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Molecular Design of Neutral Intramolecular Complexes Bearing Two Silicon Atoms Anchored by a Carbonyl Oxygen Atom: *N*,*N*′-Bis(silylmethyl)propylene Ureas

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Abstract: B3LYP and MP2 computations have been performed on a variety of *Si*,*Si*′-substituted *N*,*N*′-bis(silylmethyl)propylene ureas. According to electron-density atoms-in-molecules (AIM) and electron localization function (ELF) quantum-topological analyses, a transition from the unstable non-chelate forms of these compounds to mono- and bis-chelate forms results in the successive interaction of one and two tetracoordinate silicon atoms with the carbonyl oxygen and the formation, respectively, of one and two covalent, polar Si⋅⋅⋅O bonds. This previously unknown X−Si←O→Si−X type of bonding in isomers possessing an anchor structure may be classified as a five-center, six-electron (5c-6e) bond. The factors that favor the existence of *Si*,*Si*′-substituted *N*,*N*′-bis(silylmethyl)propylene ureas exclusively in the form of stable, bridged complexes (the size of equatorial ligands and the electronegativity of axial substituents at the silicon atom, change in the donor capability of the carbonyl group, and effect of the polar solvent) are discussed.

Keywords: ab initio calculations • bond nature • chelates • density functional calculations • ELF (electron localization function) • silicon • substituent effects

Introduction

Although few in number, intramolecular complexes containing two acceptor silicon atoms anchored by a single donor (D) center through Si←D→Si coordination bonding are of chemical interest owing to their unusual structure and stereodynamic behavior.[1] In the known examples, a vicinal (as in **1**[1b] and **2**[1c]) or geminal (as in **3**[1f]) disposition of silicon atoms in the main molecular framework imposes severe limitations on their internuclear distance (d_{Si-Si}). Therefore, the formation and stability of donor-bridged structures of this type are, to a large extent, a result of the steric constraints of the attractive interactions of the two silicon atoms with the donor atom of an appropriate size and basicity (halide anion or ether oxygen).

The recently proposed method for the preparation of *N*,*N*′-bis(dimethylhalogensilylmethyl)propylene ureas (halogen = Cl (**4**), Br (**4′**)) provides a route to another structural organization of intramolecular donor-bridged silicon complexes.[2] Indeed, contrary to compounds **1**–**3**, the stability of the possible anchor (bis-chelate) structure of various *Si*,*Si*′-substituted *N*,*N*′-bis(silylmethyl)propylene ureas should depend only on the nature of the substituents at the silicon atom. However, it is difficult to establish the nature of this dependence a priori as there is no theoretically justified model describing the effects of medium and silicon substituents on the properties of the Si←O→Si anchor bonding.[3] This hinders both the targeted synthesis of the anchor-bonded intramolecular silicon complexes and the interpretation of the existing experimental information on **4** and **4′**. Indeed, the chemical equivalence of the two silicon atoms observed in the ^{29}Si NMR spectra of these compounds may be indicative either of a pendulum (degenerate isomerization of the two mono-chelate forms being fast on the NMR timescale) or anchor structure.

We undertook an ab initio and DFT study of the structures of *Si*,*Si*′-substituted *N*,*N*′-bis(silylmethyl)propylene ureas **4**–**12** to gain an insight into the factors facilitating

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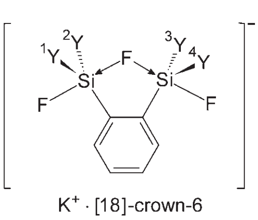
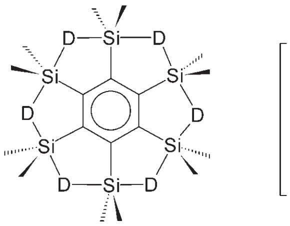
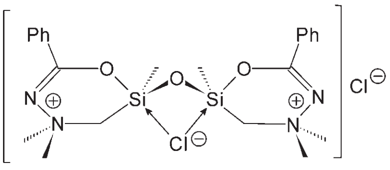
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Cartesian coordinates of all investigated structures, the absolute and relative values of the total energies, enthalpies and Gibbs free energies ($T = 298.15$ K, 1 atm) of structures **4**–**12** calculated at the different theoretical levels as well as the B3LYP/6-31G* dipole moments of these structures.



1 (Y = F, Ph)



2 (D = F⁻, OMe)



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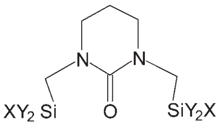


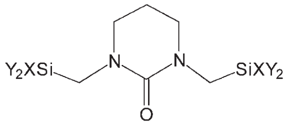
X = Cl: Y = Me (**4**), H (**5**),
F (**6**), Cl (**7**), Br (**8**);
Y = H: X = HO (**9**), F (**10**),
Br (**11**), Me (**12**)

4–12

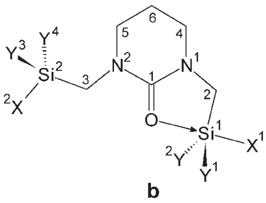
their existence in the bis-chelate form and the nature of the previously unknown multicenter X−Si←O→Si−X bond.

Results and Discussion

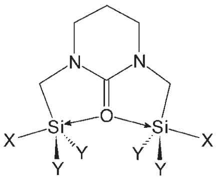
Geometry and energetics of *N,N'*-bis(silylmethyl)propylene ureas: The energies and selected geometry of the most significant ground- ($\lambda = 0$) and transition-state ($\lambda = 1$) structures of *N,N'*-bis(silylmethyl)propylene ureas **4–12** in their non-chelate (**a**), mono-chelate (**b**), and bis-chelate (**c**) forms, distinguished by the coordination number of the silicon atoms, are collected in Table 1, Table 2, and Table 3.



a



b

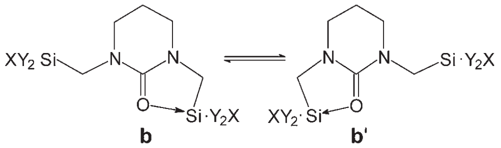


c

Non-chelate *structures* ***4a–12a***: Non-chelate structures **4a–12a** correspond to potential energy surface (PES) minima ($\lambda = 0$) and are characterized by C_S symmetry with a tetrahedral configuration of bonds at the silicon atoms and dihedral angles for Si-C-N-C1 of 95–108°. In these structures (as well as in the **b** and **c** isomers) the urea six-membered CNCCCN cycle adopts an envelope conformation: the C6 atom deviates from the C1-C4-C5 plane in the opposite direction to that of the silicon atoms and the degree of pyramidalization of the two nitrogen atoms is insignificant. Judging by the values of the differences between the total energies of the non-chelate **a** and chelate **b** and **c** forms ($\Delta E_{\mathbf{a-b}}$ and $\Delta E_{\mathbf{a-c}}$), the existence of the studied compounds in the **a** form is practically excluded (see Table 1).

Mono-chelate structures ***4b–12b***: Forming degenerate pairs, the mono-chelate **b** and **b'** forms of **4–12** ($\lambda = 0$), which may interconvert, have one penta- (denoted as Si1) and one tetracoordinated (Si2) silicon atom. They are energetically more favorable (by 1.9–9.0 kcal mol^{-1}) than the non-chelate **a** forms. At the same time, only molecules **4**, **7**, and **8**, with form **b** (**b'**) being their most stable isomer, adopt pendulum structures.

We located two mono-chelate minima (**b** and **b**$_\mathbf{c}$) on the PES of **4**, which differ in their Si2-C3-N2-C1 angles (96.1 and 40.3°). The latter conformer is more stable by 0.28 kcal mol^{-1}.



The calculated internuclear Si1···O distances ($d_{\text{Si-O}}$) in **4b–12b** are significantly shorter than the sum of the van der Waals radii of silicon and oxygen atoms (3.62 Å) and are markedly longer than the sum of their covalent radii (1.83 Å). This points to the formation of an additional Si←O coordinate bond, which closes a virtually planar chelate cycle and increases the coordination number of the Si1 atom to five. As the value of the parameter η_e (see Table 2 and Table 3) is between that characteristic of a tetrahedron ($\eta_e = 0\%$) and an "ideal" trigonal bipyramid ($\eta_e = 100\%$), the Si1 polyhedron adopts, to a large extent (with the exception of that of **12**), the structure of a distorted trigonal bipyramid (TBP).

