HETEROCYCLES, Vol. 71, No. 1, 2007, pp. 153 - 164. © The Japan Institute of Heterocyclic Chemistry
Received, 23rd October, 2006, Accepted, 30th November, 2006, Published online, 1st December, 2006. COM-06-10925

POSITIONAL EFFECT ON THE NMR SPECTROSCOPY OF ESTERS AND AMIDES OF 2- AND 3-FURANCARBOXYLIC ACIDS

Kyu Ok Jeon, Ji Sook Yu, and Chang Kiu Lee*

Department of Chemistry, Kangwon National University, Chuncheon 200-701,
S. Korea
E-mail: cklee410@kangwon.ac.kr

Abstract- Eleven derivatives of esters and amides of 2- and 3-furancarboxylic acids and their NMR spectra were obtained in DMSO-d_6. The spectra of esters were also obtained in chloroform-*d*. The chemical shift values show good correlation with the Hammett substituent parameters. The slopes, however, show contrasting phenomena depending on the position in the furan ring.

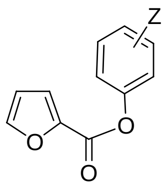
INTRODUCTION

The effect of hetero atom on the physico-chemical properties of a five-membered monoheterocyclic aromatic compound is generally understood by both inductive and conjugative sense. For example, the calculated value of the electron density of the β-carbon of furan is greater than that of the α-carbon. The results of such calculation is consistent with the upfield shift of ^{13}C signal of the β-carbon (109.9 ppm) of furan compared to that of the α-carbon (143.0 ppm).[1] However, electrophilic substitution usually takes place at the α-carbon of furan.[2] This is opposite to the observed lower electron density at the α-carbon.

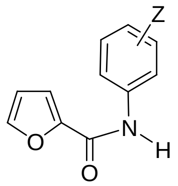
The inductive effect of the O atom may explain the greater acidity of 2-furoic acid (pK_a 3.16) compared to that of 3-furoic acid (pK_a 3.95).[3] However, the ^{13}C chemical shift of the carbonyl carbon of 2-furoic acid is upfield (159.33 ppm) whereas that of 3-furoic acid is downfield (163.79 ppm).[4] If the inductive effect is the origin of the shift, 2-CO should be more deshielding than 3-CO because the former is closer to the electronegative O atom than the latter.

In the course of our investigation of the aromaticity of five-membered monoheterocyclic compounds we observed that a plot of the chemical shifts of *m*- and *p*-substituted phenyl 2-furoate (**1**) against those of benzoate (**5**) could be used for the determination of the index of aromaticity of furan.[5] A similar method could be employed for the anilide series.[6] But the investigation was carried out with 2-substituted furan.

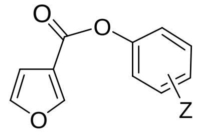
Considering the difference in the physico-chemical properties of 2- and 3-derivatives of the heterocycles it seems to be worthwhile to investigate the possible correlation with the 3-furoic acid derivatives. Here we report the striking contrast in NMR spectra of the esters and anilides of 2- and 3-furoic acids.



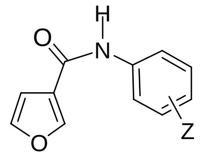
1



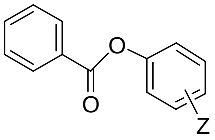
2



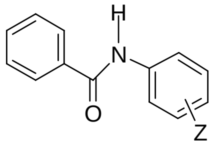
3



4



5



6

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

RESULTS AND DISCUSSION

The 3-furoates (**3**) were prepared by the reactions of 3-furoyl chloride and *m*- and *p*-substituted phenols in triethylamine. The esters were purified by recrystallization or column chromatography in order to obtain the analytically pure compounds. The *m*- and *p*-substituted anilides of the 3-furoic acid (**4**) were also prepared by reacting 3-furoyl chloride with *m*- and *p*-substituted anilines.

Both DMSO-d_6 and chloroform-*d* were used for the NMR studies of the ester (**3**), but only DMSO-d_6 was employed for the anilides (**4**) because of the poor solubility of the anilides in chloroform-*d*. The concentration of the NMR solutions was 0.1 M. The assignment of each peak was made by analysis of ^1H-^1H COSY and ^1H-^{13}C HETCOR spectra. ^1H and ^{13}C chemical shift values are listed in Table 1 and Table 2, respectively.

