Quantum-chemical study of pentacoordinated silicon compounds: Si-substituted (O—Si)dimethyl(*N*-acetylacetamidomethyl)silanes

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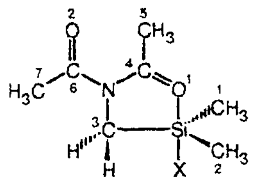
The mechanisms and self-consistency of the changes in geometric parameters, charge distribution, orbital structure and energy of the "soft" coordination center $XSiC_3O$ in Si-substituted (O—Si)dimethyl(*N*-acetylacetamidomethyl)silanes upon variation of the nature of the substituent X (X = $OCOCH_3$, $OCOCF_3$, F, Cl, Br, I) have been established by the PM3 method. They have been found to be in complete correspondence with the experimental data and the hypervalent bonding model. In contrast to the prediction of the standard donor-acceptor complex model, a decrease in the ionization potential of the donor upon the formation of the 3c—4e $XSi \leftarrow O$ bond has been demonstrated. Significant shortcomings of the PM3 method in quantitative estimations of the complexation energy and the gas-phase geometry have been pointed out.

Key words: silicon-substituted (O—Si)dimethyl(*N*-acetylacetamidomethyl)silanes, pentacoordination, semiempirical quantum-chemical methods.

The appreciable interest in new compounds of the petacoordinated silicon atoms, in particular, in the (O—Si)chelate and zwitterionic Si-substituted *N*-(dimethylsilylmethyl)-derivatives of cyclic and acyclic amides, imides, carbamides, and acylhydrazines, is related first of all to the high sensitivity of the geometry of their "soft" $XSiC_3O$ coordination center to the nature of the axial substituents at the Si atom as well as to external factors like medium and temperature.[1,2] Some particular features of the structure of such systems have already been considered by means of quantum-chemical methods.[3—6] However, a detailed quantum-chemical analysis of their electronic and molecular orbital structure has not been performed despite the significant interest in the correspondence of its results with the consequences of the three-center four-electron (3c—4e) bonding model which provides the background for the theory of chelate compounds of group 14 elements.[1]

In this paper the results of quantum-chemical MNDO/PM3 study of the structure of Si-substituted (O—Si)dimethyl(*N*-acetylacetamidomethyl)silanes (**1a—f**) are considered.



1a—f

1: X = $OCOCH_3$ (**a**), $OCOCF_3$ (**b**), F (**c**), Cl (**d**), Br (**e**), I (**f**)

The choice of this compounds as the subject of the present study is not arbitrary. According to data of X-ray structural analysis and NMR spectroscopy, crystals and solutions of the compounds **1** exhibit remarkable differences in the properties of the free acetyl group and the group involved in the hypervalent bonding with Si atom.[2] It might be expected that the former can serve as an "internal reference" for estimating the changes in the properties of the acetyl fragment upon its interaction with Si atom.

Methods of Calculations

The limited semiempirical studies on hypervalent silicon compounds do not provide unambigously the most reliable approximation for the calculations of their energetics and spatial electronic properties.[7—10] For this reason it was instructive to estimate the adequacy of the MNDO, MNDO/PM3, and AM1 approximations available from the MOPAC version 6.0 program package to study the system **1**. The lack of direct experimental data on the complex formation energies and dipole moments compelled us to consider the efficiency of these calculations only for the geometry of molecules **1d—f** available from the X-ray data.[11]

Analysis of the results of calculations (with full geometry optimization) revealed that only the MNDO/PM3 method is able to describe qualitatively the specific dependence of the structural parameters of the $XSiC_3O$ coordination center on the nature of the substituent X. In particular, this follows from a comparison of calculated and measured[11] Si—O bond lengths (d/Å) in Si-halogen-substituted molecules **1**:

1	AM1	MNDO	PM3	Exptl.
d	2.424	1.996	1.850	2.027
e	2.443	1.939	1.822	1.978
f	2.447	1.963	1.813	1.830

Therefore, below we will use only the MNDO/PM3 method.

