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Classical and Inverted Structures of SiX$_n$H$_{3-n}$Li and SiX$_n$H$_{3-n}$Na

P. C. Gómez* and M. Alcolea Palafox[†]

*Departamento de Química Física I, Facultad de Química, Universidad Complutense de Madrid,
E-28040 Madrid, Spain*

L. F. Pacios[‡]

*Departamento de Química y Bioquímica, ETSI Montes, Universidad Politécnica de Madrid,
E-28040 Madrid, Spain*

Geometry, energetics, and dipole moments of tetrahedral-like (classical) and inverted forms of SiX$_n$H$_{3-n}$Li and SiX$_n$H$_{3-n}$Na, where X stands for a halogen atom, are studied ab initio at HF, MP2, QCISD(T), and B3LYP levels of the theory using triple-ζ plus polarization and diffuse functions basis sets. The inverted form is found to be the most stable for all the cases where Li is present but not in all the cases involving Na. Energy differences between classical and inverted forms range from −2 to 24 kcal mol^{-1}. The results for SiH$_3$Li agree with previous data. Agreement of the properties determined using this methodology with the experimental results, where available, is found very satisfactory. An analysis of the bonding in these molecules in terms of atomic charges and electron density is carried out.

Introduction

It is a piece of chemical wisdom that carbon tetracoordinated compounds have only one structure of equilibrium on the potential energy surface (PES) and that it corresponds in general to a nearly tetrahedral shape called "classical structures". However, there have been a large number of cases reported of anomalous and interesting carbon species violating the conventional rules of chemical structure, such as CCl$_3$Li [1], bicyclo[1.1.1]-propellane,[2−5] and a number of others nicely reviewed in ref 6 (see also quotations therein). In these cases "inverted" forms (displaying an inverted umbrella-like shape) happen to be the lowest lying conformers of the various local minima on the PES. In the case of one-silicon derivatives including lithium, nonclassical inverted structures (those having XSiLi and HSiLi angles smaller than 90°, see figures in this paper, especially Figure 3) have also been found. That is the case of SiH$_3$Li that has been reported[7] to present two minima on its PES, one tetrahedral-like (classical) and one "inverted". The latter was found to be lower in energy by 2.4 kcal mol^{-1} in an MP4SDTQ/6-31G** calculation using optimized geometries obtained with a 6-31G* basis set. Similar species containing lithium and fluorine are also expected to have both forms. Whether this is a peculiarity of all alkali metal-containing carbenoids and silanes or rather another peculiarity of Li (an atom with a reputation of displaying special properties in chemical bonding) is not certain yet. We explore here the relative stability of the classical and inverted possible forms of one-silicon compounds containing Li, Na, and different halogen atoms.

In spite of the interest in this types of molecules, ab initio geometries and properties are scarce and we only know of HF and MP2 calculations,[8,9] where a double-ζ quality basis set was used, in addition to those already mentioned. On the experi-

mental side the information is not more abundant, experimental data being almost nonexistent to the best of our knowledge. Nevertheless, both SiH$_3$Li and SiH$_3$Na have been synthesized[10] and found stable as monomers in solution.

In this paper, we aim at contributing to the better knowledge of these species and undertake a systematic study of the structure, energetics, and properties of the SiX$_n$H$_{3-n}$Li and SiX$_n$H$_{3-n}$Na (where X stands for fluorine or bromine atoms) family of molecules. We account for the correlation effects, which have been found to be essential in the bonding of these molecules, by means of different methods and virtually saturated basis sets.

The pairs of atoms fluorine, chlorine, or bromine on the one hand and lithium or sodium on the other have been chosen because of their positions at the extremes of their rows of the periodic table of the elements, which facilitates the understanding of the trends in the bonding of the molecules studied.

Methodology

We have performed ab initio geometry optimizations and frequency calculations for both tetrahedral and inverted forms of SiF$_n$H$_{3-n}$Li and SiF$_n$H$_{3-n}$Na types of molecules (where *n* varies from 0 to 3) plus SiBr$_3$Li, SiH$_3$F, and SiH$_3$Cl using wave function and density functional theory (B3LYP) methods along with 6-311++G(3df,pd) basis sets. Atomic charges computed with the Mulliken population analysis and the Merz−Kollman procedure, with the additional option to reproduce dipole moments, have been also considered. All the calculations have been carried out using the GAUSSIAN94 suite of programs.[11]

Geometry and Energy of the Conformers

We have determined geometric parameters and energies of SiH$_3$Li using HF, MP2, B3LYP, and QCISD(T) methods along with 6-311G(d,p), 6-311G+(d,p), 6-311G+(2d,p), 6-311G++-(3df,pd), and 6-311++G(3df,3pd) basis sets. In Tables 1 and 2

* Corresponding author. E-mail: pgc@eucmos.sim.ucm.es.
[†] E-mail: alcolea@eucmos.sim.ucm.es.
[‡] E-mail: lfp@atenea.montes.upm.es.

