

Fluoromaticity: The Molecular Orbital Contributions of Fluorine Substituents to the π -Systems of Aromatic Rings

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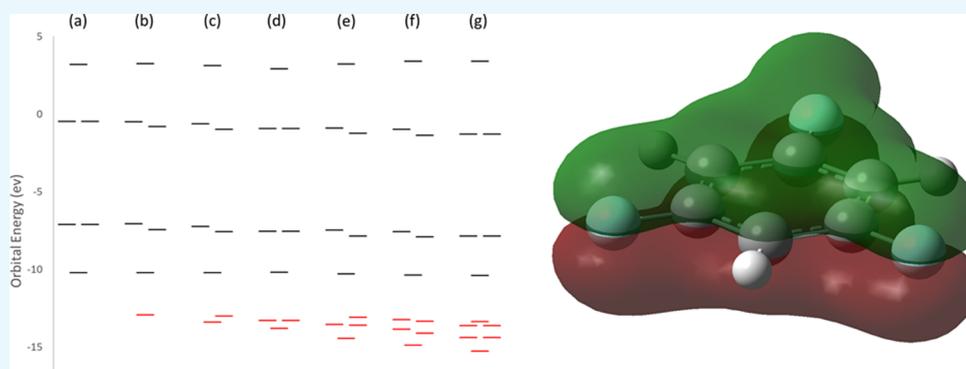
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ABSTRACT: The addition of fluorine atoms to an aromatic ring brings about an additional set of π -bonding and antibonding orbitals culminating after the addition of the sixth fluorine with a new set of π -aromatic-like orbitals that affect the molecule in a way that we will refer to hereafter as “fluoromaticity”. Depending on the number and position of the fluorine atoms, the contributed π -orbitals can even further stabilize the ring leading to smaller bond lengths within the ring and higher resistance to addition reactions. This added ring stability partially explains the high thermostability and chemical resistance found in polymers containing fluorinated aromatics in their architecture. A similar molecular orbital effect is seen with the addition of other halogen atoms to aromatic rings, though to a much smaller degree and not resulting in the additional ring stability.

INTRODUCTION

Fluoropolymers, particularly those containing fluorinated aromatics in their architecture, are widely known for their desirable properties such as chemical resistance, thermal stability, and solution and melt processability.^{1–6} Fluoroaromatics have also shown great promise for use in biomedical applications,^{7–10} including as substituents to allow medications to more easily cross the blood brain barrier^{11,12} and penetrate cells.¹³

Recently, in an effort to bring a deeper understanding to the reactions that lead to the formation of perfluoropyridine-based polymers, we published a theoretical explanation of reaction site selectivity in the addition of a phenoxy group to perfluoropyridine.¹⁴ Following this, a detailed description of the electronic structure of these and related molecules would be useful in explaining not only these reactions, but the desirable properties of the fluoropyridine or fluorophenyl polymers derived from them. To our knowledge, this kind and depth of comprehensive model of all of the fluoropyridines and fluorobenzenes has not been conducted before. In 1968, Emsley examined just the monofluoropyridine isomeric set along with monofluorobenzene and the difluorobenzene isomeric set using semiempirical methods¹⁵ and drew very

few overall conclusions related to the cause of the orbital energy differences he found.

In 1987, George, Bock, and Trachtman modeled the monofluoropyridine isomeric set using Hartree-Fock theory and the 6-31G basis set.¹⁶ This was a high level of theory for that time, but with no correlation correction, diffuse functions, or polarization. As such, these models can be computed with much higher accuracy using current computational technology. They found 2-fluoropyridine to be the most stable (lowest energy) of the monofluoropyridines while 3-fluoropyridine was the least stable of the three. They noted a lack of electronic communication between the fluorine and the nitrogen on 4-fluoropyridine with a stronger communication being seen in the other two isomers. However, they made these arguments

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based on molecular geometry rather than the electronic structure.

