

# Stand up for Electrostatics: The Disiloxane Case

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The basicity of the simplest silicone, disiloxane ( $\text{H}_3\text{Si}-\text{O}-\text{SiH}_3$ ), is strongly affected by the Si–O–Si angle ( $\alpha$ ). We use high-level *ab initio* MP2/aug'-cc-pVTZ calculations and the molecular electrostatic potential (MEP) to analyze the relationship between the increase in basicity and the reduction of  $\alpha$ . Our results clearly point out that this increase can be explained through the MEP, as the interactions between oxygen from disiloxane and the acceptors are mostly electrostatic. Furthermore, the effect of  $\alpha$  on the tetrel bond between disiloxane and several Lewis bases

can again be rationalized using the MEP. Finally, we explore the cooperativity throughout  $\alpha$  for ternary complexes where disiloxane simultaneously interacts with a Lewis acid and a Lewis base. Both non-covalent interactions remain cooperative for all  $\alpha$  values, although the largest cooperativity effects are not always those maximizing the binding energy in the binary complexes. Overall, the MEP remains a powerful predictor for noncovalent interactions.

## Introduction

Acidity and basicity are two of the most relevant properties in order to understand the behavior of molecules in terms of reactivity or interaction towards other molecules in the environment. These properties can be modulated most commonly changing the substituents in the vicinity of the acidic/basic center, in line with the seminal work of Louis Plack Hammett from 1937 regarding the substituent constant  $\sigma$  parameter.<sup>[1,2]</sup> Another important way of modulating these intrinsic properties of molecules, which we have long been interested in,<sup>[3,4]</sup> is through non-covalent interactions with other molecules. In the specific case of ditopic molecules, those that show both acidic and basic centers, the interaction with other molecules can increase or decrease its intrinsic acid/base properties, leading to cooperativity or anticooperativity (also called synergistic and antagonistic effects). The cooperative/anticooperative balance of non-covalent interactions are of uttermost importance in many chemical systems, and has been extensively explored.<sup>[5,6]</sup>

Amongst the many ditopic molecules of chemical importance, we find that disiloxane ( $\text{H}_3\text{Si}-\text{O}-\text{SiH}_3$ ) is particularly interesting. This molecule can be thought of as the simplest silicone, but it also represents the simplest molecule with a ( $\text{R}_3\text{Si}-\text{O}-\text{Si}(\text{R}_3)$ ) moiety. Disiloxane has thus often been studied as a model for both silicones and silicates, and a number of studies have used this simple molecule to understand the

"elusive"<sup>[7]</sup> nature of the ubiquitous Si–O bond.<sup>[8–17]</sup> Regarding its ditopic character, disiloxane can act as a Lewis base *via* its oxygen atom, but it can also behave as a Lewis acid by allowing tetrel bonds with the silicon atoms. Tetrel bonds are analogs to halogen bonds, but they are formed with an atom from Group 14 in the periodic table instead of a halogen atom as the Lewis acidic site.<sup>[18–21]</sup>

We have previously studied the changes (increments) in basicity that can arise through such tetrel bonds with the Si atoms of silanol and disiloxane,<sup>[22]</sup> as well as the cooperativity when ternary complexes of disiloxane with a Lewis acid and a Lewis base are formed.<sup>[23]</sup> A scheme of the different complexes that can be formed with disiloxane can be found in Figure 1.

An important fact regarding the basicity of the disiloxane linkage, that has long been known, is they are less basic than their carbon counterparts: ethers.<sup>[24,25]</sup> Just as an example, the proton affinity of dimethyl ether ( $\text{H}_3\text{C}-\text{O}-\text{CH}_3$ ) is 792.0 kJ/mol, while the proton affinity of disiloxane is quite lower, 749.0 kJ/mol.<sup>[26]</sup> The basic character of oxygen in siloxane linkages is key to understand the different cation binding capabilities of the silicon counterparts of crown ethers, the so-called silacrown ethers.<sup>[27,28]</sup> An excellent review has been published recently dealing with some of these issues in more depth.<sup>[29]</sup> There is some interest, then, also from the experimental point of view, in understanding how to tune the oxygen basicity in Si–O groups.

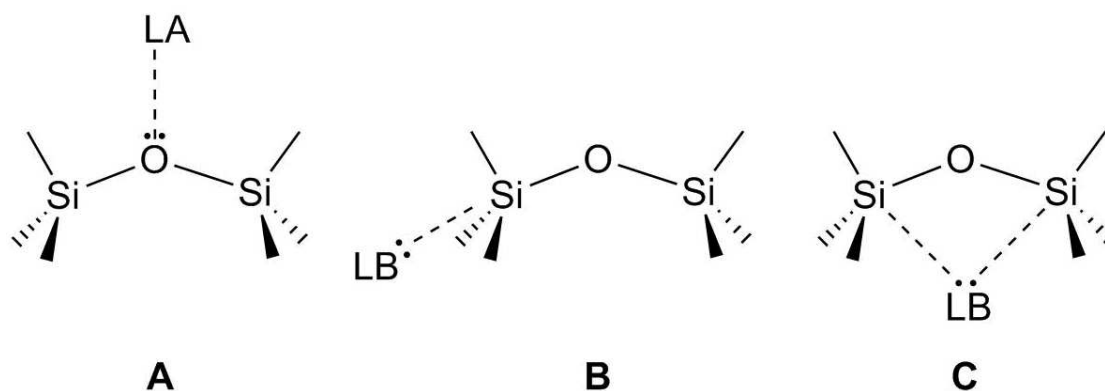
The difference in basicity is particularly surprising because the reported calculated charges on the oxygen atom are lower (more negative) in the case of Si–O–Si linkages than in C–O–C.<sup>[14,30,31]</sup> Additionally, several studies show that the siloxane linkage becomes more ionic (*i.e.* the oxygen becomes more negative) at larger angles.<sup>[13,32,33]</sup> Very surprisingly, this finding seems to be in contradiction with the observation that the disiloxane linkage turned more basic at smaller Si–O–Si angles.<sup>[14,25,32]</sup> How can a *more negative* atom be *less basic*? A number of studies in the past have dealt with this question, proposing different explanations. Some authors suggest that the difference in basicity arises from the different nature of the

