Determination of Aromaticity Indices of Thiophene and Furan by Nuclear Magnetic Resonance Spectroscopic Analysis of Their Phenyl Esters

Chang Kiu Lee*, Ji Sook Yu and Hye-Jin Lee
Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea
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A series of *m*- and *p*-substituted phenyl benzoates, 2-thienoates, and 2-furoates were prepared and their ^1H and ^{13}C nmr spectroscopic characteristics were examined. In general, good correlations were observed between the chemical shift values of protons and carbons of the acyl aromatic rings and the Hammett σ. Plots of the chemical shift values of the carbonyl carbons of the benzoates against those of the 2-thienoates and 2-furoates gave an excellent correlation and the values of the slopes are 0.85 and 0.75, respectively, in dimethyl sulfoxide-d_6 and 0.90 and 0.78, respectively, in chloroform-*d*. The values could be considered as a set of aromaticity indices.

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One of the theoretical aspects of 5-membered mono-heterocyclic aromatic compounds, namely thiophene, furan, and pyrrole, is the relative aromaticities compared to benzene. Aromaticity indices have been calculated using several methods [1-2]. Comparing the ring current the indices of aromaticity of benzene, thiophene, pyrrole, and furan are reported to be 1.00, 0.75, 0.59, and 0.46, respectively [3]. Consideration of bond length gives a different set of indices: benzene 1.00; thiophene 0.93; pyrrole 0.91; and furan 0.87 [4]. Our continued interest in the substituent effects on the chemical shifts of ^1H and ^{13}C of 5-membered heterocycles led us to investigate the possibility of using the chemical shift values for determination of the index of aromaticity [5].

Correlations of ^1H and ^{13}C chemical shifts with Hammett σ (or related parameters) in substituted benzene derivatives have been widely reported. For example, dual substituent parameter (DSP) analysis of the chemical shift value of the carbonyl carbon in compounds of the type of $XC_6H_4C(=O)Z$ (Z = NH_2, F, OEt, OH, Me, H) and $XC_6H_4OC(=O)CH_3$ show good correlation [6]. A theoretical aspect of the effect of substituent on the chemical shifts of the carbonyl system has also been investigated [7]. However, there is no systematic investigation reported on the quantitative estimation of the aromaticity of the 5-membered heteroaromatic compounds by examining the correlation of the chemical shift values and substituent constants.

We now report our approach to the indices of aromaticity by comparing the chemical shift values of a series of *m*- and *p*-substituted phenyl esters of benzoic acid, 2-thienoic acid, and 2-furoic acid.

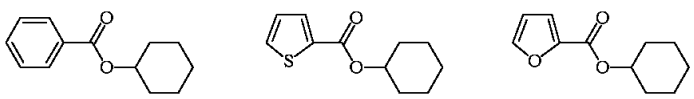
Results and Discussion.

The *m*- and *p*-substituted phenyl benzoates (**1**), 2-thienoates (**2**), and 2-furoates (**3**) were prepared by the reactions of the corresponding acyl chlorides with *m*- and *p*-substituted phenols and triethylamine in dichloromethane. Cyclohexyl esters **5-7** were prepared similarly with cyclohexanol. Substituted phenyl acetates **4** were prepared by treating basic solution of phenols with acetic anhydride in the presence of triethylamine and acetic acid in dichloromethane.

The products were purified by recrystallization or chromatography to achieve analytical purity, which is essential to the preparation of a 0.1 *M* solution. Both chloroform-*d* and dimethyl sulfoxide-d_6 were used for the nmr measurement so that solvent effects might be

1 **2** **3** **4**

Z: **a**, *m*-NO_2; **b**, *m*-Br; **c**, *m*-Cl; **d**, *m*-OCH_3; **e**, *m*-CH_3
f, *p*-NO_2; **g**, *p*-Br; **h**, *p*-Cl; **i**, *p*-OCH_3; **j**, *p*-CH_3, **k**, H



5 **6** **7**

Table 1

^{1}H Chemical Shift Values of Substituted Phenyl Esters **1-3** in Dimethyl Sulfoxide-d_6 and in Chloroform-*d* (0.1 *M*)

		o-H	*m*-H	*p*-H	2'-H	3'-H	4'-H	5'-H	6'-H
1a	[a]	8.17	7.64	7.79	8.27		8.20	7.84	7.78
	[b]	8.21	7.55	7.69	7.61		8.17	7.62	8.14
1b	[a]	8.14	7.62	7.77	7.63		7.54	7.45	7.35
	[b]	8.19	7.52	7.65	7.43		7.42	7.30	7.18
1c	[a]	8.14	7.62	7.77	7.50		7.41	7.52	7.32
	[b]	8.19	7.52	7.65	7.27		7.26	7.36	7.14
1d	[a]	8.13	7.62	7.76	6.91		6.86	7.37	6.90
	[b]	8.20	7.51	7.64	6.78		6.82	7.32	6.83
1e	[a]	8.13	7.61	7.75	7.11		7.13	7.35	7.08
	[b]	8.20	7.51	7.63	7.03		7.08	7.31	7.02
1f	[a]	8.17	7.64	7.79	7.64	8.37			
	[b]	8.21	7.55	7.69	7.43	8.33			
1g	[a]	8.14	7.62	7.76	7.30	7.67			
	[b]	8.19	7.51	7.65	7.12	7.54			
1h	[a]	8.14	7.62	7.76	7.36	7.54			
	[b]	8.19	7.52	7.65	7.17	7.39			
1i	[a]	8.13	7.61	7.75	7.21	7.01			
	[b]	8.20	7.50	7.63	7.13	6.94			
1j	[a]	8.13	7.61	7.75	7.16	7.26			
	[b]	8.20	7.50	7.63	7.09	7.22			
1k	[a]	8.14	7.62	7.76	7.30	7.49	7.33		
	[b]	8.21	7.51	7.64	7.22	7.43	7.27		
2a	[a]	8.08	7.34	8.15	8.24		8.20	7.78	7.83
	[b]	8.02	7.22	7.73	8.15		8.16	7.61	7.60
2b	[a]	8.04	7.32	8.12	7.62		7.54	7.44	7.34
	[b]	7.98	7.18	7.68	7.42		7.41	7.29	7.18
2c	[a]	8.04	7.32	8.12	7.50		7.41	7.51	7.30
	[b]	7.98	7.18	7.68	7.27		7.26	7.35	7.14
2d	[a]	8.02	7.31	8.09	6.90		6.89	7.36	6.85
	[b]	7.98	7.18	7.66	6.78		6.82	7.31	6.82
2e	[a]	8.01	7.31	8.09	7.07		7.13	7.34	7.07
	[b]	7.97	7.17	7.65	7.04		7.02	7.30	7.08
2f	[a]	8.09	7.34	8.16	7.63	8.35			
	[b]	8.02	7.22	7.74	7.43	8.32			
2g	[a]	8.04	7.32	8.11	7.29	7.66			
	[b]	7.98	7.18	7.68	7.12	7.53			
2h	[a]	8.04	7.32	8.11	7.35	7.53			
	[b]	7.98	7.18	7.68	7.17	7.38			
2i	[a]	8.01	7.31	8.08	7.20	7.00			
	[b]	7.97	7.17	7.65	7.13	6.93			
2j	[a]	8.01	7.31	8.08	7.15	7.26			
	[b]	7.97	7.17	7.65	7.09	7.21			
2k	[a]	8.03	7.32	8.10	7.28	7.48	7.32		
	[b]	7.98	7.18	7.66	7.22	7.42	7.27		
3a	[a]	7.64	6.84	8.15	8.24		8.20	7.78	7.82
	[b]	7.45	6.64	7.72	8.13		8.16	7.62	7.61
3b	[a]	7.59	6.81	8.12	7.61		7.54	7.44	7.33
	[b]	7.40	6.60	7.69	7.41		7.42	7.29	7.18
3c	[a]	7.59	6.82	8.12	7.49		7.41	7.51	7.29
	[b]	7.39	6.61	7.69	7.26		7.26	7.35	7.13
3d	[a]	7.56	6.80	8.10	6.89		6.84	7.36	6.89
	[b]	7.38	6.59	7.67	6.77		6.79	7.31	6.82
3e	[a]	7.56	6.80	8.10	7.08		7.13	7.34	7.06
	[b]	7.37	6.58	7.67	7.02		7.08	7.29	7.01
3f	[a]	7.66	6.84	8.16	7.62	8.35			
	[b]	7.43	6.64	7.72	7.44	8.32			
3g	[a]	7.59	6.81	8.12	7.28	7.66			
	[b]	7.39	6.60	7.68	7.11	7.53			
3h	[a]	7.59	6.81	8.12	7.34	7.53			
	[b]	7.38	6.60	7.68	7.16	7.38			
3i	[a]	7.55	6.79	8.09	7.19	7.00			
	[b]	7.37	6.59	7.66	7.13	6.93			
3j	[a]	7.56	6.80	8.09	7.14	7.26			
	[b]	7.37	6.58	7.66	7.09	7.21			
3k	[a]	7.58	6.81	8.11	7.27	7.47	7.30		
	[b]	7.38	6.60	7.67	7.21	7.42	7.27		

