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INVESTIGATION OF 2,5-DISUBSTITUTED SILYLFURANS BY PMR SPECTROSCOPY

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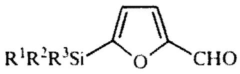
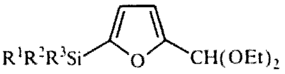
The ${}^1H$, ${}^{13}C$, and ${}^{29}Si$ NMR spectra of 5-substituted furfurals and the corresponding diethyl acetals containing various alkylsilyl substituents at position 5 of the furan ring were studied in comparison with the carbon- and sulfur-containing analogs and also with a series of monosubstituted silylfurans. In cases where the substituent was conjugated with the residue of the furan molecule the effect of the substituent at position 5 of the furan was transmitted to C_α of the aldehyde group. The reverse effect was also observed. It was determined that the contribution from the aldehyde group and the substituents at position 5 of the furan to the screening of the carbon nuclei of the furan ring was not additive.

Earlier a ${}^1H$, ${}^{13}C$, and ${}^{29}Si$ NMR spectroscopic study of carbofunctional furylsilanes was undertaken [1]. While keeping the silicon-containing substituent at position 5 of the furan (Me_3Si) unchanged, the authors changed the carbofunctional substituent at position 2 and compared the spectra of the obtained compounds, trimethyl(2-furyl)silane, and its carbon analog.

On the contrary, we examined the ${}^1H$, ${}^{13}C$, and ${}^{29}Si$ NMR spectra of 5-substituted furfurals (I) and the corresponding diethyl acetals (II), containing various alkylsilyl substituents at position 5, in comparison with the carbon- and sulfur-containing analogs and also with a series of monosubstituted silylfurans (III) (Tables 1-4, [6]).


I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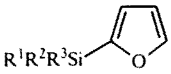
III

Change of the substituents at the silicon atom in the 2-furylsilanes (III) and 5-substituted furfural diacetals (II) has little effect on the screening of the protons in the furan ring ($\delta H^3 = 6.4 \pm 0.05$ ppm, $\delta H^4 = 6.6 \pm 0.09$ ppm, $\delta H^5 = 7.64 \pm 0.03$ ppm). The diethyl acetal group at position 2 does not have an appreciable effect on the chemical shifts of the protons in the furan ring compared with the monosubstituted silylfurans.

Unlike the silicon-containing substituents, the sulfur-containing substituents (MeS, BuS) do not give rise to descreening of the furan ring protons, whereas the aldehyde group shifts the signals of the ring protons upfield compared with the alkylsilyl substituents.

The appearance of a methylene bridge between the silicon atom and the furan gives rise to an increase in the chemical shift of H^4 ($\Delta\delta = 0.4$ ppm) in comparison with 5-trimethylsilylfurfural diethyl acetal, i.e., leads to the disappearance of the electron-withdrawing effect of the alkylsilyl group due to $d\pi - p\pi$ coupling between the unoccupied d orbitals of the silicon and the π electrons of the furan ring, as already noted earlier for the monosubstituted derivatives of furan [2].

Unlike the diethyl acetal group the aldehyde group at position 2 has an electron-withdrawing effect on the π system of the substituted furan, leading to a downfield shift of the signals for the H^3 (by 0.4-0.5 ppm) and H^4 (by 0.6 ppm) protons compared with the corresponding diethyl acetals and monosubstituted silylfurans.

The smaller downfield shift of the H^3 and H^4 protons in the PMR spectrum of furfural containing the substituent $Me_3CHC{=}CHMe_2Si-$ at position 5 of furan can presumably be explained both by weakening of the $d\pi - p\pi$ coupling of the silicon atom with the π-electron system of furan as a result of concurrent coupling with the π system of the $Me_3CHC{=}CH-$

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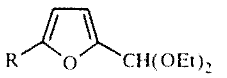
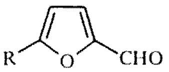
TABLE 1. ^{1}H NMR Spectra of 5-Substituted Furfural Diethyl Acetals



Obtained by the Organolithium Synthesis (deuterochloroform)