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**Figure 1.** Possible complexes that can be formed between disiloxane and a Lewis acid (LA) or a Lewis base (LB). We will refer to the different binary complexes as A, B or C. Simultaneous interaction with a LA and a LB can give rise to either A:B or A:C ternary complexes.

Si–O and C–O bonds. In the case of the Si–O bond, the oxygen lone pair is less available for hydrogen bonding due to  $p(\text{O}) \rightarrow d(\text{Si})$   $\pi$  backbonding, which has been termed an “obsolete” model,<sup>[15,32,33]</sup> or from  $\text{LP}(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{R})$  negative hyperconjugation.<sup>[14,30,34]</sup> Other authors, studying the coordination to metal cations, attribute the different basicity to the fact that the more positive Si atoms will repel the cation, and thus weaken the interaction with oxygen.<sup>[31]</sup> Importantly, these (apparently) contradictory observations regarding the charge/basicity of the oxygen in the siloxane group have been used to criticize the use of electrostatic models to understand and model non-covalent interactions and bonding.<sup>[14]</sup>

However, the failure of the calculated charges to properly predict the observed changes of disiloxane basicity is not a problem of ‘electrostatics’, but rather an intrinsic problem arising from the definition of net atomic charges. It is very well-known that the calculated values for atomic charges are very dependent on the partition method,<sup>[35,36]</sup> giving rise to a problem that Politzer and co-workers named as the “fallacy of atomic charges”.<sup>[37]</sup> In fact, the mere existence of halogen bonds came as a shock to many chemists who were used to thinking of electronic distributions in terms of partial atomic charges. In this sense, the concept of  $\sigma$ -hole has greatly helped in our understanding of these and other noncovalent interactions.<sup>[38–44]</sup>

At this point, it is important to note that the  $\sigma$ -hole was originally related to the molecular electrostatic potential (MEP) and to the finding of areas of positive potential when it was plotted on a density isosurface.<sup>[38,45–47]</sup> The MEP has been shown to be a powerful tool for the prediction of electrophilic and nucleophilic sites in a molecule, and the value of the potential can often be correlated with the strength of the interactions at those sites.<sup>[48,49]</sup> Furthermore, when mapped on an isodensity surface,<sup>[50,51]</sup> the MEP has proven to be a valuable tool in chemical education, mostly because it provides a quick, visual and simple interpretation of the electronic distribution.<sup>[52–57]</sup> The main problem of analyzing the MEP in the isolated molecules has to do with the fact that it does not account for the polarization of the electron density when these molecules interact with the environment. Different methods to account for

the effect of polarization have been proposed in the literature, such as the calculation of molecular polarization potential (MPP) maps,<sup>[58–65]</sup> and the importance of accounting for polarization is widely recognized.<sup>[66,67]</sup> In any case, the  $\sigma$ -hole concept has been extended in order to address some of these issues, but the explanation using the MEP remains the simplest and easiest to grasp.

The main objective of this work is to assess whether the observed changes in the MEP along the Si–O–Si angle ( $\alpha$ ) can be used to understand the changes found in the binding energies of the different complexes that disiloxane can form. We have chosen 7 Lewis acids (HF, HCl, HBr, H<sub>2</sub>O, H<sub>2</sub>S, HCN and HNC) and 17 Lewis bases (NH<sub>3</sub>, PH<sub>3</sub>, CO, CS, N<sub>2</sub>, NP, HCN, HNC, LiCN, FCN, ClCN, HSiN, H<sub>2</sub>O, HCl, Cl<sub>2</sub>, CH<sub>3</sub>CN and SiH<sub>3</sub>CN) that can interact with disiloxane by forming A, B or C complexes. The Lewis acids were chosen to include several hydrogen bond donors, while the Lewis bases include several electron donor atoms (N, P, C, O and Cl). We will show that the study of the MEP can easily and readily explain the observed changes in the basicity of disiloxane related to the angle, as well as the trends observed with respect to the changes in binding energies. Thus, we hold that the MEP remains a fundamental tool of important predictive power when studying weak interactions.

