NUCLEAR MAGNETIC RESONANCE SPECTRA OF FURAN DERIVATIVES OF IV B GROUP ELEMENTS* (REVIEW)

Yu. Popelis and É. Lukevits

Electronic and steric effects in furan derivatives were studied by the method of ^{1}H, ^{13}C, ^{17}O, and ^{29}Si NMR spectroscopy. The characteristic features of the influence of substituents on the screening and spin–spin interaction of ring nuclei in α-substituted derivatives of furan in the presence of a second α-substituent have been noted.

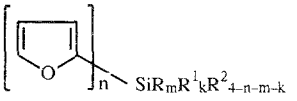
The studies in the field of chemistry, physical chemistry, and biology of furan derivatives with IV B group elements in the substituent, initiated at the institute of Organic Synthesis in 1960, have been greatly extended during the last 8 years — the characteristic features of their electronic and steric structure have been studied by the method of NMR spectroscopy. The increased interest in these compounds was due especially to the fact that many of them have neurotropic activity. Moreover, the furan derivatives are convenient models for the determination of the application limits of multinuclear magnetic resonance in studying electronic effects in organic compounds.

1. INFLUENCE OF SUBSTITUENTS ON THE MAGNETIC SCREENING OF ^{1}H, ^{13}C, ^{17}O, AND ^{29}Si NUCLEI IN MONO- AND α,α′-DISUBSTITUTED

1.1 Derivatives of (2-Furyl)silane

The parameters of ^{1}H spectra of α-substituted furans are distinguished by a certain uniqueness if the silicon atom is bound to the furan ring [1-3]. When the tert-butyl substituent is exchanged by trimethylsilyl, all the ring protons are descreened, although a shift of these signals to stronger fields could be expected (because of the lower electronegativity of silicon with respect to carbon). This effect is presumably caused by a (π–d)π-interaction between vacant d-orbitals of silicon and the π-electrons of the furan ring.

A quantitative characterization of the influence of the number of the furyl groups and other substituents at the silicon atom on the magnetic screening of the ring atoms in mono-, di- and tri- (2-furyl)silanes of type (I) was carried out by comparing the chemical shifts (CS) of the ring ^{1}H and ^{13}C with the sum of the Taft inductive constants σ^{*} of the substituents different from 2-furyl (substituents R were also selected which are not capable of undergoing the (π–d)π-interaction):



I

R = H, CH_3, C_2H_5, C_4H_9, CH_2Cl, $CH{=}CH_2$, C_6H_5, OC_2H_5, 2-thienyl; n, m = 1, 2, 3; k = 1, 2

*Dedicated to Prof. A. R. Katritsky on his 65th birthday.

Latvian Institute of Organic Synthesis, Riga LV-1006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 879-890, July, 1993. Original article submitted June 10, 1993.

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TABLE 1. Parameters of Correlations Linking the Chemical Shifts δ of the Ring ^1H and ^{13}C in 2-Furylsilanes with the Sum of Taft Inductive Constants σ^* ($\delta = A + B\Sigma\sigma^*$)

Nucleus*1	A	B	r*2	s*3
		(2-Furyl)silanes		
H_3	6,63 ± 0,03	0,14 ± 0,07	0,854	0,05
C_2	159,9 ± 0,9	-5,8 ± 2,3	0,931	0,23
C_3	120,3 ± 0,4	2,5 ± 0,9	0,925	0,25
		Di(2-furyl)silanes		
H_3	6,72 ± 0,03	0,19 ± 0,06	0,915	0,08
H_4	6,35 ± 0,03	0,10 ± 0,06	0,789	0,06
H_5	7,65 ± 0,03	0,09 ± 0,05	0,805	0,07
C_2	155,8 ± 0,9	-4,4 ± 1,5	0,900	1,01
C_3	122,5 ± 0,4	2,2 ± 0,7	0,915	0,72
C_4	110,1 ± 0,1	0,4 ± 0,2	0,852	0,33
C_5	147,8 ± 0,2	1,1 ± 0,3	0,929	0,51
		Tri(2-furyl)silanes		
H_3	6,84 ± 0,04	0,20 ± 0.03	0,893	0,01
C_2	153,4 ± 0,9	-3,2 ± 0,6	0,850	0,07
C_3	124,4 ± 0,4	1,7 ± 0,3	0,807	0,06
C_4	110,3 ± 0,1	0,40 ± 0,04	0,993	0,01
C_5	148,6 ± 0,2	0,8 ± 0,2	0,838	0,04

*1The correlation coefficients for chemical shifts of nuclei not indicated in Table 1 are lower than 0.7.

*2Correlation coefficient.

*3Standard deviation.