Substituent R	δ, ^{1}H, ppm						
	H^3	H^4	CH	$SiMe_2$	OCH_2	CH_3	Other protons
$HSiMe_2$	6,42	6,66	5,58	0,34	3,63	1,24	4,42 (SiH)
$PhSiMe_2$	6,41	6,61	5,57	0,53	3,59	1,20	7,3...7,7 (Ph)
$Cl_2HCSiMe_2$	6,45	6,80	5,57	0,51	3,60	1,22	5,4 (CH_2Cl)
ClH_2CSiMe_2	6,42	6,69	5,56	0,39	3,60	1,22	2,95 (CH_2Si)
Ph_2SiMe	6,45	6,64	5,59	0,80	3,59	1,20	7,3...7,6 (Ph)
Me_3SiH_2C-	6,05	6,56		0,32	3,88	1,50	2,35 (CH_2Si)
MeS—	6,39	6,39			3,62	1,23	2,40 (SCH_3)
BuS—	6,39	6,44	5,51		3,61	1,23	1,49 (CH_2CH_2), 0,89 (CCH_3)
OHC—	6,63	7,22	5,57		3,65	1,25	9,67 (CHO)

TABLE 2. ^{1}H NMR Spectra of 5-Substituted Furfurals (deuterochloroform)



R	δ, ^{1}H, ppm				
	H^3	H^4	CHO	Other substituents R	SSCC, Hz, H^3—H^4
$HSiMe_2$	6,85	7,26	9,72	0,42 ($SiCH_3$), 4,48 (SiH)	3,6
$PhSiMe_2$					
Ph_2SiMe	6,78	7,20	9,69	0,90 (SiMe), 7,3...7,64 (Ph_2)	
$Me_3CC\beta H{=}C\alpha HSiMe_2$	6,59	7,06	9,52	0,22 ($SiMe_2$), 0,86 (CMe_3), 5,49 (Hα), 6,07 (Hβ)	3,5
$Me_3C(CH_2)_2SiMe_2$	6,77	7,23	9,69	0,31 ($SiMe_2$), 0,75 ($SiCH_2$), 0,85 (CMe_3)	3,4
$NC(CH_2)_3SiMe_2$	7,24	6,80	9,71	0,36 ($SiMe_3$), 0,97 (CH_2Si), 1,71 (CH_2), 2,38 (CH_2CN)	
$ClCH_2SiMe_2$	6,89	7,24	9,72	0,47 ($SiMe_2$), 3,0 (CH_2Si)	
MeS—	6,41	7,23	9,52	2,58 (SCH_3)	3,7
BuS—	6,47	7,22	9,53	3,02 (SCH_2), 0,98 (CCH_3), 1,60, 1,42 (CH_2CH_2)	3,6

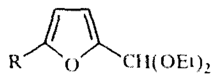
group and by the electron-donating mesomeric effect of the Me_3C- group. The latter is also favored by the fact that the proton of the aldehyde group in this compound is more screened than in the other silyl-substituted furfurals. The protons of the aldehyde group in 5-substituted furfurals containing MeS or BuS substituents are characterized by the same shift.

Analysis of the ^{13}C NMR spectra of 5-silicon-substituted furfurals and the corresponding diethyl acetals shows that the appearance of substituents at position 5 of furan containing both $-CH(OEt)_2$ and $-CHO$ groups at position 2 leads to descreening of the C^5, C^4, and C^2 carbon nuclei of the furan ring in comparison with unsubstituted furfural diethyl acetal and furfural respectively. The degree of descreening decreases in the order $C^5 > C^4 > C^2$ (Tables 5 and 6).

The chemical shifts of the C^3 nuclei of furan for the investigated 5-silyl-substituted furfural diethyl acetals change little with change in the substituents at the silicon atom ($\Delta\delta^{13}C$, ppm, ± 0.8), whereas screening of the C^3 nuclei by a large amount ($\Delta\delta = -2.1$ to -4.6 ppm) is observed for the series of aldehydes.

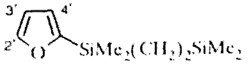
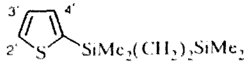
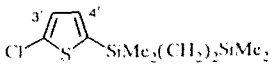
In the series of investigated 5-substituted furfural diethyl acetals change of the substituents at position 5 has practically no effect on the chemical shifts of the α-carbon (with constant solvent $\delta^{13}C\alpha = 96.8 \pm 0.4$ ppm).

