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Molecular Complexes between Silicon Derivatives and Electron-Rich Groups

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Theoretical calculations on a series of SiXY$_3$···ZW complexes, where X and Y are H, F, and Cl, and Z corresponds to an electron donor atom (ZW = NH$_3$, NCH, CNH, OH$_2$, FH), were performed. The calculations were carried out using B3LYP/6-311++G**, MP2/6-311++G** and MP2/6-311++G(2d,2p) computational methods. The electron density was characterized by means of the atoms in molecules (AIM) methodology, and the interaction nature was studied with the NBO method. Finally, the effect of the complexation on the nuclear chemical shieldings was evaluated with the GIAO method. The results display a wide range of interaction distances that vary from 2.1 to 4.1 Å. The complexes with shorter interaction distances (~2.1 Å) show important distortion effects and large dipole moment enhancements. The NBO analysis indicates that in those complexes an ionic interaction is formed between the Si and Z atoms. Comparison of the chemical shieldings of the complexes and the monomers indicates that these interactions could be detected experimentally using ^{29}Si NMR. In addition, in the case of the complexes with NH$_3$ and OH$_2$, the use of ^{15}N NMR and ^{17}O NMR could be adequate to check the potential formation of the corresponding complexes.

Introduction

Several complexes between tetracoordinated silicon derivatives and an electron-rich group, in the gas phase, have been described in the literature (SiF$_4$···NH$_3$,[1] SiF$_4$···N$_2$,[2] and SiF$_4$···CO[2]). In the particular case of the SiF$_4$···NH$_3$ complex, important changes are observed in the geometry of the SiF$_4$ molecule (the tetrahedral F−Si−F angles in the isolated monomers become 97° within the complex). An enormous enhancement of the dipole moment is associated with these changes (from 1.47 D, as the sum of the dipole moments of the isolated monomers, to 5.41 D in the complex). In the rest of the complexes studied, only small changes in the monomers were observed, as expected for weak complexes.

This kind of interaction between the silicon and electron donor atoms has been experimentally explored as well as using NMR techniques. Thus, the percentage of Si−O and Si−S bond formation, in a series of 2-pyridones and 2-thiopyridones derivatives, has been established based on the ^{29}Si NMR chemical shielding.[3,4] And, in other cases, correlations have been found between NMR shieldings and the Si···N distance in a series of silatranes.[5]

At the theoretical level, previous ab initio studies have dealt with the SiF$_4$···NH$_3$ and SiH$_4$···NH$_3$ complexes at the MP2 level,[6] in which the resulting interaction energies were 10.5 and 2.6 kcal/mol, respectively. Besides, an atom in molecules (AIM) study of the SiF$_4$···NH$_3$ found that the large dipole moment enhancement observed in this complex could be explained on the basis of geometrical changes detected in the monomers, in agreement with the experimental findings.[7] More recently, Ault and co-workers have studied the interaction between silicon tetrafluoride and water in different stoichiometric complexes as well as its hydrolysis reaction.[8] The theoretical chemical shifts and interaction energies of a series of fluoro-substituted silanes interacting with ammonia have been described while this article was in the revision process.[9]

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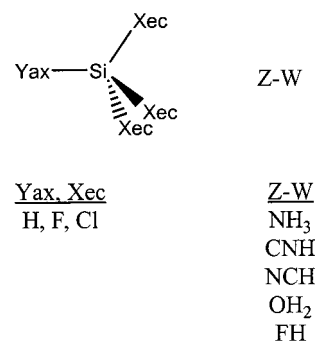

Figure 1. Schematic representation of the complexes studied.

In the present study, the influence of the substituents of silicon derivatives, in axial and equatorial positions, in their interaction with several electron donor groups has been explored. The energy of the monomers and the interaction energy of the complexes have been evaluated using the B3LYP/6-311++G**, MP2/6-311++G**, and MP2/6-311++G(2d,2p) computational levels. The atoms in molecules methodology and natural bond orbital (NBO) analyses have been used to characterize the electron density in the complexes and the orbitals responsible for the interactions between monomers. Finally, GIAO calculations have shown the sensibility of the ^{29}Si NMR shieldings to characterize these complexes.

Methods

A schematic representation of the complexes chosen for this study is shown in Figure 1. For each complex, several relative positions of the monomers have been attempted by maintaining, as starting point in all the cases, a disposition where a lone pair of the electron donor atom Z points toward the silicon atom.

The geometry and the energy of the monomers and complexes were obtained initially at the B3LYP/6-31G* level with the Gaussian-94[10] and Gaussian-98[11] packages. The nature of all the structures as a potential energy minimum was confirmed

TABLE 1: Geometrical Parameters of the Monomers[a]

	B3LYP/6-311++G**			MP2/6-311++G**		
monomers	Si$-$X$_{ec}$	Si$-$Y$_{ax}$	$\angle$Y$_{ax}-$Si$-$X$_{ec}$	Si$-$X$_{ec}$	Si$-$Y$_{ax}$	$\angle$Y$_{ax}-$Si$-$X$_{ec}$
SiH$_4$	1.484	1.484	109.47	1.474[b]	1.474	109.47
				(1.473)	(1.473)	(109.47)
SiF$_4$	1.584	1.584	109.47	1.581[c]	1.581	109.47
				(1.569)	(1.569)	(109.47)
SiCl$_4$	2.043	2.043	109.47	2.020[d]	2.020	109.47
				(2.033)	(2.033)	(109.47)
FSiH$_3$	1.479	1.631	107.95	1.469	1.625	108.01
ClSiH$_3$	1.479	2.082	108.21	1.469	2.058	108.24
ClSiF$_3$	1.590	2.013	110.56	1.585	1.998	110.38
FSiCl$_3$	2.033	1.602	108.01	2.012	1.595	108.13
HSiF$_3$	1.598	1.457	110.92	1.593	1.449	109.34
HSiCl$_3$	2.053	1.466	109.32	2.028	1.457	110.73

