Theoretical Studies of Some Fluoro Compounds with Silicon, Phosphorus and Sulphur and Establishment of Negative Hyperconjugation through Calculation of Charge

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Abstract: Hyperconjugation is an act to build π bond character into bonds that have only σ character. Negative Hyperconjugation is the flow or movements of electrons from π to σ^* orbitals and more particularly from π orbital of a carbon atom to the σ^* orbital of the C—X bond, where X is any electronegative atom. This effect is different from Inductive effects. An attempt is made to study the negative hyperconjugation (Anomeric Effect) by the calculation of the charges at the Density Functional Theory (DFT) level for some compounds with hypervalent atoms like Si, P & S

Keywords: DFT, Negative Hyperconjugation, Hypervalent atoms

Introduction

The effect of donation of electron density from filled π or n_π orbitals of the symmetry adapted σ^* orbital(s) of the σ bond(s) of a molecular entity resulting in building π character into bonds that nominally possess only σ character is termed anomeric effect. The consequences of the effect are, for example, elongation of the C-F bond in the β -fluoro ethyl anion and the stabilization of antiperiplanar conformation of fluoromethylamine¹. In short negative hyperconjugation is π or $n_\pi \rightarrow \sigma^*$ as shown in the below scheme 1.

Scheme 1.

Some of the important consequences of the negative hyperconjugation are

- (i) The shortening of the AY bond in X_nAY , where X is an electronegative element, A is any hypervalent atom and Y is any other atom or group attached to A.
- (ii) The increase in π orbital population of the X atom and thereby a change in the charge on that atom
- (iii) Widening of the XAY angle, for example, 113 degrees in the place of tetrahedral angle
- (iv) Lengthening of the AX bond.

Hyperconjugation of the C—X bond is maximum when the dihedral angle between the π -orbital of X atom and the orbital of a π system or of the same symmetry from which electrons flow, is either zero degree or 180 degree and falls to zero when the dihedral angle is 90 degree².

The presence of fluorine atoms gives rise also to inductive effect which is felt through the σ bonds and the polarization is not be confused with negative hyperconjugation. To measure the inductive effects separately, the dihedral angles around the atoms responsible for negative hyperconjugation was set to 90 degree during optimization, when at this angle anomeric effect is minimized to zero³.

The concept of bond order, bond order–bond energy relations and the Pauling relationship between bond length and bond order is quite helpful in verifying the changes in the bond length⁴. The shortening of the C—X bond and the lengthening of the A—X bond can be easily verified using these rules. The imposition of symmetry during geometry optimisation is useful in calculating the distribution of the charges both on the π or σ centers. If the substituent is phenyl ring, it can be confined to a plane to achieve the dihedral angle required for the overlap by the π orbitals of the aromatic ring and the orbitals of the same symmetry found in the hypervalent atom and the halides. The gross orbital population (GOP) is required for the calculation of the charges on the σ or π centers.

Phosphorus, sulphur and silicon were primarily studied for the anomeric effect (the effect due to negative hyperconjugation) with highly electronegative atom like fluorine. For comparison some imaginary systems without the ring or without the electronegative atoms were also included. All the possible symmetries were tried during geometry optimization and the geometry that had the lowest heat of formation was considered stable. Based on this the anomeric effect was studied. The contribution of the n -electrons of the fluorine atoms was also established.

Experimental

Computational Methods

The systems C_6H_5-A , where $A = PF_4$, SiF_3 and SF_5 were optimized and characterized using the Density Functional Theory method, B3LYP with a 6-31 G* basis set. For comparison of the results, the calculations were also performed for C_6H_5-N , where $N = CH_3$ and CF_3 at the same level of theory. The frequency calculations indicated that all the systems were minima and there was no imaginary frequency at all to suggest any transition state.

All the calculations were done using Gaussian 98 on IBMS12 machine. For optimization the geometrical parameters were allowed to vary within the given symmetry point group. The total charges and the σ and the π charges were also calculated separately from the orbital population values⁵.

