

FOURIER COMPONENT ANALYSIS OF INTERNAL ROTATION IN β -CARBOFUNCTIONAL DERIVATIVES OF GROUP IVB ELEMENTS*

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Fourier analysis of potential curves of internal rotation around C—X and C—C bonds of β -carbofunctional derivatives of the type $H_3M(CH_2)_2X$ ($M = X, Si, Ge; X = NH_2, OH, F$) has been performed and the nature of intramolecular interactions in these compounds is discussed.

In recent years experimental data on stability of conformers have been increasingly confronted with quantum chemical calculations on different levels of approximation. Such a description makes it possible not only to predict the relative stability of individual conformers but also it provides sufficiently complete information on potential curves of internal rotation. Recently, theoretical description of internal rotation barriers based on nonempirical *ab initio* calculation has led to nearly quantitative agreement with experiment¹.

Despite of these encouraging results, semiempirical methods (CNDO, INDO, PCIO) are still important in the field of theoretical organic chemistry, especially due to their relatively low time demands which enable their application to relatively complex molecules. Although as a rule, these methods do not yield results which would be in quantitative agreement with experiment, they are very useful for ascertaining trends and relative changes in series of structurally related substances.

The form of internal rotation curves is essentially determined by the nature of intramolecular interactions in a given compound and the knowledge of rotational potentials allows therefore to analyse the nature of these interactions. Recently, Pople and coworkers have proposed^{2,3} the method of the analysis of internal rotation curves which is based on their decomposition to truncated Fourier series. Individual coefficients of this expansion can be given a clear physical meaning and characterize thus different interaction mechanisms. With regard to the fact that α - and β -functional organosilicon and organogermanium compounds exhibit a number of anomalies in both physical properties and chemical reactivity compared to analogous carbon derivatives, it was of interest to study the nature of electronic effects of silyl and germyl substituents in these substances. Observed anomalies are so pronounced that the term α - and β -effect⁴⁻⁷ have even been proposed for them. For many years this phenomenon has been explained by postulating the existence of the $(p-d)_\pi$ bonding. However, on the basis of semiempirical CNDO/2 calculations it has been recently proved⁸ that for qualitative interpretation of the above anomalies, silicon d orbitals have not to be considered in calculation and the concept of $(p-d)_\pi$ bonding is increasingly replaced by the concept of $\sigma-\pi$ of $\sigma-\sigma$ conjugation⁹⁻¹¹.

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In the previous work we made Fourier analysis of the curves of internal rotation around C—X bond for a series of carbonyl derivatives of the the H_3MCH_2X ($M = C, Si, Ge; X = NH_2, OH$). In the present work we extend this study to the series of β -functional derivatives, $H_3MCH_2CH_2X$ ($M = C, Si, Ge; X = NH_2, OH, F$). With respect to the greater number of degrees of freedom, we studied rotation around both the C—X bond and the middle C—C bond.

CALCULATIONS

Quantum chemical calculations of carbon and silicon derivatives were made by the standard CNDO/2 programme¹³. This programme was further modified so as to include Group IVb elements, *i.e.* organogermanium compound in our case. Parameters for germanium were taken from Schweig¹⁴. Silicon *d* orbitals and germanium *d* orbitals were not considered in calculation. Compounds were considered in idealised tetrahedral geometries with standard bond lengths. Only Ge—C (1.945 Å, Si—C (1.87 Å), Ge—H (1.529 Å) and Si—H (1.48 Å) bond lengths were taken from experiment¹⁵⁻¹⁷. Internal rotation potential curves were calculated in the so called "rigid rotor" approximation and the corresponding rotational conformers were generated by rotating the starting conformation around C—X or C—C bonds by angles 60°, 120°, 180°, eventually by 240° and 300°. On studying rotation around C—X bond the starting conformations used were *I* for the alcohols and *II* for the amines.