In the series **5b** and **9b–12b**, which have the same equatorial substituents Y=H, a good correlation is obtained between the changes in $d_{\text{Si1-O}}$, η_e, and $\Delta E_{\mathbf{a-b}}$ caused by the variation of the axial substituent X (see Figure 1) as is expected for O−Si mono-chelates.[4] An increase in the nucleofugality of X ($CH_3 < OH < F < Cl < Br$) results in a strengthening of the Si1−O bond (decreasing $d_{\text{Si1-O}}$) and an increase in the pentacoordination character of Si1 (η_e) and its complex stability ($\Delta E_{\mathbf{a-b}}$). In contrast, by varying the equatorial substituents Y, no correlation between changes in $d_{\text{Si1-O}}$, η_e, and $\Delta E_{\mathbf{a-b}}$ was observed in the series **4b–8b**, which have axial substituents X=Cl. Nevertheless, an increase in the electronegativity of Y ($CH_3 < OH < Br < Cl < F$) results in the expected shortening of both axial X−Si1 and Si1−O bonds at

Table 1. Relative energies with and without ZPE corrections and the number of Hessian eigenvalues (λ) for molecules **4**–**12** calculated at the B3LYP/6-31G* and MP2/6-31G* (in parentheses) levels of theory.[a]

	X	Y	ΔE [kcal mol^{-1}]			$\Delta E_{+\mathrm{ZPE}}$ [kcal mol^{-1}]			λ		
			a	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**
4	Cl	Me	5.0	0.3, *0.0*[b]	0.8	4.5	0.3, *0.0*	0.5	0	0, *0*	1
			(6.4)	(1.6), *(0.0)*	(1.9)						
5	Cl	H	14.1	4.6	0.0	13.2	4.4	0.0	0	0	0
			(14.6)	(5.1)	(0.0)						
6	Cl	F	9.7	1.9	0.01, *0.0*[b]	9.3	2.1	0.0, *0.1*	0	0	1, *0*
			(11.4)	(2.8)	(0.03), *(0.0)*						
7	Cl	Cl	5.0	0.0	4.3	4.6	0.0	3.8	0	0	1
8	Cl	Br	5.2	0.0	2.4	4.6	0.0	1.9	0	0	1
9	OH	H	7.8	2.9	0.0	7.2	2.8	0.0	0	0	0
10	F	H	13.8	4.8	0.0	13.0	4.5	0.0	0	0	0
			(14.6)	(5.6)	(0.0)						
11	Br	H	13.9	4.1	0.0	13.1	4.0	0.0	0	0	0
12	Me	H	3.6	1.4	0.0	3.2	1.3	0.0	0	0	0

[a] The energies of the most stable isomers were taken to be equal to zero values. [b] Data for the $\mathbf{4b_c}$ and $\mathbf{6c_u}$ isomers are given in italics.

Table 2. Selected bond and bridge lengths, angles, and structural characteristics (η_e) of the pentacoordinate silicon atom for stable isomers of **5**, **6**, **10**, and **11** calculated at the B3LYP/6-31G* and MP2/6-31G* (in italics) levels of theory.

	$d_{\mathrm{Si-Si}}$ [Å]	$d_{\mathrm{Si1-O}}$ [Å]	$d_{\mathrm{X1-Si1}}$ [Å]	$d_{\mathrm{C1-O}}$ [Å]	X-Si1-Y [°][a]	Y-Si1-Y [°]	C1-O-Si1 [°]	Si1-C2-N1-C1 [°]	η_e [%]
5a			2.091	1.231	107.8	109.7		−98.8	
			2.070	*1.238*	*108.1*	*110.3*		*−97.3*	
5b		2.129	2.185	1.263	98.1	118.2	111.3	−4.2	86
		2.133	*2.154*	*1.268*	*98.6*	*118.3*	*110.6*	*−6.9*	*85*
5c	4.370	2.311	2.146	1.269	101.4	117.2	109.0	−7.2	72
	4.310	*2.279*	*2.122*	*1.276*	*101.5*	*117.3*	*109.0*	*−9.3*	*73*
6a			2.055	1.231	108.4	106.4		−108.1	
			2.032	*1.238*	*108.6*	*106.7*		*−104.0*	
6b		2.014	2.150	1.268	97.0	115.4	113.0	−2.2	90
		2.018	*2.119*	*1.272*	*97.4*	*115.4*	*112.3*	*−3.0*	*90*
6c	4.222	2.246	2.110	1.272	100.7	114.6	109.9	−4.5	75
	4.141	*2.205*	*2.086*	*1.280*	*100.7*	*114.7*	*110.1*	*−6.3*	*77*
10a			1.620	1.231	108.4	109.8		−102.6	
			1.625	*1.237*	*108.3*	*110.7*		*−100.0*	
10b		2.216	1.649	1.255	101.7	117.4	110.5	−6.1	74
		2.191	*1.657*	*1.263*	*101.2*	*117.7*	*110.0*	*−9.6*	*77*
10c	4.440	2.344	1.640	1.264	103.6	116.6	108.7	−8.4	64
	4.346	*2.297*	*1.648*	*1.272*	*103.0*	*117.1*	*108.9*	*−11.3*	*68*
11a			2.238	1.231	107.7	109.8		−98.9	
11b		2.123	2.339	1.263	97.7	118.3	111.4	−3.7	87
11c	4.331	2.294	2.297	1.269	101.1	117.3	109.2	−6.2	72

[a] The mean value of the X1-Si1-Y1 and X1-Si1-Y2 angles.

the TBP Si1 atom. Experimentally a similar effect has been illustrated by X-ray crystallography of some N–Si and O–Si chelates.[5]

Bis-chelate structures ***4c*****–*****12c***: Judging by the $\Delta E_{\mathbf{b-c}}$ values (Table 1), molecules **5** and **9**–**12** exist predominantly in the symmetric bis-chelate form **c,** which is characterized by the pentacoordination of both silicon atoms with virtually flat five-membered SiCNCO heterocycles.

On the PES of **6** we found two isomers very similar in energy and possessing an anchor structure, the first (**c**, $\lambda = 1$) has equivalent and the second ($\mathbf{c_u}$, $\lambda = 0$) slightly different internuclear Si–O distances ($\Delta d_{\mathrm{Si-O}} < 0.05$ Å). The symmetric form **6c** is more favorable (by 0.1 kcal mol^{-1}) than the nonsymmetric $\mathbf{6c_u}$ only if the zero-point energy (ZPE) is taken into account.

The anchor structures **4c**, **7c**, and **8c** are unstable and are related to the transition state ($\lambda = 1$) of the intramolecular "flip–flop" rearrangement of the degenerate mono-chelate $\mathbf{b} \rightleftarrows \mathbf{b}'$ forms of **4**, **7**, and **8**. However, the corresponding barriers are not high (<4 kcal mol^{-1}). Therefore, molecules **4b**, **7b**, and **8b** may be considered to be symmetric in a dynamic sense. This conclusion is consistent with the equivalence of the silicon nuclei observed experimentally in the ^{29}Si NMR spectra of **4**.[2]

The change in the status of the bridge structure for **5c**, **6c**, and **9c**–**12c** from a PES minimum to a transition-state structure for **4c**, **7c**, and **8c** is associated with the potential function describing the movement of the silicon atoms of **4**–**12** relative to the carbonyl group. This function, $\Delta E^{d_{\mathrm{Si-Si}}} = \mathrm{f}(q)$, where $E^{d_{\mathrm{Si-Si}}}$ is the total energy of the studied molecules at a fixed internuclear Si1–Si2 distance and $q = (d_{\mathrm{Si1-O}} - d_{\mathrm{Si2-O}})/2$,

Table 3. Selected bond and bridge lengths, angles, and structural characteristics (η_e) of the pentacoordinate silicon atom for stable isomers of **4**, **7**–**9**, and **12** calculated at the B3LYP/6-31G* and MP2/6-31G* (in italics) levels of theory.

	d_{Si-Si} [Å]	d_{Si1-O} [Å]	d_{X1-Si1} [Å]	$d_{C1=O}$ [Å]	X-Si1-Y [°][a]	Y-Si1-Y [°]	C1-O-Si1 [°]	Si1-C2-N1-C1 [°]	η_e [%]
4a			2.120	1.239	107.2	112.9		−95.1	
			2.093	*1.245*	*107.5*	*113.0*		*−96.2*	
4b		2.246	2.209	1.260	98.7	118.0	110.5	−3.5	88
		2.219	*2.173*	*1.266*	*99.5*	*118.4*	*110.1*	*−6.2*	*86*
4b$_c$	5.005	2.441	2.174	1.257	100.8	117.6	107.5	1.4	79
		(2.731)[b]	(2.144)		(103.6)	(115.9)	(101.2)	(40.3)	
	4.803	*2.338*	*2.151*	*1.266*	*100.4*	*118.5*	*108.4*	*0.5*	*82*
		(2.643)	*(2.118)*		*(103.4)*	*(116.8)*	*(101.2)*	*(44.7)*	
7a			2.068	1.230	108.8	108.0		−103.5	
7b		2.037	2.164	1.268	97.3	116.5	113.0	−1.7	91
8a			2.073	1.231	109.2	109.4		−99.6	
8b		2.025	2.172	1.270	97.1	116.9	113.0	−4.4	92
9a			1.677	1.235	110.9	108.3		−105.5	
9b		2.339	1.702	1.250	105.6	113.8	108.4	−14.5	60
9c	4.688	2.454	1.693	1.254	107.2	113.2	106.6	−18.6	50
12a			1.893	1.233	109.3	108.4		−98.0	
12b		2.558	1.909	1.239	105.8	113.4	105.2	−21.6	41
12c	5.041	2.625	1.905	1.243	106.6	112.8	104.0	−28.0	35
	4.958	*2.599*	*1.898*	*1.250*	*106.8*	*113.1*	*103.1*	*−36.2*	*35*

[a] Mean value of the X1-Si1-Y1 and X1-Si1-Y2 angles. [b] The structural parameters for the second silicon atom are given in parentheses.

