Physical Chemistry

Studies of electronic structures of 1,1'-disubstituted silaoxacyclohexa-3,5-dienes

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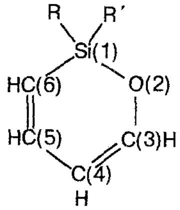
Spatial and electronic structures of 1,1'-disubstituted silaoxacyclohexa-3,5-dienes have been calculated using the AMPAC and HYPERCHEM 3.0 program packages. Interatomic distances, bond angles, torsion angles, atomic charges, electron densities, bond orders, parameters of localized molecular orbitals, *etc.* have been determined. Based on data obtained, it has been concluded that the —R'SiO— fragment in these molecules is a saturated structural linkage, which exhibits an inductive effect on the diene system; however, the linkage does not interact with the diene system by the mesomeric (resonance) mechanism.

Key words: silicon, quantum chemistry, electronic structure.

Structures and properties of unsaturated heterocyclic organosilicon compounds, which contain the —R'SiO— fragment in the cycle, have been studied repeatedly.[1–7] However, up to now, electronic structures of these molecules have not been studied in detail. We have calculated electronic and spatial structures of the simplest (of compounds synthesized to date) representatives of this series, namely, 1,1'-disubstituted silaoxacyclohexa-3,5-dienes:



R = H, Me, Cl, F
R' = H, Me, Vin, Cl,

All calculations were performed using the AMPAC and HYPERCHEM 3.0 program packages.[8,9]

Because only the structure of 1,1'-dichloro-1-sila-2-oxacyclohexa-3,5-diene (**1**) has been experimentally determined to date (see Ref. 7), there was a need to choose a computing method, which reproduces the structure of the molecule most adequately with the aim of using this method for obtaining structural parameters for other compounds of this series. Methods of molecular mechanics (MM2 force field) and quantum chemistry (LCAO MO SCF in the PM3 valence approximation[10]) adequately reproduce the principal structural features of molecule **1**. However, the best agreement between experimental and calculated values is achieved with the use of the MM method, in the framework of which the VESCF procedure (MMP) is used for optimization of the geometry of the diene fragment. Therefore, calculations of the structures of the studied molecules were thereafter performed with the use of the MM method. The obtained structural parameters of 1,1'-disubstituted silaoxacyclohexa-3,5-dienes are given in Table 1.

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Table 1. Chemical bond lengths (*d*/Å) and bond angles (ω/deg) in 1,1′-disubstituted 1-sila-2-oxacyclohexa-3,5-dienes

Bond	Experiment[7]	R = R′ = H	R = R′ = Me	R = Me, R′ = Vin	R = R′ = Cl	R = R′ = F
Si—O	1.653(9)	1.637	1.633	1.633	1.631	1.634
Si—R	2.032(6)	1.487	1.877	1.877, 1.862	2.026	1.559
Si—C	1.851(13)	1.880	1.859	1.860	1.858	1.859
C—O	1.317(9)	1.353	1.356	1.356	1.354	1.357
C=C	1.317(9)	1.347	1.346	1.346	1.349	1.351
C—C	1.481(9)	1.469	1.468	1.469	1.469	1.468
C—H	1.089(24)	1.103	1.104	1.104	1.103	1.104
Angle						
R—Si—R	108.5(6)	106.4	110.6	111.0	110.7	110.3
Si—O—C	134.3(15)	125.4	124.7	124.7	125.3	124.8
Si—C=C	121.4	118.3	118.4	118.4	118.6	118.5
C—C=C	123.7(7)	122.8	122.6	122.6	124.9	125.0
C—Si—O	97.2	104.3	105.2	105.2	104.7	105.0
O—C=C	119.7	123.9	124.0	124.1	123.7	124.0
C—C—H	119.0(10)	118.4	118.0	118.2	118.4	118.5

The LOCAL procedure of the AMPAC program package (see Ref. 8) was used for describing electronic structures of the studied compounds in terms of localized molecular orbitals. Data obtained for molecule **1** are given in Table 2. Valence MOs of this molecule contain 44 electrons, which may be distributed among 22 localized orbitals of bonds and lone electron pairs (two- and one-center orbitals). Eight predominantly one-center MOs of compound **1** correspond to lone electron pairs of oxygen and chlorine atoms (see Table 2, MOs 3—7 and 20—22). Three lowest orbitals (MOs 20—22) are purely atomic. Other one-center MOs contain the contributions of AOs of the neighboring atoms.