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*; [a] CH_3: **1d**, 3.78; **1e**, 2.35; **1i**, 3.77; **1j**, 2.34; **2d**, 3.79; **2e**, 2.34; **2i**, 3.78; **2j**, 2.33; **3d**, 3.77; **3e**, 2.38; **3i**, 3.77; **3j**, 2.33; [b] CH_3: **1d**, 3.82; **1e**, 2.39; **1i**, 3.82; **1j**, 2.36; **2d**, 3.81; **2e**, 2.38; **2i**, 3.82; **2j**, 2.37; **3d**, 3.81; **3e**, 2.38; **3i**, 3.81; **3j**, 2.36.

Table 2

^{13}C Chemical Shift Values of Substituted Phenyl Esters **1-3** in in Dimethyl Sulfoxide-d_6 and in Chloroform-*d* (0.1 *M*)

	C=O	*i*-C	*o*-C	*m*-C	*p*-C	1'-C	2'-C	3'-C	4'-C	5'-C	6'-C	
1a	[a]	164.74	128.92	130.48	129.49	134.82	151.41	118.03	148.85	121.53	131.35	129.59
	[b]	164.54	128.52	130.29	128.67	134.18	151.23	117.56	148.84	120.84	130.08	128.25
1b	[a]	164.82	129.09	130.36	129.47	134.69	151.83	125.72	122.01	129.54	131.77	121.84
	[b]	164.76	129.05	130.20	128.64	133.84	151.43	125.26	122.43	129.08	130.51	120.62
1c	[a]	164.81	129.10	130.37	129.49	134.70	151.81	122.96	133.90	126.67	131.46	121.48
	[b]	164.76	129.07	130.20	128.63	133.83	151.40	122.43	134.75	126.18	130.30	120.13
1d	[a]	164.95	129.21	130.26	129.45	134.52	152.13	108.37	160.69	112.35	130.47	114.47
	[b]	165.08	129.52	130.15	128.55	133.57	151.90	107.64	160.53	111.84	129.85	113.89
1e	[a]	165.09	129.46	130.21	129.46	134.49	151.06	122.80	139.80	127.12	129.75	119.36
	[b]	165.29	129.63	130.13	128.53	133.51	150.88	122.28	139.67	126.68	129.19	118.62
1f	[a]	164.43	128.79	130.50	129.55	134.93	156.01	123.88	125.80	145.68		
	[b]	164.22	128.50	130.31	128.78	134.24	155.70	122.62	125.26	145.38		
1g	[a]	164.84	129.14	130.33	129.47	134.66	150.37	124.82	132.91	118.82		
	[b]	164.85	129.14	130.18	128.62	133.79	149.95	123.53	132.51	118.97		
1h	[a]	164.91	129.16	130.34	129.48	134.66	149.89	124.41	129.97	130.66		
	[b]	164.93	129.16	130.18	128.62	133.78	149.40	123.09	129.53	131.26		
1i	[a]	165.36	129.53	130.21	129.43	134.42	144.46	123.19	114.92	157.49		
	[b]	165.53	129.62	130.11	128.52	133.58	144.39	122.42	114.50	157.29		
1j	[a]	165.19	129.51	130.22	129.45	134.46	148.89	122.07	130.39	135.65		
	[b]	165.34	129.67	130.13	128.51	133.47	148.69	121.35	129.98	135.49		
1k	[a]	165.08	129.43	130.26	129.47	134.53	151.12	122.42	130.07	126.51		
	[b]	165.18	129.57	130.16	128.55	133.57	150.94	121.70	129.48	125.87		
2a	[a]	160.15	131.69	136.21	129.52	136.36	150.93	117.98	148.84	121.65	131.39	129.29
	[b]	159.85	131.63	135.43	128.28	134.40	150.80	117.48	148.79	120.91	130.07	128.16
2b	[a]	160.26	131.92	135.94	129.25	136.10	151.37	125.68	122.03	129.68	131.80	121.80
	[b]	160.12	132.27	134.99	128.12	133.88	151.01	125.18	122.40	129.17	130.49	120.55
2c	[a]	160.25	131.93	135.95	129.25	136.10	151.34	122.92	133.91	126.81	131.49	121.43
	[b]	160.14	132.30	134.99	128.12	133.88	150.98	122.35	134.73	126.27	130.18	120.06
2d	[a]	160.46	132.36	135.65	129.20	135.77	151.68	108.31	160.69	112.53	130.51	114.42
	[b]	160.50	132.86	134.75	128.01	133.49	151.48	107.55	160.50	111.99	129.83	113.82
2e	[a]	160.60	132.41	135.57	129.21	135.72	150.64	122.75	139.88	127.27	129.79	119.32
	[b]	160.68	133.00	134.58	127.97	133.48	150.49	122.21	139.66	126.77	129.17	118.56
2f	[a]	159.82	131.57	136.35	129.37	136.57	155.50	123.82	125.83	145.73		
	[b]	159.52	131.66	135.50	128.32	134.52	155.26	122.51	125.26	145.41		
2g	[a]	160.31	132.01	135.90	129.26	136.05	149.94	124.79	132.96	118.99		
	[b]	160.22	132.38	134.93	128.10	133.80	149.56	123.45	132.49	119.07		
2h	[a]	160.38	132.01	135.88	129.25	136.02	149.45	124.38	130.00	130.81		
	[b]	160.30	132.41	134.90	128.09	133.78	148.99	123.02	129.50	131.35		
2i	[a]	160.90	132.47	135.48	129.17	135.59	144.05	123.19	114.98	157.57		
	[b]	160.96	132.96	134.54	127.91	133.33	144.04	122.40	114.47	157.35		
2j	[a]	160.71	132.44	135.83	129.19	135.66	148.48	122.04	130.47	135.54		
	[b]	160.79	133.02	134.55	127.96	133.32	148.32	121.29	129.96	135.62		
2k	[a]	160.58	132.35	135.66	129.23	135.79	150.70	122.38	130.11	126.65		
	[b]	160.58	132.90	134.66	128.00	133.46	150.56	121.64	129.46	125.97		
3a	[a]	156.38	143.04	121.70	113.43	149.53	150.65	117.99	148.88	121.39	131.46	129.62
	[b]	156.07	143.07	120.47	112.45	147.81	150.46	117.42	148.82	120.99	130.13	128.08
