

## QUANTUM CHEMICAL STUDY OF BASICITIES OF CARBOFUNCTIONAL ORGANOSILICON COMPOUNDS. THE $\alpha$ -EFFECT\*

R. PONEC and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

Received November 7th, 1974

Enthalpies of acid-base equilibria,  $\Delta H$ , of the compounds  $H_3M(CH_2)_nX$  ( $M = C, Si$ ;  $X = OH, NH_2$ ;  $n = 0-3$ ) were calculated by CNDO/2 method, for partially optimized geometries or for reported *ab initio* geometries without inclusion of silicon  $d$  orbitals. Calculated values of  $\Delta H$  are the measure of gas phase basicities or acidities and their order agrees with that found experimentally. The  $\alpha$ -effect is explained in terms of interaction of  $n$ -orbitals of  $X$  with low lying antibonding  $\sigma_{(M-C)}^*$  or  $\sigma_{(M-H)}^*$  orbitals.

In previous works<sup>1,2</sup> of our laboratory it was reported that the relative basicity of the alcohols  $(CH_3)_3M-(CH_2)_nOH$  ( $M = Si, Ge$ ;  $n = 1-4$ ) decreases in the order  $n = 1 > 2 > 3 > 4 \approx \approx$   $n$ -butanol, in accordance with the expected inductive effect of  $Si$  or  $Ge$ . On the other hand, in a similar study of the basicities of the compounds  $X_3M(CH_2)_nNH_2$  ( $X = CH_3, OC_2H_5$ ;  $M = Si, Ge$ ;  $n = 1-4$ ) the following order was established<sup>3,4</sup>:  $1 < 2 > 3 > 4 \approx$   $n$ -butylamine. Several explanations were already suggested for the decreased basicity of the  $\alpha$ -functional derivative, *i.e.* the so called  $\alpha$ -effect, above all in terms of  $(p-d)_\pi$  or  $(p-d)_\sigma$  coordination<sup>5</sup>. Solvent effect, which can also influence the order of basicities of the amines<sup>6</sup>, can be excluded in this case, since measurements were carried out in an inert solvent ( $CCl_4$ ). One can expect that  $\Delta v$  values include only electronic factors and that the basicities so obtained will be, at least as to their sequence, identical with gas phase basicities<sup>7</sup>. It is known that the CNDO/2 method gives the correct order of gas phase basicities of aliphatic alcohols and amines<sup>8,9</sup>.

It was of interest to make analogous calculation also for carbofunctional organosilicon compounds without inclusion of silicon  $d$  orbitals with the aim of estimating their importance for explanation of the  $\alpha$ -effect<sup>5,10</sup>. It is shown that qualitatively correct results can be achieved without considering the  $d$  orbitals.

### CALCULATIONS

Calculations by the CNDO/2 method<sup>11</sup> were made for idealized tetrahedral geometries without inclusion of silicon  $d$  orbitals. Lengths of the  $Si-X$  bonds were taken from the work<sup>12</sup>, the others from the work<sup>11</sup>. In the case of  $\alpha$ - and  $\beta$ -functional derivatives that could exist in several con-

\* Part CXXXI in the series Organosilicon Compounds; Part CXXX: This Journal 40, 2309 (1975).

formers, their geometries were optimized with respect to rotation around the C—X or C—C bonds. The most stable conformations calculated for  $\alpha$ -functional carbon derivatives were identical with both experimental data and results of *ab initio* calculations<sup>13</sup>. In the case of  $\beta$ -functional



carbon derivatives, the CNDO/2 method gives in some cases (propylamine) different optimum geometries than *ab initio* calculations<sup>14</sup>. However, energetic differences between the most stable conformations are very small. For  $\alpha$ - and  $\beta$ -functional silicon derivatives the most stable conformations were found to be identical with those of corresponding carbon analogues. Calculations of reaction enthalpies  $\Delta H$  in cases where the results of *ab initio* calculations differed from those of the CNDO/2 calculations were made for *ab initio* optimum conformations taken from literature, identical for carbon and silicon derivatives. Reaction enthalpies,  $\Delta H$ , were calculated for the following reactions:



These characterize the gas phase acidity of alcohols (Eq. (A)) and the gas phase basicity of alcohols and amines (Eqs (B) and (C)). With alcohols, energetically preferred mode of their protonation and its conformational consequences were also estimated. Results of calculations are summarized in Tables I—III.

