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MOLECULAR ORBITAL STUDY OF GAS PHASE BASICITIES OF CARBOFUNCTIONAL DERIVATIVES OF GROUP IVB ELEMENTS; STEREOCHEMICAL CONTROL

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Summary

The gas phase basicities of a series of carbofunctional derivatives H_3M-$(CH_2)_nX$ (M = C, Si, Ge; X = NH_2, OH, F; n = 1—3) were investigated by the semiempirical CNDO/2 method. The calculations indicate that the electronic effects of silyl- and germyl-substituents differ greatly from the effect of simple alkyls. Moreover, in contrast to simple carbon derivatives, the overall nature of the electronic effects of silyl- and germyl-substituents is crucially influenced by the molecular conformation.

Introduction

The increasing availability of such techniques as chemical ionisation mass spectrometry [1] and ion cyclotron resonance [2] has stimulated experimental and theoretical interest in the study of the effect of structural variations on intrinsic (gas-phase) acid and base strengths. Because of the absence of complications arising from solvation effects, the gas phase quantities represent very convenient data for direct theoretical calculation, and both ab initio [3—5] and semiempirical [6—8] calculations have proved to be very useful in rationalizing the experimental results. In contrast to the considerable effort devoted to the study of the effect of simple alkyl groups, little is known about the factors determining the influence of other substituents.

An interesting extension in this respect represents the study of basicities in a series of closely related trimethylsilyl- and trimethylgermyl-substituted aliphatic alcohols and amines [9—11] ($(CH_3)_3M(CH_2)_nX$ (M = Si, Ge; X = NH_2, OH; n = 1—4)). Because of the unavailability of direct gas phase techniques the basicity used was that measured by the IR method with phenol and deuterochloroform as proton-donors. Since the measurements were made in a very dilute solution in nonpolar CCl_4 and since the studied series form a closely structurally related set of compounds we believe that the IR data can be considered as a rough measure of the gas phase basicities. The theoretical justification for such a belief is provided by the thorough study by Arnett [12].

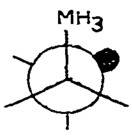
The experimental results reveal a large difference between the trends in basicity for organometallic derivatives (Si, Ge) and the corresponding alkyl derivatives. For example, the basicities in both series of organometallic alcohols decrease with increase in the number of intervening CH_2 groups, in contrast to the trend for simple alkyl alcohols. The variation in the basicities of organometallic amines is even more complex, and reflects the operation of the so-called α-effect [13].

These results suggest that in spite of expected similarity of carbon, silicon and germanium, the electronic effects of silyl and germyl groups are substantially different from those of simple alkyl groups. Stimulated by these experimental findings we undertook to investigate through semiempirical CNDO/2 calculations, the factors influencing the effects of silyl- and germyl-substituents on the gas phase basicities.

Calculations

Quantum chemical calculations were performed with the standard CNDO/2 programme [14] modified for inclusion of third-row atoms. The *d*-orbitals on silicon and germanium were neglected and parameters for germanium were taken from Schweig [15]. Ideal tetrahedral geometries were assumed, with bond lengths either standard [14] or experimental [16—18] (r(Si—C) = 1.87 Å; r(Ge—C) = 1.945 Å; r (Si—H) = 1.48 Å; r(Ge—H) = 1.53 Å). Because of the semiempirical nature of the calculations the gas phase basicities were estimated simply as the energies of protonation without any correction for zero point vibrations. Further, since we are interested in qualitative trends rather than in absolute numbers, the calculations were performed for silyl (H_3Si-) and germyl (H_3Ge-) substituted compounds rather than trimethylsilyl and trimethylgermyl derivatives.