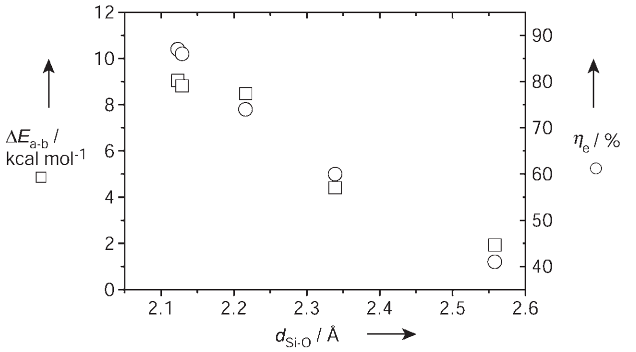


Figure 1. Relationship between the pentacoordinate character of the Si1 atom (η_e), the complex stability ($\Delta E_{\mathbf{a-b}}$), and the Si1–O bond length (d_{Si-O}) of the mono-chelate forms **5b**, and **9b**–**12b** as calculated at the B3LYP/6-31G* level of theory.

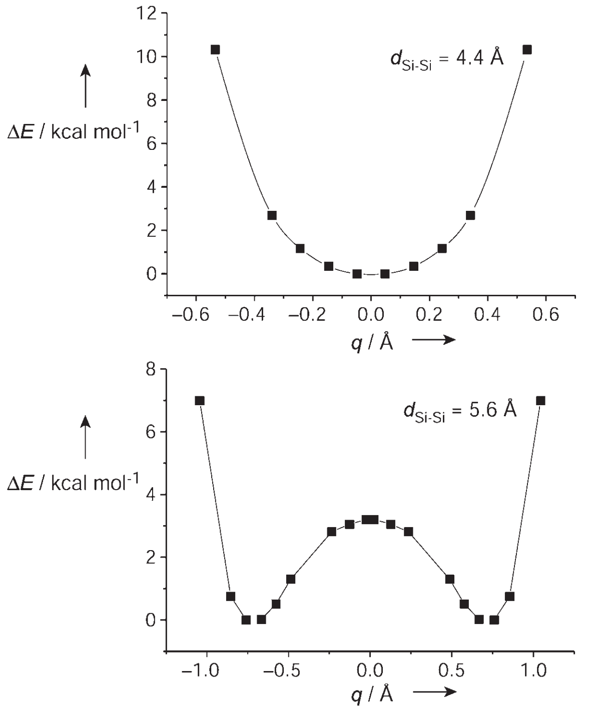


Figure 2. MP2/6-31G*//HF/6-31G* sections through the potential energy surface of molecule **5** on the coordinate d_{Si-Si} = const.

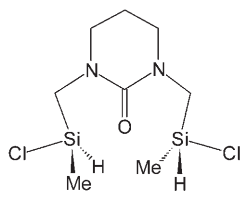
an antisymmetric coordinate, was determined at the MP2/6-31G*//HF/6-31G* level of theory by using molecule **5** as an example (see Figure 2).

At relatively large d_{Si-Si} values (>5 Å) the $\Delta E^{d_{Si-Si}} = f(q)$ relationship has a double-hollow character. The minima of this function correspond to the mono-chelate forms **b** and **b′**, and its transition state is related to a symmetric bridge structure. The main change in the form of the potential is observed at $d_{Si-Si} < 5$ Å; it becomes a single-hollow with the isomer **c** possessing an anchor structure at its minimum.

It is important to emphasize that the sections through the PES on the coordinate d_{Si-Si} = const presented in Figure 2 are similar to those known for the symmetric classic charged hydrogen-bridged structures of the $[A-H-A]^{\ddagger}$ type.[6]

Among the factors that favor a decrease in the internuclear Si–Si distance in the **c** form of the cycloureas **4**–**12** and thereby increase the probability of their existence in the form of stable intramolecular silicon complexes possessing an anchor structure, mention should be made of the following points.

Decreasing the size of the equatorial ligands Y: According to the results of the calculations at the B3LYP/6-31G* level of theory, the d_{Si-Si} values in the series **4c**–**8c** increase in the following sequence: F (**6c**: 4.22 Å) < H (**5c**: 4.37 Å) < Br (**8c**: 4.85 Å) < Cl (**7c**: 4.92 Å) < CH_3 (**4c**: 5.15 Å). The structures **4c**, **7c**, and **8c** with the bulky equatorial substituents CH_3, Cl, and Br are characterized by relatively large d_{Si-Si} values and do not correspond to PES minima. By replacing one equatorial methyl group at each silicon atom of **4** with a less bulky hydrogen atom we obtained **13**. Its bis-chelate form is a PES minimum being energetically more advantageous than the mono-chelate **13b** by 2.8 kcal mol^{-1}. Symptomatically, when the equatorial hydrogen atoms in **5c** are replaced by fluorine atoms, being more electronegative and having a larger size, a significant decrease, judging by the ΔE_{b-c} values, in the stability of corresponding species **6c** is observed though the d_{Si-Si} distance is shorter.



13

The transition from the mono-chelate **b** to the bis-chelate **c** forms of **4**–**12** results (see Table 2 and Table 3) in an appreciable lengthening of the Si←O bond ($\Delta d_{Si-O} = d_{Si-O}{}^{c} - d_{Si-O}{}^{b}$) and a decrease in the pentacoordinate character of the silicon atoms. The main reason for this apparently lies in repulsive interequatorial Y–Y interactions that are typical of anchor structures. The Δd_{Si-O} values do not exceed 0.2 Å for molecules **5** and **9**–**12** and exceed 0.4 Å for **4**, **7**, and **8**. Molecule **12** with the least stable mono-chelate form experiences the smallest change in d_{Si-O} ($\Delta d_{Si-O} = 0.06$ Å) of **4**–**12** upon **b**→**c** isomerization.

Increasing the electronegativity of the axial substituents X: The calculations at the B3LYP/6-31G* level of theory predict that values of d_{Si-Si} for the bis-chelate forms of the dihydrides **5** and **9**–**12** increase in the order **11c** (4.33 Å) < **5c** (4.37 Å) < **10c** (4.44 Å) < **9c** (4.69 Å) < **12c** (5.04 Å), which suggests a decrease in the bridging Si←O→Si bond distance with increasing nucleofugality of the axial substituents X (Me < HO < F < Cl < Br). At the same time, judging by the ΔE_{b-c} values (Table 1), the stability of the anchor structures **5c** and **9c**–**12c** increases with increasing electronegativity (Me < HO < Br < Cl < F) rather than nucleofugality of X, meanwhile the stability of mono-chelates **5b** and **9b**–**12b** relative to non-chelates **5a** and **9a**–**12a** increases with increasing X nucleofugality.

Increasing the donor capability of the carbonyl group: Replacement of one of the hydrogen atoms at each of the C4 and C5 carbon atoms of the urea CNCCCN cycle of bis-chelate **5c** with a σ-donor SiH_3 group shortens the internuclear Si···Si distance by 0.110 Å and the Si←O bond by 0.037 Å and markedly increases (by 0.9 kcal mol^{-1}) its stability with respect to the related **b** form. The predicted lengthening (by 0.003 Å) of the C–O bond in isomer **c** corresponds to an increase in the donor capability of the oxygen atom. This example strongly suggests that variation of the surroundings of the carbonyl group can efficiently affect the geometry and stability of the anchor forms of molecules **4**–**12**.

Transition from the gas phase to polar solution: According to the calculations at the B3LYP/6-31G*-SCRF level of theory (Table 4), a polar medium (with dielectric constant $\varepsilon = 45.0$) results in a significant increase in the anchor Si←O→Si bond strength (a decrease in d_{Si-Si} and d_{Si-O} values) of bis-chelates **5c** and **6c** and their increased stabilization with respect to mono-chelates **5b** and **6b**.[7]

The energy differences between the nonequilibrium **c** and equilibrium **b** forms of compounds **4** and **7** in polar solution are greater than those in the gas phase. Curiously, in solution, as opposed to in the gas phase, molecule **6** has predominantly a nonsymmetrical $\mathbf{c_u}$ structure whilst conformer **b** of compound **4** is more stable than $\mathbf{b_c}$.

Table 4. Changes in the Si–Si bridge (Δd_{Si-Si}) and Si–O (Δd_{Si-O}) bond distances of the bis-chelate species **4c**–**7c** and their stability ($\Delta\Delta E_{b-c}$) upon transition from the gas phase (B3LYP/6-31G*) to polar solution (B3LYP/6-31G*-SCRF, $\varepsilon = 45.0$).

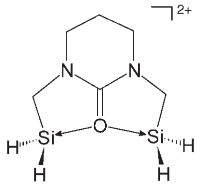
	4 (X = Cl, Y = Me)	**5** (X = Cl, Y = H)	**6** (X = Cl, Y = F)[a]	**7** (X = Cl, Y = Cl)
Δd_{Si-Si} [Å]	−0.063	−0.229	−0.219	−0.148
Δd_{Si-O} [Å]	−0.030	−0.103	−0.101 −0.097	−0.070
$\Delta\Delta E_{b-c}$ [kcal^{-1}mol^{-1}]	−4.34[b]	1.48	1.22	−0.02

[a] Data for the nonsymmetric bis-chelate form $\mathbf{6c_u}$, which is 1.9 kcal mol^{-1} more favorable in the polar solution than the symmetric **6c**. [b] In polar solution the mono-chelate isomer $\mathbf{b_c}$ is energetically less favorable (by 2.9 kcal mol^{-1}) than isomer **b**.