TABLE I  
Calculated Total Energies  $E$  (in eV) and Reaction Enthalpies  $\Delta H$  (in eV) for Reaction (A)

Compound	$E(\text{ROH})$	$E(\text{RO}^-)$	$\Delta H$
$\text{H}_2\text{O}$	— 540.667	— 514.395	— 26.262
$\text{CH}_3\text{OH}$	— 776.924	— 752.383	— 24.541
$\text{CH}_3\text{CH}_2\text{OH}$	— 1 013.483	— 989.059	— 24.424
$\text{CH}_3(\text{CH}_2)_2\text{OH}$	— 1 249.964	— 1 225.651	— 24.313
$\text{CH}_3(\text{CH}_2)_3\text{OH}$	— 1 486.381	— 1 462.107	— 24.274
$\text{H}_3\text{SiOH}$	— 676.893	— 653.151	— 23.742
$\text{H}_3\text{SiCH}_2\text{OH}$	— 919.604	— 895.739	— 23.865
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{OH}$	— 1 156.229	— 1 132.036	— 24.193
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{OH}$	— 1 392.649	— 1 368.458	— 24.191
$(\text{CH}_3)_3\text{SiOH}$	— 1 372.910	— 1 349.555	— 23.355
$(\text{CH}_3)_3\text{SiCH}_2\text{OH}$	— 1 615.540	— 1 591.877	— 23.663

## RESULTS AND DISCUSSION

As follows from comparison of  $\Delta H$  values for reaction (A), the order of the gas phase acidity of the alcohols is following (Table I):  $\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH} < n\text{-C}_3\text{H}_7\text{OH} < n\text{-C}_4\text{H}_9\text{OH}$  and  $\text{H}_3\text{SiOH} > \text{H}_3\text{SiCH}_2\text{OH} > \text{H}_3\text{Si}(\text{CH}_2)_2\text{OH} \approx \approx \text{H}_3\text{Si}(\text{CH}_2)_3\text{OH}$ . The sequence of gas phase acidities of carbon alcohols<sup>15,16</sup> agrees with  $\Delta H$  values. Gas phase acidities of silyl alcohols are not available. The

TABLE II

Comparison of the Energies of Protonation (in eV) with the Stability of Protonated Alcohols

Compound	$E(\text{ROH})$	$E(\text{ROH}_2^+)^a$	$\Delta E^b$
$\text{CH}_3\text{OH}$	- 776.924	- 788.015	-11.091
$\text{C}_2\text{H}_5\text{OH}$	-1 013.483	-1 024.921 <sup>c</sup>	-11.438 <sup>d</sup>
$n\text{-C}_3\text{H}_7\text{OH}$	-1 249.964	-1 261.457	-11.493
$\text{H}_3\text{SiOH}$	- 676.893	- 689.431	-12.538
$\text{H}_3\text{SiCH}_2\text{OH}$	- 919.604	- 931.249 <sup>e</sup>	-11.645 <sup>f</sup>
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{OH}$	-1 156.229	-1 167.818	-11.589

<sup>a</sup> The free electron pair syn (conformation *IV*); <sup>b</sup>  $\Delta E = E(\text{ROH}_2^+)_{\text{syn}} - E(\text{ROH})$ ; <sup>c</sup> Total energy for conformation *V* = -1024, 850 eV; <sup>d</sup> Difference between the total energies of conformations *IV* and *V* = -0.071 eV; <sup>e</sup> Total energy for conformation *V* = -931.037 eV; <sup>f</sup> Difference between the total energies of conformations *IV* and *V* = -0.212 eV.

TABLE III

Calculated Total Energies  $E$  (in eV) and Reaction Enthalpies  $\Delta H$  (in eV) for Reaction (C)

Compound	$E(\text{RNH}_3^+)$	$E(\text{RNH}_2)$	$\Delta H$
$\text{NH}_3$	- 390.033	- 377.447	-12.586
$\text{CH}_3\text{NH}_2$	- 627.157	- 614.021	-13.136
$\text{C}_2\text{H}_5\text{NH}_2$	- 863.862	- 850.505	-13.357
$\text{C}_3\text{H}_7\text{NH}_2$	-1 100.420	-1 086.949	-13.471
$\text{C}_4\text{H}_9\text{NH}_2$	-1 336.891	-1 323.365	-13.526
$\text{H}_3\text{SiNH}_2$	- 520.792	- 507.499	-13.293
$\text{H}_3\text{SiCH}_2\text{NH}_2$	- 770.195	- 756.669	-13.526
$\text{H}_3\text{Si}(\text{CH}_2)_2\text{NH}_2$	-1 006.886	- 993.218	-13.668
$\text{H}_3\text{Si}(\text{CH}_2)_3\text{NH}_2$	-1 243.234	-1 229.637	-13.597