Results and Discussion

Phenyltrifluorosilane

The structure **1a** was first optimized using the DFT method at the 6-31G* level under C_{2v} symmetry. Given the freedom to rotate at the Si—C axis the molecule attained C_s symmetry. This was further supported by lower heat of formation. Due to unfavourable overlap from the π -system (phenyl ring) with σ^* orbitals of fluorine atoms, the bond length was lengthened followed by an increase in tetrahedral angle. There was also an increase in the π charge on one of the three fluorine atoms. Only one of these three fluorine atoms effectively showed the presence of negative hyperconjugation. This may be due to the symmetry of the molecule, particularly with the respect to the non-bonding electrons of the F atoms and the P_z orbitals of the phenyl ring. In the C_s symmetry (**1b**), only one of the F atoms had a dihedral angle of 0 degrees with respect to the C-atom π orbital of the phenyl ring (the ipso C-atom). Only at this value the effect would be maximum. The other two F atoms did not have sufficient dihedral angle (**1c**) to show negative hyperconjugation. Hence these two atoms did not show the effect to the extent the F_1 atom showed.

Structure of phenyltrifluorosilane under two symmetries (**1a** & **1b**) and the calculated angles and dihedral angles (**1c**)

All the increased factors, like the bond length and the bond angle (shown in Table 1) point to the Anomeric effect. Due to charge withdrawal by electronegative substituents, there should be effective shrinkage of the C-Si bond length. This has been found to be true, as the theoretical value, 1.888 Å, was found using an imaginary system without an F or π system, CH_3SiH_3 . This might be of greater importance for d -orbitals of second row atoms as opposed to first row atoms, since d -functions generally lead to much greater bond length contractions in the case of hypervalent as opposed to normal valent second row compounds⁶.

This shortening of bond length was enough to prove that there is a drain of π electrons from the ring and the withdrawal of π electrons to the σ^* orbitals of the F atom through the hypervalent atom Si. The role of this atom is to provide “ d -orbitals” for effective overlapping. This was further evidenced by the fact that the gross orbital population (π orbital values obtained as a sum of $2p_z=3p_z+4zz+4xz+4yz$) for the F atom undergoing the anomeric affect was found to have a higher value compared to the other two F atoms (Table 2).

The other effect like inductive effect would be competing with this, but from the above data it was enough to conclude that negative hyperconjugation should be supported by decrease in C—Si bond length, increase in Si—F bond length along with (or without) increase in C—Si—F bond angle and increase in π orbital population number of fluorine atom. Of these three F atoms only one was more favored for the Anomeric effect due to its geometric position.

Table 1. The geometrical parameters and stabilization energies of various systems obtained by DFT 6-31 G* MO calculations.

Structure	System (symmetry)	A-X Å	A-Y Å	<XAY, degree	ΔE, Kcal
I	C ₆ H ₅ -SiF ₃ (C _S)	F ₁ =1.597 F ₂ =1.595 F ₃ =1.595	1.836	113.86 110.40 110.40	-1.3081
II	C ₆ H ₅ -CF ₃ (C _S)	F ₁ =1.354 F ₂ =1.352 F ₃ =1.352	1.889 ¹	111.8 111.9 111.9	-0.9072
III	C ₆ H ₅ -CH ₃ (C _S)	H ₁ =1.098 H ₂ =1.095 H ₃ =1.095	1.513 ²	111.3 111.5 111.5	-0.4320
IV	C ₆ H ₅ -PF ₄ (C ₂ V)	F ₁ =1.640 F ₂ =1.640 F ₃ =1.310 F ₄ =1.310	1.746	93.57 93.57 115.12 115.12	-1.5496
V	CH ₃ -PF ₄ (C ₂ V)	F ₁ =1.492 F ₂ =1.492 F ₃ =1.428 F ₄ =1.428	1.869	90.6 90.6 123.6 123.6	-0.6113
VI	C ₆ H ₅ -SF ₅ (C ₂ V)	F ₁ =1.623 F ₂ =1.630 F ₃ =1.630 F ₄ =1.630 F ₅ =1.630	1.825	180.0 90.0 90.0 90.0 90.0	-1.7990
VII	CH ₃ -SH ₅ (C _S)	H ₁ =1.415 H ₂ =1.431 H ₃ =1.431 H ₄ =1.431 H ₅ =1.431	1.896	180.0 90.0 90.0 90.0 90.0	-0.7025

A—X refers to the bond length between a hypervalent atom and an electronegative atom and A—Y to bond length between hypervalent atom and the Carbon atom

¹The ipso C—C(F₃) distance, ²The ipso C—C(H₃) distance

All the values given above were obtained using 6-31 G* basis sets. The point groups represented in parentheses are for the optimized geometry with lower ΔE values.