Table 1. ^1H Chemical Shift Values of Substituted 3-Furoate (**3**) and 3-Furoanilides (**4**) in Dimethyl Sulfoxide-d_6 (0.1 M) and in chloroform-*d* in Italic

	NH	2-H	4-H	5-H	2'-H	3'-H	4'-H	5'-H	6'-H	CH_3
3a		8.70	6.98	7.94	8.20		8.19	7.78	7.79	
3a		*8.24*	*6.89*	*7.54*	*8.10*		*8.15*	*7.61*	*7.56*	
3b		8.65	6.94	7.92	7.57		7.52	7.43	7.30	
3b		*8.19*	*6.88*	*7.51*	*7.38*		*7.40*	*7.28*	*7.15*	
3c		8.66	6.95	7.92	7.45		7.39	7.50	7.26	
3c		*8.19*	*6.86*	*7.51*	*7.23*		*7.25*	*7.34*	*7.10*	
3d		8.63	6.93	7.91	6.85		6.81	7.35	6.88	3.77

3d		*8.19*	*6.87*	*7.50*	*6.74*		*6.82*	*7.30*	*6.78*	*3.81*
3e		8.62	6.93	7.91	7.05		7.11	7.33	7.03	2.36
3e		*8.18*	*6.87*	*7.49*	*6.99*		*7.07*	*7.29*	*6.98*	*2.38*
3f		8.71	6.98	7.94	7.59	8.35				
3f		*8.24*	*6.88*	*7.54*	*7.39*	*8.31*				
3g		8.65	6.94	7.91	7.25	7.65				
3g		*8.19*	*6.86*	*7.50*	*7.08*	*7.53*				
3h		8.65	6.94	7.91	7.25	7.65				
3h		*8.19*	*6.86*	*7.51*	*7.13*	*7.38*				
3i		8.62	7.00	7.90	7.16	6.95				3.77
3i		*8.18*	*6.86*	*7.49*	*7.09*	*6.92*				*3.81*
3j		8.62	6.93	7.90	7.11	7.23				2.32
3j		*8.18*	*6.87*	*7.49*	*7.06*	*7.20*				*2.36*
3k		8.64	6.94	7.91	7.24	7.67	7.31			
3k		*8.20*	*6.88*	*7.50*	*7.18*	*7.42*	*7.26*			
4a	10.36	8.42	7.02	7.82	8.69		8.13	7.64	7.94	
4b	10.05	8.39	6.99	7.80	8.03		7.27	7.31	7.69	
4c	10.07	8.39	6.99	7.80	7.90		7.14	7.37	7.63	
4d	9.88	8.37	6.99	7.79	7.40		6.67	7.24	7.29	3.75
4e	9.83	8.36	6.99	7.78	7.52		6.91	7.21	7.51	2.30
4f	10.46	8.46	7.02	7.83	7.99	8.25				
4g	10.03	8.38	6.99	7.08	7.52	7.69				
4h	10.03	8.38	6.99	7.80	7.74	7.40				
4i	9.80	8.33	6.98	7.78	7.59	6.92				3.73
4j	9.83	8.35	6.99	7.78	7.14	7.58				2.31
4k	9.91	8.37	7.00	7.79	7.70	7.34	7.09			

Table 2. ^{13}C Chemical Shift Values of Substituted 3-Furoate (**3**) and 3-Furoanilides (**4**) in Dimethyl Sulfoxide-d_6 (0.1 M) and in chloroform-*d* in Italic

	C=O	2-C	3-C	4-C	5-C	1’-C	2’-C	3’-C	4’-C	5’-C	6’-C
3a	161.01	150.74	118.08	110.27	145.91	150.88	117.91	148.85	121.52	131.38	129.52
3a	*160.62*	*149.15.*	*118.02*	*109.92*	*144.39*	*150.68*	*117.50*	*148.81*	*120.86*	*130.07*	*128.18*
3b	161.15	150.49	118.24	110.25	145.84	151.32	125.69	122.01	129.55	131.79	121.82