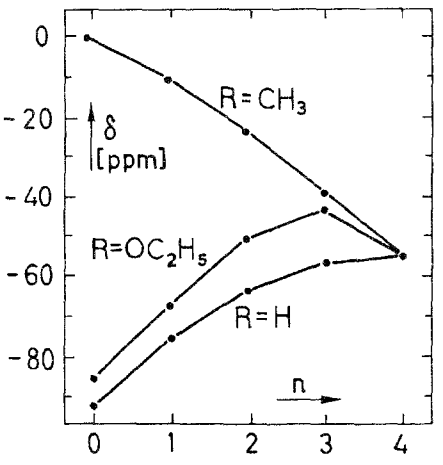


Fig. 1. Dependence of $\delta^{29}Si$ on the number of furyl groups (n) in (2-furyl)-R-silanes.

The existence in each series of compounds (with a given n) of these correlations for most of the ^1H and ^{13}C ring nuclei indicates that within this set, the nonfuryl substituents at Si influence the screening of ring atoms by an inductive mechanism. Increase in σ^* results in descreening of the ^1H and ^{13}C ring atoms (apart from C_2), such that the inductive influence of the substituents at the silicon on the screening of furan atoms is realized mainly by polarization of the ring π-electrons.

However, the sensitivity of the CS of all the protons and the C_4 and C_5 carbons to the inductive effects of the substituents increases with increase in the number of furyl groups and decreases with the distancing of the corresponding nucleus from the Si atom. The observed changes in CS of the ring nuclei may be explained within the scope of the $(\pi-d)\pi$-

TABLE 2. Parameters of Correlations Linking the Chemical Shifts of the Ring ^1H and ^{13}C in the Series of 2,5-Disubstituted Furans $\delta(2.5)$ and in 2-Substituted Furans $\delta(2)$ [$\delta(2.5) = K + M\,\delta(2)$]

Nucleus[1]*	K	M	r2*	s3*	K	M	r	s
	$X^{4*} = NO_2$ n = 9[5*]				X = $Si(CH_3)_3$ n = 6			
H_3	1,3	0,9	0,961	0,53	0,7	0,9	0,971	0,52
H_4	3,0	0,7	0,792	0,18	0,7	0,9	0,979	0,70
C_2	30,4	0,8	0,982	7,0	0,7	1,0	0,998	9,94
C_3	18,0	0,9	0,964	4,6	1,3	0,9	0,992	6,80
C_4	-	-	0,332	-	43,5	1,7	0,887	1,1
C_5	-	-	0,461	-	-9,9	1,2	0,947	3,4
	X = $Ge(CH_3)_3$ n = 6				X = $COOCH_2CF_3$ n = 6			
H_3	0,8	0,9	0,952	0,09	1,9	0,7	0,954	0,04
H_4	4,2	0,4	0,745	0,13	6,1	0,2	0,914	0,11
C_2	-15,8	1,1	0,999	7,14	-17,1	1,1	0,928	11,77
C_3	3,8	0,9	0,999	6,83	27,9	0,8	0,903	4,12
C_4	43,7	0,8	0,916	1,20	28,3	0,8	0,906	1,09
C_5	-17,6	1,3	0,906	0,54	11,2	0,9	0,993	2,24
	X = CH=NOH (Z) n = 6				X = CH=NOH (E) n = 6			
H_3	1,4	0,8	0,925	0,06	1,9	1,3	0,912	0,63
H_4	4,7	0,4	0,948	0,16	3,5	0,5	0,827	0,21
C_2	2,5	1,0	0,997	7,44	6,2	1,0	0,996	9,07
C_3	8,3	0,9	0,983	4,17	-14,7	1,1	0,997	3,16
C_4	-2,3	1,1	0,971	0,58	-25,8	1,3	0,981	1,15
C_5	13,7	0,9	0,928	2,31	-4,1	1,6	0,902	0,76

*[1]The correlation coefficients for chemical shifts of nuclei not indicated in Table 1 are lower than 0.7.

*[2]Correlation coefficient.

*[3]Standard deviation.

*[4]Fixed substituent.

*[5]Number of compounds in the series.

interaction between the Si atom and the furan ring. At the same time, this pattern of change of the numerical values of the angular coefficients in the correlations shows that on changing the number of the acceptor furyl groups in the molecule, the influence of this interaction is apparently nonadditive, since the configuration of the d-orbitals of silicon permits the existence of only one (π-d)π-bond. As a result, with increase in the number of the furyl groups at Si, the probability of the participation of each of the rings in this interaction decreases.