values of  $\Delta\nu(\text{OH})$  of these alcohols with tetrahydrofuran as proton acceptor<sup>1,2</sup>, which could serve as the measure of the acidity, differ only slightly from one another and lie essentially within the range of experimental errors. In addition to this, their order is reverse to that of  $\Delta H$  values. This can be due to the fact that in 1M tetrahydrofuran, used in measurements solvation effects cannot be neglected and the acidity order represented by  $\Delta\nu(\text{OH})$ 's is in fact "solution acidity".

It seems therefore more reasonable to compare the infrared basicities, since corresponding  $\Delta\nu(\text{OH})$  or  $\Delta\nu(\text{C—D})$  value with phenol or deuteriochloroform as proton donors are only slightly influenced by solvation effects, since these measurements are carried out in tetrachloromethane and with highly diluted compounds. Although it was shown<sup>17</sup> that in general it is not possible to identify the term "complete proton transfer" with the term "hydrogen bonding" in the sense of the measure of basicity, in our case such comparison can be made, since in a group of structurally similar compounds there exists a linear relationship between the enthalpy of hydrogen bond formation and the enthalpy of protonation<sup>17</sup>.

The order of  $\Delta\nu(\text{OH})$ 's of silyl alcohols with phenol as proton donor is the same as the order of the enthalpies of protonation (Fig. 1).

A similar situation arises also with the amines. Gas phase basicity order for the aliphatic amines  $\text{NH}_3 < \text{CH}_3\text{NH}_2 < \text{C}_2\text{H}_5\text{NH}_2 < n\text{-C}_3\text{H}_7\text{NH}_2 < n\text{-C}_4\text{H}_9\text{NH}_2$  (refs<sup>18,19</sup>) agrees again with  $\Delta H$  values (Table III). The  $\Delta H$  values of silylsubstituted amines parallel  $\Delta\nu(\text{CD})$  values<sup>3</sup> (Fig. 2).

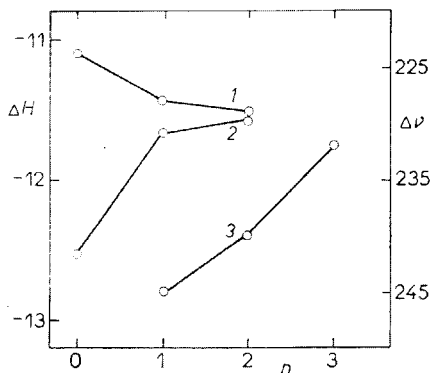


FIG. 1

Dependences of Calculated Enthalpies of Protonation of the Alcohols  $\text{H}_3\text{M}(\text{CH}_2)_n\text{OH}$  ( $\Delta H$  in eV, 1 M = C, 2 M = Si) and  $\Delta\nu(\text{OH})$ 's (in  $\text{cm}^{-1}$ ) of the Alcohols  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$  (Curve 3) on  $n$

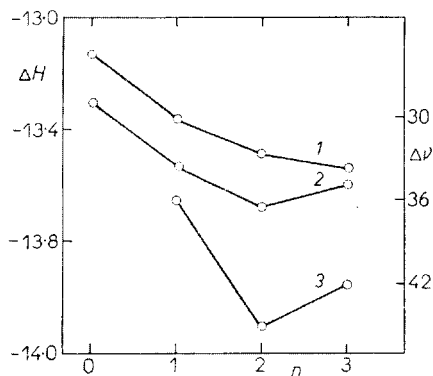
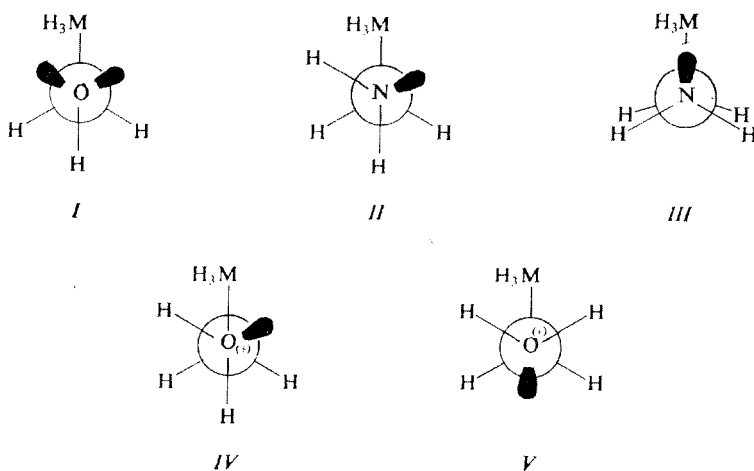


