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PHOTOELECTRON SPECTRA OF FURYLSILANES AND THEIR CARBON ANALOGS

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Summary

The first vertical π-ionization energies of substituted furans as determined by photoelectron spectroscopy are compared with the results of CNDO/2 calculations. The analysis of the photoelectron spectra and quantum chemical calculations for furylsilanes, difurylsilanes and some carbon analogs has shown the importance of the p_π–d_π interaction as well as of the conjugation and necessity of the inclusion of silicon *d*-atomic orbitals into the basic set.

Introduction

Photoelectron spectroscopy (PES) has been successfully applied to the study of interactions between atomic *d* orbitals in silicon and π molecular orbitals (MO) of vinyl and phenyl groups in vinyl- [1–3] and phenyl-silanes [4]. To deepen our knowledge of p_π–d_π interactions, we recorded photoelectron spectra of furylsilanes and some of their carbon analogs and performed quantum chemical calculations in the CNDO/2 formalism. Energies and ionization potentials (IP) calculated in *sp* and *spd* basic sets have been compared within Koopmans' Theorem. These systems attract particular interest, first, because of the presence of the furyl group which serves a good model to investigate interactions between heterocyclic π-systems and *d* atomic orbitals (AO) of silicon [5], and, second, because furylhydrosilanes are important starting products to synthesize biologically active organosilicon furan derivatives [6–8].

Results and discussion

Figures 1a and 1b show photoelectron spectra of the following compounds: furan (I), 2-furylsilane (II), 2-methylfuran (III), dimethyl(2-furyl)silane (IV), methylethyl(2-furyl)silane (V), diethyl(2-furyl)silane (VI), trimethyl(2-furyl)silane (VII), 2-

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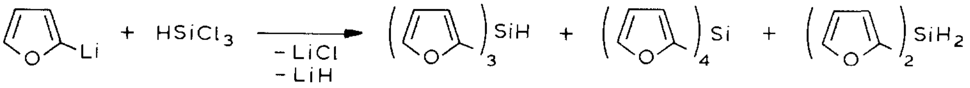
tert-butylfuran (VIII), 2-furyltriethoxysilane (IX), 2-furyltriethoxymethane (X), di(2-furyl)silane (XI), methyldi(2-furyl)silane (XII), methyldi(3-furyl)silane (XIII), dimethyldi(2-furyl)silane (XIV), ethyldi(2-furyl)silane (XV). 2-Furylsilane (II) was obtained in 35% yield by reducing 2-furyltriethoxysilane with lithium aluminum hydride:

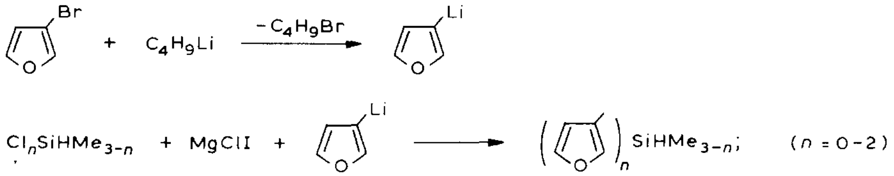
To avoid Si–C bond cleavage, lithium aluminum hydride was added to the ether solution of silane at −25°C in inert atmosphere.

Di(2-furyl)silane (XI) results from the interaction of 2-furyllithium in THF and trichlorosilane in ether. The reaction is conducted at −30°C. Along with substitution of chlorine atoms, the hydrogen of the Si–H bond is also substituted, and the Si–Cl bond is reduced by the resultant lithium hydride:



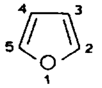
The first representatives of 3-furylhydrosilanes were prepared by successive addition to methyldichlorosilane of methylmagnesium iodide and 3-furyllithium obtained from 3-bromofuran and butyllithium at −65 to 70°C in ether:

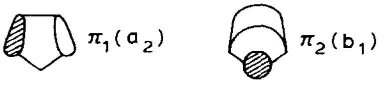
$$\mathrm{MeSiHCl_2 + MeMgI \xrightarrow{-MgClI} Cl_nSiHMe_{3-n}} \quad ; (n = 0-2)$$



Conversion of the lithium derivative into the magnesium one includes fission of the Si–H bond and formation of methyltri(3-furyl)silane. Treating 2-furyllithium with trimethylchlorosilane [9] and tetraethoxysilane [10] yields furylsilanes IV, V, VII, IX, XII, XIV. 2-tert-Butylfuran (VIII) and 2-furyltriethoxymethane (X) were synthesized as reported [9,10].