TABLE 1: Ab Initio Geometric Parameters for the Inverted Form of SiH$_3$Li^a

	Si−Li	Si−H	Li−Si−H	energy + 298
HF/6-311G(d,p)	2.339	1.572	53.7	−0.103 371 6
HF/6-311+G(d,p)	2.338	1.570	53.8	−0.103 714 6
HF/6-311+G(2d,p)	2.336	1.566	53.8	−0.106 275 8
HF/6-311++G(3df,pd)	2.334	1.567	53.8	−0.108 195 8
HF/6-311++G(3df,3pd)	2.334	1.537	53.8	−0.108 440 9
MP2/6-311G(d,p)	2.340	1.566	53.0	−0.232 286 1
MP2/6-311+G(d,p)	2.339	1.565	53.0	−0.232 935 6
MP2/6-311++G(2d,p)	2.344	1.560	53.2	−0.241 120 2
MP2/6-311++G(3df,pd)	2.348	1.561	53.1	−0.260 574 7
MP2/6-311++G(3df,3pd)	2.351	1.561	53.1	−0.264 290 5
MP4SDTQ/6-31G* ^{b}	2.386	1.568	53.0	−0.225 67
B3LYP/6-311G(d,p)	2.339	1.581	52.6	−0.833 433 4
B3LYP/6-311+G(d,p)	2.337	1.580	52.7	−0.833 815 4
B3LYP/6-311++G(2d,p)	2.331	1.575	52.8	−0.835 930 8
B3LYP/6-311++G(3df,pd)	2.331	1.575	52.8	−0.837 792 0
B3LYP/6-311++G(3df,3pd)	2.331	1.575	52.8	−0.838 030 3
QCISD(T)/6-311++G(3df,pd)	2.344	1.570	53.0	−0.296 078 6

^{a} Bond distances are in Å. Bond angles are in degrees. Energies are in E$_h$. Dihedral angles were found to be 120° or 240° always. ^{b} See ref 8.

TABLE 2: Ab Initio Geometric Parameters for the Tetrahedral-like Form of SiH$_3$Li^a

	Si−Li	Si−H	Li−Si−H$_a$	energy + 298
HF/6-311G(d,p)	2.512	1.499	115.0	−0.107 506 3
HF/6-311+G(d,p)	2.512	1.499	115.0	−0.107 608 0
HF/6-311+G(2d,p)	2.513	1.495	115.0	−0.110 697 4
HF/6-311++G(3df,pd)	2.512	1.496	115.1	−0.112 439 9
HF/6-311++G(3df,3pd)	2.512	1.496	115.1	−0.112 607 7
MP2/6-311G(d,p)	2.482	1.495	115.1	−0.228 630 0
MP2/6-311+G(d,p)	2.480	1.495	115.2	−0.229 004 2
MP2/6-311++G(2d,p)	2.489	1.492	115.5	−0.237 899 9
MP2/6-311++G(3df,pd)	2.488	1.494	115.5	−0.257 877 1
MP2/6-311++G(3df,3pd)	2.488	1.494	115.5	−0.261 540 5
MP4SDTQ/6-31G* ^{b}	2.524	1.497	115.2	−0.222 43
B3LYP/6-311G(d,p)	2.465	1.505	115.6	−0.829 221 9
B3LYP/6-311+G(d,p)	2.465	1.505	115.6	−0.829 387 9
B3LYP/6-311++G(2d,p)	2.463	1.501	115.6	−0.831 367 2
B3LYP/6-311++G(3df,pd)	2.463	1.501	115.6	−0.833 002 5
B3LYP/6-311++G(3df,3pd)	2.463	1.501	115.6	−0.833 313 4
QCISD(T)/6-311++G(3df,pd)	2.475	1.500	115.8	−0.292 597 3

^{a} Bond distances are in Å. Bond angles are in degrees. Energies are in E$_h$. Dihedral angles were found to be 120° or 240° always. ^{b} See ref 8.

the appropriate geometrical parameters and energies are collected. It can be noticed that there is practically no difference in the geometries obtained by using the three larger basis sets, especially at HF and B3LYP levels of the theory, and it is also apparent that the differences in the energy tend to be smaller when improving the basis sets. In fact, differences between the (3df,pd) and (3df,3pd) basis sets in HF and B3LYP calculations are smaller than 0.2 kcal mol^{-1}, whereas MP2 energy shows a somewhat slower convergence with the basis set size.