Fluorobenzene and the polyfluorobenzenes have been modeled more extensively than their pyridine counterparts,^{17–25} most extensively by Jezowski,²⁶ but with focus primarily on frontier orbitals rather than on the entire π -system and its effects on the structure and stability of the ring.

Since the discovery of benzene by Faraday in 1825,²⁷ there has been significant controversy over the definition and even the cause of aromaticity,^{28–33} but the classically accepted criteria for the determination of aromaticity typically includes the following:³⁴

- 1) Reduced bond lengths within the ring compared to analogous acyclic unsaturated molecules
- 2) Increased stability compared to analogous acyclic unsaturated molecules
- 3) Increased probability of undergoing substitution reactions and a decreased probability of undergoing addition reactions
- 4) Induction of a diatropic ring current by the application of an external magnetic field.³⁵

The various fluorobenzenes have been studied extensively with reference to number 4 above, making extensive use of the “nucleus-independent chemical shift” (NICS) method for calculating the magnetic shielding at the center of an aromatic ring.³⁶ In these studies, the fluorobenzenes have been found to exhibit at least slightly diminished aromaticity with respect to benzene as it pertains to the diatropic ring current.^{37–43} Table 1 shows a sample of the results of some of these computations in the literature.

Table 1. NICS(0) Values as Computed by Kaipio⁴¹ et al. and Chen⁴³ et al.

molecule	NICS(0) Kaipio	NICS(0) Chen
benzene	−8.4	−8.03
fluorobenzene	−9.8	−9.98
<i>o</i> -difluorobenzene	−11.3	−11.76
<i>m</i> -difluorobenzene	−11.3	−11.7
<i>p</i> -difluorobenzene	−11.1	−11.6
1,2,3-trifluorobenzene	−12.6	−13.39
1,2,4-trifluorobenzene	−12.7	−13.43
1,3,5-trifluorobenzene	−12.4	−13.16
1,2,3,4-tetrafluorobenzene	−14	−15.19
1,2,3,5-tetrafluorobenzene	−13.8	−14.94
1,2,4,5-tetrafluorobenzene	−14.1	−15.22
pentafluorobenzene	−15.3	−16.74
hexafluorobenzene	−16.5	−18.23

In this work, we will focus on number 3 of the criteria for aromaticity listed above. A numerical value to the energy of aromaticity has often been assigned by looking at the differences between the heats of hydrogenation of benzene, 1,3-cyclohexadiene, and cyclohexene.⁴⁴ However, a comparison of the first heat of hydration between benzene and fluorobenzenes might not be the best measure of energy of aromaticity because the fluorine atoms may cause a stabilization or destabilization of the product that has little or nothing to do with aromaticity. A more accurate measure of energy of protection against addition reactions brought by aromaticity would be the activation energy for the reaction leading to the first hydrogenation. By this measure, we will

show that some of the fluoroaromatics have an increased energy of aromaticity and, therefore, an increased aromatic character.

To explain this effect, we provide the most detailed molecular orbital analysis so far of the π -systems of all of the fluoropyridine and fluorobenzene isomeric sets and derive from that a theoretical explanation for the enhanced thermal stability found in polymers containing fluorinated aromatic rings in their architecture. We also contend that while the fluorobenzenes exhibit reduced aromatic character compared to benzene as it pertains to the induction of a diatropic ring current by a magnetic field, they exhibit similar and, in some cases, increased aromatic character over benzene as it pertains to the other three criteria listed above. This increased aromatic-like behavior is caused by the addition of molecular orbitals to the π -system as the lone pairs on each fluorine atom conjugate to the ring. We will refer to this concept as “fluoromaticity”.

