RESEARCH ON THE MOLECULAR STRUCTURE OF PHENYL-HALOSILANES II

QUANTUM CHEMICAL CALCULATION OF PHENYL-FLUORO-SILANES

By

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Introduction

The first part of our paper dealt with the preparation and the spectroscopic investigation of the phenyl-halosilanes [1].

This is a review of the quantum chemical calculations carried out for phenyl-fluoro-silanes. The molecular structure of the following compounds has been studied:

$(C_6H_5)_nSiF_{4-n}$,   where n = 1, 2, 3.

$(CH_3) (C_6H_5)SiF_2$.
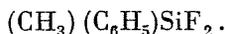
For the calculation of the σ bond system of the compounds Del Re's approximative method [2] and of the π bond system the semi-empirical SCF method, worked out by Pariser–Parr–Pople, has been used [3, 4].

1. Calculation of the σ system

The parameters used in the calculation are compiled in Table 1.

Fig. 1 contains the charge densities derived from the solution of the calculations and the degree of bond polarity, the bond dipole moment values are listed in Table 2.

2. Calculation of the π system

The PPP method calculates the Coulomb integrals as follows:

$$\alpha_i = U_i + \frac{1}{2} q_i \gamma_{ii} + \Sigma(q_j - n_j)\gamma_{ij} \qquad (eV)$$

where α_i — is the Coulomb integral of the i-th atom,

U_i — is the ionization energy in valence state,

q_i, q_j — are electron densities of the i-th and the j-th atom, resp.,

n_j — is the number of electrons donated by the j-th atom to the π system,

γ_{ii}, γ_{ij} — are symbols of the single center $[ii/ii]$ and double center integrals $[ii/jj]$, respectively.
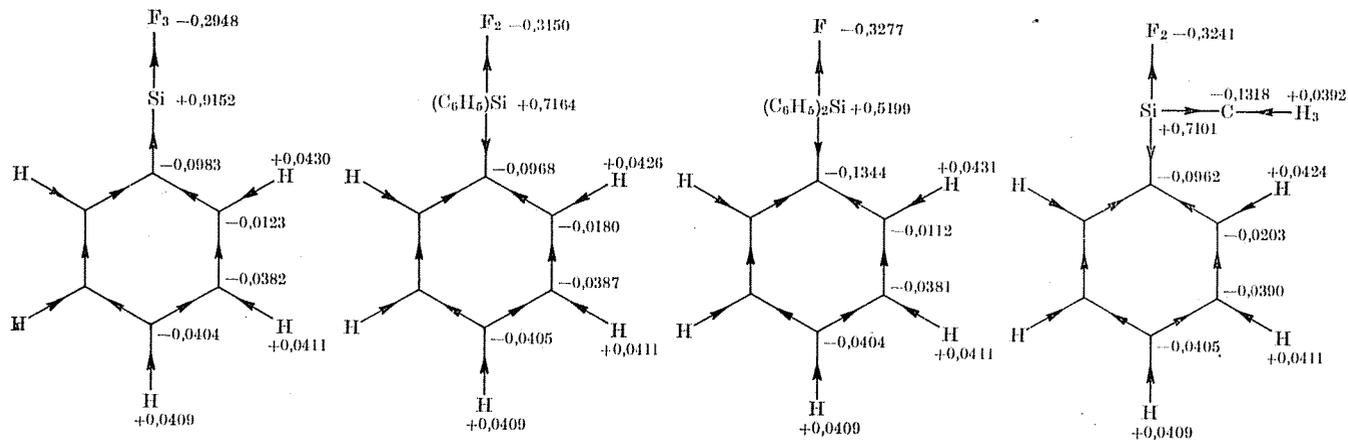
Fig. 1. σ charge distribution of phenyl-fluoro-silanes
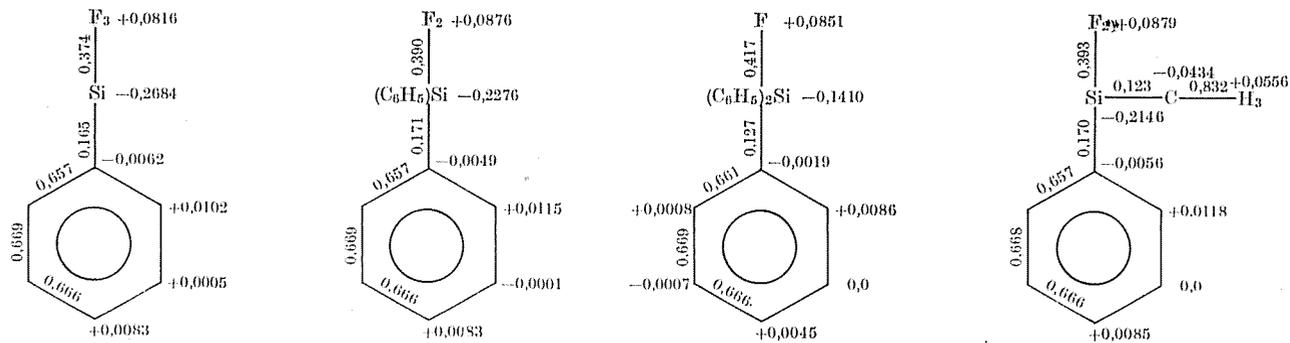
Fig. 2. π partial charges and π bond orders of phenyl-fluoro-silanes

