Ab Initio SCF and DFT Study of Configuration and Reactivity of Silacarbamic Acid

M. REMKO

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Comenius University, SK-832 32 Bratislava

Received 12 December 1996

Ab initio and DFT methods have been used to study molecular structure and reactivity of silacarbamic acid. The basis set included the double-zeta 6-31G**, triple-zeta 6-311G**, and 6-311+G* basis. Complete geometry optimization was accomplished for silacarbamic acid and its protonated species using the 6-31G** basis. The proton affinities were calculated at the HF, MP4SDTQ, CCSD, CCSD(T), and Becke3LYP levels of theory and 6-311+G* basis set. The protonation energies were found to increase in the order PA(Si—O···H) < PA(Si—N· ·H) < PA(Si=O· ·H). The absolute values of calculated gas phase proton affinities depend on the basis set used and way of evaluating the correlation energy. The decomposition of silacarbamic acid was investigated at HF and various correlated levels of theory. The decarboxylation reaction is at highest theoretical levels (MP4SDTQ/6-311+G*//MP2/6-311G** and CCSD(T)/6-311+G*//MP2/6-311G**) highly positive (226.8 kJ mol^{-1} and 248.9 kJ mol^{-1}). It means that the equilibrium (at 0 K) for this reaction is shifted towards silacarbamic acid. On the other hand, dimerization reaction is for silacarbamic acid greatly exothermic with the energy of −390.2 kJ mol^{-1} (the Becke3LYP/6-311G** computation). Changes in the natural atomic charges and atom—atom net linear NLMO/NPA bond orders were examined with respect to their dependence on protonation site of silacarbamic acid.

Most of the experimental information on configuration and reactivity of compounds containing double X=O bond available nowadays originates in a substantial body of data for carbonyl compounds [1]. The investigation of the silicon compounds containing the Si=O double bond represents a relatively new research field of the organometallic chemistry which attracts considerable attention of theoretical and experimental chemists [2, 3]. One of such examples are silicon analogues of carboxylic acids. *Withnall* and *Andrews* [4] proved the existence of silanoic acid by infrared spectroscopy, the evidence for the existence of the silaacetate species was given by *Chmielecka et al.* [5] and *Cremer et al.* [6] have experimentally proved the existence of methyl ester of silaacetic acid. As regards the structurally similar silacarbamates, no direct experimental evidence about their existence is, to our knowledge, available. The existence of silacarbamic acid and their simpler alkyl derivatives has been presumed theoretically [7—9].

The aim of our work was to gain more insight into the structure and stability of silacarbamates. We present results of more detailed theoretical study on the simplest model of silacarbamate moiety - silacarbamic acid. This derivative was chosen because extremely little is known about its intrinsic (gas-phase) reactivity and carbamates (a natural yardstick for comparison) have received a great deal of attention of theoretical chemists [10—19] because the carbamate group occurs in many biologically active compounds [20—26]. The replacement of the carbon atom in the functional group of the drug by silicon represents one of the possible isosteric substitutions leading to a considerable modification in the biological activity of such compounds. Two main topics are addressed in this work: i) The influence of the nature of the basic centre (N(sp^2) and O(sp^3, sp^2)) on the relative basicities of these centres and ii) the reactivity (decomposition and dimerization) of silacarbamate moiety. Since the correlation energy contributions to the reactivity are significant, we have also investigated the effects of electron correlation using the many-body (Moller—Plesset) perturbation theory at the fourth (MP4) order [27], the coupled-cluster CCSD and CCSD(T) methods [28, 29] and the Becke3LYP functional [30, 31] of the DFT theory [32, 33].

THEORETICAL

The *ab initio* and DFT methods were employed for the calculation of equilibrium geometries, proton affinity, acidity, and reactivity of the silacarbamic acid (Fig. 1). The basis sets included the double-zeta 6-31G** basis set [34], the triple-zeta 6-311G** basis set [35], and the triple-zeta 6-311+G* augmented with diffuse *s* and *p* functions [36] on non-hydrogen