3b	[a]	156.54	143.18	121.08	113.36	149.45	151.07	125.69	122.07	129.74	131.87	121.81
	[b]	156.40	143.53	119.86	112.27	147.41	150.64	125.11	122.43	129.26	130.54	120.48
3c	[a]	156.51	143.19	121.08	113.36	149.35	151.04	121.43	133.95	126.86	131.55	122.91
	[b]	156.41	143.55	119.86	112.28	147.41	150.62	120.00	134.78	126.36	130.22	122.29
3d	[a]	156.78	143.51	120.69	113.28	149.13	151.37	108.35	160.73	112.52	130.57	114.42
	[b]	156.81	143.97	119.43	112.16	147.12	151.09	107.54	160.52	112.01	129.88	133.76
3e	[a]	156.91	143.55	120.61	113.25	149.11	150.33	122.75	139.92	127.31	129.84	119.32
	[b]	157.02	144.08	119.29	112.12	147.04	150.10	122.15	139.71	126.86	129.20	118.51
3f	[a]	156.03	142.93	121.58	113.49	149.68	155.24	123.81	125.89	145.78		
	[b]	155.72	143.04	120.56	112.48	147.87	154.90	122.45	125.28	145.46		
3g	[a]	156.59	143.27	121.01	113.35	149.32	149.64	124.79	133.02	119.04		
	[b]	156.50	143.63	119.78	112.26	147.34	149.19	123.39	132.55	119.17		
3h	[a]	156.65	143.27	120.98	113.34	149.30	149.14	124.38	130.06	130.86		
	[b]	156.60	143.64	119.76	112.26	147.33	148.63	122.96	129.56	131.46		
3i	[a]	157.24	143.70	120.48	113.22	149.01	143.70	123.19	115.04	157.61		
	[b]	157.30	144.08	119.25	112.12	147.01	143.61	122.35	114.51	157.42		
3j	[a]	157.04	143.59	120.56	113.24	149.06	148.15	122.04	130.48	135.88		
	[b]	157.14	144.10	119.25	112.11	147.00	147.92	121.24	130.00	135.72		
3k	[a]	156.90	143.51	120.70	113.28	149.15	150.38	122.37	130.16	126.69		
	[b]	156.92	144.01	119.40	112.15	147.11	150.17	121.58	129.50	126.05		

[a] Dimethyl sulfoxide-d_6;[b] Chloroform-*d*;[a] CH_3: **1d**, 55.90; **1e**, 21.28; **1i**, 55.92; **1j**, 20.91; **2d**, 55.92; **2e**, 21.25; **2i**, 55.92; **2j**, 20.90; **3d**, 56.28; **3e**, 21.29; **3i**, 55.95; **3j**, 20.92;[b] CH_3: **1d**, 55.42; **1e**, 21.32; **1i**, 55.59; **1j**, 20.91; **2d**, 55.43; **2e**, 21.31; **2i**, 55.59; **2j**, 20.88; **3d**, 55.42; **3e**, 21.31; **3i**, 55.58; **3j**, 20.87.

examined. The ^1H and ^{13}C nmr chemical shift values of the esters **1**-**3** are listed in Tables 1 and 2, respectively. Assignment of each peak was made by analysis of ^1H-^1H COSY and ^1H-^{13}C HETCOR spectra. In addition, correlations of the values of 2-thienoyl and 2-furoyl compounds against those of benzoyl compounds (*cf.* Table 6) make the assignment unambiguous. Such plots for protons and carbons in the substituted phenyl group (not listed) show slopes of near unity with correlation coefficient of 0.999-1.000. This could also be used to make accurate assignments. The 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.

The substituent effect on the chemical shift can be analyzed by either single substituent parameter (SSP) approach or dual substituent parameter (DSP) approach as shown in Equations 1 and 2, respectively [8].

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

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

Although DSP analysis shows good correlation, the results are not listed in this report because the major objective of the present report is to determine the indices of aromaticity.

The slopes of the plots of the chemical shift values of the protons in the acyl ring against Hammett σ [9] according to Equation 1 are listed in Table 3. Other σ values such as σ^+ or $^{13}\sigma$ [9] do not show a reasonable correlation.

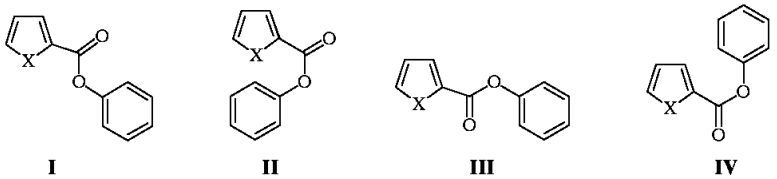
In general, the correlations are better in dimethyl sulfoxide-d_6 than in chloroform-*d*. The magnitudes of the slopes of *meta*-H's are smaller than those of others. However, *ortho*-H's of the benzoates **1** show no correlation with σ in chloroform-*d* and merely a trend in dimethyl sulfoxide-d_6. *Para*-H's of **1** show a fair correlation with large slope in chloroform-*d*. It should be pointed out that the slopes of *ortho*- and *para*-H's are pretty close in the benzene and thiophene series, showing the ρ_{ortho}/ρ_{para} of 0.98 and 1.09 for **1** and **2**, respectively, in dimethyl sulfoxide-d_6. In contrast, the ratio for the furan series (**3**) is 1.63 in the same solvent, indicating that the chemical shifts of the *ortho*-H are more sensitive to the electronic effect of the substituent

