HETEROORGANIC DERIVATIVES OF FURAN.

65.* EFFECT OF SUBSTITUENTS ON SHIELDING OF ^{1}H, ^{13}C, AND ^{29}Si AND ^{29}Si-^{13}C SPIN-SPIN COUPLING CONSTANTS IN NMR SPECTRA OF 2-SUBSTITUTED FURANS AND 5-TRIMETHYLSILYLFURANS

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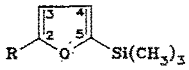
The results of an investigation of 2-substituted furans and 5-trimethylsilylfurans by NMR spectroscopy and the CNDO/2 method showed that the chemical shifts of the different nuclei do not correlate sufficiently clearly with the calculated charges because of an additional change in the electron density under the influence of a π–d interaction. The ^{13}C–^{29}Si direct spin-spin coupling constants (SSCC) are less sensitive to this interaction, since they depend primarily on the inductive effects of the substituents.

Investigations of the ^{1}H chemical shifts (CS) of heteroorganic derivatives of furan have shown that an interaction of the π–d type, the degree of which varies as a function of both the nature of the element and the number of furan rings, occurs between the heteroring and the central M atom (M = Si, Ge, Sn) [2, 3]. At the same time, a study of the ^{13}C resonance of the same compounds does not lead to such unambiguous conclusions [4, 5]. The effect of a silicon-containing substituent on the conductivity of the electronic effects of the substituents through the furan ring has not been studied. In this connection, we carried out a comparative analysis of the ^{1}H, ^{13}C, and ^{29}Si chemical shifts (CS) and ^{13}C–^{29}Si spin-spin coupling constants (SSCC) of series of 2-substituted furans I and 5-trimethylsilylfurans II, and used the CNDO/2 method to calculate the charges on the atoms and the bond orders in these molecules. The calculations were made both without and with inclusion of the d orbitals of silicon (sp and spd bases). The correlations between the CS of the $C_{(5)}$ atom of the furan ring and the total charges in series of silyl derivatives II deteriorated in the case of spd parametrization of the calculations (the r value decreased from 0.936 to 0.837). At the same time, the inclusion of the d orbitals in the parametrization led to improvement in the correlation of the $C_{(5)}$–^{29}Si SSCC with the order of this bond, as a measure of which the Wiberg indices [6] served (r increased from 0.861 to 0.926).

The measured CS and the results of calculations for both series of compounds are presented in Tables 1–3.

I



II

I R=CH_2OH, CHO, $COCH_3$, NO_2, CH_3, SCH_3, Cl, C≡N, Br, I, H, $Si(CH_3)_3$; II R=CH_3, $CH_2N(CH_2)_5$, CH_2NH_2, H, $Si(CH_3)_3$, $Sn(CH_3)_3$, CHO, $CH(OC_2H_5)_2$, C≡N, NO_2

It is generally accepted that the shielding of the nuclei in molecules is realized by both the π and σ electrons and that their effects can be examined separately. The results of our calculations show that the π and σ charges in furan molecules are interrelated: an increase in the π charge causes a decrease in the σ charge, and vice versa (Eqs. 1 and 2 in Table 4).

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*See [1] for Communication 64.

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TABLE 1. Calculated (by the CNDO/2 method) Charges on the Individual Atoms (q) and Wiberg Indices (W) for 2-Substituted Furans