If the starting conformation has a plane of symmetry, the course of internal rotation potential can be described by the simple Fourier expansion (*I*) where V_1 , V_2 and V_3 have certain physical meaning, relating to different mechanisms of substituent effect.

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

This potential is the even function of rotational angle and is thus symmetrical with respect to the axis passing through the point $\varphi = 180^\circ$. In general case one has to use the nonsymmetrical potential (2) where coefficients V_1 , V_2 and V_3 have the same meaning as in the preceding case and coefficients V'_1 and V'_2 determine the magnitude of deviations of the potential (2) from the even function of angle φ . Calculated values of Fourier components V_1 , V_2 , V_3 , V'_1 and V'_2 are presented in Tables I—III.

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

RESULTS AND DISCUSSION

Calculated potentials of internal rotation around C—X and C—C bonds provide a relatively complete cross-section of potential hypersurfaces for β -carbonyl derivatives of the type $H_3MCH_2CH_2X$. This makes it possible to determine the optimum conformations of these compounds. As far as the rotation around the C—X bond is concerned, the studied compounds can be regarded as α -functional derivatives $Y-CH_2X$ in which the substituent Y has, of course, the more complex internal

Table I

Calculated Values of Coefficients V_n (kJ/mol) of Fourier Analysis of Curves of Internal Rotation Around C—N Bond in β -Functional Amines

Compound	V_1	V_2	V_3	V'_1	V'_2
$\text{CH}_3\text{CH}_2\text{NH}_2$	9.69	-3.40	-6.51	—	—
$\text{CH}_3(\text{CH}_2)_2\text{NH}_2^a$	10.75	-3.61	-6.58	—	—
$\text{CH}_3(\text{CH}_2)_2\text{NH}_2^b$	12.84	-2.65	-6.60	-0.97	-0.32
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{NH}_2^a$	10.48	-3.78	-6.64	—	—
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{NH}_2^b$	19.89	-1.87	-6.07	-3.26	-1.71
$\text{H}_3\text{Ge}(\text{CH}_2)_2\text{NH}_2^a$	10.58	-3.98	-6.61	—	—
$\text{H}_3\text{Ge}(\text{CH}_2)_2\text{NH}_2^b$	26.27	-1.02	-5.16	-5.61	-3.56

^a Conformation IV; ^b conformation V.

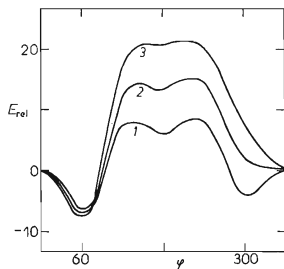


FIG. 1

CNDO/2 Calculated Potentials of Internal Rotation (E_{rel} , kJ/mol) Around C—N Bond in β -Carbofunctional Amines $\text{H}_3\text{MCH}_2\cdot\text{CH}_2\text{NH}_2$ with *gauche* Arrangements of H_3MCH_2 Fragment (1 M = C; 2 M = Si; 3 M = Ge)

The most stable conformation corresponds to structure X.

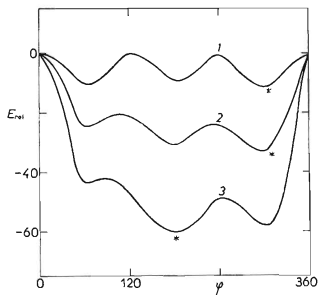


FIG. 2

CNDO/2 Calculated Potentials of Internal Rotation (E_{rel} , kJ/mol) Around C—C bond in β -Carbofunctional Amines $\text{H}_3\text{MCH}_2\text{CH}_2\cdot\text{NH}_2$ (1 M = C; 2 M = Si; 3 M = Ge)

Conformation with rotational angle $\varphi = 300^\circ$ corresponds to structure XI, conformation with the angle $\varphi = 60^\circ$ corresponds to structure XII. The most stable conformation is designated by asterisk.

structure which is given *e.g.* by the existence of different conformational arrangements of the fragment H_3MCH_2 (*IV*, *V*).