Table 3

Best Fit of the Single Substituent Parameter Equation for the ^1H Chemical Shifts of **1**-**4** in Dimethyl Sulfoxide-d_6 and in Chloroform-*d* in Hz

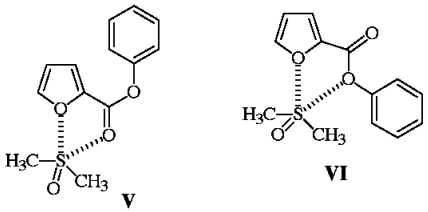
		1		**2**		**3**		**4**	
		ρ	r	ρ	r	ρ	r	ρ	r
Ortho-H	[a]	16.31	0.854	30.96	0.952	39.31	0.960	34.3 [c]	0.942
	[b]	0.85 [d]	0.075	19.90	0.866	30.56	0.910	27.2 [c]	0.869
Meta-H	[a]	12.38	0.950	14.72	0.957	18.38	0.970		
	[b]	16.94	0.932	19.63	0.941	22.13	0.939		
Para-H	[a]	16.67	0.969	28.31	0.983	24.16	0.976		
	[b]	24.03	0.958	34.82	0.963	23.71	0.958		
ρ_o/ρ_p	[a]	0.98		1.09		1.63			
	[b]	0.04 [d]		0.57		1.23			

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*; [c] CH_3; [d] The value is meaningless because there is no correlation.



I **II** **III** **IV**

X = S, O



V **VI**

than those of the *para*-H. The slope of the *ortho*-H of **3** in dimethyl sulfoxide-d_6 is the largest among all protons in the present investigation.

It is conceivable that conformations **I-IV** are possible for **2** and **3**. It seems apparent that the *ortho*-H of **3** lies close to the phenyl ring with a conformation like **IV** in which the hetero atom in the ring and the oxygen atom of the carbonyl group are *syn* so that the through-space interaction of the phenyl ring and *ortho*-H is most effective. The preference of *syn* conformation in polar solvent has been reported with 2-benzoylthiophene and 2-benzoylfuran [10]. Alkyl 2-furyl ketones and alkyl 2-thienyl ketones also prefer *syn* conformation in diethyl ether [11]. The *syn* arrangement should be favorable in dimethyl sulfoxide-d_6 because coordination of the lone pair electrons of both oxygen atoms and the sulfur atom is possible like **V**. Such an association would make free rotation along the C2-CO bond to form other conformation less favorable. This seems to be the case because the ratio of ρ_{ortho}/ρ_{para} for **3** becomes much smaller (1.23) in chloroform-*d*.

One of the striking observations in Table 4 and Figure 1 is the inverse substituent effect of carbonyl and *ipso* carbons and the normal substituent effect of *ortho*, *meta*, and *para* carbons. Brownlee, *et al*. reported reverse ^{13}C substituent chemical shift effect in the side-chain carbon of aromatic systems including the inverse correlation of the

Table 4

Best Fit of the Single Substituent Parameter Equation for the ^{13}C Chemical Shifts of **1-4** in Dimethyl Sulfoxide-d_6 and in Chloroform-*d* in Hz

		1		**2**		**3**		**4**	
		ρ	r	ρ	r	ρ	r	ρ	r
C=O	[a]	-70.6	0.953	-84.6	0.967	-97.0	0.973	-59.8	0.916
	[b]	-111.5	0.986	-124.1	0.989	-143.6	0.988	-134.9	0.992
Ipso-C	[a]	-71.1	0.983	-91.4	0.972	-71.3	0.978	-4.8 [c]	0.413
	[b]	-122.7	0.972	-146.2	0.969	-112.5	0.975	7.5 [c]	0.481
Ortho-C	[a]	30.1	0.984	94.9	0.971	117.0	0.977		
	[b]	18.4	0.974	96.7	0.985	133.4	0.978		
Meta-C	[a]	8.0	0.878	25.7	0.848	24.8	0.982		
	[b]	22.8	0.952	37.6	0.987	36.8	0.970		
Para-C	[a]	45.9	0.982	66.1	0.917	61.8	0.978		
	[b]	73.5	0.955	117.1	0.978	87.7	0.979		
ρ_o/ρ_p	[a]	0.66		1.44		1.89			
	[b]	0.25		0.83		1.52			

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*; [c] CH_3.

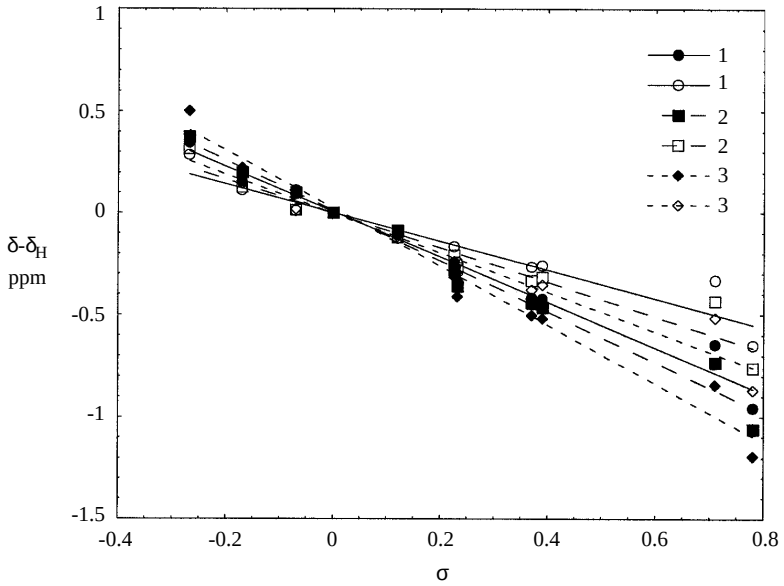


Figure 1. Correlation between σ and ^{13}C chemical shifts of carbonyl carbon in **1-3** in chloroform-*d* (closed) and in dimethyl sulfoxide-d_6 (open).