The geometries of the unprotonated and corresponding protonated compounds were partially optimised by the so-called rigid rotor approximation with respect to the rotation around the C—X bond (α-functional derivatives) and around the central C—C bond (β-functional derivatives). For unprotonated α-functional compounds the optimised geometries were found to be identical within the series of ethylamine, (silylmethyl)amine and (germylmethyl)amine (I), and also identical within the series of ethanol, silylmethanol and germylethanol (II). These geometries agree in the case of carbon compounds with both experimental and ab initio data [19]. In β-functional derivatives the geom-



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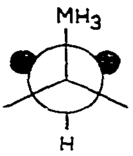

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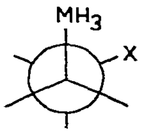

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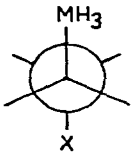
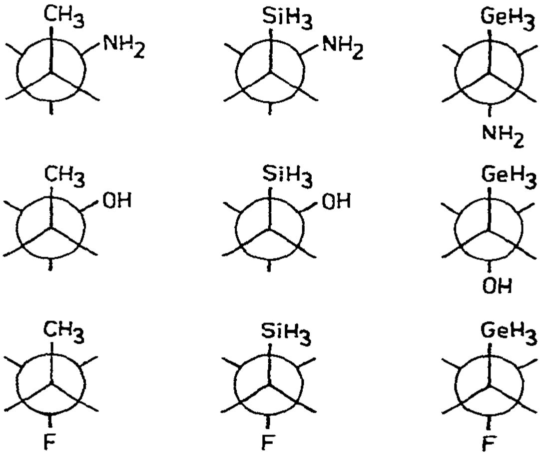


IV

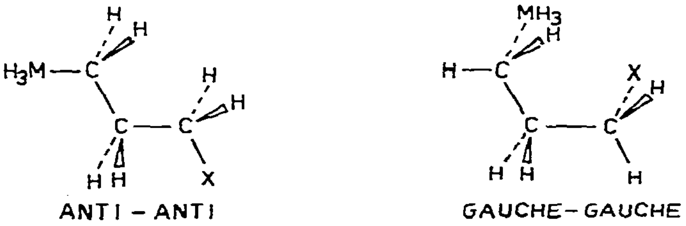
etry of the C—X fragment was fixed in the optimal arrangement found for the α-functional series, and only the rotation around the C—C bond was optimised. The calculated optimal geometries in the case of nonprotonated carbon derivatives can be compared with the results of a 4-31G ab initio study by Pople [20]. Generally both CNDO/2 and ab initio calculation predict comparable stability for "*gauche*" (III) and "*anti*" (IV) conformations, but quantitatively their prediction differ in some cases. For example, whereas in the case of n-propyl alcohol both methods predict the *gauche* conformation (III) to be the most stable, they differ in their assignments of the optimal conformations for propylamine (*anti* (IV) for ab initio vs. *gauche* (III) for CNDO/2) and for propyl fluoride (*gauche* for ab initio vs. *anti* for CNDO/2). Calculated CNDO/2 optimised geometries for all the unprotonated β-functional derivatives are presented schematically in Scheme I, from which it will be seen that the calculated optimal geometries differ in the case of alcohols and amines on going from simple alkyl to germyl derivatives, but there are no experimental or ab initio data available for comparison in these cases.

SCHEME I



Because of the large number of rotational degrees of freedom we did not optimise the geometry for γ-functional derivatives $H_3M(CH_2)_3X$. Instead, in view of the comparable importance of *gauche* and *anti* conformations in β-functional series, we have assumed for γ-functional derivatives only conformations derived from initial *gauche* and *anti* arrangements by again placing the addi-

SCHEME II



tional CH_3, SiH_3 and GeH_3 group into the *gauche* and *anti* positions. The resulting final geometries of γ-functional derivatives are shown schematically in Scheme II.

Results and discussion

The suitability of the CNDO/2 method for describing trends in the gas phase basicities of simple aliphatic alcohols and amines is well documented [6—8]. Stimulated by these results we applied the CNDO/2 method to the series of organosilicon and organogermanium derivatives. In order to eliminate the possible imperfections of the CNDO/2 method in assigning the most stable conformations, the protonation energies were calculated for all energetically preferred *gauche*, *anti* (β-functional series), *gauche-gauche* and *anti-anti* (γ-functional series) conformations in all series of compounds. The calculated values of protonation energies are summarised in Tables 1—3.

