

## PROTONATION-INDUCED VARIABILITY OF ELECTRONIC EFFECTS OF SILYL AND GERMYL SUBSTITUENTS IN $\alpha$ -CARBOFUNCTIONAL DERIVATIVES\*

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On the basis of Fourier analysis of internal rotation curves for  $\alpha$ -carbofunctional derivatives of Group IVb elements the effect of protonation of parent molecules on the nature of electronic effects of methyl, silyl and germyl substituents is discussed.

One of the fundamental concepts of organic chemistry is the concept of substituent. Its importance stems above all from the fact that it enables to quantify changes in the properties of a given molecule caused by introduction of a structural group. Such a quantification was made possible only by empirical finding that the introduction of the same structural group to different molecules induces frequently similar changes in the properties of these molecules. This finding was generalised by a rule that a given substituent exerts a certain effect in the molecule to which it is attached and that this effect is the invariant property of the substituent. Further progress in theoretical organic chemistry culminated in suggestion to divide the overall substituent effect into different components corresponding to *e.g.* resonance, inductive and steric effect, which were considered to be independent. Such an approach became the basis of multiparameter correlation analysis. Recently, development of the quantum chemical calculation methods has significantly influenced also the theory of substituent effect. It was shown that in many cases the assumption about the constant substituent effect is not valid, not even qualitatively. Thus, for example, CNDO/2 calculations proved<sup>1</sup> that methyl group acts as  $\sigma$ -donor and  $\pi$ -acceptor in toluene while in the corresponding *p*-toluenonium ion it acts as  $\sigma$ - and  $\pi$ -donor. Hence, it is obvious that substituents cannot be in general classified in terms of the effects which they exert (+I, -M, etc.) since these effects are influenced to a great extent by variable electronic demands of substrates. These, in turn, are induced by various chemical or physical perturbations, such as *e.g.* by protonation of molecule, conformational changes, external field, excitation, etc. The ease with which a given substituent "accommodates" changes in electronic demands of substrates depends above all on its polarisability. The success of the original classification of substituents according to the type of effects which they exert was mainly due to the fact that for the majority of the substituents which one encounters in organic chemistry the polarisability effects are much weaker than the effects of polarity. In order to prove experimentally the variability of electronic effects it was therefore necessary to find substituents which would exhibit sufficiently high polarisability. Recently, several examples have been reported in the field of organosilicon and organogermanium

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chemistry<sup>2-4</sup>. Thus, for example, on the basis of CNDO/2 calculations of the series of  $\beta$ -carbofunctional derivatives  $H_3MCH_2CH_2X$  ( $M = C, Si, Ge$ ;  $X = NH_2, OH$ ) it was found that the electronic effect of silyl and germyl groups is influenced dramatically by conformational changes of their molecules, in contrast to the effect of methyl group<sup>4</sup>. This interesting result could contribute to the elucidation of the mechanism of the so-called  $\alpha$ -effect<sup>5,6</sup>.

Pople and coworkers<sup>7</sup> have recently proposed a new method for characterisation of substituent effects which is based on Fourier analysis of potential curves of internal rotation around some bonds. The course of these curves is determined to a great extent by the nature of intramolecular interactions in a given compound. Since one can ascribe physical meaning to the coefficients of such a Fourier expansion, it is possible — by their comparison in a series of differently substituted derivatives — to discuss the role and magnitude of different interaction mechanisms which are generally included into the term substituent effect.

In the present work the Fourier analysis of potential curves of internal rotation has been used to study the effect of protonation of molecule on the character of electronic effects of methyl, silyl and germyl groups in the series of  $\alpha$ -carbofunctional amines, alcohols and halogenides.

