STUDY MATERIAL

VIVEKANANDA COLLEGE THAKURPUKUR

NAAC Accredited Grade—A

Topic: **Bent’s rule and its applications**

Course Title: **Core Course CC-2**

Course Paper**: Paper 2**

Unit: **NA**

Semester: **2**

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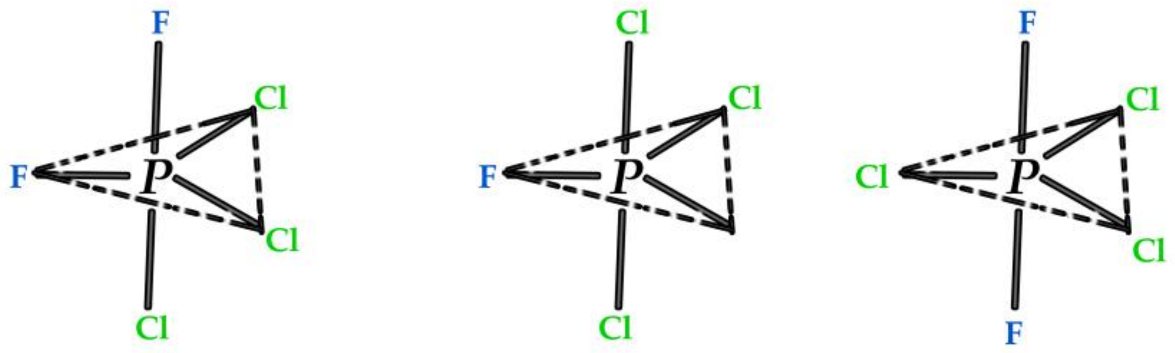
Name of the Department: **Chemistry**

Bent’s rule and its applications

In compounds with lone pairs or different substituents with trigonal bipyramidal(TBP) geometry, determining the correct structure can be difficult.It becomes mandatory to figure out the exact positions of the substituents or lone pairs , to determine the correct structure of the molecule.

e.g.– i)Consider **PCl_3F_2** molecule.In this molecule the central P atom is attached to five substituents (three Cl and two F) and so it is sp^3d hybridized (refer to the chart in earlier post). This molecule has TBP geometry and can have the following structures –

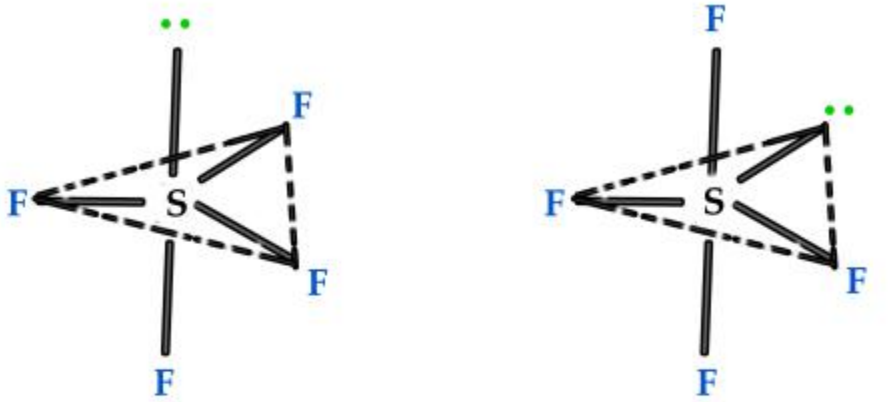
Possible structures of PCl_3F_2 molecule.



Which structure is correct ?

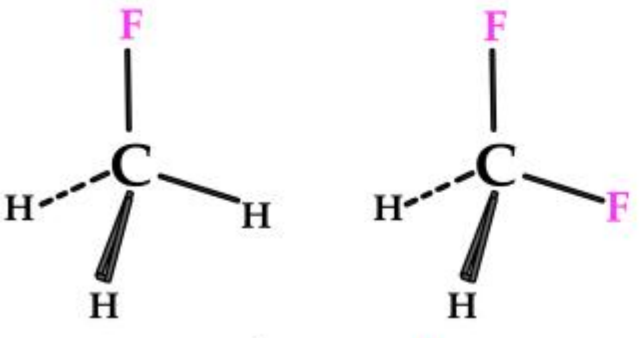
ii) SF_4 molecule has a lone pair of electrons. The structure of this molecule too can be written in two ways as follows-

Possible structures of SF_4 molecule.