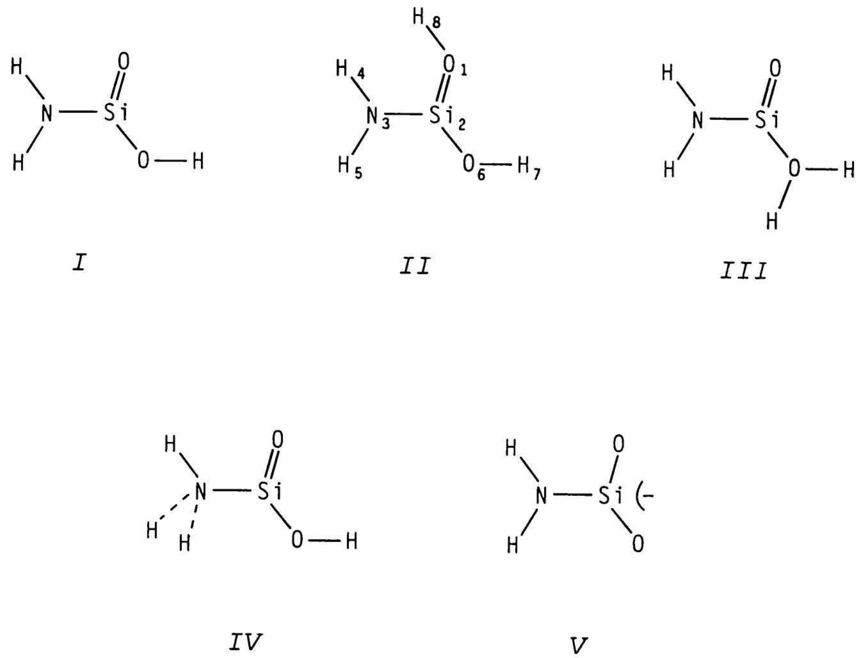


Fig. 1. Structure of silacarbamic acid and its protonized and ionized derivatives. Atom numbering is the same as in *II* for al species investigated.

atoms. A few optimizations were also carried out at the MP2(FC)/6-311G** level of theory. The correlation energies for the neutral, protonized, and ionized species were also evaluated by using the many-body (MP4SDTQ) theory, coupled-cluster CCSD and CCSD(T) methods and the 6-311+G* basis set. The vibrational frequencies computed at the HF/6-31G** level for acid, its protonated forms, anions, and reaction products studied were used to characterize stationary points and to evaluate zero-point vibrational energies (ZPE).

The proton affinities of the bases B were calculated as the negative values of the differences ΔE_{PA} between the total energies of the base B and its cation BH^+

$$\Delta E_{\mathrm{PA}} = E_{\mathrm{B}} - E_{\mathrm{BH^+}} \qquad (1)$$

for the exothermal reaction

$$\mathrm{B} + \mathrm{H}^+ \rightarrow \mathrm{BH}^+ \qquad (A)$$

The gas-phase acidity of the acid AH was defined as the energy of deprotonation (ΔE_{AC}) for reaction (*B*)

$$\mathrm{A}^- + \mathrm{H}^+ \rightarrow \mathrm{AH} \qquad (B)$$

using eqn (*2*).

$$\Delta E_{\mathrm{AC}} = E_{\mathrm{AH}} - E_{\mathrm{A^-}} \qquad (2)$$

The basis set superposition error (BSSE) corrections were not applied, as they are expected to be small. All the calculations were carried out with the aid of the GAUSSIAN94W package of computer codes [37].

RESULTS AND DISCUSSION

Structure of Silacarbamic Acid and its Protonized and Ionized Derivatives

The optimized structural parameters, total energies, and zero-point energies of the silacarbamic acid species studied are given in Table 1. An analysis of the harmonic vibrational frequencies of the optimized structures revealed that all structures have a number of imaginary frequencies equal to zero thus corresponding to the stationary points on the potential-energy surface. The *syn* form (Fig. 1) of the silacarbamic acid is by 21.8 kJ mol^{-1} more stable than the *anti* conformer. The changes with *syn-anti* isomerization result in the shortening of the Si=O and Si—O bonds and lengthening of the Si—N bond. The angles O-1—Si-2—N-3 and Si-2—N-3—H-4 were found substantially higher and the Si-2—N-3—H-5 and Si-2—O-6—H-7 considerably lower in the *syn* form. The major differences are clearly due to the steric repulsion between the hydrogen atoms in the *anti* conformer.

