

## A QUANTUM CHEMICAL STUDY OF EFFECTS OF SILYL SUBSTITUENTS IN PHENYL- AND BENZYL-SILANES\*

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Charge-transfer spectra of series of substituted phenyl- and benzylsilanes and some carbon analogues were measured with tetracyanoethylene as the acceptor in dichloromethane solutions in the 15000–35000  $\text{cm}^{-1}$  region. The obtained results can be interpreted by interaction with  $\Sigma^*$  orbitals of ( $\text{CH}_2\text{—Si}$ ) or ( $\text{Si—X}$ ) bonds, without assuming the participation of silicon  $d$  orbitals. These conclusions are supported by the results of quantum chemical calculations performed for phenylsilanes and for corresponding carbon analogues by a simple HMO method. The wavenumbers of charge-transfer bands correlate well with calculated values of the highest occupied molecular orbital energies (HOMO).

The results obtained in our laboratory<sup>1,2</sup>, and previously also in other laboratories<sup>3,4</sup>, show that to explain electron acceptor character of silicon, it is not necessary to invoke the participation of its  $3d$  orbitals through the so-called ( $p \rightarrow d$ ) <sub>$\pi$</sub>  bonds. The same conclusions can be reached by assuming the interaction with low-lying antibonding orbitals,  $\sigma^*(\text{Si—X})$  or  $\sigma^*(\text{CH}_2\text{—Si})$ , which becomes increasingly important as the electronegativity of X increases. To prove the correctness of these assumptions on a more sophisticated level than orbital diagrams, it was of interest to perform quantum chemical calculations with a model of a silyl group which would enable these effects to be at least qualitatively included. These requirements were not met in the earlier proposed model of the silicon atom for HMO calculations<sup>5</sup>. This latter model, which assumes that only one unoccupied silicon orbital is engaged in conjugation, does not render it possible to explain the donor properties of trimethylsilyl group which were established by *e.g.* photoelectron spectroscopy (I.P. of benzene = 9.24 eV, I.P. of phenyltrimethylsilane = 8.94 eV) (ref.<sup>6</sup>).

A model of the  $\text{MX}_3$  group was therefore suggested which assumes that atom M and atom X contributes to conjugation, each by one orbital occupied by one electron. This, in dependence on the values of corresponding coulombic and resonance integrals, makes it possible to obtain both acceptor and donor properties of the  $\text{MX}_3$

group. The calculations were performed for phenylsilanes and corresponding carbon compounds with substituents  $X = F, Cl, H,$  and  $CH_3$ .

### EXPERIMENTAL

*Model compounds.* All the compounds under study, except those commercially available, were prepared by reported procedures. In Table I are therefore recorded only their boiling points and references to the original literature. The purity of the compounds was checked by gas chromatography. The compounds all contained less than 1% of impurities.

Benzene (UV spectrograde, Lachema, Brno) was dried by refluxing it with sodium and then rectified. The fraction collected at 80–80.5°C was stored in a small flask over Nalsit 4 A molecular sieve. Toluene (UV spectrograde, Lachema, Brno) was dried and purified similarly as benzene. A fraction boiling at 110–111°C was stored over Nalsit 4 A molecular sieve. Ethylbenzene (*puris.*, Fluka), *t*-butylbenzene (*puris.*, Fluka), benzotrifluoride (*purum*, Fluka), benzotrichloride (*purum.*, Fluka), and tetracyanoethylene (*purum*, Fluka), all were used without further purification. Dichloromethane (analytical purity grade, Lachema, Brno) was purified by the method described earlier<sup>1</sup>.