Table 2. Characteristics of localized MOs of 1,1′-dichloro-1-sila-2-oxacyclohexa-3,5-diene

MO	Energy /eV	Composition; contributions of AOs (%)	Number of centers
1	−10.8	C(6) 52.2; C(5) 44.0; Si(1) 1.8; C(3) 1.1	2.14
2	−10.9	C(4) 55.5; C(3) 41.0; C(5) 2.1; C(6) 1.0	2.09
3	−11.0	Cl 97.5; Si(1) 2.0	1.05
4	−11.0	Cl 97.5; Si(1) 2.0	1.05
5	−11.1	Cl 98.0; Si(1) 1.5	1.04
6	−11.1	Cl 98.0; Si(1) 1.5	1.04
7	−13.6	O(2) 90.1; C(3) 3.6; Si(1) 3.5	1.22
8	−16.6	C(6)60.1; Si(1)39.2	1.94
9	−17.0	Cl 67.4; Si(1) 32.1	1.79
10	−17.0	Cl 67.4; Si(1) 32.1	1.79
11	−18.4	C(6) 54.8; H 44.3	2.01
12	−18.9	C(5) 54.3; H 45.1	2.00
13	−18.9	C(4) 55.5; H 43.9	1.99
14	−19.8	C(3) 55.3; H 43.8	2.00
15	−20.8	C(4) 50.6; C(5) 48.3	2.04
16	−22.4	O(2) 72.2; Si(1) 26.9	1.68
17	−22.6	C(6) 49.8; C(5) 49.3	2.03
18	−23.3	C(4) 50.2; C(3) 49.1	2.02
19	−23.6	O(2) 57.3; C(3) 41.2	2.00
20	−24.1	O(2) 98.9	1.02
21	−50.9	Cl 99.9	1.00
22	−50.9	Cl 99.9	1.00

Of two-center localized MOs (see Table 2, MOs 1—2 and 8—19), the MOs of bonds of the silicon atom are of most interest in the case under consideration. The contribution of AOs of the silicon atom ranges from 39.2 % (the Si—C bond) to 26.9 % (the Si—O bond); the number of centers varies from 1.94 to 1.68, which is determined by a strong polarization of the bond of the silicon atom. As is evident from Tables 3 and 4, silicon atoms have the smallest valence electron density of all heavy atoms of the studied molecules. The ΔQ^* values for the bonds of the silicon atom are substantially larger than the analogous values for the C—O, C—C, and C=C bonds; the orders of the the bonds of the Si atom with electronegative substituents like O or Cl are less than unit. Absolute values of the energies of pairwise valence interactions of the silicon atom with substituents are smaller than those for the C—O, C=C, and =C—C= bonds.

The enhanced polarity of the bonds of the Si atom is clearly seen in the electron density distribution map of the Cl—Si—Cl fragment of molecule **1** (Fig. 1). Electron clouds of chlorine atoms are substantially larger and more dense than that of the Si atom. These clouds are deformed and shifted toward the Si atom under the effect of a large positive charge on the Si atom.

The π-MOs of the C=C bonds are the highest orbitals (see Table 2, MOs 1 and 2). These orbitals are of rather complex composition: π bonding occurs not only through p_z-AOs of carbon atoms of C=C bonds but through p_z-AOs of the neighboring carbon and silicon atoms as well. The contribution of the latter to π bonding is very small (>2 %); the p_z-AO of the oxygen atom is not involved in π bonding at all.

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* Absolute values of differences of atomic charges of the Si—X bond.

Table 3. Characteristics of valence bonds of six-membered cycles of 1,1′-disubstituted 1-sila-2-oxacyclohexa-3,5-dienes

Molecule	Bond	ΔQ	Bond order (according to Wiberg)	Partial energy /eV
1-Oxa-2-silacyclohexa-3,5-diene	Si—C	1.17	0.95	12.2
	Si—O	1.22	0.90	14.0
	Si—H	1.07	0.93	9.5
	C—O	0.44	1.07	16.0
	C—C	0.29	1.05	15.4
	C=C	0.24	1.88	21.5
Dimethyl-1-sila-2-oxacyclohexa-3,5-diene	Si—C	1.06	0.91	12.0
	Si—O	1.08	0.87	13.8
	Si—C_{Me}	0.99	0.94	11.2
	C—O	0.48	1.09	16.4
	C—C	0.25	1.06	15.5
	C=C	0.30	1.87	21.5
1-Methyl-1-vinyl-1-sila-2-oxacyclohexa-3,5-diene	Si—C	1.11	0.92	12.0
	Si—O	1.14	0.88	14.0
	Si—C_{Me}	1.03	0.94	11.1
	Si—C_{Vin}	1.06	0.89	11.8
	C—O	0.47	1.08	16.4
	C—C	0.25	1.06	15.4
	C=C	0.28	1.87	21.5
Dichloro-1-sila-2-oxacyclohexa-3,5-diene	Si—C	1.48	0.91	12.7
	Si—O	1.48	0.86	14.6
	Si—Cl	1.36	0.89	10.4
	C—O	0.53	1.07	16.4
	C—C	0.31	1.06	15.5
	C=C	0.41	1.81	21.6
Difluoro-1-sila-2-oxacyclohexa-3,5-diene	Si—C	1.54	0.87	12.7
	Si—O	1.54	0.83	14.5
	Si—F	1.41	0.93	13.0
	C—O	0.53	1.08	16.5
	C—C	0.27	1.06	15.5
	C=C	0.38	1.87	21.5