To measure the effect of hypervalent atoms, a study was made with another system without the Si atom, C₆H₅CF₃, **II**. It was found that there was a decrease in the C—F bond length of F atoms 2 & 3. But due to the absence of hypervalent atom the effect of negative hyperconjugation was not felt by a significant decrease in change of bond angle. Hence in such systems, it can be concluded that the effect has to be followed up by change in bond angles involved. To sum up, the effect would be more enhanced in the presence of hypervalent atom like silicon and with a favourable angle for overlapping.

Trifluoromethylbenzene and the bond lengths in angstroms

In the absence of silicon atom, the inductive effect would compete with Anomeric effect and this could be recognized by calculating the σ and π charges⁷. The negative hyperconjugation was present in this case even in the absence of silicon atom, but without any marked change in the geometry of the molecule.

Table 2. The Gross orbital population number (π orbital electron number) of the different systems obtained by DFT 6-31 G* MO calculations at the B3LYP level and the π charges at the ipso carbon atom.

Structure	System (symmetry)	Gross Orbital Population	π - charges on the ipso C	Sigma charges on the ipso C
I	$C_6H_5-SiF_3$ (C_s)	$F_1=1.895$ $F_2=1.765$ $F_3=1.765$	0.085	-0.164
II	$C_6H_5-CF_3$ (C_s)	$F_1=1.906$ $F_2=1.665$ $F_3=1.665$	0.106	-0.113
III	$C_6H_5-CH_3$ (C_s)		0.118	0.057
IV	$C_6H_5-PF_4$ (C_{2V})	$F_1=1.928$ $F_2=1.928$ $F_3=1.794$ $F_4=1.794$	0.113	-0.148
VI	$C_6H_5-SF_5$ (C_{2V})	$F_1=1.507$ $F_2=1.937$ $F_3=1.937$ $F_4=1.937$ $F_5=1.937$	0.145	-0.288
VII	$C_6H_5-NO_2$ (C_s)		0.302	-0.031
VIII	C_6H_6 (S_6)		0.000	-0.128

Phenyltetrafluorophosphorane

Some possible structures for the system $C_6H_5PF_4$ under symmetry considerations are given as per the structures **IV a, b & c**. Given the freedom to rotate at the phosphorus atom, during optimization, the system assumed **IVa** structure. The heat of formation values also showed that this structure was stable compared to the other two, **IV b & c**. The bond lengths and bond angles are tabulated in Table 1. There was an increase in P—F bond length

(from 1.31 to 1.64) followed by an increase in the CPF angle (90° as per the C_{2v} symmetry before optimization) which indicated the presence of anomeric effect. There is also the shortening of the C—P bond and a system without π electrons and F atoms *viz.* CH_3PH_4 was studied using the same parameters and the bond lengths were also tabulated. It was found that the C—P bond decreased from 1.869 to 1.746 Å when moving from an alkyl system to an aromatic system. This was indicative of the fact that there is a built up of π character into the σ^* bonds of the molecule and hence the shortening of the bond length.

Structures of Phenyltetrafluorophosphorane showing deviation in bond angles from 90° (IV d) and Gross Orbital Population (IV e)

Moreover, the F atoms 1 & 2 alone are at a dihedral angle 0 or 180° with respect to the π orbitals of the phenyl ring (the ipso C atoms **IV d**) and hence show more negative hyperconjugation compared with the rest of the two F atoms, which are in the plane of the phenyl ring and hence have a dihedral angle of 90° - where the effect is very minimum. Also the split valence orbital population of F atoms suggested F1 and F2 as having higher gross orbital population (GOP) compared to F3 and F4 (**IV e**).