Should the lone pair be placed at equatorial or axial position?

iii) Why does the C-F bond length vary in fluoromethane and difuoromethane?



C- F length = 1.388 Å   C- F length = 1.358 Å

Why do C- F bond lengths vary?

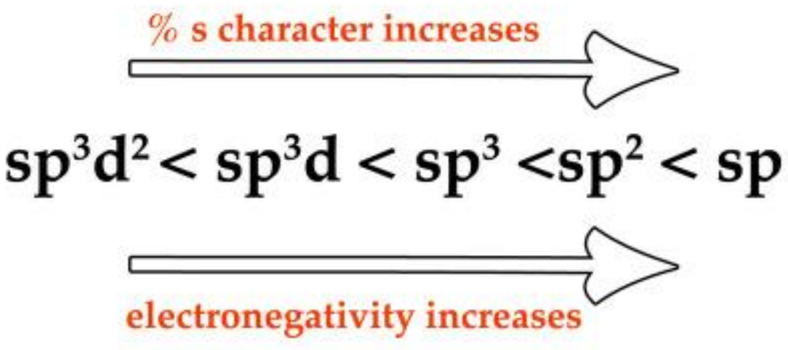
Bent’s rule is the answer to all the above questions. The rule is helpful in explaining bond lengths , bond angles , position of substituents in a molecule and structure of many molecules.

We have studied why substituents have their own preferences, in deciding which position they occupy, earlier in post 59.Now , we shall study that same concept again with a different approach.

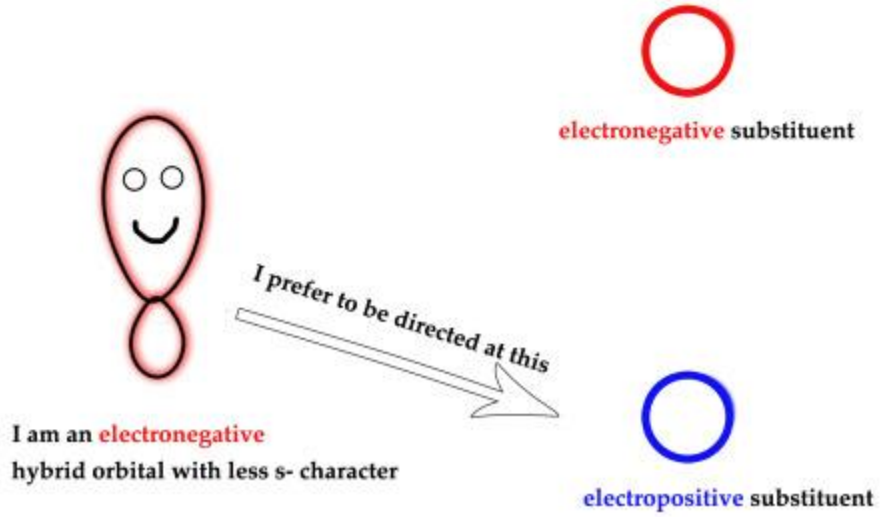
Bent’s rule

” Atomic s character tends to concentrate in orbitals that are directed towards electropositive groups and atomic p character tends to concentrate in orbitals that are directed towards electronegative groups.”

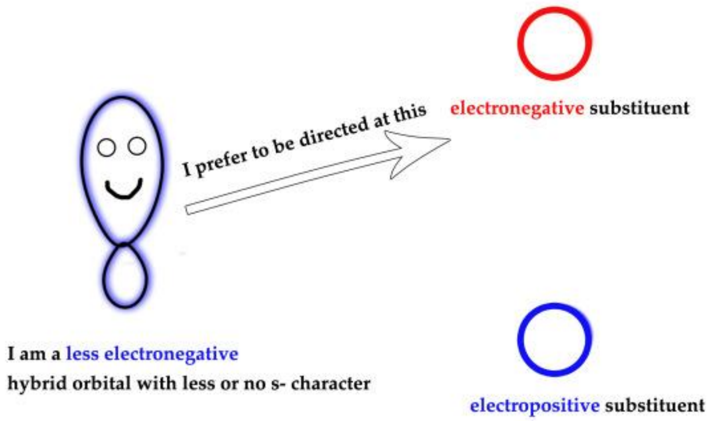
We know that ,the s- orbital is closer to the nucleus and so as the s-character in a hybrid orbital increases, its electronegativity increases too.