We first examine the trends in protonation energies in a series of homologous carbofunctional derivatives. Experimental data on gas phase basicities of aliphatic amines, alcohols, and halides indicate that there is a regular increase in basicity on going from methyl to higher alkyl derivatives. This effect has been explained in terms of the increasing polarisability of the alkyl groups [5]. The experimental results are completely reproduced by the CNDO/2 calculations. As can be seen from Table 1 the absolute values of the protonation energies for all three series of simple alkyl derivatives (amines, alcohols, fluorides) increase regularly with increasing length of the alkyl chain. It is important to note that the trends in the experimental data are correctly reproduced irrespective of the conformation of the alkyl chain (see the series CH_3CH_2X, *anti* $CH_3CH_2CH_2X$, *anti-anti* $CH_3CH_2CH_2CH_2X$ or CH_3CH_2X *gauche* $CH_3CH_2CH_2X$, *gauche-gauche* $CH_3CH_2CH_2CH_2X$).

TABLE 1

CNDO/2 CALCULATED VALUES OF PROTONATION ENERGIES (kJ/mol) FOR A SERIES OF SIMPLE ALKYLDERIVATIVES $CH_3(CH_2)_nX$

Compound	ΔE
$CH_3CH_2NH_2$	—1288.7
$CH_3CH_2CH_2NH_2$ [a]	—1293.6
$CH_3CH_2CH_2NH_2$ [b]	—1299.6
$CH_3CH_2CH_2CH_2NH_2$ [c]	—1296.9
$CH_3CH_2CH_2CH_2NH_2$ [d]	—1304.9
CH_3CH_2OH	—1103.5
$CH_3CH_2CH_2OH$ [a]	—1112.4
$CH_3CH_2CH_2OH$ [b]	—1117.0
$CH_3CH_2CH_2CH_2OH$ [c]	—1116.0
$CH_3CH_2CH_2CH_2OH$ [d]	—1123.4
CH_3CH_2F	—908.9
$CH_3CH_2CH_2F$ [a]	—915.7
$CH_3CH_2CH_2F$ [b]	—925.7
$CH_3CH_2CH_2CH_2F$ [c]	—919.0
$CH_3CH_2CH_2CH_2F$ [d]	—933.5

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

TABLE 2

CNDO/2 CALCULATED VALUES OF PROTONATION ENERGIES (kJ/mol) FOR A SERIES OF CARBOFUNCTIONAL ORGANOSILICON DERIVATIVES

Compound	ΔE
$SiH_3CH_2NH_2$	—1305.0
$SiH_3CH_2CH_2NH_2$ [a]	—1292.6
$SiH_3CH_2CH_2NH_2$ [b]	—1318.7
$SiH_3CH_2CH_2CH_2NH_2$ [c]	—1298.0
$SiH_3CH_2CH_2CH_2NH_2$ [d]	—1311.9
SiH_3CH_2OH	—1123.6
$SiH_3CH_2CH_2OH$ [a]	—1118.1
$SiH_3CH_2CH_2OH$ [b]	—1141.7
$SiH_3CH_2CH_2CH_2OH$ [c]	—1117.0
$SiH_3CH_2CH_2CH_2OH$ [d]	—1132.0
SiH_3CH_2F	—948.7
$SiH_3CH_2CH_2F$ [a]	—928.3
$SiH_3CH_2CH_2F$ [b]	—954.2
$SiH_3CH_2CH_2CH_2F$ [c]	—921.8
$SiH_3CH_2CH_2CH_2F$ [d]	—944.0

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

In contrast, a completely different picture holds for the series of organosilicon and organogermanium compounds for which the trends in the protonation energies depend greatly on the molecular conformation. This is illustrated in Figure 1 for a representative series of silyl and germyl substituted alcohols, but practically the same pattern holds also for amines and fluorides. In a series of silyl and germyl derivatives H_3MCH_2X, *gauche* $H_3MCH_2CH_2X$, and *gauche-gauche* $H_3MCH_2CH_2CH_2X$, the trends in protonation energy correspond to a regular decrease of gas phase basicity, in complete contrast to the situation for