TABLE 3. ^{13}C and ^{29}C NMR Spectra of the Diethyl Acetals of 5-Substituted Furfurals (deuterochloroform)



R	δ, ^{13}C, ppm							
	C^2	C^3	C^4	C^5	CH	SiMe	Carbon atoms of substituents R	δ, ^{29}Si, ppm
1	2	3	4	5	6	7	8	9
$HSiMe_2$	157,4	108,3	121,7	157,2	96,8	-4,6	61,3 (OCH_2), 15,2 (CH_3)	-28,7
$Cl_2CHSiMe_2$	154,3	109,0	124,1	158,6	97,0	-5,6	61,8 (OCH_2), 15,6 (CH_3), 62,1 ($CHCl_2$)	
$ClCH_2SiMe_2$	156,8	108,7	122,6	158,0	97,2	-4,5	61,8 (OCH_2), 15,6 (CH_3), 29,8 (CH_2Cl)	-10,6
Me_3SiCH_2	150,0	109,5	104,6	155,2	97,1	-1,25	61,7 (OCH_2), 15,6 (CH_3), 18,9 (CH_2Si)	-10,9
MeS–	155,0	110,2	115,2	148,1	96,8		61,9 (OCH_2), 15,6 (CH_3), 19,2 (SCH_3)	
BuS–	155,3	110,2	117,3	146,8	96,8		61,7 (OCH_2), 15,6 (CH_3), 36,1 (SCH_2), 32,4 ($SC\underline{C}H_2$), 22,1 ($SCC\underline{C}H_2$), 14,0 (CH_3)	
CHO–	159,0	111,2	121,5	153,4	96,7		62,5 (OCH_2), 15,6 (CH_3), 178,5 (CHO)	
$Me_3CC\beta H{-}C\alpha HSiMe_2$	156,4	107,8	120,6	159,2	96,5		60,9 (OCH_2), 35,1 (*tert*-C), 28,9 ($CC\underline{H}_3$), 15,1 ($OC\underline{C}H_3$), 159,8 ($C\beta$), 119,2 ($C\alpha$)	-18,4
$H_3C(CH_2)_6C\beta H{-}C\alpha HSiMe_2$	157,2	108,5	121,2	159,9	97,2	-2,4	61,6 (OCH_2), 14,4 (CH_3), 37,2 (CCH_2), 32,2, 29,6, 29,0 (CH_2), 15,5 (CH_3), 150,5 ($C\beta$), 126,5 ($C\alpha$)	-19,5
$Me_3SiC\beta H{-}C\alpha HSiMe_2$	156,4	107,9	120,8	158,5	96,4		60,9 (OCH_2), 15,0 (CH_3), 153,4 ($C\beta$), 146,3 ($C\alpha$)	-19,7, -7,4
$PhC\beta H{-}C\alpha HSiMe_2$	156,8	107,9	121,0	158,4	96,5	-3,1	61,0 (OCH_2), 14,9 (CH_3), 131,8 (*i*), 128,1 (*p*), 128,4 (*o*), 126,5 (*m*), 145,8 ($C\beta$), 125,5 ($C\alpha$)	-17,8