Among the bond distances obtained using either of the two largest basis sets in this paper, Si−Li bond at MP2 level appears to be the largest one provided by the correlated methods we have used, both in the inverted and tetrahedral forms, but still is slightly shorter than the values obtained[7] by Scheleyer and Clark (2.386 Å for the inverted form and 2.524 Å for the tetrahedral). It is noticeable also that there is some basis set effect on MP2 Si−Li bond distance that is not present in the other methodologies used. On the other hand, B3LYP Si−Li bond distances are the shorter ones in the list for both forms whereas QCISD(T) looks always somewhat intermediate; therefore, considering the possible ionic character of the Si−Li bond, we tend to trust better QCISD(T) results and feel inclined to consider values larger than 2.34 Å as probably too long. In the Si−H distance, QCISD(T) still provides intermediate results in tetrahedral and inverted isomers, the differences between the

various methodologies used and the QCISD(T) values now being rather small (in the order of a few thousandths of Å). Finally, H−Si−Li angles coincide in all our three correlated calculations, and in those in ref 7 rather satisfactorily.

From results in Tables 1 and 2 the energy differences between the tetrahedral and inverted forms of SiH$_3$Li can be calculated. It is clear again that the two largest basis sets provide practically the same value for this energy difference, so that we have adopted the 6-311++G(3df,pd) as the reference basis set to be used throughout this paper as a reasonable choice to reach high accuracy, except for the estimates of the zero-point energy correction (ZPE) which have been done by using 6-311++G-(2d,p).

The values of the classical-form energy minus inverted-form energy for SiH$_3$Li found at the various levels of the theory using the reference basis set are −2.7 kcal mol^{-1} for HF, 1.7 kcal mol^{-1} for MP2, 3.0 kcal mol^{-1} for B3LYP, and 2.2 kcal mol^{-1} for QCISD(T). It is worth noting that the extra stability of the inverted form compared to the tetrahedral one is a correlation effect since HF predicts always, independently of the basis set used, the tetrahedral isomer to be the lowest lying one. MP2 provides a value for this energy difference somewhat smaller than B3LYP and QCISD(T) when the two longest basis sets are employed, whereas larger values are obtained with the more modest basis sets displayed in Tables 1 and 2. This might be due to the already mentioned slow convergence of MP2 energies and Si−Li bond distances with basis set size; this method probably requires even larger basis sets than 6-311++G(3df,-3pd) to yield values similar to those of the other methods in these particular molecules. In any event the agreement of QCISD(T) and B3LYP in providing values above 2.2 kcal mol^{-1} suggests that MP2 values are probably underestimates of the real energy difference between conformers. The ZPE correction has been done only at the B3LYP level which produces corrected energy differences between tetrahedral and inverted forms of SiH$_3$Li at this level of the theory of 3.1 kcal mol^{-1}, in reasonable agreement with the value found previously[7] though about 0.7 kcal mol^{-1} larger. When this correction is applied to the QCISD(T) value, merely as a rough estimate of the ZPE influence, an energy difference of 2.2 kcal mol^{-1} is found, very close to the 2.4 kcal mol^{-1} in ref 7, so we think our QCISD(T) to be closest to the real value of this property.

Silanes involving halogen atoms instead of lithium, such as SiFH$_3$ and SiClH$_3$, have also been investigated but no minima for the inverted forms were found. However, we have included these two molecules in the present work to establish the reliability of our methodological choice (B3LYP/6-311++G-(3df,pd)) since experimental data are available for them. In Table 3 calculated geometric parameters and dipole moments are compared with their experimental counterparts[12−15] and with other density functional calculations.[16] It can be seen that the concordance is remarkably good, the differences in bond distances being smaller than 0.02 Å and differences in bond angles smaller than 0.3°. As for the calculated dipole moments, they agree with the experimental values within a few hundredths of a debye which is also excellent. Harmonic vibrational frequencies have been calculated for SiClH$_3$ at the same level of the theory and using the same basis set as those used to calculate all the ZPE corrections in this paper, namely B3LYP/6-311++G(2d,p). The values obtained in cm^{-1}, along with the frequencies reported as experimental[17] in parentheses, are as follows: 522 (551), 656 (663), 656 (663), 950 (945), 960 (952),

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TABLE 3: Ab Initio and Experimental Geometric Parameters and Dipole Moments for SiFH$_3$ and SiClH$_3$[a]

	SiFH$_3$		SiClH$_3$	
	B3LYP[b]	expt[c]	B3LYP[b]	expt[c]
SiX[d]	1.611	1.591	2.067	2.049
SiH	1.476	1.470	1.475	1.485
XSiH	108.2	108.4	108.5	
HSiH	110.8	110.52	110.5	110.23
μ	1.358, 1.110[e]	1.299	1.353, 1.118[e]	1.303

[a] Bond distances are in Å. Bond angles are in degrees. Dipole moments are in debyes. Dihedral angles were found to be 120° or 240°. [b] B3LYP/6-311++G(3df,pd) calculations, this work. [c] See refs 12–15. [d] X stands for Cl or F as required. [e] Density functional computation in ref 16.

960 (952), 2262 (2201), 2276 (2211), 2276 (2211). As can be seen, the calculated harmonic frequencies agree rather well with the experimental, errors being smaller than 3% except for the lowest frequency where the error is 5%. The above results support the choice made to determine geometrical structures and to calculate ZPE estimates.