Table 5

^{1}H and ^{13}C Chemical Shift Values of Substituted Phenyl Acetates(**4**)in Dimethyl Sulfoxide-d_6 and in Chloroform-*d* (0.1 *M*)

	CH_3	2-H	3-H	4-H	5-H	6-H	C=O	CH_3	1-C	2-C	3-C	4-C	5-C	6-C
4a [a]	2.32	8.08		8.14	7.73	7.65	169.45	21.31	151.27	117.89	148.75	121.28	131.29	129.43
[b]	2.35	8.00		8.12	7.57	7.46	168.71	20.97	150.89	117.37	148.76	120.76	130.01	128.06
4b [a]	2.27	7.44		7.48	7.39	7.17	169.45	21.27	151.72	125.60	121.88	129.26	131.69	121.69
[b]	2.29	7.04		7.37	7.24	7.04	168.98	21.01	151.13	125.10	122.35	129.01	130.44	120.45
4c [a]	2.27	7.31		7.34	7.45	7.13	169.43	21.28	151.68	121.33	133.74	126.39	131.38	122.81
[b]	2.30	7.13		7.22	7.30	7.00	169.00	21.03	151.11	119.97	134.66	126.11	130.13	122.26
4d [a]	2.28	6.70		6.83	7.31	6.72	169.54	21.34	152.00	108.31	160.58	114.41	130.38	111.99
[b]	2.29	6.64		6.78	7.27	6.68	169.38	21.12	151.60	107.60	160.45	113.76	129.80	111.64
4e [a]	2.25	6.94		7.06	7.28	6.90	169.63	21.24	150.94	122.71	139.62	126.85	129.63	119.25
[b]	2.29	6.89		7.04	7.25	6.88	169.61	21.12	150.60	122.14	139.60	126.63	129.12	118.48
4f [a]	2.33	7.45	8.31				169.10	21.37	155.87	123.70	125.74	145.47		
[b]	2.35	7.29	8.27				168.36	21.09	155.34	122.42	125.19	145.30		
4g [a]	2.27	7.12	7.60				169.47	21.29	150.22	124.69	132.80	118.52		
[b]	2.29	6.98	7.49				169.19	21.05	149.65	123.36	132.45	118.89		
4h [a]	2.27	7.18	7.47				169.54	21.28	149.75	124.27	129.86	130.37		
[b]	2.29	7.03	7.34				169.20	21.04	149.10	122.92	129.46	131.19		
4i [a]	2.23	6.94	7.04				169.97	21.26	144.38	123.07	114.86	157.28		
[b]	2.28	6.89	7.00				169.90	21.04	144.15	122.28	114.43	157.22		
4j [a]	2.24	6.99	7.20				169.76	21.31	148.77	121.96	130.26	135.34		
[b]	2.28	6.96	7.17				169.74	20.84	148.40	121.21	129.92	135.46		
4k [a]	2.27	7.12	7.25	7.42			169.67	21.34	150.99	122.30	129.94	126.23		
[b]	2.30	7.08	7.23	7.38			169.50	21.13	150.65	121.55	129.41	125.81		

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*; [a] CH_3: **4d**, 3.75, 55.83; **4e**, 2.31, 21.32; **4i**, 3.75, 55.87; **4j**, 2.29, 20.85; [b] CH_3: **4d**, 3.79, 55.38; **4e**, 2.36, 21.28; **4i**, 3.79, 55.55; **4j**, 2.34, 21.10.

carbonyl carbon of substituted aryl acetates [6]. For a series of benzoyl derivatives, X-C_6H_4-C(=O)Y (Y = NH_2, F, OEt, OH, Me, H) the electron-withdrawing substituents X cause an upfield shift of the carbonyl carbon. π-Polarization is attributed to the observation [6]. The magnitude of such an effect is weakening in cases of substituted phenylacetic acids and substituted phenyl acetates because the methylene and oxygen atom separate the carbonyl carbon thus pushing the substituents farther apart.

For the purpose of comparison we prepared a similar series of substituted phenyl acetates (**4**) and the nmr data are listed in Table 5. The plot of the chemical shift of the carbonyl carbon of 0.1 *M* solution against Hammett σ shows an inverse correlation as reported [6]. The ρ values of such plots are -59.8 Hz with r = 0.916 in dimethyl sulfoxide-d_6 and -134.9 Hz with r = 0.992 in chloroform-*d*. However, the methyl carbon's chemical shifts values show no correlation with σ, giving values of 4.8 Hz (r = 0.413) in dimethyl sulfoxide-d_6 and 7.5 Hz (r = 0.481) in chloro-

Table 6

Slopes and Correlation Coefficients of the Plots of ^{13}C Chemical Shift Values of the Aryl Benzoates (**1**) vs. Those of the Aryl 2-Thienoates (**2**) and Aryl 2-Furoates (**3**) in Dimethyl Sulfoxide-d_6 and in Chloroform-*d*

		Thiophene		Furan			Thiophene		Furan	
		slope	r	slope	r		slope	r	slope	r
C=O	[a]	0.85	0.998	0.75	0.996					
	[b]	0.90	0.999	0.78	0.999					
i-C	[a]	0.80	0.965	1.03	0.966					
	[b]	0.84	0.999	1.03	0.999					
o-C	[a]	0.32	0.987	0.26	0.990	*o*-H	0.61	0.962	0.50	0.943
	[b]	0.19	0.992	0.14	0.990		0.93 [c]	0.528	0.80 [c]	0.422
m-C	[a]	0.46	0.958	0.39	0.925	*m*-H	0.85	0.996	0.69	0.993
	[b]	0.65	0.963	0.65	0.961		0.87	0.999	0.78	0.998
p-C	[a]	0.68	0.944	0.75	0.989	*p*-H	0.60	0.991	0.70	0.996
	[b]	0.65	0.990	0.86	0.994		0.69	0.999	1.01	0.999

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*; [c] No correlation due to *ortho*-H of **1** do not correlate with σ.

form-*d*. The protons of the methyl group show merely a trend of correlation (ρ = 34.3 Hz, r = 0.942 in dimethyl sulfoxide-d_6 and ρ = 27.16 Hz, r = 0.869 in chloroform-*d*).

It should also be pointed out that the ρ values of *ortho*-, *meta*- and *para*-C's of **1** are much smaller than the corresponding values of **2** and **3**. The ratios for **1** are 0.66 in dimethyl sulfoxide-d_6 and 0.25 in chloroform-*d*, but they are 1.89 and 1.52 for **3**, respectively.

Correlation of the chemical shifts of benzoyl with those of the heterocycles may be related to the relative magnitude of the ring current of each ring. This is especially true with the chemical shift of the carbonyl carbon because the ring current of the attached ring should affect the magnitude of the shift.

The plot of the chemical shifts of the benzoyl protons and carbons against those of the 2-thienoyl and the 2-furoyl counterparts show quite an interesting phenomenon. As shown in Table 6, the slopes of such plots of carbonyl carbon in dimethyl sulfoxide-d_6 are 0.85 (r = 0.998) and 0.75 (r = 0.996) for the thiophene and the furan, respectively. The values are 0.90 (r = 0.999) and 0.78 (r = 0.999) in chloroform-*d*. The correlations are excellent with both series, indicating that the magnetic property of the heterocyclic ring is correlated to that of the benzene ring. Therefore, the value of the slope may be taken as the value of aromaticity index of the heterocycle when that of benzene is set at 1.00.

The observed difference in values (*e.g.*, 0.85 in dimethyl sulfoxide-d_6 and 0.90 in chloroform-*d* for thiophene) suggest that the aromaticity of heterocyclic compounds strongly depend on the solvent. This, in turn, implies that the heterocyclic compounds behave like benzene more in chloroform than in dimethyl sulfoxide.

