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SYNTHESIS AND ^{1}H, ^{13}C, AND ^{29}Si SPECTROSCOPIC INVESTIGATION OF 2-THIENYL(2′-FURYL)- AND 2-THIENYL[2′-(4′,5′-DIHYDROFURYL)]SILANES

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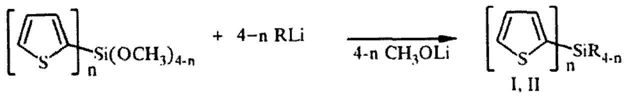
The complete series of 2-thienyl(2′-furyl)- and 2-thienyl[2′-(4′,5′-dihydrofuryl)]silanes have been synthesized, and the influence of the character and number of substituents on the chemical shifts in the ^{1}H, ^{13}C, *and* ^{29}Si *spectra has been investigated.*

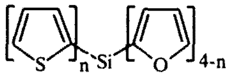
Aromatic and heteroaromatic derivatives of Group IV-B elements provide a convenient model for the investigation of (p−d)π interaction of a central atom of silicon, germanium, tin, or lead with the π-electrons of the ring [1]. Thus, it has been found that in the case of (2-furyl)silanes, -germanes, -stannanes, and -plumbanes, the chemical shifts of the protons are determined by the nature of the heteroorganic substituent, the number of furan rings in the molecule, and the character of coupling of the π-electron system with the heteroatom, as well as the geometric parameters of the π-donor and the heteroatom [2]. Substituent effects that are analogous in character and magnitude have been observed in less highly conjugated π-electron systems [3]. In (2-furyl)- and (2-thienyl)alkoxysilanes, competing interactions have been observed: Interaction between the central silicon atom with the π-electron system of the furan or thiophene ring on the one hand, and with the p-electrons of oxygen on the other hand [4].

In order to study the mutual influence of the heteroring on electronic effects in furylsilanes and thienylsilanes in reactions of (2-thienyl)methoxysilanes with 2-furyl- or 2-(4,5-dihydrofuryl)lithium, we synthesized two series of compounds:



I) R = 2-furyl, n = 1-3; II) R = 4,5-dihydrofuryl, n = 1-3

The analytical characteristics of the new compounds are listed in Table 1. The tetra(4,5-dihydrofuryl)silane, tetra(2-furyl)silane, and tetra(2-thienyl)silane were obtained by organolithium and organomagnesium syntheses, using methods described in [3, 5, 6].



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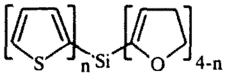

II

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*Deceased

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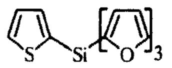
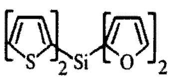
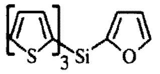
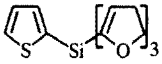
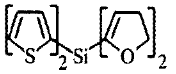
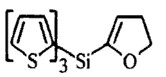
TABLE 1. Analytical Characteristics of 2-Thienyl(2'-furyl)- and 2-Thienyl[2'-(4',5'-dihydrofuryl)]silanes

Compound	mp, °C	Empirical formula	Elemental analyses (found/calculated), %		
			C	H	S
	62...63	$C_{16}H_{12}O_3SSi$	61,45 61,51	3,84 3,87	10,22 10,26
	56...57	$C_{16}H_{12}O_2S_2Si$	58,41 58,50	3,61 3,68	19,41 19,52
	90...92	$C_{16}H_{12}OS_3Si$	55,59 55,78	3,24 3,51	27,80 27,92
	101...102	$C_{16}H_{18}O_3SSi$	60,35 60,34	5,39 5,70	10,12 10,07
	69...70	$C_{16}H_{16}O_2S_2Si$	58,04 57,79	4,70 4,85	19,13 19,29
	71...72	$C_{16}H_{14}OS_3Si$	55,30 55,45	3,99 4,07	27,59 27,76