Thus, polar media ensure the stabilization of the anchor structures of *Si,Si'*-substituted *N,N'*-bis(silylmethyl)propylene ureas stable in the gas phase and increase the barrier to the "flip–flop" rearrangement of the pendulum structures.

The X–Si bonds at the pentacoordinated silicon atom in bis-chelates **5c**, **6c**, and **9c**–**11c** are markedly longer than those at the tetracoordinated silicon in non-chelates **5a**, **6a**, and **9a**–**11a**, and the shorter the d_{Si-Si} bridge distance in **5c**, **6c**, and **9c**–**11c**, the greater the difference between these bonds. Such an effect (existence of an inverse correlation between the axial bonds) is typical of TBP silicon atom compounds and has been repeatedly observed experimentally.[4a,c,d,8]

An important consequence of the interaction of the two electrophilic silicon sites in the **c** form (or single site in form **b**) of compounds **5**, **6**, and **9**–**12** with the carbonyl oxygen is a lengthening by 0.01–0.04 Å of the C–O bond.[9] Relatively large Δd_{C-O} [$\Delta d_{C-O} = d_{C-O}{}^{a} - d_{C-O}{}^{c(b)}$] values occur for structures **5c**, **6c**, and **11c** which have the strongest O→Si bonds. In magnitude the increasing Δd_{C-O} values compare well with those known for complexes of Lewis acids (for example, $AlCl_3$, AlH_3, BF_3, and BH_3)[10] with carbonyl-containing molecules and point to a noticeable activation of the C–O bond in the formation of O–Si chelate forms of the studied cycloureas. In marked contrast to the situation with intermolecular complexes,[10] a reduction in the stability of **5c**, **6c**, and **9c**–**12c** (see Table 1, Table 2, and Table 3) is accompanied by a decrease rather than an increase in the Si-O-C bond angle describing the approach of the acid center to the O−C fragment.



14

A maximum Δd_{C-O} value (0.15 Å according to calculations at the B3LYP/6-31G* level of theory) is observed for the dication **14**, which is characterized by the shortest Si···Si contact ($d_{Si-Si} = 3.503$ Å; $d_{Si-O} = 1.879$ Å) of the species studied in this work.

The results of the computations on the **a**–**c** isomers of molecules **4**–**6**, **10**, and **12** at the B3LYP/6-31G* and MP2/6-31G* levels of theory are in good agreement (see Table 1, Table 2, and Table 3). Differences in the values of the torsion and bond angles do not exceed 5 and 1°, respectively, and the maximum difference in the bond lengths (<0.06 Å) is reached when estimating the Si−O and X−Si bond distances of the hypervalent X−Si←O fragment. Judging by the $\Delta E_{\mathbf{a-b}}$ and $\Delta E_{\mathbf{b-c}}$ values (without the ZPE correction), the B3LYP/6-31G* method underestimates (by less than 1 kcal mol^{-1}) the stability of the chelate **b** and **c** forms compared with the MP2/6-31G* method.

By using **10** as an example, we found that extension of the basis set from 6-31G* to 6-311+G* at the MP2 and B3LYP levels of theory results in insignificant changes in the estimates of the structural and energetic characteristics of **4**–**12**. At the B3LYP level of theory, the bond lengths, bond angles, and $\Delta E_{\mathbf{b-c}}$ values change by <0.03 Å, <2°, and <0.4 kcal mol^{-1}, and with MP2 by <0.02 Å, <2°, and <0.1 kcal mol^{-1}, respectively. Note that by using the 6-311+G* rather than the 6-31G* basis set the quantitative discrepancy between the results of the MP2 and B3LYP calculations for **4**–**12** may decrease. Indeed, the values of d_{Si-O}(B3LYP)−d_{Si-O}(MP2) and $\Delta E_{\mathbf{b\text{-}c}}$(B3LYP)−$\Delta E_{\mathbf{b\text{-}c}}$(MP2) for **10a** are equal to 0.046 Å and 0.79 kcal mol^{-1} using the 6-31G* basis set and 0.029 Å and 0.50 kcal mol^{-1} using the 6-311+G* basis set, respectively.

The nature of the Si←O bond in the mono-chelate forms and the Si←O→Si bonds in the bis-chelate forms of *Si*,*Si*′-substituted *N*,*N*′-bis(silylmethyl)propylene ureas: By using compound **5** as an example, we determined that there are three maxima [(3,−3) critical points] of the negative Laplacian of the electron density [$-\nabla^2\rho(\mathbf{r}_c)$] in the vicinity of the carbonyl oxygen atom of the non-, mono-, and bis-chelate isomers of **4**–**12**, as in the formamide molecule.[11] One of them, located in the internuclear C···O region, is of little interest to us. The other two correspond to the electron pairs (EP)[12] that can interact with the silicon atoms. The electron properties of these maxima differ noticeably in forms **a**–**c** (Table 5). The EPs of the oxygen atom in the bridge structure **c** are more delocalized than the unambiguously nonbonding (lone) EPs (LPs) of the non-chelate isomer **a** and are characterized by a smaller radial curvature μ_3 and electron-density concentration $\nabla^2\rho(\mathbf{r}_c)$ and a greater distance from the oxygen atom r_0. According to Bader et al.,[13] this reflects their bonding character. In the mono-chelate form **5b** the electron properties of maximum 1 (see Table 5) are similar to those of **5c** and the properties of maximum 2 resemble those of **5a**. Both EPs in the anchor structure and one in the pendulum complex are oriented toward the corresponding silicon atoms. This is evident from a comparison of the 1−O−2 angle between the oxygen electron pairs and the Si1−O−Si2 bond angle of **5c** as well as the 1−O−C1 and Si1−O−C1 angles of **5b**.

As postulated in the well-known structural model of Gillespie et al.,[14a] the bonding EPs should be smaller in size than the nonbonding ones. A graphic illustration (see Figure 3) of the shape and size of the carbonyl oxygen EPs in isomers **a**–**c** of molecule **5** was obtained by locating the

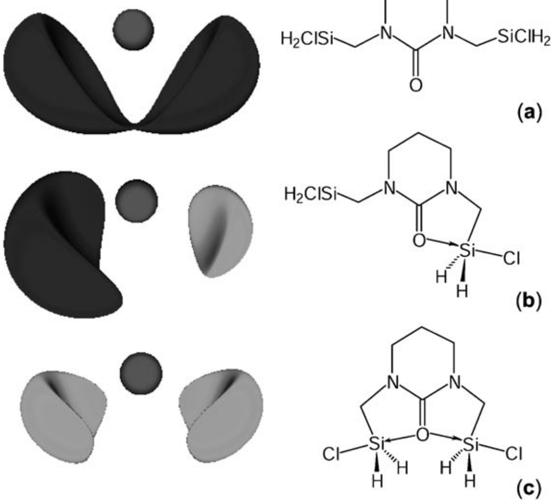


Figure 3. Domains of the electron localization function [ELF=0.86, MP2-(full)/6-31G* wave functions] in the vicinity of the oxygen atom of the non-chelate (**a**), mono- (**b**), and bis-chelate (**c**) forms of molecule **5**.

Table 5. Properties [r_0, $-\nabla^2\rho(\mathbf{r}_c)$, μ_3][a] of the two maxima of the negative density Laplacian $-\nabla^2\rho(\mathbf{r}_c)$ and bond angles between atoms and LPs in the vicinity of the carbonyl group oxygen atom for species **5a**–**c** determined at the MP2/6-31G* level of theory.

Form	Maximum[b]	r_0 [Å]	$-\nabla^2\rho(\mathbf{r}_c)$ [e a_0^{-5}]	μ_3	1-O-2[c] [°]	Si1-O-Si2 [°]	1-O-C1[d] [°]	Si1-O-C1 [°]
a	1 (2)	0.639	5.629	637.6	147.9		106.1	
b	1	0.649	4.862	549.3	145.6		110.9	110.6
	2	0.640	5.475	624.9			103.5	
c	1 (2)	0.648	4.943	561.4	142.8	142.0	108.6	109.0

[a] r_0 is the distance from the respective maximum to the oxygen atom and μ_3 is the radial curvature of $\nabla^2\rho$. [b] The maximum denoted by 1 is the maximum located at the side of Si1 and that denoted by 2 is located at the side of Si2. [c] The bond angle between the LPs of the oxygen atom. [d] The bond angle between the atoms C1, O, and one LP of the O atom.

domains of the electron localization function[15] in the vicinity of the oxygen atom. Figure 3 shows clearly that the EPs in the anchor form are markedly smaller in size than those in the non-chelate form, whereas in the mono-chelate form one localization domain (oriented towards the Si1 atom) is reduced in size relative to the another.