Independently of conformation of this fragment, the rotational potential minimum was found in all cases to be at $\varphi = 60^\circ$ for the amines (*VI*) and at $\varphi = 180^\circ$ for the alcohols (*VII*). The curves of internal rotation around C—N bond of β -carbofunctional amines for "gauche" (*V*) arrangement of the H_3MCH_2 fragment are shown in Fig. 1. It is seen that the curves for Si and Ge derivatives differ substantially from the curve for propylamine. On the other hand, for the *anti* arrangement of this fragment, the curves for C, Si and Ge derivatives are nearly identical and do not deviate significantly from the curve for propylamine (*cf.* Fig. 1). Similar results were obtained also for the series of β -functional alcohols. The values of Fourier components V_n for rotation around C—O and C—N bonds of the alcohols and amines, respectively, are given in Tables I and II and will be discussed later.

As far as the rotation around the C—C bond is concerned, the conformation of the C—X fragment was fixed so that it corresponded to the most stable arrangement for both the amines (*VI*) and the alcohols (*VII*). The resulting rotational potentials for X = NH_2 , OH and F are shown in Figs 2–4. The potentials for carbon derivatives could be confronted with the results of 4–31G *ab initio* study by Pople¹⁸. From this comparison it follows that both CNDO/2 and *ab initio* calculations predict correctly the crossed conformations *VIII* and *IX* as energetically very similar, although in some cases (propylamine and propyl fluoride) they differ in predicting energetically most favored conformations. On comparing C, Si and Ge derivatives in individual series (amines, alcohols, fluorides) one observes the change of optimum conformation in some cases (*e.g.* propylamine *vs.* $\text{H}_3\text{Ge}(\text{CH}_2)_2\text{NH}_2$, propanol *vs.* $\text{H}_3\text{Ge}(\text{CH}_2)_2\text{OH}$). However, in these cases the experimental and *ab initio* data are not

TABLE II

Calculated Values of Coefficients V_n (kJ/mol) of Fourier Analysis of Curves of Internal Rotation Around C—O Bond in β -Carbofunctional Alcohols

Compound	V_1	V_2	V_3	V'_1	\hat{V}'_2
$\text{CH}_3\text{CH}_2\text{OH}$	— 8.50	2.34	—3.06	—	—
$\text{CH}_3(\text{CH}_2)_2\text{OH}^a$	— 9.85	2.28	—3.17	—	—
$\text{CH}_3(\text{CH}_2)_2\text{OH}^b$	— 9.27	2.12	—3.15	0.25	—0.11
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{OH}^a$	— 8.90	2.85	—3.04	—	—
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{OH}^b$	—17.13	1.02	—2.92	2.88	1.42
$\text{H}_3\text{Ge}(\text{CH}_2)_2\text{OH}^a$	— 8.91	3.09	—3.02	—	—
$\text{H}_3\text{Ge}(\text{CH}_2)_2\text{OH}^b$	—24.07	0.07	—2.49	5.37	3.32

^a Conformation *IV*; ^b conformation *V*.

still available, which makes it impossible to test the reliability of CNDO/2 data. Since even in such cases differences between two most stable conformations are not too great, we believe that for purposes of qualitative discussion based on Fourier analysis of internal rotation curves the CNDO/2 rotational potentials are sufficiently reliable. Furthermore, Figs 2–4 show that on going from carbon to germanium