[a] The results obtained at MP2/6-311++G(2d,2p) are given in parentheses. Distances in Å and angles in deg. [b] Experimental value 1.481.[21] [c] Experimental value 1.552.[22] [d] Experimental value 2.019.[23]

by frequency calculations (no imaginary frequencies detected) at the same computational level. Further geometry optimization was carried out at the B3LYP/6-311++G**[12,13] and MP2/6-311++G**[14] levels. A selection of the complexes has been studied at the MP2/6-311++(2d,2p) level to consider the effect of a second set of polarization function in the description of the systems. A one-dimensional scan of the potential energy surface was carried out along the C_{3v} axes in selected cases. The interaction energy, E_I, was calculated as the difference between the energy of the complex and those of the isolated monomers. The inherent basis set superposition error (BSSE) has been taken into account using the full counterpoise method proposed by Boys and Bernardi.[15] In addition, the basis set saturation method has been used to compute an alternative interaction energy by performing MP2/6-311++G(3df,2p)// MP2/6-311++G** calculations.

The topological properties of the electron density, calculated at the B3LYP/6-311++G** level, were characterized using the AIM methodology[16] with the AIMPAC package.[17]

The natural bond orbital analysis was used to evaluate the corresponding atomic charges and to determine the nature of the interactions in the formation of the complexes. These calculations were performed with the NBO code implemented in Gaussian-98.[18]

Nuclear magnetic resonance (NMR) spectroscopic shieldings of the isolated molecules and complexes were calculated using the gauge-independent atomic orbital (GIAO) perturbation method[19] as implemented in the Gaussian-94 and Gaussian-98 programs. This perturbation method, as suggested by London, proposes local gauge origins to define the vector potential of the external electric field.[20]

Results and Discussion

A selection of the geometric parameters obtained for the monomers and complexes calculated is gathered in Tables 1 and 2, respectively. In all the starting geometries for the optimizations, the electron donor atom was pointing toward the silicon atom (see Figure 1). The inclusion of a second set of polarization functions on the isolated silicon derivatives results in a Si$-$F bond distance of SiF$_4$ more similar to the experimental data, while the Si$-$H of SiH$_4$ is almost unaltered. On the contrary, the Si$-$Cl of SiCl$_4$ becomes less similar to the corresponding experimental bond distance.[21$-$23] The comparison of the geometries of the complexes with one or two polarization functions does not indicate any significant change.

The only available experimental geometry, that of the SiF$_4\cdots$NH$_3$ complex (Si$\cdots$N distance of 2.090 Å and F$_{ax}-$Si$-$F$_{eq}$ angle

of 97°),[1] is well reproduced by our calculations (2.099 Å and 97.3° at the B3LYP/6-311++G** level and 2.087 Å and 97.5° at the MP2/6-311++G** level).

Independently of the computational method used, calculations with the largest basis set, B3LYP/6-311++G** and MP2/6-311++G**, provide similar parameters. Only significant differences between both methods are found in the cases of weak complexes with long interaction distances ($>$3.5 Å) due to the problems associated with the inadequate representation of the dispersion forces in the DFT methods that produces longer interaction distances.

Two relative dispositions for the complexes with NH$_3$, OH$_2$, and FH have been explored, with the hydrogen atoms either alternated or eclipsed with respect to the equatorial substituents of the silicon atom (X$_{ec}$ in Figure 1). In all the complexes with NH$_3$, a minimum with a C_{3v} configuration was obtained. In this configuration, the hydrogen atoms are alternated to the silicon equatorial substituents as found previously experimentally[1] and theoretically[7] for the SiF$_4\cdots$NH$_3$ complex. On the contrary, the eclipsed dispositions show one imaginary frequency with a very small relative energy ($\sim$1.0 kcal/mol) that connects two minima by rotation of the NH$_3$ moiety. In the complexes with OH$_2$, both dispositions are minima, the eclipsed disposition being more stable. The coexistence of both minima indicates a small rotational barrier and an effective C_{3v} symmetry for these complexes. Finally, in the complexes with FH the minimum obtained is that in which the hydrogen atom points toward one of the axial substituents of the silicon atom (see Figure 2). Thus, in the case of the SiH$_4\cdots$FH complex a dihydrogen bond is obtained with a H$\cdots$H distance of 1.882 Å, similar to other dihydrogen bonds described in the literature.[24] The alternated dispositions of these complexes show one small imaginary frequency and small relative energy (less than 0.2 kcal/mol) with respect to the minima, indicating low barriers between the three symmetrical minima.

Surprisingly, and in addition to the minima mentioned before, a double minimum (confirmed by frequency calculations) has been found with similar symmetry, C_{3v}, for the complexes between Y$_{ax}$SiCl$_3$ and NH$_3$. The first minimum (Figure 3, I) corresponds to the situation in which the silicon and the nitrogen atoms are very close ($<$2.2 Å) and an important distortion in the silicon derivative is observed. In the second case (Figure 3, II), however, the distance between the silicon and the nitrogen is very large ($>$3.3 Å) and a small distortion of the monomers is observed. A relax scan of the energetic surface has been carried out for the Si$\cdots$N coordinate for all the complexes studied here with NH$_3$. The results (Figure 4) indicate that in