The somewhat different character of change in the CS of the ring C_2 and C_3 atoms under the influence of the inductive properties of the substituents or on changing the number of the furyl groups [a decrease in the CS of C_2 with increase in σ^* is observed and also a decrease in the sensitivity of CS of C_2 and C_3 to the inductive effect of the substituents on transition from tri(2-furyl)silane to (2-furyl)silanes] can be explained on the basis of the supposition that the screening of these atoms is due to a larger extent to the π-inductive effect of the central atom, and due to a lesser extent to a change in the electron density on this carbon atom on changing the substituents at Si; with increase in the number of furyl groups this effect diminishes.

The chemical shifts of ^{29}Si nuclei of the organosilicon compounds we studied change on gradual exchange of the furyl groups by other substituents forming characteristic slacking curves, the course of which depends on the difference between the electron-acceptor or electron-donor properties of the attached substituents and furan (Fig. 1). At the same time, increase in the number of the acceptor furyl groups in (2-furyl)methyl silanes additively increases the electronic density on silicon. However, the absence of a linear dependence between the chemical shifts of ^{29}Si and the value of the charge makes it impossible to use the former for the analysis of the electronic effects during a change of the substituent in the first coordination effects during a change of the substituent in the first coordination sphere.

TABLE 3. Values of Certain ΔH_i and ΔC_i Increments for Fixed Substituents X in 2,5-Disubstituted Furans

R	X			
	NO_2	CH_3	$Si(CH_3)_3$	$Ge(CH_3)_3$
		ΔH_4; ΔH_3		
CH_3	1,29; 0,54	-0,38; -0,14	0,40; 0,07	0,25; 0,03
H	1,25; 0,48	-0,40; -0,13	0,31; 0,03	0,29; 0,11
$Si(CH_3)_3$	0,87; 0,08	-0,36; -0,04	0,24; -0,04	0,10; -0,04
CHO	1,01; 0,21	—	0,21; -0,06	0,04; -0,08
NO_2	1,06; 0,29	-0,34; -0,09	-0,09; -0,38	—
CH=CH—COOH	1,02; 0,33	-0,37; -0,12	0,22; -0,04	0,09; -0,09
$CH=NNHCONH_2$	1,37; 0,41	-0,23; -0,17	0,42; 0,0	0,34; -0,01
$COOCH_2CF_3$	0,85; 0,07	-0,39; -0,08	—	0,08; -0,03
		ΔC_5; ΔC_4		
CH_3	9,6; 3,8	—	16,8; 9,5	19,8; 9,8
H	8,9; 4,2	—	16,4; 10,2	21,9; 10,4
$Si(CH_3)_3$	10,0; 2,0	—	17,7; 10,1	18,3; 8,6
NO_2	3,0; 1,2	—	20,2; 8,5	—
CH=CH—COOH	5,8; -1,3	3,5; -6,0	17,5; 7,0	18,9; 5,4
$CH=NNHCONH_2$	6,8; 0,9	4,4; -2,8	17,1; 10,2	18,1; 9,1

TABLE 4. ^{17}O NMR Parameters of α-Substituted Furans ($CDCl_3$, 313 K)

R	Ring hetero atom		$q\pi(O)$*1	
	$\delta^{17}O$, ppm	$\Delta\nu_{1/2}$, Hz	CNDO/2	*Ab initio*
NO_2	231,1*2	260	0,235	0,288
CHO	235,9*3	150	0,260	0,287
H	237,5	100	0,273	0,290
$C(CH_3)_3$	237,5	130	0,222	0,287
CH_2NH_2	237,7	140	—	—
$COOCH_3$	238,8*4	240	0,261	—
CH_2OH	239,2*5	190	0,255	0,288
$C\equiv N$	243,7	110	0,255	0,289
CH_3	249,6	90	0,252	0,283
Br	249,6	160	—	—
$Si(CH_3)_3$	252,7	150	0,233*6	—

*1The π-charge density of the ring hetero atom was calculated by the CNDO/2 method (our data) or ab initio (the data were taken from the literature [8]).

*2The NO_2 signal 558.6 ppm.

*3The C=O signal 528.0 ppm.

*4The C=O signal 325.9 ppm.

*5The OH signal 4.6 ppm.

*6The charge of oxygen $q_\pi O$ in the spd-basis is 0.264.