We now consider the photoelectron spectra of furylsilanes I–X (Fig. 1a). The spectrum of furan (I) has been investigated earlier [11]; identification of the bands was performed on the basis of calculation and analysis of the band vibration structure. The first band was assigned by the authors to the ionization of the π MO of a_2 symmetry localized at C(2)–C(3) and C(4)–C(5), whereas the second band to that of b_1 symmetry localized at oxygen and C(3)–C(4):





Before we interprete the photoelectron spectra of substituted furans, we attempt to predict qualitatively a change in ionization potentials of molecular π_1 and π_2

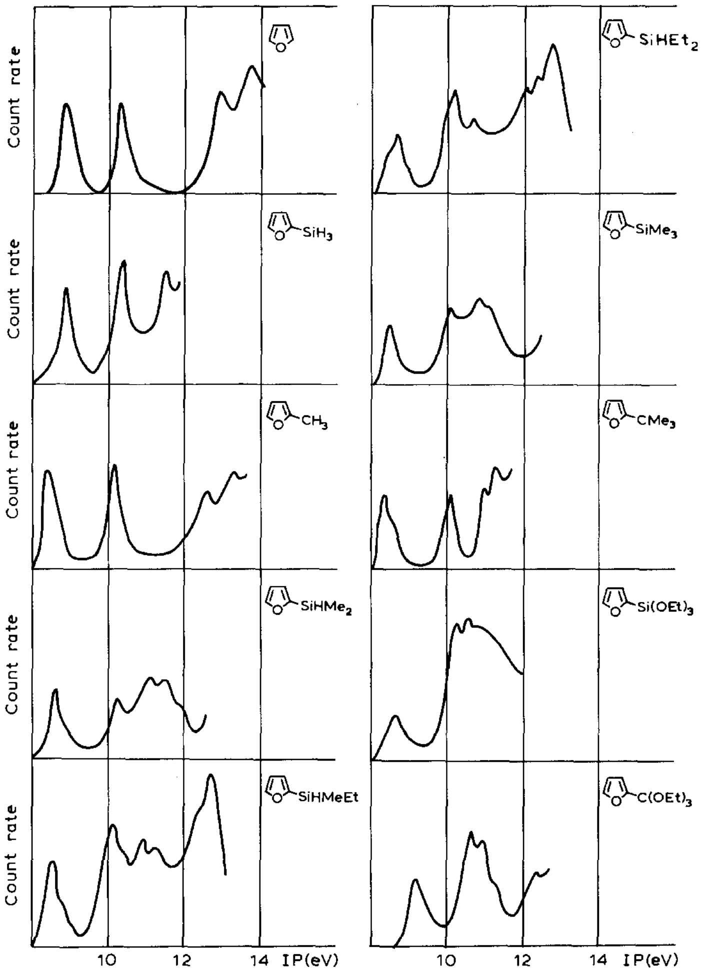
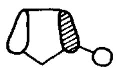


Fig. 1. a) He(I) photoelectron spectra of compounds I–X; b) He(I) photoelectron spectra of compounds XI–XV.