SiXY$_3$···ZW Complexes *J. Phys. Chem. A, Vol. 105, No. 4, 2001* **745**

TABLE 2: Selected Geometrical Parameters of the Complexes[a]

complexes		B3LYP/6-311++G**				MP2/6-311++G**			
$Y_{ax}-Si-(X_{ec})_3···Z$	spatial config	interactn dist	$\Delta(Si-X_{ec})$	$\Delta(Si-Y_{ax})$	$\Delta(\angle Y_{ax}-Si-X_{ec})$	interactn dist	$\Delta(Si-X_{ec})$	$\Delta(Si-Y_{ax})$	$\Delta(\angle Y_{ax}-Si-X_{ec})$
SiH₄···NH₃	C_{3v}	3.263	−0.002	0.007	−1.54	3.181	−0.002	0.007	−1.72
						(3.216)	(−0.002)	(0.007)	(−1.77)
SiH₄···NCH	C_{3v}	3.695	−0.001	0.003	−0.64	3.399	−0.001	0.004	−0.85
SiH₄···CNH	C_{3v}	3.881	−0.001	0.003	−0.58	3.591	−0.001	0.004	−0.83
SiH₄···OH₂ (A)	C_s, A[b]	3.245	−0.002	0.005	−1.06	3.135	−0.001	0.005	−1.21
SiH₄···OH₂ (E)	C_s, E[b]	3.251	−0.002	0.005	−1.07	3.139	−0.001	0.005	−1.18
SiH₄···FH	C_s[c]	1.789				1.882			
SiF₄···NH₃	C_{3v}	2.099	0.038	0.037	−12.17	2.087	0.036	0.036	−12.00
						(2.099)	(0.040)	(0.034)	(−11.85)
SiF₄···NCH	C_{3v}	3.128	0.000	0.008	−2.07	3.078	0.000	0.008	−2.08
SiF₄···CNH	C_{3v}	3.265	0.000	0.008	−2.16	3.215	0.000	0.009	−2.25
SiF₄···OH₂ (A)	C_s, A[b]	2.767	0.003	0.011	−3.43	2.785	0.001	0.010	−3.09
SiF₄···OH₂ (E)	C_s, E[b]	2.772	0.003	0.011	−3.44	2.786	0.002	0.010	−3.12
SiF₄···FH	C_s[c]	1.914				1.952			
SiCl₄···NH₃ (I)	C_{3v}, I[d]	2.181	0.056	0.075	−12.23	2.143	0.054	0.069	−11.98
						(2.070)	(0.081)	(0.060)	(−13.14)
SiCl₄···NH₃ (II)	C_{3v}, II[d]	3.534	0.001	0.011	−1.72	3.389	0.011	0.001	−1.71
						(3.446)	(0.011)	(0.001)	(−1.74)
SiCl₄···NCH	C_{3v}	3.957	−0.001	0.007	−0.70	3.567	−0.001	0.008	−0.79
SiCl₄···CNH	C_{3v}	4.166	−0.001	0.007	−0.67	3.828	−0.001	0.007	−0.80
SiCl₄···OH₂ (A)	C_s, A[b]	3.504	−0.001	0.009	−1.13	3.333	0.000	0.008	−1.14
SiCl₄···OH₂ (E)	C_s, E[b]	3.504	0.000	0.008	−1.19	3.325	0.000	0.008	−1.24
SiCl₄···FH	C_s[c]	2.441				2.441			
FSiH₃···NH₃	C_{3v}	2.639	−0.002	0.024	−4.50	2.598	−0.001	0.023	−4.64
ClSiH₃···NH₃	C_{3v}	2.681	−0.004	0.047	−4.73	2.651	−0.003	0.040	−4.65
ClSiF₃···NH₃	C_{3v}	2.125	0.033	0.075	−12.57	2.123	0.031	0.068	−11.97
FSiCl₃···NH₃ (I)	C_{3v}, I[d]	2.122	0.063	0.031	−12.39	2.081	0.060	0.032	−12.34
FSiCl₃···NH₃ (II)	C_{3v}, II[d]	3.312	0.004	0.007	−2.43	3.217	0.004	0.007	−2.44
HSiF₃···NH₃	C_{3v}	2.139	0.041	0.013	−12.22	2.125	0.039	0.014	−11.98
HSiCl₃···NH₃ (I)	C_{3v}, I[d]	2.118	0.071	0.007	−13.22	2.091	0.065	0.009	−13.01
HSiCl₃···NH₃ (II)	C_{3v}, II[d]	3.475	0.002	0.002	−1.97	3.344	0.002	0.003	−1.96

[a] The results obtained at MP2/6-311++G(2d,2p) are given in parentheses. Distances in Å and angles in deg (see Figure 1) compared to the isolated monomers. [b] (A) stands for the alternated configuration of the hydrogen of the OH₂ and the equatorial substituents of Si, and (E) for the eclipsed one. [c] The reported interaction is between the hydrogen of the FH molecule and one of the eclipsed substituents of the silicon atom. [d] See Figure 3.

the absence of chlorine atoms in the equatorial positions only one minimum is found. The two minima found for the complexes with $Y_{ax}SiCl_3$ correspond to two extreme situations. In the first minimum, the loss of energy due to a large distortion of the Si derivative is compensated with a strong interaction with the NH₃ molecule. Yet, in the second minimum, the weak interaction between both molecules corresponds to a small loss of the energy related to the slight distortion of the monomers. The presence of the three hydrogen atoms and their potentiality to interact with the chlorine atoms could be the reason for the existence of the two minima.

The most favored minimum depends on the substituent in the axial position (Y_{ax}). Thus, when a fluorine atom is in that disposition, the minima I is favored. In the case of $Y_{ax} = H$, both minima are similarly stable and, in the case of $Y_{ax} = Cl$, complex II is the most stable (see interaction energies in Table 3).

The substitution of a hydrogen atom of the silane molecule, SiH₄, by a chlorine atom in axial or equatorial positions, produced a shortening of the interaction distance of approximately 0.6 Å in the complex with ammonia (in SiH₄···NH₃, Si···N distance is 3.2 Å). However, if both positions are substituted simultaneously, a lengthening of the interaction distance is observed (in SiCl₄···NH₃, Si···N is 3.4 Å). In contrast, the substitution of the silane hydrogen in the axial position by a fluorine atom produces a shortening of 0.6 Å in the interaction distance. If this substitution takes place in the

three equatorial positions the shortening rises to 1.2 Å, which is similar to that found in the silicon tetrafluoride complex.