Since protonation and/or ionization can result in appreciable changes in the geometry, particularly in the vicinity of the protonation site, the geometries and energies of ionized forms of the more stable *syn* silacarbamic acid were also optimized (Table 1). The protonation of the carbonyl oxygen of the Si=O group can occur in the *cis* as well as in *trans* position with

Table 1. Optimized Geometries, Energies (in a.u.[a]), and Zero-Point Energies (in kJ mol^{-1}) of the Silacarbamic Acid Species Studied (Fig. 1) (6-31G** Basis Set)

Parameter	Species					
	Ia	*Ib*	*II*	*III*	*IV*	*V*
			Bond lengths r/pm			
O-1—Si-2	149.6	149.3	156.0	147.6	147.5	152.5
Si-2—N-3	166.4	167.3	162.7	163.1	185.2	172.5
N-3—H-4	99.5	99.6	99.9	100.3	101.4	99.3
N-3—H-5	99.5	99.4	100.1	99.8	101.4	99.3
Si-2—O-6	161.3	161.0	155.9	178.9	156.9	152.5
O-6—H-7	94.4	94.1	94.7	96.1	94.9	
X—H-8[b]			94.5	95.6	101.4	
			Bond angles Φ/°			
O-1—Si-2—N-3	128.1	125.3	124.3	145.7	116.9	112.6
Si-2—N-3—H-4	122.2	120.4	124.7	119.5	109.8	122.6
Si-2-N-3—H-5	123.2	126.3	122.0	128.0	112.5	122.6
N-3—Si-2—O-6	105.8	105.9	117.0	104.7	99.6	112.6
Si-2—O-6—H-7	117.6	123.1	130.5	115.8	127.1	
Si-2—X—H-8[b]			134.5	131.4	112.4	
$-E$/a.u.	494.93669	494.92837	495.30518	495.21227	495.24617	494.35533
Symmetry	C_s	C_s	C_s	C_1	C_1	C_s
ZPE	127.6	125.9	156.9	158.2	164.8	92.5

a) 1 a.u. = 2625.5 kJ mol^{-1}; *b*) X = N, O.

Table 2. Computed Protonation and Deprotonation Energies E/(kJ mol^{-1}) for the Species Studied

Method	Species			
	II	*III*	*IV*	*V*
HF/6-31G**//HF/6-31G**	967.3	723.4	812.5	−1526.3
MP4SDTQ/6-311+G*//HF/6-31G**	889.5	710.9	807.1	−1427.2
CCSD/6-311+G*//HF/6-31G**	906.3	709.6	802.9	−1441.0
CCSD(T)/6-311+G*//HF/6-31G**	898.7	709.6	804.6	−1434.3
Becke3LYP/6-311+G*//HF/6-31G**	899.1	705.4	797.5	−1430.1
MP4SDTQ + ΔZPE	860.2	680.3	769.9	−1392.0

respect to the nitrogen atom (Fig. 1). According to our computations the *cis* isomer was found to be more stable (by 0.4 kJ mol^{-1}). The major effect of the Si—X· ·H protonation (X = N, O) is a considerable lengthening of the Si—X bond. The values of the X· · ·H length increase in the order r(O-1· · ·H) < r(O-3· ·H) < r(N· · ·H). The bond angles are subject to higher or lower changes in the protonated species studied according to the protonation site. The deprotonation of the silacarbamic acid is connected with the appreciable lengthening of the Si=O and Si—N bonds and shortening of the Si—O length (Table 1). The net repulsion between the oxygen atoms in the anion results in a dramatic decrease of the valence angle O-1—Si-2—N-3 in anion in comparison with the neutral molecule. The computed zero number of imaginary frequencies for the ionized species confirms that also these forms of silacarbamic acid are true minima at the HF/6-31G** potential energy surface.

Protonation and Deprotonation Energies

Table 2 shows computed protonation and deprotonation energies for ionization reactions of silacarbamic acid. The zero-point energy correction (at the HF/6-31G** level of theory) reduces (about 30—40 kJ mol^{-1}) the computed reaction energies. The effect of the electron correlation correction of the protonation and deprotonation energies was studied using single-point calculations and the three methods for the evaluation of correlation energies (Moller—Plesset perturbation theory, coupled-cluster method, and Becke3LYP method of the density functional theory). All levels of theory applied give the same stability order of proton affinities (PA)

PA(Si=O· · ·H) > PA(Si—N· ·H) > PA(Si—O· ·H)

The Becke3LYP protonation and deprotonation energies are close to those computed at the highest levels of the electron correlation by the Hartree—Fock method (MP4SDTQ and CCSD(T)).

