

FOURIER COMPONENTS ANALYSIS OF INTERNAL ROTATION IN CARBOFUNCTIONAL DERIVATIVES OF GROUP IV B ELEMENTS*

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On the basis of Fourier component analysis of internal rotation around the C—X bond in α - and β -functional derivatives of the type $Y-(CH_2)_n-X$ ($X = NH_2, OH$; $Y = CH_3, SiH_3, GeH_3$; $n = 1, 2$) the nature of intramolecular interactions in these compounds was analysed. Electronic effects of polarisable silyl and germyl groups were found to be dramatically influenced by the molecular conformation.

The important position among the carbofunctional organosilicon compounds belongs to α and β derivatives. The differences in chemical reactivity as well as in physical properties of these compounds are in comparison with analogous carbon derivatives so striking that the term α and β effect was even proposed¹⁻⁵. One of the important manifestations of the α effect in physical properties is *e.g.* the distinctly decreased basicity of trimethylsilylmethylamine in homological series of amines of the type⁶ $(CH_3)_3Si(CH_2)_nNH_2$ ($n = 1-4$), while in analogous series of trimethylsilyl-substituted alcohols their basicity decreases monotonously with increasing numbers of CH_2 groups⁷. Another important demonstration of the α -effect is documented by the decrease in electron density on the chlorine atom of chloromethyl-substituted silanes, as indicated by NQR method⁸.

Mechanism of both the α - and β -effects has been frequently discussed in terms of the silicon valence sphere expansion *via* utilization of $3d$ orbitals. However, in recent years, the concept of $(p-d)_\pi$ or $(p-d)_\sigma$ interaction has been mostly forsaken in favour of the concept of $\sigma-\pi$ interaction^{9,10}, when the original idea of Nesmeyanov about the so called $\sigma-\sigma$ conjugation has been scarcely noticed¹¹. The revival of the concept of hyperconjugation has been significantly influenced by quantum chemistry. Thus, for example, CNDO/2 calculations even without silicon d orbitals were used to interpret differences in the basicities of series of silylsubstituted alcohols and amines¹². The same calculations confirmed also significant differences between some calculated quantum chemical characteristics of carbon and silicon analogues (*e.g.* P_{M-C}, Q_X) in a series of α -functional derivatives H_3MCH_2X ($M = C, Si$; $X = NH_2, OH, F$). On the basis of analysis of orbital interactions in these compounds it was

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proposed¹³ that the greater polarisability of silicon compared to carbon is the main factor responsible for the differences mentioned.

The next higher analogue of silicon in the Periodic system is germanium, the polarisability of which – in comparison with silicon – is even greater. It seems therefore likely that a number of anomalies in properties of α - and β -functional organosilicon derivatives could be observed also for germanium analogues. A very useful tool for the study of intramolecular interactions is the recently reported Fourier analysis of the curves of internal rotation¹⁴ around some of the bonds. The aim of this work was to compare on the basis of Fourier analysis of internal rotation curves differences in the nature of intramolecular interactions in a series of carbon, silicon and germanium compounds.

CALCULATIONS

Quantum chemical calculations of potential curves of internal rotation around the C—X bond in α - and β -carbofunctional compounds of the type Y—CH₂—X (X = NH₂, OH; Y = GeH₃, H₃GeCH₂, H₃SiCH₂, CH₃CH₂) were performed by the modified CNDO/2 programme¹⁵ both with and without inclusion of germanium and silicon *d* orbitals. The parameters for germanium were taken from Schweig¹⁶. The compounds were considered in idealized tetrahedral geometries with standard bond lengths¹⁵. Only Si—C, Si—H, Ge—C and Ge—H bond lengths were taken from experiment¹⁷⁻¹⁹ ($r_{\text{Si-C}} = 1.87 \text{ \AA}$, $r_{\text{Si-H}} = 1.48 \text{ \AA}$, $r_{\text{Ge-C}} = 1.945 \text{ \AA}$, $r_{\text{Ge-H}} = 1.529 \text{ \AA}$). Potential curves were calculated in the so called "rigid rotor" approximation, starting from initial conformations *I* and *II*. The structure *I* was used for X = OH and the structure *II* for X = NH₂. This choice of initial conformations comports with the original proposal of Pople¹⁴.

RESULTS AND DISCUSSION

Rotation around the C—N and C—O bond of substituted methylamines and substituted methanols, respectively, can be expressed by potential (1) in cases where potential curves are the even functions of the rotation angle φ .