Concerning the effect of the interaction in the geometry of the monomers involved, an important distortion of the silicon derivative is observed in all the cases in which the electron-rich molecule is close (Si···Z distance ∼ 2.1 Å). In those cases, the $Y_{ax}-Si-X_{eq}$ angle can reach values as small as 97° in the SiF₄···NH₃ complex. An exponential relationship has been found between the distortion of the angle and the Si···Z distance (Figure 4). Other parameters that suffer the effect of the interaction are the bond distances of the silicon derivatives. In all cases, a lengthening of the $Si-Y_{ax}$ is observed that is more important in the close Si···Z contacts. In addition, a significant lengthening of the $Si-X_{ec}$ bond is observed in the complexes with Si···Z distances of about 2.1 Å.

The distortion energy (difference between the energies of the isolated monomer in their minima configuration and of the monomer in its geometry in the complex) calculated for the silicon derivatives in the six complexes with short interaction distances ranges between 19 and 21 kcal/mol. This distortion energy drops to 1.6 kcal/mol in those complexes with a Si···Z distance of ∼2.6 Å (ClSiH₃···NH₃ and FSiH₃···NH₃).

The interaction energies calculated with both B3LYP and MP2 methods and using the 6-311++G** basis set are gathered in Table 3. The calculated interaction, E_I, and corrected interaction energies, E_{I+BSSE}, are gathered in Table 3. The BSSE correction seems to be inadequate for those complexes with large
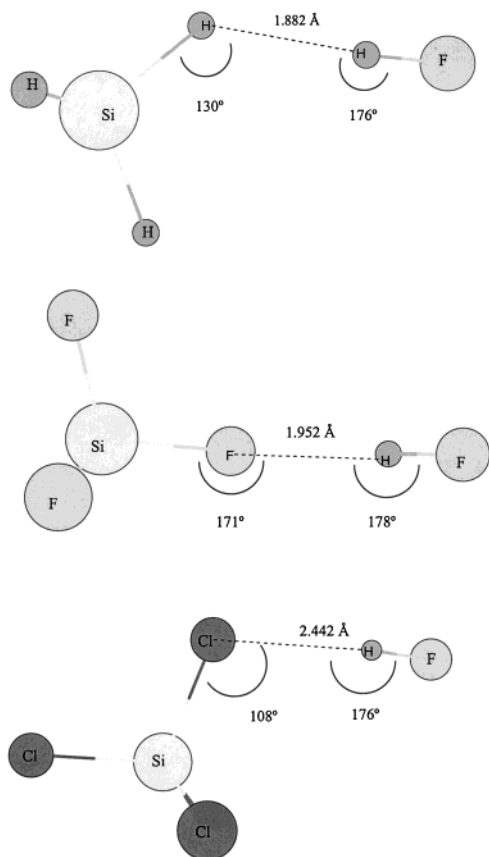
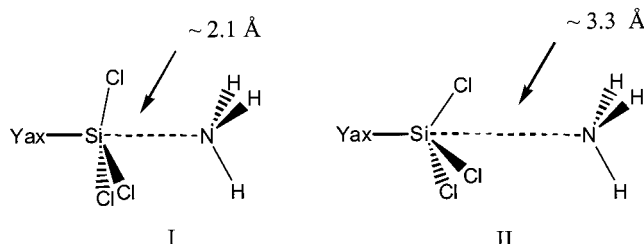**Figure 2.** Complexes with FH obtained at the MP2/6-311++G** level.

Figure 3. Schematic representation of the double minima found for the trichlorosilicon derivatives in their interaction with ammonia (Y_{ax} = H, F, Cl).

changes in the electronic structure of the monomers. In the present study, the trichlorosilicon derivatives complexes with ammonia that are more stable in the (I) configuration became less stable than II and with a positive E_{I+BSSE} after the inclusion of the BSSE correction. Another complex with irregular of E_{I+BSSE} values is the $SiCl_4\cdots CNH$ which interaction became repulsive. Thus, the results including the mentioned correction should be considered with caution. In addition, the MP2/6-311++G(3df,2p)//MP2/6-311++G** energies provide similar results to the uncorrected MP2/6-311++G** ones.

The calculations carried out at the MP2/6-311++G(2d,2p) provide similar interaction energies to the MP2/6-311++G** ones except for the $SiCl_4\cdots NH3$ complexes where the configuration (I) became more stable with the largest basis set. In general, they range from −11 kcal/mol for the $SiF_4\cdots NH_3$ to positive or almost positive values for the local minima found in the complexes with hydrogen or chlorine atoms in equatorial positions. These last series of local minima are trapped in a compromise between the intermolecular interaction and the strain generated in the silicon derivatives due to close contacts.
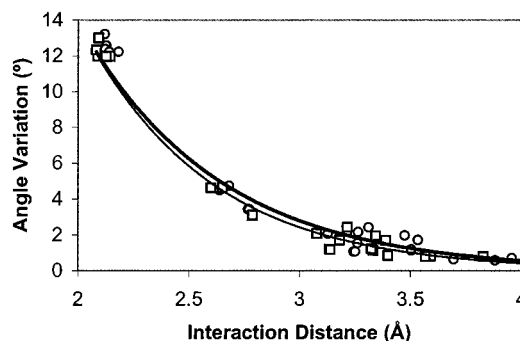

Figure 4. Interaction distance vs $Y_{ax}-Si-X_{eq}$ angle variation in the complexes calculated at MP2/6-311++G** (squares) and B3LYP/6-311++G** (circles) levels. The fitted equation corresponds to angle variation = 462.08 exp(−1.7493 × interaction distance), $n = 24$, $r^2 = 0.94$ for the MP2/6-311++G** results (thin line) and angle variation = 344.38 exp(−1.6043 × Interaction distance), $n = 24$, $r^2 = 0.94$ for the B3LYP/6-311++G** results (thick line).