In the ^1H spectra of compounds I and II, we observe signals of three-spin systems of the AMX type, the chemical shifts and SSCCs of which are characteristic for α-substituted furans or thiophenes, respectively ([7], pp. H285 and H305), and also multiplets of the AM_2X_2 type, characteristic for protons of the 4,5-dihydrofuryl ring [8]. An unambiguous assignment of signals in the ^{13}C NMR spectra was made on the basis of the ^{13}C-^1H SSCCs, measured in spectra without any wideband suppression of protons. The signals of the thiophene and furan carbons are readily distinguishable, since in all cases, the values of ^1J(C-H) do not fall outside the limits of variation of values characteristic for α- and β-carbons in derivatives of thiophene (182-184 and 167-168 Hz) and furan (198-200 and 174-176 Hz) ([7], p. C220). The chemical shifts of the ^1H, ^{13}C, and ^{29}Si nuclei are listed in Tables 2 and 3.

The results of a graphical analysis performed for the chemical shifts of the NMR signals of compounds I and II (Figs. 1-4) show that the effects of substituents attached to the central silicon atom are nonadditive. It should also be noted that with the appearance of any of the heterocycles in the molecule of I or II, the signals of the ring protons are shifted downfield relative to the unsubstituted heterocycle of the same type, with $\Delta\delta$(3-H) > $\Delta\delta$(5-H) > $\Delta\delta$(4-H) for the 2-thienyl and 2'-furyl groups, and with $\Delta\delta$(3'-H) of the 2'-(4',5'-dihydrofuryl) group comparable in magnitude to the corresponding value for the 2'-furyl substituent. At the same time, we observe a greatly different character for the changes in chemical shifts of the 2-C carbon, which is closest to the silicon atom: for the furyl and 4',5'-dihydrofuryl groups, with increasing number of heterocyclic substituents we observe shielding of the 2'-C signal; for the thienyl groups, in contrast, we observe deshielding of the analogous signal. In the latter case, the 2-C signals in series II are shielded relative to the signals of the same carbon in series I in accordance with the smaller −I-effect of the 4',5'-dihydrofuryl group. In accord with such an influence on the chemical shifts of the ^1H and ^{13}C nuclei of the heterocycles, the (2-thienyl)-, (2-furyl)-, and 2-(4,5-dihydrofuryl)silyl substituents, regardless of their number on the silicon atom, are electron acceptors. If we compare the changes in chemical shifts of the 4-H and 5-H protons of the thiophene ring, we find that the electron-acceptor strength of the (2'-furyl)silyl group is somewhat higher than that of the [2'-(4',5'-dihydrofuryl)]silyl group. It is difficult to use the chemical shifts of the 3-H signal for the same purposes, since shielding of this proton experiences the anisotropic influence of the other heterocycles.

In parallel with the analysis of chemical shifts of the various nuclei in series I and II compounds, we attempted to calculate the atomic charges. We intended to use these values in a correlation analysis of the chemical shifts. The theoretical calculations were performed by the semiempirical AM1 method for fully optimized structures. In the course of the optimization, we found that the I and II compounds have minimal energy with a completely disordered position of the heteroaromatic rings.

TABLE 2. Chemical Shifts of ^1H, ^{13}C, and ^{29}Si Nuclei in 2-Thienyl(2′-furyl)silanes (I)

n	Thiophene ring*							Furan ring*								Si
	3-H	4-H	5-H	2-C	3-C	4-C	5-C	3'-H	4'-H	5'-H	2'-C	3'-C	4'-C	5'-C		
0 †	—	—	—	—	—	—	—	6,89	6,36	7,67	151,4	125,5	110,4	149,1		-56,0
1	7,56	7,26	7,74	129,4	138,5	128,4	133,2	6,96	6,47	7,78	151,8	124,9	109,9	148,6		-50,0
2	7,53	7,26	7,75	130,8	138,5	128,4	133,2	6,93	6,47	7,79	152,8	124,8	109,9	148,5		-44,7
3	7,50	7,24	7,73	132,1	138,4	128,4	133,1	6,90	6,46	7,78	153,7	124,6	109,8	148,4		-39,4
4	7,50	7,26	7,70	134,0	138,4	129,3	134,0	—	—	—	—	—	—	—		-34,1

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*Upon transition from n = 0 to n = 4, the changes in interproton SSCC are no greater than 0.1 Hz: $J_{35} = 3.5$, $J_{45} = 4.6$, $J_{3'4'} = 3.4$, $J_{3'5'} = 0.6$, $J_{4'5'} = 1.7$ Hz.