So, it should come as no surprise that an orbital containing more %s character (more electronegative) will prefer to be directed towards more electropositive groups.This is because – an electronegative group and a electronegative substituent will repel each other more, thus increasing the overall energy of the system.So, an electronegative hybrid orbital (with more %s character) will always prefer to be directed at an electropositive group.*e.g.* sp hybrid orbital



A hybrid orbital with lesser or no s- character can easily be directed towards an electronegative substituent.*e.g.* p-orbital.



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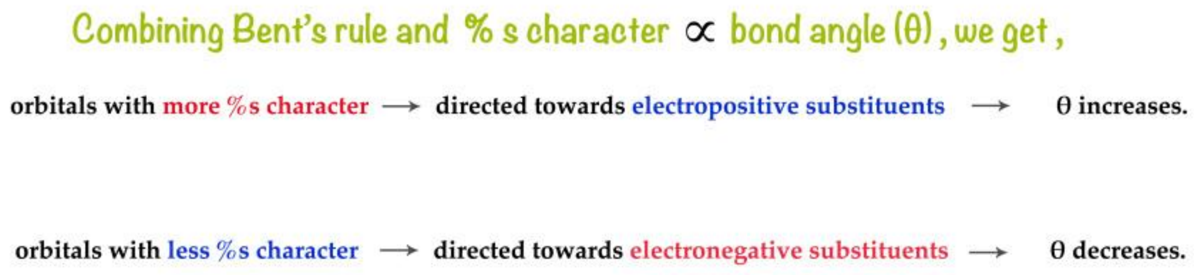
We know that *bond angle(θ)* $\propto$ *% s character* (from post no 71) .Then , according to Bent's rule,



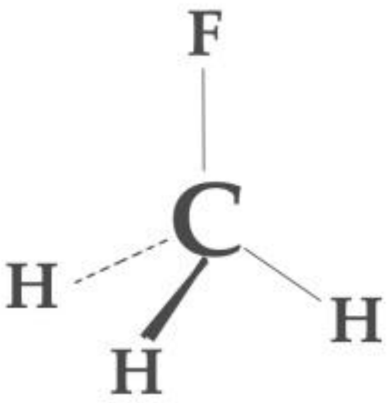
Combining Bent's rule and % s character $\propto$ bond angle (θ) , we get ,

orbitals with more %s character → directed towards electropositive substituents → θ increases.

orbitals with less %s character → directed towards electronegative substituents → θ decreases.

Now let us apply this to various examples and study Bent's rule .

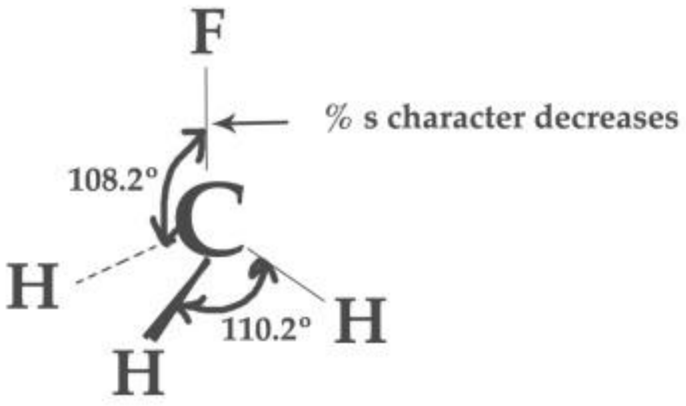
Example 1 – Methyl Fluoride (CH_3F molecule) .



In a methyl fluoride molecule , **fluorine** is the most **electronegative element**. Just like methane (CH_4) , this molecule is sp^3 hybridised too.However, the distribution of s- character is not uniform in all hybrid orbitals and so bond angles change too.This change is due to the presence of F atom. We can predict the change in bond angles using Bent's rule.