Substitute	$WC_{(5)}-H$	Charge	Ring atoms					Substituent atoms			
			$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	O				
CH_3	0,964	q_σ	0,146	0,021	0,040	0,173	0,577	−0,052	C		
		q_π	−0,099	−0,075	−0,063	−0,076	−0,748	0,014			
		q_H	—	0,011	0,006	0,006	—	0,015			
CH_2OH	0,964	q_σ	0,139	0,020	0,040	0,171	0,584	0,095	C	0,727	O
		q_π	−0,112	−0,064	−0,065	−0,071	−0,747	0,038		−0,977	
		q_H	—	0,015	0,008	0,008	—	−0,013		0,138	
$C(CH_3)_3$	0,963	q_σ	0,158	0,030	0,013	0,176	0,604	0,059	C		
		q_π	−0,014	−0,108	−0,044	−0,081	−0,778	−0,014			
		q_H	—	0,008	0,000	−0,001	—	—			
H	0,965	q_σ	0,120	0,042	0,042	0,120	0,552	—			
		q_π	−0,129	−0,056	−0,056	−0,129	−0,727				
		q_H	0,005	0,010	0,010	0,005	—				
$Si(CH_3)_3$	0,963	q_σ	−0,034	0,027	0,019	0,160	0,597	−0,105	C	0,408	Si
		q_π	−0,055	−0,056	−0,061	−0,053	−0,768	−0,078		0,160	
		q_H	—	−0,003	0,004	−0,006	—	0,016		—	
CHO (O,O-cis)	0,964	q_σ	0,140	−0,016	0,045	0,149	0,587	0,089	C	−0,027	O
		q_π	−0,151	0,009	−0,080	−0,026	−0,740	0,141		−0,202	
		q_H	—	0,017	0,013	0,015	—	−0,039		—	
CHO (O,O-trans)	0,964	q_σ	0,144	−0,013	0,045	0,148	0,575	0,086	C	−0,017	O
		q_π	−0,159	0,021	−0,083	−0,022	−0,741	0,154		−0,220	
		q_H	—	0,025	0,015	0,013	—	−0,049		—	
$C\equiv N$	0,964	q_σ	0,175	0,006	0,043	0,161	0,587	0,021	C	−0,069	N
		q_π	−0,137	−0,023	−0,073	−0,046	−0,745	0,048		−0,073	
		q_H	—	0,021	0,015	0,014	—	—		—	
NO_2	0,965	q_σ	0,202	−0,005	0,026	0,146	0,625	0,185	O	0,547	N
		q_π	−0,146	0,033	−0,073	0,001	−0,765	−0,578		0,107	
		q_H	—	0,037	0,030	0,023	—	—		—	

TABLE 2. Shielding of the Nuclei of 2-Substituted Furans I and 2-Substituted 5-Trimethylsilylfurans II

Substituent	δ, ppm																
	I (in deuteroacetone)							II (in deuterodimethyl sulfoxide)									
	$C_{(2)}$	$C_{(3)}$	3-H	$C_{(4)}$	4-H	$C_{(5)}$	5-H	$C_{(2)}$	$C_{(3)}$	3-H	$C_{(4)}$	4-H	$C_{(5)}$	^{29}Si*	C_{Me}	CH_3
CH_3**	152,7	106,3	5,93	111,1	6,22	141,7	7,27	156,9	106,3	6,13	120,9	6,73	158,9	−11,7	−1,2*	0,26
$CH_2N(CH_2)_5$	—	—	—	—	—	—	—	157,5	108,9	6,24	120,9	6,67	159,9	−11,6	−1,1*	—
CH_2NH_2	155,0	106,8	6,18	110,9	6,33	142,2	7,42	160,0	105,6	6,22	121,0	6,67	161,8	−11,4	−0,6	0,25
H**	143,6	110,4	6,36	110,4	6,36	143,6	7,46	146,7	109,7	6,49	120,0	6,77	160,4	−11,5	−1,3*	0,30
$Sn(CH_3)_3$	160,9	121,5	6,42	109,8	6,64	147,7	7,79	165,8	120,6	6,53	119,3	6,62	165,0	−11,5	−1,3*	0,27
$Si(CH_3)_3$	160,4	120,4	6,70	110,0	6,41	147,4	7,74	164,4	119,8	6,73	119,8	6,73	164,4	−11,4	−1,3*	0,27
$CH(OC_2H_5)_2$	153,5	108,5	6,41	110,8	6,41	143,1	7,52	156,9	108,3	6,40	120,4	6,70	160,3	−11,1	−0,9	0,27
CHO**	154,3	122,4	7,45	113,6	6,74	149,5	7,94	157,5	122,2	7.55	121,6	7,06	168,9	−8,7	−1,5*	0,34
C≡N**	126,9	123,4	7,35	112,6	6,68	149,4	7,86	130,2	121,9	7,61	122,1	7,05	168,9	−8,4	−1,3	0,34
NO_2	153,7	114,5	7,54	112,6	6,88	146,9	7,91	156,7	111,7	7,38	122,0	6,85	167,4	−7,5	−1,8*	0,41

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*In deuterochloroform.