FIG. 2

Dependences of Calculated Enthalpies of Protonation of the Amines  $\text{H}_3\text{M}(\text{CH}_2)_n\text{NH}_2$  ( $\Delta H$  in eV, 1 M = C, 2 M = Si) and  $\Delta\nu(\text{CD})$ 's (in  $\text{cm}^{-1}$ ) of the Amines  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{NH}_2$  (Curve 3) on  $n$

This shows that calculation without inclusion of silicon  $d$  orbitals reproduces experimental results. It seems therefore worthwhile to interpret these results in the form which is more common to the chemist and explain thus why the  $\alpha$ -amines show decreased basicity, whilst the  $\alpha$ -alcohols do not. Such explanation can be based on the analysis of the symmetry and shape of wave functions of corresponding compounds and can be depicted by the following orbital diagram (Scheme 1). The most



stable conformations of  $\text{H}_3\text{SiCH}_2\text{OH}$  and  $\text{H}_3\text{SiCH}_2\text{NH}_2$  are *I* and *II*, conformation *III* being, however, not much different in energy from conformation *II*. Conformations *I* and *III* have the plane of symmetry with respect to which classification of orbitals can be made. This renders it possible to analyze orbital interactions. Due to the lesser electronegativity of nitrogen compared to oxygen, the stronger interaction takes place between  $n$ -electron pair and the Si—C bond, which leads to an additional decrease of the  $n$ - $\sigma$  orbital by interaction with antibonding  $\sigma_{\text{SiC}}^*$  or  $\sigma_{\text{SiH}}^*$  orbitals. The contributions of  $\sigma_{\text{SiH}}^*$  orbitals can in fact be found in the form of HOMO:

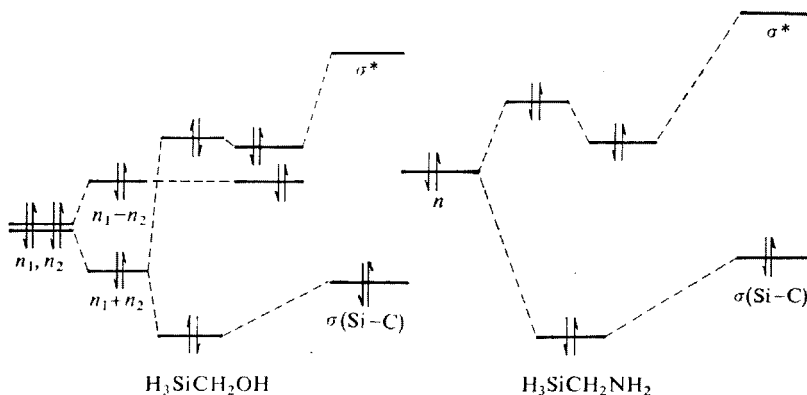
$$\psi_{\text{HOMO}} = [-0.536(p_z)_N + 0.496(p_z)_C - 0.430(p_z)_{\text{Si}}]_{n-\sigma_{\text{Si-C}}} + \\ + [0.123(s)_{\text{Si}} - 0.095(s)_H - 0.095(s)_H - 0.15(s)_H]_{\sigma_{\text{Si-H}}^*}$$

The above interaction results in charge transfer from the nitrogen to the silicon which manifests itself in a decrease of basicity. Situation is more complicated with the alcohols due to the presence of two electron pairs and also due to the greater electronegativity of oxygen. Here only the  $n_1 + n_2$  orbital can interact with  $\sigma_{\text{SiC}}$ , which

causes that also interaction with antibonding orbitals is weaker. This is shown also by relative contributions of  $\sigma_{\text{SiH}}^*$  to HOMO:

$$\psi_{\text{HOMO}} = [0.333(p_z)_O - 0.585(p_z)_C + 0.505(p_z)_{\text{Si}}]_{n-\sigma_{\text{Si-C}}} - \\ - [0.085(s)_{\text{Si}} - 0.164(s)_H - 0.164(s)_H - 0.111(s)_H] \sigma_{\sigma_{\text{SiH}}^*}.$$

Basicities of the alcohols are therefore governed above all by the +I effect of silicon.



