Challenges in Studying Steric Interactions in Highly Strained Perhalogenated Alkanes and Silanes.

Luís Simões[1] and RODRIGO CORMANICH[1]

[1]Universidade Estadual de Campinas

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Abstract

The decomposition of the molecular total energy in their hyperconjugative, steric and electrostatic effects can lead to interesting interpretations about the stereoelectronic effects that govern their geometry and properties. In this work, we have studied homologous series of perfluoroalkanes, perchloroalkanes, perfluorosilanes and perchlorosilanes, and all molecules have preference for helical geometries. According to Natural Bond Orbitals (NBO) calculations, the silanes have their helical geometry stabilised by hyperconjugative interactions, as well as the perfluoroalkanes. However, it was surprisingly difficult to disclose that steric interactions are ruling the helical geometry preference in perchloroalkanes by comparing the NBO analysis and the Quantum Theory of Atoms ins Molecules (QTAIM). Although perchloroalkanes have extremely intense steric interactions between Cl lone pairs, some of them were underestimated by the NBO analysis, which showed the opposite behaviour compared with QTAIM that indicates steric effects as the leading forces to helical geometry preference.

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Luís H. Simões and Rodrigo A. Cormanich*

University of Campinas, Institute of Chemistry, Monteiro Lobato Street, Campinas, Sao Paulo, Brazil - 13083-862.

*email: cormanich@unicamp.br

website: cormanich.iqm.unicamp.br

ABSTRACT: The decomposition of the molecular total energy in their hyperconjugative, steric and electrostatic effects can lead to interesting interpretations about the stereoelectronic effects that govern their geometry and properties. In this work, we have studied homologous series of perfluoroalkanes, perchloroalkanes, perfluorosilanes and perchlorosilanes, and all molecules have preference for helical geometries. According to Natural Bond Orbitals (NBO) calculations, the silanes have their helical geometry stabilised by hyperconjugative interactions, as well as the perfluoroalkanes. However, it was surprisingly difficult to disclose that steric interactions are ruling the helical geometry preference in perchloroalkanes by comparing the NBO analysis and the Quantum Theory of Atoms ins Molecules (QTAIM). Although perchloroalkanes have extremely intense steric interactions between Cl lone pairs, some of them were underestimated by the NBO analysis, which showed the opposite behaviour compared with QTAIM that indicates steric effects as the leading forces to helical geometry preference.

Introduction

Halogenated polymers are widespread molecules in our daily routine: polytetrafluorethylene and polyvinylchloride are two of the most well-known carbon-based polymers,[1] while fluorosilicon polymers have recently became leading motifs of rubbery materials.[2]–[4] Fluoroalkanes have proved to be interesting molecules even

beyond their economic importance, but also concerning debates about the dominant stereoelectronic effects on their geometry.[5]–[9] Recent advances have been recently achieved by our group, relating stereoelectronic effects and geometry on perfluoroalkanes[10] and multivicinalfluoroalkanes.[11] The systematic study of perchlorinated molecules have been raised since early 70's[12] and had reached significant advances with the arising of computational chemistry.[13]–[20] Despite the experimental limitations on synthesizing and isolating perchloroalkanes with more than 4 carbon atoms,[21], [22] theoretical studies about them are particularly interesting once they allow to analyse stereoelectronic effects in sterically overcrowded molecules. Moreover, perfluoro and perchlorosilanes are the perfect analogues to be studied with perfluoro and perchloroalkanes, once their larger bond length in the silicon backbone is expected to minimize steric effects, reducing overcrowding and allowing other stereoelectronic effects to arise as leading effects. However, for the best of our knowledge, there is a lack of advances in this topic after the seminal study of Neumann,[15] which presented a model to understand and predict geometric preferences in small halogenated molecules for the first time. In order to bring advances to this important topic, this study compares homologous series of perfluoro and perchloro alkanes and silanes using modern quantum mechanic methods as the Natural Bond Orbital (NBO)[23] and the Quantum Theory of Atoms in Molecules (QTAIM)[24], in order to understand their conformational preferences and to rationalize the stereoelectronic effects that rule such preferences.