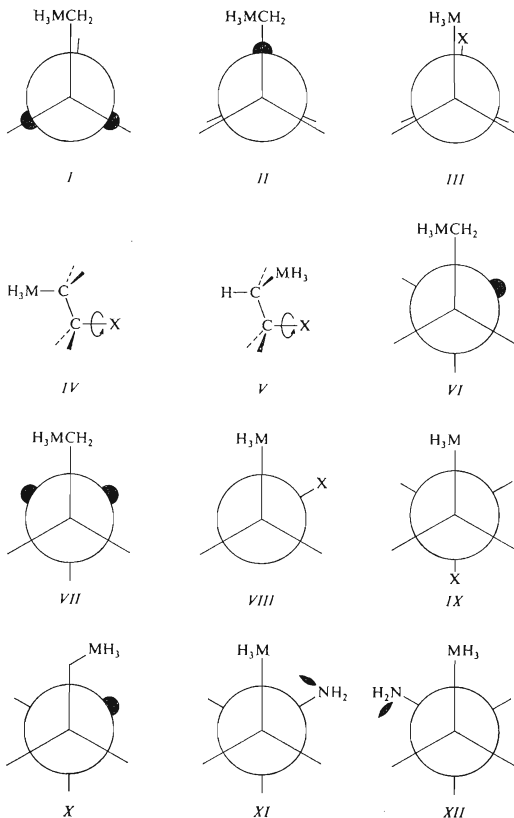


TABLE III

Calculated Values of Coefficients V_n (kJ/mol) of Fourier Analysis of Curves of Internal Rotation Around C—C Bond in Series of β -Carbofunctional Derivatives $H_3MCH_2CH_2X$

Compound	V_1	V_2	V_3	V'_1	V'_2
$H_3CCH_2CH_2F$	3.85	3.98	-9.74	—	—
$H_3SiCH_2CH_2F$	-6.87	-4.69	-14.24	—	—
$H_3GeCH_2CH_2F$	-19.57	-13.86	-19.51	—	—
$H_3CCH_2CH_2OH$	4.58	3.39	-8.72	—	—
$H_3SiCH_2CH_2OH$	-2.93	-3.34	-12.49	—	—
$H_3GeCH_2CH_2OH$	-13.81	-11.53	-17.52	—	—
$H_3CCH_2CH_2NH_2$	1.04	-0.93	-10.27	0.66	0.64
$H_3SiCH_2CH_2NH_2$	-17.00	-12.34	-15.20	2.56	2.41
$H_3GeCH_2CH_2NH_2$	-37.83	-25.37	-21.69	4.71	4.45

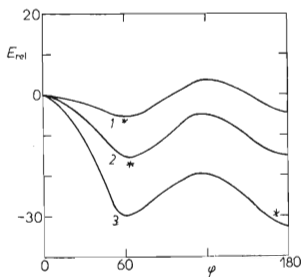


FIG. 3

CNDO/2 Calculated Potentials of Internal Rotation (E_{rel} , kJ/mol) Around C—C Bond in β -Carbofunctional Alcohols $H_3MCH_2\cdot CH_2OH$ (1 M = C; 2 M = Si; 3 M = Ge)

The most stable conformation is designated by asterisk.

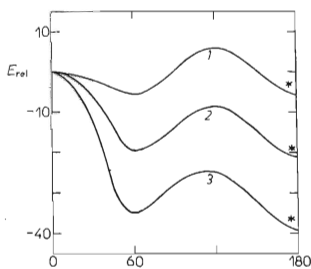


FIG. 4

CNDO/2 Calculated Potentials of Internal Rotation (E_{rel} , kJ/mol) Around C—C Bond in β -Carbofunctional Fluorides $H_3MCH_2\cdot CH_2F$ (1 M = C; 2 M = Si; 3 M = Ge)

The most stable conformation is designated by asterisk.

derivatives a similar trend in all the series is observed, *i.e.* qualitative change in the shape of curves and minima positions does not take place, the result being only an increase in the barriers to rotation. Values of Fourier components V_n and V'_n calculated from data presented in Figs 2–4 are listed in Table III.