Experimental evidence indicates that in the gas phase carbonyl compounds XCOY (X, Y are heteroatoms endowed with lone pairs (potential basic sites)) protonate on the carbonyl oxygen [38—40]. *Ab initio* SCF calculations [16] of protonation of carbamic acid and its methyl derivatives confirmed that the principal protonation site in carbamates is carbonyl oxygen. The protonation of silacarbamate moiety in silacarbamic acid also determined that this acid behaves as silacarbonyl base in the gas phase. The presence of quite basic alternative centres (nitrogen and sp^3 oxygen) shows that the protonation at other basic centres is not competitive with protonation at silacarbonyl oxygen (Table 2). The value of computed proton affinity of the carbonyl protonation of silacarbamic acid (Table 2) is substantially higher than that found for analogous protonation of carbamic acid [16] (820 kJ mol^{-1}, MP2/6-31G*//6-31G** calculation). Thus the replacement of the central carbon atom by silicon leads to the substantial enhancing of basicity of silicon compounds in comparison with the parent carbonyl compounds.

The deprotonation of silacarbamic acid is an endothermic reaction (Table 2). However, the deprotonation of silacarbamic acid is much easier than the analogous reaction in the case of parent carbamic acid [8] (for deprotonation of carbamic acid a value of −1513.9 kJ mol^{-1} has been found from the MP2/6-31G**//HF/6-31G** calculations). Thus the substitution of carbon atom by silicon in carbamic acid leads to the increase of acidity.

The higher basicity and acidity of sila derivatives in comparison with their parent carbonyl compounds could be explained by the concept of softness (polarizability) and electronegativity, which show opposite trends in a given column of periodic table [41]. These two effects are shown to be competing [41]. Although silicon ($\chi = 1.74$) is less electronegative than carbon ($\chi = 2.5$), it is softer and therefore exhibits a larger charge capacity. The increased softness could lead in the gas phase to an increased rearrangement of charge close to it which results in higher basicity and acidity of silacarbamic acid. The same sequences in acidity were recently obtained with carboxylic and silacarboxylic acids [42].

Table 3. Computed Energy of the Decomposition Reaction $H_2NSiO_2H \rightarrow NH_3 + SiO_2$

Method	ΔE/(kJ mol^{-1})
HF/6-311G**//HF/6-311G**	320.9
B3LYP/6-311G**//B3LYP/6-311G**	266.5
MP4SDTQ/6-311+G*//MP2/6-311G**	226.8
CCSD/6-311+G*//MP2/6-311G**	263.6
CCSD(T)/6-311+G*//MP2/6-311G**	248.9
MP4SDTQ + ΔZPE	215.5

Decomposition and Dimerization

It is well known [43] that the carbamic acid and its substituted R—NHCOOH derivatives are unstable compounds and break down to carbon dioxide and the amine. Because the sila-substituted species of the carbamates – silacarbamates were not yet studied experimentally, we applied the strength of theory to bear on this problem. The calculated reaction energies, ΔE for the decomposition reaction

$$H_2NSiO_2H \rightarrow NH_3 + SiO_2 \qquad (C)$$

Table 4. Optimized Geometries and Energies of *syn* Silacarbamic Acid (6-311G** Basis)

Parameter	NH_2SiO_2H		
	RHF	MP2	B3LYP
		Bond lengths r/pm	
O-1—Si-2	149.2	152.7	152.4
Si-2—N-3	165.8	165.9	167.7
Si-2—O-6	160.7	163.5	163.7
O-6—H	94.1	95.9	96.1
N-3—H-4	99.4	100.6	100.7
N-3—H-5	99.4	100.6	100.8
		Bond angles Φ/°	
O-1—Si-2—N-3	128.1	128.8	128.3
O-1—Si-2—O-6	126.2	127.4	127.2
Si-2—O-6—H	119.5	114.9	116.5
Si-2—N-3—H-4	122.6	122.8	122.4
Si-2—N-3—H-5	123.2	122.8	123.0
$-E$/a.u.[a]	495.01099	495.68065	496.67809

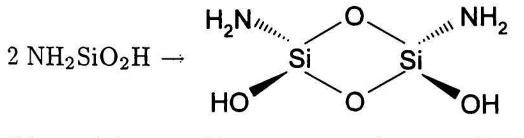
a) 1 a.u. = 2625.5 kJ mol^{-1}

Table 5. Optimized Geometries and Energies of NH_3 and SiO_2

Method	NH_3			SiO_2		
	N—H/pm	H—N—H/°	$-E^a_{SCF}$/a.u.	Si=O/pm	O=Si=O/°	$-E^a_{SCF}$/a.u.
HF/6-311G**//HF/6-311G**	100.1	107.4	56.21039	147.6	179.9	438.67842
MP2/6-311G**//MP2/6-311G**	101.4	105.9	56.40879	152.1	179.9	439.17377
B3LYP/6-311G**//B3LYP/6-311G**	101.6	106.5	56.57603	151.4	179.9	440.00047