TABLE 5. ^{17}O NMR Parameters of Heteroorganic Furan Derivatives*

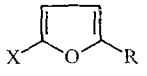
Compound	$\delta^{17}O$, ppm	$\Delta\nu_{1/2}$, Hz	Compound	$\delta^{17}O$, ppm	$\Delta\nu_{1/2}$, Hz
R—H	237,5	100	R—SiH(CH$_3$)(C$_4$H$_3$S)**	253,4	230
R—CH$_3$	244,8	90	R$_2$—SiH$_2$	253,8	180
R—SiH$_3$	255,3	130	R$_2$—Si(CH$_3$)$_2$	253,2	290
R—C(CH$_3$)$_3$	237,5	130	R$_2$—SiH(CH$_3$)	253,2	200
R—Si(CH$_3$)$_3$	252,7	150	R$_2$—SiH(C$_2$H$_5$)	253,6	250
R—Si(OC$_2$H$_5$)$_3$	250,5	310	R$_2$—SiH(C$_4$H$_9$)	254,2	260
R—Ge(CH$_3$)$_3$	252,3	110	R$_2$—Si(CH$_3$)CH$_2$Cl	252,3	330
R—Sn(CH$_3$)$_3$	259,3	230	R$^1_2$—SiH(CH$_3$)	250,2	170
R—SiH(CH$_3$)$_2$	253,0	150	R$_3$—SiH	252,7	350
R—SiH(CH$_3$)C$_2$H$_5$	253,6	200	R$_3$—SiCH$_3$	252,7	300
R—SiH(C$_2$H$_5$)$_2$	254,2	170	R$_3$—SiC$_2$H$_5$	252,9	400
R—SiH(CH$_3$)C$_4$H$_9$	254,0	200	R$_3$—SiC$_4$H$_9$	253,8	590
R—SiH(C$_4$H$_9$)$_2$	254,2	240	R$_4$—Si	253,2	410
R—SiH(CH$_3$)C$_6$H$_5$	253,6	350			

*R = furyl, R^1 = 3-furyl.
**C$_4$H$_3$S - the 2-thienyl group.

Decrease of the chemical shifts of ^{13}C of the Si(CH$_3$)$_3$ substituent in (2-furyl)methylsilanes with increase in the number of the furyl groups is, as expected, accompanied by a decrease in the electron density on this atom, which is characteristic for the inductive effect of neighboring groups. The deviation from the linearity of the shift-charge correlation can be possibly explained by the influence of the above mentioned $(\pi-d)\pi$-effect.

1.2. 2,5-Disubstituted Furans

The effectiveness of the influence of the substituents on the screening of the ring nuclei depends not only in the number of the furyl groups, but also on the change in the electronic properties of the heterocyclic ring when a second α-substituent appears in them. We therefore studied the ^1H and ^{13}C NMR parameters of certain groups of 2,5-disubstituted furans (II) [3-6]:



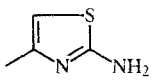
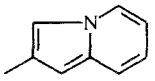
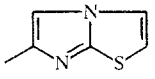
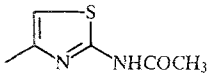
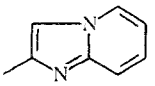
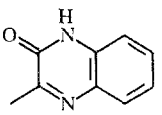
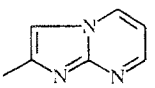
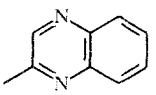
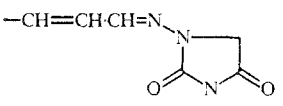
II

X = CH$_3$, NO$_2$, COOC$_2$H$_5$, CH=NOH, Si(CH$_3$)$_3$, Ge(CH$_3$)$_3$; R = NO$_2$, C≡N , CHO, COCH$_3$, CF$_3$, COOCH$_3$, COOH, CONH$_2$, CHCl$_2$, I, Si(CH$_3$)$_3$, CH$_3$, CH=CH-CONH$_2$, CH=CH-COOH, CH=CHCHO, CH=NNH(CO)NH$_2$, COOH, CH=NNH(CS)NH$_2$, Br, CH=NN(CONH$_2$)CH$_2$COOH, CH(OC$_2$H$_5$)$_2$, Sn(CH$_3$)$_3$, Cl, Ge(CH$_3$)$_3$, CH$_2$NH$_2$, CH=NNH$_2$, CH$_2$N$^+$(CH$_3$)$_3$I$^-$

From the satisfactory correlation of CS of the ring nuclei in (II) with those in 2-substituted furans (see Table 2) it was stipulated that the susceptibility of the screening to the influence of substituents R is determined by the electronic properties of the second substituent X: The acceptor groups reduce the electron density on the ring atoms, and as a result lower the sensitivity of the CS. In methylfurans there are no such decreases in sensitivity. For the H_4, C_4 and C_5 derivatives II (X = NO_2), there are practically no correlations with CS in 2-substituted furans. This is explained by the fact that for nitrofurans the rotation of the nitro groups around the C_5-N bond changes according to the electronic properties of substituents R.