TABLE 3

CNDO/2 CALCULATED VALUES OF PROTONATION ENERGIES (kJ/mol) FOR A SERIES OF CARBOFUNCTIONAL ORGANOGERMANIUM DERIVATIVES

Compound	ΔE
$GeH_3CH_2NH_2$	—1317.2
$GeH_3CH_2CH_2NH_2$ [a]	—1289.6
$GeH_3CH_2CH_2NH_2$ [b]	—1329.5
$GeH_3CH_2CH_2CH_2NH_2$ [c]	—1299.9
$GeH_3CH_2CH_2CH_2NH_2$ [d]	—1317.2
GeH_3CH_2OH	—1138.1
$GeH_3CH_2CH_2OH$ [a]	—1124.9
$GeH_3CH_2CH_2OH$ [b]	—1154.8
$GeH_3CH_2CH_2CH_2OH$ [c]	—1118.9
$GeH_3CH_2CH_2CH_2OH$ [d]	—1138.1
GeH_3CH_2F	—971.1
$GeH_3CH_2CH_2F$ [a]	—936.7
$GeH_3CH_2CH_2F$ [b]	—969.0
$GeH_3CH_2CH_2CH_2F$ [c]	—924.5
$GeH_3CH_2CH_2CH_2F$ [d]	—951.0

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

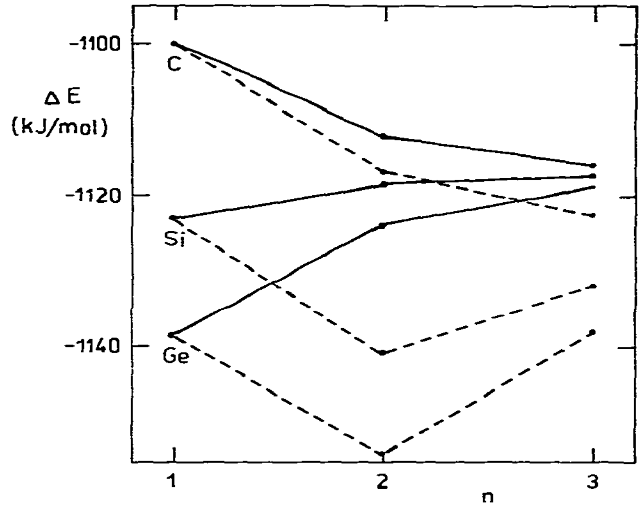


Fig. 1. Dependence of calculated protonation energies in a series of carbofunctional alcohols $H_3M(CH_2)_n$-OH on the value of n. Full line: *gauche* and *gauche-gauche* conformations; dotted line: *anti* and *anti-anti* conformations.

the simple alkyl derivatives, and this decrease of basicity has been previously found experimentally for a series of trimethylsilyl- and trimethylgermyl substituted alcohols [9,11]. On the other hand, the trend in protonation energy in a series of H_3MCH_2X, *anti* $H_3MCH_2CH_2X$ and *anti-anti* $H_3MCH_2CH_2CH_2X$ is much more complex, and reflects the operation of the so called α-effect [13]. This trend is exactly reproduced by experimental results for a series of trimethylsilyl substituted amines [10].

These results suggest that CNDO/2 data rationalise the experimental results provided that the conformation of the molecular chain is *gauche* for β- and *gauche-gauche* for γ-functional alcohols and *anti* for β- and *anti-anti* for γ-functional amines. This assumption cannot be, however, checked because of the lack of reliable experimental or theoretical data on the molecular conformations of silyl and germyl derivatives. It is noteworthy, however, that 4-31G ab initio calculations [20] indicate that the *gauche* conformation is the most stable for n-propyl alcohol and the *anti* conformation for n-propylamine.

These results indicate that the appearance of the so-called α-effect [13] in basicity data is crucially connected with the *anti* conformation of the molecular chain, and consequently the α-effect is probably of conformational origin. The calculations also clearly demonstrate that the electronic effect of silyl and germyl groups is substantially different from that of simple alkyls and moreover that this effect crucially depends on the molecular conformation. The same conclusion follows also from the analysis of the barrier to internal rotation around the C—X bond in a series of β-functional derivatives $H_3MCH_2CH_2X$ [21].

The predicted trends in the gas phase basicities of organosilicon and organogermanium compounds could be perhaps demonstrated experimentally on properly chosen rigid models. The results of our analysis also suggest that there is a considerable potential for theoretical studies aimed of deeper understanding of the electronic effects of organometallic substituents.

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