The higher total charge of the first two F atoms compared to the rest of the two may be because of the combined effect of negative hyperconjugation (higher) and the inductive effect (lower) which is absent in the rest of the fluorine atoms 3 & 4 as they lie in the plane of the ring i.e. 90° to the π orbital of the carbon atom in the ring when the negative hyperconjugation effect falls to zero. When in plane, the F atoms 3 & 4 might be showing higher inductive effect compared to F atoms 1 & 2. The inductive effects can be guessed from the σ or the total charges as they are operative only through the σ bonds, but since there is a hypervalent atom the anomeric effect predominates, which is supported by the gross orbital population⁸ (GOP), as in Table 2.

It was also found that all the four fluorine atoms, upon optimization tend to lie nearly in plane. Optimization without symmetry enforcement resulted in the two fluorine atoms 1 & 2 at the apex of the trigonal bipyramidal geometry **IV c** (in accordance with Bent's rule)⁹. After optimisation it was found that the F atoms have moved away from the ring by a few degrees, resulting in larger P—F bond length. This lengthening should have been caused by the inflow of more electrons by both effects and hence the increased total charge.

The magnitude of bond lengthening was also compared with the systems **I** and **IV** and it was found that the more the number of F atoms, the greater was the increase in the bond length of the C—X. This was also proportional with the decrease in the A—Y bond lengths when moving from three F atoms in **I** to four F atoms in **IV**.

Phenylpentafluorosulphorane

The structure $C_6H_5SF_5$ was studied at the same level. During the optimisation the molecule was allowed to rotate freely along the C—S—F axis (**VI b**) under the C_{2v} symmetry. The molecule assumed **VI a** orientation and this structure was found to be stable. The bond length and charge calculations are presented in Table 1 and 2 respectively. The theoretical bond length value for the S—F was found to be $1.59 \text{ \AA}$.

Structures of Phenylpentafluorosulphorane under different symmetries (VI a & b) and the bond lengths and angle under Anomeric effect

In this system the π charge on the apex F_a -atom (opposite to the phenyl ring in an octahedral geometry) was found to increase in support of negative hyperconjugation, but two of the geometrical information viz. the bond length and the bond angle, did not support this. The S—F bond length should have increased (compared to other F atoms), but it had a reduced value. At the same time a bond angle (ipso C-S- F_a) of 180° meant a dihedral angle of 90° with π orbital of the ipso C-atom-C-S-F, where the negative hyperconjugation effect is either zero or most minimum. Hence the only effect possible with this F-atom was the inductive effect. This was evident from the sigma charges present on the ipso C-atom, which is the highest value in the table 2. The overall effect was supported by a decreased C—S bond length¹⁰.

For F atom that is responsible for negative hyperconjugation the value of gross orbital population should have been higher compared with other F atoms in the same molecule. All other F atoms which are at 90° degrees to the phenyl ring having a favourable dihedral angle for overlap with π orbital should show negative hyperconjugation. In this case the dihedral angle between π of ipso C-C-P- F_b was 45° (VI c), which is just a minimum for a favourable overlap to give anomeric effect. Hence the effect is less marked compared to the inductive effect.

Conclusion

Negative hyperconjugation is found in the systems having hypervalent atoms attached to highly electronegative atoms and π systems in a geometrically anti-periplanar structure. This effect is found along with the inductive effect and can be differentiated in atoms having different geometry in the same system. By this way some atoms have high “anomeric effect”, while some just show “inductive effect”. Geometry of the system and the charges on the electronegative and the ipso atoms through which the π systems are attached are the helpful factors for establishing negative hyperconjugation. This is because the anomeric

effect is maximum when the π orbital, C- atom, Hypervalent atom and the electronegative atom have a dihedral angle of either 0 degree or 180 degrees (antiperiplanar, in this sense). Equally important is the inductive effect, which is operative through the sigma bonds. The charges both on the σ and π orbitals help in evaluating the types of effect. Of the three systems of interest studied, *viz.*, C_6H_5-A , where $A=SiF_3$, PF_4 and SF_5 , the last system showed less anomeric effect compared with the former two. In the last system, the inductive effect was competing with the anomeric effect. Wherever necessary the imaginary systems should be employed to study and compare the effects¹¹.

The overall effects should thus be calculated specifically for each system and with hypervalent atoms and electronegative atoms the effect was significant.

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