RESULTS AND DISCUSSION

Activation Energies of Hydrogenation. A quick look at the computed energies of hydrogenation for benzene, 1,3,5-trifluorobenzene, and hexafluorobenzene would suggest that the substitution of fluorine atoms onto benzene reduces the aromatic character (see Table 2 below). However, complete

Table 2. Activation Energy of Hydrogenation (ΔE^\ddagger) and Change in Energy of Hydrogenation (ΔE) for the Selected Aromatic Compounds

molecule	ΔE^\ddagger hydrogenation (kcal/mol)	ΔE hydrogenation (kcal/mol)
benzene	54.04	4.90
1,3,5-trifluorobenzene	58.10	0.14
hexafluorobenzene	58.29	−9.61

energies of the reaction include energetic effects other than the protection aromaticity brings to the ring, particularly how the fluorine atoms stabilize or destabilize the products. The computed activation energy of hydrogenation (ΔE^\ddagger) gives a much more realistic view of the protection given to the ring by its aromaticity. 1,3,5-trifluorobenzene and hexafluorobenzene each have about 4 kcal/mol greater activation energies of hydrogenation. To put it another way, the energy of aromaticity is about 4 kcal/mol greater for these fluoroaromatics than for benzene.

If we state that the fluorinated aromatics are more aromatic than their nonfluorinated counterparts, we at least partially answer our previous question of why polymers with fluoroaromatic architectures are so resistant to high temperature and chemical attack.^{2,6} However at the same time, we beg the question of why so many previous works, several cited in the introduction above, show them to be less aromatic from the point of view of diatropic ring currents.^{37,38,41,42} One possible explanation for this phenomenon invokes the particle on a ring model of basic quantum mechanics and how that model would be affected by the charges on the atoms in the rings. If the π -electrons, whose ring currents are being measured, are seen as particles on a two-dimensional ring, they will behave most ideally when allowed to flow around a ring under constant potential energy. In a benzene ring, the carbon atoms have nearly identical Millikan charges of about −0.4 due to the larger electronegativity of carbon compared to

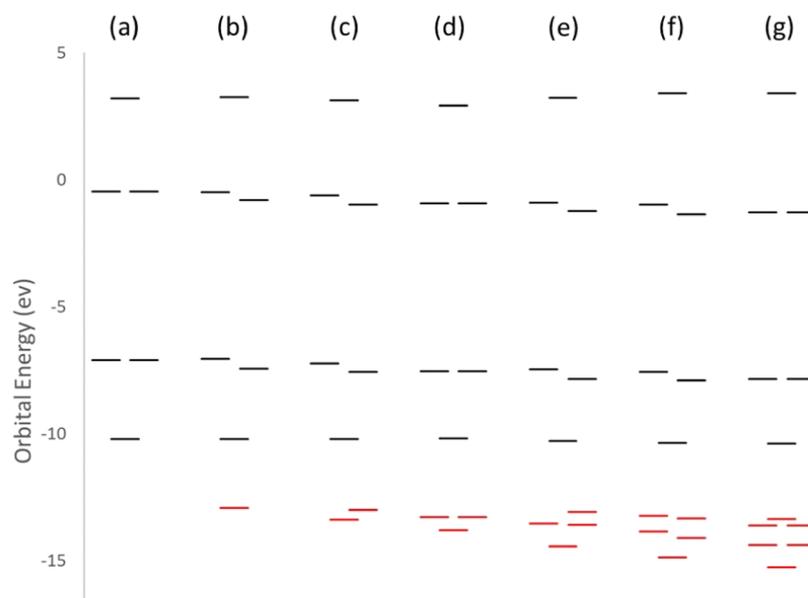


Figure 1. π -molecular orbital diagrams for (a) benzene, (b) fluorobenzene, (c) *m*-difluorobenzene, (d) 1,3,5-trifluorobenzene, (e) 1,2,3,5-tetrafluorobenzene, (f) pentafluorobenzene, and (g) hexafluorobenzene. Conventional aromatic orbitals are shown in black while additional π -orbitals formed by the conjugation of substituents to the ring are shown in red (note: the highest three orbitals in each set are unoccupied).