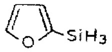
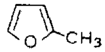
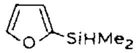
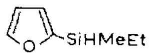
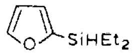
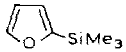
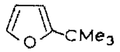
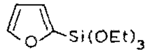
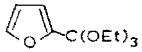
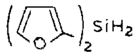
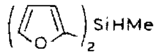
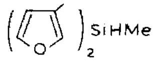
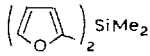
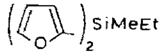
orbitals. Furylsilanes and some of their carbon analogs have been obtained by substituting hydrogen at carbon-2 (C(2)). As follows from perturbation theory, this should lead to a more pronounced change in the energy of the π_1 MO than in that of the π_2 MO, for the second orbital has in this position practically a node. CNDO/2 calculations give the highest occupied molecular orbital (HOMO) of π-type with a node on the C(2)–M bond where M = C, Si. The analysis of relative changes in IP$_1$ and IP$_2$ (see Table 1) in the series of compounds I–X confirmed the above predictions. Thus, based on calculations and change of IP$_1$ and IP$_2$ in the series of substituted furans, we assigned the first two bands in PES of compounds II–X to the ionization of π_1 and π_2 MO's:


π_1


π_2

TABLE 1

VERTICAL IP's OF COMPOUNDS I–XV

IP (eV)		IP_1	IP_2	IP_3
I		8.90	10.30	13.0
II		8.92	10.40	11.57
III		8.37	10.14	12.63
IV		8.62	10.22	11.20
V		8.53	10.14	11.0
VI		8.62	10.13	10.67
VII		8.53	10.07	10.88
VIII		8.38	10.08	10.98
IX		8.66	10.20	
X		9.23	10.7	11.03
XI		8.79	10.31	11.39
XII		8.71	10.20	11.14
XIII		8.84	10.07	11.16
XIV		8.60	10.18	10.95
XV		8.75	10.33	10.94

The third band in the PE spectra of furan I occurs at 12.5–13.5 eV (vertical IP = 13.0 eV). The spectra of substituted furans II–X show additional bands in the region 10.5–12.5 eV, which may be attributed to the ionization of the orbitals associated with substituents. The comparison of ionization potentials of σ MO's of vinylsilanes and their carbon analogs [1] with the third IP of compounds II–VIII and also the analysis of changes in IP_3 and calculated energies of C(2)–M σ bond orbitals in the above-mentioned series of compounds establishes that the third IP corresponds to the removal of electrons from the C(2)–M bond σ MO. For compounds IX–X, calculations assign IP_3 to the ionization of the orbital localized predominantly on oxygens of the substituents. Photoelectron spectra of difurylsilanes XI–XV (Fig. 1b) show in the region 8.0–10.5 eV two well resolved bands; their positions are identical to those of the first two bands in the spectra of furylsilanes I–X, which we have assigned to π_1 and π_2 MO's.

As follows from the comparison of the linewidths in spectra of difurylsilanes and furylsilanes and analysis of the ratio integrated intensities of bands in spectra of difurylsilanes (the ratio of integrated intensities of the first three bands in the spectrum of di(2-furyl)silane (XI) is 2 : 2 : 1), the first two bands in spectra of XI–XV appear to be due to the ionization of doubly degenerate or weakly interacting (splitting $\Delta E \leqslant 0.06$ eV). Calculations performed with a *spd* basic set for difurylsilane molecules with *trans*-furan rings allowed the first bands in the PE spectra of these compounds to be assigned to ionization of two π MO's of energies differing by $\Delta E = 0.11$–0.02 eV, which arise from the weak interaction across a silicon atom of two π MO's of a_2 symmetry in the symmetry group of furan. Based on comparison of PE spectra of substituted furans I–X, of the band shapes and integrated relative intensities of the first and second bands, the second band in spectra of difurylsilanes XI–XV has been assigned to ionization of the two π MO's which represent a combination of π orbitals of b_1 symmetry in the local symmetry group of the heterocycle. From the results of calculations, the difference between these π MO energies is as small as $\Delta\ E = 0.11$–0.04 eV, with the exception of methyldi(3-furyl)silane for which $\Delta E = 0.92$ eV, but since no splitting of the second band in the PE spectra of this molecule is observed, the divergence of experimental and calculated values appears to result from the non-planar conformation of the molecule considered. Therefore, the position of the first two bands in the PE spectra of difurylsilanes, the ratio of integrated intensities as well as the absence of splitting supported by quantum chemical calculation allowed to us assign the bands discussed to ionization of the non-interacting a_2-π_1', π_1'' and b_1-π_2', π_2'' orbitals, respectively.