†Data for ^{13}C and ^{29}Si are taken from [9].

TABLE 3. Chemical Shifts of ^1H, ^{13}C, and ^{29}Si Nuclei in 2-Thienyl[2′-(4′,5′-dihydrofuryl)]silanes (II)

n	Thiophene ring*							4′,5′-Dihydrofuran ring*								Si
	3-H	4-H	5-H	2-C	3-C	4-C	5-C	3'-H	4'-H	5'-H	2'-C	3'-C	4'-C	5'-C		
0 †	—	—	—	—	—	—	—	5,70	2,68	4,35	153,8	118,0	31,3	71,3		-51,9
1	7,59	7,21	7,68	130,0	138,3	128,8	132,9	5,63	2,66	4,38	154,6	117,8	30,9	71,1		-47,4
2	7,56	7,22	7,70	130,0	138,3	128,3	132,9	5,56	2,63	4,41	155,9	117,8	30,9	71,2		-43,0
3	7,51	7,22	7,71	131,7	138,4	128,3	133,0	5,51	2,67	4,42	157,0	117,7	30,9	71,3		-38,6
4	7,50	7,26	7,70	134,0	138,4	129,3	134,0	—	—	—	—	—	—	—		-34,1

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*Upon transition from n = 0 to n = 4, the changes in interproton SSCC are no greater than 0.1 Hz: $J_{34} = 3.3$, $J_{35} = 0.8$, $J_{45} = 4.7$, $J_{3'4'} = 2.6$, $J_{3'5'} = 0$, $J_{4'5'} = 9.6$ Hz.

†Data for ^{13}C and ^{29}Si are taken from [9].

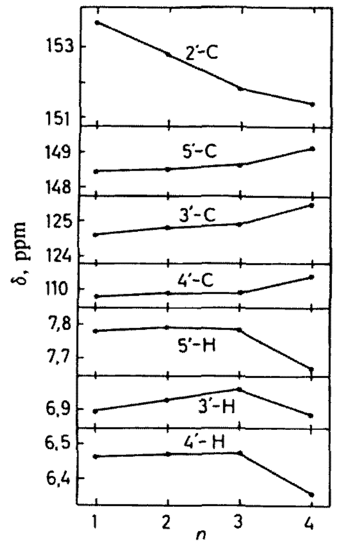

Fig. 1

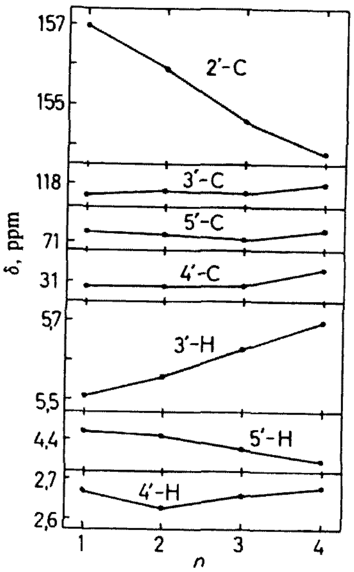

Fig. 2

Fig. 1. Chemical shifts of ^1H and ^{13}C nuclei of 2-furyl fragment as functions of number of furyl groups in 2-thienyl(2′-furyl)silanes (I).

Fig. 2. Chemical shifts of ^1H and ^{13}C nuclei of 2′-(4′,5′-dihydrofuryl) fragment as functions of number of 4′,5′-dihydrofuryl groups in 2-thienyl[2′-(4′,5′-dihydrofuryl)]silanes (II).