Interesting results were also obtained in studying energetically most preferred protonation of ethanol and silylmethanol. As follows from the results given in Table II, the most stable conformation of protonated alcohols is IV and  $\text{H}_3\text{SiCH}_2\text{OH}_2^+$  is more stable than  $\text{H}_3\text{CCH}_2\text{OH}_2^+$ . Stabilizing factor is here superjacent orbital interaction<sup>20</sup>. Relative rates of the addition of the alcohols  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$  to phenyl isocyanate and ketene<sup>1</sup> lead to the conclusion that the basicity of these alcohols decreases with increasing  $n$ , in accordance with the  $\Delta\nu(\text{OH})$  values with phenol as proton donor. In contradistinction to the acidity order, inferred from  $\Delta\nu(\text{OH})$ 's with tetrahydrofuran or acetonitrile as proton acceptor<sup>1</sup> and discussed above, calculated enthalpies  $\Delta H$  for reaction (A) allow us to conclude that trimethylsilylmethanol is the most acidic of the alcohols studied. This is not surprising, since measurement of the gas phase acidities and basicities of aliphatic alcohols and amines<sup>21-23</sup> lead to the same conclusion (the acidity and basicity change in the same order, *i.e.* increase with the size and branching of the adjacent alkyl group). This is connected with the fact that alkyl groups are able to stabilize both positive and negative charges<sup>8,9,24</sup>.

## REFERENCES

1. Pola J., Bažant V., Chvalovský V.: This Journal 37, 3885 (1972).
2. Krumpolc M., Bažant V., Chvalovský V.: This Journal 37, 711 (1973).
3. Fialová V., Bažant V., Chvalovský V.: This Journal 38, 3837 (1973).
4. Cadenas J., Chvalovský V.: Unpublished results.
5. Voronkov M. G., Feshin V. P., Mironov V. F., Gar T. K.: Zh. Obshch. Khim. 41, 2211 (1971).
6. Arnett E. A., Jones F. M., Taagepera M., Henderson V. G., Beauchamp J. L., Holz D., Taft R. W.: J. Amer. Chem. Soc. 94, 4725 (1972).
7. Beauchamp J. L.: Annu. Rev. Phys. Chem. 1971, 527.
8. Lewis P. T.: Tetrahedron 25, 4117 (1969).
9. Hermann R. B.: J. Amer. Chem. Soc. 92, 5298 (1970).
10. Pola J., Schraml J., Chvalovský V.: This Journal 38, 3158 (1973).
11. Pople J. A., Beveridge D. L.: *Approximate MO Theory*. McGraw Hill, New York 1970.
12. Sutton L.: *Tables of Interatomic Distances*, Supplement (Special publ. No 18). The Chemical Soc., London 1965.
13. Pople J. A.: Tetrahedron 30, 1605 (1974).
14. Radom L., Lathan W. A., Hehre W. J., Pople J. A.: J. Amer. Chem. Soc. 95, 693 (1973).
15. Brauman J. I., Blair L. K.: J. Amer. Chem. Soc. 90, 6561 (1968).
16. Böhme D. K., Ruff L. E., Young B. I.: J. Amer. Chem. Soc. 93, 4608 (1971).
17. Arnett E. M., Mitchell E. J.: J. Amer. Chem. Soc. 93, 4052 (1971).
18. Aue D. H., Webb H. M., Bowers M. T.: J. Amer. Chem. Soc. 94, 4726 (1971).
19. Brauman J. I., Riveros J. M., Blair K. L.: J. Amer. Chem. Soc. 93, 3914 (1971).
20. Hoffmann R. W., Hehre W. J., David S., Salem L., Eisenstein O.: J. Amer. Chem. Soc. 95, 3806 (1973).
21. Brauman J. I., Blair L. K.: J. Amer. Chem. Soc. 91, 2126 (1969).
22. Brauman J. I., Blair L. K.: J. Amer. Chem. Soc. 93, 3911 (1971).
23. Munson M. S. B.: J. Amer. Chem. Soc. 87, 2332 (1965).
24. Hehre W. J., Pople J. A.: Tetrahedron Lett. 34, 2959 (1970).

Translated by J. Hetflejš.