It is obvious that the role of alkali metals in the stabilization of inverted forms of tetracoordinate silanes is essential since they join a large difference of electronegativity with respect to Si, to a relatively small size. In order to explore the effect of increasing the charge differences among the Li atom and the substituents in the inverted form of Si X$_n$H$_{3-n}$Li, we have studied molecules with increasing number of fluorine atoms: SiFH$_2$Li, SiF$_2$HLi and SiF$_3$Li. Energies and optimized geometric parameters at B3LYP/6-311++G(3df,pd) and zero-point energy corrections are summarized in Table 4. It is found that energy differences between the tetrahedral and inverted forms in the previous series are (in kcal mol^{-1}) 7.9, 11.4, and 17.3 which yield after ZPE correction 8.1, 11.7, and 17.4. That shows clearly the stabilizing effect of partial negative charges on fluorine atoms and the positive ones on Li in the inverted form as summarized in Table 6. It may be supposed that this trend would not continue if more voluminous atoms were present in the place of fluorine atoms, but we have found that even when bromine replaces fluorine atoms in SiX$_3$Li the inverted form is still the most stable. To our great surprise the extra stability of the nonclassical form was in this case 23.8 kcal mol^{-1}, clearly larger than in any of the other species studied here, although angles (SiLiBr is now ca. 57°) and especially SiLi distance (which has grown 0.4 Å with respect to the bond in SiF$_3$Li) are considerably distorted now.

Geometries have also been optimized for SiH$_3$Na at the same level of the theory and using the same basis set to learn whether the inverted form occurs also as the lowest lying conformer in silanes with alkali metals other than lithium. Two minima corresponding to a tetrahedral and an inverted form are found (see Table 5); however, in this case the inverted form is calculated to be 2.0 kcal mol^{-1} higher in energy than the tetrahedral one after allowing for zero-point correction, so Na displays a rather different behavior from Li in this case. Substitution of H atoms by F, more voluminous but also more electronegative, is expected to produce a similar effect to that of the Li series of compounds. This is in fact the case, but two fluorine atoms are needed at least to obtain an inverted form clearly more stable than the classical one as can be deduced from Table 7. Replacement of just one H for one F atom produces energy differences between both conformers practically negligible (tetrahedral more stable by 0.2 kcal mol^{-1}, which is certainly beyond our accuracy limit) which can be interpreted as a sort of compensation between the larger charge differences

between the alkali metal and the halogen on the one hand and the increase in steric repulsion on the other. Finally, when the three H are replaced by fluorine atoms, as in SiF$_3$Na, the inverted form is more stable than the tetrahedral by 11.5 kcal mol^{-1}. We can conclude that a qualitatively similar trend is found in Li and Na series of compounds though the extra stability of the inverted form in the Li family is larger.

Discussion

The results of the relative stability of the inverted and tetrahedral forms are clear from the ab initio calculations summarized in Table 7; however, a rationalization of whole picture in terms of more "chemical" concepts should be desirable. Figures 1 and 2 display contour maps of the electron density computed at B3LYP level using our reference basis set in planes defined by Si, Li, and halogen atoms in SiF$_3$Li and SiBr$_3$Li. Charge dsitributions show a very different pattern in inverted and tetrahedral structures. The existence of two different domains is visible in the tetrahedral forms, namely, the lithium atom on the one hand and silicon—halogen bond on the other. This feature is consistent with the clearly larger dipole moments found in tetrahedral geometries, as displayed in Table 6: 4.2 D for inverted and 9.3 D for tetrahedral forms in the fluorine containing molecule and 2.5 and 9.7 D for the respective structures in the bromine case. Charges on the atoms seem the obvious choice to visualize interactions among them and this viewpoint has been in fact already adopted before (see ref 7). There are several schemes for partitioning electron density to get atomic charges, all having well-known weaknesses and advantages. Because of the desirable property of reproducing the molecular electrostatic potential, the Merz—Kollman (MK) analysis is known to be one of the most appealing in providing atomic charges of higher reliability than other population schemes. Therefore, we have chosen MK atomic charges with the additional condition to reproduce the ab initio computed dipole moment to carry out the following analysis, although the charges obtained from conventional MK procedure are very similar.