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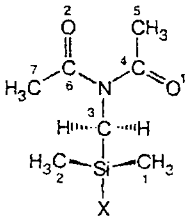
Results and Discussion

In principle, molecules of Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes can exist in four forms. Two of them (**1** and **2**) correspond to *trans* arrangement of the carbonyl groups. In the *trans*-bonded form **1** the central Si atom is pentacoordinated, whereas in the non-bonded form **2** its coordination number is equal to four. The rotation of one of the acetyl groups around the C(6)—N bond transforms structures **1** and **2** into two conformers with *cis* arrangement of the carbonyl fragments (**3** and **4**).



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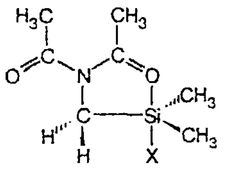

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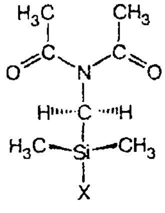

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Calculations of all possible *trans*- and *cis*-forms of the compounds under study were performed by means of the MNDO/PM3 method with full geometry optimization. The positive values of the corresponding Hessians confirmed the evaluation of true minima on the potential energy surfaces.* The results presented in Table 1 demonstrate that *trans* arrangement of the carbonyl groups in the structures **1** and **2** is energetically more favorable than *cis* in structures **3** and **4**, perhaps due to steric reasons.

As follows from NMR spectroscopy[13] and X-ray analysis data,[11] the diacetamines in solution and in the solid phase indeed exist in the *trans*-conformations. We therefore restricted ourselves to the consideration of *trans*-forms **1** and **2** of the Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes.

The structural parameters of bonded **1** and non-bonded **2** forms calculated by the MNDO/PM3 method are presented in Tables 2 and 3. According to these data, the coordination center in the derivatives **1a—f** has the structure of a distorted trigonal bipyramid. Indeed, the valence angles X—Si—O, X—Si—C, C—Si—C and the displacement of Si atom from the equatorial plane of three C atoms (Δ_{Si}) markedly differ from the "ideal" ones, *i.e.*, from 180°, 90°, 120° and 0 Å, respectively (see Table 2). At the same time, the chelate cycle SiCNCO has almost planar geometry in all cases. In contrast, the valence angles X—Si—C(2), C(1)—Si—C(2) and the value of Δ_{Si} for the non-bonded **2a—f** forms correspond unambiguously to an almost tetrahedral configuration of the Si atom (see Table 3).

Table 1. The relative energies (kcal mol^{-1}) of the *cis*-, *trans*-bonded (ΔE_{3-1}), *trans*-, *cis*-non-bonded (ΔE_{4-2}), and *trans*-bonded and non-bonded (ΔE_{1-2}) forms of the Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes calculated by the MNDO/PM3 method

X	ΔE_{3-1}	ΔE_{4-2}	ΔE_{1-2}
$OCOCH_3$	3.1	2.5	13.7
$OCOCF_3$	3.2	2.1	8.5
F	3.5	2.5	13.4
Cl	3.7	2.3	2.8
Br	3.9	1.7	−7.5
I	3.7	1.8	−13.5

Analysis of the results presented in Tables 2 and 3 made it possible to deduce the following conclusions.

1. On going from the silane **1a** to **1f**, the range of equatorial Si—Me bond length variation is *ca.* two times smaller than that of axial Si—O bond lengths (see Table 2). This fact unambiguously points out the predominantly *trans*-effect of the substituent X.

2. The bond length between the substituent X and pentacoordinated Si atom exceeds the distance between X and tetracoordinated one (see Tables 2 and 3). Thus, the bonding between Si and O atoms in the structure **1** weakens the X—Si bond.

3. As follows from the Si—O bond lengths listed in Table 2, the strength of this bond in the compounds **1a—f** increases along the following sequence of substituents X: $OCOCH_3 \approx F < OCOCF_3 < Cl < Br < I$.