The sensitivity and the character of the change in the screening of the ring nuclei due to substituents R changes qualitatively if a heteroorganic substituent is present in the second α-position of the ring. Compared with the 2-substituted furans, the sensitivity of the CS of protons to the resonance effects increases in derivatives of trimethylsilylfuran and is greater still in trimethylgermylfurans.

TABLE 6. σ_p^+ Values of Substituents Calculated from Chemical Shifts of H_5 Protons in 2-Substituted Furans

Substituent	δH_5, ppm	σ_p^+, calc	Substituent	δH_5, ppm	σ_p^+, calc
	7,48	0,03	—CH=NNHCONH$_2$	7,66	0,29
	7,50	0,06	—CH=CHCOCH$_3$	7,70	0,34
			—CH=NNHC(S)NH$_2$	7,71	0,36
	7,51	0,07	—CH=CH—COOH	7,74	0,40
			—Si(CH$_3$)$_3$	7,74	0,40
	7,55	0,13	—Ge(CH$_3$)$_3$	7,75	0,41
			—Sn(CH$_3$)$_3$	7,79	0,47
—COC(CH$_3$)=NOH (*E*)	7,55	0,13	—COC$_2$H$_5$	7,78	0,46
	7,58	0,17	—CH=CH—CHO	7,80	0,48
—COC(C$_2$H$_5$)=NOH (*Z*)	7,60	0,20		7,85	0,56
	7,62	0,23		7,86	0,57
	7,63	0,24	—COCH=NOH (*E*)	7,91	0,64
—CH=NOH (*Z*)	7,63	0,24	—COC(Cl)=NOH	7,96	0,71
—CH=NN(CONH$_2$)CH$_2$COOH	7,64	0,25	—COCOOH	8,03	0,81

The effectiveness of the influence of certain substituents on the CS of the ring nuclei of substituted furans was evaluated from ΔH_i and ΔC_i increments for four fixed substituents X = NO_2, CH_3, $Si(CH_3)_3$ and $Ge(CH_3)_3$ in various 2,5-disubstituted furans.

The increments for the CH_3 group in 2-substituted methylfurans vary little. Hence, in the methylfuran derivatives the influence of the substituents on the CS of the ring protons is additive. The considerable scattering of the increment values for other X means that the NO_2, $Si(CH_3)_3$ and $Ge(CH_3)_3$ groups change the properties when the variable α-substituent is changed. Decrease of the increments by the acceptor substituents R in the nitrofuran derivatives means that the intensification of the electron acceptor properties of R results in an increase in the rotation of the nitro group relative to the furan plane. Then, the lower the conjugation between the hetero ring and the nitro group, the weaker is its ability to draw the electrons to itself and the smaller the increments.

On the contrary, increase in the electron donor properties of R leads to increase in ΔH_i and ΔC_i, and hence can be explained by the maximal flattening of the nitrofuran molecules. To this was later related the fact that the CS of oxygen in furan and the nitro group in 2-substituted derivatives of nitrofurans changes on transition from acceptor (NO_2) to donor (CH_3) substituents. The irregularity of the influence of the $Si(CH_3)_3$ and $Ge(CH_3)_3$ groups on the CS of the ring ^1H cannot be caused by a change in the conformation of the molecule, and therefore the scattering of their increments can be explained by the change in the contribution of the $(\pi-d)\pi$-interaction of the central atom of substituent X with the furan ring when the variable substituent R is varied. Within the whole series of R the increments for $Ge(CH_3)_3$ are smaller than the increments for the $Si(CH_3)_3$ group. This agrees with the lower effectiveness of the $(\pi$-d$)\pi$-binding in the Ge-derivatives.

TABLE 7. Direct $^{13}C-^{29}Si$ SSCC (Hz) in (2-Furyl)- and (2-Thienyl)silanes

The R = 2-furyl, R^1 = 2-thienyl series	C_2—Si				Si—CH_3 (Si—H)*			
	n = 1	n = 2	n = 3	n = 4	n = 0	n = 1	n = 2	n = 3
$R_nSi(CH_3)_{4-n}$	76,2	83,0	90,3	97,3	50,3**	53,7	57,1	60,5
R_nSiH_{4-n}	84,0	87,8	92,0	97,3	(202)***	(210)	(214)	(224)
$R^1_nSi(CH_3)_{4-n}$	66,1	71,5	77,1	82,7	50,3	53,5	56,6	59,6
$R^1_nSiH_{4-n}$	73,2	75,4	78,7	82,7	(202)	(208)	(214)	(218)
$R^1_nSiCl_{4-n}$	129,4	108,6	93,7	82,7	—	—	—	—

*The Si-H SSCC values are given in brackets.

