

MULTIVARIATE REGRESSION WITH SUBSTITUENT SHIFT INCREMENTS. III. 2,5-DISUBSTITUTED FURANS⁺Miroslav HOLÍK^{a,*}, Zdeněk FRIEDL^b and Štefan MARCHALÍN^c^a Department of Theoretical and Physical Chemistry, Masaryk University, CZ-611 37 Brno, Czech Republic; e-mail: holik@chemi.muni.cz^b Faculty of Chemistry, Technical University Brno, CZ-612 00 Brno, Czech Republic; e-mail: friedl@fch.vutbr.cz^c Department of Organic Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovak Republic; e-mail: smarchal@chtf.stuba.skReceived June 18, 1999
Accepted September 13, 1999*Dedicated to Professor Otto Exner on the occasion of his 75th birthday.*

Six series of 2-X-5-Y-substituted furans were used for multivariate regression of ¹³C NMR chemical shifts with four substituent shift increments (SSI). Some of these series were measured in CDCl₃ and DMSO-*d*₆ on different spectrometers to exclude possible sources of deviation from the general trends. Program ASSIGN was written for visual and numerical estimation of correct assignment of ¹³C NMR spectra in the series of derivatives. Multivariate regression proved that the corresponding position in benzenes and furans are not affected by the substituents in the same way: in 2-X-5-Y-substituted furans, the “*ortho*” position requires correction for the different bond order, the “*meta*” ¹³C chemical shift is probably affected by change in diamagnetic contribution of the Y group, and “*para*” position behaves like another “*ortho*” position in the molecule.

Key words: Substituent shift increments; ¹³C NMR substituent chemical shifts; Assignment of ¹³C NMR signals; Linear regression; Furans; NMR spectroscopy; Substituent effects.

For more than twenty years a single-variable regression analysis has been used to explore non-additivity of substituent shift increments (SSI) in calculating chemical shifts of *p*-disubstituted-X,Y-benzenes^{1,2}. Such an approach is equivalent to the use of the SSI as *substituent constants*; this kind of linear regression is sometimes called *proportionality relationship*¹, Eq. (1), or “*Lynch*”

+ For Parts I and II of this series see refs^{7,8}.

plot" (ref.³) according to the author¹ who introduced it to the ¹³C NMR spectroscopy.

$$\delta_{Cj} = b_0 + b_j z_j(X) + \varepsilon \quad Y \text{ fixed} \quad (1)$$

In this equation, δ_{Cj} is the carbon chemical shift for a given position j and substituent X in disubstituted benzene, b_0 is an estimate of the shift in the parent compound ($X = H$, $Y \approx H$), z_j is the SSI obtained⁴ from the ¹³C NMR chemical shift of the X -monosubstituted benzene ($Y = H$), b_j is the slope of the regression, and ε is the residual. Ideally, b_j should not differ substantially from one: if it does, an estimated parameter is biased and another explanatory variable has to be added to the regression equation. It was shown that in p -disubstituted benzenes with the fixed Y substituent possessing a group with diamagnetic anisotropy effect, a variable expressing variation of the Y group conformation caused by substituent X must be added⁵ in order to properly explain chemical shifts for proximal C_m carbon atoms. As an additional variable, σ_p or σ_r^0 can be used⁵; another choice is SSI for *para* position, z_p , which correlates very well with both σ values. Not only the diamagnetic anisotropy effect but also "the electron demand" (ref.⁶) of the substituent Y can be accounted for by an additional variable in regression equation⁷, e.g., in p -disubstituted benzenes, an additional explanatory variable for δ_{C1} is z_m if Y is an electron donor, or z_o and z_p if it is an acceptor⁸.