This trend coincides with a sequence established by NMR spectroscopy[13] and reveals the increase of Si—O bond strength with enhancement of the nucleophilic character of substituent X among the series of derivatives **1** considered here. In other words, if the X—Si bond weakens, the interaction between Si and O atoms grows. As should be expected, this is accompanied by the elongation of the C=O and shortening of the C—N bonds in the coordinated N—C=O fragment with respect to those in the free group (see Table 2).

Such an inverse correlation between the energies of axial X—Si and Si—O bonds should lead to the conservation of the sum of their orders. Indeed, the systems **1a—f** can be considered as the stable intermediates that exist on the optimal reaction path of intramolecular S_N2-substitution at the tetrahedral Si atom (Scheme 1). Non-bonded form **2** and ionic pair **5** with the tetrahedral Si atom correspond to the initial and final points on the reaction path.

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* The calculated barriers for the rotation of the free acetyl group around the C(6)—N bond depend weakly on the nature of substituent X and lies in the 4.4—4.6 kcal mol^{-1} range, being ~4 kcal mol^{-1} smaller than the experimental values for the *N*,*N*-diacetyl-derivatives of aliphatic amines.[12]

Table 2. The structural parameters of the *trans*-bonded form **1** of the Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes calculated by the MNDO/PM3 method

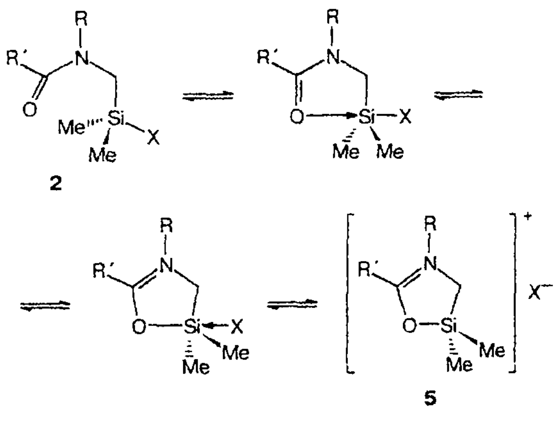
Compound	Bond length, d/Å							Valence angle, ω/deg			Displacement /Å, Δ_{Si}*
	X—Si	Si—O	Si—Me	C(4)—N	C(6)—N	C(4)—O	C(6)—O	X—Si—O	X—Si—Me	C(1)—Si—C(2)	
1a	1.755	1.905	1.928	1.414	1.444	1.247	1.219	164.85	101.43	118.55	0.198
1b	1.769	1.878	1.922	1.408	1.449	1.252	1.217	164.70	98.79	118.18	0.137
1c	1.637	1.896	1.933	1.414	1.442	1.246	1.220	170.54	97.98	116.68	0.190
1d	2.299	1.850	1.899	1.406	1.450	1.257	1.217	168.49	93.26	117.87	0.024
	(2.259)	(2.027)	(1.871)	(1.361)	(1.421)	(1.251)	(1.181)	(171.62)	(95.03)	(119.34)	(0.160)
1e	2.481	1.822	1.885	1.399	1.455	1.266	1.216	162.94	91.11	117.57	−0.111
	(2.467)	(1.978)	(1.838)	(1.371)	(1.366)	(1.253)	(1.211)				(0.052)
1f	2.671	1.814	1.882	1.395	1.458	1.270	1.216	162.91	90.75	117.30	−0.127
	(3.030)	(1.830)	(1.864)	(1.368)	(1.436)	(1.268)	(1.203)				(−0.090)

Note. The values determined by the X-ray analysis[11] are given in parentheses. *The positive sign of Δ_{Si} corresponds to the displacement of the Si atom toward the substituent X.