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9
$\mathrm{EtOOCC\beta H{-}C\alpha HSiMe_2}$	156,6	107,9	121,6	157,0	96,3	-3,8	60,9 ($\mathrm{OCH_2}$), 14,9 ($\mathrm{OC\underline{C}H_3}$), 162,7 ($\mathrm{C{=}O}$), 156,08 ($\mathrm{C\beta}$), 145,16 ($\mathrm{C\alpha}$), 141,05, 135,64 ($\mathrm{C{=}CH_2}$)	-17,8, -16,1
$\mathrm{(CH_2)_4NCH_2C\beta H{-}C\alpha HSiMe_2}$	156,6	107,8	120,7	158,7	96,5	-3,2	61,0 ($\mathrm{OCH_2}$), 14,9 ($\mathrm{CH_3}$), 146,4 ($\mathrm{C\alpha}$), 128,3 ($\mathrm{C\beta}$), 61,4 ($\mathrm{CH_2N}$)	-19,2
$\mathrm{(CH_2)_5NCH_2CH{-}CHSiMe_2}$	156,6	107,8	120,6	158,8	96,6	-3,9	61,0 ($\mathrm{OCH_2}$), 14,9 ($\mathrm{CH_3}$), 140,5, 110,0, 104,0, 22,0, 13,3 [$\mathrm{(CH_2)_5N}$]	-19,4
$\mathrm{Me_3C(CH_2)_2SiMe_2}$	156,2	107,8	120,2	159,3	96,4	-3,8	9,2 ($\mathrm{SiCH_2}$), 30,8 (*tert* -C), 28,6 ($\mathrm{CCH_3}$), 37,5 ($\mathrm{CCH_2}$)	
	156,5	107,8	120,5	159,4	96,6	-4,2	146,5 ($\mathrm{C^{2'}}$), 109,2 ($\mathrm{C^{3'}}$), 119,9 ($\mathrm{C^{4'}}$), 159,4 ($\mathrm{C^{5'}}$), 7,1 ($\mathrm{SiCH_2}$)	-8,0, -5,6
	157,3	108,6	121,2	159,8	97,2	-1,9 -3,5	131,0 ($\mathrm{C^{2'}}$), 128,6 ($\mathrm{C^{3'}}$), 134,9 ($\mathrm{C^{4'}}$), 135,5 ($\mathrm{C^{5'}}$), 7,98 ($\mathrm{SiCH_2}$)	-7,7, -3,7
	156,6	107,8	120,6	159,2	96,6	-2,9, -4,2	134,7 ($\mathrm{C^{2'}}$), 127,3 ($\mathrm{C^{3'}}$), 133,6 ($\mathrm{C^{4'}}$), 139,1 ($\mathrm{C^{5'}}$), 7,2 ($\mathrm{SiCH_2}$)	-7,8, -3,5
$\mathrm{NC(CH_2)_3SiMe_2}$	157,6	108,6	121,7	158,9	97,2	-3,1	15,5 ($\mathrm{SiCH_2}$), 20,9 ($\mathrm{CH_2CH_2}$), 21,0 ($\mathrm{CH_2CN}$), 120,1 (CN)	
$\mathrm{(CH_2)_4N(CH_2)_3SiMe_2}$	156,4	107,7	120,3	159,4	96,5	-3,7	12,9 ($\mathrm{SiCH_2}$), 23,1 ($\mathrm{CH_2CH_2}$), 59,7 ($\mathrm{CH_2N}$), 53,9, 23,3 [$\mathrm{(CH_2)_4N}$]	-9,4
$\mathrm{(CH_2)_5N(CH_2)_3SiMe_2}$	156,4	107,7	120,3	159,4	96,5	-3,7	12,8 ($\mathrm{SiCH_2}$), 24,4 ($\mathrm{CH_2CH_2}$), 62,7 ($\mathrm{CH_2N}$), 54,5, 25,9, 20,9 [$\mathrm{(CH_2)_5N}$]	-9,5
$\mathrm{H_{13}C_6HN(CH_2)_3SiMe_2}$	156,4	107,8	120,4	159,3	96,6	-3,7	12,6 ($\mathrm{SiCH_2}$), 24,2 ($\mathrm{CH_2CH_2}$), 53,0 ($\mathrm{CH_2N}$), 49,8, 31,6, 30,1, 29,0, 27,2, 22,4, 13,7 ($\mathrm{C_6H_{13}}$)	-9,5
$\mathrm{Me_3Si}$*	157,6	108.7	121,2	160,3	97,2			-11,1

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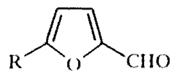
*Spectrum was recorded in DMSO-d_6 [1].

TABLE 4. ^{13}C and ^{29}Si NMR Spectra of 5-Substituted Furfurals (deuterochloroform)