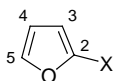
Therefore, it seems reasonable to model chemical shifts in disubstituted derivatives⁷ by regression equation of Eq. (2) possessing all SSI values, z_j , then to test the significance of the slope parameters, b_j , and finally to recalculate the regression equation only with those variables z_j for which the slope b_j is statistically significant.

$$\delta_{Cj} = b_0 + b_1 z_i + b_2 z_o + b_3 z_m + b_4 z_p + \varepsilon \quad Y \text{ fixed} \quad (2)$$

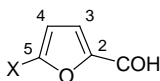
This approach proved to be usable also in the case of other than benzene aromatic. It is generally accepted, that *ortho*-SSI, i.e., z_o , cannot be used for prediction of ¹³C NMR chemical shifts in 2- X -naphthalenes^{9,10}. It is attributed to the fact that C2-C1 and C2-C3 π -bond orders in naphthalene are distinctly non-equivalent while the corresponding π -bond order in benzene is close to their mean value. However, the ¹³C chemical shifts for both C1 and C3 atoms can be predicted⁷ by proper combination of z_o and z_p values:

addition and subtraction of z_p multiples simulates the increase and decrease in the bond order between C2–C1 and C2–C3 atoms, respectively.

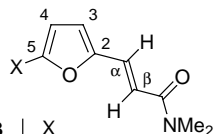
In the early days of ^{13}C NMR spectroscopy, it was assumed that the positions 3, 4, and 5 in 2-substituted furans and the *ortho*, *meta*, and *para* positions of a monosubstituted benzenes are affected by the 2-substituent in similar ways¹¹. Since our preliminary calculations with Eq. (2) in series of 2-X-5-Y-disubstituted furans gave slightly different results, we have decided to collect more such series to make our predictions statistically more significant. Now we present the results of our calculations on 2-substituted furans 1 and five series of 2-X-5-Y-disubstituted furans 2–6.



1	X
a	H
b	MeO
c	MeS
d	Cl
e	Br
f	I
g	Me
h	CH ₂ OH
i	CH=O
j	MeC=O
k	COOH
l	CN
m	NO ₂



2	X
a	Me ₂ N
b	PhS
c	Br
d	I
e	Ph
f	Me
g	H
h	PhSO ₂
i	COOMe
j	CN
k	NO ₂

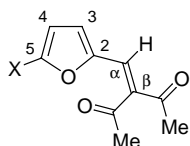


3	X
a	Me ₂ N
b	PhO
c	PhS
d	Cl
e	Br
f	I
g	Ph
h	Me
i	H
j	PhSO ₂
k	COOMe
l	CN
m	NO ₂
n	MeS
o	MeSO ₂
p	MeC=O

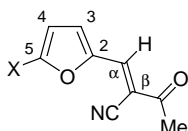
CALCULATIONS

All calculations were carried out with double precision on a PC with Pentium-S/150 MHz processor and 32 MB RAM. Standard subrutines were used for linear regression; for assignment and multivariate regression, program ASSIGN was written⁺⁺.

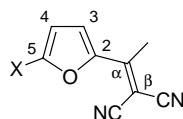
⁺⁺Listing of the ASSIGN program written in Matlab is available from the author (M. H.) on request. Matlab is a commercial product of The MathWorks Inc. Natick, U.S.A. supplied by Humusoft s.r.o., Prague.



4	X
a	Me ₂ N
b	PhS
c	Cl
d	Br
e	I
f	Ph
g	Me
h	H
i	PhSO ₂
j	COOMe
k	CN
l	NO ₂
m	MeS



5	X
a	Me ₂ N
b	PhO
c	PhS
d	Cl
e	Br
f	I
g	Ph
h	Me
i	H
j	COOMe
k	CN
l	NO ₂



6	X
a	Me ₂ N
b	PhO
c	PhS
d	Cl
e	Br
f	I
g	Ph
h	Me
i	H
j	COOMe
k	CN
l	PhSO ₂

PROGRAM ASSIGN

1. Matrix of data, $D(m,4)$, and matrix of variables, $M(m,5)$, are introduced; m is number of measurements - X derivatives - in series. Matrix D is composed from individual column vectors of chemical shifts, e.g., δ_{C5} , δ_{C4} , δ_{C3} , and δ_{C2} of furan ring. Matrix M contains four SSI vectors, i.e., z_i , z_o , z_m , and z_p with a column of 128.5s (i.e., δ_0) added as the first column into the M matrix.

2. Projection matrix $H = M(MM)^{-1}M'$ is calculated (M' being a tranpose of M matrix) and used for projecting the data matrix D (experimental values) into the matrix Q (calculated values): $Q = HM$.