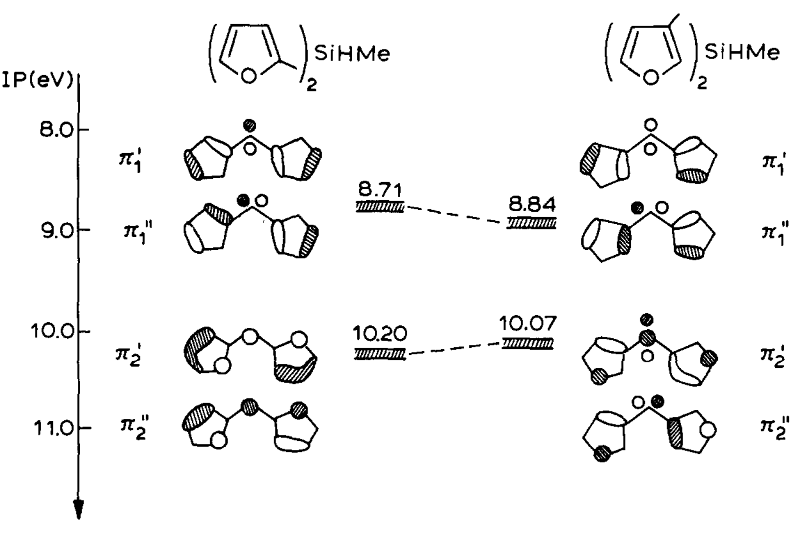


Fig. 2. Energies of π MO levels for methyldi(2-furyl)silane and methyldi(3-furyl)silane.

This identification is substantially confirmed by a change in the first two ionization potentials in the series of molecules with the same substituents in different positions. The comparison of the PE spectra of methyldi(2-furyl)silane (XII) and methyldi(3-furyl)silane (XIII) whose $IP_1 = 8.71$ eV (XII), 8.84 eV (XIII) and $IP_2 =$ 10.20 eV (XII), 10.07 eV (XIII) shows that the HOMO's for XIII are more stabilized and a second MO destabilized relative to XII. This can be explained by the assumption that the highest occupied MO's are in fact degenerate π_1' and π_1'' MO's followed by π_2'- and π_2'' MO's in their energies. Indeed, because of the π electron density of the a_2 orbital, a change in the position of substitution from 2 to 3 is expected to lead to an similarity of the π MO levels in the methyldi(3-furyl)silane as compared with the methyldi(2-furyl)silane, which is observed in the experiment (Fig. 2).

The absence of splitting of the first two bands in the spectra of difurylsilanes suggests that there is no apparent interaction taking place between the π systems of heterocycle. It should be noted that in diphenylsilanes and diarylsilanes no interaction between the π systems across the saturated silicon atom has been established [12,13].

The third IP in the series of difurylsilanes XI–XV changes from 11.16 eV (XIII) to 10.94 eV (XV). From comparison of IP_3 values in the series of corresponding furylsilanes it follows that IP_3 of difurylsilanes is due to ionization of the σ MO localized on the C–Si–C bonds, where the carbon atoms belong to heterocycles. Tables 1 and 2 show vertical IP's of molecules I–XV under consideration, as well as the energies calculated by a CNDO/2 method in *sp* and *spd* basic sets.