TABLE I

Characteristic Constants of Studied Compounds and Wavenumbers of the Maxima of Their Charge-Transfer Bands with Tetracyanoethylene in Dichloromethane

Compounds	B.p., °C/Torr	B.p., °C/Torr (ref.)	$\nu$ , $cm^{-1}$	$\nu$ , $cm^{-1a}$
Benzene (1)	80–80.5	80.1 <sup>8</sup>	26 000 ± 100	26 050
Toluene (2)	110–111	110.6 <sup>8</sup>	24 600 ± 200	24 650
<i>t</i> -Butylbenzene (3)	167–169	169.1 <sup>8</sup>	24 000 ± 200	24 000
Benzotrichloride (4)	90–91/15	214 <sup>8</sup>	28 700 ± 500	—
Benzotrifluoride (5)	100–103	102.4 <sup>8</sup>	30 500 ± 500	—
Phenyltrimethylsilane (6)	168–170	170.6 <sup>9</sup>	24 500 ± 100	24 650
Phenylsilane (7)	120–121	120 <sup>10</sup>	25 700 ± 200	26 000
Phenyltriethoxysilane (8)	—	108.5/3 <sup>11,12</sup>	26 200 ± 200	—
Phenyltrichlorosilane (9)	197–200	201.1 <sup>13</sup>	29 300 ± 300	—
Phenyltrifluorosilane (10)	100–101	101.8 <sup>14</sup>	30 600 ± 500	—
<i>p</i> -Tolylsilane (11)	147–148	147–148 <sup>16</sup>	23 700 ± 200	—
<i>p</i> -Tolyltrimethylsilane (12)	188–191	190–191 <sup>15</sup>	23 500 ± 200	—
Ethylbenzene (13)	134–136	136.1 <sup>8</sup>	24 000 ± 100	24 200
Benzyltrimethylsilane (14)	189–191	191–192 <sup>17</sup>	20 400 ± 100 <sup>b</sup>	20 550 <sup>b</sup>
			24 200 ± 100	24 050
Benzylsilane (15)	149–150	150.3 <sup>18</sup>	24 500 ± 200	—
Benzyltrichlorosilane (16)	212–215	140–142/100 <sup>19</sup>	25 300 ± 300	25 300
Benzyltrifluorosilane (17)	134–135	134–135 <sup>14</sup>	25 800 ± 300	25 700
Benzyltriethoxysilane (18)	245–250	170–175/70 <sup>19</sup>	24 100 ± 300	—

<sup>a</sup> Data reported by Bock<sup>7</sup>; <sup>b</sup> two separate bands.

Charge-transfer spectra of all the compounds studied were measured with the use of tetra-cyanoethylene as an acceptor in dichloromethane solution on a double-beam  $\text{SiO}_2$ -prism Specord, Zeiss, spectrophotometer (Jena, GDR) in the  $15000\text{--}35000\text{ cm}^{-1}$  region under the conditions reported in a previous work<sup>1</sup>. Experimental wavenumbers of charge-transfer band maxima are recorded in Table I. For purposes of comparison, also the data reported by Bock<sup>7</sup> are included.

## RESULTS AND DISCUSSION

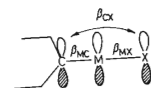
The model of the  $\text{MX}_3$  group suggested in this work is based on Bishop's<sup>21</sup> semiempirical model of hyperconjugation, but it is of course modified to HMO level. The orbitals of  $\sigma(\text{M}\text{--}\text{X})$  bonds can be, due to their symmetry ( $\text{C}_{3v}$ ), combined into group orbitals, two of which are of suitable symmetry for interaction with the phenyl  $\pi$  system. When going from these equivalent orbitals to atomic orbitals, one obtains

$$\Sigma_{\pi}^{\text{M}} = \frac{1}{\sqrt{6}} (2\varphi_{\text{M}}^1 - \varphi_{\text{M}}^2 - \varphi_{\text{M}}^3)$$

$$\Sigma_{\pi}^{\text{X}} = \frac{1}{\sqrt{6}} (2\varphi_{\text{X}}^1 - \varphi_{\text{X}}^2 - \varphi_{\text{X}}^3).$$

These orbitals then serve as the basis for our model. Each orbital is occupied by one electron, and because of identical symmetry they may interact. This manifests itself in the formation of the "bonding" combination  $\Sigma_{\pi} = (\Sigma_{\pi}^{\text{M}} + \Sigma_{\pi}^{\text{X}})$ , occupied by two electrons, and of the unoccupied "antibonding" combination  $\Sigma_{\pi}^* = \Sigma_{\pi}^{\text{M}} - \Sigma_{\pi}^{\text{X}}$ .