## Computational Details

All the calculations were performed using the MP2<sup>[68]</sup> method and the aug-cc-pVTZ basis set, which means the cc-pVTZ basis was used for the H atoms, and the aug-cc-pVTZ one for the rest.<sup>[69,70]</sup> We have previously shown that this level of theory is needed to properly describe the disiloxane molecule, as well as tetrel bonds.<sup>[23]</sup> We would like to highlight that our calculated binding energies for the disiloxane–H<sub>2</sub>O hydrogen-bonded A complex at different angles are in very good agreement with those reported by Fugel et al.<sup>[15]</sup> using the highly accurate W1-F12 composite method (see Table S6). All calculations were carried out using the Gaussian 09 program.<sup>[71]</sup>

Angular scans were performed by fixing the Si–O–Si angle ( $\alpha$ ) from  $90^\circ$  to  $180^\circ$  in steps of  $5^\circ$  and allowing the rest of coordinates to relax within certain symmetry constraints. The  $C_{2v}$  point group was maintained for the isolated disiloxane, most of the hydrogen-bonded A complexes and most of the C complexes. The  $C_s$  point group was used for all of the B complexes, the A complexes with  $H_2O$  and  $H_2S$ , as well as the rest of C complexes (those with  $NH_3$ ,  $PH_3$ ,  $CH_3CN$ ,  $SiH_3CN$ ,  $HCl$  and  $Cl_2$ ). In the case of the ternary complexes  $C_{2v}$  symmetry was used for the A:C complexes in which it can be maintained, and  $C_s$  symmetry was used whenever possible for the rest of A:C and A:B complexes. We have verified that the difference in terms of binding energies between the symmetry-constrained and the fully relaxed complexes is small ( $\pm 1$  kJ/mol), which means that for the sake of the interpretation the results are fully valid (see Table S7).

The binding energies ( $\Delta E$  or  $E_b$ ) of a dimer X:Y or a trimer X:Y:Z are defined in Equation (1). In order to study the angular dependence, then,  $E(Y)$  will correspond to the energy of the disiloxane molecule at a fixed  $\alpha$  angle, while  $E(X)$  and/or  $E(Z)$  will simply be the energy of the corresponding Lewis Acid or Base in their equilibrium geometry. The  $E(X:Y)$  and  $E(X:Y:Z)$  energies are also calculated at a fixed  $\alpha$  angle for the complexes, as described above. The more negative binding energies (larger in absolute value) will correspond to stronger interactions.

$$\begin{aligned}\Delta E(X:Y) &= E(X:Y) - [E(X) + E(Y)] \\ \Delta E(X:Y:Z) &= E(X:Y:Z) - [E(X) + E(Y) + E(Z)]\end{aligned}\quad (1)$$

As a measure of cooperativity, we will calculate the non-additivity ( $\delta\Delta E$ ) as defined in Equation (2). A negative value for  $\delta\Delta E$  can, then, be understood as positive cooperativity, while a positive value would mean that the interactions are anti-cooperative. The same definition for non-additivity has been used previously to study cooperative effects.<sup>[72–76]</sup>

$$\delta\Delta E = \Delta E(X:Y:Z) - [\Delta E(X:Y) + \Delta E(Y:Z)]\quad (2)$$

Electron-rich and electron-deficient regions on the molecular space were identified by calculating the molecular electrostatic potential (MEP).<sup>[50,51]</sup> The electrostatic potential values mapped on the 0.001 a.u. electron density isosurface (labeled as  $V_s$ ) were obtained at all the angles of the scan for the isolated disiloxane molecule, as well as for three representative complexes A, B and C with  $HF$ ,  $NH_3$  and  $HCN$ , respectively. The WFA-SAS program was used to locate the minima and maxima of the electrostatic potential on the electron density isosurface.<sup>[77]</sup>

## Results and Discussion

Our discussion will start with the analysis of the MEP changes at different values of the Si–O–Si angle ( $\alpha$ ) for the isolated disiloxane molecule and three representative binary complexes formed at the different binding sites A, B and C (Figure 1). This analysis can provide the necessary insight in order to make

predictions regarding the angular behavior of disiloxane when forming complexes. Then, we will analyze the changes in binding energies with respect to  $\alpha$  for the three kinds of complexes that can be formed at sites A, B and C. Finally, we will discuss the impact of changing the angle on the observed cooperativity effects for ternary A:B and A:C complexes.