R	δ, ^{13}C, ppm							δ, ^{29}Si, ppm
	C^2	C^3	C^4	C^5	CHO	$SiMe_n$	Carbon atoms of substituents R	
Me_3Si*	157,2	123,2	123,2	168,7	179,3	-1,2		-8,7 [24]
$HSiMe_2$	157,2	122,5	123,5	166,1	178,8	-4,6		-26,7
$PhSiMe_2$*	158,8	123,0	124,3	166,8	179,4	-2,6	134,9 (*o*), 129,2 (*m*), 130,9 (*p*), *136,3 (i)* (C_{Ph})	-14,1
Ph_2SiMe*	158,4	122,9	125,8	165,0	179,6	-3,7	135,8 (*o*), 129,3 (*m*), 131,3 (*p*), 134,5 (*i*) (C_{Ph})	-19,0
Ph_3Si*	158,8	123,0	127,4	163,1	180,0		136,8 (*o*), 129,6 (*m*), 131,8 (*p*), 132,6 (*i*) (C_{Ph})	-23,2
$Me_3CC_\beta H{=}C_\alpha HSiMe_2$	156,6	117,6	120,1	167,3	177,4	-3,4	35,0 (*tert* -C), 28,6 (CH_3), 160,8 ($C\beta$), 121,7 ($C\alpha$)	-16,7
$Me_3C(CH_2)_2SiMe_2$	156,7	120,2	121,6	167,3	177,5	-4,1	37,2 (CCH_2), 26,5 ($\underline{C}Me_3$), 8,73 ($Si\underline{C}H_2$)	-6,3
$NC(CH_2)_3SiMe_2$	157,7	120,1	123,0	167,3	178,6	-3,4	20,9 (CH_2CH_2), 14,9 ($SiCH_2$), 120,1 ($C \equiv N$)	
$ClCH_2SiMe_2$	157,8	120,7	123,7	164,8	178,6	-4,6	29,0 (CH_2Cl)	-8,6
MeS–	154,5	124,3	112,1	158,5	176,5		16,2 (SCH_3)	
BuS–	154,8	123,6	114,4	157,1	176,7		34,1 (CH_2S), 32,2 (CH_2CS), 22,1 ($SCC\underline{C}H_2$), 13,9 (CH_3)	
$(EtO)_2HC$–	153,4	121,5	111,2	159,0	178,5		62,5 (OCH_2), 15,6 (CH_3), 96,7 (CH)	

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*Spectrum was recorded in DMSO-d_6.

TABLE 5. Changes in the Chemical Shifts of the Carbon Nuclei in the Furan Ring in the ^{13}C NMR Spectra of Furfural with the Introduction of Substituents R at Position 5

R	$\Delta\delta$, ^{13}C, ppm ($CDCl_3$)				
	C^2	C^3	C^4	C^5	C=O
Me_3Si*	4,1	1,0	10,3	20,1	1,2
Me_2SiH	4,1	0,3	10,6	17,5	0,7
Me_2SiPh*	5,7	0,8	11,4	18,2	1,3
$MeSiPh_2$*	5,3	0,7	12,9	16,4	1,5
Ph_3Si	5,7	0,8	14,5	14,5	1,9
$Me_2Si(CH_2)_3CN$	4,6	-2,1	10,1	18,7	0,5
$Me_2SiCH{=}CHCMe_3$	3,5	-4,6	7,2	18,7	-0,6
$Me_2Si(CH_2)_2CMe_3$	3,6	-2,0	8,7	18,7	-0,6
$CH(OEt)_2$	0,3	-0,7	-1,7	10,4	0,4
MeS—	1,4	2,1	-0,8	9,9	-1,6
BuS—	1,7	1,4	1,5	8,5	-1,4

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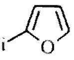
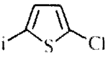
*Spectra were recorded in DMSO-d_6. $\Delta\delta^{13}C_i = \delta^{13}C_i$ (5-substituted furfural) − $\delta^{13}C_i$ (furfural).

TABLE 6. Changes in the Chemical Shifts of the Carbon Nuclei in the Furan Ring in the ^{13}C NMR Spectra of Furfural Diethyl Acetals with the Introduction of Substituents R at Position 5

R	$\Delta\delta$, ^{13}C, ppm ($CDCl_3$)*				
	C^2	C^3	C^4	C^5	C—O
Me_3Si	4,1	0,2	10,4	17,2	0,2
Me_2SiH	3,5	-0,2	10,5	14,1	-0,2
$Me_2SiCHCl_2$	0,8	0,5	13,3	15,5	0
Me_2SiCH_2Cl	3,3	0,2	11,8	14,9	0,2
Me_3SiCH_2	-3,5	-1,0	-6,2	12,1	0,1
$Me_2Si(CH_2)_2CMe_3$	2,7	-0,7	9,4	16,2	-0,6
$Me_2SiCH{=}CHCMe_3$	2,9	-0,7	9,8	16,1	-0,6
$Me_2SiCH{=}CHPh$	3,3	-0,6	10,8	13,9	-0,7
$Me_2SiCH{=}CHCOOEt$	3,1	-0,6	10,8	13,9	-0,7
$Me_2SiCH{=}CHC_7H_{15}$	3,7	0	10,4	16,8	0,2
$Me_2SiCH{=}CHCH_2N(CH_2)_4$	3,1	-0,7	9,9	15,7	-0,5
$Me_2Si(CH_2)_3N(CH_2)_4$	2,9	-0,8	9,5	16,3	-0,5
$Me_2Si(CH_2)_3N(CH_2)_5$	2,9	-0,8	9,5	16,3	-0,5
$Me_2Si(CH_2)_3NHC_6H_{13}$	2,9	-0,7	9,8	16,1	-0,5
$Me_2Si(CH_2)_3NEt_2$	2,9	-0,8	9,5	16,3	-0,5
$Me_2Si(CH_2)_3CN$	4,1	0,1	10,9	15,8	0,2
$Me_2Si(CH_2)_2Me_2Si$ 	3,0	-0,7	9,7	16,3	-0,4
$Me_2Si(CH_2)_2Me_2Si$ 	3,8	0,1	10,4	16,7	-0,8
$Me_2Si(CH_2)_2Me_2Si$ 	3,1	-0,7	9,8	16,1	-0,4
$Me_2SiCH{=}CHSiMe_3$	2,9	-0,6	10,0	15,4	-0,6
MeS—	1,5	1,7	4,4	5,0	-0,2
BuS—	1,8	1,7	6,5	3,7	-0,2
CHO—	5,5	2,7	10,7	10,3	-0,3