Atomic charges have been calculated for all the molecules studied in this paper using the above-mentioned scheme along with the traditional Mulliken (M) analysis. In the case of SiH$_3$-Li we have carried out calculations at HF/6-311G(d,p), HF/6-311++G(3df,pd), and B3LYP/6-311++G(3df,pd) levels of the theory. We have found a strong basis set effect on M charges, which is consistent with a great deal of knowledge regarding this population partitioning. As an example it can be pointed out that the value for the HF/6-311++G(3df,pd) charge on Si in the inverted form is almost 10 times smaller than the one obtained when using HF/6-311G(d,p), whereas MK values for Si remained equal, up to the second decimal place, for these two basis sets. A rather similar behavior was found in the tetrahedral form. In general, MK charges look much more stable under changes in the basis set. However, it must be underlined that values obtained with these two population analyses are very different; actually the MK charge on Si in the mentioned case has a negative value (−0.18). The effect of the method was also noticeable on the atomic charges, even for MK partition, but that was somewhat expected since our charges are meant to reproduce the dipole moment which is clearly dependent on the methodology used. Since we are using in this paper the B3LYP plus 6-311++G(3df,pd) combination and also considering that the B3LYP dipole moment found using this basis set was in very good agreement with the experimental values in

TABLE 4: B3LYP/6-311++G(3df,pd) Geometric Parameters, Energy, and Zero-Point Energy for Tetrahedral-like and Inverted Forms of Some of the $SiX_nH_{3-n}Li$ Type of Molecules[a]

	$SiFH_2Li^b$	$SiFH_2Li^c$	SiF_2HLi^b	SiF_2HLi^c	SiF_3Li^b	SiF_3Li^c	$SiBr_3Li^b$	$SiBr_3Li^c$
SiLi	2.348	2.481	2.363	2.483	2.369	2.458	2.765	2.451
SiX^d	1.807	1.658	1.771	1.641	1.741	1.626	2.452	2.300
SiH	1.576	1.503	1.584	1.503				
SiLiH	55.6	118.7	57.3	125.2				
SiLiX	48.0	109.6	50.2	111.2	52.5	115.7	56.8	114.3
β	123.9	118.3	117.3	122.7	120.0	120.0	120.0	120.0
energy	−0.187 315 4	−0.174 697 7	−0.548 468 2	−0.530 369 8	−0.924 146 0	−0.896 521 2	−0.692 947 81	−0.655 044 84
ZPE	11.9	12.1	8.78	9.07	5.70	8.80		

[a] Bond distances are in Å. Bond angles and dihedral (β) angles are in degrees. Energies (in E_h) are relative to −398 in SiH_2FLi, to −497 in $SiHF_2Li$, to −596 in SF_3Li, and to −8019 in $SiBr_3Li$. ZPE, calculated using 6-311++G(2d,p) basis set, in kcal mol^{-1}. [b] Inverted form. [c] Tetrahedral-like form. [d] X stands for F or Br as required.

TABLE 5: B3LYP/6-311++G(3df,pd) Geometric Parameters, Energy, and Zero-Point Energy for Tetrahedral-like and Inverted Forms of $SiF_nH_{3-n}Na$ Type of Molecules[a]

	SiH_3Na^b	SiH_3Na^c	$SiFH_2Na^b$	$SiFH_2Na^c$	SiF_3Na^b	SiF_3Na^c
SiNa	2.706	2.758	2.705	2.774	2.741	2.753
SiH	1.56	1.500	1.576	1.503		
SiF			1.774	1.656	1.729	1.629
NaSiF			52.8	109.1	54.5	115.8
NaSiH	56.3	115.2	56.3	118.6		
β	120.0	120.0	122.4	118.0	120.0	120.
energy	−0.609 900 55	−0.613 789 69	−0.954 361 358	−0.955 601 46	−0.694 340 8	−0.676 472 8
ZPE	13.8	14.3	11.0	11.6	5.05	5.32

[a] Bond distances are in Å. Bond angles and dihedral (β) angles are in degrees. Energies (in E_h) are relative to −435 in SiH_3Na, −552 in SiH_2FNa, and −751 in SiF_3Na. ZPE, calculated using 6-311++G(2d,p) basis set, in kcal mol^{-1}. [b] Inverted form. [c] Tetrahedral-like form.

TABLE 6: B3LYP/6-311++G(3df,pd) Merz−Kollman Atomic Charges for Inverted and Tetrahedral Forms[a]

	inverted					tetrahedral				
	Si	Li, Na	H	F, Br	μ	Si	Li, Na	H	F, Br	μ
SiH_3Li	−0.082	0.795	−0.238		5.641	−0.359	0.554	−0.065		7.161
$SiFH_2Li$	0.059	0.850	−0.250	−0.410	5.151	−0.214	0.557	−0.066	−0.211	7.743
SiF_2HLi	0.122	0.853	−0.212	−0.382	4.748	−0.072	0.568	−0.069	−0.214	8.381
SiF_3Li	0.239	0.863		−0.367	4.209	−0.242	0.666		−0.141	9.302
$SiBr_3Li$	0.242	0.591		−0.278	2.480	−0.854	0.830		0.079	9.660
SiH_3Na	−0.085	0.780	−0.232		7.247	−0.160	0.477	−0.106		7.294
$SiFH_2Na$	0.012	0.888	−0.262	−0.376	7.443	−0.101	0.497	−0.087	−0.223	7.891
SiF_3Na	0.218	0.947		−0.388	6.853	−0.098	0.622		−0.175	10.02

[a] Dipole moments (μ) are in debyes.