**The CS of derivatives I were taken from [7].

TABLE 3. Calculated (by the CNDO/2 method) Charges on the Individual Atoms (q) and Wiberg Indices (W) for 2-Substituted 5-Trimethylsilylfurans

Substituent	W $C_{(5)}$—Si	W Si—C_{Me}	Basis	Charge	Ring atoms				Substituent atoms				
					$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	O	Si	CH_3	others	
CH_3	0,948	0,967	*sp*	q_σ	0,165	0,021	0,020	0,041	0,601	0,407	−0,105	−0,055 } C	
				q_π	−0,023	−0,089	−0,044	−0,070	−0,776	0,161	−0,078	0,016 }	
				q_H	—	0,003	−0,005	—	—	—	0,016	0,013	
	1,134	1,204	*spd*	q_σ	0,153	0,020	0,012	0,056	0,622	0,033	−0,085	−0,055 } C	
				q_π	−0,003	−0,097	0,003	−0,026	−0,771	−0,174	−0,104	0,015 }	
				q_H	—	0,004	−0,002	—	—	—	0,082	0,015	
H	0,947	0,968	*sp*	q_σ	0,160	0,019	0,027	0,034	0,597	0,408	−0,105	—	
				q_π	−0,053	−0,061	−0,056	−0,055	−0,768	0,160	−0,078		
				q_H	−0,006	0,004	−0,003	—	—	—	0,016		
	1,129	1,205	*spd*	q_σ	0,149	0,018	0,019	0,051	0,618	0,034	−0,086	—	
				q_π	−0,033	−0,069	−0,010	−0,013	−0,761	−0,174	−0,104		
				q_H	−0,004	0,005	0,004	—	—	—	0,082		
$Si(CH_3)_3$	0,953	0,967	*sp*	q_σ	0,031	0,023	0,023	0,031	0,595	0,400	−0,106	−0,106 } C	0,400 } Si
				q_π	−0,053	−0,055	−0,055	−0,053	−0,770	0,161	−0,078	−0,078 }	0,161 }
				q_H	—	−0,007	−0,007	—	—	—	0,015	0,015	—
	1,131	1,201	*spd*	q_σ	0,035	0,020	0,020	0,035	0,408	0,031	−0,087	−0,087 } C	0,031 } Si
				q_π	0,008	−0,016	−0,016	0,008	0,160	−0,168	−0,103	−0,103 }	−0,168 }
				q_H	—	−0,003	−0,003	—	—	—	0,081	0,081	—
CHO (O,O-cis)	0,942	0,969	*sp*	q_σ	0,082	−0,016	0,027	0,012	0,611	0,413	−0,106	0,086 } C	−0,027 } O
				q_π	−0,074	−0,005	−0,065	−0,017	−0,771	0,156	−0,077	0,143 }	−0,206 }
				q_H	—	0,008	0,001	—	—	—	0,018	−0,041	—
	1,116	1,209	*spd*	q_σ	0,146	−0,012	0,019	0,034	0,616	0,033	−0,086	0,087 } C	−0,029 } O
				q_π	−0,059	−0,015	−0,020	0,019	−0,764	−0,172	−0,103	0,141 }	−0,199 }
				q_H	—	0,009	0,003	—	—	—	0,086	−0,040	—
CHO (O,O-trans)	0,943	0,969	*sp*	q_σ	0,080	−0,012	0,026	0,011	0,599	0,412	−0,106	0,084 } C	−0,016 } O
				q_π	−0,082	0,006	−0,067	−0,014	−0,772	0,156	−0,077	0,156 }	−0,223 }
				q_H	—	0,016	0,002	—	—	—	0,018	−0,052	—
	1,117	1,208	*spd*	q_σ	0,151	−0,012	0,018	0,033	0,620	0,034	−0,086	0,085 } C	−0,018 } O
				q_π	−0,063	−0,004	−0,022	0,027	−0,765	−0,172	−0,103	0,154 }	−0,217 }
				q_H	—	0,017	0,004	—	—	—	0,084	−0,050	—
NO_2	0,930	0,972	*sp*	q_σ	0,264	−0,014	0,035	0,001	0,615	0,426	−0,107	0,234 } O	0,373 } N
				q_π	−0,132	0,024	−0,077	0,011	−0,769	0,150	−0,076	−0,556 }	0,057 }
				q_H	—	0,033	0,016	—	—	—	0,021	—	—
	1,095	1,215	*spd*	q_σ	0,254	−0,014	0,032	0,029	0,634	0,040	−0,087	0,233 } O	0,374 } N
				q_π	−0,114	0,013	−0,033	0,043	−0,762	−0,173	−0,103	−0,554 }	0,055 }
				q_H	—	0,033	0,018	—	—	—	0,087	—	—