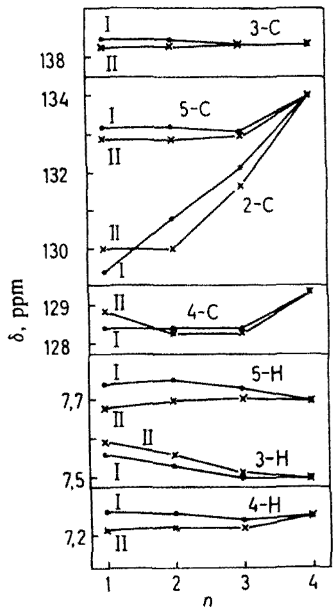

Fig. 3. Chemical shifts of ^1H and ^{13}C nuclei of 2-thienyl fragments as functions of number of thienyl groups in 2-thienyl[2′-furyl]silanes (I) and 2-thienyl[2′-(4′,5′-dihydrofuryl)]silanes (II).

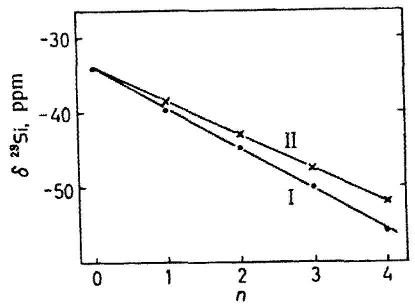

Fig. 4

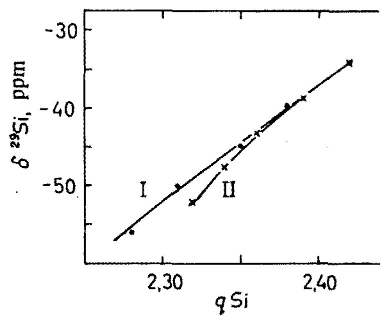

Fig. 5

Fig. 4. Chemical shifts of ^{29}Si nuclei as functions of number of furyl or 4′,5′-dihydrofuryl groups in 2-thienyl(2′-furyl)silanes (I) and 2-thienyl[2′-(4′,5′-dihydrofuryl)]silanes (II).

Fig. 5. Chemical shifts of ^{29}Si nuclei as functions of magnitude of charge on silicon atom in 2-thienyl(2′-furyl)silanes (I) and 2-thienyl[2′-(4′,5′-dihydrofuryl)]silanes (II).

As a consequence, for monotypical nuclei, the calculation gave several values of the charge, and the averaging of these values led to a loss of sensitivity to substituent effects. The dependence of the chemical shift on the magnitude of the charge on the central silicon atom (Fig. 5) shows that with increasing number of 2-furyl or 2′-(4′,5′-dihydrofuryl) groups, the charge on this atom decreases, the effect being greater for the 2-thienyl(2′-furyl)silanes.

Thus, the NMR data indicate a complex character of the mutual influence of heterocyclic substituents on shielding of the nuclei, i.e., we can assume the presence of several effects, including inductive and congruent (p-d)π interaction.

EXPERIMENTAL

NMR spectra of solutions of the compounds in $CDCl_3$ were registered in a Bruker AM-360 spectrometer with working frequencies (in MHz) 360.13 (^{1}H), 90.56 (^{13}C), and 71.55 (^{29}Si). The chemical shifts were measured relative to TMS as an internal standard (^{1}H, ^{13}C) or as an external standard (^{29}Si). The calculations of the total charges on the atoms were performed by A. Dishs (for which the authors wish to express their gratitude) for fully optimized structures, by the semiempirical AM1 method that is included in MOPAC 6.0 [10].

2-Thienyltri(2′-furyl)silane. To a solution of 4.15 g (0.02 mole) of 2-thienyltrimethoxysilane in 30 ml of absolute ether, at 0°C, 2-furyllithium was added dropwise over the course of 2 h (the furyllithium was prepared from 0.06 mole of furan in 60 ml of absolute tetrahydrofuran and 0.06 mole of 1.5 N n-butyllithium in hexane, at −20°C). After all of the furyllithium had been added, the reaction mixture was held for 30 min at 0°C and then left at room temperature for 17 h. The product was filtered through a layer of neutral aluminum oxide and treated with 0.1 ml of acetic acid. The solvent was removed under reduced pressure, and the resulting precipitate was filtered off and washed with absolute pentane. Obtained 2.88 g (yield 45%) of 2-thienyltri(2′-furyl)silane.

The compounds listed in Table 1 were synthesized analogously from the corresponding 2-thienylmethoxysilane and 2-furyllithium or 4,5-dihydrofuryllithium.

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