3. Matrices Q and D are sorted in the ascending order and data of matrix D (rows are called sets) are plotted against selected column j (called block) of matrix Q as points together with the line obtained from plotting vector q_j against q_j (slope = 1). Since the points for different carbon atoms (blocks) are plotted in different marks (e.g., \circ , $*$, \times , $+$), it is easy to judge if the corresponding data lie properly distributed around the line with the slope one (Fig. 1). Coefficients of determination, CD, for each individual columns and also for all data taken as one vector (= total coefficient of determination), TCD, are calculated.

4. If there is a point of another column which is closer to the line than the point of column corresponding to displayed block, then it can be exchanged (e.g., in Fig. 1, in set 4, $+$ is closer to unity line of block 1 than \circ).

The improvement caused by this exchange can be checked by an increase in TCD and corresponding CDs. For calculation of new values of TCD and CDs, the program first recalculates the projection matrix \mathbf{H} and then projects unsorted corrected \mathbf{D} matrix to new matrix \mathbf{Q} . This procedure is then repeated for all the blocks (columns of \mathbf{Q}) present.

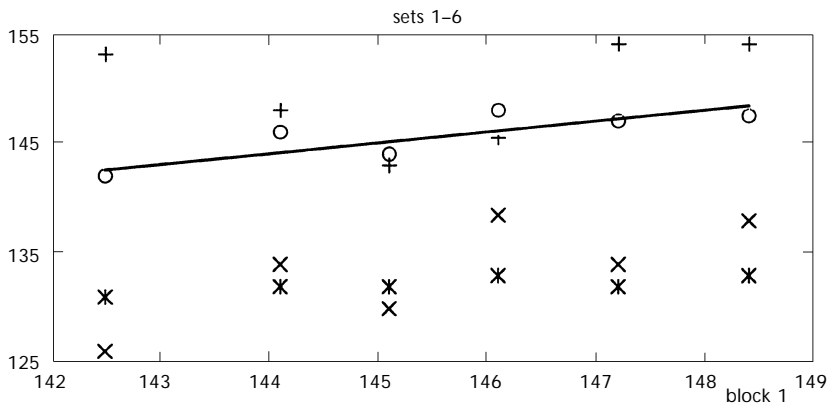
5. Finally, the matrix of parameters b_j , \mathbf{B} , calculated according to Eq. (3) is presented and all slopes are tested for their statistical significance at the 95% confidence level dividing them by corresponding standard deviation and comparing the results with critical Student's t -value: $t = b_j/s_{b_j} > t_{(0.05, m-5)}$.

$$\delta_{Cj} = b_0 \delta_0 + b_1 z_i + b_2 z_o + b_3 z_m + b_4 z_p + \varepsilon \quad \delta_0 = 128.5 \quad (3)$$

6. Then the individual equations are recalculated according to reduced Eq. (3) with only significant variables, e.g.: $\delta_{C3} = b_0 \delta_0 + b_3 z_m + b_4 z_p + \varepsilon$, $\delta_0 = 128.5$.

NMR CHEMICAL SHIFT DATA

The origin of the data used for present calculations is evident from Table I and following comments. ^{13}C NMR chemical shifts of 2-substituted furans **1**



Similarity = coefficient of determination * 100				
TCD	CD1	CD2	CD3	CD4
96.7726	71.9482	86.7180	65.2473	97.5483
97.2833	87.8222	86.7180	65.2473	99.8153

FIG. 1

An example of re-assignment procedure with ASSIGN program. \circ d_1 ; * d_2 ; \times d_3 ; + d_4

were taken from ref.^{11a} without any change; they were obtained^{11a} at 25.142 MHz on a Varian XL-100-15 spectrometer with an accuracy of ± 0.1 ppm; recently published paper^{11b} contains another derivative ($X = \text{SPh}$), unfortunately, measured in another solvent and therefore, could not be added into the investigated series. 5-X-2-furaldehydes **2**, 3-[(5-X-2-furyl)methylene]pentane-2,4-diones **4**, and 2-[(5-X-2-furyl)methylene]malononitriles **6** were measured at 500 MHz (125 MHz) on a Bruker Avance DRX-500 spectrometer ($c = 0.1 \text{ mol dm}^{-3}$) and standardized on the central peak of solvent used¹²: CDCl_3 δ 76.91, $\text{DMSO}-d_6$ δ 39.56. Alternatively, ^{13}C NMR spectra of **2**, **4**, and 2-acetyl-3-(5-X-2-furyl)prop-2-enitriles **5** were measured at 75.426 MHz on a Varian VXR 300 spectrometer under conditions given in ref.¹³. Chemical shifts of 3-(5-X-2-furyl)-*N,N*-dimethylprop-2-enamides **3** were taken from Table III in ref.¹⁴, but in five spectra the signals were re-assigned using program ASSIGN and 2D-heterocorrelated NMR experiments; new assignments are collected in Table II. After these changes, the data gave mostly better coefficients of determination: C5 (0.9299 \rightarrow 0.9412), C4 (0.9339 \rightarrow 0.9216), C3 (0.2792 \rightarrow 0.7006), and C2 (0.8260 \rightarrow 0.9483).