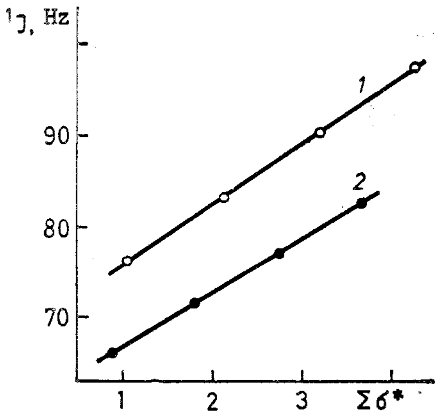

Fig. 1. Correlation between the direct $C_{(2)}$–^{29}Si SSCC of (2-furyl)- (1) and (2-thienyl)methylsilanes (2) and $\Sigma\sigma^*$ of all the substituents attached to the silicon atom.

TABLE 4. Correlation Equations for the NMR Parameters and Charges on the Individual Atoms of 2-Substituted Furans I and 5-Trimethylsilylfurans II*

Eq. No.	Equation	*r*	*s*	*N*
1	$q_\sigma^{I}=0,141-0,397q_\pi^{I}$	0,953	0,02	11
2	$q_\sigma^{II}=0,005-0,514q_\pi^{II}$	0,998	0,02	6
3	$q\ C_{(3)}^{II}=-0,26+0,728q\ C_{(3)}^{I}$	0,908	0,02	5
4	$q\ C_{(5)}^{II}=-10,778+0,818q\ C_{(5)}^{I}$	0,996	0,02	5
5	$q\ Si^{II}=0,564+0,483q\ H_{(5)}^{I}$	0,976	0,08	5
6	$\delta\ C_{(5)}^{I}=114,2+286,8q\ C_{(5)}^{I}$	0,949	0,21	5
7	$\delta\ H_{(3)}^{I}=5,51+53,5q\ H_{(3)}^{I}$	0,975	0,07	7
8	$\delta\ H_{(4)}^{I}=6,05+28,5q\ H_{(4)}^{I}$	0,991	0,05	7
9	$\delta\ C_{(5)}^{II}=170,3+382,6q\ C_{(5)}^{II}$	0,936	0,23	5
10	$\delta\ H_{(4)}^{II}=6,95+37,5q\ H_{(4)}^{II}$	0,921	0,03	4
11	$\delta\ C_{(2)}^{II}=-12,03+1,10\delta\ C_{(2)}^{I}$	0,993	0,37	7
12	$\delta\ C_{(3)}^{II}=1,47+0,98\delta\ C_{(3)}^{I}$	0,999	4,82	6
13	$\delta\ C_{(4)}^{II}=40,32+0,72\delta\ C_{(4)}^{I}$	0,977	0,81	7
14	$\delta\ C_{(5)}^{II}=-15,76+1,22\delta\ C_{(5)}^{I}$	0,984	3,11	6
15	$\delta\ ^{29}Si^{II}=-51,43+5,41\delta\ H_{(5)}^{I}$	0,976	0,63	6
16	$\delta\ C_{(5)}^{II}=160,8+8,47F-4,81R$	0,997	2,33	5
17	$^1J_{(^{13}C_{Me}-^{29}Si)}=59,9-0,08\cdot{}^1J_{(^{13}C_{(5)}-^{29}Si)}$	0,946	0,22	10
18	$^1K(^{13}C_{(5)}-Si)=(221,2-31,0\sigma_p)\cdot10^{-16}$	0,989	$2,0\cdot10^{-9}$	9
19	$^1K(^{13}C_{(5)}-H)=(666,2+37,6\sigma_p)\cdot10^{-18}$	0,960	$1,8\cdot10^{-9}$	12
20	$^1J_{(C_{(5)}-Si)}=255,5-292,9B(C_{(5)}-Si)$	0,926	0,25	5
21	$^1J_{(C_{Me}-Si)}=115,9-175,5B(C_{Me}-Si)$	0,910	0,03	5
22	$^1J_{(C_{(5)}-Si)}=-76,6+9,41F-1,80R$	0,999	0,64	6

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*Symbols: r, correlation coefficient; s, mean square error; N, number of points.