Computational Details

Perchloroalkanes, perfluorosilanes and perchlorosilanes with backbone containing n=4 to 20 C or Si atoms were fully optimised at the B3LYP/6-31G** level of theory for zigzag and helical geometries. Frequency calculations were performed on all optimised geometries at the same theoretical level to ensure only positive eigenvalues for all helical geometries. Relative energies between zigzag and helical geometries for compounds with backbone containing n=4 to 10 C or Si atoms were compared with single point calculations from *gold standard* [25], [26] DLPNO-CCSD(T)/cc-pVTZ with cc-pVTZ/C as auxiliary basis set. Figure S5 show the comparison between theoretical levels. The B3LYP/6-31G** level of theory showed consistent results in comparison with DLPNO-CCSD(T)/cc-pVTZ and was used to all remaining calculations. NBO 6.0 calculations were performed on fully optimised geometries, as well as QTAIM calculations. Natural Steric Analysis calculations were first performed at B3LYP/6-31G** level of theory and subsequently calculated at HF/6-31G** to search for eventual artifacts.[27] All optimisations, frequency calculations and NBO calculations were performed in Gaussian09 program, Revision D.01. DLPNO-CCSD(T)/cc-pVTZ single point calculations were performed in ORCA 4.2.1.[28], [29] QTAIM calculations were performed in AIMALL package, version 19.10.12.[30]

Results and Discussion

Helical geometries with C-C-C-C or Si-Si-Si-Si dihedral angles of ˜160º were the overall preference for all molecules - perfluoroalkanes, perchloroalkanes, perfluorosilanes and perchlorosilanes. The calculated molecular central dihedral angle values are showed in Figure 1.

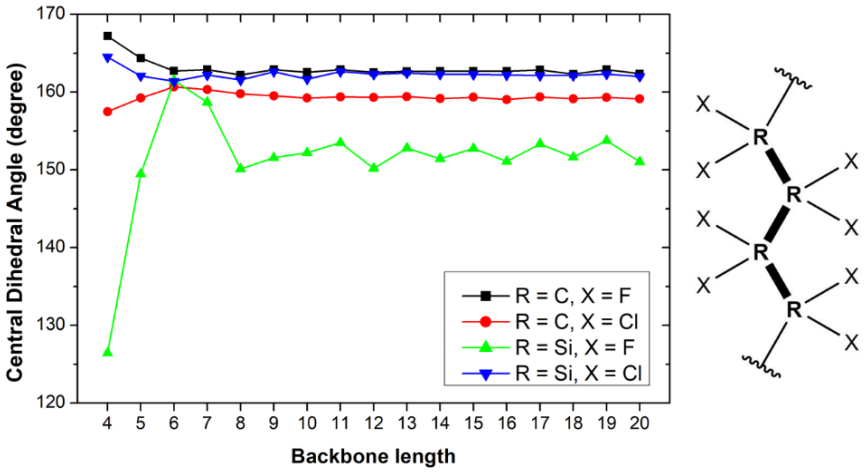


Figure 1. Calculated central C-C-C-C or Si-Si-Si-Si- dihedral angles for each molecule at the B3LYP/6-31G* level (in degrees). At the right side, a generic example of the central dihedral angle (highlighted). In the case of the molecules with odd number of atoms in the backbone, it was considered the average value between the two central dihedral angles.

Total Energetic barriers ΔE (T) were calculated at the B3LYP/6-31G** level and were decomposed using the NBO analysis: ΔE (L) represents the Lewis energy[31], [32] of the molecule when hyperconjugation is not taken into account, ΔE (NL) is the non Lewis energy that represents the stabilisation by hyperconjugation, ΔE (NCE) stands for Natural Coulomb Electrostatic analysis [27] and ΔE (NSA) represents the steric energies obtained from the Natural Steric Analysis.[33], [34] Energetic barriers were calculated using the equation$_{\text{barrier}} = E_{\text{zigzag}} - E_{\text{helical}}$ and their results are showed in Figure 2 for perchloroalkanes and Figure S1 in the Supporting Information for perfluorosilanes and perchlorosilanes. Positive values represent helical and negative values represent zigzag favouring interactions.