TABLE 7: Energy Difference between Classical and Inverted Forms at the B3LYP/6-311++G(3df,pd) Level[a]

|	$\Delta E^{C\ b}$		$\Delta E^{C\ b}$
SiH_3Li	3.1	SiH_3Na	−2.0
$SiFH_2Li$	8.1	$SiFH_2Na$	−0.2
SiF_2HLi	11.7		
SiF_3Li	17.4	SiF_3Na	11.5
$SiBr_3Li^c$	23.8		

[a] ΔE^C: Zero-point energy corrected energy difference between classical and inverted forms in kcal mol^{-1}. Positive values correspond to a larger stability for inverted forms. [b] Zero-point energy correction was done at B3LYP/6-311++G(2d,p) level in all cases. [c] No zero-point energy correction was done.

SiClH$_3$ and SiFH$_3$ (see Table 3), we have bound ourselves to this methodology and to MK charges to analyze the molecules studied in this paper.

MK atomic charges provide some understanding on the peculiar bonding in all these molecules. It can be seen from Table 6 that excess of charge on H (and halogens) and the deficiency on alkali atoms is much larger in the inverted form than in the tetrahedral one, which may explain the stabilization of the former by electrostatic interaction of the alkali atom with the rest of the molecule, mainly with H or the corresponding halogen atoms. That seems to suggest a certain ionic character in the bonding.

The analysis of data collected in Table 6 for SiF$_n$H$_{3-n}$Li family of molecules shows that the inclusion of an increasing number of F atoms does not affect greatly the charge over Li, F or H (although charges on Si change noticeably), and this leads to a more intense interaction with the alkali metal which makes the inverted form more stable with respect to the tetrahedral. That is reflected in the energy calculations in the previous section.

An interesting case is SiBr$_3$Li whose inverted form is largely more stable than the tetrahedral one in spite of the voluminous substituents attached to Si. What is more surprising about this molecule is that this stability of the nonclassical form is not accompanied by large opposite charges on Br and Li atoms; actually they are smaller than those on F and Li in the similar SiF$_3$Li molecule, so that a possible electrostatic interaction would not justify the extra stability of the inverted form in this molecule compared to the case of trifluorinated silicon. This relatively smaller ionic character is also visible in the little dipole moment found for this species, only 2.48 D where the rest of inverted molecules in Table 6 display values between 4 and 7.5 D. All this is confirmed by the study of bond distances. A very large value has been found for Si−Li bond distance, 2.765 Å, whereas distance between Li and Br atoms calculated from data in Table 4 is 2.496 Å, only about 0.04 Å larger than the SiBr where chemical intuition would advise to draw a bond.