3b	*160.92*	*148.85*	*118.42*	*109.97*	*144.17*	*150.86*	*125.21*	*122.40*	*129.11*	*130.49*	*120.57*
3c	161.16	150.51	118.26	110.27	145.86	151.31	122.93	133.91	126.69	131.51	121.47
3c	*160.93*	*148.85*	*118.44*	*109.97*	*144.17*	*150.84*	*122.37*	*134.72*	*126.21*	*130.18*	*120.08*
3d[a]	161.36	150.23	118.57	110.26	145.78	151.62	108.38	160.68	112.34	130.50	114.49
3d[a]	*161.30*	*148.66*	*118.82*	*110.03*	*144.03*	*151.33*	*107.62*	*160.50*	*111.85*	*129.84*	*113.85*
3e[a]	161.51	150.16	118.61	110.25	145.78	150.57	122.81	139.82	127.74	129.77	119.37
3e[a]	*161.51*	*148.60`*	*118.91*	*110.04*	*143.99*	*150.32*	*122.25*	*139.66*	*126.72*	*129.17*	*118.58*
3f	160.70	150.86	118.02	110.25	145.98	155.15	150.86	125.83	145.65		
3f	*160.28*	*149.20*	*118.05*	*109.91*	*144.42*	*155.15*	*122.54*	*125.25*	*145.37*		
3g	161.20	150.44	118.30	110.24	145.83	149.86	124.81	132.93	118.83		
3g	*161.02*	*148.81*	*118.51*	*109.98*	*144.15*	*149.40*	*123.48*	*132.50*	*119.00*		
3h	161.29	150.45	118.33	110.26	145.85	149.39	124.41	130.00	130.68		
3h	*161.12*	*148.80*	*118.53*	*109.98*	*144.14*	*148.85*	*123.05*	*129.51*	*121.29*		
3i[a]	161.84	150.10	118.64	110.27	145.74	143.98	123.23	114.99	157.49		
3i[a]	*161.78*	*148.57*	*118.87*	*110.04*	*143.97*	*143.85*	*122.42*	*114.47*	*157.30*		
3j[a]	161.63	150.14	118.62	110.26	145.75	148.40	122.09	130.41	135.67		
3j[a]	*161.62*	*148.58*	*118.91*	*110.05*	*143.96*	*148.13*	*121.31*	*129.96*	*135.55*		
3k	161.48	150.24	118.57	110.26	145.79	150.62	122.42	130.08	126.51		
3k	*161.40*	*148.66*	*118.75*	*110.04*	*144.05*	*150.38*	*121.66*	*129.46*	*125.91*		
4a	161.42	146.90	123.01	109.67	145.01	140.60	114.62	148.42	118.55	130.67	126.41
4b	161.08	146.62	123.18	109.68	144.85	140.99	122.84	121.91	126.63	131.17	119.25
4c	161.63	146.64	123.20	109.70	144.86	140.86	120.01	133.46	123.76	130.88	118.89
4d[a]	160.90	146.35	123.51	109.74	144.72	140.54	106.38	159.93	109.54	129.93	112.87
4e[a]	160.33	146.29	123.57	109.77	144.71	139.26	121.25	138.32	124.81	129.01	117.90
4f	161.54	147.16	122.99	109.78	145.04	145.75	120.12	126.10	142.91		
4g	160.97	146.53	123.30	109.71	144.80	138.75	122.52	131.98	115.74		
4h	160.97	146.52	123.30	109.71	144.80	138.33	122.16	129.07	127.68		
4i[a]	160.54	146.11	123.59	109.71	144.64	132.32	122.38	114.28	156.01		
4j[a]	160.69	146.20	123.57	109.74	144.65	136.78	120.75	129.53	133.04		
4k	160.89	146.34	123.51	109.77	144.71	139.33	120.71	129.15	124.10		

[a] CH$_3$: **3d**, 55.41 (*55.90*); **3e**, 21.31 (*21.27*); **3i**, 55.57 (*55.93*); **3j**, 20.87 (*20.90*); **4d**, 55.49; **4e**, 21.95; **4i**, 55.66; **4j**, 20.96.

The substituent effect on the chemical shift were analyzed by a single substituent parameter approach as shown in Equation (1).[7]

$$\delta = \rho\sigma + \delta_o \qquad (1)$$

The chemical shift values of the protons and carbons were plotted against the Hammett σ values[8] according to Eqn. (1) as shown in Figure 1. The results of such plots are listed in Table 3.