RESULTS AND DISCUSSION

For the ^{13}C chemical shifts on *ipso* carbon atom (C2 in **1**, C5 in others) almost all measured sets gave a good regression with z_i increments only when z_m variable is also included. Only in the case of series **6**, the slope b_3 in the

TABLE I
Sets of chemical shifts data and measurement conditions used

Experiment	Series	Solvent	Spectrometer	Reference
A	1	acetone- d_6	V 100	ref. ¹¹
B	2	CDCl_3	B 500	Table III
C	2	CDCl_3	V 300	ref. ¹⁵
D	3	CDCl_3	J 60	ref. ¹⁴
E	4	CDCl_3	V 300	ref. ^{15,16}
F	4	$\text{DMSO}-d_6$	V 300	ref. ^{15,16}
G	4	$\text{DMSO}-d_6$	B 500	Table IV
H	5	CDCl_3	V 300	ref. ¹³
I	5	$\text{DMSO}-d_6$	V 300	ref. ¹⁵
J	6	CDCl_3	B 500	Table V ref. ¹⁷

regression equation is only significant at the 90% confidence level. For series **4** measured on a Bruker spectrometer, also the slope at z_p was significant at 95% but not at 99% level. These two exceptions from the general trend point out to variations caused probably by sample selection.

In the *p*-disubstituted (X,Y)benzene series⁸ significantly negative b_3 slope was also observed, but only when Y substituent was an electron donating

TABLE II
Corrected assignments^a of several derivatives of **3** (original data in ref.¹⁴)

3	X	C5	C4	C3	C2	C _a	C _b
c	PhS	145.06 ^a	121.16 ^b	115.25 ^b	154.99 ^a	128.43	116.49
g	Ph	155.29	107.73	116.23 ^c	151.26	129.10	114.42 ^c
j	PhSO ₂	150.32	119.40 ^d	113.93 ^d	156.31	127.86	120.11
n	MeS	153.53 ^e	115.00 ^f	115.52 ^f	150.15 ^e	128.58	114.87
o	MeSO ₂	149.80	119.40 ^g	113.86 ^g	156.12	127.86	120.24

^a Values assigned by the same letter were interchanged.

TABLE III
Chemical shift data of 5-X-2-furaldehydes **2** (experiment B)

2	X	C5	C4	C3	C2	C _α	H4	H3	H _α
a	Me ₂ N	163.99	86.06	131.77	144.22	170.49	5.24	7.20	8.95
b	PhS	153.70	116.99	121.65	154.50	176.89	6.57	7.21	9.57
c	Br	130.79	114.58	122.32	154.39	176.14	6.57	7.19	9.54
d	I	98.92	123.07	122.16	157.88	175.98	6.78	7.11	9.51
e	Ph	159.24	107.50	123.30	151.89	177.02	6.82	7.29	9.63
f	Me	158.24	109.24	123.61	151.62	176.58	6.25	7.19	9.50
g	H	147.93	112.40	120.88	152.80	177.72	6.62	7.27	9.67
h	PhSO ₂	153.83	117.60	118.48	154.54	178.19	7.24	7.30	9.71
i	COOMe	153.79	118.51	118.66	158.27	178.79	7.27	7.27	9.81
j	CN	129.29	122.80	122.48	154.44	177.49	7.27	7.32	9.78
k	NO ₂	152.93	111.62	118.90	150.82	178.15	7.45	7.39	9.84

TABLE IV
Chemical shift data of 3-[(5-X-2-furyl)methylene]pentane-2,4-diones **4** (experiment G)