Selected results of the topological analysis of the electron density ρ of the stable chelate forms of **4**–**12** by the AIM approach[11] at the B3LYP/6-31G* level of theory are presented in Table 6. They confirm the bis-chelate structures of **5c**, **6c**, and **9c**–**12c** by the detection of two (3,−1) bond critical points (BCPs) in the O−Si1 and O−Si2 internuclear regions of the Si···O···Si bridge and two (3,+1) ring critical points (RCP) in the centers of five-membered SiCNCO heterocycles. Mono-chelates **4b**–**12b** are characterized by only one BCP(Si−O) and one RCP in the SiCNCO fragment. The molecular graph of the chelate forms of molecule **5** (Figure 4), which follows from the quantum-topological analysis of the electron distribution, is consistent with their suggested structures and is typical of the chelate forms of **4**–**12**.

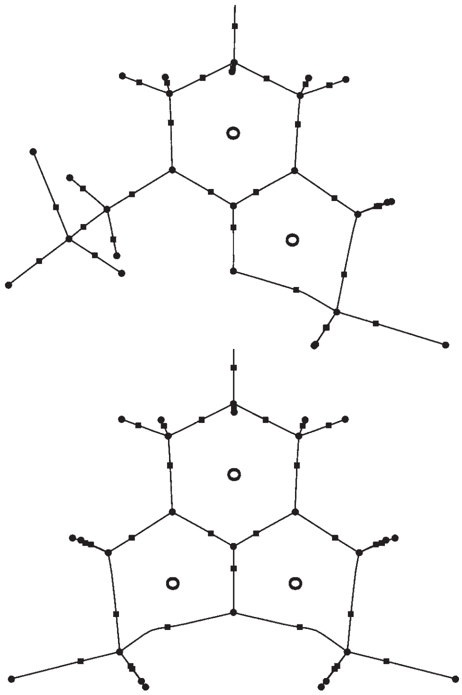


Figure 4. Molecular graphs of the mono-chelate **b** (top) and bis-chelate **c** (bottom) isomers of molecule **5**. The bond critical points are denoted by solid squares, and the ring critical points are designated by large open cycles.

At the BCP(Si←O) of the pendulum and anchor isomers of **4**–**11**, the Laplacian of the electron density $[\nabla^2\rho(\boldsymbol{r}_\mathrm{c})]$ is positive whilst the electron energy density $[E(\boldsymbol{r}_\mathrm{c})]$ is negative (see Table 6). Analogous AIM characteristics are typical of all the X−Si bonds known in the literature (X = O, NH, C, Cl, Br) regardless of the coordination number (4, 5, or 6) of the silicon atom.[7f,16] Bonds with such topological characteristics $[\nabla^2\rho(\boldsymbol{r}_\mathrm{c})>0$ and $E(\boldsymbol{r}_\mathrm{c})<0]$ have been assigned[16a,17] to the intermediate type of interatomic interactions (transit closed shell class): they are ionic as judged by the magnitude and positive sign of $\nabla^2\rho(\boldsymbol{r}_\mathrm{c})$ at the related BCPs, but covalent based on the negative sign and the absolute value of $E(\boldsymbol{r}_\mathrm{c})$. We used the criteria of Cremer and Kraka[18a,b] to gain an insight into the nature of the Si←O bonds in **4**–**12**, that is, to determine which component, ionic or covalent, is dominant in these bonds. A corresponding analysis of the topological properties at BCP(Si←O) (see Table 6) suggests the Si←O bonding in chelate structures **4**–**11** (excluding species **9c**) has a highly polar, covalent character. The O···Si interactions in **9c**, **12b**, and **12c** may be assigned to ionic–type bonding. These species are characterized by the largest $d_{\mathrm{Si-O}}$ values in the series **4**–**12**.

Table 6. Electron density $[\rho(\boldsymbol{r}_\mathrm{c})]$, Laplacian $[\nabla^2\rho(\boldsymbol{r}_\mathrm{c})]$, and electron energy density $[E(\boldsymbol{r}_\mathrm{c})]$ at (3,−1) bond critical points of the Si−O bonds in the mono- and bis-chelate forms of **4**–**12** calculated at the B3LYP/6-31G* level of theory.[a]

	X	Y	$\rho(\boldsymbol{r}_\mathrm{c})$ [e Å^{-3}]	$\nabla^2\rho(\boldsymbol{r}_\mathrm{c})$ [e Å^{-5}]	$E(\boldsymbol{r}_\mathrm{c})$ [hartree Å^{-3}]	Bond character[b]
4b	Cl	Me	0.275	1.137	−0.09	weakly covalent
$\mathbf{4b}_\mathbf{c}$	Cl	Me	0.203	1.087	−0.04	weakly covalent
			0.132[c]	1.171	0.00	ionic
5b	Cl	H	0.325	2.077	−0.12	weakly covalent
5c	Cl	H	0.240	1.222	−0.06	weakly covalent
6b	Cl	F	0.406	3.326	−0.16	weakly covalent
6c	Cl	F	0.274	1.034	−0.09	weakly covalent
7b	Cl	Cl	0.407	2.799	−0.17	weakly covalent
8b	Cl	Br	0.416	3.047	−0.17	weakly covalent
9b	OH	H	0.234	1.190	−0.06	weakly covalent
9c	OH	H	0.193	1.187	−0.03	ionic
10b	F	H	0.281	1.455	−0.09	weakly covalent
10c	F	H	0.226	1.243	−0.05	weakly covalent
			0.227[d]	1.389	−0.05	weakly covalent
11b	Br	H	0.329	2.153	−0.12	weakly covalent
11c	Br	H	0.247	1.259	−0.07	weakly covalent
12b	Me	H	0.170	1.096	−0.02	ionic
12c	Me	H	0.154	1.094	−0.02	ionic

[a] 1 au of $\rho = 1\,\mathrm{e\,a_0^{-3}} = 6.748\,\mathrm{e\,Å^{-3}}$; 1 au of $\nabla^2\rho = 1\,\mathrm{e\,a_0^{-5}} = 24.099\,\mathrm{e\,Å^{-5}}$; 1 au of $E(\boldsymbol{r}_\mathrm{c}) = 1\,\mathrm{e^2\,a_0^{-4}} = 6.748$ hartree Å^{-3}. [b] Determined according to the quantitative criteria given by Cremer and Kraka and coworkers.[18] [c] Data for the second silicon atom. [d] Geometry optimization and wavefunction computations were performed at the B3LYP/6-311+G(d) level of theory.

Species **5c**, **6c**, and **9c**–**12c** are characterized by smaller $\rho(\boldsymbol{r}_\mathrm{c})$ values and a less negative $E(\boldsymbol{r}_\mathrm{c})$ value at BCP(Si−O) than **5b**, **6b**, and **9b**–**12b**. This supports the conclusion made earlier (comparing the $d_{\mathrm{Si-O}}$ values) about the weakening of the Si−O bonds on going from mono- to bis-chelates.

The mono-chelate isomer $\mathbf{b}_\mathbf{c}$ of molecule **4** has two BCPs-(Si−O) (see Table 6). However, the density characteristics of these BCPs suggest the formation of a covalent bond between only the oxygen and Si1 atoms with the O···Si2 interaction being of an ionic nature.

With **10c** we have demonstrated that the basis-set size only slightly affects the values of $\rho(\boldsymbol{r}_c)$ and $E(\boldsymbol{r}_c)$ used for determining the nature of the bond interaction using the criteria of Cremer and Kraka.[18a,b]

Taking into account the mechanism of formation (involving a lone electron pair of the donor center) of the Si←O bond in the molecules studied, this bond should be described as a dative or a donor–acceptor bond.[19] A change in the nature of such bonds from covalent to ionic, depending on the properties of the donor and acceptor fragments, has been demonstrated with a wide range of intermolecular complexes using the AIM approach.[20] The results presented in Table 6 show that a similar situation takes place for the dative Si←O bonds in the series of chelate structures **4–12** as well, according to the AIM criteria of Cremer and Kraka and co-workers.[18]

As a rule, the relatively low values of $\rho(\boldsymbol{r}_c)$ and $E(\boldsymbol{r}_c)$ at the (3,−1) critical points of the dative bonds pose major problems when determining the nature of such bonds.[16c,17b,21] In connection with this it is worthwhile using the strength of the ELF analysis.[15] The examples of molecules **5c** and **12** demonstrate that the ELF analysis and the analysis based on the AIM criteria of Cremer and Kraka and co-workers[18] (see Table 6) lead to similar conclusions concerning the character of the Si←O bonds in chelates **4–12**. Indeed, the valent basin V(Si,O) in **5c** has a disynaptic character, that is, according to Silvi and Savin,[15b] the EPs of the carbonyl oxygen atom are shared between the cores of the silicon and oxygen atoms. This is indicative of the covalent nature of the Si←O bonds in **5c**. In contrast, the synaptic order of the basins of weaker Si←O dative bonds in **12c** is equal to unity. In this case the EPs belong only to the oxygen atom and the Si←O bonds are ionic.

