EFFECTS OF GROUP IVB SUBSTITUENTS ON THE PROTON AFFINITY OF ALCOHOLS AND AMINES: A THEORETICAL STUDY *

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(Received July 12th, 1983)

Summary

The effects of α- and β-silyl- and -germyl- substituents on the proton affinity of alcohols and amines have been considered on the basis of a recently proposed method of analysis of the protonation energy. This method permits discussion of the origin of the stereospecificity of the substituent effects of silyl and germyl groups, which may contribute to the understanding of the nature of the α-effect on the chemistry of Group IVB elements.

Introduction

Several experimental observations indicate that the effects of silyl and germyl substituents considerably differs from those of simple alkyls. Thus for example in a series of trimethylsilyl- and trimethylgermyl-substituted carbofunctional alcohols $Me_3M(CH_2)_nOH$ (M = Ge, Si; n = 1, 2, 3), the basicity decreases with the increasing length of the alkyl chain [1,2]. In contrast, in an analogous series of carbofunctional amines $Me_3M(CH_2)_nNH_2$ the data indicate an unusual sequence of basicity, characteristic for the operation of the so-called α-effect [3,4]; in this sequence the maximum basicity is observed for the β-derivatives, the basicities of both α and γ-derivative being lower.

Theoretical quantum chemical calculations were applied to the elucidation of these results [5,6]. Besides interpreting the observed experimental results, the calculations also disclosed a very interesting conformational dichotomy for silyl and germyl substituent effects [6]. In a preliminary communication [7] we outlined our attempts to analyse the origin of the stereospecificity of the substituent effects for a series of carbofunctional organosilicon derivatives. In the present paper we apply the same

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* Dedicated to Prof. R. Calas on the occasion of his 70th birthday.

method to a series of organogermanium compounds. This extension permits a discussion of the general factors governing the substituent effects of Group IVB substituents and thus contributes to the elucidation of the nature of the α-effect.

Calculations

The calculations were of two types. The first one involves determination of the total protonation energies ΔE of all the studied compounds in terms of the general equation 1 as the difference between the total energy of the nonprotonated molecule B and that of the corresponding conjugate acid BH^+.

$$\Delta E = E(BH^+) - E(B) \tag{1}$$

For these calculations a standard CNDO/2 programme [8] was modified for inclusion of third row elements. Because of the semi-empirical nature of the CNDO/2 method, and since we are interested in general trends rather than in absolute numbers, the calculations were performed for the hypothetic silyl-(SiH_3) and germyl-(GeH_3)-substituted compounds rather than for trimethylsilyl and trimethylgermyl derivatives. The d-orbitals on silicon and germanium were neglected. Parameters for germanium were taken from Schweig [9]. All molecules were, as in our previous study, considered in idealised tetrahedral geometries with bond lengths either standard [8] or experimental [10,11] (r(SiC) 1.87 Å, r(GeC) 1.945 Å, r(SiH) 1.48 Å, r(GeH) 1.53 Å). The geometries of all the compounds were partially optimised with respect to rotation around the C–X bond (in α-functional derivatives) and to the central C–C bond (in β-functional derivatives). For β-derivatives there are two energetically comparable conformations corresponding to "*gauche*" and "*anti*" arrangements of the molecular chain (A and B). Despite the comparable

(A)   (B)
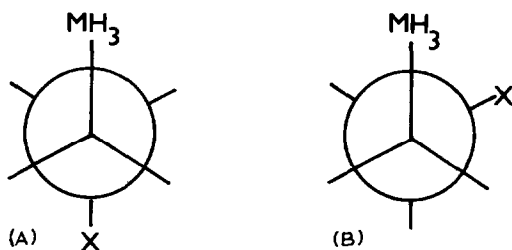
stability of these two conformations, the substituent effects displayed by silyl and germyl groups depends greatly on the actual arrangement of the molecular chain. Thus on going from an α- to a β-derivative, the basicities of silyl- and germyl-substituted compounds increase for the *anti*-conformation, but falls for the *gauche* conformation [6]. In order to analyse in detail the dichotomy of the substituent effect mentioned above, in a second step the total protonation energies were broken down by the procedure described in our original paper [12].