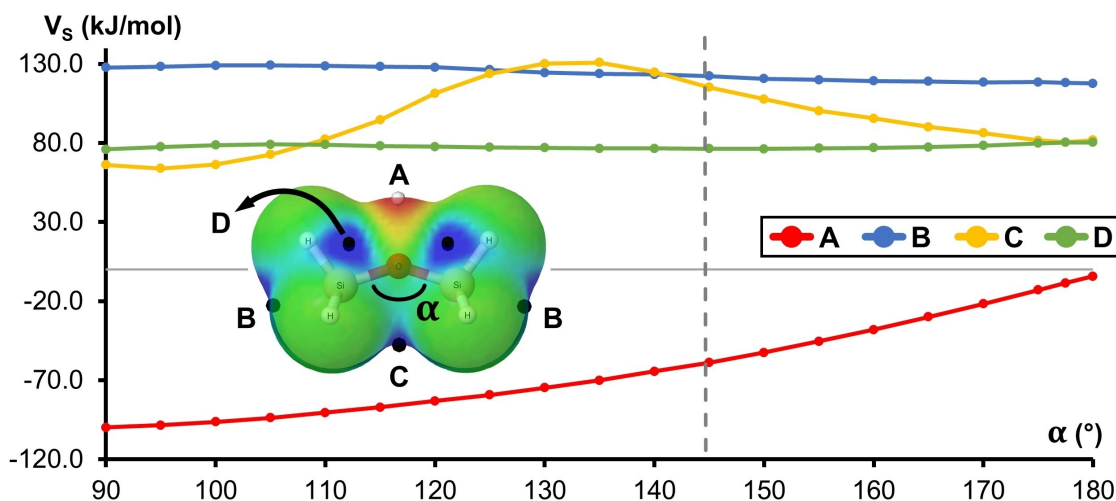
### Angular Behavior of the MEP

The MEP (on the 0.001 au density isosurface) of disiloxane at equilibrium shows one minimum (A) and seven local maxima (two degenerate B, a single C, and four degenerate D), as we have shown previously.<sup>[23]</sup> These points are plotted on top of the MEP in the inset of Figure 2. The minimum A arises from the oxygen lone pair. Maxima B can be understood as the  $\sigma$ -holes created by the polarization along the Si–O bond, while maxima D correspond to  $\sigma$ -holes arising from two Si–H bonds. Finally, maximum C can be rationalized as a combination of the  $\sigma$ -holes from the upward-pointing hydrogen atoms and a certain LP-hole character from the oxygen.<sup>[78–83]</sup> Disiloxane can, then, act as a Lewis base through the minimum A and as a Lewis acid through maxima B, C and D.

In order to shed some more light on the discussion around the basicity of the oxygen atom in siloxane linkages, we decided to study the behavior of the MEP along the Si–O–Si bending potential (see Figure 2 and Table S1 in the Supporting Information). As it has been pointed out in the Introduction, a number of studies in the past have looked into the electronic changes of disiloxane depending on  $\alpha$  by using Natural Bonding Orbital analyses,<sup>[14,15]</sup> or analyzing the electron density with topological tools such as the Quantum Theory of Atoms in Molecules (QTAIM),<sup>[13,15,33]</sup> the electron localization function (ELF)<sup>[32]</sup> or the electron localizability indicator (ELI-D).<sup>[15,33]</sup> Notably, the MEP, a simple yet insightful approach, has still not been used in this discussion, to the best of our knowledge.

The previously reported calculations<sup>[14,15,32]</sup> show an increase in oxygen basicity for smaller angles, thus making the oxygen atom a better electron donor. Regarding the change in Lewis acidity of disiloxane with respect to the angle no claim has ever been done that we are aware of. Since the value of the potential at the  $\sigma$ -hole is mostly related to the electronegative atom that causes the  $\sigma$ -hole, these interactions tend to be strongly directional.<sup>[40]</sup> Thus, if the  $\sigma$ -hole values are fairly independent from  $\alpha$ , we expect that the Lewis acidity will be somewhat insensitive as well.

In Figure 2 we can find the variation of the critical points of the MEP with respect to the different Si–O–Si angles (see also Table S1). The minimum A becomes larger in absolute value at smaller angles (fitting to a second order polynomial yields  $R^2 = 0.9999$ ), which is consistent with the observation that smaller  $\alpha$  make disiloxane a better Lewis base. Interestingly, stationary point A becomes divided into three points at an angle of  $165^\circ$ . At  $165^\circ$  the A point located along the symmetry axis has a potential value of  $-30$  kJ/mol, and the two new symmetrically equivalent minima have a potential value of  $+5.4$  kJ/mol. All these points get equal values of  $-4.2$  kJ/mol at  $180^\circ$ , having



**Figure 2.** Angular dependence of the critical points of the MEP of disiloxane (isosurface of electron density 0.001 a.u.) at the MP2/aug'-cc-pVTZ level. Also shown is the MEP plotted at the equilibrium geometry (indicated in the graph by a dashed grey line,  $\alpha = 144.5^\circ$ ) from  $-53$  (red) to  $+53$  (blue) kJ/mol. The minimum (A) and maxima (B, C, D) are indicated with white and black dots, respectively. The values of the potential are in kJ/mol and the angles in degrees ( $^\circ$ ).