Besides the linear relationship of the chemical shifts with the Hammett σ there are other interesting trends in the chemical shifts. One of the notable observations in the averaged chemical shifts (Table 7) is the slight downfield shift (0.06-0.44 ppm) of the acyl ring protons in dimethyl sulfoxide-d_6 except for the *ortho*-H of the benzoates (**1**) that shows an upfield shift by 0.06 ppm. The downfield shift in general may be understandable because the solvation of thiophene and furan rings in polar solvent should be more favorable due to the presence of sulfur and oxygen atoms. Such solvation also explains the fact that the chemical shift of *para*-Hs of **2** and **3** are more sensitive to solvent than those of **1** (Δδ 0.43-0.44 ppm vs. 0.12 ppm). However, the upfield shift of the *ortho*-H of **1** in dimethyl sulfoxide-d_6 is a little unusual. Anisotropic deshielding of carbonyl group in benzoyl compounds usually causes downfield shift of *ortho*-H, as observed in the benzoyl ester **1** in both solvents.

In order to examine the solvent effect we obtained the spectra of unsubstituted benzene, thiophene, and furan in 0.1 *M* solution. The results are listed in Table 8. Indeed, the effect of solvent on the chemical shift of both proton and carbon of benzene is trivial showing downfield shifts by only 0.01 ppm for proton and 0.47 ppm for carbon as the solvent changed from chloroform-*d* to dimethyl sulfoxide-d_6. However, the effect is quite significant in thiophene and in furan being greater on α-H and α-C than β-H and β-C.

The solvent-solute interaction like **V** will likely decrease the diamagnetic deshielding effect of the carbonyl group on the *ortho*-H, but it will enhance the ring current effect of the phenyl ring on the *ortho*-H of the heterocycles. It will cause the downfield shift of the *para*-H by enhanced polarization. This type of interaction is not possible with the benzoates **1** and the polar solvent may effectively solvate the ester group, causing a decrease in the diamagnetic anisotropic effect. Therefore, the chemical shift of the *ortho*-H is further downfield in chloroform-*d*.

Table 7
Averaged Chemical Shift Values of Substituted Phenyl Esters **1**-**3** in Dimethyl Sulfoxide-d_6 (0.1 *M*) and in Chloroform-*d* (0.1 *M*) and Their Difference

		o-H	*m*-H	*p*-H	C=O	*i*-C	*o*-C	*m*-C	*p*-C
1	[a]	8.14	7.62	7.77	164.75	129.21	130.32	128.47	133.63
	[b]	8.20	7.52	7.65	164.95	129.22	130.18	128.60	133.76
	diff.	-0.06	0.10	0.12	-0.20	-0.01	0.14	-0.13	-0.13
2	[a]	8.04	7.30	8.11	160.44	132.11	135.88	129.26	135.95
	[b]	7.98	7.18	7.69	160.33	132.49	134.89	128.08	133.76
	diff.	0.06	0.12	0.43	0.11	-0.38	1.06	1.16	2.12
3	[a]	7.59	6.81	8.12	156.69	143.34	120.95	113.33	149.28
	[b]	7.38	6.66	7.68	156.63	140.70	119.77	112.24	147.31
	diff.	0.21	0.15	0.44	0.06	2.64	1.18	1.09	1.97
4	[a]	2.27 [c]			169.55	21.30 [c]			
	[b]	2.30 [c]			169.23	21.04 [c]			
	diff.	-0.03			0.32	0.26			
5	diff.	-0.08	0.10	0.12	-0.51				
6	diff.	0.00	0.12	0.40	-0.39				
7	diff.	0.12	0.19	0.39	-0.43				

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*; [c] CH_3.

Table 8

Chemical Shift Values of 0.1 *M* Solutions of Benzene, Thiophene, and Furan in Dimethyl Sulfoxide-d_6 and in Chloroform-*d*

		α-H	β-H	Δ(α-β)	α-C	β-C	Δ(α-β)
Benzene	[a]	7.37	7.37	0	128.80	128.80	0
	[b]	7.36	7.36	0	128.33	128.33	0
	diff.	0.01	0.01	0	0.47	0.47	0
Thiophene	[a]	7.57	7.15	0.42	126.20	127.56	-1.36
	[b]	7.35	7.13	0.22	125.11	126.86	-1.75
	diff.	0.22	0.02	0.20	1.09	0.70	0.39
Furan	[a]	7.67	6.48	1.19	143.37	110.17	33.20
	[b]	7.45	6.39	1.06	142.52	109.44	33.08
	diff.	0.22	0.09	0.13	0.85	0.73	0.12

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*.

The averaged chemical shift values of *ortho* and *para*-H's of **2** are very close, δ 8.04 and 8.11, respectively, in dimethyl sulfoxide-d_6 as shown in Table 7. But the values are not only far apart but the order is reversed in chloroform-*d*, showing *ortho*-H at δ 7.98 and *para*-H at δ 7.69. The assignment was made based on the coupling constants. They are $J_{3,4}$ = 3.57 Hz and $J_{4,5}$ = 4.94 Hz in average. These values are consistent with the values in literature [12].

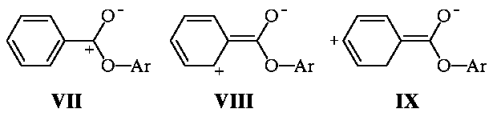
The α-H of furan is shifted downfield by 0.10 ppm from that of thiophene in both solvents, but the β-H of furan is shifted upfield by 0.67 ppm from that of thiophene in dimethyl sulfoxide-d_6 and 0.74 ppm in chloroform-*d* (Table 8). Therefore, the close, if not the same, chemical shift values (δ 8.11-8.12 in dimethyl sulfoxide-d_6 and 7.68-7.69 in chloroform-*d*) for para-H of **2** and **3** (Table 7) may be strong evidence that the polar electronic effect of the ester group should be very similar. In other words, both **2** and **3** prefer similar rotameric conformation, such as **IV**.

The ^{13}C signals of **2** and **3** are also influenced to a greater extent (1.06-2.64 ppm toward downfield) by changing the solvent from chloroform-*d* to dimethyl sulfoxide-d_6 than those of **1** (0.01-0.20 ppm upfield except *ortho*-C which shows 0.14 ppm downfield). The difference in the averaged chemical shift of *ortho*- and *para*-Hs of **2** is merely 0.07 ppm in dimethyl sulfoxide-d_6, *ortho*-H appearing upfield. In chloroform-*d*, however, the difference is relatively large (1.13 ppm) and, in contrast with the *ortho*-H appears downfield.