The results of the NBO analysis of **5c** and **9c–12c** presented in Table 7 give us an insight into the donor–acceptor interaction between the C=O and $XSiY_2$ fragments of the anchor structures on an orbital level. They are indicative of the involvement of both LPs (LP1 and LP2) of the carbonyl oxygen in the formation of the X−Si←O→Si−X bridge. An increase in the acceptor ability of the Si−X bond (Si−CH_3 < Si−OH < Si−F < Si−Cl < Si−Br) in **5c** and **9c–12c** is accompanied by a decrease in the $d_{\text{Si-O}}$ values and an increase in the energy of interaction of the oxygen LPs with the antibonding orbitals ($\sigma^*_{\text{Si-X}}$) of the Si−X bonds ($E_{\text{LP},\sigma^*_{\text{Si-X}}}$) and low electron-density transfer from LP1 and LP2 to $\sigma^*_{\text{Si-X}}$ (Figure 5). Similar behavior has previously been established for the O−Si mono-chelates that possess a Si←O coordination bond.[16a,b]

Table 7. NBO characteristics [Δn(LP), $n(\sigma^*_{\text{Si-X}})$, $E_{\text{LP},\sigma^*_{\text{Si-X}}}$] of bis-chelates **5c** and **9c–12c** according to HF/6-31G*//B3LYP/6-31G* calculations.

	X	Y	Δn(LP1) [e][a]	Δn(LP2) [e][a]	$n(\sigma^*_{\text{Si-X}})$ [e][b]	$E_{\text{LP},\sigma^*_{\text{Si-X}}}$ [kcal^{-1}mol^{-1}][c] LP1	LP2
11c	Br	H	0.091	0.135	0.066	12.8	7.2
5c	Cl	H	0.087	0.135	0.063	11.4	6.6
10c	F	H	0.074	0.131	0.061	8.9	5.7
9c	OH	H	0.063	0.129	0.051	7.0	4.6
12c	CH_3	H	0.051	0.126	0.034	4.7	3.1

[a] $\Delta n(\text{LP}) = 2 - n(\text{LP})$ is a decrease in the population (n) of the orbital (LP1 or LP2) of the oxygen atom electron pair with respect to the population of the unperturbed LP orbital ($n = 2$). [b] Population of the antibonding orbital ($\sigma^*_{\text{Si-X}}$) of the Si−X bond. [c] The energy of interaction between the LP1 (LP2) orbital of the oxygen atom and $\sigma^*_{\text{Si-X}}$ (calculated using second-order perturbation theory).

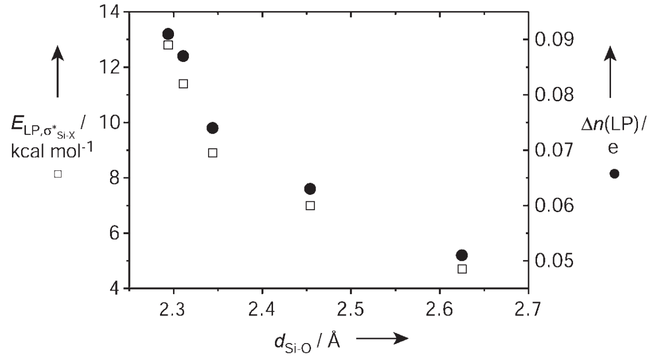


Figure 5. Relationship between the energy of interaction of the oxygen LP1 orbital with $\sigma^*_{\text{Si-X}}$ ($E_{\text{LP},\sigma^*_{\text{Si-X}}}$), the extent of the charge transfer from LP1 to $\sigma^*_{\text{Si-X}}$ [Δn(LP1)], and the Si1−O bond length ($d_{\text{Si-O}}$) for the bis-chelate structures **5c** and **9c–12c** according to calculations at the B3LYP/6-31G* level of theory.

The values of $E_{\text{LP},\sigma^*_{\text{Si-X}}}$ for LP1 and LP2 differ significantly. Consequently we have considered a situation in which only one atomic orbital (AO) of the oxygen atom (LP1) interacts with the orbitals of two X−Si bonds when performing a qualitative analysis of the conditions favorable for the electron stabilization of the bis-chelate forms of *Si,Si′*-substituted *N,N′*-bis(silylmethyl)propylene ureas. Corresponding to this case, a simple MO diagram (one p-type AO from each atom) for the formation of Ψ_1–Ψ_5 MOs of the X−Si←O→Si−X moiety is presented in Figure 6.

The formation of the bonding Ψ_1 MO and the lowering (as a consequence of the interaction between LP1 and $\sigma^*_{\text{Si-X}}$) of the two-node Ψ_3 MO relative to the LP1 level can pro-

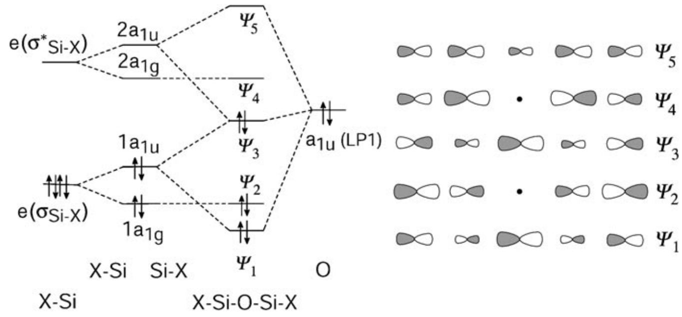


Figure 6. Formation of MOs of the X−Si←O→Si−X bridge fragment of the stable anchor complexes of *Si,Si′*-substituted *N,N′*-bis(silylmethyl)propylene ureas from the $\sigma_{\text{Si-X}}$ and $\sigma^*_{\text{Si-X}}$ orbitals of the Si−X bonds and one p-type carbonyl oxygen LP.

vide a five-center six-electron (5c-6e) orbital stabilization of the anchor structures. Indeed, among the molecular orbitals of **4c**–**12c** one can recognize those that correspond, according to their amplitudes and node properties, to composite Ψ_1–Ψ_5 MOs of the X−Si←O→Si−X fragment (see Figure 6 and Figure 7). This was demonstrated with **5c** at the HF/6-31G*//B3LYP/6-31G* level of theory.

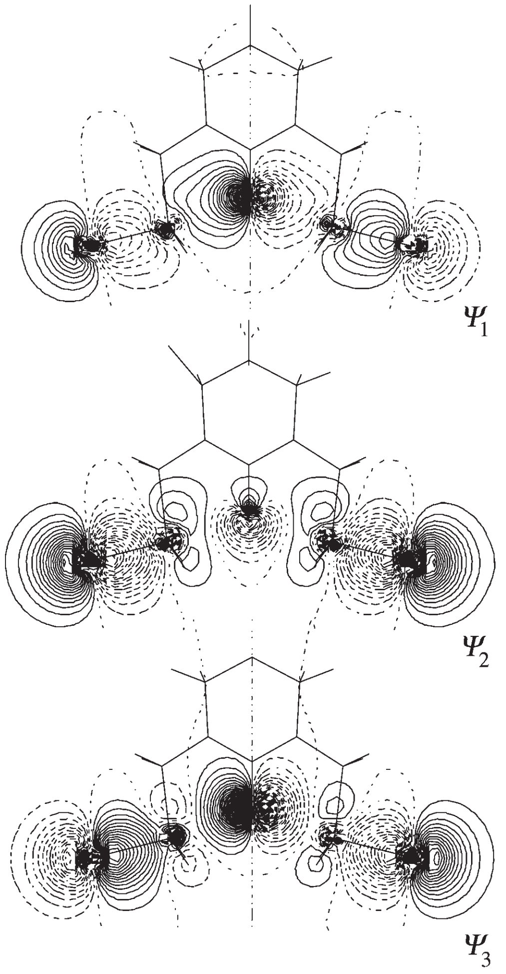


Figure 7. Contour plots of the HF/6-31G*//B3LYP/6-31G* MOs of the X−Si←O→Si−X fragment of species **5c** corresponding to the reconstructed filled Ψ_1–Ψ_3 orbitals. The increment between successive contours is 0.01 bohr$^{-3/2}$. For clarity we have shown only the atomic orbitals of the X, silicon, and oxygen atoms.

The results of this investigation will hopefully enable the targeted synthesis of the first representatives of neutral intramolecular silicon complexes possessing the previously unknown multicenter X−Si←O→Si−X bond.

Conclusions

B3LYP and MP2 calculations virtually reject the existence of the studied *Si*,*Si'*-substituted *N*,*N'*-bis(silylmethyl)propylene ureas in their non-chelate forms. Their bis-chelate isomers, possessing electronegative axial (X = Cl, F, Br) and relatively small equatorial (Y = H, F) ligands at the silicon atom, are energetically more favorable (by more than 2 kcal mol^{-1}) than the mono-chelate isomers. Anchor structures with bulky substituents (Y = CH_3, Cl, Br) are the transition states of the "flip–flop" rearrangement of mono-chelates which possess a pendulum structure. The Si−C−N−C−O heterocycles in the mono- and bis-chelate forms are closed, according to the data from AIM and ELF analyses, by weak covalent Si←O bonds, which are stronger in the former than in the latter. In terms of MOs, the previously unknown type of bonding in the X−Si←O→Si−X moiety of the anchor chelates of *Si*,*Si'*-substituted *N*,*N'*-bis(silylmethyl)propylene ureas may be classified as a five-center, six-electron (5c-6e) bond.