a) 1 a.u. = 2625.5 kJ mol^{-1}

are shown in Table 3. The ΔE values were computed as the difference between total energies of reaction products and reactants. The geometries of *syn* silacarbamic acid optimized on various levels are shown in Table 4. The calculated structural data and energies for SiO_2 and NH_3 are given in Table 5. The highest absolute value of the reaction energy 320.9 kJ mol^{-1} is yielded by the 6-311G** calculation. The single-point calculations using 6-311+G* basis set and the higher level correlation energy corrections (MP4SDTQ, CCSD, and CCSD(T)) in various degree lowered the reaction energy. This lowering was, however, not sufficient for the reversing the sign of the reaction energy. On the contrary, the calculations of the decomposition of carbamic acid have shown that this reaction is slightly exothermic [9]. The different energy content of decomposition of carbamic and silacarbamic acids can be partly explained by the different behaviour of oxides of carbon and silicon. The carbon dioxide exists as individual molecule species, whereas silicon dioxide forms giant molecules containing tetravalent SiO_4 units. It is probable that, if one considers that the final products of reaction (*C*) are the tetravalent oxides that exhibit continuous three-dimensional structures, the resulting reaction will be exothermic. It is a well known fact that the compounds with the Si=O double bonds are highly reactive species [2, 3, 44] and undergo polymerization [2, 44]. One of the possible reaction products are the cyclo-$(R^1R^2SiO)_2$ dimers. We therefore decided to investigate another possible reaction – dimerization of silacarbamic acid leading to the formation of the cyclic product containing four-membered ring



(*D*)

For this cyclobutane-like structure (*cis*-2,4-diaminocyclodisiloxane-2,4-diol) we performed optimization in which the bond lengths, bond angles, and torsion angles were varied. The Becke3LYP/6-311G** minimized structure of this compound is shown in Fig. 2*a*. The product is a cyclic structure with practically planar four-membered ring. The Si—O—Si angle is quite acute (91.5°) and the Si· ·Si length surprisingly short (0.242 nm). This "short" Si· ·Si distance is of about the same range as the normal Si—Si bond (0.235 nm). For rationalization of this short silicon—silicon separation several models have been proposed [45—47]. *Grev* and *Schaefer* [46] explained the short Si· ·Si contact in cyclic disiloxanes with the existence of "unsupported π bond" between silicon atoms. The ^{29}Si NMR measurements by *West et al.* [47] supported this model. Another view is that repulsion between the oxygen atoms dominates the structure, forcing the silicon atoms into antibonding contact [45, 48]. According to this theory the "short" Si· ·Si distance should be a result of a strong repulsion between oxygen atoms of this ring. The B3LYP/6-311G** computed O· ·O length is indeed very short (0.236 nm). The NPA computed charges of oxygens of the ring are highly negative (about – 1.2 *e*). The silicon atoms carry large positive charge (about + 2.3 *e*) (Fig. 2*b*). Then the

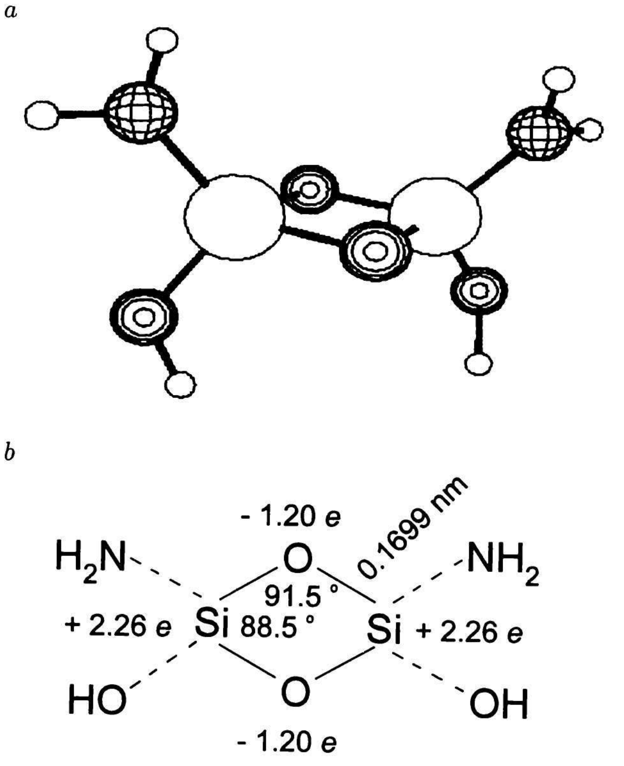


Fig. 2. The Becke3LYP/6-311G** optimized structure of dimeric *cis*-2,4-diaminocyclodisiloxane-2,4-diol.