4	X	C5	C4	C3	C2	C _α	C _β	CO-E	CO-Z	Me-E	Me-Z
a	Me ₂ N	163.12	87.40	124.56	129.19	127.69	139.22	194.45	204.37	25.53	31.76
b	PhS	147.72	120.27	120.55	151.83	124.28	138.75	196.62	203.28	25.95	30.57
c	Cl	139.48	110.58	120.92	148.56	124.12	138.09	196.64	203.44	25.93	30.90
d	Br	127.08	115.36	120.99	150.70	123.99	138.11	196.63	203.44	25.92	30.69
e	I	99.36	123.43	120.91	153.63	123.74	138.08	196.56	203.46	25.91	30.96
f	Ph	157.06	109.23	121.57	148.25	124.88	137.46	196.54	204.00	25.86	31.07
g	Me	157.37	109.96	120.65	147.28	125.12	136.53	196.44	203.86	25.82	30.96
h	H	147.59	113.20	119.01	148.66	123.18	137.80	196.70	203.66	25.89	31.14
i	PhSO ₂	151.13	118.54	119.39	152.91	124.64	138.60	196.77	202.90	26.11	30.64
j	COOMe	145.81	119.90	118.94	151.58	125.19	141.00	196.83	203.29	26.13	30.70
k	CN	126.92	123.40	118.41	152.97	123.38	141.55	196.89	203.15	26.15	30.90
l	NO ₂	152.66	114.16	119.77	150.39	124.30	142.46	196.76	202.96	26.26	30.65
m	MeS	153.70	112.93	121.15	149.66	124.38	136.99	196.44	203.77	25.84	31.13

group and the absolute value of b_3 was less than one. Since the Y group in our 2-X-5-Y-disubstituted furans **1–6** is rather an electron withdrawing substituent, then the large negative slope at z_m probably reflects a specific modification of Y substituent by the furan ring.

Chemical shift of *ortho* carbon atom in *p*-disubstituted (X,Y)benzenes significantly⁸ depends only on z_o . However, in 2-substituted naphthalenes⁷, chemical shifts in both *ortho* positions can be explained by a regression with z_o and z_p variables; positive slope +0.52 for δ_{C1} and negative slope -0.49 for δ_{C3} follow the increase and decrease in the *ab initio* bond order between C2–C1 (1.535) and C2–C3 (1.331) atoms, respectively, as compared with benzene CC bond (1.432). In furans **1–6**, the ¹³C chemical shift in *ortho* position to the X-substituent (C3 in **1**, C4 in others) needs, besides z_o , also z_p in regression. The values of b_4 in the range 0.728–1.051 correspond very well to the increase in the bond order; in furan, the C2–C3 bond order has been calculated as 1.660.

Position *meta* in furans **1–6** (C4 in **1**, C3 in others) substantially differs from that in substituted benzenes; the corresponding ¹³C chemical shift does not depend on the z_m increment but on the z_p one. Generally, the

TABLE V
Chemical shift data of 2-[(5-X-2-furyl)methylene]malononitriles **6** (experiment J)

6	X	C5	C4	C3	C2	C $_{\alpha}$	C $_{\beta}$	CN-Z	CN-E
a	Me ₂ N	164.95	91.41	133.25	140.29	134.89	59.51	116.33	117.59
b	PhO	164.14	91.66	127.72	139.99	141.07	72.27	113.18	114.50
c	PhS	157.69	116.33	124.68	149.44	141.19	76.00	112.61	113.90
d	Cl	147.26	111.56	124.75	145.29	141.46	77.54	112.16	113.39
e	Br	149.63	116.54	124.60	132.34	141.39	77.70	112.18	113.38
f	I	100.67	124.34	125.08	153.00	141.10	77.80	112.20	113.37
g	Ph	161.37	109.36	126.24	147.21	141.18	75.43	113.28	114.27
h	Me	161.80	111.64	125.51	146.91	142.06	74.62	112.90	114.21
i	H	149.40	114.27	123.33	147.91	142.91	77.36	112.43	113.63
j	COOMe	148.52	119.61	121.83	149.41	143.13	82.05	111.77	112.76
k	CN	130.20	120.88	123.52	150.32	141.73	83.80	111.31	112.30
l	PhSO ₂	155.01	118.04	121.89	150.25	142.11	82.86	111.40	112.54