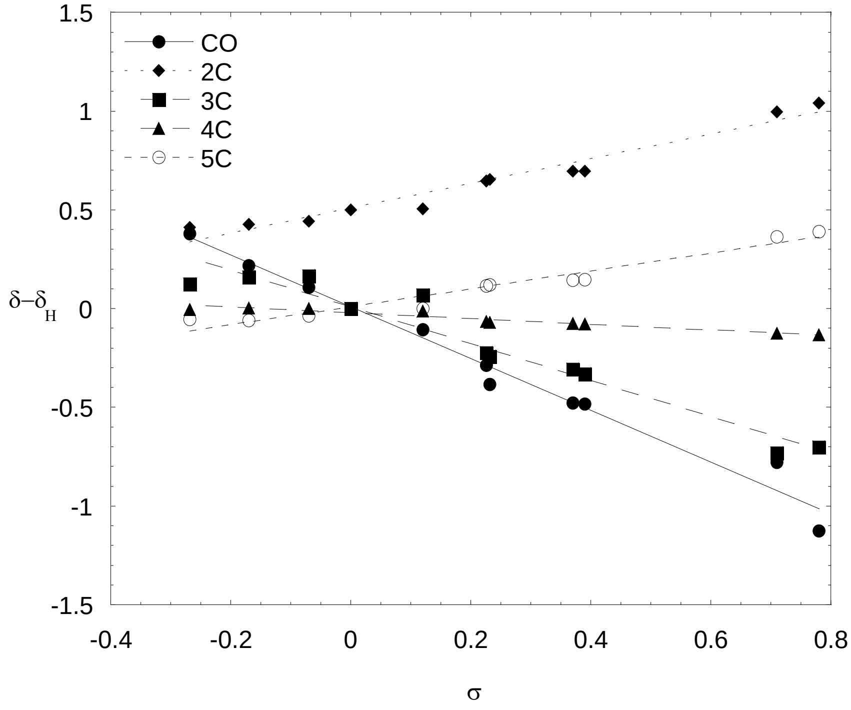


Figure 1. Correlation between σ and ^{13}C chemical shifts of **3** in chloroform-*d*.

Table 3. Best Fit of the Single Substituent Parameter Equation for ^{1}H and ^{13}C Chemical Shifts of the Esters (**1** and **3**) and the Anilides (**2** and **4**) in Dimethyl Sulfoxide-d_6 (0.1 M) and in chloroform-*d* in Italic

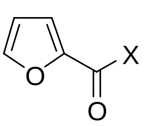
	Esters				Anilides			
	1[a]		**3**		**2**[a]		**4**	
	ρ	r	ρ	r	ρ	r	ρ	r
2-H			30.91	0.957			40.34	0.966
			20.11	*0.858*				
3-H	39.31	0.960			53.70	0.964		
	30.56	*0.910*						
4-H	18.38	0.970	20.26	0.911	25.15	0.981	11.24	0.814

	22.13	*0.939*	*5.40*	*0.501*				
5-H	24.16	0.976	15.63	0.966	36.83	0.992	19.89	0.990
	23.71	*0.958*	*18.98*	*0.942*				
N-H					266.37	0.966	241.51	0.953
C=O	-97.0	0.973	-89.9	0.971	50.3	0.976	85.2	0.984
	-143.6	*0.988*	*-131.0*	*0.989*				
2-C	-71.3	0.978	72.8	0.984	-89.0	0.992	90.0	0.982
	-112.5	*0.975*	*62.7*	*0.977*				
3-C	117.0	0.977	-65.1	0.970	157.0	0.987	-64.9	0.975
	133.4	*0.978*	*-92.7*	*0.968*				
4-C	24.8	0.982	-0.2	0.066	34.6	0.990	-2.6	0.236
	36.8	*0.970*	*-14.5*	*0.956*				
5-C	61.8	0.978	20.5	0.967	93.0	0.987	39.6	0.988
	87.7	*0.979*	*45.3*	*0.975*				
1’-C	622.1	0.760	603.5	0.756	799.2	0.824	794.4	0.822
	605.0	*0.753*	*606.1*	*0.754*				

[a] From reference 5 and 6.

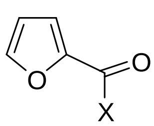
One of the noteworthy observations in the correlation is that the 2-furoates (**1**) and 2-furoanilides (**2**) show good correlations in both solvents with the correlation coefficient r values ranging 0.910-0.992 for proton and 0.970-0.992 for carbon. The 3-furoates (**3**) and 3-furoanilides (**4**) show similar correlations except for the 4-H and 4-C. For example, there is no correlation for 4-H of **3** in chloroform-*d* (r = 0.501) and 4-C of **3** (r = 0.066) and **4** (r = 0.236) in DMSO-d_6. The correlation for 4-H of **4** is significantly poorer (r = 0.814) compared to 2-H (r = 0.966) and 5-H (r = 0.990). Both the 2- and 4-positions of **3** and **4** are ortho to the carbonyl group and a similar trends in correlation are expected. However, only the 2-H and 2-C show fair correlations.

The observations seem to be related to the conformation of the carbonyl groups in 2- and 3-furoic acids. It has been reported that the syn conformation in which both oxygen atoms are on the same side is favored in the 2-series (c.f. **I**),[9] whereas the anti conformation (**III**) is favored in the 3-series.[10] The observed upfield shift of the carbonyl signal in 2-furoyl derivatives is consistent with the syn conformation. The interaction between the lone-pair electrons of both O atoms should push the electron pair in the carbonyl oxygen atom to the π^* orbital of the carbonyl C=O bond, which should result in shielding of the carbonyl carbon, and consequently, the upfield shifting of the signal.



