A HMO STUDY OF HYPERCONJUGATION,
# CHARGE-TRANSFER SPECTRA
OF SUBSTITUTED SILAFLUORENES*

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Charge-transfer spectra of substituted silafluorenes and corresponding carbon analogs with tetracyanoethylene were measured in the 15000—35000 cm^{-1} region in dichloromethane solution. Wavenumbers of charge-transfer bands correlate well with calculated values of orbital energies. As no unoccupied orbital on silicon (d orbital) was considered explicitly in calculations, the results show that experimental data can explained without assuming the participation of silicon d orbitals. The participation of the d orbitals is excluded also by the symmetry of wave functions

As it has been shown several times[1,2], to explain electron acceptor properties of silicon it is not necessary to assume the participation of its d orbitals through the so-called $(p$-$d)_\pi$ bond. The same conclusions can be reached by assuming the interaction with low lying antibonding orbitals of (Si—X) or (Si—CH$_2$) bonds[1,3] which becomes increasingly important as the electronegativity of X increases. The importance of these interactions was pointed out by Hoffmann[4], who made the suggestion to call them "superjacent orbital interaction", and also by Epiotis[5] and Schweig[3]. These interactions can be visualized by the orbital diagram.
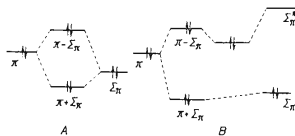
Similar orbital diagrams are used to explain changes in ionization potentials of vinylsilane, vinyl-trimethylsilane, allylsilane, allyltrimethylsilane and corresponding carbon analogs[6,7], with the difference that a decrease in HOMO energy according to scheme B is ascribed to the interaction with silicon 3d orbitals. Arguments of the perturbation theory[1,4] support rather the participation of the $\sum_\pi^*$ orbital.

In the cases studied so far[1,8,9] the symmetry of wave functions did not allow a direct experimental distinguishing between the interaction with a d_{yz} orbital and $\sum_{\pi}^{*}$ orbital, and, as already stated, the participation of the $\sum_{\pi}^{*}$ orbital was preferred only on the basis of the perturbation theory. However, it is evident that in the cases where the participation of the $\sum_{\pi}^{*}$ and d_{yz} orbitals is not possible due to symmetry, the only possibility remaining is the interaction with a d_{xz} orbital.

TABLE I

Compounds Studied

Compound	M.p., °C	M.p., °C (lit.)	
Fluorene (1)	114	115	(10)
9,9-Dichlorofluorene (2)	104	103	(11)
9,9-Dimethylfluorene (3)	93—94	94·5—95[a]	(13)
9,9-Difluorosilafluorene (4)	59—60	59·5	(14)
9,9-Dichlorosilafluorene (5)	98	97—98[b]	(14)
9,9-Diethoxysilafluorene (6)	51—52	—	
9,9-Diphenylsilafluorene (7)	147—148	147—148	(14)
Silafluorene (8)	36—37	36·5	(14)
9,9-Dimethylsilafluorene (9)	59—60	59·1[c]	(14)
3,6,9,9-Tetramethylsilafluorene (10)	128—129	128—129	(16)

[a] Ref.[12] m.p. 95—96°C; [b] ref.[15] m.p. 108—110°C; [c] ref.[16] m.p. 59—60·5°C.

TABLE II

Wavenumbers of Charge-Transfer Bands of Studied Compounds with Tetracyanoethylene in Dichloromethane

Compd.[a]	ν_{CT}(I) 10^{-3}, cm^{-1}	ν_{CT}(II) 10^{-3}, cm^{-1}	ν_{CT}(III) 10^{-3}, cm^{-1}
1	17·8 ± 0·1	24·1 ± 0·2	—
2	19·8 ± 0·3	24·0 ± 0·3	—
3	17·5 ± 0·1	24·0 ± 0·2	—
4	20·8 ± 0·1	24·0 ± 0·2	—
5	20·3 ± 0·2	23·9 ± 0·2[a]	—
6	18·8 ± 0·1	24·0 ± 0·1	25·5 ± 0·3
7	18·5 ± 0·1	24·1 ± 0·2	25·3 ± 0·2
8	18·5 ± 0·1	24·2 ± 0·2	25·3 ± 0·3
9	17·8 ± 0·1	24·0 ± 0·2	25·3 ± 0·3
10	16·8 ± 0·1	22·2 ± 0·2	23·6 ± 0·3

[a] Shoulder.

In this sense silafluorenes are ideal model compounds, since, as follows from HMO calculations, their two highest occupied molecular orbitals differ in symmetry. In the absence of the participation of silicon d orbitals one can expect that changes in

TABLE III

Calculated Quantum Chemical Data on Studied Compounds

m_1 Energy of highest occupied orbital (HOMO) (in β units), m_2 energy of second highest occupied orbital (HOMO-1), m_3 energy of (HOMO-2), m_{-1} energy of lowest free molecular orbital (LFMO), q_M electron density on atom M (M=Si, C), and q_X electron density on atom X.