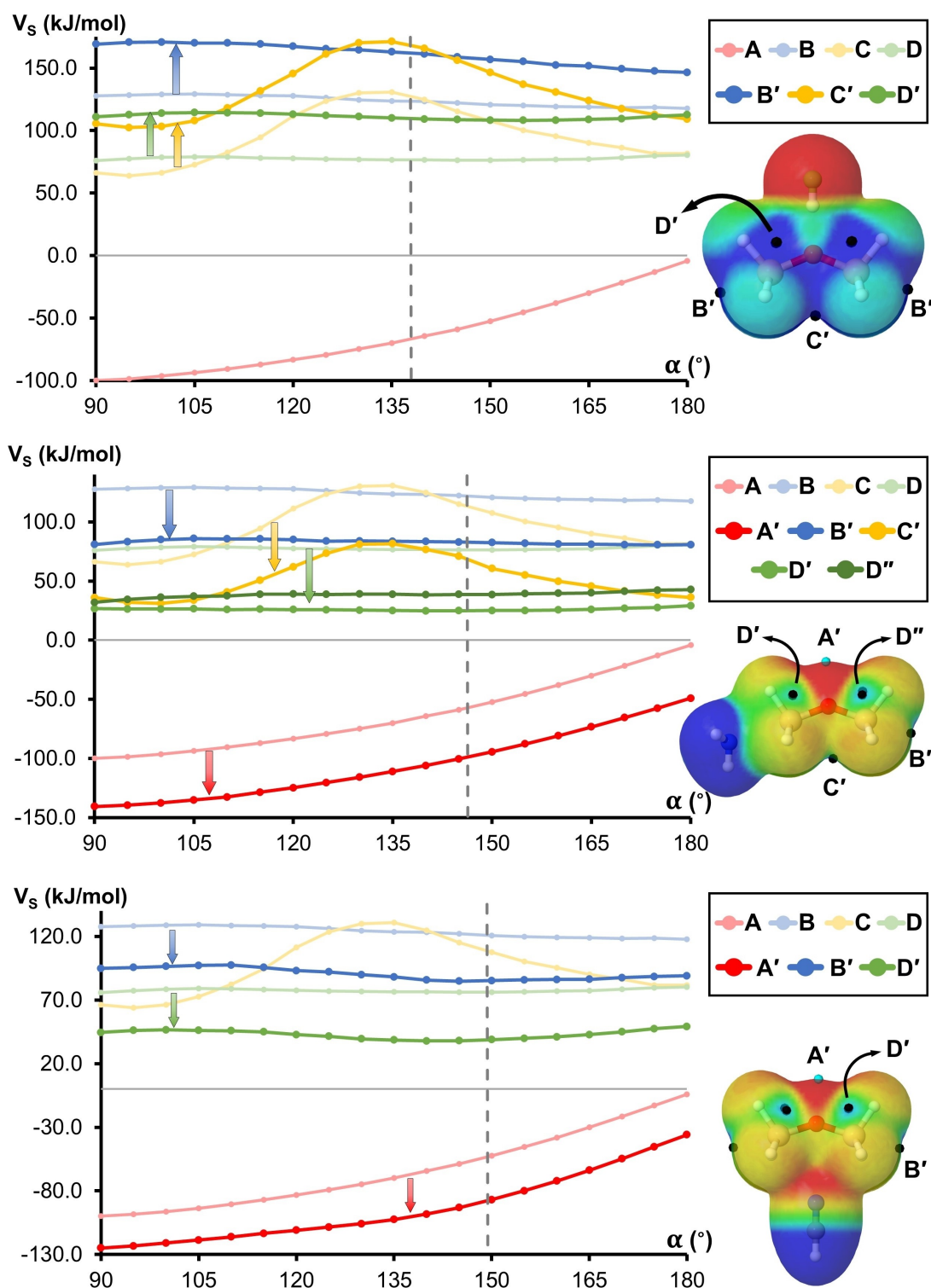
decreased around 50 kJ/mol in absolute value from the equilibrium geometry. This result is in agreement with the observed variation of the ELF,<sup>[32]</sup> where the two attractors associated to the O lone pair are divided into three at an angle of  $165^\circ$ , and finally create a torus around the O atom when the  $\alpha$  angle becomes  $180^\circ$ . In terms of possible binding with a Lewis acid, and based on this MEP analysis alone, one would predict that the stronger interactions will take place at lower values of  $\alpha$ .

Regarding the maxima, points B and D remain basically constant along the whole potential curve, once again showing that  $\sigma$ -holes will lead to strongly directional (close to linear) interactions.<sup>[40]</sup> Furthermore, this result suggests that the strength of a possible tetrel bond at point B/D will not be very dependent on the angle, which is the opposite behavior of the expected for an interaction with A. Finally, studying point C is somewhat more complex because at large angles it will be divided into two different (equivalent) maxima, and eventually it will become degenerate with the other  $\sigma$ -holes (D) arising from the Si-H bonds. For angles below  $100^\circ$ , maxima D have larger values than C, then C grows reaching its maximum value at an angle of  $135^\circ$ , and then it starts decreasing until it converges with D at the  $D_{3h}$  symmetric  $180^\circ$  structure. It is important to note that it will become two maxima for  $\alpha > 145^\circ$ . This changing behavior across the angular bending potential can enforce our view on the amalgamated nature ( $\sigma$ - and LP-holes) of this maximum of the MEP: at large angles it is very similar in nature to maxima D, at intermediate angles it turns more positive due to the favorable combination of  $\sigma$ - and LP-holes, and at smaller angles its potential value is quite diminished. It is also worth noting that at  $\alpha$  angles between  $125^\circ$  and  $140^\circ$  maximum C is even comparable in value with maxima B, that arise from the  $\sigma$ -hole created by the very electronegative oxygen atom.

From this MEP analysis alone we can predict the observed trend of increased basicity for the oxygen atom at reduced  $\alpha$  angles. Furthermore, our results can be used to stress that it is not the *charge* (an ill-defined chemical concept whose quantum chemical derivation is strongly dependent on the partition method used to define it)<sup>[35,36]</sup> at the oxygen atom that can give an indication on whether it is more or less basic. Rather, it is the *electrostatic potential* (which can be experimentally derived)<sup>[48,49]</sup> that plays a very important role in determining the basicity of oxygen towards potential interaction with Lewis acids. For this reason, the MEP can be used to rationalize the observed trends, once again showing the important role of electrostatics in describing and studying this kind of weakly interacting complexes.

In a previous work,<sup>[23]</sup> we have shown that interaction of disiloxane with a LA/LB will change the behavior of the MEP not only due to the change in  $\alpha$  when forming a complex, but mostly because of the polarization induced by the LA/LB. When interacting with a LA through minimum A, the potential of the maxima will be shifted upwards (will become more positive). For the case of interactions with a LB through maxima B or C we observed that the potentials are shifted downwards to more negative values. Is this observation conserved throughout the bending potential or is it also angle dependent?