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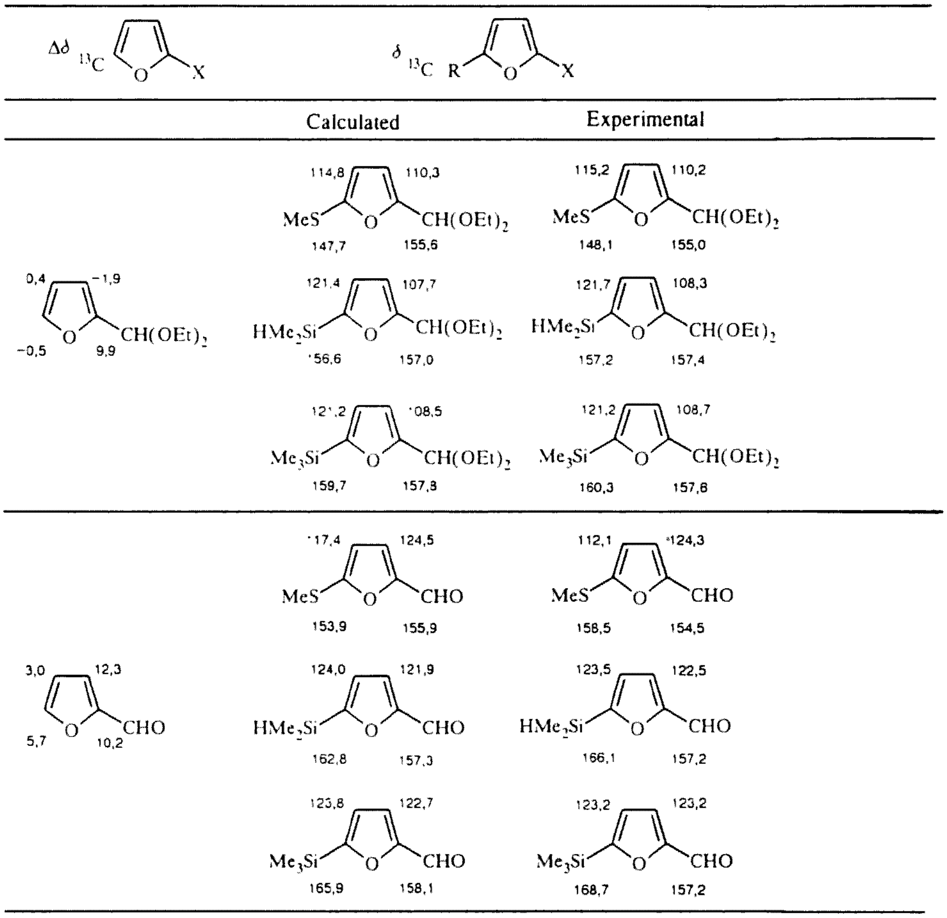
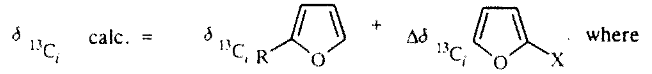
*$\Delta\delta^{13}C_i = \delta^{13}C_i$ (5-substituted furfural) − $\delta^{13}C_i$ (furfural diethyl acetal).