In order to understand the effect of the silicon substituents in the axial and equatorial position, a Free–Wilson model[25] has been carried out with all the ammonia complexes. The Free–Wilson model correlates a given property, in this case the interaction energy, with the presence/absence of the substituents in different positions. In this case, the silane (SiH_4) has been considered as the base molecule and the effect of the substitution of hydrogen atoms by fluorine or chlorine in axial and equatorial position has been taken into account. The obtained model using the B3LYP/6-311++G** and MP2/6-311++G** interaction energies is as follows:

B3LYP/6-311++G**:

$$E_I = -2.06 - 4.18(nF_{ax}) - 1.35(nF_{eq}) - 2.27(nCl_{ax}) + 0.68\,(nCl_{eq}) \qquad n = 9, r^2 = 0.94$$

MP2/6-311++G**:

$$E_I = -1.09 - 4.15(nF_{ax}) - 1.20(nF_{eq}) - 1.69(nCl_{ax}) - 0.03(nCl_{eq}) \qquad n = 9, r^2 = 0.93$$

The constant term of these equations provides a very close value to that of the interaction energy of the $SiH_4\cdots NH_3$ complex. The rest of the coefficients indicate a stabilization of about 4.1 kcal/mol when a fluorine atom is in axial, 1.3 for each fluorine atom in equatorial position and approximately 2 for the chlorine atoms in axial position. It is worth mentioning that the presence of chlorine atoms in equatorial position does not stabilize or slightly destabilize the complex formation when compared to that with hydrogen atoms in the same position.

The analysis of the electron density shows positive Laplacians at the bond critical points (BCP), indicating ionic interactions between the silicon and the electron donor atoms (see Table 4). The ellipticity of the electron density at the BCP is, in all the cases studied, close to zero (exactly zero for the C_{3v} symmetry systems). The position of the bond critical point is approximately in the middle of the interaction distance except for those cases with short interaction distances where the BCP is much closer to the silicon atom than to the nitrogen of ammonia, which corresponds to the small values of the relative position of the BCP gathered in Table 3. The value of the electron density at the bond critical point depends on the interaction distance as have been shown previously for other systems.[26-29] Thus, the large number of data obtained for Si···

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TABLE 3: Total Energy (hartrees), E_T, and Interaction, E_I, and Corrected Interaction Energies (kcal/mol), EI + BSSE, of the Complexes Studied at B3LYP/6-311++G and MP2/6-311++G** Levels of Computation[a]**

	B3LYP/6-311++G**			MP2/6-311++G**			MP2/6-311++G(3df,2p)// MP2/6-311++G**
	E_T	E_I	E_{I+BSSE}	E_T	E_I	E_{I+BSSE}	E_I
SiH$_4$···NH$_3$	−348.498 87	−1.17	−0.89	−347.791 46	−2.26	−1.33	−2.15
				(−347.822 13)	(−2.01)	(−1.61)	
SiH$_4$···NCH	−385.369 29	−0.32	−0.24	−384.577 70	−1.34	−0.88	−1.57
SiH$_4$···CNH	−385.346 21	−0.24	−0.20	−384.547 76	−1.17	−0.80	−1.50
SiH$_4$···OH$_2$ (A)	−368.374 23	−0.89	−0.60	−367.650 37	−1.95	−0.97	−1.66
SiH$_4$···OH$_2$ (E)	−368.374 24	−0.90	−0.59	−367.650 39	−1.96	−0.94	−1.66
SiH$_4$···FH	−392.398 72	−1.29	−1.12	−391.653 60	−1.49	−0.77	−1.53
SiF$_4$···NH$_3$	−745.868 91	−10.92	−8.57	−744.424 14	−11.42	−5.57	−11.39
				(−744.568 08)	(−9.59)	(−5.51)	
SiF$_4$···NCH	−782.727 24	−2.47	−1.68	−781.199 82	−3.87	−2.10	−3.86
SiF$_4$···CNH	−782.704 07	−2.34	−1.63	−781.169 78	−3.65	−2.03	−3.77
SiF$_4$···OH$_2$ (A)	−765.734 22	−4.33	−2.89	−764.274 33	−5.64	−2.71	−4.46
SiF$_4$···OH$_2$ (E)	−765.734 25	−4.34	−2.87	−764.274 58	−5.80	−2.67	−4.56
SiF$_4$···FH	−789.755 58	−2.76	−2.17	−788.274 09	−3.00	−1.96	−2.70
SiCl$_4$···NH$_3$ (I)	−2187.194 08	0.02	2.42	−2184.222 99	−3.65	5.48	−5.82
				(−2184.347 54)	(−4.79)	(0.49)	
SiCl$_4$···NH$_3$ (II)	−2187.196 46	−1.47	−0.64	−2184.224 48	−4.59	−1.42	−3.49
				(−2184.344 45)	(−2.85)	(−1.54)	
SiCl$_4$···NCH	−2224.066 78	−0.55	−0.12	−2221.010 17	−3.32	−1.02	−3.04
SiCl$_4$···CNH	−2224.043 64	−0.43	0.01	−2220.979 62	−2.77	−0.94	−2.75
SiCl$_4$···OH$_2$ (A)	−2207.071 94	−1.26	−0.53	−2204.082 77	−3.89	−1.02	−2.76
SiCl$_4$···OH$_2$ (E)	−2207.071 94	−1.26	−0.51	−2204.082 55	−3.75	−0.90	−2.76
SiCl$_4$···FH	−2231.096 06	−1.43	−0.78	−2228.084 48	−2.47	−0.44	−2.24
FSiH$_3$···NH$_3$	−447.839 74	−6.08	−5.09	−446.947 80	−7.17	−4.87	−6.94
ClSiH$_3$···NH$_3$	−808.1803 5	−5.38	−4.46	−806.903 96	−6.44	−4.18	−6.21
ClSiF$_3$···NH$_3$	−1106.200 59	−8.14	−5.78	−1104.373 15	−8.70	−2.85	−9.60
FSiCl$_3$···NH$_3$ (I)	−1826.864 70	−3.73	−1.17	−1824.276 91	−7.59	1.64	−8.97
FSiCl$_3$···NH$_3$ (II)	−1826.862 14	−2.12	−1.24	−1824.272 69	−4.91	−1.91	−3.97
HSiF$_3$···NH$_3$	−646.524 53	−5.71	−3.61	−645.263 44	−6.54	−1.12	−6.55
HSiCl$_3$···NH$_3$ (I)	−1727.524 95	−1.30	1.08	−1725.118 24	−4.93	4.34	−5.62
HSiCl$_3$···NH$_3$ (II)	−1727.524 72	−1.16	−0.46	−1725.117 17	−4.26	−1.19	−3.04