Experimental Section

General methods: The basic computations on species **4**–**12** were performed with full geometry optimization at the B3LYP and MP2 levels of theory using the 6-31G* (and also the 6-311+G* for **5**) basis set in the Gaussian 98[22] package of programs. The stationary points on the potential energy surface (PES) corresponding to the B3LYP-calculated structures were identified by the number (λ) of negative Hessian eigenvalues. Sections through the PES of molecule **5** for $d_{\text{Si-Si}}$ = const were determined by varying the Si−O bond distances in the range of 1.8–2.7 Å and by optimizing all other geometrical parameters. The effect of solvent on the geometry of **4**–**12** was determined by using the Onsager reaction field cavity model (SCRF).[23] The Onsager radii of **4**–**12** were calculated quantum chemically using the procedure described by Wong et al.[24] The stability of the studied complexes was estimated as the difference in the total energies (corrected for zero-point vibrations) of the non- and mono-chelate forms in the case of the pendulum structures ($\Delta E_{\mathbf{a-b}}$) and as the difference in the total energies of the mono- and bis-chelate forms for the anchor structures ($\Delta E_{\mathbf{b-c}}$). Because of the insignificant effect of the correction for temperature on the values of $\Delta E_{\mathbf{a-b}}$ and $\Delta E_{\mathbf{b-c}}$ for **4**–**12** the Gibbs free energies and enthalpies have not been discussed in the text.[25] The pentacoordinate character of the silicon atom was determined using Equation (1),[1b] where θ_n are the equatorial angles at the silicon atom.

$$\eta_e = 1-[(120-{}^{1}\!/_{3}\sum_{n=1}^{3}\theta_n)/(120-109.5)] \qquad (1)$$

Analysis of the electron density in terms of the atoms-in-molecules (AIM) theory[11] was performed using the MORPHY1.0[26] program. The electron localization functions of Bekke and Edgecombe[15a] (ELF) were calculated using the TopMod[27] program package and visualized using the GOpenMol[28] package of programs. The molecular orbital (MO) and NBO[29] analyses were carried out on the B3LYP/6-31G* geometries and the HF/6-31G* wavefunctions.[30] Two-dimensional plots of the orbital amplitudes were generated using the PLTORB program of the GAMESS[31] package of programs.

Overview of the atoms-in-molecules (AIM) theory: According to Bader,[11] the topology of the electronic charge density [$\rho(\mathbf{r})$] gives an accurate mapping of the chemical concepts of atom, bond, and structure. The principal topological properties are summarized in terms of their critical points (CP). A bond critical point (BCP) is found between each pair of nuclei, which are considered to be linked by a chemical bond. BCPs are denoted as (3,−1) CPs, they are characterized by two negative curvatures (λ_1, λ_2) and one positive curvature (λ_3). The ring CPs possess a single negative curvature. Each BCP generates a pair of gradient paths originating at this CP and terminating at neighboring attractors [which behave topologically as local maxima in $\rho(\boldsymbol{r})$; usually attractors correspond to the nuclear positions]. This gradient path defines a line through the charge distribution linking the neighboring nuclei. Such a line is referred to as an atomic interaction line. The presence of an atomic interaction line in such an equilibrium geometry indicates that the atoms are bonded together.

The Laplacian of the electronic charge density $[\nabla^2\rho(\boldsymbol{r})]$ describes two extreme situations. In the first $\rho(\boldsymbol{r})$ is locally concentrated $[\nabla^2\rho(\boldsymbol{r})<0]$ and in the second it is locally depleted $[\nabla^2\rho(\boldsymbol{r})>0]$. Thus, a value of $\nabla^2\rho(\boldsymbol{r}_c)<0$ at a BCP is unambiguously related to a covalent bond, showing that charge has been shared. In closed-shell interactions, a value of $\nabla^2\rho(\boldsymbol{r}_c)>0$ is expected.

Cremer and Kraka and co-workers pointed out that an analysis of $\nabla^2\rho(\boldsymbol{r}_c)$ is not always sufficient to distinguish between covalent and closed-shell interactions.[18] The chemical bonding can be described sufficiently only when both the electron-density-based criteria and the energetic contributions are taken into account. They therefore proposed an analysis of the electronic kinetic-energy density $G(\boldsymbol{r}_c)$ and the electronic potential-energy density $V(\boldsymbol{r}_c)$ at the bond critical point since the magnitudes of both are related to the Laplacian by $2G(\boldsymbol{r}_c)+V(\boldsymbol{r}_c)={}^1\!/_4\nabla^2\rho(\boldsymbol{r}_c)$.[11] For covalent bonds it has been shown that the local energy density $E(\boldsymbol{r}_c)=G(\boldsymbol{r}_c)+V(\boldsymbol{r}_c)$ is less than zero.[18b] The sign of $E(\boldsymbol{r}_c)$ determines whether the accumulation of charge at a given point $\boldsymbol{r}$ is stabilizing $[E(\boldsymbol{r}_c)<0]$ or destabilizing $[E(\boldsymbol{r}_c)>0]$.[18,32]

Overview of the ELF analysis: The electron localization function (ELF) was introduced by Becke and Edgecombe as a "simple measure of electron localization in atomic and molecular systems", enabling regions of space associated with different electron pairs to be defined.[15,32b] The original formula is based on the Taylor expansion of the spherically averaged conditional same-spin pair probability density to find an electron close to a same-spin reference electron. This definition gives ELF values between 0 and 1, with large values when two antiparallel spin electrons are paired in space and small ones in regions between electron pairs. Considering the scalar character of the ELF function, analysis of its gradient field yields its attractors (local maxima) and its corresponding basins (domains). There are two types of basins: the core basins labeled by C(atom symbol) and the valence basins V(list of atoms). The valence basins are characterized by their synaptic order (the number of core basins with which they share a common boundary). Accordingly, they can be classified as mono-, di- and polysynaptic, corresponding to the lone pair, bicentric, and polycentric bonding regions, respectively. Monosynaptic basins are nonbonding, whereas di- and polysynaptic ones are bonding (corresponding to shared-electron interactions). According to Silvi and Savin,[15b] ELF analysis complements and augments the AIM theory.

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[1] a) K. Tamao, T. Hayashi, Y. Ito, M. Shiro, *J. Am. Chem. Soc.* **1990**, *112*, 2422–2424; b) K. Tamao, T. Hayashi, Y. Ito, M. Shiro, *Organometallics* **1992**, *11*, 2099–2114; c) K. Ebata, T. Inada, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **1994**, *116*, 3595–3596; d) D. Brondani, F. H. Carré, R. J. P. Corriu, J. J. E. Moreau, M. Wong Chi Man, *Angew. Chem.* **1996**, *108*, 349–352; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 324–326; e) T. Hoshi, M. Takahashi, M. Kira, *Chem. Lett.* **1996**, 683–684; f) I. Kalikhman, O. Girshbery, L. Lameyer, D. Stalke, D. Kost, *J. Am. Chem. Soc.* **2001**, *123*, 4709–4716.

[2] a) L. I. Belousova, O. B. Kozyreva, A. E. Pestunovich, V. A. Pestunovich, M. G. Voronkov in *The XVI International Conference on Organometallic Chemistry. Book of Abstracts*, Sussex, UK, July 10–15, **1994**, p. 331; b) A. I. Albanov, A. Bassindale, E. Belogolova, N. Chipanina, G. Gavrilova, N. Lazareva, V. Pestunovich, V. Sidorkin, P. Taylor, V. Turchaninov in *The 12th International Symposium on Organosilicon Chemistry. Program, Abstracts, and List of Participants*, Sendai, Japan, May 23–28, **1999**, p. 171.

[3] Only one theoretical work on complexes bearing two silicon atoms anchored by a donor atom has been published: L. P. Davis, L. W. Burggraf, M. S. Gordon, *Int. J. Quant. Chem.* **1992**, *44*, 691–698. In this paper ab initio and semiempirical methods have been applied to the study of anionic intermolecular complexes $[\mathrm{Y{-}SiH_3{-}D{-}SiH_3{-}Y}]^-$, where D = H, Me, $\mathrm{NH_2}$, OH, F, Cl.

[4] a) V. A. Pestunovich, V. F. Sidorkin, M. G. Voronkov in *Progress in Organosilicon Chemistry* (Eds.: B. Marciniec, J. Chojnowski), Gordon and Breach Science Publishers, New York, **1995**, pp. 69–82; b) V. F. Sidorkin, E. F. Belogolova, V. A. Pestunovich, *Izv. Akad. Nauk, Ser. Khim.* **1998**, 230–235; *Russ. Chem. Bull. (Engl. Transl.)* **1998**, *47*, 225–230; c) D. Kost, I. Kalikhman in *The Chemistry of Organic Silicon Compounds, Vol. 2*, *Part 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 1339–1445; d) M. G. Voronkov, V. A. Pestunovich, Yu. I. Baukov, *Metalloogan. Khim.* **1991**, *4*, 1210–1227; *J. Organomet. Chem. USSR (Engl. Transl.)* **1991**, *4*, 593–608.