Table 6. Natural Atomic Charges (NAC) and Bond Orders from the HF/6-31G** NBO Analysis (NAC)/*e*

Parameter	Species				
	I	*II*	*III*	*IV*	*V*
=O	−1.28	−1.13	−1.18	−1.17	−1.38
Si	2.43	2.58	2.44	2.44	2.39
N	−1.37	−1.34	−1.35	−1.07	−1.36
—O	−1.13	−1.12	−0.96	−1.13	−1.38
H	0.51	0.55	0.59	0.56	
H(+)		0.56	0.57	0.45	
Si=O	0.673	0.416	0.756	0.774	0.563
Si—N	0.455	0.539	0.525	0.288	0.368
Si—O	0.363	0.425	0.192	0.410	0.563
O—H	0.490	0.436	0.409	0.435	
X—H (X = N, O)		0.433	0.418	0.543	
TNL/%	0.95	0.81	0.78	0.84	1.04

equilibrium geometry of this four-membered ring is a result of a compromise between nonbonding repulsion (O· ·O and Si· ·Si) and attractive bonding (Si—O) forces. The Si—O bond lengths were computed slightly longer (about 0.004 nm) and Si—O—Si bond angles considerably shorter (by 45°) than those parameters found for cyclo-($R^2SiO)_3$ trimers [45]. NBO analysis [48] of the $(H_2XO)_2$ rings (X = C, Si, Ge, Sn, and Pb) does not support the X· ·X π interaction model of *Grev* and *Schaefer* [46]. The covalent metal—metal interactions were found very small and there is no direct X—X bond. The Wiberg bond index of the *cis*-2,4-diaminocyclodisiloxane-2,4-diol (0.04) is close to that found for the $(H_2SiO)_2$ (0.03) in Ref. [48].

The computed energies for this dimerization reaction using HF/6-31G**, B3LYP/6-31G**, and B3LYP/6-311G** methods are quite large (−461.5 kJ mol^{-1}, −404.6 kJ mol^{-1}, and −390.2 kJ mol^{-1}). The frequency calculations showed that this structure is a minimum at the HF/6-31G** level. The reaction energy is at all levels of theory highly negative, *i.e.* the reaction (*D*) is shifted towards the reaction products.

Our calculations thus demonstrated that also in the case of the double bond Si=O containing silacarbamates the energetically favoured compounds with single Si—O bonds may exist as most stable species. Another question arises concerning a possible barrier to the formation of this cyclic structure. The activation energy of the reaction (*D*) is not known, but its magnitude may have some influence on the gas phase stability.

Natural Population Analysis

The protonation and deprotonation reactions are connected with the considerable charge redistribution within the atoms of the reaction centre. For the quantifying differences in density from one molecule to another the partial charges on atomic centres usually serve as a convenience. The atomic charges of the species studied were also evaluated by natural population analysis (NPA) [49—51] using the NBO program [52].

The NAC charges, atom—atom net linear NLMO/NPA bond orders, and percentage of the total non-Lewis (TNL) structure contributions for the *syn* silacarbamic acid and its ionized species are seen in Table 6. Protonation is accompanied by only slight changes in charges on heavy atoms. The negative charge on the silacarbonyl oxygen upon protonation decreases (about 0.1 *e*) regardless of the protonation site. Similarly, negative charge decreases on both oxygen and nitrogen atoms (0.2 *e*) in NH and OH protonated species *III* and *IV* The net positive charge on the central Si atom slightly increases in the Si=O· ·H$^+$ system *II* and remains practically unchanged in the rest two cations. The H-8 proton (Fig. 1) carries a high positive charge the magnitude of which depends on the protonation site. Ionization of silacarbamic acid results in an increase of the net negative charge (0.1—0.2 *e*) on both oxygen atoms (Table 6). The computed atom—atom net linear NLMO/NPA bond orders and percentage of the total non-Lewis structure for silacarbamic acid and its charged species are also shown in Table 6. The calculated bond orders for Si=O bond are about twice as high as those for Si—O bond; this is, together with the nonequal bond lengths for these bonds in neutral acid (Table 1), a clear evidence for the double bond character between silicon and oxygen. In dependence on the site of protonation the bond orders are substantially changing. The Si=O· ·H$^+$ protonation in complex *II* causes an increase of both Si—O and Si—N bond orders and a substantial lowering of the Si=O bond order. Similarly, O· ·H$^+$ and N· ·H$^+$ protonation (cations *III* and *IV*) results in appreciable weakening of Si—O and Si—N bonds with a tendency for chopping of these bonds. The geometrical equivalence of two Si—O bonds in anion *V* (Table 1) is also demonstrated by computed equal bond orders for these bonds. The Si—N bond order in anion in comparison with parent acid is slightly reduced.