[a] The MP2/6-311++G(2d,2p) results are given in parentheses. The basis set saturation energies computed at the MP2/6-311++G(3df,2p)// MP2/6-311++G** level.

N interactions (15 cases) has allowed to verify this hypothesis. In addition, two simple covalently bonded systems (H$_3$SiX, X = NH$_2$ and NC) have been included in the regression to verify the generality of the given relationship (see Figure 5). The results obtained for this family of interactions is in agreement with our previous findings referred to the correlation between the electron density at the bond critical point and the bond distance for different bonds both theoretically[20−22] and experimentally.

The charge transfer, dipole moment enhancement, and nature of the interaction using the NBO method at the B3LYP/6-311++G** level are gathered in Table 5. Large charge transfer and dipole moment enhancement due to the formation of the complexes are observed in those cases where the Si···Z distance is short (∼2.1 Å) which corresponds to complexes where the silicon derivatives suffered large distortions. The larger values (over 4 D) are in agreement with the experimental finding for the dipole moment of the SiF$_4$···NH$_3$ complex. An analysis of the atomic charge variation indicates that most of the electron gain of the silicon derivatives goes to the axial substituent.

The NBO analysis (Table 5) shows the formation of an ionic Si−N bond, with over 90% contribution of the nitrogen in complexes with short Si···N distances (<2.1 Å). The molecular orbital responsible of the mentioned bond shows an important contribution of the p and d orbitals of the silicon (in average sp^{4}d$^{2.75}$) and a sp^3 hybridization of the nitrogen atom. In the rest of the complexes (Si···N > 2.1 Å), a lone pair of the electron donor atom, Z, interacts with the antibonding Si−Y$_{ax}$ orbital. This interaction is similar to that found in hydrogen bonds with the difference being that the electron acceptor atom is a silicon instead of a hydrogen atom. In the HSiF$_3$···NH$_3$

TABLE 4: Electron Density at the Interaction Bond Critical Point (e/au^3), Its Corresponding Laplacian (e/au^5), Distance of the Bond Critical Point to the Silicon Atom (Å), and Relative Position of the BCP to the Interaction Distance Calculated at the B3LYP/6-311++G Level of Theory**

	ρ_{BCP}	$\nabla^2\rho_{BCP}$	BCP···Si distance	relative position of the BCP[a]
SiH$_4$···NH$_3$	0.009	0.021	1.580	0.48
SiH$_4$···NCH	0.003	0.010	1.891	0.51
SiH$_4$···CNH	0.003	0.008	1.940	0.50
SiH$_4$···OH$_2$ (A)	0.007	0.021	1.643	0.51
SiH$_4$···OH$_2$ (E)	0.007	0.019	1.662	0.51
SiF$_4$···NH$_3$	0.062	0.123	0.815	0.39
SiF$_4$···NCH	0.008	0.029	1.535	0.49
SiF$_4$···CNH	0.008	0.024	1.564	0.48
SiF$_4$···OH$_2$ (A)	0.014	0.045	1.338	0.48
SiF$_4$···OH$_2$ (E)	0.015	0.048	1.413	0.51
SiCl$_4$···NH$_3$ (I)	0.057	0.054	0.860	0.39
SiCl$_4$···NH$_3$ (II)	0.007	0.016	1.757	0.50
SiCl$_4$···NCH	0.003	0.008	2.079	0.53
SiCl$_4$···CNH	0.002	0.007	2.137	0.51
SiCl$_4$···OH$_2$ (A)	0.005	0.017	1.829	0.52
SiCl$_4$···OH$_2$ (E)	0.005	0.017	1.921	0.55
FSiH$_3$···NH$_3$	0.022	0.045	1.185	0.45
ClSiH$_3$···NH$_3$	0.021	0.042	1.219	0.45
ClSiF$_3$···NH$_3$	0.059	0.105	0.827	0.39
FSiCl$_3$···NH$_3$ (I)	0.062	0.089	0.827	0.39
FSiCl$_3$···NH$_3$ (II)	0.009	0.020	1.624	0.49
HSiF$_3$···NH$_3$	0.057	0.098	0.834	0.39
HSiCl$_3$···NH$_3$ (I)	0.063	0.085	0.826	0.39
HSiCl$_3$···NH$_3$ (II)	0.007	0.017	1.723	0.50

[a] Calculated as the "Si···BCP distance" divided by the "Si···Z interaction distance".
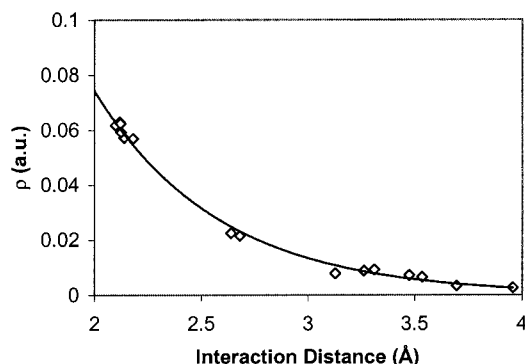
Figure 5. Interaction distance vs electron density at the bond critical point (ρ_{bcp}) calculated at the B3LYP/6-311++G** level. The fitted equation corresponds to interaction distance = 0.5109 − 0.576 ln(ρ_{bcp}), $n = 17$, $r^2 = 0.989$.