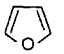
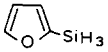
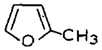
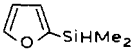
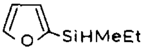
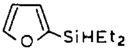
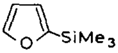
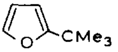
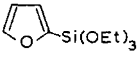
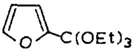
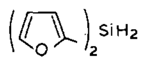
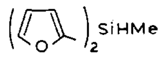
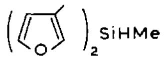
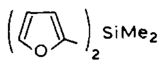
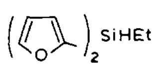
Using the data of Tables 1 and 2 the measured IP's and calculated energies have been compared. The correlation coefficients obtained for the relationships of experimental IP_1, IP_2 and those calculated by CNDO/2, $E(\pi_1)$, $E(\pi_2)$ for compounds I–X and $\tilde{E}(\pi_1', \pi_1'')$, $\tilde{E}(\pi_2', \pi_2'')$ where $E(\pi_i', \pi_i'') = E(\pi_i') + E(\pi_i'')/2$ for compounds XI–XV, respectively, suggest merely an approximate agreement between the experimental and calculated values. However, comparison of the changes in ΔIP_π and their corresponding ΔE_π in the series of molecules investigated shows that in calculations both in the *sp* and *spd* basic sets, the effects of σ–π and p_π–d_π conjugations are overestimated. Therefore, a correlation analysis has been performed for molecules I–VIII and XI–XV involving π MO energy values averaged through the two basic sets: $\tilde{E}_\pi = (E_\pi(sp) + E_\pi(spd))/2$ (Table 2). As a result, the correlation coefficient $r = 0.974$ has been determined for the IP_1 relationship and the corresponding $\tilde{E}_{\pi_1}$ in the series of thirteen molecules I–VIII and XI–XV which, indicates a semiquantitative agreement between the experimental and calculated values (Fig. 3).

Using the data from quantum chemical calculations in the two basic sets, the experimental data and taking into consideration the correlation relationships, we have carried out an evaluation of the inductive effect, σ–π conjugation and p_π–d_π interaction, whose values are shown in Table 3.

We briefly discuss below the appropriate values. Since CNDO/2 calculations showed that a change in the π_2 MO energies in these molecules mainly resulted from the inductive effect of substituents, the magnitude of this effect was determined directly by experimental changes relative to the furan IP_2. In calculations of the conjugation effects, the overestimation of these effects has been taken into account: from the correlation equation $IP_i = -kE_i + b$, i = the number of members of the series, $k = 0.66$, $b = 0.84$ for example: $\Delta IP^{1,i}_{\sigma\text{-}\pi} = -k(E^1_\pi - E^i_\pi)$ where E^1_π = energy of

TABLE 2

CALCULATED EIGENVALUES (eV) BY CNDO/2

Compounds		$-E(\pi_1)$			$-E(\pi_2)$		
		sp	*spd*	$\frac{sp+spd}{2}$	*sp*	*spd*	$\frac{sp+spd}{2}$
I		12.19	-	12.19	14.85	-	14.85
II		11.62	12.82	12.22	14.75	15.35	15.05
III		11.48	-	11.48	14.78	-	14.78
IV		11.46	12.16	11.81	14.77	14.93	14.85
V		11.31	12.01	11.66	14.69	14.93	14.81
VI		11.33	12.06	11.695	14.67	14.82	14.745
VII		11.43	12.01	11.72	14.71	14.68	14.695
VIII		11.34	-	11.34	14.83	-	14.83
IX		12.05	12.44	12.245	15.35	15.08	15.215
X		11.99	-	11.99	15.04	-	15.04
		$-(\frac{E(\pi_1')+E(\pi_1'')}{2})$			$-(\frac{E(\pi_2')+E(\pi_2'')}{2})$		
XI		11.69	12.54	12.11	14.75	15.06	14.90
XII		11.62	12.22	11.92	14.72	14.80	14.76
XIII		11.84	12.26	12.05	14.14	14.46	14.30
XIV		11.56	12.0	11.78	14.68	14.72	14.70
XV		11.56	12.22	11.89	14.75	14.85	14.80

furan π_1 MO. $E^i_\pi = \pi_1$ MO, *i*th member of the series.