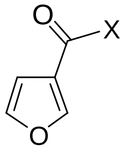
syn

I



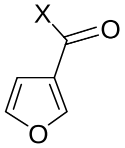
anti

II



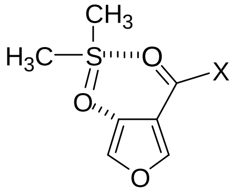
anti

III



syn

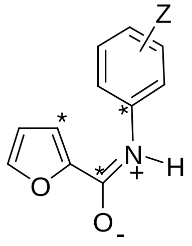
IV



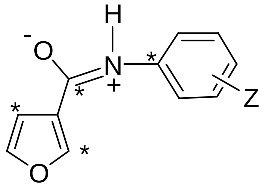
V

The anti conformation of **3** and **4** may also the cause of no correlation of 4-C in DMSO-d_6 with σ. The solvent may form a six membered ring like **V**. The field effect of O atom of the sulfoxide may overcome the electronic effect of the substituent that is transmitted through the bonds. Consequently, the electronic effect may not linearly correlate with the σ value of the substituent.

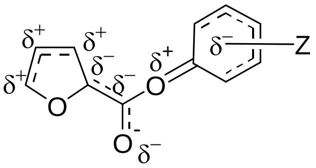
It should also be pointed out that both the carbonyl and ipso carbons of the esters (**1** and **3**) show inverse correlation but only the ipso carbons of the anilides (**2** and **4**) show inverse correlation. This is consistent with the favorable conjugation of the anilide like **VI** and **VII** so that the anilide may be considered structural analogs of cinnamoyl compound. It is known that the unstarred carbons show an inverse correlation in such a conjugated system. The esters, on the other hand, seem to follow the π polarization mechanism (like **VIII**) in transmitting the effect of the substituent.[11,12]



VI



VII



VIII

When the chemical shift values of the furoates (**1** and **3**) and furoanilides (**2** and **4**) were plotted against the benzoate and benzanilides (Figure 2), there were excellent correlations for most of the H and C except for the 2-H and 4-C of **3** and **4**, respectively. The results are listed in Table 4.

Table 4. Slopes and Correlation Coefficients of the Plots of ^{1}H and ^{13}C Chemical Shift Values of the Benzoates (**5**) vs. Those of 2-Furoates (**1**) and 3-Furoates (**3**) in Dimethyl Sulfoxide-d_6 and in Chloroform-*d* in Italic, and Benzanilides (**6**) vs. Those of the 2-Furoanilides (**2**) and 3-Furoanilides (**4**) in Dimethyl Sulfoxide-d_6

	1		**3**		**2**		**4**	
	Slope	r	Slope	r	Slope	r	Slope	R
N-H					1.04	0.999	0.95	0.999
2-H			1.87	0.950			1.65	0.883
			1.09	*0.528*				
3-H	2.02	0.943			2.18	0.877		

	1.25	*0.422*						
4-H	1.44	0.993	1.14	0.978	1.33	0.987	0.59	0.955
	1.29	*0.998*	*0.84*	*0.884*				
5-H	1.43	0.996	1.24	0.996	1.34	0.997	1.04	0.981
	1.46	*0.973*	*1.11*	*0.998*				
C=O	1.34	0.996	1.24	0.997	0.52	0.998	0.88	0.993
	1.28	*0.999*	*1.17*	*0.999*				
2-C	0.97	0.966	2.41	0.995	0.96	0.998	2.95	0.986
	0.91	*0.999*	*3.37*	*0.995*				
3-C	3.88	0.990	0.89	0.962	5.10	0.980	0.71	0.996
	7.14	*0.990*	*0.76*	*0.995*				
4-C	2.56	0.925	0.00	0.002	1.78	0.976	0.01	0.043
	1.53	*0.961*	*-0.76*	*0.994*				
5-C	1.34	0.989	2.23	0.955	1.24	0.997	2.07	0.984
	1.16	*0.994*	*1.87*	*0.959*				
1’-C	1.00	0.999	0.97	0.999	1.01	0.999	1.01	0.999
	1.00	*0.999*	*1.00*	*1.000*				