Table 3. Calculated values of the structural parameters of the *trans*-non-bonded form **2** of the Si-substituted dimethyl-(*N*-acetylacetamidomethyl)silanes

X	Bond length, d/Å		Valence angle, ω/deg		Displacement/Å,
	Si—X	Si—Me	X—Si—C(1)	C(1)—Si—C(2)	Δ_{Si}
OCOCH$_3$	1.718	1.890	112.25	111.32	0.587
OCOCF$_3$	1.724	1.885	111.13	111.70	0.565
F	1.600	1.886	108.33	111.16	0.571
Cl	2.115	1.872	107.08	112.62	0.523
Br	2.314	1.864	105.55	114.55	0.496
I	2.539	1.861	106.29	115.00	0.450

Scheme 1



R = MeC(O), R′ = Me

It should be noted that the structures of iodo- and bromo-derivatives of **1** with inverted configuration of Si atom and weak coordination bond (see Table 2) represent the case when the reaction is almost completed. The changes in the distances between the Si atom and attacking and leaving groups Δd_i are related by the logarithmic (Pauling's) dependences with the corresponding bond orders n_{SiO} and n_{XSi}[14]:

$$\Delta d_{XSi} = d_{XSi} - d^0{}_{XSi} = c\log n_{XSi}, \qquad (1)$$

$$\Delta d_{SiO} = d_{SiO} - d^0{}_{SiO} = c\log n_{SiO}. \qquad (2)$$

Here Δd_{XSi} and Δd_{SiO} are the differences of the bond lengths in the complex **1** and in the reactant or product ($d^0{}_{XSi}$ and $d^0{}_{SiO}$ are the values for the non-bonded state and cation **5**, respectively). By definition,[3] $n_{XSi} = (\Delta_m + \Delta_i)/(\Delta_m - \Delta_c)$ and $n_{SiO} = (\Delta_m - \Delta_i)/(\Delta_m - \Delta_c)$, where Δ_m is the maximum displacement of the Si atom from the plane of three C atoms for the non-bonded form **2**, whereas Δ_i and Δ_c are the same quantities for the complex **1** and the cation **5**, respectively.

Using the data of Tables 2 and 3 and the calculated values $d^0{}_{SiO}$ = 1.754 Å and Δ_c = −0.432 Å for cation **5**, we found that the correlations (1) and (2) can be reduced to the forms

$$\Delta d_{XSi} = -0.526\log(n_{XSi} \cdot 1.045);\ r = 0.801,\ s = 0.032, \qquad (1')$$

$$\Delta d_{SiO} = -0.322\log(n_{SiO} \cdot 0.911);\ r = 0.997,\ s = 0.003. \qquad (2')$$

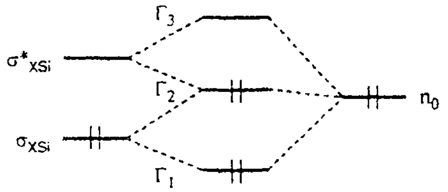
According to equations (1′) and (2′), $n_{XSi} + n_{SiO} = 1.133 + 0.026\Delta_i$. Therefore, to a good approximation the sum of orders of axial Si—O and X—Si bonds for the complexes **1a—f** is constant. If the standard definition of the bond order[14] ($n_{XSi} = (\Delta_m + \Delta_i)/2\Delta_m$, $n_{SiO} = (\Delta_m - \Delta_i)/2\Delta_m$) is used, the conclusion on the conservation of the bond order sum remains unaltered, but the accuracy of the correlation relations (1) and (2) becomes markedly worse.

Conclusions 1—3 deduced from the results of calculations (see above) are typical for organic derivatives of silicon in trigonal-bipyramidal coordination.[1,2,15] They follow from the hypervalent (3c—4e)-bond model, which is the basis of the theory of their structure.[16] According to MNDO/PM3 data, the two filled (Γ_1 and Γ_2) and one vacant (Γ_3) molecular orbitals (MO's) considered within this model are mainly localized on the XSiO fragment of

Table 4. Changes in charges (Δq) and dipole moments ($\Delta\mu$) upon the transition from the non-bonded form **2** to the bonded one **1** calculated by the MNDO/PM3 method