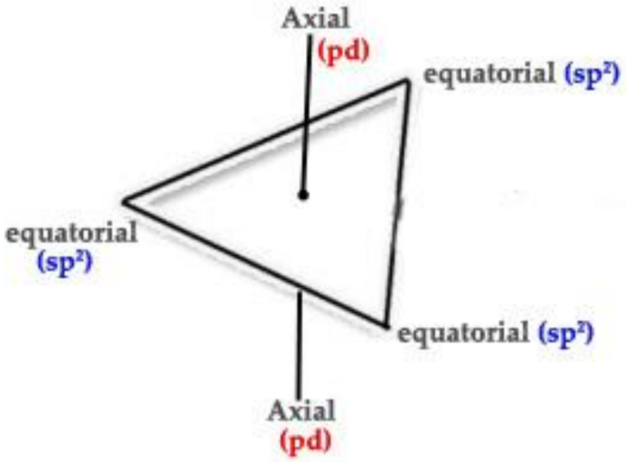
According to Bent's rule, the orbital with less %s character will be directed towards the more electronegative element. So, we can conclude that , the bond between C- F has **less % s-character** compared to C-H bonds. Also, the bond angle will decrease. Experimentally the H-C-F bond angle is found to be 108.2º , which is less than 109.5º .

When the %s character in C- F bond decreases, it is accounted for by increase in the %s-character in the other three C-H bonds. So, C-H bonds have more %s character than expected ,resulting in increase in bond angle between them. Experimentally , the H-C-H bond is found to be 110.2º.



Example 2 – Sulphur tetrafluoride (SF_4) .

We were skeptical about the structure of this molecule in the earlier post.Let us study it's structure using Bent's rule. SF_4 is sp^3d hybridized and has TBP geometry .There are four fluorine atoms and a lone pair in this molecule. As we know, according to Pauling scale of electronegativity , fluorine is the most electronegative element in the periodic table (refer post no 46) . In the TBP geometry , there are three equatorial positions and two axial positions.



We can **split sp^3d as sp^2 + pd.**

As seen above , the sp^2 orbitals occupy the equatorial positions and the pd orbitals occupy the axial position. How can we be sure of this ? Let's check whether this is true –

Experimentally , we find out that the angle between equatorial substituents is 120º. We also know,

$i = -1/\cos\theta$
$\therefore i = -1/\cos 120$
$i = -1/-(1/2)$ ..As $\cos 120 = -1/2$
$\therefore i = 2$

So, as the hybridization index is equal to 2 , the equatorial orbitals are sp^2 orbitals.

Or we can use the formula from post 69 – $\mathbf{f_s = \cos\theta/(\cos\theta - 1)}$

∴fraction of s- character in equatorial positions with θ = 120º is ,

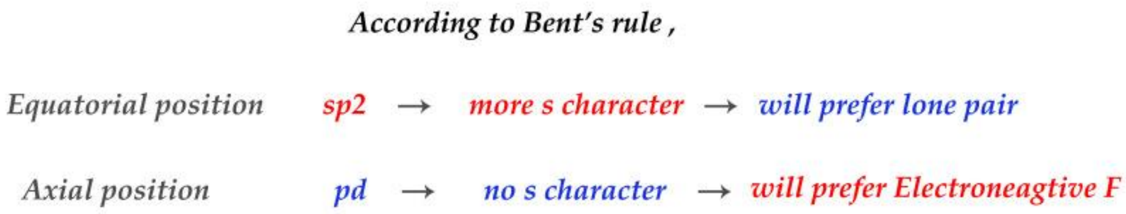
f_s= cos(120) / (cos 120 -1)
= (-1/2) /(-1/2 -1)
=(-1/2)/ (-3/2)
= 1/3
=0.33.

We know that it is sp^2 orbitals which have 33% s- character , so the equatorial hybrid orbitals are sp^2 hybridized.

lll^{ly} we know experimentally , that the angle with axial substituents is 90º. So,

f_s=cosθ/(cosθ-1)
= cos 90 / cos90 – 1
= 0/(0-1)
=0.

So, the amount of s- character in axial orbitals is zero i.e the pd part(no s character)occupies the axial position. Applying Bent's rule –