TABLE 5: Charge Transfer (e), Dipole Moment Enhancement, and Orbital Interaction Energy (kcal/mol) or Bond Composition Calculated at the B3LYP/6-311++G Level with the NBO Method**

	charge transfer	μ enhancement	$E(2)^a$ or bond hybridization
$SiH_4\cdots NH_3$	0.016	0.65	2.23
$SiH_4\cdots NCH$	0.003	0.36	0.48
$SiH_4\cdots CNH$	0.004	0.34	0.68
$SiH_4\cdots OH_2$ (A)	0.007	0.36	1.27
$SiH_4\cdots OH_2$ (E)	0.007	0.31	1.28
$SiH_4\cdots FH$	0.002	0.08	
$SiF_4\cdots NH_3$	0.181	4.69	Si(sp$^{3.74}$ d$^{2.75}$)N(sp$^{3.13}$)
$SiF_4\cdots NCH$	0.001	0.95	0.41
$SiF_4\cdots CNH$	0.004	0.96	0.55
$SiF_4\cdots OH_2$ (A)	0.013	1.01	1.37
$SiF_4\cdots OH_2$ (E)	0.015	0.89	1.39
$SiF_4\cdots FH$	0.002	0.24	
$SiCl_4\cdots NH_3$ (I)	0.193	4.44	Si(sp$^{4.48}$d$^{2.76}$)N(sp$^{2.76}$)
$SiCl_4\cdots NH_3$ (II)	0.004	0.78	1.03
$SiCl_4\cdots NCH$	−0.001	0.58	0.14
$SiCl_4\cdots CNH$	−0.001	0.52	0.17
$SiCl_4\cdots OH_2$ (A)	0.000	0.51	0.54
$SiCl_4\cdots OH_2$ (E)	0.001	0.33	0.6
$SiCl_4\cdots FH$	0.000	−0.02	
$FSiH_3\cdots NH_3$	0.067	1.70	9.07
$ClSiH_3\cdots NH_3$	0.069	2.86	9.62
$ClSiF_3\cdots NH_3$	0.184	3.90	Si(sp$^{3.96}$d$^{2.77}$)N(sp$^{2.89}$)
$FSiCl_3\cdots NH_3$ (I)	0.203	3.83	Si(sp$^{3.59}$d$^{2.49}$)N(sp$^{2.84}$)
$FSiCl_3\cdots NH_3$ (II)	0.009	2.26	1.44
$HSiF_3\cdots NH_3$	0.177	4.50	13.58
$HSiCl_3\cdots NH_3$ (I)	0.211	4.05	Si(sp$^{4.18}$d$^{2.80}$)N(sp$^{2.74}$)
$HSiCl_3\cdots NH_3$ (II)	0.004	0.66	0.85

^{a} $E(2)$ between the lone pair of the Z atom and the antibonding Si−Y_{ax} bond.

complex, even though the interaction distance is 2.1 Å, no ionic bond was found between the silicon and nitrogen atoms, as should have been the case for complexes with short Si$\cdots$N distances. On the contrary, an interaction between the N lone-pair and the antibonding Si−H$_{ax}$ orbital [$E(2)$ 13.58] and three interactions between the N lone-pair and the three antibonding Si−F$_{eq}$ orbitals [$E(2)$ 18.20] were found.

The absolute chemical shieldings of the monomers and complexes are gathered in Table 6. Only negative $\Delta\sigma$ due to the formation of the complexes are observed in the SiH_4 cases. The larger differences are obtained for those complexes with NH_3 reaching values of 70−80 ppm for the silicon derivatives with chlorine atoms in the equatorial positions. The shielding difference in the Z atom is negative for ammonia and water and positive for HCN and NCH. In addition, the large differences observed in the ammonia and water complexes, even

TABLE 6: Absolute NMR Shieldings of the Isolated Monomers and Complexes and Shielding Differences at the B3LYP/6-311++G Level Calculated with the GIAO Method**

	Si		Z
	σ	$\Delta\sigma$	$\Delta\sigma$
SiH_4	448.288		
$SiH_4\cdots NH_3$	444.097	−4.192	−7.60
$SiH_4\cdots NCH$	444.946	−3.342	1.20
$SiH_4\cdots CNH$	444.351	−3.938	1.12
$SiH_4\cdots OH_2$ (A)	444.617	−3.671	−5.86
$SiH_4\cdots OH_2$ (E)	444.788	−3.501	−6.13
SiF_4	443.806		
$SiF_4\cdots NH_3$	469.925	26.119	−42.37
$SiF_4\cdots NCH$	445.144	1.338	8.94
$SiF_4\cdots CNH$	445.186	1.379	1.05
$SiF_4\cdots OH_2$ (A)	446.824	3.017	−14.02
$SiF_4\cdots OH_2$ (E)	446.836	3.030	−15.37
$SiCl_4$	314.152		
$SiCl_4\cdots NH_3$ (I)	387.513	73.361	−85.35
$SiCl_4\cdots NH_3$ (II)	314.396	0.244	−11.80
$SiCl_4\cdots NCH$	314.758	0.606	1.32
$SiCl_4\cdots CNH$	314.771	0.619	4.96
$SiCl_4\cdots OH_2$ (A)	314.309	0.157	−10.01
$SiCl_4\cdots OH_2$ (E)	314.292	0.140	−11.19
$FSiH_3$	353.923		
$FSiH_3\cdots NH_3$	396.357	42.434	−18.92
$ClSiF_3$	408.009		
$ClSiF_3\cdots NH_3$	442.617	34.609	−42.19
$FSiCl_3$	341.520		
$FSiCl_3\cdots NH_3$ (I)	410.865	69.345	−85.76
$FSiCl_3\cdots NH_3$ (II)	341.348	−0.173	−17.18
$HSiF_3$	406.418		
$HSiF_3\cdots NH_3$	437.702	31.284	−43.23
$HSiCl_3$	317.472		
$HSiCl_3\cdots NH_3$ (I)	397.635	80.163	−86.41
$HSiCl_3\cdots NH_3$ (II)	319.497	2.025	−13.70