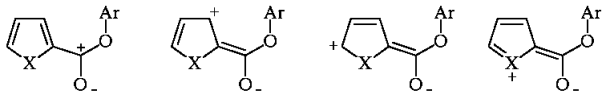
The ester group causes a downfield shift of *ipso*-, *ortho*-, *meta*- and *para*-Cs of the benzoyl ring in **1** by 0.21, 1.52, 0.33, and 4.83 ppm, respectively, in dimethyl sulfoxide-d_6 and 0.81, 1.85, 0.27, and 5.43 ppm, respectively, in chloroform-*d*. The magnitude of the effect on the *para*-C is about three times of that on the *ortho*-C in both solvents. On the other hand, similar effects of 2-ester group on furanyl ring are: *ipso* -0.03, *ortho* 10.88, *meta* 3.16 and *para* 5.91 ppm in dimethyl sulfoxide-d_6 and *ipso* -1.82, *ortho* 10.33, *meta* 2.80, and *para* 4.79 ppm in chloroform-*d*. In this case the effect on the *para*-C is about half of that on the *ortho*-C. It is also quite unusual that the *ipso*-Cs show upfield shift in both solvents. In case of 2-thienoyl ester **2** the effects of the ester group on the chemical shift of the carbons are most significant: *ipso* 5.91, *ortho* 8.32, *meta* 1.70, and *para* 9.75 in dimethyl sulfoxide-d_6; and *ipso* 7.38, *ortho* 8.03, *meta* 1.22, and *para* 8.65 ppm in chloroform-*d*. Here, the effect of the ester group on the *ortho*- and the *para*-Cs are relatively similar in magnitude, and the effect on the *ipso*-C is significantly deshielding.

The small downfield shift in the benzoate carbon signals can be readily explained by the relatively insignificant contribution of the resonance structures **VIII** and **IX**. Such structures should lose the requirement of 6π electrons for aromaticity. Among the resonance structures of the benzoates **VII** is the most significant contributor. In this structure the positive end of the dipole passes through the *para*-C and, consequently, the *para*-C should appear farthest downfield.

On the other hand, the contribution of **X**-**XII** are relatively important in the 2-thienoates **2** and the 2-furoates **3**. In case of **3** further conjugation like **XIII** (X = O) is possible, which should diminish the positive character of the *para*-C so that the magnitude of the downfield shift of the *para*-C is about half of that of the *ortho*-C. But the size of the sulfur atom should disfavor similar conjugation with **2**. Therefore, the magnitude of the shift of the *ortho*- and the *para*-C's are about the same.

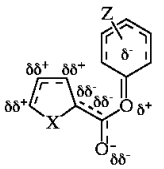


VII **VIII** **IX**



X **XI** **XII** **XIII**

The contrasting observations of the substituent effect on the chemical shift (which is quite significant on the *para* position in **1** and the *ortho* position in **3**) may be explained by two different mechanisms of transmission of the substituent effect. The aryloxy group may induce local polarization in benzoyl group like **XIV**.



XIV

X: HC = CH, S, O

Table 9

^{1}H Chemical Shift Values of Substituted Cyclohexyl Esters **5**-**7** in Dimethyl Sulfoxide-d_6 (0.1 *M*) and in Chloroform-*d* (0.1 *M*)

		o-H	*m*-H	*p*-H	1'-H	2'*a*-H	2'*b*-H	3'*a*-H	3'b-H	4'a-H	4'b-H
5	[a]	7.97	7.53	7.66	4.94	1.88	1.54	1.73	1.42	1.54	1.32
	[b]	8.05	7.43	7.54	5.03	1.94	1.58	1.79	1.43	1.58	1.33
6	[a]	7.79	7.21	7.93	4.89	1.86	1.51	1.70	1.39	1.51	1.31
	[b]	7.79	7.09	7.53	4.99	1.92	1.57	1.79	1.43	1.57	1.33
7	[a]	7.28	6.66	7.95	4.88	1.87	1.49	1.71	1.38	1.49	1.27
	[b]	7.16	6.49	7.56	5.00	1.94	1.55	1.78	1.42	1.55	1.30

		C=O	*i*-C	*o*-C	*m*-C	*p*-C	1'-C	2*a*-C	3'-C	4'-C
5	[a]	165.49	130.73	129.52	129.17	133.63	72.89	31.48	23.50	25.39
	[b]	165.97	131.02	129.51	128.24	132.64	73.01	31.63	23.65	25.47
6	[a]	161.30	134.05	133.94	128.78	134.17	73.26	31.49	23.50	25.33
	[b]	161.69	134.75	133.01	127.59	131.93	73.37	31.58	23.59	25.41
7	[a]	157.84	144.66	118.62	112.71	147.88	73.10	31.57	23.62	25.30
	[b]	158.27	145.26	117.44	111.67	145.99	73.38	31.66	23.76	25.35

[a] Dimethyl sulfoxide-d_6; [b] Chloroform-*d*.

Table 10

Yields, Mp, and Elemental Analysis Data of Compounds **1**-**7**

Compound	Yield	Mp	Calcd				Observed			
	%	°C	C, %	H, %	X, %	S, %	C, %	H, %	X, %	S, %
1a	84	93-94	64.20	3.73	5.76 [a]		64.35	3.77	5.85 [a]	
1b	75	83-85	56.34	3.27	28.84 [b]		56.25	3.30	28.76 [b]	
1c	68	65-68	67.11	3.90	15.24 [c]		67.40	3.78	15.05 [c]	
1d	69	liquid	73.67	5.30			73.85	5.21		
1e	64	liquid	79.23	5.70			79.01	5.62		
1f	70	143-144	64.20	3.73	5.76 [a]		64.48	3.54	5.55 [a]	
1g	63	102-103	56.34	3.27	28.84 [b]		56.22	3.23	28.65 [b]	
1h	62	86-87	67.11	3.90	15.24 [c]		67.35	3.88	14.99 [c]	
1i	84	84-86	73.67	5.30			73.41	5.66		
1j	89	66-69	79.23	5.70			79.35	5.56		
1k	83	68-69	78.77	5.09			78.52	4.89		
2a	60	98-100	53.01	2.83	5.62 [a]	12.86	52.85	2.64	5.58 [a]	12.65
2b	38	60-62	46.66	2.49	28.22 [b]	11.32	46.85	2.54	28.48	11.12
2c	52	47-49	55.35	2.96	14.85 [c]	13.43	55.55	2.82	14.69	13.22
2d	21	liquid	61.52	4.30		13.69	61.64	4.55		13.43
2e	48	80-81	66.03	4.62		14.69	66.32	4.45		14.39
2f	60	98-100	53.01	2.83	5.62 [a]	12.86	52.90	2.72	5.63	12.65
2g	50	92-93	46.66	2.49	28.22 [b]	11.32	46.78	2.52	28.02	11.24
2h	69	82-83	55.35	2.96	14.85 [c]	13.43	55.48	2.85	14.65	13.24
2i	60	104-105	61.52	4.30		13.69	61.77	4.58		13.48
2j	60	85-87	66.03	4.62		14.69	66.28	4.85		14.42
2k	53	44-46	64.69	3.95		15.67	64.68	4.22		15.45
3a	68	77-80	56.66	3.03	6.01 [a]		56.45	3.32	5.99 [a]	
3b	69	51-53	49.47	2.64	29.92 [b]		49.23	2.68	29.75 [b]	
3c	51	40-47	59.35	3.17	15.92 [c]		59.28	2.99	15.84 [c]	
3d	82	liquid	66.05	4.62			66.24	4.52		
3e	34	35-38	71.28	4.98			71.02	5.21		
3f	74	162-165	56.66	3.03	6.01 [a]		56.72	3.28	6.11 [a]	
3g	65	89-91	49.47	2.64	29.92 [b]		49.55	2.48	30.11 [b]	
3h	57	74-82	59.35	3.17	15.92 [c]		59.19	3.41	15.68 [c]	
3i	67	83-85	66.05	4.62			66.21	4.48		