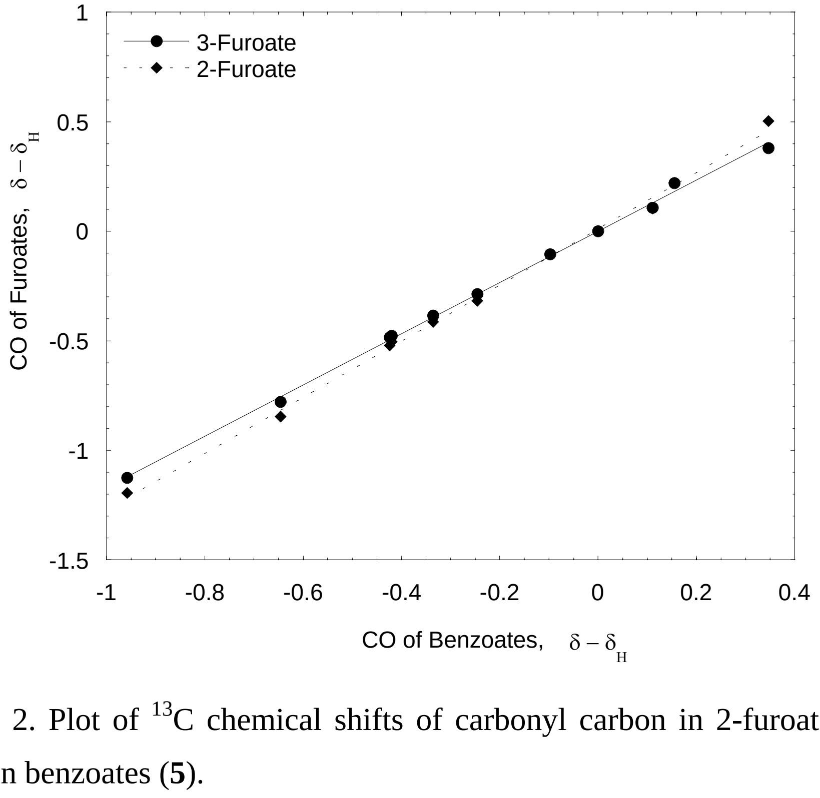


Figure 2. Plot of ^{13}C chemical shifts of carbonyl carbon in 2-furoates (**2**) and 3-furoates (**3**) against those in benzoates (**5**).

The exceptions are not surprising because the nuclei show no correlation with the Hammett σ. The esters (**1** and **3**) show generally larger values of the slopes than those of the anilides (**2** and **4**) with the exception of 3-Cs of **1** and **2** that are significantly larger than any other values. It seems apparent that the favorable conjugation of the amide makes the anilides (**2** and **4**) stilbene system in which the two aromatic rings are completely conjugated. The transmission of the effect of the substituent from one ring to another should be most favorable when two rings are connected by a C-C double bond.

On the other hand, such transmission is less favorable in the esters and the effect of the hetero atom in the furan ring should predominate. The conformation should also play an important role in transmitting the substituent effect. Both rings are in cis arrangement for the furoates (**1** and **3**) and furoanilides (**2** and **4**), but the two phenyl rings are trans for the benzoates (**5**) and benzanilides (**6**).

Plotting like Figure 3 can show the solvent effects on the chemical shift. The effects are quite contrasting for 2-furoates (**1**) and 3-furoates (**3**) as shown in Table 5. The substituent effect on the chemical shift of the carbons of **1** are about 1.13-1.54 times larger in chloroform-*d* than in DMSO-d_6. But the effect appears differently in **3**: larger for the C=O, the 3-C, and the 5-C and smaller for the 2-C and no correlation for the 4-C.