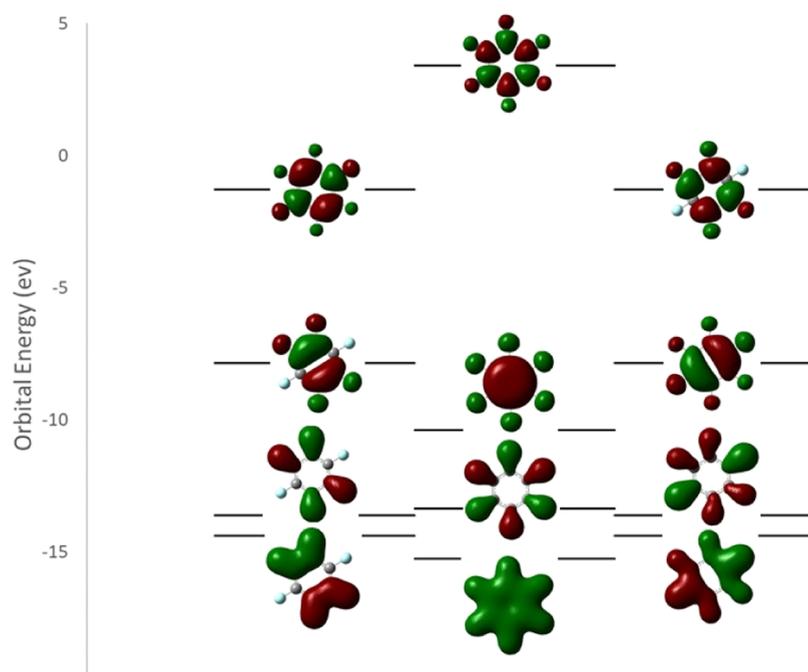


Figure 2. π -system molecular orbitals for hexafluorobenzene (highest three orbitals are unoccupied).

hydrogen. This creates the near ideal environment for ring current flow. Each fluorine atom that replaces a hydrogen atom causes its carbon atom to gain a net positive charge, creating a barrier for the π -electrons to flow through and disrupt the ring current. Even though the ring current is reduced, the next several sub-sections of this paper will show that the π -density of the ring is increased with the substitution of fluorine atoms for hydrogen and that this is the most important factor for determining energy of aromaticity, rather than diatropic ring current.

Fluorobenzenes. Each substitution of a fluorine atom onto a benzene ring creates a new π -orbital in conjugation with

the aromatic ring. Each of these newly created π -orbitals is lower in energy than the original six aromatic orbitals (three of which are still occupied and three unoccupied) and has little if any effect on the energetic positioning of the original six, as shown in Figure 1 below. The isomers chosen for (c–e) were the lowest energy isomers for that isomeric set.

The pattern exhibited by these orbitals is similar to that of the original six π -aromatic orbitals with the lowest being entirely bonding between the ring and the fluorine, and the next several as the added accruing increasing antibonding character (see Figure 2 below).

Notice that the upper six orbitals on hexafluorobenzene each have similar nodes, ring geometry, and energy analogous to orbitals on benzene. These upper six orbitals all are π -antibonded to the attached fluorine atoms. The lower six orbitals have geometries analogous to the upper set, but with the fluorine atoms bonded rather than antibonded to their ring atoms. This means that as we work our way across **Figure 1**, adding another fluorine atom and therefore another π -molecular orbital from the lower set, the amount of the total bonding character around the ring increases as we add the first, second, and third fluorine atoms. Once we add the fourth, and then the fifth and sixth fluorine atoms, the new orbitals are primarily antibonding around the ring. As such, the average bond length within the ring should reach a minimum at 1,3,5-trifluorobenzene. This is the trend that we see in **Table 3** below.