#### CALCULATIONS

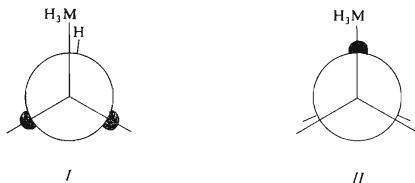
Quantum chemical calculations of potential curves of internal rotation around C—X bond of the series  $Y-CH_2X$  and  $Y-CH_2XH^+$  ( $Y = CH_3, SiH_3, Si(CH_3)_3, GeH_3$ ;  $X = NH_2, OH, F$ ) were made by using a modified version of CNDO/2 programme<sup>8</sup> without inclusion of silicon and germanium  $d$  orbitals. Parameters for germanium were taken from Schweig<sup>9</sup>. The compounds were considered in idealised tetrahedral geometries with standard bond lengths<sup>8</sup>. Si—C (1.87 Å), Si—H (1.48 Å), Ge—C (1.945 Å) and Ge—H (1.529 Å) bond lengths were taken from experiment<sup>10-12</sup>.

#### RESULTS AND DISCUSSION

Due to the symmetry of studied compounds, rotation around their C—X bond can be described by the potential ( $I$ )

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

The calculation of coefficients  $V_1$ ,  $V_2$  and  $V_3$  requires the knowledge of energies of three different conformations relative to the energy of the starting conformation for which  $\varphi = 0$ . These starting conformations were taken different for alcohols ( $I$ ) and amines ( $II$ ), in accordance with Pople's work<sup>7</sup>. The choice of starting conformations for protonated molecules originates from the fact that protonated alcohols are isosteric with amines ( $II$ ) and protonated fluorides with alcohols ( $I$ ).



In order to demonstrate variability of electronic effects of methyl, silyl and germyl substituents, let us compare first the potentials of internal rotation for the series of isosteric derivatives, *i.e.*  $Y-CH_2NH_2$  *vs.*  $Y-CH_2OH_2^+$  and  $Y-CH_2OH$  *vs.*  $Y-CH_2FH^+$ . For purposes of illustration, data for germylmethylamine and protonated germylmethanol are represented graphically in Fig. 1. It is seen that both curves are very similar. This is due to the isostericity of the molecules. The more pronounced difference appears in the magnitude of barriers for internal rotation. This difference can be expressed quantitatively by the coefficients of Fourier expansion (1). Calculated values of coefficients  $V_1 - V_3$  for the isosteric series of amines and protonated alcohols are listed in Table I and analogous data for the series of alcohols and protonated fluorides are summarised in Table II.

Data in Table I show that difference in constants  $V_1$  and  $V_2$  between the amines and protonated alcohols are relatively much smaller in the series of carbon compounds than they are in the series of silyl and germyl derivatives. This documents the markedly increased polarisability of the latter groups. This greater polarisability

TABLE I

Calculated Values of Coefficients  $V_n$  (kJ/mol) of Fourier Expansion of Curves of Internal Rotation Around C—X Bond for Isosteric Series of  $\alpha$ -Carbofunctional Amines and Protonated Alcohols

Compound	$V_1$	$V_2$	$V_3$
$CH_3CH_2NH_2$	9.68	-3.41	-6.52
$SiH_3CH_2NH_2$	16.61	0.29	-8.41
$SiMe_3CH_2NH_2$	17.47	0.45	-8.89
$GeH_3CH_2NH_2$	20.58	2.99	-9.88
$CH_3CH_2OH_2^+$	6.87	-2.08	-4.29
$SiH_3CH_2OH_2^+$	30.44	3.18	-7.36
$SiMe_3CH_2OH_2^+$	28.43	2.23	-7.58
$GeH_3CH_2OH_2^+$	40.72	6.10	-9.08

also manifests in that in comparison with methyl group, silyl and germyl groups exert simultaneously both donor (dipole-dipole) and acceptor (delocalisation) character. By contrast, the methyl group acts here only as the electron donor. Similar

TABLE II

Calculated Values of Coefficients  $V_n$  (kJ/mol) of Fourier Expansion of Curves of Internal Rotation Around C—X Bond for Isosteric Series of  $\alpha$ -Carbofunctional Alcohols and Protonated Fluorides