**The SSCC for $Si(CH_3)_4$ was published previously in [11].

***The SSCC for SiH_4 was taken from [12].

TABLE 8. Values of Direct $^{13}C-^{29}Si$ SSCC (Hz) in 2-Substituted 5-Trimethylsilylsilanes

Substituent	C_5—Si	Si—CH_3	Substituent	C_5—Si	Si—CH_3
—NO_2	66,8	54,7	—$Sn(CH_3)_3$	75,9	53,7
—C≡N	69,0	54,4	—H	76,2	53,7
—CHO	69,4	54,3	—CH_2NH_2	76,4	53,9
—$CH(OC_2H_5)_2$	75,7	54,0	—$CH_2N(CH_2)_5$	76,7	53,9
—$Si(CH_3)_3$	75,7	53,9	—CH_3	77,9	53,8

The influence of a change in substituents on the $\delta^{29}Si$ of the trimethylsilyl group was studied in the series of 2-substituted 5-trimethylsilylfurans. The resonance signals are shifted into weak fields on substitution of the H_2 proton by electron-acceptor groups, while, on the contrary, they are shifted to stronger fields when electron-donor substituents are introduced. Since the perturbation center, i.e., the 2-position of furan is considerably distanced from the nucleus studied, the anisotropy effects of the substituents can be neglected. Hence the change in the screening of Si under the influence of substituent R is preferentially determined by the local diamagnetic contribution of the electrons and can be explained without taking the π-bonding into account.

On the other hand, the change of the chemical shifts of ^{29}Si of a substituent when an acceptor nitro group is introduced into the ring of 5-trimethylsilylfuran exceeds twofold its increment in trimethylsilylbenzene. On the contrary, the increment due to the methyl group is larger in the latter. This difference in the effectiveness of the transfer of the influence of the substituents through the ring is due to the change in the electron density of the ring nuclei: The acceptor groups reduce it, as a result of which the (π-d)π- interaction becomes weaker and the inductive effect becomes stronger. In n-substituted trimethylsilylbenzenes, the amplitude of the effects is smaller, since the size of the benzene ring is larger than that of the furan ring, while the (π-d)π-conjugation is less effective.

1.3 Chemical Shifts of the Ring ^{17}O Hetero Atom in 2-Substituted and 2,5-Disubstituted Furans

In 2-substituted furans (R = NO_2, CHO, H, $C(CH_3)_3$, CH_2NH_2, $COOCH_3$, CH_2OH, C≡N, CH_3, Br, $Si(CH_3)_3$) the screening of the ring hetero atom is increased by electron-acceptor and reduced by electron-donor substituents [7].

Comparison of the chemical shifts of ^{17}O of furan with the Swayne–Lapton reaction constants of substituents R shows that the transfer of their influence to the ^{17}O is preferentially realizable:

$$\delta\,^{17}O = 238{,}63 + 4{,}78\,F - 30{,}04R\,, \quad (1)$$
$$r = 0{,}985,\ s = 4{,}61,\ n = 9.$$

The resonance and inductive effects thereby act on the screening of ^{17}O in opposite directions. Our CNDO/2 calculations (the s,p-basis) made it possible to explain this situation within the scope of the redistribution of the π-charge on the oxygen atom: a correlation was detected of the $\delta^{17}O$ of 2-substituted furans with the π-charge value on the hetero atom:

$$\delta^{17}O = -2146 + 1337\ q\pi(O), \quad (2)$$
$$r = 0{,}952,\ s = 0{,}09,\ n = 9.$$

To study the interaction of the furan ring with the central IV B group atom in the substituent, we obtained for the first time the ^{17}O NMR spectra of more than 25 heteroorganic derivatives of furan [9].

An exchange of the α-hydrogen of furan by an SiH_3 group is accompanied by an increase in the CS of oxygen, which is almost 2.5 times greater than the shift due to the methyl group. Introduction of the trimethylgermyl and trimethylstannyl group into the α-position also shifts the signal of the oxygen atom of furan into weak fields. It was thus concluded that Si, Ge and Sn atoms may also exhibit π-acceptor properties with respect to the furan ring. The considerable positive charge on the element atom leads to a redistribution of the π-electron density in the furan ring, which is manifested by the increase in the energy of the upper occupied molecular orbital of furan. As a result effectiveness of the p,π-interaction of the unshared pair of electrons of oxygen with the ring π-electrons increases, and the heteroatom of furan is descreened. If the ^{17}O increments are taken as a measure of the acceptor properties of the element-containing substituents, then they will increase in the series of C < Ge ≈ Si < Sn, which agrees with the increase in the π-acceptor properties detected upon screening of C_5 of the heterooganic derivatives of furan.

