text{H}$ , the  $^{13}\text{C}$  chemical shifts are difficult to correlate with an index of aromaticity. Introduction of the benzoyl group causes downfield shift of the *i*-C signal. Such a shift is the most significant with the thiophene series showing an average shift of 18.08 ppm. On the other hand, benzene shows the least effect by the presence of the benzoyl group and 8.92 ppm is observed. The inductive effect of oxygen atom in furan causes the most deshielding of  $^1\text{C}$  and the difference between  $^1\text{C}$  and  $^2\text{C}$  is 33.08 ppm for furan itself. But introduction of a benzoyl group at  $^3\text{C}$ -position causes a similar magnitude of deshielding of both the  $^1\text{C}$  and  $^2\text{C}$  and the difference between *i*- and *o*-Cs is 31.48 ppm for **4**.

The difference between the shifts of *i*- and *o*-Cs of **1-4** may be used as a base for calculation of the aromaticity index. If we divide  $\delta$  of **1** by those of **2**, **3**, and **4**, 0.87, 0.65, and 0.23 are obtained, respectively, which may be considered as a set of aromaticity indices. The exceptionally low value of 0.23 for **4** may be due to the profound electronic effect of the oxygen atom in the furan ring.

In conclusion, a set of aromaticity indices is proposed based on the correlation of the chemical shifts of a series of substituted benzophenones to an identical series of substituted benzoyl derivatives of thiophene, pyrrole, and furan. The indices thus obtained are 0.72, 0.44, and 0.35, respectively.

## EXPERIMENTAL

Melting points were determined on a Fischer MEL-TEMP apparatus and are uncorrected. 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 concentration of the solution was 0.10 M in chloroform-*d*. Infrared spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Elemental analyses were performed by the Central Lab of Kangwon National University.

*Meta*- and *p*-substituted benzoic acids are all commercially available from which the corresponding benzoyl chlorides were prepared by a standard procedure using thionyl chloride. Benzoyl chloride, 2-furoyl chloride, and 2-thiophenecarbonyl chloride are also commercially available. Compounds **1c**, **1e**, **1g**, **1h**, **1i**, **1j**, and **1k** are also commercial products.

Preparation of the Ketones.

An Illustrative Procedure.

Benzoyl chloride (7 mmoles) was added dropwise over 10 minutes to a mixture of benzene (15 ml) and aluminum chloride (1.44 g, 10 mmoles) with rapid stirring. The mixture was heated at reflux for 36 hours. After neutralization with saturated sodium bicarbonate solution the aqueous mixture was extracted with dichloromethane (6 x 25 ml). The organic layer was washed with water (25 ml) and then dried with magnesium sulfate overnight. After suction filtration the solution was concentrated to give a

pale yellow liquid which was purified by chromatography on a column of silica gel eluting with hexane-ethyl acetate. Solid recrystallization was repeated until analytical purity was achieved. Yield, mp, elemental analysis data, and carbonyl stretching frequencies are listed in Table 7.

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## REFERENCES AND NOTES

- [1a] M. J. Cook and A. R. Katritzky, *Adv. Heterocyclic Chem.*, **17**, 255 (1974); [b] B. Y. Simkin, V. I. Minkin and M. N. Glukhovtsev, *Adv. Heterocyclic Chem.*, **56**, 303 (1993); [c] A. R. Katritzky, M. Karelson and N. Malhotra, *Heterocycles*, **32**, 127 (1991); [d] F. R. Cordell and J. E. Boggs, *J. Mol. Struct.*, **85**, 163 (1981); [e] C. W. Bird, *Tetrahedron*, **41**, 1409 (1985).
- [2] Elvidge, J. A. *Chem. Commun.*, 160 (1965).
- [3] A. Julg and P. Francois, *Theor. Chim. Acta*, **8**, 249 (1967).
- [4a] C. K. Lee, J. S. Yu and H.-J. Lee, *J. Heterocyclic Chem.*, **39**, 1207 (2002); [b] C. K. Lee, J. S. Yu and J. S. Park, *Bull. Korean Chem. Soc.*, **21**, 49 (2000).
- [5] C. K. Lee, J. S. Yu and Y. R. Ji, *J. Heterocyclic Chem.*, **39**, 1219 (2002).
- [6] F. Fringuelli, G. Marino, A. Taticchi and G. Grandolini, *J. Chem. Soc. Perkin Trans. II*, 332 (1974).
- [7] J. Bromilow, R. T. C. Brownlee, D. J. Craik, P. R. Fiske, J. E. Rowe and M. Sadek, *J. Chem. Soc. Perkin Trans. II*, 753 (1981).
- [8] H. Neuvonen, K. Neuvonen, A. Koch, E. Kleinpeter and P. Pasanen, *J. Org. Chem.*, **67**, 6995 (2002).
- [9] N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964, p 241.
- [10] M. Fiorenza, A. Ricci, G. Sbrena, G. Pirazzini, C. Eaborn and J. G. Stamper, *J. Chem. Soc. Perkin Trans. II*, 1232 (1978).
- [11] Reference 9, p 243.
- [12a] D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.*, **14**, 1 (1983); [b] S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973); [c] C. K. Lee, J. H. Jun and J. S. Yu, *J. Heterocyclic Chem.*, **37**, 15 (2000); [d] K. O. Jeon, J. S. Yu and C. K. Lee, *Bull. Korean Chem. Soc.*, **23**, 1241 (2002).
- [13] F. Ruff and I. G. Csizmadia, *Organic Reactions: Equilibria, Kinetics and Mechanism*, Elsevier, Amsterdam, 1994, p 164.
- [14] C. D. Slater, C. N. Robinson, R. Bies, D. W. Bryan, K. Chang, A. W. Hill, W. H. Moore Jr., T. G. Oray, M. L. Poppelreiter, J. R. Reisser, G. G. Stablein, V. P.; Wilkinson, W. D. Waddy III and W. A. Wray, *J. Org. Chem.*, **50**, 4125 (1985).
- [15a] H. Suezawa, T. Yuzuri, M. Hirota, Y. Ito and Y. Hamada, *Bull. Chem. Soc. Jpn.*, **63**, 328 (1990); [b] T. Yuzuri, H. Suezawa and M. Hirota, *Bull. Chem. Soc. Jpn.*, **67**, 1664 (1994).
- [16] C. N. Robinson, G. E. Stablein and C. D. Slater, *Tetrahedron*, **46**, 335 (1990).
- [17] E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3<sup>rd</sup> Ed., VCH: Weinheim, Germany, 1987; p 117.
- [18] O. Exner, in *The Chemistry of Double-bonded Functional Groups*, Supplement A, Part 1; Patai, S. Ed., Wiley, New York, 1977, p 81.
- [19] R. T. C. Brownlee and D. J. Craik, *J. Chem. Soc. Perkin Trans. II*, 760 (1981).