The percentage contribution of non-Lewis structures in silacarbamic acid and its anion is practically the same and low (about 1 %). With protonation the percentage of the total electron density which cannot be described by its Lewis structure slightly decreases (Table 6).

CONCLUSION

Ab initio and DFT methods have shown that the *syn* form of the silacarbamic acid is by 21.8 kJ mol^{-1} more stable than the *anti* conformer.

The preferred structure for monoprotonated silacarbamic acid is the protonated Si=O form *II*.

The net effect of substitution of the central carbon atom in carbamic moiety by silicon is an increase of both basicity and acidity of sila acid in comparison with its parent carbon derivative.

The decomposition of silacarbamic acid has been found an endothermic process. On the other hand, dimerization of this acid leads to the formation of a stable four-membered ring product.

Acknowledgements. Support of this work by the Slovak Ministry of Education (Grant No. 1224/97) and from EC Program COPERNICUS (Grant No. ERB3512PL941009) is gratefully acknowledged.

REFERENCES

1. March, J., *Advanced Organic Chemistry. Reactions, Mechanisms and Structure.* Fourth Edition. Wiley & Sons, New York, 1992.
2. Raabe, G. and Michl, J. *Chem. Rev. 85*, 419 (1985).
3. Damrauer, R. and Hankin, J. A., *Chem. Rev. 95*, 1137 (1995).
4. Withnall, R. and Andrews, L., *J. Phys. Chem. 89*, 3261 (1985).
5. Chmielecka, J., Chojnowski, J., Eaborn, C., and Stancyk, W. A., *J. Chem. Soc. Chem. Commun. 1987,* 1337
6. Patyk, A., Sander, W., Gauss, J., and Cremer, D., *Angew. Chem., Int. Ed. 28,* 898 (1989).
7. Remko, M., *Chem. Papers 43*, 601 (1989).
8. Remko, M., Liedl, K. R., and Rode, B. M., *J. Chem. Soc., Faraday Trans. 89*, 2375 (1993).
9. Remko, M. and Rode, B. M., *Theochem, J. Mol. Struct. 339*, 125 (1995).
10. Kydd, R. A. and Rauk, A., *J. Mol. Struct. 77*, 227 (1981).
11. VanAlsenoy, C., Williams, J. O., and Schaefer, L., *Theochem, J. Mol. Struct. 76,* 179 (1981).
12. Manning, J. Klimkowski, V J., Siam, K., Ewbank, J. D., and Schaefer, L., *Theochem, J. Mol. Struct. 139,* 305 (1986).
13. Buckingham, A. D., Handy, N. C., Rice, J. E., Somasundram, K., and Dijkgraaf, C., *J. Comput. Chem. 7,* 283 (1986).
14. Remko, M. and Scheiner, S., *Theochem, J. Mol. Struct. 180,* 175 (1988).
15. Remko, M. and Scheiner, S., *Theochem, J. Mol. Struct. 181,* 19 (1988).
16. Remko, M., *Collect. Czech. Chem. Commun. 53,* 1141 (1988).
17. Remko, M., *Z. Phys. Chem.* (Leipzig) *271,* 575 (1990).
18. Baudekar, J. and Okuzumi, Y. *Theochem, J. Mol. Struct. 281,* 113 (1993).
19. Wang, Q., Stidham, H. D., and Papadimitrakopolos, F., *Spectrochim. Acta, A 50,* 421 (1994).
20. Wolff, M. E. (Editor), *Burger's Medicinal Chemistry.* Wiley, New York, 1981.
21. Čižmárik, J., Borovanský, A., and Švec, P., *Pharmazie 33,* 297 (1978).
22. Kozlovský, J., Čižmárik, J., Pešák, M., Inczinger, F and Borovanský, A., *Arzneim.-Forsch./Drug Res. 32,* 1032 (1982).
23. Gregáň, F., Kettmann, V., Novomeský, P., Račanská, E., and Švec, P., *Farmaco 48,* 375 (1993).