Table 3. Computed Bond Lengths and Standard Deviations of Bond Lengths for all of the Fluorobenzenes (Most Energetically Stable for Each Isomeric Set Shown in Bold Print)

molecule	average bond length (Å)	bond length std dev
benzene	1.39065	0.00001
fluorobenzene	1.38839	0.00383
<i>o</i> -difluorobenzene	1.38758	0.00407
<i>m</i> -difluorobenzene	1.38620	0.00330
<i>p</i> -difluorobenzene	1.38592	0.00358
1,2,3-trifluorobenzene	1.38714	0.00319
1,2,4-trifluorobenzene	1.38542	0.00365
1,3,5-trifluorobenzene	1.38437	0.00000
1,2,3,4-tetrafluorobenzene	1.38667	0.00393
1,2,3,5-tetrafluorobenzene	1.38527	0.00243
1,2,4,5-tetrafluorobenzene	1.38492	0.00226
pentafluorobenzene	1.38683	0.00281
hexafluorobenzene	1.38851	0.00002

As predicted by the molecular orbital distributions shown in **Figures 1** and **2**, 1,3,5-trifluorobenzene has the smallest average carbon–carbon bond lengths of any of the molecules studied. The argument can be made that 1,3,5-trifluorobenzene is more aromatic than benzene itself because of its symmetry and shorter carbon–carbon bond lengths.

Table 4 shows parameters thought to be indicators of aromaticity, including the HOMA (harmonic oscillator model of aromaticity),⁴⁵ the polarizability, and the band gap. Larger band gaps, smaller polarizability, and HOMAs closer to 1.00 are thought to be indicators of increased aromaticity.²⁶ The reference bond length for the HOMA calculation was set to the average carbon–carbon bond length found in our benzene model so that benzene's HOMA would be normalized to 1.00. Notice that the band gap for 1,3,5-trifluorobenzene does not begin to differ with that of benzene until the third decimal place. There are several species on this table with slightly larger HOMA than 1,3,5-trifluorobenzene but that is likely more of an artifact of how HOMA is calculated than an indicator of any lack of aromaticity because the HOMA formula considers the benzene bond length to be the perfect aromatic bond length, but as we stated earlier, shorter bond lengths in a ring π -system are indicative of increased aromaticity.

An additional paradox in the data is that the lowest energy isomers in the difluorobenzene set and the tetrafluorobenzene set are not the isomers with the smallest carbon–carbon bond

Table 4. Parameters Related to Aromaticity Including HOMA, Polarizability, and Band Gap for all of the Fluorobenzenes (Most Energetically Stable for Each Isomeric Set Shown in Bold Print)

molecule	HOMA	polarizability (Å ³)	band gap (eV)
benzene	1.0000	10.2589	6.6154
fluorobenzene	0.9955	10.2781	6.2434
<i>o</i> -difluorobenzene	0.9940	10.3492	6.2145
<i>m</i> -difluorobenzene	0.9926	10.3196	6.2421
<i>p</i> -difluorobenzene	0.9915	10.2855	5.8850
1,2,3-trifluorobenzene	0.9946	10.4350	6.5313
1,2,4-trifluorobenzene	0.9901	10.3862	5.9626
1,3,5-trifluorobenzene	0.9898	10.3892	6.6120
1,2,3,4-tetrafluorobenzene	0.9926	10.5224	6.2140
1,2,3,5-tetrafluorobenzene	0.9913	10.5017	6.2216
1,2,4,5-tetrafluorobenzene	0.9905	10.4839	5.8475
pentafluorobenzene	0.9945	10.6349	6.1985
hexafluorobenzene	0.9988	10.7800	6.2037

lengths nor the smallest polarizabilities. In the case of difluorobenzene, the para isomer has the smallest bond lengths and the smallest polarizability in the set despite not having the lowest energy. This is because the stabilization of the ring and the shortening of its bond lengths are at the expense of the stability of the carbon–fluorine bonds, which are slightly elongated for the para isomer compared to the other two (see **Table 5** below).