Structures of SiX$_n$H$_{3-n}$Li and SiX$_n$H$_{3-n}$Na
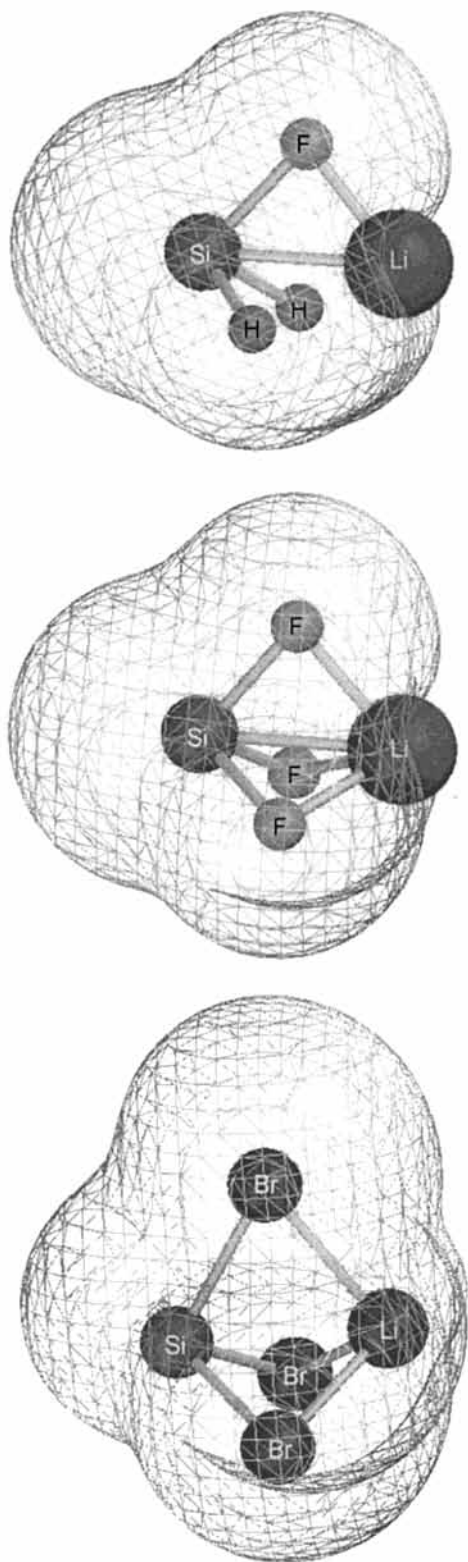
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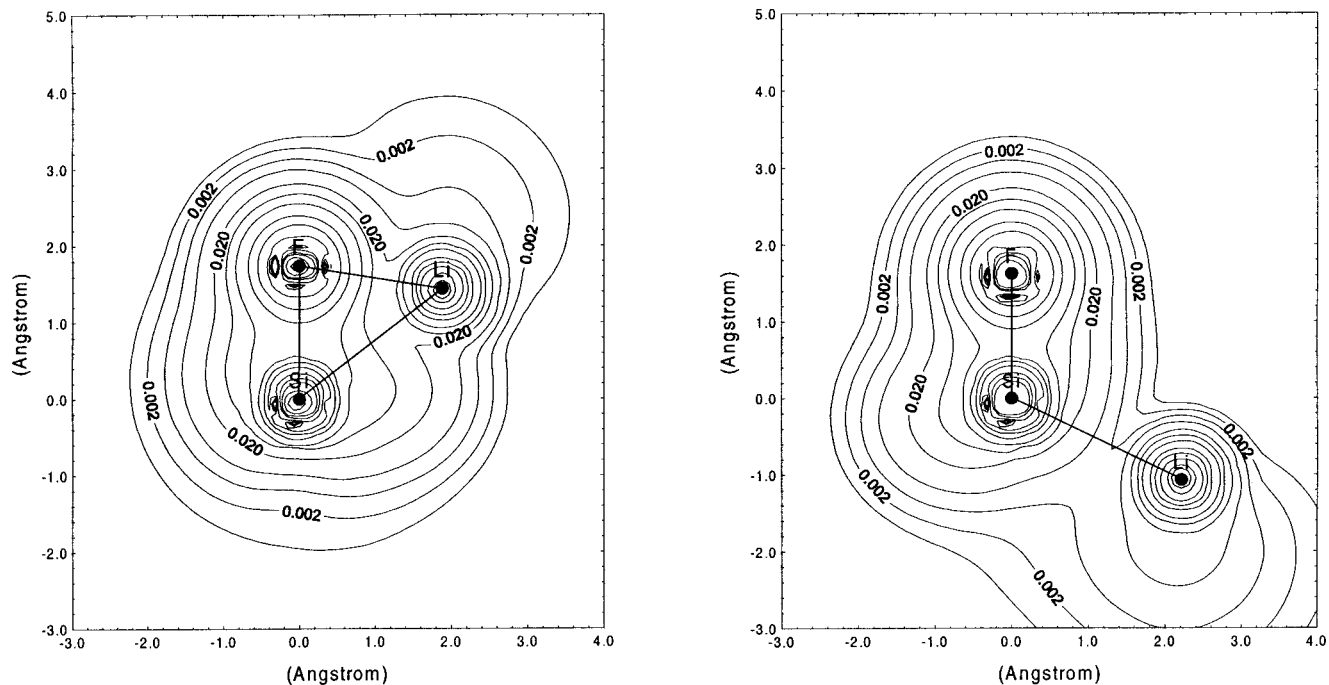
Figure 1. Contour maps of the B3LYP/6-311++G(3df,pd) electron density in the plane $(-3.0, -3.0)-(4.0, 5.0)$ Å defined by Si (located at the origin), F, and Li atoms in the inverted form (left) and tetrahedral geometry (right) of SiF$_3$Li. The outer contour has the value 0.001 au, and the remaining contours increase in the order 2×10^n, 4×10^n, and 8×10^n with $n = -3, -2, -1$, and 0.
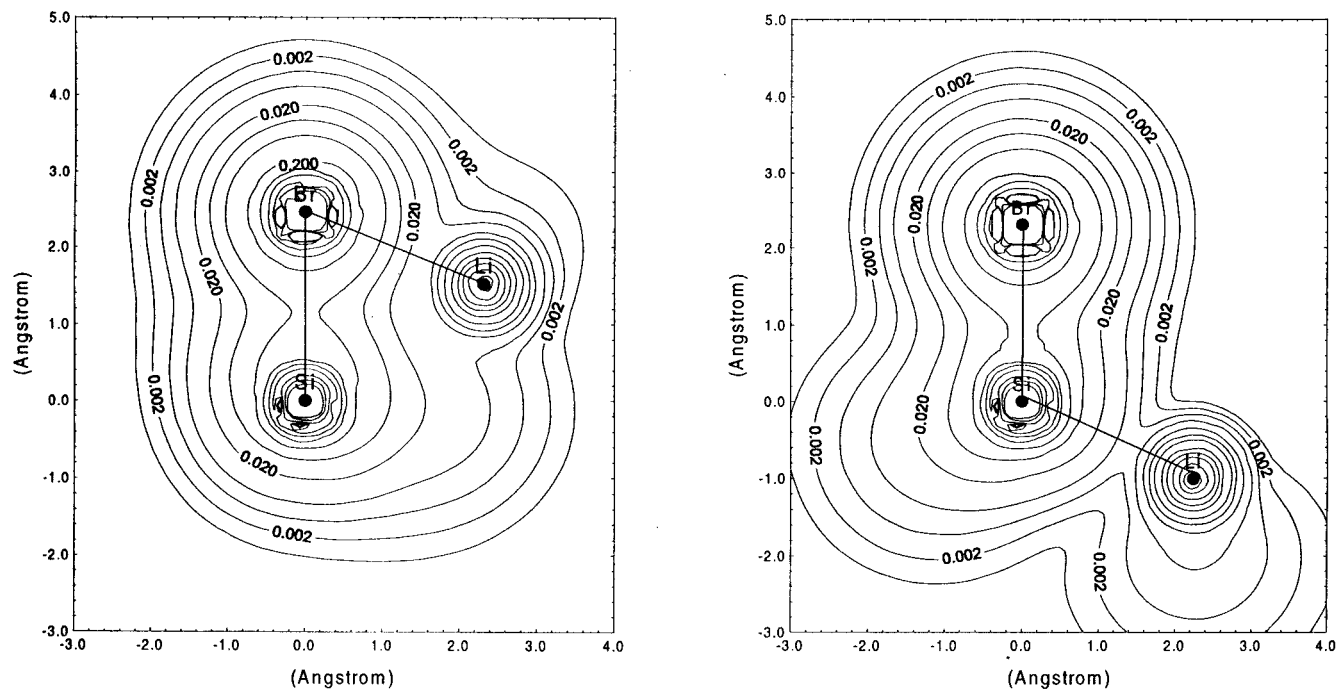
Figure 2. Contour maps of the B3LYP/6-311++G(3df,pd) electron density in the plane $(-3.0, -3.0)-(4.0, 5.0)$ Å defined by Si (located at the origin), Br, and Li atoms in the inverted form (left) and tetrahedral geometry (right) of SiBr$_3$Li. The outer contour has the value 0.001 au, and the remaining contours increase in the order 2×10^n, 4×10^n and 8×10^n with $n = -3, -2, -1$, and 0.