Table 4. Valence electron density of the atoms of 1,1′-disubstituted 1-sila-2-oxacyclohexa-3,5-dienes

Substituent		Valence electron density					
R	R′	O(2)	Si(1)	C(3)	C(4)	C(5)	C(6)
H	H	6.52	2.76	4.00	3.75	4.18	3.72
Me	Me	6.61	2.58	4.02	3.73	4.30	3.74
Me	Vin	6.62	2.58	4.01	3.74	4.30	3.72
Cl	Cl	6.49	2.28	4.00	3.68	4.22	3.67
F	F	6.70	1.88	4.04	3.70	4.45	3.80

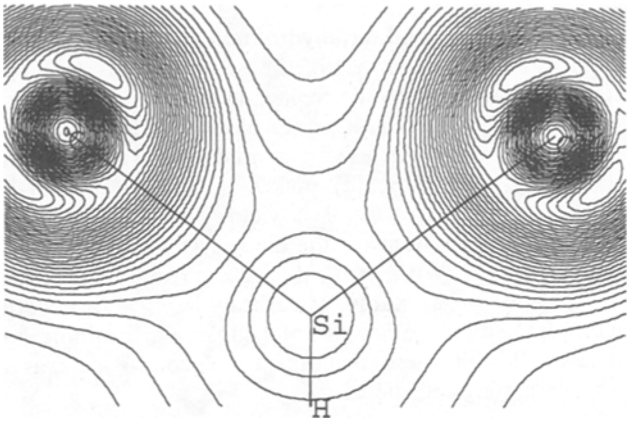

Fig. 1. Electron density distribution in the Cl—Si—Cl fragment of 1,1′-dichloro-1-sila-2-oxacyclohexa-3,5-diene (the section through the silicon and chlorine atoms perpendicular to the cycle of the molecule).

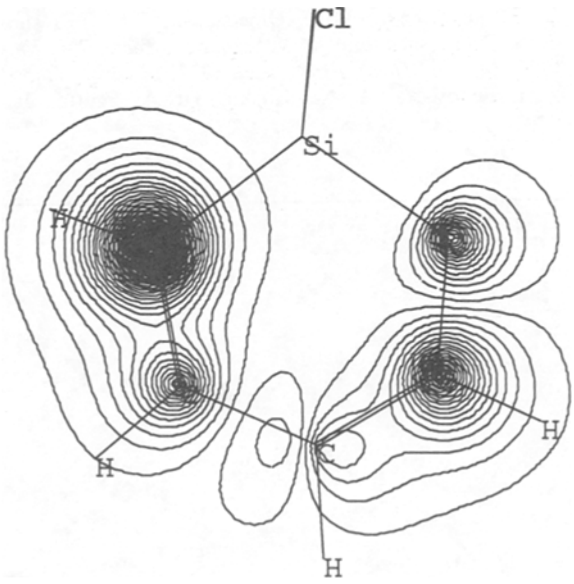

Fig. 2. Highest occupied molecular orbital of 1,1′-dichloro-1-sila-2-oxacyclohexa-3,5-diene (the section coincides with the plane of the cycle of the molecule).

Analogous structures are also typical of other 1,1′-disubstituted silaoxacyclohexa-3,5-dienes. Closed electron systems formed by p_z-AOs of atoms of six-membered cycles do not occur in these compounds. The change of substituents at the silicon atom substantially affects only its valence electron density; for carbon and oxygen atoms bonded to Si atoms, these values are changed only slightly, and for other carbon atoms, these values remain virtually unchanged (see Table 4). Therefore, in the studied molecules, the R′SiO fragment is a structural linkage, which inductively affects the diene system but does not interact with this system by the mesomeric (resonance) mechanism.

Figure 2 shows the canonically highest occupied molecular orbital of compound **1**, which determines the direction of the attack of nucleophilic and electrophilic reagents. Doubtlessly, the Si atom is most susceptible to the attack of nucleophilic reagents. Because of the above-mentioned weakening of the Si—C, Si—O, and Si—Cl bonds on methylation of molecule **1** with Grignard reagent in ether and tetrahydrofuran in the temperature range 0—20 °C, cleavage of the Si—C and Si—O bonds occurs in addition to the replacement of the Cl atom by the Me group to form a trimer of dimethylsilanone and 1-butenal. Only the use of a mild ethoxylation agent (trimethyl orthoformate) makes it possible to obtain diethoxy derivatives in 70 % yield. The other target of the nucleophilic attack is the diene system. Reactions of compound **1** with iron dodecacarbonyl (with the formation of a stable tricarbonyliron heterocyclic complex), dichlorosilylene, and molecular bromine are known. In all these reactions, molecule **1** acts as a simple conjugated diene.

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