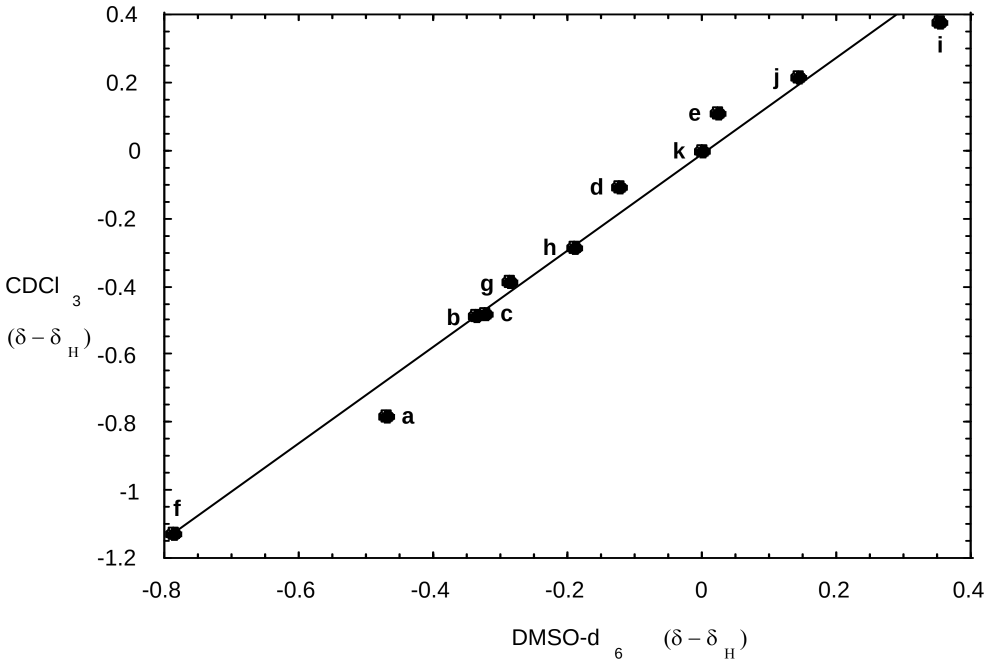


Figure 3. Plot of ^{13}C chemical shifts of carbonyl carbon in 3-furoates (**3**) in chloroform-*d* against those in DMSO-d_6.

Table 5. Slopes and Correlation Coefficients of the Plots of ^{1}H and ^{13}C Chemical Shift Values of the 2-Furoates (**1**) and 3-Furoates (**3**) in Dimethyl Sulfoxide-d_6 vs. Chloroform-*d*

	1		**3**			**1**		**3**	
	Slope	r	Slope	r		Slope	r	Slope	r
					C=O	1.45	0.995	1.42	0.990
2-H			0.59	0.946	2-C	1.54	0.971	0.86	0.990
3-H	0.79	0.997			3-C	1.13	0.992	1.40	0.984
4-H	1.23	0.988	0.35	0.721	4-C	1.48	0.981	0.23	0.052
5-H	2.12	0.970	1.23	0.986	5-C	1.38	0.973	2.12	0.970
					1’-C	0.98	0.999	1.00	0.999

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 for the NMR experiments was 0.10 M. Infrared spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Elemental analyses were performed by the Central Lab of Kangwon National University.

Mea- and *p*-substituted phenols and anilines are all commercially available and used without purification. 3-Furoyl chlorides were prepared by a standard procedure from 3-furoic acid using thionyl chloride. The yields and analytical data of **3** and **4** are listed in Table 6.

Preparation of *m,p*-substituted 3-furoates (3). An illustrative procedure: A solution of phenol (9 mmoles) in CH_2Cl_2 (10 mL) was cooled in a water bath at 0-5 °C and Et_3N (1.3 mL, 9 mmoles) was added. With stirring and cooling the solution, 3-furoyl chloride (1.04 g, 8 mmoles) was added dropwise. The resulting solution was stirred at rt for 4-5 h. Water (50 mL) was added to the reaction mixture and the mixture was separated. The aqueous layer was extracted with CH_2Cl_2 (4 x 10 mL). The organic layers were combined and then washed with 1 M-NaOH (20 mL), 1 M-HCl ((20 mL), and water (20 mL) successively. The organic layer was dried over $MgSO_4$. The dried solution was filtered and the solvent was evaporated to give a residue that was purified further by crystallization or column chromatography using silica gel (EtOAc-hexane).

Preparation of *m,p*-substituted 3-furoanilidies (4). An illustrative procedure: 3-Furoyl chloride (10 mmoles) was added slowly to a solution of substituted aniline (16 mmoles) and triethylamine (10 mmoles) in CH_2Cl_2 (15 mL) at 0°C with vigorous stirring. After the completion of the addition the solution was heated at reflux for 1 h. The mixture was cooled to rt and then treated with saturated aqueous $NaHCO_3$ solution until the aqueous layer was slightly basic (pH ~8). The organic layer was washed with water (10 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed and the resulting solid was crystallized from EtOH.