Since the substituents at silicon are quite remote from the indication center, they hardly influence the chemical shifts of the ^{17}O of furan (the shift with respect to the signal in the $Si(CH_3)_3$ derivative does not exceed 1.5 ppm). A certain degree of screening of the oxygen nuclei (3 ppm) observed during the transition from (2-furyl)- to (3-furyl) derivatives, is probably due to a weakening of the π-acceptor influence of the Si atom in the latter case. A similar value of the screening of the ^{17}O nuclei is also obtained on transition from the $Si(CH_3)_3$ to $Si(OC_2H_5)_3$ derivatives of furan. In this case it can be assumed that the effectiveness of the (π-d)π-bonding between the Si and the ethoxy group oxygen exceeds the effectiveness of the silicon–furan (π-d)π bond in the competition for the vacant d-orbitals of Si.

The chemical shifts of the ring hetero atom in the nitrofuran derivatives are more sensitive to the influence of substituents than in furans, which is due to the increase in the conjugation effect. Under the influence of the acceptor nitro group the contribution of the p, π-interaction of the oxygen atom with ring π-electrons probably decreases, and this in turn leads to increase in the charge of the oxygen atom, and hence to increase in the amplitude of its change during the variation of the electronic properties of the variable substituent R. We believe that the correctness of this interpretation is confirmed by the simultaneous decrease in the $\Delta^{13}C$ increments on transition from the furan derivatives to the 2-substituted 5-nitrofuran derivatives.

The $\delta^{17}O$ of the nitro group exhibit a still greater sensitivity to the effects of the substituents. This results in a weakening of the conjugation between the furan ring and the nitro group because of the change in the magnitude of the torsional angle formed with the plane of the aromatic ring and the nitro group under the influence of the second substituent.

1.4. Furan as an Indicator of Electronic Properties of Substituents [10]

The chemical shifts of the ring proton in the 5-position of 2-substituted furans correlate linearly with the electrophilic constant σ_p^+, the value of which is a function of the degree of conjugation of the reaction center with the substituent in the transition state. This dependence was used in the calculation of the σ_p^+ constant of 25 new compounds.

The values of the σ_p^+ found for the trimethylsilyl and trimethylgermyl groups are in agreement with the concept of the (π-d)π-interaction between the furan ring and the Si (or Ge) atom. The presence of the π-acceptor properties in these groups

is manifested in the different reactivity of (2-furyl)trimethylsilanes, -germanes and 2-tert-butylfuran: The addition of dichlorocarbene in the first two compounds proceeds at the $C_4 = C_5$ bond of furan, while in the tert-butylfuran, it occurs, on the contrary, at the $C_2 = C_3$ double bond.

The behavior of 2-substituted furans in the nitration processes is strongly dependent on the donor-acceptor properties of the substituents. The furan ring is characterized by high stability if 2-quinoxalinyl, 3-(2-oxo-1,2-dihydroquinoxalinyl) or trimethyl silyl groups, which have augmented values of σ_p^+, are present at the 2-position. However, in the case of weaker electron-acceptor imidazo[1,2-a]pyridyl and imidazo[1,2-a]pyrimidyl groups, in addition to nitration, splitting of the furan ring takes place by the action of the nitrating mixture. On further decrease in the electron-acceptor properties of the substituents. for example, in the case of the 2-acetamino-4-thiazolyl group, the nitration can be realized at both the 5- and (partially) the 3-position of furan.

2. SPIN–SPIN INTERACTION IN ORGANOSILICON DERIVATIVES OF FURAN

The spin-spin coupling constants of the ring protons of the 2-substituted furans studied are practically constant and are independent of the solvent used: The scattering of SSCC does not exceed 0.2 Hz. In 2,5-disubstituted furans, the interprotonic constants also change little. Only such a strong acceptor as the NO_2 group in 2-substituted 5-nitrofurans increases the value of this constant to 0.6 Hz.

The direct $^{13}C-^{29}Si$ SSCC studied by us in five series of (2-furyl)- and (2-thienyl)silanes show that these constants increase with increase in the number of furyl or thienyl groups [3].

An opposite tendency is observed in the series of (2-thienyl)chlorosilanes. A comparison of $^1J(C-Si)$ with the Taft inductive constants σ^* of the substituents different from ^1H and not containing unshared electron pairs results in close to linear dependences:

$$^1J(^{29}Si—^{13}C_2) = 69{,}03 + 6{,}54\ \Sigma\sigma^*,$$

(2-furyl)silanes $r = 0{,}998,\ s = 2{,}78,\ n = 8;$

$$^1J(^{29}Si—^{13}C_2) = 60{,}50 + 5{,}96\ \Sigma\sigma^*,$$

(2-thienyl)silanes $r = 0{,}999,\ s = 2{,}76,\ n = 5.$

The similar angular coefficients in the dependences mean that the influence of the electronic effects of the substituents at the silicon atom on the value of $^1J(^{29}Si-^{13}C)$ is the same for both types of compounds. This means that the interpretation of $^1J(C-Si)$ is possible within the scope of the inductive effect of the substituents, while the $(\pi-d)\pi$-interaction is in no way reflected in the SSCC.