In order to solve this question, we have calculated the angular changes of the MEP when disiloxane is interacting through points A, B or C with HF, NH<sub>3</sub> or HCN, respectively, and the results have been summarized in Figure 3 (see also Tables S2–S4 in the Supporting Information). In all cases, the variation of the different critical points of the MEP along the whole  $\alpha$  range is remarkably similar to the one observed for the isolated molecule. The main difference in the case of the complexes is that the potential is overall shifted to more positive values when disiloxane acts as a Lewis base (on average  $+35.7$  kJ/mol for the HF A complex), or to more



**Figure 3.** Angular dependence of the critical points of the MEP of and its complexes with (from top to bottom) HF, NH<sub>3</sub> and HCN (dark colored lines) at the MP2/aug-cc-pVTZ level (isosurface of electron density 0.001 a.u.). A, B, C, D notation stands for the reference MEP values of isolated disiloxane (light colored lines), whereas A', B', C', D', D'' are the MEP values in the complexes (dark colored lines). The arrows indicate whether the potential in the complexes is shifted up or down with respect to the isolated disiloxane. Also shown is the MEP plotted at the equilibrium geometry of each complex (indicated in each graph by a dashed grey line) from -53 (red) to +53 (blue) kJ/mol. On the complexes the location of the minimum (A') and the maxima (B', C', D', D'') from disiloxane are indicated with cyan and black dots, respectively. The values of the potential are in kJ/mol and the angles in degrees (°).



negative ones when disiloxane acts as a Lewis acid (on average  $-43.4$  kJ/mol for the  $\text{NH}_3$  B complex, and  $-32.7$  kJ/mol for the HCN C complex).

## A Complexes

A relationship between the disiloxane angle and the basicity of the oxygen was established from the experimental observation that cyclic siloxanes with smaller angles formed stronger hydrogen bonds.<sup>[25]</sup> Recent theoretical works agree with the experimental observation regarding the angle-basicity relation in disiloxane, and these works have focused on the specific case of hydrogen bonds with  $\text{H}_2\text{O}$  and  $\text{H}_3\text{SiOH}$  as hydrogen bond donors.<sup>[14,15,32,33]</sup> Those studies were performed at different levels of theory, and so with different degrees of accuracy, but in all of them an increase in binding energies for smaller  $\alpha$  angles was observed.

As noted in the Computational Details section, our results for the particular case of the complex with  $\text{H}_2\text{O}$  compare very well with the previously published<sup>[15]</sup> high-level W1-F12 results (see Table S6), showing a mean absolute error of only 0.51 kJ/mol. Aside from water, in this work we have studied other hydrogen bond donors of different strength, namely HF, HCl, HBr,  $\text{H}_2\text{S}$ , HCN and HNC. The hydrogen bond (HB) results have been summarized in Figure 4, and can be found in the Supporting Information (Table S5).

All the studied HB interactions share a common trend: at smaller  $\alpha$ , the interaction is stronger, *i.e.*, the binding energies increase in absolute value. This behavior matches the previously observed trend for hydrogen bonds, and fits our expectation from the MEP calculations. It can be noted that all the hydrogen-bonded complexes have binding energies below 10 kJ/mol when  $\alpha=180^\circ$ , which is a decrease in more than 20 kJ/mol for the strongest interactions (with HNC and HF). The lowest binding energy is always found at  $180^\circ$ , and the largest one is usually obtained at angles between  $90^\circ$  and  $100^\circ$ . The largest difference is found for the HF complex (26.2 kJ/mol),

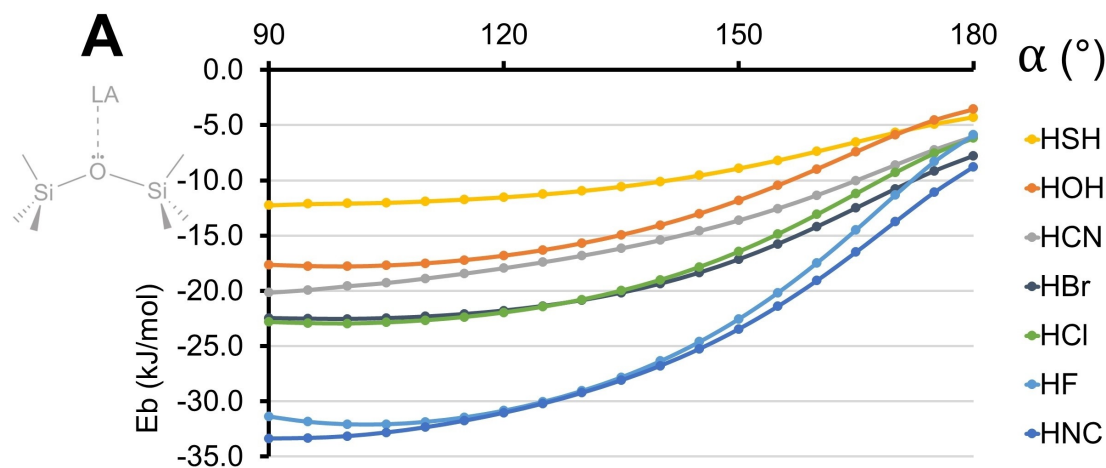
while the smallest difference is that of the  $\text{H}_2\text{S}$  complex (8.0 kJ/mol), evidencing the HB distance, linearity of the interaction and H polarization due to the neighboring atom size (second row vs third row) as key factors.