Table 10 (continued)

Yields, Mp, and Elemental Analysis Data of Compounds **1**-**7**

Compound	Yield	Mp	Calcd				Observed			
	%	°C	C, %	H, %	X, %	S, %	C, %	H, %	X, %	S, %
3j	71	56-58	71.28	4.98			71.35	4.78		
3k	77	37-40	70.21	4.29			70.00	4.45		
4a	89	liquid	53.04	3.90	7.73 [a]		53.25	4.02	7.57 [a]	
4b	84	liquid	44.68	3.28	37.16 [b]		44.39	3.55	37.41 [b]	
4c	90	liquid	56.33	4.14	20.78 [c]		56.45	4.22	20.52 [c]	
4d	82	liquid	65.05	6.07			65.31	6.22		
4e	97	liquid	71.98	6.71			71.73	6.77		
4f	82	75-77	53.04	3.90	7.73 [a]		53.14	4.05	7.60 [a]	
4g	82	liquid	44.68	3.28	37.16 [b]		44.71	3.38	37.01 [c]	
4h	78	liquid	56.33	4.14	20.78 [c]		56.19	3.99	20.81 [c]	
4i	93	liquid	65.05	6.07			65.12	6.22		
4j	85	liquid	71.98	6.71			71.81	6.95		
4k	80	liquid	70.58	5.92			70.74	5.88		
5	50	liquid	76.44	7.90			76.67	8.11		
6	65	liquid	62.83	6.71		15.25	62.95	6.88		15.05
7	55	liquid	68.02	7.26			68.28	7.45		

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

Similar type of local π-polarization has been discussed in literature [6,13]. The induced polarization should explain the negative ρ values of the carbonyl- and *ipso*-Cs and the positive ρ values of the *ortho*-, *meta*-, and *para*-Cs (Table 4). On the other hand, the effect of the dipole seems to be most significant in determining the size of ρ values, especially in case of **1**, which show the largest value for the *para*-H and *para*-C. In contrast, through space transmission of the substituent effect is more significant than anything else in **3** in which the *syn* conformation is more favorable in dimethyl sulfoxide-d_6. Such conformation brings the *ortho*-H and *ortho*-C close to the phenyl ring.

In order to examine the effect of the phenyl ring on the chemical shift of the benzoyl, 2-thienoyl, and 2-furoyl rings, we prepared cyclohexyl esters **5**-**7** and obtained their ^{1}H and ^{13}C nmr spectra in both solvents. The data are listed in Table 9. Comparison of the chemical shift values of the phenyl esters **1k**, **2k**, and **3k** with the corresponding cyclohexyl esters **5**, **6**, and **7** reveals that the difference of the *ortho*-H and *ortho*-C are largest for the furoate (**3k** and **7**): $\Delta\delta_{ortho\text{-H}}$ 0.30 ppm and $\Delta\delta_{ortho\text{-C}}$ 2.08 ppm in dimethyl sulfoxide-d_6. They are 0.17 and 0.74 ppm, respectively, for the benzoates (**1k** and **5**) and 0.24 and 1.72 ppm, respectively, for the 2-thienoates (**2k** and **6**) in the same solvent. The observation may be an evidence of the importance of the through-space effect of the phenyl group in **2** and **3**.

Interestingly, the order of the chemical shifts of the thienyl carbons changes by the solvent: from downfield *para*>*ipso*>*ortho*>*meta* in dimethyl sulfoxide-d_6 and *ipso*>*ortho*>*para*>*meta* in chloroform-*d*. The order for benzoyl and furoyl carbons is the same regardless of the solvent: *para*>*ipso*>*ortho*>*meta*.

In conclusion, we have found that a correlation of the chemical shift values with the Hammett σ can be used in determining the aromaticity index of 5-membered monoheterocyclic compounds. The indices are benzene 1.00, thiophene 0.85 and furan 0.75 when the chemical shift values are obtained in dimethyl sulfoxide-d_6. In chloroform-*d* the values are benzene 1.00, thiophene 0.90 and furan 0.78.

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}H and 100 MHz for ^{13}C and were referenced to tetramethylsilane. The concentration of the solution was 0.10 *M* in dimethyl sulfoxide-d_6 and chloroform-*d*. The Central Lab of Kangwon National University performed elemental analyses.

An Illustrative Procedure for Preparation of *m*- and *p*-Substituted Phenyl Esters **1**-**3**.

To an ice-cold solution of phenol (11 mmoles), triethylamine (11 mmoles) in dichloromethane (10 ml) was added drop-wise an acyl chloride (10 mmoles). The mixture was stirred at room temperature for 30 minutes and washed with 1 *M* hydrochloric acid solution (5 x 2 ml). The organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation of the

solvent, colorless solid formed, which was recrystallized from ethanol-hexane. The yields, mp, and elemental analysis data are listed in Table 10.

An Illustrative Procedure for Preparation of *m*- and *p*-Substituted Phenyl Acetates **4**.

To an ice-cold solution of phenol (7 mmoles), triethylamine (10 mmoles) in dichloromethane (5 ml) was added drop-wise a solution of acetic anhydride (10 mmoles) in dichloromethane (5 ml). After the addition of the anhydride, 3-5 drops of glacial acetic acid was added. The resulting solution was heated at reflux for 30 minutes. The solution was mixed with water (20 ml). The pH was adjusted to 5 by adding 1.0 *M* hydrochloric acid. The organic layer was separated. The aqueous layer was extracted with dichloromethane (2 x 30 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (30 ml) and then with water (30 ml). After drying over sodium sulfate and removal of the solvent, the residual liquid was purified by distillation under vacuum or chromatography with silica gel, eluting with hexane-ethyl acetate (4:1). The yields, mp, and elemental analysis data are listed in Table 10.

An Illustrative Procedure for Preparation of Cyclohexyl Esters **5-7**.

A solution of cyclohexanol (13.3 mmoles) in dichloromethane (5 ml) was added drop-wise to a solution of acyl chloride (2.7 mmoles) in dichloromethane (10 ml). The resulting solution was heated at reflux for 1 hour. The solution was partitioned in dichloromethane (50 ml) and water (80 ml) and the organic layer was separated. After drying over sodium sulfate and evaporation of the solvent, the residual liquid was purified by chromatography with silica gel, eluting with hexane-ethyl acetate (4:1). The yields, mp, and elemental analysis data are listed in Table 10.

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