Table 1

Del Re parameters

A—B	δ_A^2	δ_B^2	γ_{AB}	γ_{BA}	ε_{AB}
C—H	0.12	0	−0.2	0.4	1.00
C—C	0.12	0.12	0.1	0.1	1.00
Si—C	−0.10	0.12	0.2	0.4	0.90
Si—F	−0.10	0.57	0.12	0.15	0.742

Table 2

Bond polarities and bond moments in the σ- system of phenyl-fluoro-silanes

Bond A—B	$(C_6H_5)SiF_3$		$(C_6H_5)_2SiF_2$		$(C_6H_5)_3SiF$		$CH_3(C_6H_5)SiF_2$	
	Q_{AB}	μ_{AB}	Q_{AB}	μ_{AB}	Q_{AB}	μ_{AB}	Q_{AB}	μ_{AB}
F—Si	0.2948	2.2106	0.3156	2.3662	0.3277	2.4568	0.3241	2.4301
Si—C_1	0.0306	0.2768	0.0426	0.3845	0.0641	0.5787	0.0475	0.4286
C_1—C_2	0.0338	0.2270	0.0271	0.1821	0.0351	0.2357	0.0244	0.1636
C_2—C_3	0.0032	0.0212	0.0025	0.0170	0.0033	0.0220	0.0023	0.0152
C_3—C_4	0.0003	0.0018	0.0002	0.0015	0.0003	0.0019	0.0002	0.0013
C_2—H	0.0430	0.2239	0.0426	0.2217	0.0431	0.2243	0.0424	0.2209
C_3—H	0.0411	0.2140	0.0411	0.2138	0.0411	0.2140	0.0410	0.2137
C_4—H	0.0409	0.2132	0.0409	0.2131	0.0409	0.2131	0.0409	0.2131
Si—C_{Me}	—	—	—	—	—	—	0.0144	0.1297
C_{Me}—H	—	—	—	—	—	—	0.0392	0.2056

The data for silicon and carbon can be found in the literature [5, 6]. One electron pair, i. e., two electrons, are donated by the fluorine atom to the π system. For this reason the double ionization energy of fluorine is to be determined. SANDERSON [7] summarized the experimental results for the single and multiple ground- state ionization energies. If the corresponding promotion energies are known [8], the double ionization energy of the valence state can be calculated by the following relationship:

$$U^{++} = U_A^{++} + P^{++} - P^{+},$$

where U^{++} — is the double ionization energy in valence state,

U_A^{++} — is the double ionization energy in ground state,

P^{+} and P^{++} — are the promotion energies.

We remark that the effect of the promotion energy decreases in the $F \to I$ row, in the case of chlorine the ground- and valence- state double ionization energies are nearly equal and in the case of bromine and iodine the difference may be neglected.

To the suggestion of PARISER [9], the γ_{ij} single center integrals are taken as equal to the difference between the corresponding valence- state ionization energy and the electron affinity.

On the other hand, the determination of the $\gamma_{FF}^{\pm\pm}$ single- center double electron repulsion integrals causes some problems.

The doubly positive oxygen atom electron repulsion integral is given by NISHIMOTO and FORSTER [6] as the difference between the experimentally determined first and second ionization energy of the free oxygen atom. For other elements of the second period this method can not be applied, but for fluorine and other elements of the second row the following expression can be used:

$$\frac{\gamma_{OO}^{\pm+}}{\gamma_{OO}^{\pm}} = \frac{\gamma_{FF}^{\pm\pm}}{\gamma_{FF}^{\pm}}.$$

From the known $\gamma_{FF}^{\pm}$ single integral of fluorine $(\gamma_{FF}^{\pm} = U_F^{\pm} - A_F^{\pm})$ and from the data for oxygen $\gamma_{FF}^{\pm\pm}$ can be calculated.