Table 5. Comparison of Average Carbon–Fluorine Bond Lengths for the Difluorobenzene and Tetrafluorobenzene Isomeric Sets

molecule	average C–F bond length (Å)
<i>o</i> -difluorobenzene	1.34367
<i>m</i> -difluorobenzene	1.34904
<i>p</i> -difluorobenzene	1.35218
1,2,3,4-tetrafluorobenzene	1.33745
1,2,3,5-tetrafluorobenzene	1.33946
1,2,4,5-tetrafluorobenzene	1.34051

A similar effect can be seen in the tetrafluorobenzene isomeric set. The 1,2,3,5 isomer is the most energetically stable isomer while the more symmetric 1,2,4,5 isomer has the smallest carbon–carbon bond lengths and smallest polarizability (**Table 6**). The additional energy in the 1,2,4,5 isomers is found in the carbon–fluorine bonds, which are slightly elongated compared to the carbon–fluorine bonds in the other two isomers. This demonstrates another characteristic of increased aromaticity for these particular isomers: an increased reactivity of the substituent atoms and decreased reactivity of the ring.³⁴ To put it another way, 1,2,4,5-tetrafluorobenzene and *p*-difluorobenzene have an increased probability of undergoing substitution reactions and a decreased probability of undergoing addition reactions compared to the rest of their respective isomeric sets.

Fluoropyridines. The substitutions of fluorine atoms for the hydrogen atoms on pyridine produces a very similar molecular orbital effect to that just described for benzene. As shown in **Figure 3** below, the conjugation of each new fluorine atom adds a new molecular orbital to the π -system below the original six and otherwise following the energetic and geometric patterns exhibited by the original six with the

Table 6. Computed Bond Lengths and Standard Deviations of Bond Lengths for all of the Fluoropyridines (Most Energetically Stable for Each Isomeric Set Shown in Bold Print)

molecule	average bond length (Å)	bond length std dev
pyridine	1.37089	0.02847
2-fluoropyridine	1.36628	0.03562
3-fluoropyridine	1.36846	0.02819
4-fluoropyridine	1.36855	0.02744
2,3-difluoropyridine	1.36500	0.03692
2,4-difluoropyridine	1.36436	0.03405
2,5-difluoropyridine	1.36407	0.03461
2,6-difluoropyridine	1.36224	0.03857
3,4-difluoropyridine	1.36786	0.02801
3,5-difluoropyridine	1.36653	0.02784
2,3,4-trifluoropyridine	1.36484	0.03614
2,3,5-trifluoropyridine	1.36317	0.03650
2,3,6-trifluoropyridine	1.36105	0.03909
2,4,5-trifluoropyridine	1.36392	0.03483
2,4,6-trifluoropyridine	1.36059	0.03722
3,4,5-trifluoropyridine	1.37686	0.02269
2,3,4,5-tetrafluoropyridine	1.36458	0.03734
2,3,4,6-tetrafluoropyridine	1.36109	0.03902
2,3,5,6-tetrafluoropyridine	1.36019	0.04012
pentafluoropyridine	1.36176	0.04120

exception that the fluorine atoms are π -bonded to the ring in the new lower orbitals and are π -antibonded to the ring in the orbitals analogous to the original six pyridine π -orbitals (see also Figure 4). Because pyridine only has five carbon atoms and, therefore, five hydrogen atoms that can be substituted,

perfluorobenzene has only five π -orbitals of the new lower energy type and they correspond in geometry to the five analogous π -orbitals on pentafluorobenzene.

It is also worth noting that the highest of the new π -orbitals (symbolized with red lines in Figure 4) caused by fluorine atoms on pentafluoropyridine is about 2.35 eV lower in energy than the lowest of the original six orbitals (symbolized with black lines in Figure 4). For pentafluorobenzene, that difference is 2.89 eV, so the stabilizing effect of the fluorine atoms is a bit stronger in fluorinated benzenes than in fluorinated pyridines.