## B and C Complexes

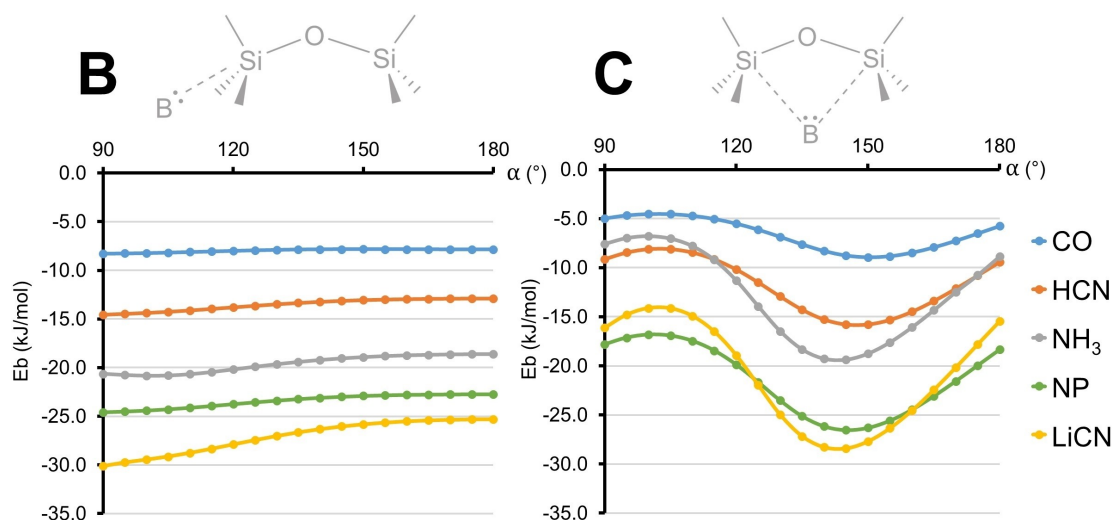
The dependence of the binding energy of disiloxane with five selected Lewis bases with respect to  $\alpha$  can be found in Figure 5. The results are comparable for all the 17 bases studied (see Figures S1–S2 and Tables S7–S9 of the Supporting Information).

Regarding the B complexes, from our MEP calculations (Figure 3) we expected that the binding energy would remain essentially unchanged along the bending potential, just like the value potential at point B does not change. This expectation is clearly fulfilled for the B complexes. Again, it is important to note that this behavior is opposite the one observed for the A complexes, whose dependence on  $\alpha$  is quite large. The minimum is always located at an angle of  $90^\circ$  (except for the  $\text{NH}_3$  complex, with the minimum at an angle of  $100^\circ$ ), and we see a decrease in  $E_b$  (in absolute value) for larger angles. From this reduced set, the largest decrease is of 4.8 kJ/mol for the LiCN complex, and the smallest one arises in the CO complex (0.5 kJ/mol). For a non-polar ligand such as  $\text{N}_2$  this decrease is virtually zero (0.2 kJ/mol, Table S8).

For the C complexes we observe larger variations, consistent with the variations of point C on the MEP along the bending potential. In this case the largest observed difference between the maximum and the minimum is 14.3 kJ/mol for the LiCN complex, and the smallest difference is 4.4 kJ/mol for the CO complex. Outside the selected cases represented in Figure 5 (see Table S10), it is interesting to note that both of the tested Lewis bases with Cl as the electron donor atom (HCl and  $\text{Cl}_2$ ) show the least pronounced curves for the C complexes, the smallest difference of the whole set being 3.3 kJ/mol for  $\text{Cl}_2$ . We also see that the behavior of the binding energies mirrors that of the MEP, showing stronger (weaker) interactions where the



**Figure 4.** Angular dependence of the binding energies in A complexes (schematically shown in at the left side) with different hydrogen bond donors at the MP2/aug'-cc-pVTZ level. Energies are in kJ/mol and angles in degrees ( $^\circ$ ).



**Figure 5.** Angular dependence of the binding energies of selected Lewis Bases tetrel-bonded in configurations B and C (schematically shown in grey on top of the graphs) at the MP2/aug-cc-pVTZ level. Energies are in kJ/mol and angles in degrees ( $^{\circ}$ ).

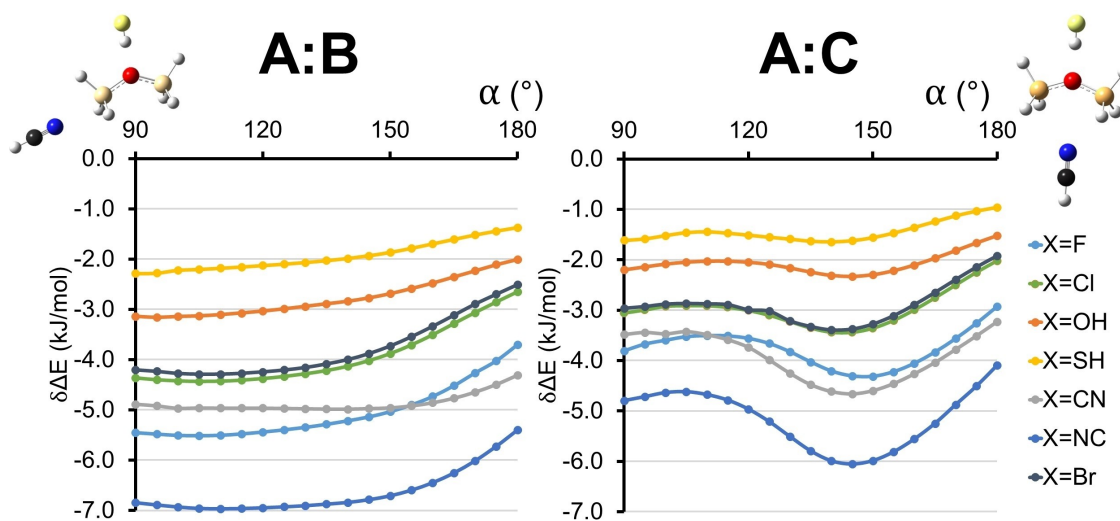
MEP is a maximum (minimum) along  $\alpha$ . Interestingly, the binding energy is often largest (in absolute value) at around an angle of  $145^{\circ}$ , close to the minimum for isolated disiloxane.