for the weak ones, indicate that this technique could be appropriate to characterize these interactions.

Conclusions

The complexes of a series of silicon derivatives, SiX_3Y (X,Y = H, F, Cl), and several electron donor atoms (NH_3, NCH, CNH, OH_2, and FH) were studied. The calculations were carried out at the B3LYP/6-311++G** and MP2/6-311++G** levels. An interaction between the silicon and the electron donor atoms is observed for all the cases except for the complexes with FH where the hydrogen atom interacts with the silicon substituents. Several conformations were explored for each system. Thus, the complexes with OH_2 present two minima connected by a small barrier. In the $YSiCl_3\cdots NH_3$ complexes, two minima were found with C_{3v} symmetry.

The interaction distances, Si$\cdots$Z, were obtained for all the complexes range between 2.1 and 4.1 Å, and a correlation has been found between this interaction distance and the silicon monomer distortion. The interaction energies can reach values of −10 kcal/mol for the stronger complexes, and a numerical relationship has been found between this interaction energy and the substituents in equatorial and axial positions.

The analysis of the electron density of the complexes indicates an ionic interaction between the silicon and the electron donor atoms. An exponential correlation has been found between the electron density at the bond critical point and the interaction distance.

The NBO analysis corroborates the ionic interaction between the silicon and electron donor atoms in the complexes with short Si$\cdots$Z distances (<2.1 Å). In the rest of the cases (distances >

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2.1 Å), the lone pair of the electron donor atom interacts with the Y$_{ax}$−Si antibonding orbital to stabilize the complex.

Finally, important chemical shielding variations are found in the silicon nucleus due to the complex formation (up to 80 ppm). In the case of the complexes with NH$_3$ and OH$_2$, the O and N nuclei experience important variations of their chemical shieldings which make them adequate for experimental validation of complex formation.

References and Notes

(1) Ruoff, R. S.; Emilsson, T.; Jaman, A. I.; Germann, T. C.; Gutowsky, H. S. *J. Chem. Phys.* **1992**, *96*, 3441.

(2) Urban, R. D.; Rouille, G.; Takami, M. *J. Mol. Struct.* **1997**, *413*−*414*, 511.

(3) Bassindale, A. R.; Borbaruah, M.; Glynn, S. J.; Parker, D. J.; Taylor, P. G. *J. Chem. Soc., Perkin Trans 2* **1999**, 2099.

(4) Bassindale, A. R.; Parker, D. J.; Taylor, P. G. *J. Chem. Soc., Perkin Trans 2* **2000**, 1059.

(5) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 1066.

(6) Rossi, A. R.; Jasinski, J. M. *Chem. Phys. Lett.* **1990**, *169*, 399.

(7) Keith, T. A.; Bader, R. F. W. *J. Chem. Phys.* **1992**, *96*, 3447.

(8) Ignatov, S. K.; Sennikov, P. G.; Ault, B. S.; Bagatur'yants, A. A.; Simdyanov, I. V.; Razuvaev, A. G.; Klimov, E. J.; Gropen, O. *J. Phys. Chem. A* **1999**, *103*, 8326.

(9) Schoeller, W. W.; Rozhenko, A. *Eur. J. Inorg. Chem.* **2000**, 375.

(10) *Gaussian 94*, revision E.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortìz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonz·lez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

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

(12) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) Krishnam, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 3265.

(14) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(15) Boys, S. B.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(16) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University: New York, 1990.

(17) Bieger-Konig, F. W.; Bader, R. F. W.; Tang, T. H. J. *J. Comput. Chem.* **1982**, *3*, 317.

(18) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(19) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(20) London, F. *J. Phys. Radium* **1937**, *8*, 397.

(21) Dang-Dhu, M.; Pierre, G.; Saint-Loup, R. *Mol. Phys.* **1974**, *28*, 447.

(22) Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 1549.

(23) Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*; North-Holland: Amsterdam, 1968.

(24) Alkorta, I.; Foces-Foces, C.; Elguero, J. *Chem. Commun.* **1966**, 1633.

(25) Hansch, C.; Leo, A. *Exploring QSAR*; American Chemical Society: Washington, DC, 1995; p 208. Free, S. M.; Wilson, J. W. *J. Med. Chem.* **1964**, *7*, 395. Fujita, T. Ban, T. *J. Med. Chem.* **1971**, *14*, 148.

(26) Alkorta, I.; Rozas, I.; Elguero, J. *J. Struct. Chem.* **1998**, *9*, 243.

(27) Alkorta, I.; Barrios, L.; Rozas, I.; Elguero, J. *Theochem* **2000**, *496*, 131.

(28) Pendas, A. M.; Costales, A.; Luaña, V. *J. Phys. Chem. B* **1998**, *102*, 6937.

(29) Espinosa, E.; Souhassou, M.; Lachekar, H.; Lecomte, C. *Acta Crystallogr.* **1999**, *B55*, 563.