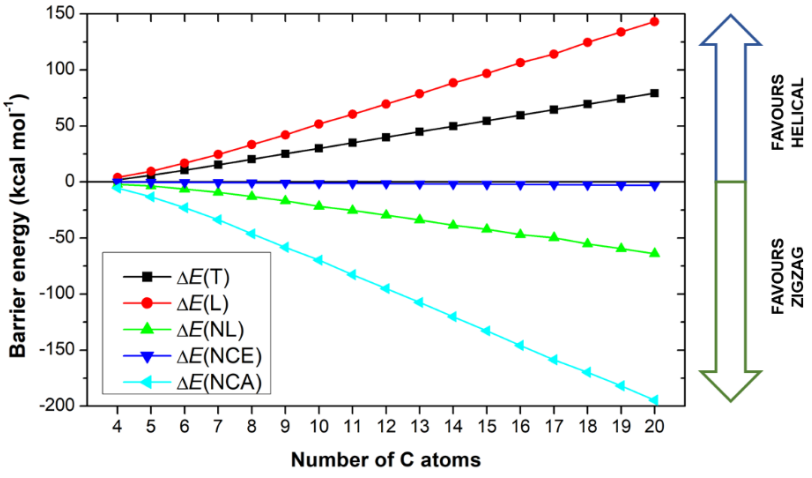


Figure 2. Energetic barriers between zigzag and helical conformers [E (zigzag) - E (helical)] calculated for perchloroalkanes according to their backbone length, where positive values indicate helical stabilization and negative values indicate zigzag stabilization.

All molecules have their helical geometries as the most stable ones according to ΔE (T), but for different reasons. While both perfluoro- and perchlorosilanes exhibit the same trend of perfluoroalkanes, in which hyperconjugation stabilises helical geometries, perchloroalkanes helical geometries are favoured by Lewis energies [ΔE (L)] and hyperconjugation favours zigzag geometries, as well as both steric and electrostatics. Steric zigzag favouring is especially peculiar, once perchloroalkanes are steric overcrowded because of short C-C bond lengths (˜154 pm) and large Cl van der Waals radii (˜175 pm). These results raise an intriguing situation: if hyperconjugation, electrostatics and sterics are driving perchloroalkanes to zigzag geometries, which component (steric or electrostatic) of the Lewis energy [ΔE (L)] is the source of helical stabilisation? To highlight the helical preference, we used the following criteria: geometric parameters, detailed NBO analysis and by applying the QTAIM method.

2.1 Geometric parameters, Electronic Distribution and Orbital Hybridization. The analysed geometric parameters were 1,3-Cl,Cl distances, C-C-C bond angles and the dihedral angles showed in Figure 1. Perchloroalkane zigzag geometries have 1,3-Cl,Cl shorter distances than helical ones: the average 1,3-Cl,Cl distance in zigzag perchloroicosane is 306 pm versus 316 pm in helical geometry (Table S1 in the Supporting Information). As 1,3-Cl,Cl distances are expected to represent the most important repulsive Cl-Cl steric interactions, this result indicate that zigzag geometries should experience higher sterical effects. Also, zigzag geometries have higher C-C-C bonding angle values, closer to 120°, than helical ones (average angle is 118.8° in zigzag perchloroicosane versus 116.4° in helical), suggesting a higher *s*character in σ_{CC} orbitals for zigzag geometries, which in turn would indicate higher electronegativities for its C atoms.

Comparing electronic populations obtained from the Natural Electron Configuration for s and p orbitals of zigzag and helical perchloroicosane (Table S3), one can observe that s orbitals have higher electronic population in the zigzag than in the helical geometries. Orbital hybridizations in Tables S4 and S5 show that σ_{CCl} orbitals have 22.2% s character in zigzag geometries and 21.6% in helical geometries. Thus, both geometric and electronic data point to higher s character in σ_{CCl} bonding orbitals in the zigzag geometry, indicating higher electronegativity to C atoms in this geometry.