Thus the molecule is probably better viewed as triangular bypiramidal structure where Br atoms are simultaneously linked to Si and Li. We display in Figure 3 three-dimensional images of SiFH$_2$Li, SiF$_3$Li, and SiBr$_3$Li showing the geometrical structure and the outer electron density contour which allows a good representation of the molecular shape. In this figure the compact electron density distribution obtained for SiBr$_3$Li is a further indication in support of a predominantly covalent structure, as suggested above. The case in SiF$_3$Li is different since the bond distance between Si$-$F (1.42 Å) is clearly shorter

than the calculated Li$-$F distance 1.903 Å, so stabilization of the inverted forms in the fluorinated molecules must be, as mentioned before, basically electrostatic.

Referring to the Na-containing molecules, we have found them more reluctant to display extra stability in the nonclassical forms, probably because atomic charges (see Table 6) are not so different from those on the lithium family, but now Na is much more voluminous. So we can see that SiH$_3$Na has a tetrahedral form about 2 kcal mol^{-1} more stable than the inverted one and SiFH$_2$Na has an inverted form approximately as stable

Li-containing counterpart, but to a lesser extent. Finally, SiF_2-HNa has not been calculated, but it looks reasonable, considering the reasoning above, to expect it to be an intermediate case with an inverted form more stable than the classical tetrahedral structure.

Conclusions

We have carried out a systematic high-level ab initio study of the $SiX_nH_{3-n}Li$ and $SiH_{3-n}X_nNa$ types of molecules. Increasing stability of the inverted forms is found as the number of halogen atoms increases. Although all forms of lithium-containing species studied here show this behavior, SiH_3Na and $SiFH_2Na$ do not show any preference for inverted forms, at least several fluorine atoms being necessary to obtain more stable inverted isomers.

The analysis of atomic charges suggests that highly polarizable alkali metals allow electrostatic interaction with the more electronegative H and halogen atoms, stabilizing the inverted forms in $SiF_nH_{3-n}Li$ and $SiF_nH_{3-n}Na$, whereas the electron density representation and the analysis of bond distances indicate a stronger covalent-like linking between the halogen and lithium atoms that stabilizes extraordinarily the inverted form, in the case of $SiBr_3Li$.

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Figure 3. Three-dimensional plots of the molecular electron density computed at the B3LYP/6-311++G(3df,pd) level of theory for the optimized geometry of inverted forms for $SiFH_2Li$ (upper), SiF_3Li (middle), and $SiBr_3Li$ (lower). The outer contour of the electron density has the value 0.002 au.

as the tetrahedral. However, calculations on trifluorinated species show a more stable inverted form, just as happened with its