Analysis of data given in Table 3 shows that, despite the predominance of the value for σ–π conjugation over the other effects in all the silicon-containing compounds, the p_π–d_π interaction is also important. The results of calculations on

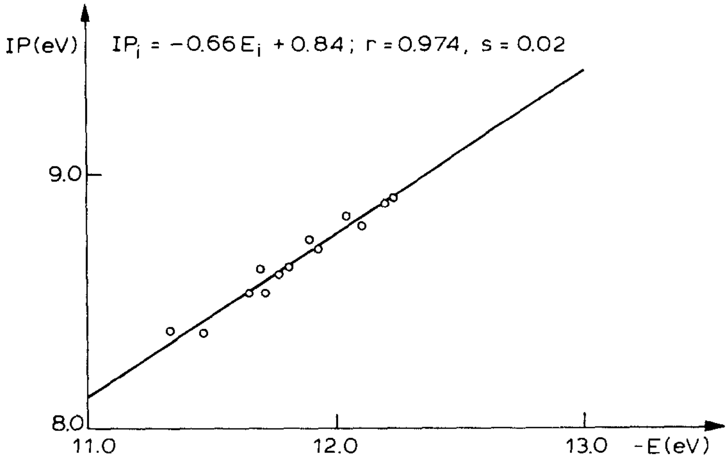


Fig. 3. Correlation between IP_1 and $\bar{E}(sp, spd)$ for compounds I–VIII and XI–XV.

2-furyltriethoxysilane (IX) and 2-furyltriethoxymethane (X) did not allow inclusion of the data for these molecules into corresponding correlations on the following reasons: first, the considerable stabilization of both π_1 and π_2 MO's which occurred according to the PE experimental data for 2-furyltriethoxymethane was not represented quantitatively in the calculation; second, the analysis of π_1 MO composition of 2-furyltriethoxysilane showed that silicon d AO's were not involved in the π_1 MO under consideration, their largest contribution being observed in the orbitals of the unshared electron pairs of the oxygen atoms (n_0) of the $Si(OEt)_3$ substituent, i.e. there is competition between n_0 and the π MO for the d AO, as already shown [14]. Thus, satisfactory correlation with $r = 0.956$ was obtained only with the inclusion of the data for this molecule calculated in the sp basic set, without averaging the energy values through these two basic sets. Nevertheless the results of calculations on 2-furyltriethoxysilane explained the reversal in the IP_1 change in 2-furyltriethoxysilane (IX) and 2-furyltriethoxymethane (X) in contrast to the pairs of analogs: 2-furylsilane (II) and 2-methylfuran (III) and trimethyl(2-furyl)silane (VII) and 2-tert-butylfuran (VIII) (Fig. 4).

TABLE 3

ESTIMATES OF INDUCTIVE, $\sigma-\pi$ AND $p_\pi-d_\pi$ EFFECTS ON FURAN π VERTICAL IONIZATION ENERGIES

Compounds	Inductive effect	$\sigma-\pi$ effect	$p_\pi-d_\pi$ effect
II	−0.1	0.47	−0.39
III	0.16	0.34	–
IV	0.08	0.41	−0.23
V	0.16	0.43	−0.24
VI	0.17	0.41	−0.32
VII	0.23	0.28	−0.16
VIII	0.22	0.27	–

Table 2 shows the average energy values $\bar{E}(\pi_1', \pi_1'')$ and $\bar{E}(\pi_2', \pi_2'')$ of highest occupied MO's of difurylsilanes, e.g. π_1' MO and π_1'' MO calculated in the *spd* basic set, and the agreement between the values of the splitting $\Delta E = E(\pi_1') - E(\pi_1'')$ with experimental data; calculations in the *sp* basic set lead to large values of ΔE not supported by experimental data (see Fig. 5).