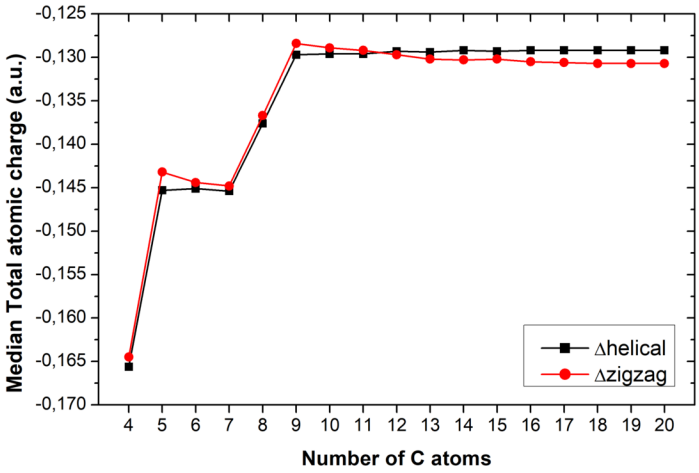
Geometric and electronic evidence support that helical favouring is essentially provided by steric effects, as it would be intuitively expected for these perchloroalkanes. Moreover, short C-C bond lengths and the large Cl atomic radii promotes geometrical deformation to diminish steric repulsion between Cl orbitals. Such geometric deformation makes C atoms more electronegative, thus in agreement with Bent's rule,[35] and withdraw electron density from Cl atoms. The steric NBO energy [ΔE (NSA)] is calculated from the difference between the Natural Localised Molecular Orbitals (NLMO) and the correspondent Preorthogonal NLMO, which allows to estimate the effect of Pauli exchange antisymmetry and spatial confinement on the molecular energy.[27] As both NLMO and PNLMO energies are dependent on electron density, the electron density withdrawing from Cl to C could presumably be the responsible for NBO underestimation of steric effects in zigzag geometries.

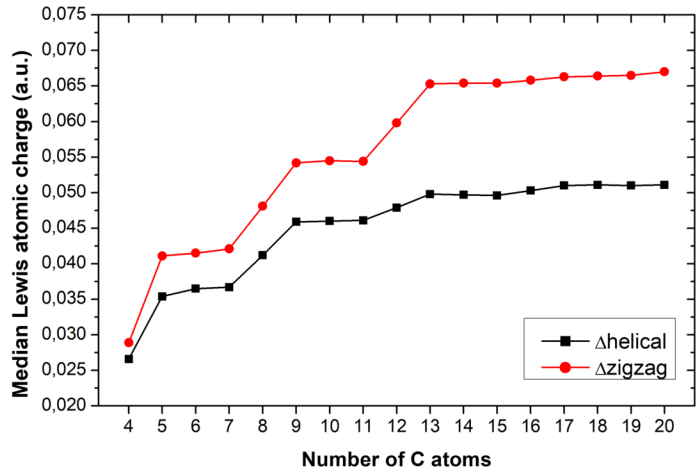
2.2 Steric Interactions. Despite the sum of all individual steric interactions in perchloroalkanes results in a negative value according to NBO (Table S6), indicating that zigzag geometries suffer less steric effects, there are two interactions with large positive values. The most important one is the 1,3-Cl-Cl repulsion, and these local destabilising interactions are more intense in zigzag than in helical geometries. These interactions would supposedly be capable to dominate the zigzag/helical steric relative energies if they were not underestimated by NBO, as a result of Cl electron density withdrawing by C atoms. It is worth mentioning perfluoroalkanes and both perfluoro- and perchlorosilanes do not show relevant repulsive interactions leading to helical geometries, as expected by considering F smaller radii and Si-Si longer bonds.

Because zigzag geometries showing overall smaller steric effects than helical ones in perchloroalkanes are unexpected, they were recalculated using the HF/6-31G** level (Table S7) in order to investigate possible artifacts, as recommended by Weinhold.[27] Despite numerical expected differences, there is just one significant qualitative difference: steric interactions between LP of Cl atoms and σ_{CC} orbitals become strongly zigzag favouring in the HF/6-31G** level. However, the steric interactions between the LPs of Cl atoms are more destabilising in zigzag geometries and remain helical favouring.

2.3 Electrostatic Interactions. Figure 3 shows total charges for C atoms obtained from the Natural Population Analysis[36] (NPA) and its decomposition into its Lewis and non Lewis (NL) contributions for perchloroalkanes, represented as the median value for all C atom for each molecule/geometry.

a) b) c)