Table 6. Yields, Melting Points, Elemental Analysis, Infrared, and Mass Spectral Data of **3** and **4**

Compd	Yield	Mp	Anal. Calcd (Found)			IR	MS, *m/z* (%)	
	%	°C	C	H	N or X	cm^{-1}	M^+	Base
3a	68	78	56.66 (56.85)	3.03 (3.21)	6.01 (6.28)	1745, 1530, 1360,	233 (2)	95
3b	51	72-74	49.47 (49.45)	2.64 (2.43)	[a]29.92 (29.71)	1740, 1310, 1185	266 (10)	95
3c	61	52-53	59.35 (59.46)	3.17 (3.28)	[b]15.92 (15.66)	1732, 1318, 1150	222 (0.3)	95
3d	64	98	66.05 (66.30)	4.62 (4.55)		1740, 1310, 1140	218 (62)	95
3e	82	49	71.28 (71.20)	4.98 (4.72)		1725, 1315, 1140	202 (20)	95
3f	76	112	56.66 (56.70)	3.03 (3.25)	6.01 (6.23)	1740, 1520, 1350	233 (9)	95
3g	28	64	49.47 (49.25)	2.64 (2.58)	[a]29.92 (29.68)	1740, 1310, 1095	266 (11)	95
3h	62	48	59.35 (59.27)	3.17 (3.35)	[b]15.92 (15.78)	1740, 1305, 1140	222 (18)	95
3i	52	98	66.05 (66.23)	4.62 (4.45)		1725, 1315, 1140	218 (78)	95
3j	64	liquid	71.28 (71.00)	4.98 (4.87)		1735, 1310, 1115	202 (36)	95
3k	56	liquid	70.21 (70.35)	4.29 (4.33)		1735, 1310, 1180	188 (75)	95
4a	27	131	56.90 (56.78)	3.47 (3.25)	12.06 (11.92)	3280, 1660, 1530	232 (65)	95
4b	62	146-147	49.65 (49.88)	3.03 (3.25)	[a]30.03 (29.89)	3250, 1650, 1598	265 (58)	95
4c	44	133	59.61 (59.82)	3.64 (3.50)	[b]16.00 (15.98)	3250, 1650, 1545	221 (35)	95
4d	44	140	66.35 (66.21)	5.10 (5.23)	6.45 (6.18)	3280, 1645, 1535	217 (70)	95
4e	65	116	71.63 (71.47)	5.51 (5.45)	6.96 (6.88)	3260, 1645, 1540	201 (75)	95
4f	19	200-201	56.90 (56.65)	3.47 (3.38)	12.06 (11.99)	3240, 1660, 1545	232 (50)	95
4g	38	178	49.65 (49.42)	3.03 (3.20)	[a]30.03 (29.79)	3290, 1642, 1525	265 (26)	95
4h	42	155	59.61 (59.66)	3.64 (3.38)	[b]16.00 (15.78)	3290, 1645, 1525	221 (11)	95
4i	46	142	66.35 (66.28)	5.10 (5.29)	6.45 (6.25)	3320, 1645, 1520	217 (75)	95
4j	45	148-149	71.63 (71.58)	5.51 (5.57)	6.96 (6.68)	3280, 1640, 1530	201 (85)	95
4k	50	128	70.58 (70.65)	4.85 (4.64)	7.48 (7.66)	3270, 1658, 1540	187 (80)	95

[a] Br. [b] Cl.

ACKNOWLEDEMENT

We thank Dr. Gary Kwong of the 3M Co. for help in preparing the manuscript. This research was supported by Korea Research Foundation (KRF-2003-005-C00021).

REFERENCE

1. A. R. Katritzky and A. F. Pozharskii, “Handbook of Heterocyclic Chemistry,” 2nd ed., Pergamon, New York, 2000, p. 58.
2. ibid., p. 302.
3. ibid., p. 351.
4. C. J. Pouchert and J. Behnke, “The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra,” volume 3, 1993, p. 27.
5. C. K. Lee, J. S. Yu, and H.-J. Lee, *J. Heterocycl. Chem.*, 2002, **39**, 1207.
6. C. K. Lee, J. S. Yu, and Y. R. Ji, *J. Heterocycl. Chem.*, 2002, **39**, 1218.
7. D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.*, 1983, **14**, 1.
8. F. Ruff and I. G. Csizmadia, “Organic Reeactions, Equilibria, Kinetics, and Mechanism,” 1994, p. 164.
9. H. Lumbroso, D. M. Bertin, F. Fringuelli, and A. Taticchi, *J. Chem. Soc., Perkin Trans. 2*, 1966, 775.
10. R. J. Abraham, D. J. Chadwick, and F. A. E. G. Sancassan, *Tetrahedron*, 1982, **38**, 3245.
11. J. Bromilow, R. T. C. Brownlee, D. J. Craik, P. R. Fiske, J. E. Rowe, and M. Sadeh, *J. Chem. Soc., Perkin Trans. 2*, 1981, 753.
12. T. Yuzuri, H. Suezawa, and M. Hirota, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1664.