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

This is the case when the initial conformation of a given molecule has the plane of symmetry. Generally it is necessary, however, to consider in the Fourier expansion also the terms containing odd functions of rotation angle φ such as $\sin \varphi$, $\sin 2\varphi$... *etc.* In such cases Pople and coworkers¹⁴ suggested to use the generalized potential (2).

$$V(\varphi) = \sum_{n=1}^3 V_n/2(1 - \cos n\varphi) + \sum_{m=1}^2 V'_m \sin m\varphi. \quad (2)$$

The V_1 , V_2 and V_3 constants correspond to different mechanisms of intramolecular interactions such as dipole-dipole interactions (V_1), delocalisation (V_2) and H...H nonbonding interactions (V_3). Constants V_1' and V_2' describe deviations of rotational potential from the perfect symmetry with respect to the axis passing through the point $\varphi = 180^\circ$ which is characteristic of the even potential (I). The values of coefficients V_1 , V_2 , and V_3 for the α -functional organogermanium alcohols and amines are presented in Table I. As in Table III of our previous work²⁰ on rotational potentials of organosilicon compounds the values of coefficients V_n for CNDO data are erroneously doubled, their correct values are listed in Table I of this work.

α -Carbofunctional amines. Owing to the symmetry of the starting conformation II for the α -functional amines, the course of the curves of internal rotation can be described by the simple potential (I). The actual form of these curves for series of carbon, silicon and germanium derivatives of the type $H_3MCH_2NH_2$ is represented graphically in Fig. 1. It is seen that the chemical similarity of C, Si and Ge manifests itself also in the similarity of the curves of internal rotation. This similarity can be found, however, only if d orbitals on silicon or germanium are neglected. As it is seen in Fig. 1, the inclusion of these orbitals leads to a completely unrealistic course of the rotational potential $V(\varphi)$. For that reason only calculations neglecting the silicon and germanium d orbitals will be further considered.

TABLE I

Calculated Values of Fourier Expansion Coefficients V_n (kJ/mol) for the Curves of Integral Rotation Around the C—X Bond for α -Carbofunctional Amines and Alcohols

Compound	V_1	V_2	V_3
CH_3NH_2	—	—	—6.56
FCH_2NH_2	—3.22	3.59	—5.77
$CH_3CH_2NH_2$	9.69	—3.40	—6.51
$SiH_3CH_2NH_2$	16.61	0.29	—8.41
$SiMe_3CH_2NH_2$	17.47	0.46	—8.89
$GeH_3CH_2NH_2$	20.58	2.99	—9.88
CH_3OH	—	—	—3.28
FCH_2OH	7.21	—2.86	—2.74
CH_3CH_2OH	—8.50	2.34	—3.06
SiH_3CH_2OH	—20.67	—0.93	—4.33
$SiMe_3CH_2OH$	—20.94	—0.79	—4.54
GeH_3CH_2OH	—26.69	—3.08	—5.13

Let us turn now to the individual coefficients V_n . As follows from the magnitude and the sign of the coefficient V_1 , the dipole of the C—Y bond is polarised in the direction Y→C for all substituents, except Y = F. Comparison of the series with Y = CH₃, SiH₃, Si(CH₃)₃ and GeH₃ shows that the magnitude of the Y→C dipoles increases in the sequence CH₃ < Si(CH₃)₃ < GeH₃, in accordance with the expected order of the +I effect of these substituents. This donation effect of the substituent Y is partially compensated by back donation from the free electron pair on the amino group to antibonding orbitals of the Y—C bond. The extent of this back donation is determined by the magnitude of the V_2 coefficient. Calculated data demonstrate that the extent of the back donation decreases in the sequence F > > GeH₃ > Si(CH₃)₃ > SiH₃. For Y = CH₃ the sign of coefficient V_2 indicates that the above back donation does not take place. Hence, electronic shifts parallel the +I effect of the methyl group and can be ascribed to the interaction of the type $\sigma_{C-Y} \rightarrow \sigma_{N-H}^*$. Both $n_X \rightarrow \sigma_{C-Y}^*$ and $\sigma_{C-Y} \rightarrow \sigma_{N-H}^*$ interactions representing two alternative mechanisms of delocalisation cause the partial double bond character of the

TABLE II

Calculated Values of Fourier Expansion Coefficients V_n (kJ/mol) for the Curves of Internal Rotation Around the C—X Bond for β -Carbofunctional Amines and Alcohols