Compound	$m_1{}^b$	$m_2{}^c$	$m_3{}^c$	$m_{-1}{}^d$	q_M	q_X
1	−0·618	−0·704	−1·000	0·354	0·933	0·926
2	−0·622	−0·704	−1·000	0·372	0·906	1·146
3	−0·607	−0·704	−1·000	0·200	0·945	0·836
4	−0·636	−0·704	−1·000	0·570	0·890	1·453
5	−0·609	−0·704	−1·000	0·613	0·914	1·298
8	−0·588	−0·704	−1·000	0·500	0·947	1·142
9	−0·578	−0·704	−1·000	0·400	0·960	1·092
10	−0·552^a	—	—	—	—	—

^{a} Calculated by means of first-order perturbation theory $\Delta\varepsilon_i = c_{i\eta}^2 \, \Delta\alpha_\eta \; \Delta\alpha_\eta \approx 0·1 \, \beta$, similarly as in the case of substituted phenylsilanes[9]; ^{b} symmetry B_1; ^{c} symmetry A_2.
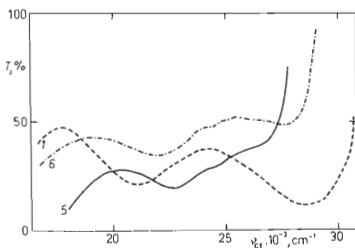

FIG. 1

Charge-Transfer Spectra of Some Compounds Studied
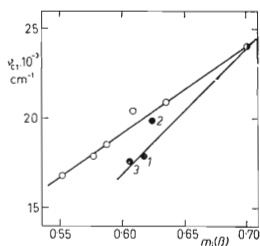
For numbering see Table I.

FIG. 2

Dependence of Wavenumbers of Charge-Transfer Bands on Calculated Orbital Energies

(Silafluorenes ○, ⊙, from left to right 10, 9, 8, 5, 4 fluorenes 1st CT band ●), 2nd CT band ◑. For numbering see Table I.

the wavenumbers of ν_{CT} of first two charge-transfer bands due to substitution on silicon will be markedly different.

EXPERIMENTAL

Model compounds. All compounds studied, except those commercialy available, were prepared by reported procedures. Table I presents therefore only characteristic constants and references to the literature. Dichloromethane (analytical purity, Lachema, Brno) was purified by the method reported earlier[1]. Fluorene (*purum*, Fluka) was purified by repeated crystallization until the compound had a constant melting point. Tetracyanoethylene (*purum*, Fluka) was used without further purification.

Charge-transfer spectra of the compounds studied with tetracyanoethylene were measured in dichloromethane solution with a double beam SiO_2-prism Specord, Zeiss spectrometer (Jena, GDR). The conditions were described in a previous work[1]. Charge-transfer spectra of some compounds are shown in Fig. 1. Wavenumbers of charge-transfer bands of all compounds studied are listed in Table II.

RESULTS AND DISCUSSION

The fact that the highest occupied molecular orbital (HOMO) is formed by the $\pi\text{-}\sum_\pi$ combination is taken as the basis for hyperconjugation explanation of the origin and essence of the effect of silyl substituents[6,7]. We believe, however, that the interaction of orbitals depicted in scheme A cannot be considered as hyperconjugation in the sense that it should lead to total stabilization of a system, similarly as does conjugation. Nor leads this interaction to change in charge distribution[17]. Total stabilization is solely due to the interaction with unoccupied orbitals, as shown in scheme B. We therefore believe that it is possible to talk about hyperconjugation only in the case B. From the foregoing it is obvious that a HMO model which is to describe, at least qualitatively, hyperconjugation effects should not obscure the fact that to each bonding orbital which is engaged in the interaction with a π-system it belongs also the $\sum_\pi^*$ antibonding orbital. The simplest way of the consideration of both orbitals led us to suggest a HMO model of hyperconjugation[9]. The above mentioned requirements were not met by the earlier suggested model of silicon atom for HMO calculations[18], since this model assumed that silicon contributes to conjugation by only one unoccupied orbital. The parameters used in HMO calculations were the same as in a previous work[9]. Calculated values of orbital energies of three highest occupied molecular orbitals are listed in Table III, along with some electron densities.

Calculations correctly reproduce the trend in the values of ν_{CT} which decrease for the first band in the order $SiF_2 > SiCl_2 > SiH_2 > Si(CH_3)_2$ and $CCl_2 > CH_2 > C(CH_3)_2$. Changes of the wavenumbers of the second and third band are very small, in harmony with the fact that corresponding orbitals are antisymmetrical.

with respect to the plane passing through the Si(C) atom. The only interaction which could lead to changes in wavenumbers of these charge-transfer bands is the interaction with the d_{xz} orbital. As the changes of $v_{CT}(II)$ and $v_{CT}(III)$ are within experimental errors, the participation of silicon $3d$ orbitals seems improbable. This is supported also by the fact that the same results were obtained with a series of analogous carbon compounds.

Correlations of calculated orbital energies with experimental wavenumbers, v_{CT}, of charge-transfer bands are graphically represented in Fig. 2. The fact that the wavenumbers of first two charge-transfer bands are described by the same regression equation is fortuitous, since corresponding orbitals, (HOMO) and (HOMO-1), differ in symmetry, and hence also the geometry of respective complexes will be different. The deviations of the values of v_{CT} from the regression line, which is greatest in the case of chloro derivatives, can be ascribed to steric effects which prevent the molecule to achieve in the complex the equilibrium state identical with the geometry of other cases. This is indicated also by the fact that greater deviations were observed in the carbon series than in the silicon one. The order of acceptor strength of MX_2 groups is therefore the same in both series $(M = C, Si)$ $F > Cl > (OC_2H_5) > H > > (C_6H_5) > CH_3$, agrees with the order of the electronegativity of X and also with the order of $\sigma^*(M—X)$.

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