Let us turn our attention to the values of Fourier components, first to those for the rotation around the C—X bond. As follows from the positive sign of coefficient V_1 for the parent ethylamine (Table I), the $\text{CH}_3\text{—CH}_2$ bond dipole is oriented in the direction $\text{CH}_3\rightarrow\text{CH}_2$. The negative value of coefficient V_2 speaks for delocalisation interaction of the type $\sigma_{\text{C—C}}\rightarrow\sigma_{\text{N—H}}^*$. Further data from Table I indicate that the introduction of the MH_3 substituent to the *anti* position in the parent ethylamine (IV) does not practically influence the values of Fourier coefficients. This means that the donor character of the substituent H_3MCH_2 expressed by dipole-dipole (V_1) and delocalisation (V_2) mechanism does not differ much from the effect of methyl group itself. Significant changes are observed, however, when the substituent MH_3 is introduced to the *gauche* position (V), and that especially for silyl and germyl derivatives. This result is not surprising if one compares differences in the course of rotational potential, *e.g.* in Fig. 1. Increasing values of the V_1 coefficient indicate an increase in the donor character of the substituent H_3MCH_2 by dipole-dipole mechanism (V_1) while the magnitude of $\sigma_{\text{C—C}}\rightarrow\sigma_{\text{N—H}}^*$ delocalisation interaction decreases somewhat on going from carbon to germanium. Values of the V_3 coefficient are roughly identical in the whole series under study and their negative sign speaks for the preference of the staggered conformation compared to the eclipsed one. Similar conclusions can be drawn also from the analysis of Fourier coefficients for the alcohols (Table II). For *gauche* conformation of the substituent MH_3 (V) also here the dipole of $\text{MH}_3\rightarrow\text{CH}_2$ bonds strongly increases which is accompanied by decreasing $\sigma_{\text{C—C}}\rightarrow\sigma_{\text{O—H}}^*$ delocalisation interaction. Values of coefficients V_3 are roughly half of these for the amines, in agreement with the corresponding decrease in the number of H···H nonbonding interactions.

Let us proceed to the analysis of Fourier coefficients for the rotation around the middle C—C bond. From data presented in Table III it is seen that in the case of carbon derivatives the dipole of the $\text{CH}_3\text{—CH}_2$ bond is oriented in the direction $\text{CH}_3\rightarrow\text{CH}_2$. The same results are obtained also by the analysis of internal rotation curves for ethylamine and ethanol. On the other hand the $\text{H}_3\text{Si—CH}_2$ and $\text{H}_3\text{Ge—CH}_2$ bond dipoles are oriented in the direction $\text{H}_3\text{M}\leftarrow\text{CH}_2$ and their magnitude increases on going from silicon to germanium. This orientation of the H_3MCH_2 bond dipole is opposite to that which was found in the α -carbonyl derivatives¹² $\text{H}_3\text{MCH}_2\text{X}$ and does not agree with the proposed order of the +I effects of silyl and germyl substituents. This result documents clearly the limited applicability of the widely accepted assumption about constancy of bond dipole moments as well as restrictions in the classification of substituents on the basis of different, not clearly defined effects. This holds above all for polarisable substituents since the character

of their electronic effects can be markedly changed by different internal perturbations, e.g. by protonation of molecule. The question about duality of the silyl and germyl substituent effects especially with regard to the role of protonation, is discussed elsewhere¹⁹. The positive values of coefficient V_2 for propyl fluoride and propanol indicate that we deal here with charge transfer in the direction $\text{CH}_3\text{—CH}_2 \rightarrow \sigma_{\text{C—X}}^*$ via delocalisation mechanism. On the other hand, the negative values of coefficient V_2 in all the other cases document that delocalisation mechanism prefers the conformation with dihedral angle $\text{MCCX} = 90^\circ$. Due to the acceptor character of silyl and germyl substituents it seems likely that partially double character of the middle C—C bond in these cases is caused by the interaction of occupied C—H orbitals of the CH_2X group with unoccupied M—C bond orbitals. The negative sign of coefficient V_3 speaks again for the preference of staggered conformations, and their increasing absolute value on going from carbon to germanium corresponds to the increasing steric demands of silyl and germyl groups compared to methyl substituent.

This result suggests that the values of V_3 , or in another words the magnitude of three-fold rotational barrier, could be used to characterise steric effect of substituents alternatively to and independently of Taft E_s constants.

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