

FOURIER COMPONENT ANALYSIS
OF INTRAMOLECULAR INTERACTIONS
IN α -CARBOFUNCTIONAL SILANES*

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Fourier analysis of potential curves of internal rotation around the C—X bond in α -carbofunctional organosilicon compounds of the type Y—CH₂—X (X = NH₂, OH; Y = SiH₃, Si(CH₃)₃) has been used to study the character of intramolecular interactions in relation to the mechanism of the so-called α -effect. The results obtained are in accordance with previous conclusions based on the analysis of orbital correlation diagrams.

Although experimental data on rotation barriers and stability of conformers become increasingly available¹⁻⁴, quantum chemical calculations remain the simplest way how to get complete information about potential barriers. Calculations made with the use of *ab initio* method are now in nearly quantitative agreement with experiment⁵. Semiempirical methods do not yield in general the correct values of energetic barriers. Nevertheless, in most cases, they describe correctly the course of potential curves and predict correctly the most stable conformer.

α -Carbofunctional organosilicon compounds exhibit a number of anomalous physical properties compared to carbon analogues. This led to the concept of the α -effect⁶⁻⁹. Based on quantum chemical calculations and the analysis of correlation diagrams¹⁰, the participation of silicon 3d orbitals does not seem now to be essential for qualitative explanation of the operation of the α -effect. Fourier analysis of potential curves of internal rotation¹¹ allows to distinguish individual mechanisms of intramolecular interaction. By this way, a series of substituted methanols and methylamines has been analysed¹¹⁻¹³. It was of interest to extend this analysis also to silyl-substituted analogues.

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CALCULATIONS

Quantum chemical calculations of potential curves for compounds of the type $Y-CH_2-X$ ($X = H, F, CH_3, SiH_3$; $X = OH, NH_2$) were made by CNDO/2 method¹⁴ without inclusion of silicon d orbitals. For all the molecules ideal tetrahedral geometries with standard bond lengths¹⁴ were adopted. Potential curves ($0-180^\circ$) were calculated for conformations formed by rotation of initial arrangements *I* and *II* by $0^\circ, 60^\circ, 120^\circ$ and 180° around the $C-X$ bond. Struc-



TABLE I

Calculated and Experimental Relative Energies (kJ/mol) for Conformers of Substituted Methylamines

Compound	Conformation	$E(\text{CNDO})$	$E(\text{ab initio})^{12}$
CH_3NH_2	0°	6.56	13.63 ^a
	180°	0.00	0.00 ^b
FCH_2NH_2	0°	8.99	28.75
	60°	5.11	27.46 ^c
	120°	9.26	32.45 ^d
	180°	0.00	0.00
$CH_3CH_2NH_2$	0°	6.65	8.06
	60°	0.00	0.00 ^e
	120°	11.36	11.50
	180°	9.82	2.18
$H_3SiCH_2NH_2$	0°	4.04	
	60°	0.00	
	120°	16.72	
	180°	12.24	
$(CH_3)_3SiCH_2NH_2$	0°	4.18	
	60°	0.00	
	120°	17.62	
	180°	12.76	

^a $E(\text{exp})$ 8.29 (ref.¹⁵), ^b $E(\text{exp})$ 0.00 (ref.¹⁵), for ^c 40° , ^d 95° , ^e 55° .

TABLE II
Calculated and Experimental Relative Energies (kJ/mol) for Conformers of Alcohols

Compound	Conformation	$E(\text{CNDO})$	$E(\text{ab initio})^{1,2}$
CH ₃ OH	0°	3.28	8.90 ^a
	180°	0.00	0.00 ^b
FCH ₂ OH	0°	3.08	5.46
	60°	0.00	0.00 ^c
	120°	6.34	
	180°	7.55	23.42
CH ₃ CH ₂ OH	0°	11.56	8.64
	60°	8.13	2.63 ^d
	120°	6.94	5.59 ^e
	180°	0.00	0.00
H ₃ SiCH ₂ OH	0°	25.00	
	60°	14.81	
	120°	8.80	
	180°	0.00	
(CH ₃) ₃ SiCH ₂ OH	0°	25.48	
	60°	15.11	
	120°	9.18	
	180°	0.00	

^a $E(\text{exp})$ 4.46 (ref.¹⁶), ^b $E(\text{exp})$ 0.00 (ref.¹⁶), for ^c 55°, ^d 65°, ^e 115°.