X	Δq/eu							$\Delta\mu$
	X	Si	N	O(1)	O(2)	C(1)	C(2)	/D
$OCOCH_3$	0.360	−0.015	−0.102	−0.002	−0.022	−0.029	−0.034	−1.90
$OCOCF_3$	0.393	−0.014	−0.115	−0.009	−0.023	−0.030	−0.027	−4.58
F	0.610	0.001	−0.117	−0.017	−0.016	−0.037	−0.040	−0.10
Cl	0.226	−0.041	−0.128	0.003	−0.022	−0.050	−0.054	−3.17
Br	0.261	−0.033	−0.143	0.009	−0.023	−0.045	−0.050	−4.48
I	0.232	0.007	−0.148	0.009	−0.023	−0.048	−0.040	−5.19

the molecules **1a—f** and correspond to the following correlation diagram:



The existence of internal reference, *i.e.*, free carbonyl group, in the silanes **1** makes it relatively easy (unlike the other intramolecular complexes of silicon[10]) to establish that the Γ_2 MO level of the complexes **1a—f** possesses higher energy than the level of the donor, *i.e.*, the lone electron pair (LEP) of oxygen atom n_O. For instance, in the framework of Koopmans' theorem, ionization potentials of the Γ_2 and n_O MO's of the complex **1c** (X = F) are equal to 9.81 eV and 11.41 eV, whereas those of the compound **1d** (X = Cl) are equal to 9.02 eV and 11.95 eV, respectively. It is worth noting that such a situation cannot in principle be ascribed to the restricted two-orbital scheme of interaction between the LEP orbital of the donor and the anti-bonding orbital of the X—Si bond (n_O and σ^*_{XSi} in our case; the concept of p,σ^*-conjugation), which is sometimes used for interpretation of some properties of trigonal-bipyramidal silicon derivatives. Hence, the experimental study of the orbital structure of the compounds **1** by means of photo-electron spectroscopy is of special importance.

It is difficult to compare the X-ray structural data and calculated geometric parameters for the compounds **1** (Table 2), because for silatranes containing the XSi←N 3c—4e-bond the extreme sensitivity of the geometry of hypervalent organic silicon derivatives to the state of aggregation was observed experimentally.[17] On going from solid to gas phase the Si←N bond in 1-fluoro- and 1-methylsilatranes becomes longer by 0.28 Å.[18,19]

The results of *ab initio* and semiempirical (MINDO/3, MNDO, AM1, MNDO/PM3) calculations[8,20—23] reproduce the significant elongation of the silatrane Si—N bond in the gas phase. This effect can be explained by the extremely "soft" character of the corresponding potential function. According to indirect NMR spectroscopy data,[13] the same effect of the medium should be expected for silicon compounds with the hypervalent XSi←O 3c—4e-bond as well.

However, the MNDO/PM3 method predicted too short Si—O bond lengths in the Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes that are too short in comparison with those established by X-ray analysis (see Table 2). Moreover, the calculated value of the Δ_{Si} displacement for the bromine derivative **1e** implies the formation of the Br→Si rather than Si←O bonding pertinent to the solid phase. This might be interpreted as a preliminary (due to the lack of direct experimental data) indication that the MNDO/PM3 method is not perfectly valid for estimating the geometric parameters of the $XSiC_3O$ coordination centers of silanes **1** in the gas phase.* At the same time, these calculations point out the labile character of the XSi←O 3c—4e-bond. For instance, elongation of the Si←O bond in the compound **1e** by 0.1 Å from the equlibrium value requres 1.5 kcal mol^{-1}, whereas for the compound **1c** this energy amounts to only 0.4 kcal mol^{-1}.

According to the data of Table 4, the dipole moment of the bonded form **1** is higher than that of the non-bonded one **2**. This is typical also for other silicon chelates.[24] Upon the formation of the $XSiC_3O$ coordination center in the silanes **1** the charge on the substituent X markedly increases, while the charges on Si, donor O(1), and equatorial C atoms change in magnitude to a much smaller extent. Depending on the nature of substituent X both increase and decrese in the positive charge on Si atom and negative charge on O(1) were observed (see Table 4).