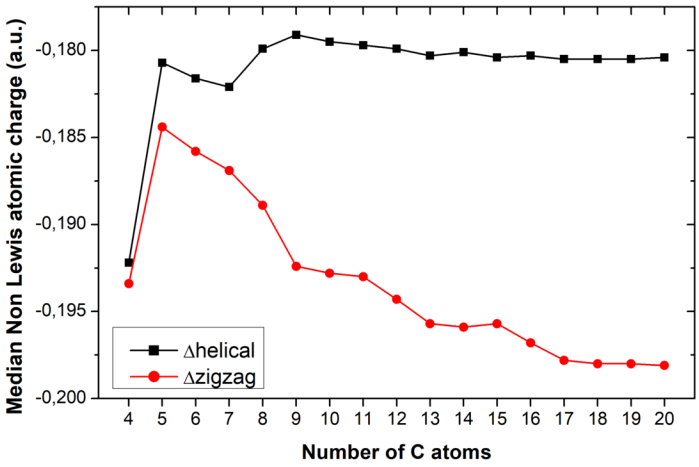


Figure 3. Median values of **a)** NBO Total charges, **b)** NBO Lewis charges and**c)** NBO non Lewis charges for carbon atoms according to their backbone length, comparing helical and zigzag geometries.

NPA calculated total charges are the opposite of expected values based on atom electronegativities: C atoms are negatively and Cl atoms are positively charged, respectively. This effect has already been observed by Neumann,[15] and could be an indication of unexpected high C electronegativity. Furthermore, NPA non Lewis charges indicate that C atoms receive more electron density in the zigzag geometries, while Lewis charges indicate that C atoms are also the ones that experience higher electronic density withdrawals. These results confirm that there is a backdonation in perchloroalkanes, in a manner that NL mechanisms promote Cl to C electron donation through hyperconjugation, but Lewis mechanisms promote C to Cl electron donation according to electronegativity difference. Both mechanisms are more intense in zigzag geometries.

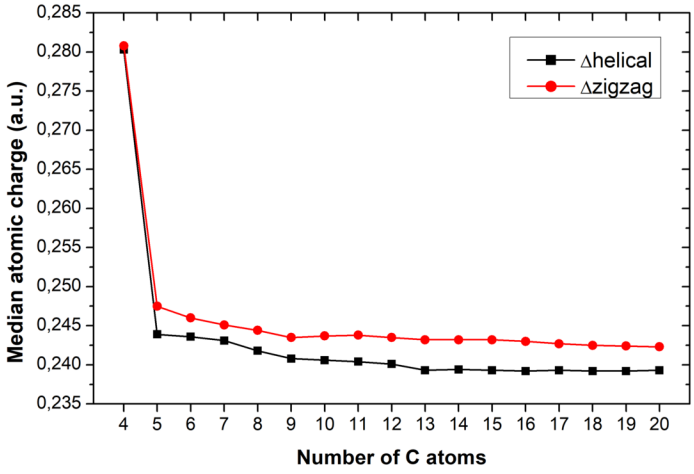
The NPA total charge graph in Figure 3 is complemented by Figure S3, where individual charges are plotted according to the atomic sequence. The central part of both conformers is well-behaved and indicate that C atoms are negatively charged and Cl atoms positively charged in the zigzag geometry. Therefore, the balance between NL and Lewis charges indicate that the NL term governs the total charge, both in positive/negative sign as in trend. The NL donation is coherent with the argument of Cl to C electron donation caused by intense steric repulsions.

2.4 Hyperconjugative Interactions. There are two important hyperconjugative interactions that provide donation from Cl lone pairs to C atoms: n_{Cl} - σ^*_{CC} andn_{Cl} - σ^*_{CCl}. These hyperconjugative interactions increase according to the backbone length, always favouring zigzag geometries and sum up to 72 kcal mol^{-1} for perchloroicosane (Tables S8 and S9). This result reinforces and complement NL charges results: NL charges indicate more charge donation from Cl to C in zigzag geometries and NBO analysis confirm that this occurs via hyperconjugation.

Also, there is geometric and electronic data supporting the NBO results, showing that there is high electron donation from Cl to C atoms in the zigzag geometries; and there are steric interactions that would favour the helical geometry in case of higher electron density in Cl atoms. However, as the Natural Steric Analysis indicates that zigzag geometries have lower steric effects overall, the QTAIM method was applied in order to evaluate steric effects from a different perspective.