We reported for disiloxane in a previous work that there was a quite good linear correlation between the Si–O bond length and the binding energy ( $R^2=0.97$ ) at the equilibrium geometry for tetrel-bonded complexes.<sup>[23]</sup> In line with this observation, linear correlations of similar quality are observed for the A complexes between the isolated critical point A of the MEP and the binding energy along the disiloxane angle ( $R^2 > 0.97$  for all cases). In some of the B complexes we find a good linear correlation between the binding energy and the variation of critical point B throughout the angle (for instance the complex with  $\text{NH}_3$  shows  $R^2=0.96$ ), but the quality of the correlation varies amongst the different Lewis bases. Finally, no

correlation of this kind was found for site C, as a consequence of the sinusoidal behavior of the binding energy and the potential with respect to  $\alpha$  (see Figures 2, 3 and 5). Nonetheless, the relationship between binding energies and MEP clearly points to the electrostatic nature of the interactions.

### Cooperativity Effects

In our previous study<sup>[23]</sup> we showed that simultaneous interaction of a Lewis Acid at A and a Lewis Base at B/C will result in positive cooperativity, that is, both interactions are reinforced. Also, in the same study, we observed that the MEP  $\sigma$ -holes B, C and the minimum associated to the lone pair in A are strongly correlated.<sup>[23]</sup> Considering the difference in angular behavior of



**Figure 6.** Angular behavior for the non-additivities of the A:B and A:C complexes with HCN as the Lewis base and HX (X=F, Cl, Br, OH, SH, CN and NC) as the Lewis acids. Energies are in kJ/mol and angles in degrees ( $^{\circ}$ ).

the different interactions, one can also think about whether the cooperativity will change or not across the Si–O–Si bending potential.

In order to explore this question in a simple way, we considered only the interactions with HB donors (HF, HCl, HBr, H<sub>2</sub>O, H<sub>2</sub>S, HCN and HNC) at A, having HCN as the Lewis base for both A:B and A:C complexes. Since the behavior of the different binary complexes was always comparable for different LAs and LBs, it is reasonable to expect that the observations for these ternary complexes will be qualitatively transferrable to other combinations of Lewis acids and Lewis bases.

In Figure 6 (and Tables S11–S12) we can see the values of the non-additivities  $\delta\Delta E$  at different angles for the different complexes. As mentioned in the Computational Details section, negative non-additivities mean positive cooperativity between interactions, which is the case for all complexes represented in Figure 6. As observed before for the binding energies, the Si–O–Si angle has a certain impact on the cooperativity for ternary complexes. In terms of the trends followed, for the A:B complexes the maximum cooperativity is often found at angles below 140°, in many cases showing a plateau. In this set of complexes, we observe that the minimum (at which cooperativity is largest) is located at an angle of ~110° instead of at 90° as was often the case with the binding energies for both A and B complexes. On the other hand, for A:C complexes we find a maximum cooperativity around 145°, which is the same value where we often found the minimum for the binding energies in the case of C complexes, but a reduced cooperativity towards either lower or higher values of  $\alpha$ . In relative terms, the energy gained by cooperativity with respect to the binding energies is always significant, as exemplified for the particular case of the disiloxane:HCN:HF complex in Figure S3. All in all, in both types of ternary complexes B and C we observe that the cooperativity always decreases when  $\alpha$  approaches linearity, but still the interactions remain cooperative.

## Conclusions

By means of MP2/aug'-cc-pVTZ calculations on isolated disiloxane and some of its complexes, regarding the effect of the Si–O–Si angle ( $\alpha$ ) on several properties, we have shown that:

1. The observed relation between oxygen basicity in siloxane linkages and Si–O–Si angle is easily explained using the molecular electrostatic potential (MEP).
2. Electrostatics-based considerations can explain all the observed trends in terms of binding energies for the weak interactions studied.
3. The changes in the electrostatic potential across the angle correlate (qualitatively) with the observed changes in binding energies for complexes where disiloxane acts as a Lewis base/acid.
4. The observed changes in binding energies for interaction of disiloxane with Lewis acids are larger than those observed in the Lewis bases cases.
5. Simultaneous A:B and A:C interactions remain cooperative throughout  $\alpha$ .

6. The largest cooperativity effect for ternary complexes is found, in some cases, at a different  $\alpha$  angle than the one that yields the highest binding energies of the corresponding binary complexes.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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