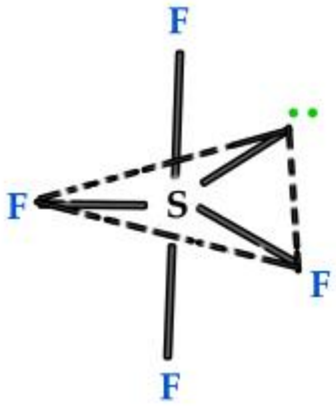


According to Bent's rule ,

Equatorial position *sp2* → *more s character* → *will prefer lone pair*

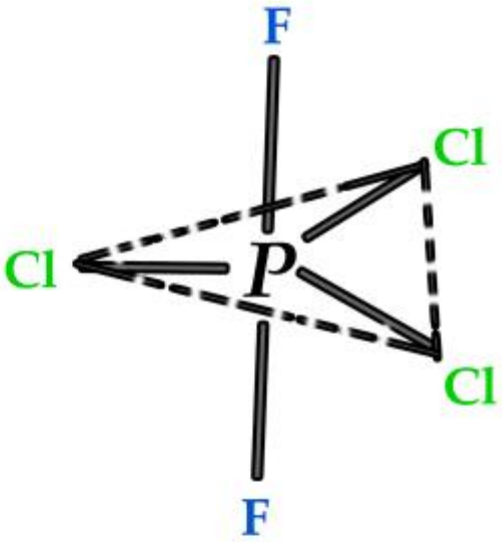
Axial position *pd* → *no s character* → *will prefer Electroneagtive F*

So the correct structure for this compound is –



Example 3 – PCl_3F_2 molecule .

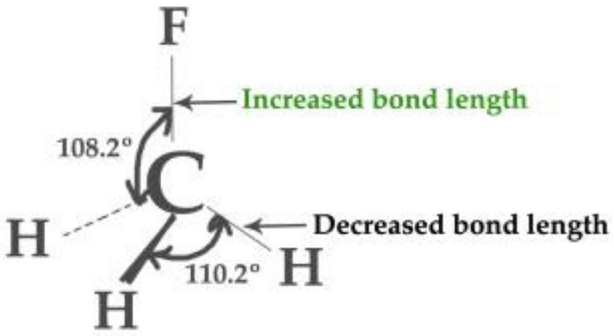
This molecule has TBP geometry with two F atoms and three Cl atoms as substituents. According to Bent's rule – F atoms are more electronegative and so they will prefer the axial position , where there is no s-character (less electronegative).The three Cl atoms will occupy the equatorial positions. Thus, the correct structure of this molecule is –



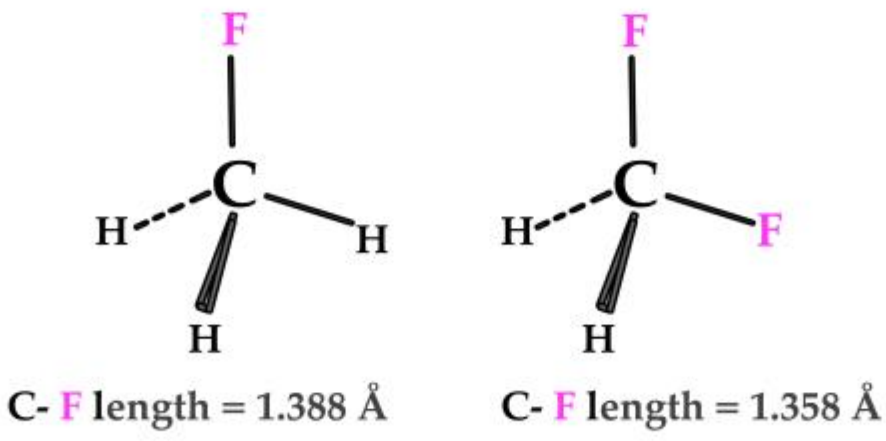
Relationship between bond length and Bond angle:

We already know what bond angle means. The distance between the centers of two nuclei of atoms connected by a chemical bond is ‘bond length’.

In general , there is an *inverse* relationship between the bond angle and bond length. However, some very strained molecules show different behaviour too. We shall study the normal behaviour of simple molecules , where bond length decreases as bond angle increases and vice versa.



We have studied the above example before and we saw that the H-C – F bond angle is lesser than expected and thus, the bond length is more and vice versa.



C- F length = 1.388 Å

C- F length = 1.358 Å

Why do C- F bond lengths vary?

Using Bent's rule we can answer the above question .

In fluoromethane ,according to Bent's rule ,

F is more electronegative than H → so %s character in C- F bond less → θ decreases → Bond length increases.

Here, all four bonds are NOT equal.In C-F bond , fluorine being more electronegative, will pull the electron density more towards itself. So, the electron density near C atom is reduced. To make up for this loss, the s- character in hybrid orbitals is shifted towards the other three C-H bonds. This increases the electron density on carbon , thus making C-H bonds more stable.