The extent of the electron density transfer from the donor O(1) atom to the acceptor $XSiC_3$ fragment upon the formation of the XSi←O 3c—4e-bond is of special interest. As was shown above, the standard approach based on the comparison of the total charges on the O(1) atoms in the structures **1** and **2** does not provide

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* The adequacy of other methods is less clear. We found that for the compounds **1d—f** in the gas phase the AM1 method underestimates the lengths of Si—O bonds, whereas the MNDO scheme can either overestimate or underestimate them. An analogous picture was observed in MNDO calculations of the other (O—Si)chelate structures.[3,6] It is likely that the applicability of semiempirical methods for describing the geometry of X—SiO 3c—4e-bond requires additional investigations.

definite solution* (see Table 4). Moreover, as was demonstrated for other compounds with the $XSiC_3O$ coordination center, the formation of XSi$\leftarrow$O bond is not accompanied by the charge transfer.[6] At the same time, according to the hypervalent bonding model, such transfer must take place, but for its observation it is necessary to consider the population of the LEP orbital of the donor O atom involved in the XSi$\leftarrow$O coordination interaction.

The diagonalization of the density matrix block which corresponds to the O(1) atom in the structures **1** and **2** allowed us to specify the sp^2-hybrid orbital of its lone pair and estimate the change in its population** (ΔN). Depending on the nature of substituent X, the ΔN value for compounds **1a—f** was found to decrease along the following sequence : **1f** ($\Delta N = 0.25$) > **1e** ($\Delta N = 0.23$) > **1d** ($\Delta N = 0.19$) > **1b** ($\Delta N = 0.18$) > **1c** ($\Delta N = 0.15$) = **1a** ($\Delta N = 0.15$). Therefore, the extent of electron density transfer from the donor O(1) atom to the $XSiC_3O$ coordination center increases when the Si—O bond strength is increased.

The complex formation energies ΔE_{1-2} for the molecules **1** can be determined as the differences in total energies of these trigonal-bipyramidal derivatives and of the corresponding non-bonded structures **2** with tetracoordinated Si atom (see Table 1). Analysis of the data from Table 1 reveals that only iodo- and bromo-derivatives of the Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes exist in the gas phase in the form **1** which has the pentacoordinated Si atom. Thus, the question of possible equilibrium $\mathbf{1} \rightleftharpoons \mathbf{2}$ in the gas-phase remains unanswered, although it is evident that the estimations of the ΔE_{1-2} energies by MNDO/PM3 are quantitatively unreliable.

Indeed, according to NMR spectroscopy data,[13] all Si-substituted dimethyl(*N*-acetylacetamidomethyl)silanes in the solutions exist in the non-bonded form **1**.*** Even if the higher polarity of the **1a—f** structures is taken into account (see Table 4), the theoretical estimations of their relative stability in solutions should not be very different from those calculated for the gas phase. The chloro-derivative **1d** can be the only exception.

Obviously, the appreciable contribution to ΔE_{1-2} corresponds to the energy of the additional Si—O bond E_{SiO} which can be estimated using the two-center part of the total energy and the normalization procedure.[25] Such estimations provided the following values of E_{SiO} = 31.4, 36.2, 32.3, 39.2, 44.7, and 47.0 kcal mol^{-1} for the compounds **1a—f**, respectively. The correction factor was determined at $E_{N-C(Si)}$ = 72.8 kcal mol^{-1}.

Therefore, the calculated results reproduce correctly the effect of the substituent X on such well-correlated properties characterizing the Si—O bond strength as its length, energy, and extent of the electron density transfer from the donor atom to the acceptor fragment $XSiC_3$.

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* The negative charge on the O(2) atom in the free carbonyl group is significantly higher than that on the O(1) one in the bonded and non-bonded forms

** The population of the LEP of O(2) atom of the free carbonyl group was estimated similarly. It is almost independent of the substituent X and coincides with that of O(1) atom in the non-bonded form **2** ($N = 1.89$).

*** The question on the possibility of $\mathbf{1} \rightleftharpoons \mathbf{2}$ equilibrium in solutions is also unclear.

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