The model can be schematically depicted in the following way:

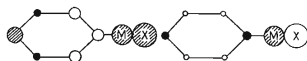


The values of coulombic integrals  $\alpha_{\pi}^{\text{M}}$   $\alpha_{\pi}^{\text{X}}$  are taken as being roughly proportional to corresponding orbital ionization potentials<sup>21,22</sup> and, along with the values of corresponding resonance integrals, are listed in Table II.

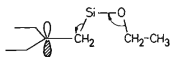
Bock<sup>7</sup> reported that the charge-transfer band of substituted phenyl- and benzylsilanes is formed by two overlapping bands which originate from the degenerate  $e_{1g}$  orbital of benzene. The observed maximum of the charge-transfer band does not correspond to the energy of the highest occupied molecular orbital. However, with regard to the fact that Bock<sup>7</sup> did not succeed in separating the above two bands and that experimental values of  $\nu_{\text{CT}}$  correlate with available values of first ionization potentials<sup>6,23</sup>, we used the wavenumber of the maxima of the charge-transfer band

also in correlations with calculated energies of HOMO. The suitability of the parameters was further verified with a series of substituted silafluorenes<sup>24</sup>, where difficulties with degeneration do not exist. The correlation of the wavenumbers of charge-transfer bands with calculated values of  $\epsilon(\text{HOMO})$  for substituted phenylsilanes and some carbon analogues are graphically represented in Fig. 1.

The calculations correctly reproduce the trend in the values of  $\nu_{\text{CT}}$  which decrease in the order  $\text{SiF}_3 > \text{SiCl}_3 > \text{SiH}_3 > \text{Si}(\text{CH}_3)_3$  and in the order  $\text{CF}_3 > \text{CCl}_3 > \text{CH}_3 > \text{C}(\text{CH}_3)_3$ . It is seen that there is no qualitative difference between silicon and carbon. The greater deviations of the values of  $\nu_{\text{CT}}$  from the regression line found for the chloro-substituted derivatives can be ascribed to steric effects which prevent the molecule of the acceptor (TCNE) from achieving in the complex the equilibrium geometry identical with the geometry of the other cases. This agrees with the fact that the greater deviations were observed in the carbon series than in the silicon one. Calculations also correctly reproduce the symmetry and form of the highest occupied orbital ( $B_1, \pi - \Sigma_\pi$ ). The lowest free molecular orbital (LFMO) is in all cases nearly pure  $\Sigma_\pi^*$  orbital. The values of orbital energies of HOMO and LFMO, and the values of electron densities on atom X are listed in Table III.



The order of acceptor strength of group  $\text{MX}_3$  is the same in both series ( $\text{M} = \text{C}, \text{Si}$ )  $\text{F} > \text{Cl} > (\text{C}_2\text{H}_5\text{O}) > \text{H} > \text{CH}_3$ , parallels the electronegativity of X, and thus also the order of  $\sigma^*(\text{M}-\text{X})$ . It is necessary to stress that on the basis of symmetry alone it is not possible to decide whether in the series of substituted silanes the interaction of the  $\pi$ -system occurs with a  $d_{yz}$  orbital or with a  $\Sigma_\pi^*$  orbital. Arguments of the perturbation theory<sup>1</sup>, together with the fact that the same trend is observed also in the analogous series of carbon compounds, support the assumption about the participation of the  $\Sigma_\pi^*$  orbital. The same order of acceptor strength is always observed when the  $\pi$  system interacts directly with  $(\text{M}-\text{X})$  bonds (phenylsilanes, silafluorenes<sup>24</sup>). A somewhat different order is found, however, in the series of benzyl- and allylsilanes<sup>1</sup>:  $\text{X} = \text{F} > \text{Cl} > \text{H} > \text{C}_2\text{H}_5\text{O} > \text{CH}_3$ . This difference can be understood when one considers that in this case the  $\pi$  system is interacting with the  $\sigma$  orbital of the  $(\text{CH}_2-\text{Si})$  bond. This orbital, because the ethoxy group is not a monoatomic substituent, may also be influenced by other factors than by the electronegativity of oxygen, as shown *e.g.* by the following scheme:



Another complication stems from the lack of knowledge of the steric arrangement of the three ethoxy groups on the silicon atom, since the above-mentioned interaction requires syn-clinal arrangement of ( $\text{CH}_2\text{—Si}$ ) and ( $\text{O—CH}_2$ ) bonds.