TABLE VI
Regression parameters, correlation coefficients, and standard deviation of data for C_{ipso} carbon atoms

C_{ipso}	Experiment	b_0	b_1	b_3	b_4	r	s_y
1	A	1.120	1.008	-10.339		0.9858	19.12
2	B	1.168	0.939	-10.426		0.9893	19.08
2	C	1.139	0.905	-6.578		0.9657	18.05
3	D	1.108	0.960	-7.392		0.9691	17.51
4	E	1.126	0.940	-7.145		0.9684	18.19
4	F	1.124	0.880	-6.980		0.9703	17.12
4	G	1.142	0.915	-9.478	(-0.341) ^a	0.9963	17.21
5	H	1.144	0.879	-7.395		0.9564	18.83
5	I	1.140	0.850	-6.363		0.9640	17.58
6	J	1.145	0.961	(-5.329) ^b		0.9679	18.75

Parameters b calculated according to reduced Eq. (3) which are significant by Student t -test at the 95% confidence level. ^a Not significant at the 99% level; ^b significant at the 90% level.

TABLE VII
Regression parameters, correlation coefficients, and standard deviation of data for C_{ortho} carbon atoms

C_{ortho}	Experiment	b_0	b_2	b_4	r	s_y
1	A	0.870	1.309	1.381	0.9576	10.98
2	B	0.880	1.177	0.886	0.9859	10.19
2	C	0.875	1.248	0.882	0.9597	11.38
3	D	0.887	1.206	1.051	0.9598	10.94
4	E	0.885	1.232	0.858	0.9736	10.70
4	F	0.890	1.198	0.942	0.9742	10.83
4	G	0.891	1.110	0.901	0.9699	9.28
5	H	0.888	1.188	0.728	0.9756	10.65
5	I	0.891	1.218	0.810	0.9855	11.06
6	J	0.889	1.159	0.804	0.9797	10.81

Parameters b calculated according to reduced Eq. (3) which are significant by Student t -test at the 95% confidence level.

TABLE VIII
Regression parameters, correlation coefficients, and standard deviation of data for C_{meta} carbon atoms

C_{meta}	Experiment	b_0	b_3	b_4	r	s_y
1	A	0.870	0.734	0.147	0.6878	0.96
2	B	0.951		-0.680	0.9183	3.66
2	C	0.953		-0.635	0.9334	3.19
3	D	0.896		-0.220	0.7204	1.49
4	E	0.930		-0.383	0.9345	1.96
4	F	0.937		-0.315	0.8973	1.68
4	G	0.937		-0.301	0.8933	1.57
5	H	0.960		-0.616	0.9642	3.09
5	I	0.965	(1.734) ^a	(-0.196) ^b	0.6218	2.41
6	J	0.965		-0.674	0.9629	3.27

Parameters b calculated according to reduced Eq. (3) which are significant by Student t -test at the 95% confidence level. ^a Significant only at the 90% level; ^b significant only at the 80% level.

TABLE IX
Regression parameters, correlation coefficients, and standard deviation of data for C_{para} carbon atoms

C_{para}	Experiment	b_0	b_1	b_2	b_4	r	s_y
1	A	1.128		0.440	0.587	0.9504	4.17
2	B	1.193		0.558		0.8968	3.80
2	C	1.187		0.574		0.9635	3.80
3	D	1.191		0.402	0.445	0.9643	4.03
4	E	1.166		0.437	0.372	0.9593	4.13
4	F	1.166		0.436	0.403	0.9620	4.24
4	G	1.159	(0.122) ^a	1.014	0.558	0.9803	6.25
5	H	1.162		0.471	0.243	0.9778	4.04
5	I	1.160		0.459	0.302	0.9770	4.20
6	J	1.154		0.459	(0.217) ^b	0.9489	3.92

Parameters b calculated according to reduced Eq. (3) which are significant by Student t -test at the 95% confidence level. ^a Not significant at the 99% level; ^b significant only at the 90% level.

variance of the shift data is relatively small (standard deviation, s_y , is below two); these results can be questioned, but in a few cases with higher variance, the trend is obvious. In *p*-disubstituted (X,Y)benzenes, a negative slope at the variable for *para* position either confirms the donor character⁸ of the Y substituent or reflects a contribution of diamagnetic anisotropy due to changing the position of the multiple bond in Y group^{5b} relative to the plane of the ring. Since chemical shifts of β carbon in the Y substituent of **3–6** correlate very well with z_p increments, different polarization of the $C_\alpha=C_\beta$ bond can be expected and the diamagnetic anisotropy field around it can be changed with variation of the X substituent.