If the main contribution to the $^{13}C-^{29}Si$ spin-spin interaction is introduced by the Fermi contact interaction, the change in the $^1J(C-Si)$ can be caused by: a) a change in the mean energy of excitation of electrons ΔE, b) the value of the effective charge on the interacting nuclei, and c) the change in the s-character of C–Si bond. The chemical shifts of the SiH protons and the carbon atom of the CH_3 groups, and also in the SSCC $^1J(Si-H)$ and $^2J(Si-C-H)$ increase with increase in the number of hetaryl groups (n) in the (2-furyl)- or (2-thienyl)methylsilanes. This means that the value of ΔE can be considered to be constant. Therefore the increase in $^1J(C-Si)$ with increase in n may be mainly due to the increase in the positive charge on the silicon atom, and to a lesser extent to the increase in the s-character of the Si–C bond. The value of the direct SSCC is also determined by the type of the hetaryl: the correlations are different for ^1J of furan and thiophene derivatives and are probably explained by the different π-acceptor properties with respect to the heterocyclic rings.

We examined the influence of the more remote substituent R on the SSCC $^1J(^{29}Si-^{13}C)$ using the interaction of the ring C_5 carbon atom with the silicon atom in 2-R-5-trimethylsilylfurans as an example.

There exists a satisfactory linear correlation between the above SSCC and σ_p of the substituents:

$$^1K(C_5—Si) = (221{,}2 - 31{,}0\sigma_p) \times 10^{-16}, \qquad (3)$$

$$r = 0{,}960,\ s = 1{,}8 \times 10^{-9},\ n = 10.$$

Comparison of the linear term coefficients (31×10^{-16}) with those from the equation for the monosubstituted derivatives of furan (37×10^{-18}) shows that the sensitivity of C_5-Si SSCC to the effects of the substituents is by almost two orders of magnitude than the C_5-H SSCC higher.

In the series of 5-trimethylsilylfurans the degree of conjugation of the silicon atom and furan increases on transition from the nitro- to the methyl derivatives: The order of the C_5-Si bond we calculated increases from 1.0948 to 1.1336. The C_5-Si SSCC and the order of this bond correlate linearly. Hence the interpretation of these $^1J(C_5-Si)$ constants should be carried out according to the redistribution mechanism of the s-character of the silicon orbitals, i.e., redistribution of the p-electron density on the C–Si bond. Since an spd-parametrization was used in the calculations of the bond orders, the participation of the d-orbitals does not arouse any doubts, while the increased order of the C_5-Si bond can be explained by either the (π-d)π-conjugation or the σ,π-conjugation of the pσ-orbitals of Si having a π-symmetry with the pπ-orbitals of the ring.

In the study of the SSCC $^1J(^{29}Si-^{13}C)$ of other furyl derivatives of silicon it was found that in 2-furyl(vinyl)silanes these have different values for the two α-carbon atoms. Despite their formally identical state of hybridization, the difference reaches 12 Hz. This difference in the value of ^1J cannot be caused by differences in the inductive effects of the heterocyclic rings, since the positive charge on the silicon atom should equally influence the values of these SSCC.

It can be assumed that the above facts are due to the effect of the unshared electron pairs (UEP) of the heteroatom. For the cis-orientation the steric overlapping of the sp^2-hybridized UEP with antibonding orbitals of the Si–C bond should lead to a noticeable increase in the Fermi contact contribution to the SSCC $^1J(Si-C_2)$. In fact, we also observed the same influence of the UEP on the value of the direct Si–C constants also in the nitrogen heterocycles: to reveal it we compared two series of compounds with a silicon-containing substituent in 2- and 3-positions of the heterocyclic rings [13]. For the former the UEP has a cis-orientation with respect to the Si–C bond, while in the case of the 3-substituted derivatives the two pairs are separated so much that their orbital-orbital interaction is completely absent. In 2-substituted pyridines and quinolines the SSCC $^1J(^{29}Si-^{13}C)$ is 10-13 Hz higher than in the 3-substituted derivatives. At the same time the alkylation of the nitrogen atom leads to the levelling of the direct SSCC values in both series of compounds.

Comparison of the $^1J(^{29}Si-^{13}C)$ values in the series studied shows that influence of the unshared pair of electrons on the value of these SSCC decreases in the series azines > furans > thiophenes.

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