TABLE III
Potential Constants of Fourier Expansion V_n (kJ/mol)

Compound	CNDO/2			<i>Ab initio</i> ^{1,2}		
	V_1	V_2	V_3	V_1	V_2	V_3
CH ₃ NH ₂	—	—	-13.12	—	—	-8.91
FCH ₂ NH ₂	-6.45	7.18	-11.53	-20.34	17.91	-8.41
CH ₃ CH ₂ NH ₂	19.37	-6.82	-13.04	3.72	0.88	-9.58
H ₃ SiCH ₂ NH ₂	33.21	0.57	-16.82			
(CH ₃) ₃ SiCH ₂ NH ₂	34.94	0.91	-17.78			
CH ₃ OH	—	—	-6.56	—	—	-4.69
FCH ₂ OH	14.42	-5.73	-5.47	21.97	-9.21	-4.02
CH ₃ CH ₂ OH	-17.01	4.67	-6.12	-3.89	-0.21	-4.77
H ₃ SiCH ₂ OH	-41.35	-1.86	-8.65			
(CH ₃) ₃ SiCH ₂ OH	-41.88	-1.59	-9.07			

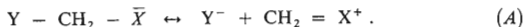
ture *I* was starting for $X = OH$ (two free electron pairs on X) and structure *II* was used as the initial arrangement for $X = NH_2$ (one free electron pair on X). In Tables I and II are presented calculated relative energies of the corresponding conformations with respect to the most stable conformation and for purposes of comparison also available *ab initio* and experimental data. V_n coefficients of Fourier expansion (*I*) used in the analysis are listed in Table III.

$$V(\varphi) = \sum_{n=1}^3 V_n (1 - \cos n\varphi) / 2 \quad (I)$$

RESULTS AND DISCUSSION

Rotation around the C—N and C—O bond in substituted methylamines and methyl alcohols can be described by potential (*I*). Constants V_1 , V_2 and V_3 of this expansion can be regarded as Fourier components reflecting different mechanisms of intramolecular interaction^{11,13}. The V_1 coefficient corresponds to dipole-dipole interaction of the free electron pair on X with the dipole of the C—Y bond. The V_2 coefficient includes the effect of $n_x - \sigma_{C-Y}^*$ back donation from the free electron pair of X to antibonding σ_{C-Y}^* orbitals of the CH_2 —Y bond. The V_3 coefficient determines the magnitude of 3-fold rotation barrier in ethane, methanol, and methylamine. Its magnitude is roughly independent of substituent Y and is proportional to the number of $H \cdots H$ nonbonded interactions. From this it follows that V_3 for the above compounds are in the ratio: $V_3(\text{ethane}) : V_3(\text{methylamine}) : V_3(\text{methanol}) = 3 : 2 : 1$.

Substituted amines. From the magnitude and sign of V_1 coefficient it follows that the dipole of the C—Y bond is polarised in the direction $Y \rightarrow C$ for all the substituents except $Y = F$. The magnitude of this dipole decreases in the sequence $Si(CH_3)_3 > SiH_3 > CH_3 > H$, in agreement with the greater electropositivity of silicon and the stronger +I effect of silyl substituents connected with it. However, this effect of substituent Y is opposed by the $n_x \rightarrow \sigma_{C-Y}^*$ back donation whose extent is determined by the value of the V_2 coefficient. Calculated data indicate a decrease in the back donation in the order $F \gg Si(CH_3)_3 > SiH_3$. This sequence comports with the values of overlap populations p_{C-N} and p_{C-Y} and speaks for a partial double character of the C—N bond in the sense of limit mesomeric structure (A).