Compound	V_1	V_2	V_3	V'_1	V'_2
CH ₃ CH ₂ NH ₂	9.69	-3.40	-6.51	—	—
CH ₃ (CH ₂) ₂ NH ₂ ^a	10.75	-3.61	-6.58	—	—
CH ₃ (CH ₂) ₂ NH ₂ ^b	12.84	-2.65	-6.60	-0.97	-0.32
SiH ₃ (CH ₂) ₂ NH ₂ ^a	10.48	-3.78	-6.64	—	—
SiH ₃ (CH ₂) ₂ NH ₂ ^b	19.89	-1.87	-6.07	-3.26	-1.71
GeH ₃ (CH ₂) ₂ NH ₂ ^a	10.58	-3.98	-6.61	—	—
GeH ₃ (CH ₂) ₂ NH ₂ ^b	26.27	-1.02	-5.16	-5.61	-3.56
CH ₃ CH ₂ OH	-8.50	2.34	-3.06	—	—
CH ₃ (CH ₂) ₂ OH ^c	-9.85	2.88	-3.17	—	—
CH ₃ (CH ₂) ₂ OH ^d	-9.27	2.12	-3.15	0.25	-0.11
SiH ₃ (CH ₂) ₂ OH ^c	-8.90	2.85	-3.04	—	—
SiH ₃ (CH ₂) ₂ OH ^d	-17.13	1.02	-2.92	2.88	1.42
GeH ₃ (CH ₂) ₂ OH ^c	-8.91	3.09	-3.02	—	—
GeH ₃ (CH ₂) ₂ OH ^d	-24.07	0.07	-2.49	5.44	3.32

^a Conformation III, ^b conformation IV, ^c conformation V, ^d conformation VI.

C—X bond, as indicated by the results of Mulliken population analysis. The absolute value of coefficient V_3 increases in the sequence $F < \text{CH}_3 < \text{SiH}_3 < \text{GeH}_3$, in accordance with the expected magnitude of the steric effect of these substituents. Its negative sign indicates the preference of staggered conformations of the $\text{CH}_2\text{—NH}_2$ fragment.

β -Carbofunctional amines. Interesting results were obtained also by the study of the curves of internal rotation for β -carbofunctional derivatives. These derivatives can be still considered as α -functional as far as the rotation around the CN bond is concerned. The only difference is that the substituent Y has here the more complex internal structure. This complexity manifests itself *e.g.* in the existence of several possible arrangements of fragments Y ($\text{Y} = \text{CH}_2\text{CH}_3$, CH_2SiH_3 , CH_2GeH_3) represented for example by the initial structures III and IV. Conformation III retains still the plane of symmetry so that the curves of internal rotation can be described by the simple potential (1). The rotational potential for conformation IV has to be described by the more generalized expansion (2). Fig. 2 shows calculated curves of internal rotation around the C—N bond for two starting conformations (III and

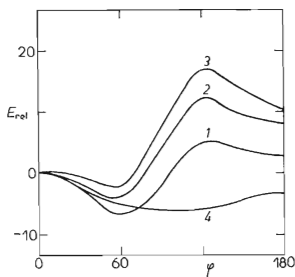


FIG. 1

CNDO/2 Calculated Potentials of Internal Rotation (E_{rel} , kJ/mol) Around the C—N Bond for a Series of α -Functional Amines of the Type $\text{H}_3\text{MCH}_2\text{NH}_2$

1 M = C; 2 M = Si (*d* orbitals neglected);
3 M = Ge (*d* orbitals neglected); 4 M =
= Ge (*d* orbitals considered).

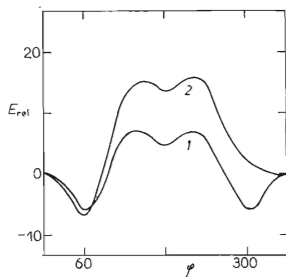
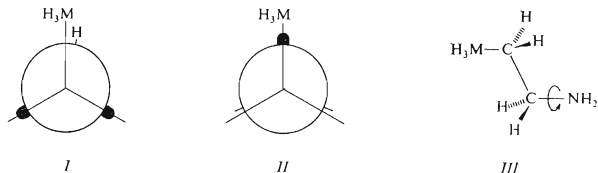


FIG. 2

CNDO/2 Calculated Potentials of Internal Rotation (E_{rel} , kJ/mol) Around the C—N Bond for Different Conformations of the H_3SiCH_2 Fragment in Silylethylamine
1 Conformation III, 2 conformation IV.