Compound	$V_1$	$V_2$	$V_3$
$\text{CH}_3\text{CH}_2\text{OH}$	-8.50	2.34	-3.06
$\text{SiH}_3\text{CH}_2\text{OH}_2$	-20.67	-0.93	-4.32
$\text{SiMe}_3\text{CH}_2\text{OH}$	-20.94	-0.79	-4.53
$\text{GeH}_3\text{CH}_2\text{OH}$	-26.69	-3.08	-5.13
$\text{CH}_3\text{CH}_2\text{FH}^+$	-2.57	3.20	-1.59
$\text{SiH}_3\text{CH}_2\text{FH}^+$	-35.55	-4.35	-3.91
$\text{SiMe}_3\text{CH}_2\text{FH}^+$	-31.87	-2.54	-4.08
$\text{GeH}_3\text{CH}_2\text{FH}^+$	-49.75	-8.27	-5.09

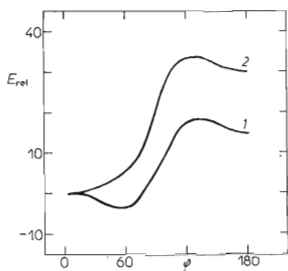


FIG. 1

CNDO/2 Calculated Potentials ( $E_{rel}$ , kJ/mol) of Internal Rotation Around C—X Bond for Germylmethanamine (1) and Protonated Germylmethanol (2)

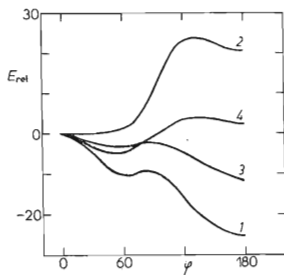


FIG. 2

CNDO/2 Calculated Potentials of Internal Rotation ( $E_{rel}$ , kJ/mol) Around C—O Bond for Unprotonated and Protonated Trimethylsilylmethanol and ethanol

1  $\text{Me}_3\text{SiCH}_2\text{OH}$ ; 2  $\text{Me}_3\text{SiCH}_2\text{OH}_2^+$ ; 3  $\text{CH}_3\text{CH}_2\text{OH}$ ; 4  $\text{CH}_3\text{CH}_2\text{OH}_2^+$ .

conclusions can be drawn also from the values of coefficients  $V_1 - V_3$  for the series of alcohols and protonated fluorides (Table II). Thus, for example, comparison of the  $V_1$  coefficients in the carbon series indicates a decrease in the dipole-dipole donor effect of the methyl group in protonated fluorides while in the series of silicon and germanium compounds one observes significant increase in both donor-dipole ( $V_1$ ) and acceptor delocalisation ( $V_2$ ) character of silyl and germyl substituents.

TABLE III

Calculated Values of Coefficients  $V_n$  (kJ/mol) of Fourier Expansion of Potential Curves of Internal Rotation Around C—O Bond for Series of Unprotonated and Protonated  $\alpha$ -Carbofunctional Alcohols

Compound	$V_1$	$V_2$	$V_3$
CH <sub>3</sub> CH <sub>2</sub> OH	- 8.50	2.34	-3.06
SiH <sub>3</sub> CH <sub>2</sub> OH	-20.67	-0.93	-4.32
SiMe <sub>3</sub> CH <sub>2</sub> OH	-20.94	-0.79	-4.53
GeH <sub>3</sub> CH <sub>2</sub> OH	-26.69	-3.08	-5.13
CH <sub>3</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>+</sup>	6.87	-2.08	-4.29
SiH <sub>3</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>+</sup>	30.44	3.18	-7.36
SiMe <sub>3</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>+</sup>	28.43	2.23	-7.58
GeH <sub>3</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>+</sup>	40.72	6.10	-9.08

TABLE IV

Calculated Values of Coefficients  $V_n$  (kJ/mol) of Fourier Expansion of Potential Curves of Internal Rotation Around C—N Bond for Series of Unprotonated and Protonated  $\alpha$ -Carbofunctional Amines