Theoretical

The protonation energies defined by eq. 1 represent overall properties which incorporate the influence of several different factors. When attempting a detailed interpretation of the influence of structural factors on molecular properties it is

usual to break down the global characteristics into various components corresponding to different mechanisms of intramolecular interaction. Such a procedure forms the basis of e.g., Morokuma's method [13]. However, Morokuma's approach is not the only possible one. We recently proposed an alternative procedure for breakdown of the total protonation energies based on Longuet–Higgins theory of proton affinity [14].

The method is described in detail in our original paper [12] and so we present here only the basic concepts necessary for the purpose of this study. The total protonation energy is broken down into two additive contributions $\Delta\epsilon$ and $\Delta\eta$ (eq. 2).

$$\Delta E = \Delta\epsilon + \Delta\eta (1) \tag{2}$$

The breakdown is based on the following simple idea. The protonation energy defined by eq. 1 represents the energy which has to be supplied to transfer the proton in the electric field of the attacked molecule from infinity to the distance r_0 corresponding to the length of the newly formed bond in the protonated molecule. The process of approaching the proton can be divided, in keeping with Longuet–Higgins' theory, into two separate steps. In the first, the vacant $1s$ orbital localised on a hypothetical particle carrying the core charge $\lambda = 0$ is transferred from infinity to the distance r_0. In the second step this particle is continuously charged up to $\lambda = 1$. At the end of this charging process we are thus in a situation in which the proton is placed at the distance r_0 from the molecule. The individual contributions $\Delta\epsilon$ and $\Delta\eta$ then correspond to the two steps. The first term $\Delta\epsilon$, which appears as a consequence of different extent of AO basis sets for nonprotonated and protonated molecules, is entirely analogous to function counterpoise correction introduced by Boys and Bernardi [15]. The second term $\Delta\eta$ (1) describes the energetic contribution resulting from the reorganisation of the electron distribution due to the presence of the charged particle in the vicinity of the molecule. The magnitude of this term depends, of course, on the charge, and eq. 2 is valid for $\Delta\eta$ corresponding to $\lambda = 1$.

In order to obtain a more detailed insight into the nature of this term it is possible to break it down further into contributions corresponding to the electrostatic and polarisation parts of the interaction energy (eq. 3).

$$\Delta\eta(1) = \Delta E_{elst} + \Delta E_{polar} \tag{3}$$

The original eq. 2 can then finally be rewritten in the form of eq. 4, which serves as a basis for our discussion.

$$\Delta E = \Delta\epsilon + \Delta E_{elst} + \Delta E_{polar} \tag{4}$$

Results and discussion

The calculated values of the total protonation energies and of their individual components are summarised for a series of organosilicon- and organogermanium-substituted amines and alcohols in Tables 1 and 2. For comparison, the same Tables also include data for simple aliphatic derivatives. In a detailed discussion of the results our first aim is to analyse the differences in substituent effect of silyl and germyl groups (with respect to methyl) in α-functional derivatives H_3MCH_2X. For

TABLE 1

CALCULATED PROTONATION ENERGIES AND THEIR INDIVIDUAL COMPONENTS FOR THE SERIES OF ALCOHOLS $H_3M(CH_2)_nOH$ (all quantities in atomic units)

Compound	ΔE	$\Delta\epsilon$	ΔE_{elst}	ΔE_{polar}
CH_3CH_2OH	−0.420	−0.385	0.101	−0.136
$CH_3CH_2CH_2OH$ [a]	−0.425	−0.385	0.098	−0.138
$CH_3CH_2CH_2OH$ [b]	−0.423	−0.386	0.102	−0.139
SiH_3CH_2OH	−0.428	−0.387	0.100	−0.141
$SiH_3CH_2CH_2OH$ [a]	−0.435	−0.385	0.093	−0.143
$SiH_3CH_2CH_2OH$ [b]	−0.424	−0.391	0.110	−0.143
GeH_3CH_2OH	−0.433	−0.388	0.099	−0.144
$GeH_3CH_2CH_2OH$ [a]	−0.440	−0.384	0.091	−0.147
$GeH_3CH_2CH_2OH$ [b]	−0.424	−0.391	0.114	−0.147