IV) of silylethylamine. While in the case of symmetrical conformation *III* the calculated curve is nearly identical with the curve for ethylamine (the same holds also for symmetrical conformation *III* for propylamine and germylethylamine), the

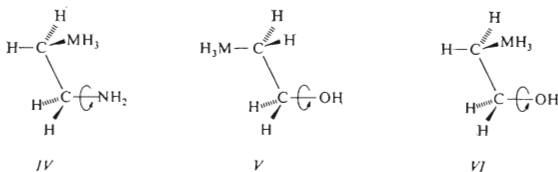


change in conformation of the silyl group (*III–IV*) leads to a dramatical change of the potential, which is demonstrated by the magnitude of coefficients V_n and V'_n of Fourier expansion. These values for standard ethylamine and its methyl, silyl and germyl derivatives are listed in Table II. From this Table it is seen that the values of coefficients V_1 for silyl and germylamines in conformation *III* are roughly equal to the value for the parent ethylamine. On the other hand, in the case of conformation *IV* the coefficient V_1 is significantly altered, above all for silyl and germyl derivatives. This increase in the V_1 coefficient corresponds to a dramatical increase in the dipole of the $Y \rightarrow C$ bond for silicon and germanium derivatives, while for analogous carbon compound this change is practically negligible. Similar conclusions can be arrived at also from comparison of coefficients V_2 . This shows that for CH_3 -, SiH_3 - and GeH_3 -substituted compounds in conformation *III*, the $\sigma_{C-C} \rightarrow \sigma_{N-H}^*$ delocalisation is slightly strengthened, while the same substituents in Conformation *IV* lead to considerable weakening of delocalisation interaction mentioned above. At the same time, these changes are again much more pronounced for polarisable silyl and germyl substituents. From the preceding facts it is evident that the electronic effect of the H_3MCH_2 group ($M = Si, Ge$) depends dramatically on the conformation of molecular chain.

α -Carbofunctional alcohols. Similarly to the α -carbofunctional amines the course of internal rotation curves for these alcohols can be again described by the simple expansion (*I*). The sign of the V_1 coefficient shows that the dipole of the $C-Y$ bond is oriented in the direction $Y \rightarrow C$ for all substituents except fluorine. This trend was found also for the substituted amines. The absolute magnitude of the V_1 coefficient agrees again with the sequence of +I effects of the substituents. The negative sign of the coefficient V_2 for $Y = F, SiH_3, Si(CH_3)_3$ and GeH_3 speaks for stabilization of the conformation formed by rotation of the starting conformation *I* by angle

$\varphi = 90^\circ\text{C}$ in which one can expect significant back donation of the type $n_o \rightarrow \sigma_{\text{C}-\text{N}}^*$. On the other hand, for $\text{Y} = \text{CH}_3$ this delocalisation interaction is of the type $\sigma_{\text{CH}_3\text{CH}_2} \rightarrow \sigma_{\text{OH}}^*$. Values of coefficients V_3 show similar trend as in the case of the α -functional amines. Their approximately half value compared to analogous amines comports with the decreased number of nonbonding $\text{H}\cdots\text{H}$ interactions in former compounds.

β -Carbofunctional alcohols. As in the case of β -carbofunctional amine; also here there is a significant dependence of electronic effects of substituents H_3SiCH_2 and H_3GeCH_2 on conformation (*V*, *VI*). For symmetrical conformation *V* no substantial



difference exists between the curves of internal rotation for CH_3CH_2 -, H_3SiCH_2 - and H_3GeCH_2 -substituted derivatives, as compared to ethanol. On the other hand, for unsymmetrical conformation *VI* one observes a significant increase in the donor dipole-dipole effect of substituents H_3SiCH_2 and H_3GeCH_2 (V_1). The carbon derivatives show again only negligible dependence on conformation. The positive value of the V_2 coefficient for the whole series of β -functional alcohols demonstrates that delocalisation electron shifts take place in the direction $\sigma_{\text{CH}_3\text{CH}_2} \rightarrow \sigma_{\text{OH}}^*$, similarly as in ethanol. Changes in the magnitude of coefficient V_2 in dependence on conformation of the H_3MCH_2 fragment are analogous to those observed for the β -functional amines. For symmetrical conformation *V* the donor $\sigma_{\text{CH}_3\text{CH}_2} \rightarrow \sigma_{\text{OH}}^*$ delocalisation interaction is slightly strengthened, while in "gauche" conformation *VI*, there exists a significant weakening of this interaction, above all for the silyl and germyl derivatives. The magnitude of coefficient V_3 is again roughly constant for the whole series studied, as expected. In addition, this coefficient is approximately one half of that found for the β -functional amines.

These calculated results document clearly that the electronic effects of silyl and germyl substituents are substantially stronger than those of simple alkyl groups. In addition to these quantitative differences, one encounters also a somewhat surprising fact that electronic effect of silyl and germyl groups depends strongly on the molecular conformation. This result clearly demonstrates that any classification of substituents in terms of different effects (+I, -M) is restricted especially in the case of highly polarisable substituents.

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