Compound	$V_1$	$V_2$	$V_3$
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	9.68	-3.41	- 6.52
SiH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	16.61	0.29	- 8.41
GeH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	20.58	2.99	- 9.88
CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	—	—	- 8.29
SiH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	—	—	-11.71
GeH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	—	—	-13.89

In connection with the problem of mechanism of the  $\alpha$ -effect, let us turn now to the study of variability of electronic substitution effects caused by protonation of molecule. As it is seen from Fig. 2, which shows potential curves of internal rotation around C—O bond in unprotonated and protonated trimethylsilylmethanol and ethanol, the protonation of molecule results in marked changes in the form of rotational potential. Calculated values of Fourier coefficients  $V_1 - V_3$  for the series of unprotonated and protonated alcohols are given in Table III and those for the series of unprotonated and protonated amines are summarised in Table IV. Let us discuss first these coefficients for the series of carbofunctional alcohols. The difference in the signs of constants  $V_1$  and  $V_2$  for the series of protonated and unprotonated molecules is worth mentioning. This difference is due to the different starting conformations of protonated (*II*) and unprotonated (*I*) alcohols. This fact has to be taken into account in interpretation of individual constants  $V_1$  and  $V_2$ . The values of coefficients  $V_1$  demonstrate that protonation of molecule does not result in principal change of the resultant donor character of the substituent Y ( $\text{CH}_3$ ,  $\text{SiH}_3$ ,  $\text{Si}(\text{CH}_3)_3$ ,  $\text{GeH}_3$ ) by dipole-dipole mechanism. In dependence on the type of substituent Y protonation however leads to significant relative changes in the magnitude of this donor effect. Thus in the series of carbon alcohols protonation decreases slightly the donor dipole-dipole effect while in the series of silyl and germyl derivatives this effect is strengthened. More pronounced changes can be observed in the effect of these substituents *via* delocalisation mechanism, which is characterized by the  $V_2$  constant. In the series of carbon alcohols, in which the methyl group acts essentially as the electron donor also by the  $\sigma_{\text{CH}_2-\text{CH}_3} \rightarrow \sigma_{\text{O}-\text{H}}^*$  delocalisation mechanism, protonation leads only to insignificant decrease in the magnitude of this interaction. In contrast to it, in the series of silyl and germyl alcohols, in which  $\text{SiH}_3$  or  $\text{GeH}_3$  groups act as electron acceptors due to back donation of the type  $n_{\text{O}} \rightarrow \sigma_{\text{C}-\text{M}}^*$ , protonation strengthens very strongly this acceptor mechanism. The values of coefficients  $V_3$  exhibit expected decrease with protonation, in agreement with doubled H...H nonbonding interactions.

On the other hand, protonation influences quite differently substituent effects of  $\text{CH}_3$ ,  $\text{SiH}_3$  and  $\text{GeH}_3$  groups in the  $\alpha$ -carbofunctional amines. The values of coefficients  $V_1$  summarised in Table IV document a significant decrease in the donor effect of all these substituents by the mechanism of direct dipole-dipole interaction. Similarly, both the donor ( $\text{CH}_3$ ) and acceptor effects ( $\text{SiH}_3$ ,  $\text{GeH}_3$ ) are markedly weakened by delocalisation mechanism ( $V_2$ ). As expected, the  $V_3$  coefficients decrease with protonation, again as a result of the increased number of H...H nonbonding interactions.

Obtained results document clearly the higher sensitivity of silyl and germyl substituents in  $\alpha$ -carbofunctional derivatives to secondary induced changes caused by protonation of molecule. This means also that the whole series of experimental results, in which protonation of molecule or formation of hydrogen bond plays

a role (*e.g.* the order of basicity of trimethylsilyl substituted alcohols and amines) and which at the same time are often characteristic of the action of the so-called  $\alpha$ -effect, cannot be interpreted only on the basis of the properties and electronic structure of parent unprotonated molecules. In these cases it seems necessary to consider also the effect of secondary protonation-induced changes on the electronic effects of polarisable silyl and germyl substituents.

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