In this case the acceptor orbitals are antibonding σ_{C-Y}^* orbitals. This mechanism of back donation explains the operation of the α -effect in the series of substituted silylmethylamines. This donation does not take place for $Y = CH_3$. The partial double C—N bond can be accounted for in this case by the electron flow character $\sigma_{C-CH_3} \rightarrow \sigma_{N-H}^*$.

Negative V_3 values agree with the higher stability of staggered conformation of the $-CH_2-NH_2$ fragment. The fact that V_3 decreases in the order $Si(CH_3)_3 >$

$> \text{SiH}_3 > \text{CH}_3 > \text{F}$ is in accordance with the +I effect of these substituents. Increasing donor ability of the above substituents leads to the increase in the electron density on hydrogen atoms and therefore also to the increase in the potential rotation barrier. These conclusions are confirmed by calculated values of $\text{H}\cdots\text{H}$ overlap populations listed in Table IV.

Substituted alcohols. From the sign of the V_1 coefficient it follows that similarly to the case of substituted amines the C—Y bond dipole is oriented in the direction $\text{C} \rightarrow \text{Y}$ for $\text{X} = \text{F}$ and $\text{Y} \rightarrow \text{C}$ for $\text{Y} = \text{Si}(\text{CH}_3)_3$, SiH_3 and CH_3 . Calculated V_1 values agree with the expected magnitude of the +I effect, analogously as in the series of substituted amines. Negative values of coefficient V_2 point to the stabilisation of the arrangement which arises by rotation of the initial conformation *II* by 90° and are due to the overlap facilitated $n_x \rightarrow \sigma_{\text{C}-\text{Y}}^*$ back donation. The positive values of V_2 for $\text{Y} = \text{CH}_3$ demonstrate the greater stability of the conformation *II* (0°) in this case. The values of overlap populations $p_{\text{C}-\text{O}}$ and $p_{\text{C}-\text{Y}}$ parallel the sequence of V_2 values. They are, however, smaller than the corresponding values for analogous substituted methylamines. The values of V_3 coefficients show the same trend as in the series of amines, *i.e.* the preference of staggered conformations of — CH_2OH fragments and the increase in the expected +I effect of substituents Y. With regard to the half number of $\text{H}\cdots\text{H}$ nonbonded repulsion interactions one can expect the following ratio: $V_3^{\text{NH}_2} : V_3^{\text{OH}} \approx 2$. This assumption is justified very well in the series of compounds with the same substituent Y. The V_n values calculated by CNDO/2

TABLE IV

CNDO/2 Mulliken Overlap Populations for Substituted Alcohols and Amines (for energetically most favourable conformations)

Compound	$p_{\text{Y}-\text{C}}$	$p_{\text{C}-\text{X}}$	$p_{\text{H}-\text{H}}$
FCH_2NH_2	1.0118	1.3108	-0.0167
HCH_2NH_2	1.3522	1.3067	-0.0185
$\text{CH}_3\text{CH}_2\text{NH}_2$	1.4334	1.2886	-0.0182
$\text{H}_3\text{SiCH}_2\text{NH}_2$	1.3876	1.2963	-0.0192
$(\text{CH}_3)_3\text{SiCH}_2\text{NH}_2$	1.3509	1.2982	-0.0193
FCH_2OH	1.0206	1.1317	-0.0159
HCH_2OH	1.3618	1.1296	-0.0175
$\text{CH}_3\text{CH}_2\text{OH}$	1.4393	1.1100	-0.0172
$\text{H}_3\text{SiCH}_2\text{OH}$	1.3940	1.1183	-0.0181
$(\text{CH}_3)_3\text{SiCH}_2\text{OH}$	1.3569	1.1189	-0.0182

method are in general greater than those found by *ab initio* calculation. This can be likely ascribed to the overestimation of delocalisation in the CNDO/2 method. Despite of this fact, our CNDO/2 calculations described qualitatively correctly trends in series of compounds with similar structure and justify thus the application of semiempirical methods to the study of intramolecular interactions.

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