[a] *anti*-Conformation. [b] *gauche*-Conformation.

this purpose only the relative changes $\delta\Delta E$ in the total protonation energy and in its components are decisive (eq. 5).

$$\delta\Delta E = \delta\Delta\epsilon + \delta\Delta E_{elst} + \delta\Delta E_{polar} \tag{5}$$

The calculated values (Table 3) demonstrate the progressive increase in basicity on going from the carbon to the germanium derivatives. The classical explanation of this result based on the concept of $+I$ effect is not, however, completely satisfactory, since it fails to account for the experimental results for β-functional derivatives. This suggests, that the intuitive classical ideas have to be replaced by more general and more sophisticated concepts. In this respect we believe that our breakdown procedure represents a useful alternative. Its advantage lies in the fact that it allows us to extract from the original global quantities the specific contributions characterising the substituent effect in terms of clearly defined molecular characteristics.

As demonstrated by the data in Table 3, the basis set correction $\Delta\epsilon$ as well as the electrostatic contributions are practically unaffected by silyl and germyl substitution. This implies that these substituents practically do not affect the electrostatic potential in the vicinity of the protonated nucleus compared with these in the carbon

TABLE 2

CALCULATED PROTONATION ENERGIES AND THEIR INDIVIDUAL COMPONENTS FOR THE SERIES OF AMINES $H_3M(CH_2)_nNH_2$ (all quantities in atomic units)

Compound	ΔE	$\Delta\epsilon$	ΔE_{elst}	ΔE_{polar}
$CH_3CH_2NH_2$	−0.491	−0.383	0.049	−0.157
$CH_3CH_2CH_2NH_2$ [a]	−0.495	−0.383	0.048	−0.160
$CH_3CH_2CH_2NH_2$ [b]	−0.493	−0.384	0.049	−0.158
$SiH_3CH_2NH_2$	−0.497	−0.385	0.049	−0.161
$SiH_3CH_2CH_2NH_2$ [a]	−0.502	−0.383	0.042	−0.161
$SiH_3CH_2CH_2NH_2$ [b]	−0.492	−0.388	0.058	−0.162
$GeH_3CH_2NH_2$	−0.501	−0.385	0.048	−0.164
$GeH_3CH_2CH_2NH_2$	−0.506	−0.381	0.041	−0.166
$GeH_3CH_2CH_2NH_2$	−0.491	−0.388	0.061	−0.164

[a] *anti*-Conformation. [b] *gauche*-Conformation.

TABLE 3

VARIATIONS IN TOTAL PROTONATION ENERGIES AND IN THEIR COMPONENTS FOR A SERIES OF α-FUNCTIONAL DERIVATIVES OF GROUP IVB ELEMENTS (all quantities in atomic units)

M	X	$\delta\Delta E$ [a]	$\delta\Delta\epsilon$ [a]	$\delta\Delta E_{elst}$ [a]	$\delta\Delta E_{polar}$ [a]
Si	OH	−0.008	−0.002	−0.001	−0.005
Ge	OH	−0.013	−0.003	−0.002	−0.008
Si	NH$_2$	−0.006	−0.002	0.000	−0.004
Ge	NH$_2$	−0.010	−0.002	−0.001	−0.007

[a] Variations with respect to carbon compound as a standard are defined by expression:
$\delta\Delta Q(H_3MCH_2X) = \Delta Q(H_3MCH_2X) - \Delta Q(CH_3CH_2X)$

analogues. The basicity increase on going from carbon to germanium therefore cannot be regarded as a consequence of differences in the static distribution of electronic density, but instead reflects the changes in the polarisability of corresponding molecules. As Fig. 1 shows, there is a very simple linear relationship between the variations in total basicity and the polarisation contributions. This suggests that the basicity increase is due to secondary dynamic effects induced by the protonation of the molecule. The importance of these secondary effects was stressed in our earlier paper [16].