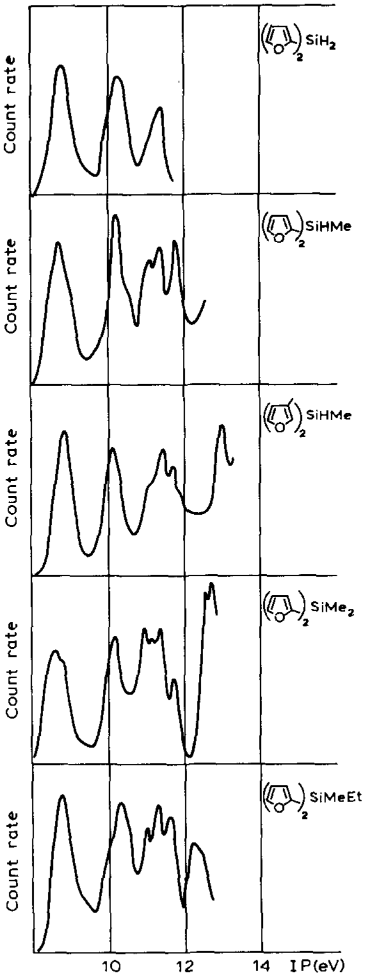


Fig. 4. Energies of π_1 MO levels for compounds II–III, VII–VIII and IX–X.

Conclusion

The analysis of photoelectron spectra and quantumchemical calculations for furylsilanes, difurylsilanes and some carbon analogs showed that although in CNDO/2 calculations the effects of σ–π conjugation and p_π–d_π interaction are overestimated, use of experimental data, which allowed quantitative evaluation of various substituent electronic effects, demonstrated the importance of p_π–d_π interac-

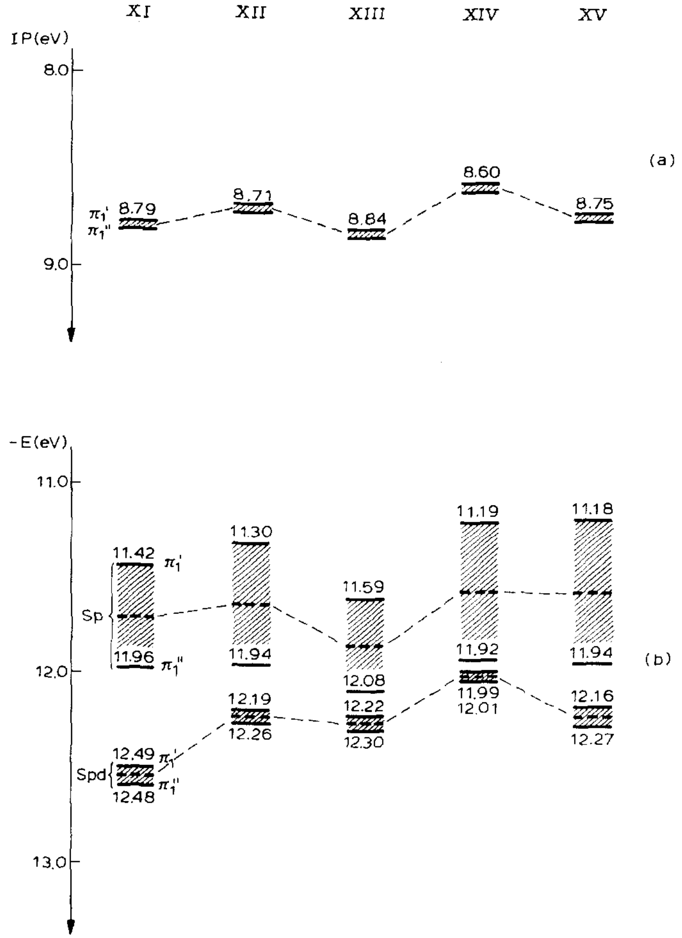


Fig. 5. Energies of π_1' and π_1''-MO levels of difurylsilanes from a) PE spectra b) CNDO/2 calculations.

tion and of σ–π conjugation as well as of the inclusion of silicon *d* AO's into the basic sets. The results obtained both from the experimental and theoretical calculations on 2-furyltriethoxysilane indicate an absence of marked p_π–d_π conjugation. The main effect of the Si atom *d* AO's are on the orbitals of unshared electron pairs of oxygen atoms.