[5] a) G. Klebe, J. W. Bats, K. Hensen, *J. Chem. Soc. Dalton Trans.* **1985**, 1–4; b) Yu. T. Struchkov, Yu. E. Ovchinnikov, A. G. Shipov, Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.* **1995**, 1774–1779; *Russ. Chem. Bull. (Engl. Transl.)* **1995**, *44*, 1705–1710.

[6] a) S. Scheiner, L. B. Harding, *J. Am. Chem. Soc.* **1981**, *103*, 2169–2173; b) S. Scheiner, *J. Phys. Chem.* **1982**, *86*, 376–382; c) R. M. Minyaev, *J. Struct. Chem.* **1986**, *27*, 140–163.

[7] a) The effect of the shortening of dative bonds in intramolecular silicon complexes under the influence of a polar medium has repeatedly been demonstrated at the theoretical level (see ref. [7b–f]) under the framework of SCRF and PCM models and has been supported by experimental investigations (see ref. [4a,4c,7g]); b) M. W. Schmidt, T. L. Windus, M. S. Gordon, *J. Am. Chem. Soc.* **1995**, *117*, 7480–7486; c) V. F. Sidorkin, E. F. Belogolova, V. A. Pestunovich, *J. Mol. Struct. (THEOCHEM)* **2001**, *538*, 59–65; d) E. F. Belogolova, V. F. Sidorkin *Izv. Akad. Nauk, Ser. Khim.* **2003**, 1392–1396; *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 1472–1476; e) S. G. Shevchenko, Yu. L. Frolov, A. V. Abramov, M. G. Voronkov, *J. Organomet. Chem.* **2005**, *690*, 2922–2933; f) V. F. Sidorkin, E. F. Belogolova, V. A. Pestunovich, *Organometallics* **2004**, *23*, 2389–2396; g) V. Pestunovich, S. Kirpichenko, M. Voronkov in *The Chemistry of Organic Silicon Compounds, Vol. 2*, *Part 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 1447–1537.

[8] a) V. F. Sidorkin, V. A. Pestunovich, M. G. Voronkov, *Usp. Khim.* **1980**, *49*, 789–813; *Russ. Chem. Rev. (Engl. Transl.)* **1980**, *49*, 414–438; b) E. Lukevics, O. A. Pudova, *Teor. Eksp. Khim. Khim. Geterotsikl. Soedin.* **1996**, 1605–1646; *Chem. Heterocycl. Compd. (Engl. Transl.)* **1996**, *32*, 1381–1422; c) R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927–950.

[9] In the open form **a** the $d_{\mathrm{C=O}}$ values are practically independent of the nature of X.

[10] T. J. LePage, K. B. Wiberg, *J. Am. Chem. Soc.* **1988**, *110*, 6642–6650.

[11] R. F. W. Bader, *Atoms in Molecules: a Quantum Theory*, Clarendon Press, Oxford, **1990**, p. 458.

[12] The presence of maxima of the negative Laplacian $-\nabla^2\rho$, that is, regions of local concentration of electron density ρ, is not a rigorous proof of the existence of real electron pairs (see ref. [11]).

[13] R. F. W. Bader, P. J. MacDougall, C. D. H. Lau, *J. Am. Chem. Soc.* **1984**, *106*, 1594–1605.

[14] a) R. J. Gillespie, R. S. Nyholm, *Q. Rev. Chem. Soc.* **1957**, *11*, 339–380; b) R. F. W. Bader, S. Johnson, T.-H. Tang, *J. Phys. Chem.* **1996**, *100*, 15398—15415.

[15] a) A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397–5403; b) B. Silvi, A. Savin, *Nature* **1994**, *371*, 683–686; c) see additional information and the literature on the ELF analysis at a legal part of the web site of the Max Planck Institute for the Chemical Physics of Solids (http://www.cpfs.mpg.de/ELF/).

[16] a) A. A. Korlyukov, K. A. Lyssenko, M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.* **2002**, 1314–1322; Russ. Chem. Bull. *(Engl. Transl.)*, **2002**, *51*, 1423–1432; b) E. F. Belogolova, V. F. Sidorkin, *J. Mol. Struct. (THEOCHEM)* **2004**, *668*, 139–145; c) N. Kocher, J. Henn, B. Gostevskii, D. Kost, I. Kalikhman, B. Engels, D. Stalke, *J. Am. Chem. Soc.* **2004**, *126*, 5563–5568; d) J. M. Anglada, C. Bo, J. M. Bofill, R. Crehuet, J. M. Poblet, *Organometallics* **1999**, *18*, 5584–5593; e) K. A. Lyssenko, A. A. Korlyukov, M. Yu. Antipin, S. P. Knyazev, V. N. Kirin, N. V. Alexeev, E. A. Chernyshev, *Mendeleev Commun.* **2000**, 88–90.

[17] a) V. G. Tsirel'son, *J. Phis. Khim.* **2000**, *74*, 1529–1532; *Russ. J. Phys. Chem. (Engl. Transl.)* **2000**, *74*, 1383–1386; b) G. Gervasio, R. Bianchi, D. Marabello, *Chem. Phys. Lett.* **2004**, *387*, 481–484.

[18] a) D. Cremer, E. Kraka, *Croat. Chem. Acta* **1984**, *57*, 1259–1281; b) D. Cremer, E. Kraka, *Angew. Chem.* **1984**, *96*, 612–614; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 627–628; c) J. P. Ritchie, S. M. Bachrach, *J. Am. Chem. Soc.* **1987**, *109*, 5909–5916; d) L. Olsson, C.-H. Ottosson, D. Cremer, *J. Am. Chem. Soc.* **1995**, *117*, 7460–7479; e) C.-H. Ottosson, D. Cremer, *Organometallics* **1996**, *15*, 5309–5320. f) According to Cremer and co-workers (see ref. [18d,18e]), the Si←O bonds were characterized as weak covalent ones if $\rho(\mathbf{r}_c)$ and $E(\mathbf{r}_c)$ at BCP(Si–O) were greater than some boundary values (about 0.2 e Å^{-3} and −0.04 hartree Å^{-3}, respectively), and they were assigned to ionic interactions at lesser values of $\rho(\mathbf{r}_c)$ and $E(\mathbf{r}_c)$. Rigorous quantitative criteria for the choice of boundary values for $\rho(\mathbf{r}_c)$ and $E(\mathbf{r}_c)$ are absent from the literature.

[19] a) A. Haaland, *Angew. Chem.* **1989**, *101*, 1017–1032; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992–1007; b) X. Krokidis, S. Noury, B. Silvi, *J. Phys. Chem. A* **1997**, *101*, 7277–7282.

[20] V. Jonas, G. Frenking, M. T. Reetz, *J. Am. Chem. Soc.* **1994**, *116*, 8741–8753.

[21] a) R. Bianchi, G. Gervasio, D. Marabello, *Inorg. Chem.* **2000**, *39*, 2360–2366.

[22] Gaussian 98w, version 5.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian Inc., Pittsburgh, PA, **1998**.

[23] a) J. G. Kirkwood, *J. Chem. Phys.* **1934**, *2*, 351–361; b) L. Onsager, *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493; c) M. Szafran, M. M. Karelson, A. R. Katritzky, J. Koput, M. C. Zerner, *J. Comput. Chem.* **1993**, *14*, 371–377, and references therein.

[24] M. W. Wong, K. B. Wiberg, M. J. Frisch, *J. Chem. Phys.* **1991**, *95*, 8991–8998.

[25] An insignificant effect of the temperature correction on the stability of compounds has been also observed for other intramolecular silicon complexes (see ref. [16b]).

[26] a) P. L. A. Popelier, *Comput. Phys. Commun.* **1996**, *93*, 212–240; b) P. L. A. Popelier, *Chem. Phys. Lett.* **1994**, *228*, 160–164.

[27] a) TopMod, S. Noury, X. Krokidis, F. Fuster, B. Silvi, Universite Pierre et Marie Curie, France, **1997**; b) S. Noury, X. Krokidis, F. Fuster, B. Silvi, *Computers & Chemistry* **1999**, *23*, 597–604.

[28] a) L. Laaksonen, *J. Mol. Graphics* **1992**, *10*, 33–34; b) D. L. Bergman, L. Laaksonen, A. Laaksonen, *J. Mol. Graphics* **1997**, *15*, 301–306.

[29] a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926; b) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **1995**.

[30] We have obtained similar results by NBO analysis using the Hartree–Fock (HF) and Kohn–Sham orbitals (KS, B3LYP method). Nonetheless, when considering the orbital structure of the molecules studied a preference was given to the HF orbitals as they are strictly one-electron and well-tried in contrast to the KS orbitals (see the discussion on the applicability of the KS orbitals in: R. Stowasser, R. Hoffman, *J. Am. Chem. Soc.* **1999**, *121*, 3414–3420).

[31] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347–1363.

[32] a) W. Scherer, P. Sirsch, D. Shorokhov, M. Tafipolsky, G. S. McGrady, E. Gullo, *Chem. Eur. J.* **2003**, *9*, 6057–6070; b) J. Molina, J. A Dobado, *Theor. Chem. Acc.* **2001**, *105*, 328–337.

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