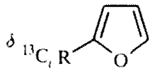
The chemical shift of the aldehyde carbon atom proved more sensitive to change of substituent at C^5 of furan. The smallest change in $\delta^{13}C\alpha$ (an upfield shift of 2 ppm) is brought about by substitution of the silicon-containing substituents by sulfur-containing substituents. In a number of cases change of the substituent at the silicon atoms also affects $\delta^{13}C\alpha$. For R = $Me_3CCH{=}CHSiMe_2$ and $Me_3C(CH_2)_2SiMe_2$ screening of the aldehyde was observed ($\Delta\delta^{13}C \sim 1$ ppm). In view of the

TABLE 7. Obtained Chemical Shifts and the Additive Chemical Shifts of the Carbon in the Diethyl Acetals of 5-Substituted Furfural and in 5-Substituted Furfurals

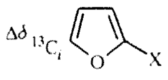




where



the chemical shift of nucleus *i* in the ring of furan derivatives (R = HSiMe₂, Me₃Si, MeS).



the change in the chemical shift of nucleus *i* in the ring of furfural diethyl acetal [X = $CH(OEt)_2$, calculated from data in [1]] and of furfural [X = CHO, calculated from data in [1, 7]] in relation to unsubstituted furan.

fact that the ^{13}C NMR spectra of 5-phenyldimethylsilylfurfural, 5-diphenylmethylsilylfurfural, and 5-triphenylsilylfurfural were recorded in DMSO-d_6, which leads to a downfield shift of the resonance of the carbon nuclei by 0.6 ppm compared with deuterochloroform, it is possible to speak of a tendency for descreening of the Cα nuclei in these compounds.

Thus, the effect of the substituent at position 5 of the furan is transmitted to Cα of the aldehyde group in cases where the substituent is conjugated with the residue of the furan molecule (alkyl sulfide substituents, silyl substituents in which the silicon atom is linked to a carbon atom in the sp_2 hybridization state).

The opposite effect is also observed: Substitution of the diethyl acetal group by an aldehyde group shifts the ^{29}Si resonance downfield by 2 ppm (R = $HSiMe_2$, Me_2SiCH_2Cl, $Me_2SiCH{=}CHCMe_3$, $SiMe_3$).

The appearance of the diethyl acetal group at position 2 of furan does not lead to change in $\delta^{29}Si$ compared with the corresponding silyl-substituted furan.

Comparison of the experimental and additive chemical shifts of the carbon nuclei in the furan rings of 5-methylthiofurfural, 5-dimethylsilylfurfural, 5-trimethylsilylfurfural, and the corresponding diethyl acetals (the choice of compounds was determined by the existence of $\delta^{13}C$ NMR data for the substituted silylfurans) shows that the contribution from the aldehyde group and the substituents at position 5 of furan to the screening of the carbon nuclei of the furan ring in these compounds is nonadditive. The experimental and calculated values of the chemical shifts of the carbon nuclei in the furan rings of the diethyl acetals of the above-mentioned 5-substituted furfurals coincide, indicating in the latter case an independent electron-withdrawing effect from the substituents on the furan ring (Table 7).

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker WH-90/DS (90 MHz) and WH-360 (360 MHz) spectrometers in deuterochloroform with TMS as internal standard. The ^{1}H chemical shifts are given in Tables 1 and 2, and the ^{13}C and ^{29}Si chemical shifts are given in Tables 3 and 4. For the data on the ^{1}H NMR spectra of 5-substituted furfural diethyl acetals and 5-dimethylsilylfurfural diethyl acetals obtained as a result of the hydrosilylation of the monosubstituted derivatives of ethylene and acetylene, see [6].

Some of the silicon-substituted furfural diethyl acetals (II) ($R^1R^2R^3Si$ = Me_3Si, HMe_2Si, $ClCH_2Me_2Si$, Cl_2CHMe_2Si, $PhMe_2Si$, Ph_2MeSi, Ph_3Si), the sulfide analogs, and also 5-formylfurfural diethyl acetal were obtained by organolithium synthesis from furfural diethyl acetal by analogy with the known procedures in [3-5]. The others were obtained by hydrosilylation of the monosubstituted derivatives of ethylene and acetylene by 5-dimethylsilylfurfural diethyl acetal [6]. The corresponding aldehydes were obtained by boiling ether solutions of the diethyl acetals of the substituted furfural in the presence of p-toluenesulfonic acid (an aqueous solution).

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