In difluoromethane , the bond length increases sightly due to presence of two fluorine atoms. Here, the s- character is shifted towards only two C-H bonds (instead of three in fluoromethane). So, less s- character in total is directed away from F- atoms(There's a limit to how much s-character can be directed at an substituent). This slightly decreases the bond length.

This trend continues as we go on adding more F- atoms in the structure –

Name	Average C-F bond length
Fluromethane	1.388 Å
Difluoromethane	1.358 Å
Trifluoromethane	1.329 Å
Tetrafluoromethane	1.323 Å

Bent Rule Energetics:

Any system in the universe always tries to lower its energy as lower energy corresponds to more stability. How does Bent's rule explain the lowering of energy ?

According to Bent's rule , in isovalent hybridization (hybridization in asymmetric molecules) ,

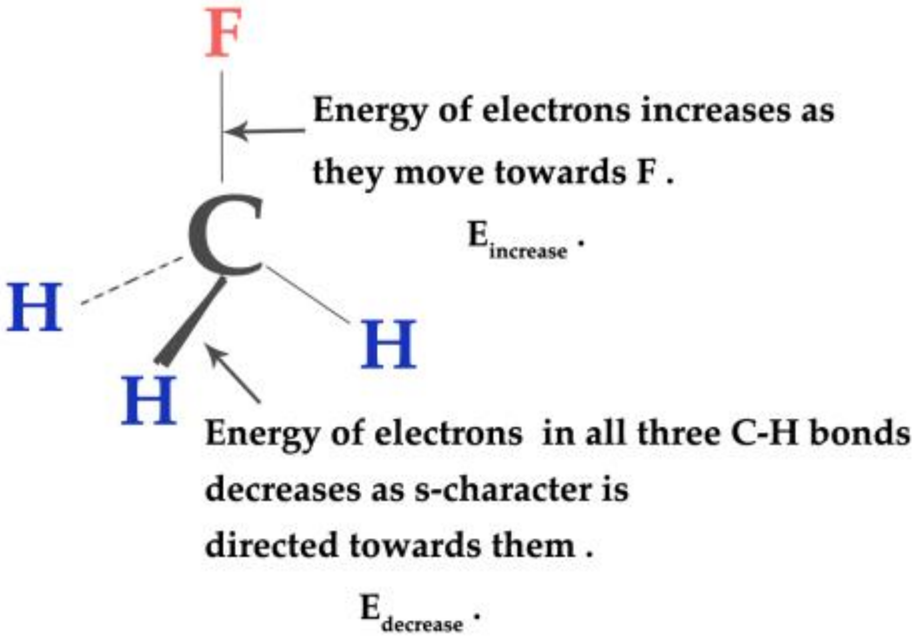
%s character is directed more towards electropositive elements &
%s character is directed less towards electronegative elements .

An electronegative substituent draws electron density away from the central atom. This results in the central atom being less stable. So, automatically , the molecule adjusts the s- character in such a way as to render stability to the central atom. So, what happens? The s- character (which has more electron density) is directed towards the less electronegative atoms. In the bond between the less electronegative atoms(*e.g.- H atoms*) and carbon, carbon is more electronegative.So, now the electron density in C-less electronegative bonds gets concentrated near carbon. What happens in the overall molecule ?

1)The electronegative element wants more electron density (as it has a tendency to accept electrons). So, the electrons from C-electronegative substituent bond get closer to the electronegative element(*e.g. – F*).So, the electronegative element is happy ! However, the energy of the bonding electrons slightly increases in this case. Let us assume that , the increase in energy of bonding electrons = $E_{increase}$.

2)The transfer of s character towards electropositive elements ,leads to maximum bonding between C- electropositive substituent bonds.Thus, there is decrease in the energy of the electrons in these orbitals. Let us assume that ,

the decrease in energy of bonding electrons = $E_{decrease}$.



F = electronegative substituent.

H= electropositive substituent.

The decrease in the energy due to shifting the s-character towards the electropositive substituents is more than the increase in energy due to shifting of electrons(in C- electroneagative element) towards the more electronegative element i.e

$$E_{decrease} > E_{increase} .$$

$$E_{increase} – E_{decrease} = – \Delta E$$

$– \Delta E$ = Net decrease in overall energy of the system.

Thus , the overall the energy of the molecule becomes less(the negative sign on ΔE indicates there is decrease in energy) and the molecule tends to be more stable.

Reference: https://madoverchemistry.com