The suitability of the discussed hyperconjugation model can be further verified, *e.g.* by examining whether it is able to describe, at least qualitatively, the order of acidity of some hydrocarbons of similar structure containing ( $\text{CH}_2$ ) or ( $\text{CH}_3$ ) group. A rough estimate is provided by comparison of the electron densities on hydrogen atoms of the  $\text{CH}_2(\text{CH}_3)$  group: cyclopentadiene (0.898) < indene (0.911) < fluorene (0.926) < toluene (1.007). In the series of silicon derivatives  $q_{\text{H}} > 1$ , which corresponds to the generally accepted polarity of the  $\text{Si}^{\delta+}\text{—H}^{\delta-}$  bond (Table III). A theoretically more correct measure of basicity is the difference in total  $\pi$ -elec-

TABLE II

Values of Empirical Parameters in Hyperconjugation Model of  $\text{MX}_3$  Group (in  $\beta$  Units)

M	( $\alpha_{\text{M}}$ )	X	$\alpha_{\text{X}}$	$\beta_{\text{C-X}}$	$\beta_{\text{M-C}}$	$\beta_{\text{M-C}}$
Si	(-0.3)	F	-4.0	-2.0	-2.0	-0.8
		Cl	-2.5	-1.7	-1.7	-0.8
		H	-1.3	-1.2	-1.2	-0.8
		$\text{CH}_3$	-1.0	-1.0	-1.0	-0.8
C	(-1.0)	F	-4.0	-2.0	-2.5	-1.0
		Cl	-2.5	-1.7	-2.0	-1.0
		H	-1.3	-1.2	-1.5	-1.0
		$\text{CH}_3$	-1.0	-1.0	-1.2	-1.0

FIG. 1  
Dependence of Wavenumbers of Maxima of Charge-Transfer Bands of Studied Compounds on Calculated Values of HOMO Energy

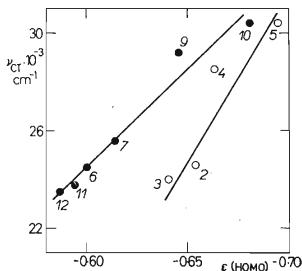


TABLE III

Calculated Quantum Chemical Quantities for Some Compounds Studied

 $\epsilon$  (HOMO) the energy of the highest occupied molecular orbital,  $\nu$  (LFMO) the energy of the lowest free molecular orbital,  $q_X$  the electron density on atom X.

Compound	$\epsilon$ (HOMO) ( $\beta$ )	$\nu$ (LFMO) ( $\beta$ )	$q_X$
2	-0.654	0.356	1.0069
3	-0.639	0.200	0.9199
4	-0.662	0.380	1.2361
5	-0.694	0.417	1.4136
6	-0.600	0.408	1.2225
7	-0.614	0.500	1.2636
9	-0.645	0.619	1.4129
10	-0.680	0.570	1.5659
11	-0.594 <sup>a</sup>	—	—
12	-0.597 <sup>a</sup>	—	—

<sup>a</sup> Values calculated by means of first-order perturbation theory from wave functions for phenylsilane (7) and phenyltrimethylsilane (6) according to the relation  $\Delta\epsilon_i = c_{i\mu}^2 \Delta\alpha_\mu$ ;  $\Delta\alpha_\mu \approx 0.1\beta$ .

tron energies between parent hydrocarbons and their anions. Their order also parallels the order of experimentally found acidity of hydrocarbons<sup>25</sup>: ( $\Delta W_\pi(\beta)$ ) for cyclopentadiene 5.18, indene 5.21, and fluorene 5.26.

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