Not less interesting results were found in regression of ¹³C chemical shifts of C5 in **1** and C2 in others furans. They correlate both with z_o and z_p making from this position another “*ortho*” position to substituent X, however, with slopes about half of those in Table VII.

CONCLUSIONS

Multivariate regression proved that the corresponding position in benzenes and furans are not affected by substituents in the same way: in 2-X-5-Y-substituted furans, the “*ortho*” position requires correction on the different bond order, the “*meta*” ¹³C chemical shift is probably affected by change in diamagnetic contribution of the Y group, and “*para*” position behaves like another *ortho* position in the molecule. These general findings are not substantially affected either by change of NMR solvent (CDCl₃ for DMSO-*d*₆) or by the spectrometer frequency and quality. Program ASSIGN based on the multivariate regression can be used to check and eventually improve the assignment of ¹³C NMR chemical shifts in a series of compounds with one variable and one fixed substituent.

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REFERENCES

1. Lynch B. M.: *Can. J. Chem.* **1977**, *55*, 541.
2. Holík M.: *Org. Magn. Reson.* **1977**, *9*, 491.
3. a) Membrey F., Ancian B., Doucet J.-P.: *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391; b) Chandrasekaran R., Perumal S., Wilson D. A.: *Magn. Reson. Chem.* **1987**, *25*, 1001.
4. Ewing D. F.: *Org. Magn. Reson.* **1979**, *12*, 499.
5. a) Holík M., Matějková B.: *Collect. Czech. Chem. Commun.* **1990**, *55*, 261; b) Holík M.: *Chemom. Intell. Lab. Syst.* **1993**, *19*, 225.

6. Bromilow J., Brownlee R. T. C., Craik D. J., Sadek M., Taft R. W.: *J. Org. Chem.* **1980**, *45*, 2429.
7. Holík M.: *Collect. Czech. Chem. Commun.* **1996**, *61*, 713.
8. Holík M.: *J. Mol. Struct.* **1999**, 482–3, 345.
9. Craig D. J., Ternai B.: *Org. Magn. Reson.* **1981**, *15*, 268.
10. Johnels D., Edlund U., Johansson E., Wold S.: *J. Magn. Reson.* **1983**, *55*, 316.
11. a) Gronowitz S., Johnson I., Hörnfeldt A.-B.: *Chem. Scr.* **1975**, *7*, 211; b) Alvarez-Ibarra C., Quiroga-Feijoo M. L., Toledano E.: *J. Chem. Soc., Perkin Trans. 2* **1998**, 679.
12. a) Levy G. C., Cargioli J. D.: *J. Magn. Reson.* **1972**, *6*, 143; b) Günther H.: *NMR Spectroscopy, Basic Principles, Concepts, and Applications in Chemistry*, 2nd ed., p. 532. Wiley, New York 1995.
13. Marchalín Š., Mamani L. N. H., Ilavský D., Prónayová N., Leško J.: *Collect. Czech. Chem. Commun.* **1993**, *58*, 1388.
14. a) Friedl Z., Böhm S., Goljer I., Piklerová A., Poórová D., Ríčková A., Kováč J.: *Collect. Czech. Chem. Commun.* **1987**, *52*, 409; b) Holík M., Friedl Z.: *Proceedings of CHEMOMETRICS IV Conference*, p. 91. Masaryk University, Brno 1996.
15. Marchalín Š.: Unpublished ¹³C NMR data are available on request.
16. Marchalín Š., Ilavský D., Kováč J.: *Z. Chem.* **1987**, *27*, 406.
17. a) Musumarra G., Ballistreri F. P.: *Chem. Scr.* **1981**, *18*, 209; b) Ilavský D., Goljer I., Kováč J.: *Z. Chem.* **1990**, *30*, 99.