In the molecules of I and II, as in substituted benzenes [8], an increase in the σ charge leads to a weak-field shift of the ^{13}C resonance, while an increase in the π charge, on the other hand, leads to a strong-field shift of the ^{13}C resonance. A proportionality exists between the calculated charges of most of the carbon atoms in both series (Eqs. 3–5). At the same time, a correlation of the CS with the calculated values of the total charges on the individual atoms is absent for most of the ^{13}C and ^1H nuclei of I and II (the r values range from 0.1 to 0.9). The CS of the $C_{(5)}$ atom and the 3-H and 4-H protons (I), as well as the $C_{(5)}$ and 4-H atoms (II, Eqs. 6–10), constitute an exception.

The numerical value of the slope of the line corresponding to Eq. 9 (382 ppm/electron) is quite close to the analogous value in the correlation for p-substituted benzenes (385 ppm/electron [8]) and greater than the value (286 ppm/electron) from Eq. 6 for monosubstituted furans. The CS of the corresponding nuclei in both series of compounds are interrelated (Eqs. 11–15). The sensitivity of the CS of the carbon atoms of the heteroring to the effect of substituent R changes with the appearance of an $Si(CH_3)_3$ group in the α position of the furan ring. The effect of the substituent is intensified for the $C_{(5)}$ and $C_{(2)}$ atoms, while it becomes weaker for the $C_{(3)}$ atom and particularly for the $C_{(2)}$ atom (Eqs. 11–14). In addition, our quantum-chemical calculations show that the introduction of an $Si(CH_3)_3$ group should decrease the sensitivity of the electron charge to the effect of substituents R for both of the above-indicated group of carbon nuclei (Eqs. 3 and 4). The increased ρ value in Eqs. 11 and 14 can therefore probably be ascribed to a change in the density of the more mobile π electrons, i.e., to the existence of a π–d interaction between the furan ring and the silicon atom.

The signals of ^{29}Si resonance in the II series are shifted to weak field when the α proton of the furan ring is replaced by an electron-acceptor group and, on the other hand, are shifted to strong field from electron-donor substituents R. Despite the absence of a satisfactory correlation between the CS of silicon and the charge on this atom, it should nevertheless be noted that the transition from donor substituents to acceptor substituents in the furan ring is reflected as a decrease in the calculated electron density on the silicon atom.

The existence of a linear correlation (Eq. 15) with a positive slope of the line leads to the conclusion of monotypic character of the effects of the substituents on the shielding of 5-H and ^{29}Si in the I and II series, respectively. For the protons the shielding is determined primarily by a local diamagnetic contribution [9]. Since the center of perturbation is located at a significant distance from the investigated nucleus, the effect of the anisotropy of substituent R can be disregarded. Consequently, the change in the shielding of the silicon atom under the influence of R is determined primarily by the local diamagnetic contribution of the electron cloud around the nucleus under consideration. It should be noted that for p-substituted trimethylsilylbenzenes similar effects of the substituents on the ^{29}Si resonance can also be explained without invoking additional π bonding [10].

The analysis of the shielding of individual nuclei under the influence of substituents is usually carried out using different reactivity constants of the substituents. We have previously made this sort of evaluation for α-substituted furan derivatives using the Swain–Lupton constants F and R and found that the CS of the $C_{(5)}$ atom are equally sensitive to the inductive and mesomeric effects of the substituents in the 2 position ($\rho_F/\rho_R = 1.07$) [11]. We obtained a similar two-parameter equation (Eq. 16 in Table 4) for the CS of the $C_{(5)}$ atom of II [R = H, CH_3, CHO, $Si(CH_3)_3$, NO_2]. The ρ_F and ρ_R slopes in the II series show that the fraction of the mesomeric effect in the shielding of $C_{(5)}$ decreased substantially as compared with that in the I series. This can be ascribed to the well-known π-acceptor capacity of silicon substituents [12].