2.5 Quantum Theory of Atoms in Molecules. QTAIM results are the opposite from NBO, exhibiting positively charged C atoms and negatively charged Cl atoms (Figure 4a). However, the difference between QTAIM and NBO in calculated charges are expected[37], [38] and can be useful. In this case, QTAIM charges agree with the calculated NBO Lewis charges, which is an indication that QTAIM calculation methodology is not affected by Cl to C backdonation represented by NBO non Lewis charges.

a) b)



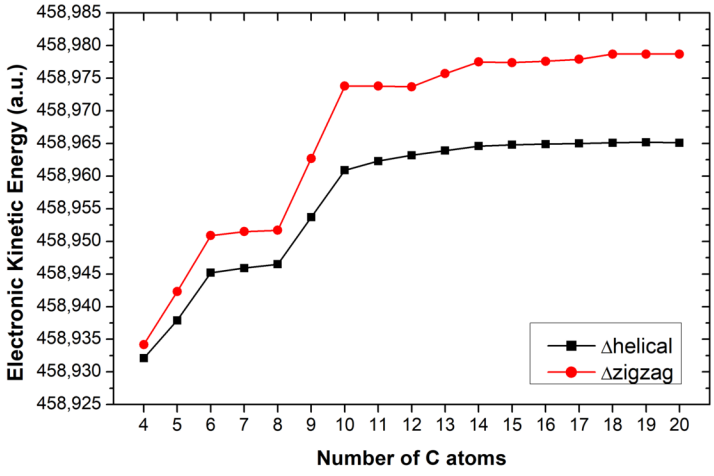


Figure 4. Median values of **a)** QTAIM charges for C atoms and **b)** QTAIM electronic kinetic energy for chlorine atoms, according to their backbone length, comparing helical and zigzag geometries.

The electron delocalisation (Figure S3) results agree with such argument since C atoms in the zigzag geometry have lower electron donation than those in the helical geometry. Therefore, it is reasonable to assume that QTAIM will represent the steric interactions more closely with the expected by chemical intuition on this group of molecules, which will not be affected by the electron withdrawing from Cl to C.

Furthermore, according with QTAIM, Cl atomic kinetic energy is consistently higher in zigzag than in helical geometries (Figure 4b): the median difference between individual atoms reaches 0.01 a.u (˜6 kcal mol^{-1}) in perchloroicosane. The higher the atomic kinetic energy, the higher the atomic kinetic energy pressure, and hence, the higher the steric effects.[39], [40] As Cl atoms are more affected by steric effects and their kinetic energy is higher in zigzag geometries, this data indicates that steric effects are higher in the zigzag geometry. Thus, QTAIM results confirms the proposal in which steric effects are the driving force for helical geometry in perchloroalkanes.

Conclusions

Steric effects are the driving force to helical geometry in perchloroalkanes. Because steric effects are diminished for F smaller radii and longer Si-Si bonds, it was observed that perfluorosilanes and perchlorosilanes have their helical geometry stabilised by hyperconjugative interactions, following the same trend observed for perfluoroalkanes. Furthermore, we confirmed that NBO steric analysis can lead to incorrect conclusions if careless analysed. This warning was raised by Weinhold, who first indicated that superficial usage of the STERIC keyword in the NBO software output can be a two-edged sword.[27] It might be thought that these problems would mainly occur in molecules not highly sterically hindered, where any kind of deviation in calculations could lead to wrong conclusions. However, this case shows the opposite: electronic effects affect NSA results when interactions are so intense that they become hidden among other interactions. In this situation, it is necessary to have another QM tool for comparison. As QTAIM is based on the electron density and therefore has a different approach for describing electrons in molecules, it is and should be used as a useful tool in combination with NBO.

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ORCID

Rodrigo A. Cormanich - https://orcid.org/0000-0001-7659-1749

Luís H. Simões - https://orcid.org/0000-0002-2123-4629

Keywords

Stereoelectronic effects, hyperconjugation, steric effects, perfluoroalkanes, perchloroalkanes

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SUPPORTING INFORMATION

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GRAPHICAL ABSTRACT

AUTHORS: Luís H. Simões and Rodrigo A. Cormanich*

TITLE: Challenges in Studying Steric Interactions in Highly Strained Perhalogenated Alkanes and Silanes

TEXT: Natural Bond Orbitals analysis and the Quantum theory of Atoms in Molecules were used to disclose the contribution of hyperconjugative, steric and electrostatic effects for the preferred helical geometry of perfluoro and perchloroalkanes and silanes.