For the determination of the γ_{ij} double- center electron- repulsion integrals the empirical expression of MATAGA and NISHIMOTO [10] has been used:

$$\gamma_{ij} = \frac{14{,}397}{r_{ij} + a_{ij}} \qquad (eV)$$

where r_{ij} is the bond length between the i-th and j-th atom and a_{ij} can be calculated from the relationship:

$$a_{ij} = \frac{2 \cdot 14{,}397}{\gamma_{ii} + \gamma_{jj}}.$$

The resonance integral was calculated by the following equation:

$$\beta_{ij} = \beta_{ij}^0 - \frac{1}{2} p_{ij}\gamma_{ij}.$$

where p_{ij} is the bond order and β_{ij}^0 was determined from the Helmholz— Wolfsberg [11] formula:

$$\beta_{ij}^0 = \frac{1}{2} k(U_i + U_j)S_{ij}.$$

The value of the overlap integral S_{ij} was determined by means of an integral table [12] as a function of bond length and effective nuclear charge. The effective nuclear charge was calculated by BURNS' [13] method. The proportional factor k was determined from the experimental and calculated resonance

integrals of ethylene for the Si—F bond, and from the experimental and calculated resonance integrals of benzene for the other bonds:

$$k(\text{benzene}) = 0,7637; \quad k(\text{ethylene}) = 0,6206.$$

In the case of $d\pi - p\pi$ bond the maximum overlap of the d and p orbitals is achieved if the axis of the p orbital includes an angle $45°$ with the two perpendicular axes of the d orbital. If there is a tetrahedral orientation, the angle alters and the overlap decreases. The difference is $19° 28'$, which was taken into consideration in the following way:

$$S' = S \cdot \cos \alpha$$

$\alpha = 19° 28'$.

X-ray diffraction investigations on the triphenyl-fluoro-silane molecule [14] revealed the "propeller"-like arrangement of the phenyl rings, with planes at an angle $45°$ to each other. This was also considered in the calculation of the overlap:

$$S'_{\text{SiC}} = S_{\text{SiC}} \cdot \cos \alpha \cdot \cos \beta$$

where $\beta = 45°$.

Calculating the methyl-phenyl-difluoro-silane molecule, the hyperconjugative effect of the methyl group was taken into account. The necessary parameters were selected according to the work of NAGY [15] who studied hyperconjugation in connection with the calculation of methyl-fluoro-silanes.

The input data necessary for the calculation of the system are listed in Table 3.

Table 3

Starting data for the calculation of the π-system of phenyl-fluoro-silanes (in eV)

$U_F^{++} = -36.18$	$\beta_{CC} = -2.308$	$\gamma_{FF}^{++} = 24.53$
$U_{Si}^{+} = -1.10$	$\beta_{SiC} = -1.2610$	$\gamma_{CC} = 11.13$
$U_{C_{Ar}}^{+} = -11.16$	$\beta_{SiF} = -1.3694$	$\gamma_{SiSi} = 3.762$
$U_{C_{Al}} = -11.19$	$\beta_{SiC_{Al}} = -1.5521$	$\gamma_{C_{Al}C_{Al}} = 9.71$
$U_{H_3}^{+} = -10.26$	$\beta_{C_{Al}H_3} = -7.4013$	$\gamma_{H_3H_3} = 9.33$

In the case of triphenyl-fluoro-silane $\beta_{SiC} = -0.8917$ eV was used in the calculation because of the over-turn of the phenyl groups.

Computations were made in computer type RASDAN-3 of the Technical University of Budapest, applying the SCF—LCAO—MO—PPP program by J. C. PACKER and B. FORD.

The eigenvalues, linear coefficients, partial charges, electron densities and bond orders were determined for each compound. The energy values of the singlet and triplet transitions were determined by means of configuration interactions. The results are represented in Fig. 2, Tables 4 and 5.

Table 4

Eigenvalues of phenyl-fluoro-silanes

(eV)	$(C_6H_5)SiF_3$	$(C_6H_5)_2SiF_2$	$(C_6H_5)_3SiF$	$(C_6H_5)(CH_3)SiF_2$
E_1	-13.4457	-13.4239	-13.3047	-16.9126
E_2	-13.0656	-13.2591	-13.2217	-13.3489
E_3	-12.1541	-12.8483	-13.2176	-12.8749
E_4	-12.1535	-12.2069	-12.7212	-12.2301
E_5	-10.3961	-10.4422	-10.4053	-10.3922
E_6	-10.3836	-10.3614	-10.3204	-10.3646
E_7	-1.4843	-10.3595	-10.3156	-1.5713
E_8	-1.0226	-10.3119	-10.3150	-1.0028
E_9	0.0493	-1.8235	-10.2865	-0.1223
E_{10}	2.0156	-1.0002	-10.2745	2.0220
E_{11}		-0.9980	-1.7974	4.9359
E_{12}		-0.9826	-0.9601	
E_{13}		0.2063	-0.9556	
E_{14}		1.9225	-0.9550	
E_{15}		2.1585	-0.9459	
E_{16}			-0.9436	
E_{17}			0.0090	
E_{18}			1.9615	
E_{19}			1.9655	
E_{20}			2.1252	