Let us now turn to an examination of the effect of substituents on the ${}^1J_{^{13}C-^{29}Si}$ value. The small number of measurements of the constants of direct SSC between the $C_{(2)}$ atom of furan and element M (M = Sn, Pb) in compounds of the I type indicate their high sensitivity to a change in the number of heterocyclic groups [4]. We investigated the constants of direct $^{13}C-^{29}Si$ SSC in two series of 2-furylsilanes (Table 5). It is apparent from the data in Table 5 that the ${}^1J_{^{13}C-^{29}Si}$ constants decrease with an increase in the number of heterorings.†

To elucidate the effect of the heteroring and other substituents attached to the silicon atom on the ${}^1J_{^{13}C-^{29}Si}$ values the latter were also measured in three series of 2-thienylsilanes and compared with the Taft σ^* induction constants (Fig. 1). For substituents that do not contain unshared electron pairs these dependences are close to linear. In the (2-thienyl)-chlorosilane series VII, where the number of thienyl groups and chlorine (an element with an unshared electron pair) atoms attached to the central silicon atom changes, the direct $C_{(2)}-^{29}Si$ SSCC decreases from 129.4 Hz (n = 1) to 82.7 Hz (n = 4), and its correlation with $\Sigma\sigma^*$ becomes nonlinear. The slope of the line increases with an increase in the number of attached chlorine atoms, i.e., the effectiveness of their action on ${}^1J_{^{13}C-^{29}Si}$ increases. A similar effect of halogen atoms and other substituents with an unshared electron pair was previously observed for ${}^1J_{^{13}C-^{199}Hg}$ in symmetrical $(RR'R''C)_2Hg$ compounds [16]. This effect is explained by a combination of two effects: transfer of p electrons from the C–Si bond to the Si–Cl bond and a nonadditive increase in the positive charge on the silicon nucleus with an increase in the number of attached chlorine atoms. Nonadditivity of the effect of the substituents because of steric effects is also not excluded.

The existence of two different correlation lines for the ^{1}J SSCC of furan and thiophene derivatives is probably explained by the different π-acceptor properties of silicon with respect to these heterocycles, which is due to a π–d interaction, as well as to the different acceptor effects of the heterorings themselves.

We examined the effect of the more remote substituent R on the ${}^1J_{^{13}C-^{29}Si}$ SSCC in the case of II (Table 6). An analysis of the data in Table 6 indicates the existence of a satisfactory mutual linear correlation between ${}^1J_{^{13}C_{(5)}-^{29}Si}$ and ${}^1J_{^{13}C_{Me}-^{29}Si}$ (Eq. 17). The negative sign of the slope is evidently due to the alternating influence of the electronic effects along the chain. The existence of this correlation means that both SSCC are determined by the same mechanism of transmission of the spin-spin coupling with predominance of the Fermi-contact contribution in it. The ratio of their values averages 0.75. The fractions of s character in sp^3 and sp^2 hybridization of carbon atoms have the same ratio.

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†For furylhydrosilanes IV this is in agreement with the increase in the length of the $C_{(2)}-^{29}Si$ bond on passing from n = 3 (1.857 Å) to n = 2 (1.869 Å) and to n = 1 (1.871 Å) [15].

TABLE 5. Direct ^{13}C–^{29}Si SSCC (Hz) of (2-Furyl)- and (2-Thienyl)silanes

Series, R = 2-furyl, R^1 = 2-thienyl	$C_{(2)}$–Si				Si–CH_3 (Si–H)*		
	n=1	n=2	n=3	n=4	n=1	n=2	n=3
$R_nSi(CH_3)_{4-n}$	76,2	83,0	90,3	97,3	53,7	57,1	60,5
R_nSiH_{4-n}	84,0	87,8	92,0	97,3	(209,8)	(214,2)	(224,0)
$R^1{}_nSi(CH_3)_{4-n}$	66,1	71,5	77,1	82,7	53,5	56,6	59,6
$R^1{}_nSiH_{4-n}$	73,2	75,4	78,7	82,7	(208,3)	(213,5)	(218,0)
$R^1{}_nSiCl_{4-n}$	129,4	108,6	93,7	82,7	—	—	—

*The Si–H SSCC are presented in parentheses. In the case n = 0, the SSCC were taken from the literature: 50.3 Hz for $Si(CH_3)_4$ [13] and 202.0 Hz for SiH_4 [14].