24. Gregáň, F., Remko, M., Račanská, E., and Csöllei, J. *Boll. Chim. Farm. 134,* 454 (1995).
25. Gregáň, F., Račanská, E., and Remko, M., *Pharmazie 50,* 772 (1995).
26. Gregáň, F., Kettmann, V., Novomeský, P., Polášek, E., and Sivý, J., *Farmaco 50,* 829 (1995).
27. Krishnan, R., Frisch, M. J., and Pople, J. A., *J. Chem. Phys. 72,* 4244 (1980).
28. Raghavachari, K., Trucks, G. W., Pople, J. A., and Head-Gordon, M., *Chem. Phys. Lett. 157,* 479 (1989).
29. Bartlett, R. J., *J. Phys. Chem. 93,* 1697 (1989).
30. Gill, P. M. W., Johnson, B. G., and Pople, J. A., *Chem. Phys. Lett. 197,* 499 (1992).
31. Becke, A. D., *Phys. Rev., A 38,* 3098 (1988).
32. Parr, R. G. and Yang, W., *Density-Functional Theory of Atoms and Molecules.* Oxford University Press, Oxford, 1994.
33. Neumann, R., Nobes, R. H., and Handy, N. C., *Mol. Phys. 87,* 1 (1996).
34. Hariharan, P. C. and Pople, J. A., *Theor. Chim. Acta 28,* 213 (1973).
35. Krishnan, R., Binkley, J. S., Seeger, R., and Pople, J. A., *J. Chem. Phys. 72,* 650 (1980).
36. Frisch, M. J., Pople, J. A., and Binkley, J. S., *J. Chem. Phys. 80,* 3265 (1984).
37. *Gaussian 94* (Revision B.2). Frisch, M. J. Trucks, G. W., Schlegel, H. B., Gill, P M. W., Johnson, B. G. Robb, M. A., Cheeseman, J. A., Keith, T. A., Peterson, A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Ayala, C. Y. Chen, W. Wong, M. W Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Barker, J., Stewart, J. P., Head-Gordon, M. Gonzales, C., and Pople, J. A., Gaussian Inc., Pittsburgh, 1995.
38. Taft, R. W. and Thompson, R. D., *Prog. Phys. Org. Chem. 16,* 1 (1987).
39. Bagno, A., Lucchini, V. and Scorrano, G., *J. Phys. Chem. 95,* 345 (1991).
40. Rasul, G., Prakash, G. K. S., and Olah, G. A., *J. Org. Chem. 59,* 2552 (1994).
41. Politzer, P., Huheey, J. E., Murray, J. S., and Grodzicki, M., *Theochem, J. Mol. Struct. 259,* 99 (1992).

42. Remko, M., Liedl, K. R., and Rode, B. M., *J. Chem. Soc., Perkin Trans. II 1996*, 1743.
43. March, J. *Advanced Organic Chemistry. Reactions, Mechanisms and Structure.* Fourth Edition, p. 886. Wiley & Sons, New York, 1992.
44. West, R., Yokelson, H. B., Gillette, G. R., and Millevolte, A. J., in *Silicon Chemistry.* (Corey, J. Y., Corey, F. R., and Caspar, P. P., Editors.) P. 269—281. Ellis Korwood, Chichester, 1988.
45. Kapp, J., Remko, M., and Schleyer, P. V. R., *J. Am. Chem. Soc. 118*, 5745 (1996).
46. Grev, R. S. and Schaefer III, H. F., *J. Am. Chem. Soc. 109*, 9577 (1987).
47. Yokelson, H. B. Millevolte, A. J., Adams, B. R., and West, R., *J. Am. Chem. Soc. 109*, 4116 (1987).
48. Kapp, J., Remko, M. and Schleyer, P V. R., *Inorg. Chem.*, in press.
49. Reed, A. E., Weinstock, R. B., and Weinhold, F. A., *J. Chem. Phys. 83*, 735 (1985).
50. Reed, A. E. and Weinhold, F *J. Chem. Phys. 83*, 1786 (1985).
51. Reed, A. E. and Schleyer, P V R. *J. Am. Chem. Soc. 112*, 1434 (1990).
52. Glendening, E. D., Reed, A. E., Carpenter, J. E., and Weinhold, F *The NBO Program, Version 3.1.*

Translated by M. Remko