Experimental

2-Furylsilane (II)

Dry lithium aluminium hydride (2.2 g, 0.058 mol) was added under nitrogen at −25°C to 2-furyltriethoxysilane (IX) (15 g, 0.065 mol) in 100 ml of ether. The reaction mixture was warmed to room temperature and the residue was filtered off on a Shott's filter. The filtrate was fractioned. Yield 2.2 g (35%), b.p. 73°C/760 mmHg, d_4^{20} 0.9033, n_D^{20} 1.4550, MR_D 29.49, calculated 29.75.

Reaction of trichlorosilane with 2-furyllithium

2-Furyllithium, prepared from 42 g (6.05 mol) of lithium, 277.5 g (3.0 mol) of butyl chloride, and 204 g (3.0 mol) of furan in 1.4 l THF, was added at −30°C to 100 g (0.74 mol) of trichlorosilane in 100 ml of ether. An additional 29 g (0.21 mol) trichlorosilane introduced at −25 to −15°C neutralized the unreacted 2-furyllithium. The mixture was left for 12 h at room temperature. The precipitate was filtered off, the solvent distilled, and the residue fractioned. Yield: 5 g of di(2-furyl)silane (XI), b.p. 40°C/0.5 mmHg, d_4^{20} 1.0745, n_D^{20} 1.5112, MR_D 46.81, calculated 46.83; 61 g of tri(2-furyl)silane, b.p. 126°C/1.5 mmHg, d_4^{20} 1.1493, n_D^{20} 1.5459, MR_D 63.44, found 63.90; 94 g of tetra(2-furyl)silane, m.p. 93°C (lit. [9] 93°C).

Dimethyl(3-furyl)silane and methyldi(3-furyl)silane (XIII)

Methylmagnesium iodide, prepared from methyl iodide (85 g, 0.6 mol) and magnesium (14.5 g, 0.6 mol) in 300 ml of ether, was added to methyldichlorosilane (115 g, 1.0 mol). Then, 3-furyllithium was added at −65 to −70°C. The latter was synthesized by adding 3-bromofuran (220 g, 1.5 mol) to butyllithium, prepared from lithium (27 g, 3.9 mol) and butyl chloride (139 g, 1.5 mol) in 600 ml of ether. The reaction mixture was warmed to room temperature, then heated to 35°C for an hour, and left for two days at room temperature. The precipitate was filtered off, the solvent distilled, and the residue fractioned. Yield: 14.5 g of dimethyl(3-furyl)silane * together with butylbromide, b.p. 100–107°C, and 47 g of methyldi(3-furyl)silane (XIII), b.p. 46°C/1 mmHg, d_4^{20} 1.1006, n_D^{20} 1.4992, MR_D 47.49, calculated 47.06.

Using methylchlorosilane, ethylmagnesium bromide, and 2-furyllithium, we obtained, in an analogous way, diethyl(2-furyl)silane, b.p. 62°C/18 mmHg (lit. [15] 50°C/10 mmHg), and ethyldi(2-furyl)silane, b.p. 51°C/1 mmHg, d_4^{20} 1.0248, n_D^{20} 1.5042, MR_D 55.58, calculated 55.83.

Photoelectron spectra were recorded on a spectrometer designed at the Department of Physics and Mathematics of the Bashkirian Branch of the U.S.S.R. Academy of Sciences. A resonance lamp served as the photon source, wavelength $\lambda = 584$ Å (He-I). All spectra were calibrated against an internal standard of xenon, line halfwidth ca. 0.06 eV, and were recorded by an F-36 data storing computer. Calculations were carried out on the ES-1033 at the computer center of the Bashkirian Branch of the U.S.S.R. Academy of Sciences, Ufa.

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* Used for synthetic purposes without isolation from the mixture.

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