We now consider the origin of stereospecificity of the silyl and germyl substituent effects in β-functional derivatives. For this purpose we compare the variations of the individual components of the protonation energies for the *anti-* and *gauche-*conformations of the β-functional derivatives and the corresponding α-compound

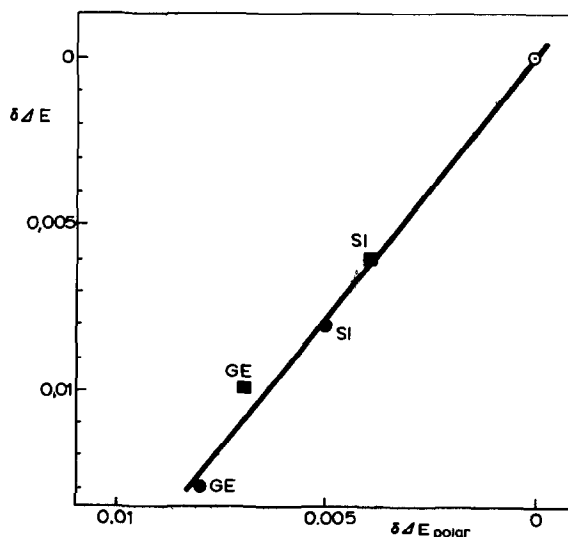Fig. 1. Variations $\delta\Delta E$(a.u.) of total protonation energies as a function of the relative polarisability contributions $\delta\Delta E_{polar}$ (a.u.) for a series of α-functional organosilicon and organogermanium derivatives (● alcohols, ■ amines).

TABLE 4

VARIATIONS IN PROTONATION ENERGIES AND IN THEIR COMPONENTS FOR A SERIES OF β-FUNCTIONAL DERIVATIVES OF GROUP IVB ELEMENTS (all quantities in atomic units)

M	X	$\delta\Delta E^{c}$	$\delta\Delta\epsilon^{c}$	$\delta\Delta E_{elst}{}^{c}$	$\delta\Delta E_{polar}{}^{c}$
Si	OH ^{a}	−0.007	0.002	−0.007	−0.002
	OH ^{b}	+0.004	−0.004	+0.010	−0.002
Ge	OH ^{a}	−0.007	0.004	−0.008	−0.003
	OH ^{b}	+0.009	−0.003	+0.015	−0.003
Si	NH$_2$ ^{a}	−0.005	0.002	−0.007	0.000
	NH$_2$ ^{b}	+0.005	−0.003	+0.009	−0.001
Ge	NH$_2$ ^{a}	−0.005	0.004	−0.007	−0.002
	NH$_2$ ^{b}	+0.010	−0.003	0.013	0.000

^{a} *anti*-Conformation. ^{b} *gauche*-Conformation. ^{c} Variations with respect to corresponding α-functional derivatives as a standard are defined by expression:

$$\delta\Delta Q(H_3MCH_2CH_2X) = \Delta Q(H_3MCH_2CH_2X) - \Delta Q(H_3MCH_2X)$$

H_3MCH_2X. The relevant data are listed in Table 4. The calculations indicate that the lengthening of the molecular alkyl chain on going from H_3MCH_2X to $H_3MCH_2CH_2X$ primarily influences the electrostatic contribution without significantly altering the polarisability of the molecule. The increase in basicity characteristic of the *anti*-conformation of the molecular chain can thus be directly related to the decrease of the electrostatic potential at the protonated nucleus. Similarly the basicity decreases predicted for *gauche*-conformations result from the increase of the electrostatic potential. These results confirms our earlier conclusions about the static character of the α-effect [17] and about the crucial influence of stereoelectronic factors on it [6].

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