TABLE 6. Direct ^{13}C–^{29}Si SSCC (Hz) of 2-Substituted 5-Trimethylsilylfurans II

Substituent	$C_{(5)}$–Si	Si–CH_3
CH_3	77,9	53,8
$CH_2N(CH_2)_5$	76,7	53,9
CH_2NH_2	76,4	53,9
H	76,2	53,7
$Si(CH_3)_3$	75,9	53,7
$Si(CH_3)_3$	75,7	53,9
$CH(OC_2H_5)_2$	75,7	54,0
CHO •	69,3	54,3
$C{\equiv}N$	69,0	54,4
NO_2	66,8	54,7

Regression analysis of the data in Table 6 shows that a satisfactory linear correlation exists between the $^{13}C_{(5)}$–^{29}Si SSCC presented and the σ_p substituent constants (Eq. 18). A similar analysis of the direct ^{13}C–^{1}H SSCC of monosubstituted furans (the data for the I series were taken from [7]) leads to Eq. 19. A comparison of the slopes of the correlation lines (Eqs. 18 and 19) shows that the sensitivity of the $^{13}C_{(5)}$–^{29}Si SSCC to the substituent effects is almost two orders of magnitude higher than for the ^{13}C–^{1}H SSCC and, in addition, has the opposite sign.

Our calculations of the bond orders (the Wiberg indices) in the II series (Table 3) show that the degree of conjugation of the silicon atom and the furan ring increases from 1.095 for the NO_2 derivative to 1.134 for the CH_3 derivative. Since spd parametrization was used in the calculations, there is no doubt about the participation of the d orbitals, and the increased order of the $C_{(5)}$–Si bond should be explained by both π–d conjugation and σ,π conjugation of the p_σ orbitals of Si (which have π symmetry) with the p_π orbitals of the ring. It is interesting to note that the order of the Si–C_{Me} bond in many cases exceeds the order of the direct Si–$C_{(5)}$ bond (Table 3). This indicates that a significant fraction of the population of the d orbital of the silicon atom is expended in interaction with the methyl group. It is possible that this result constitutes evidence for the existence of hyperconjugation between the CH bonds of the $SiCH_3$ group and the vacant d orbitals of the silicon atom. Thus, the results of the calculations show that the interpretation of the changes in the $^1J_{^{13}C_{(5)}-^{29}Si}$ constants of derivatives II should apparently be made with respect to the mechanism of the redistribution of the s character of the orbitals of the silicon atom, as was proposed in [17].

Electron-donor substituents lead to enrichment in the p-electron density of the C–Si bond (on the part of the substituent), while electron-acceptor substituents lead to its impoverishment due to delocalization of the p electrons on the adjacent bonds [16, 18]; the order of the $C_{(5)}$–Si bond changes in the order CH_3 > H > CHO > NO_2; the direct $^1J_{^{13}C_{(5)}-Si}$ SSCC increases in almost the same order. A completely satisfactory linear correlation exists between the two parameters (Eq. 20). The reason for the rather low correlation coefficient should be sought in the change in the geometry of the molecules in cases in which, in addition to an $Si(CH_3)_3$ group, strong acceptor substituents appear in the ring (in fact, our calculations by the INDO method of the optimal geometry of 2-nitro-5-trimethylsilylfuran revealed lengthening of the $C_{(5)}$–Si bond by 0.01 Å relative to the length in 2-trimethylsilylfuran).

The existence of a correlation of the Eq. 18 type for the $^1J_{C(5)-Si}$ SSCC of II derivatives indicates that analysis by means of two-parameter equations is also possible for these SSCC. The most satisfactory r value is obtained when the F and R substituent constants are used (Eq. 22). This correlation constitutes evidence for the predominant role of the inductive effect in the determination of the $^1J_{C(5)-Si}$ value.

EXPERIMENTAL

The ^{13}C and ^{29}Si NMR spectra of 30-50% solutions of the compounds in $CDCl_3$ were investigated with a Bruker WH-90/DS spectrometer (resonance-excitation frequencies 22.63 MHz and 17.88 MHz, respectively); the pulse duration was 5 μsec (30° pulses), and their sequential frequency was 0.25-0.35 Hz. The spectra with widths of 6 or 3 kHz were recorded in an operative memory with a volume of 8 K, which determined an accuracy in the measurement of the ^{13}C and ^{29}Si chemical shifts of ±0.1 ppm. The direct ^{13}C-^{29}Si SSCC were measured with an accuracy of ±0.1 Hz in the ^{29}Si spectra using the method of internuclear polarization transfer (see [19, 20]). The number of accumulation was 10-13 thousand. The ^1H NMR spectra were recorded with the same spectrometer (resonance-excitation frequency 90 MHz) under standard conditions.

The substituent constants were taken from a monograph [21]. The theoretical calculations by the CNDO/2 method with sp and spd parametrization, as well as by the INDO method, were carried out for the optimal geometries of the furan ring [22] and the substituents [23].

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