Table 5

Energy values of the $^1E_{CI}$ and $^3E_{CI}$ singlet and triplet energy transitions of phenyl-fluoro-silanes (in eV)

	$(C_6H_5)SiF_3$		$(C_6H_5)_2SiF_2$		$(C_6H_5)_3SiF$		$(CH_3)(C_6H_5)SiF_2$	
	$^1E_{CI}$	$^3E_{CI}$	$^1E_{CI}$	$^3E_{CI}$	$^1E_{CI}$	$^3E_{CI}$	$^1E_{CI}$	$^3E_{CI}$
1	4.8318	3.1848	4.7516	3.1111	4.8129	3.1758	4.6648	2.9258
2	5.8336	4.0268	4.7521	3.1135	5.1621	3.3456	5.7673	3.7745
3	6.6388	4.1231	5.6027	3.9374	5.2826	3.3634	6.5312	3.8153
4	6.6621	4.8156	5.7587	3.9378	5.6953	4.0101	6.5370	4.6879
5	7.1839	6.5637	6.3427	3.9861	5.7574	4.0223	6.7692	5.1562
6	7.1857	6.5699	6.3847	3.9882	5.8928	4.2423	7.3529	6.7738
7	8.2183	8.2179	6.4276	4.7389	6.2808	4.2752	7.4238	6.9907
8	8.2382	8.2377	6.4940	4.7400	6.3130	4.8101	8.3121	8.3121

Discussion

From the σ- and π- charge distributions of the compounds the bond polarities, bond moments and the resultant μ_σ, μ_π and $\mu_{\sigma\pi}$ dipole moments were calculated. As shown in Table 6, our results are in good agreement with the experimental dipole moment values.

Table 6

Calculated and measured dipole moment values of phenyl-fluoro-silanes (in Debye)

Compound	μ_σ	μ_π	$\mu_{\sigma\pi}$	$\mu_{exp.}$	
$(C_6H_5)SiF_3$	2.408	0.21	2.198	2.77	[16]
$(C_6H_5)_2SiF_2$	2.815	0.27	2.545	2.59	[16]
$(C_6H_5)_3SiF^*$	2.363	0.21	2.153	1.85	[17]
$(C_6H_5)_3SiF$	2.363	0.43	1.933	1.85	[17]
$(C_6H_5)(CH_3)SiF_2$	2.905	0.398	2.514	2.55	[18]

The dipole moment vector of the methyl-phenyl-difluoro-silane does not coincide with the bisectrix of the two fluorine atoms and silicon atom. The deviation is represented in Fig. 3.
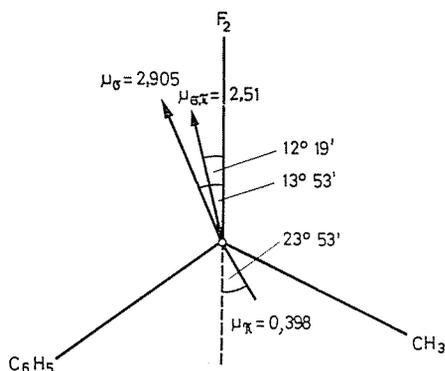
Fig. 3. Orientation of the σ- and π- dipole- moment vectors of methyl-phenyl-difluoro-silane

The larger deviation for phenyl-trifluoro-silane may be due to the approximative method used for the calculation of the σ- system. The further refinement of our calculations will be discussed in a subsequent paper.

In Table 7 the calculated singlet transition values are compared to the ultraviolet absorption spectra. Also here, the measured and calculated values show a good agreement.

Table 7

Measured ultraviolet absorption maxima [1] and calculated
singlet energy transitions of phenyl-fluoro-silanes

Compound	α-band [eV]		p-band [eV]	
	meas.	calc.	meas.	calc.
$(C_6H_5)SiF_3$	4.70	4.83	5.90	5.83
$(C_6H_5)_2SiF_2$	4.69	4.75	5.89	5.76
$(C_6H_5)_3SiF^*$	4.71	4.71	5.90	5.72
$(C_6H_5)_3SiF$	4.71	4.81	5.90	5.89
$(C_6H_5)(CH_3)SiF_2$	4.70	4.66	5.87	5.77

In Tables 6 and 7 asterisks refer to a calculation where the propeller-shape arrangement of the phenyl rings was left without consideration.

Summary

Quantum chemical calculations were carried out for various fluoro-silanes. The Del Re method has been used for the calculation of the σ bond system and the PPP method for the calculation of the π system. Results were evaluated in comparison with the experimental dipole moment and ultraviolet spectroscopic data. Calculated values are in good agreement with experimental data.

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