Bond distances within the ring tend to follow similar trends for the fluoropyridines to those seen for the fluorobenzenes. One notable difference here is that there is a tetrafluoropyridine (2,3,5,6) with shorter average bond lengths in the ring than that of the trifluoropyridine with the shortest ring bonds (2,4,6). Pentafluorobenzene's ring bond lengths are also shorter than one might expect based on the benzene trends.

A further look at the other aromaticity-related parameters (see Table 7 below) tells a bit more of the rest of the story. The HOMAs are likely not as useful in the case of the fluoropyridines for reasons discussed earlier, but the band gaps and polarizabilities give us something to look at. Many of the fluoropyridines have significantly larger band gaps than pyridine itself, especially those with a fluorine atom at the 4-position (para to the nitrogen). The lowest energy and smallest polarizability isomers in each set always have a fluorine atom at the 2-position (ortho to the nitrogen), suggesting that the fluorine atoms interact more effectively with a π -system when they are ortho or para to the nitrogen atom.

The average carbon to fluorine bond lengths on the fluoropyridines are shown in Table 8 below. As in the

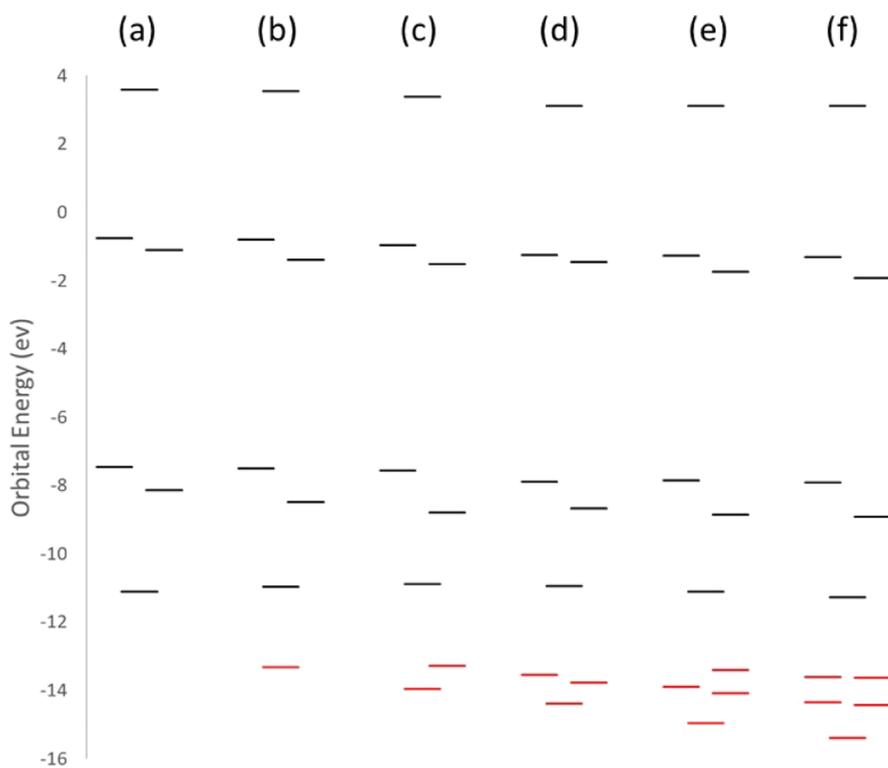


Figure 3. π -molecular orbital diagrams for (a) pyridine, (b) 2-fluoropyridine, (c) 2,6-difluoropyridine, (d) 2,4,6-trifluoropyridine, (e) 2,3,4,6-tetrafluoropyridine, and (f) pentafluoropyridine. Conventional aromatic orbitals are shown in black while additional π -orbitals formed by the conjugation of substituents to the ring are shown in red (note: the highest three orbitals in each set are unoccupied).

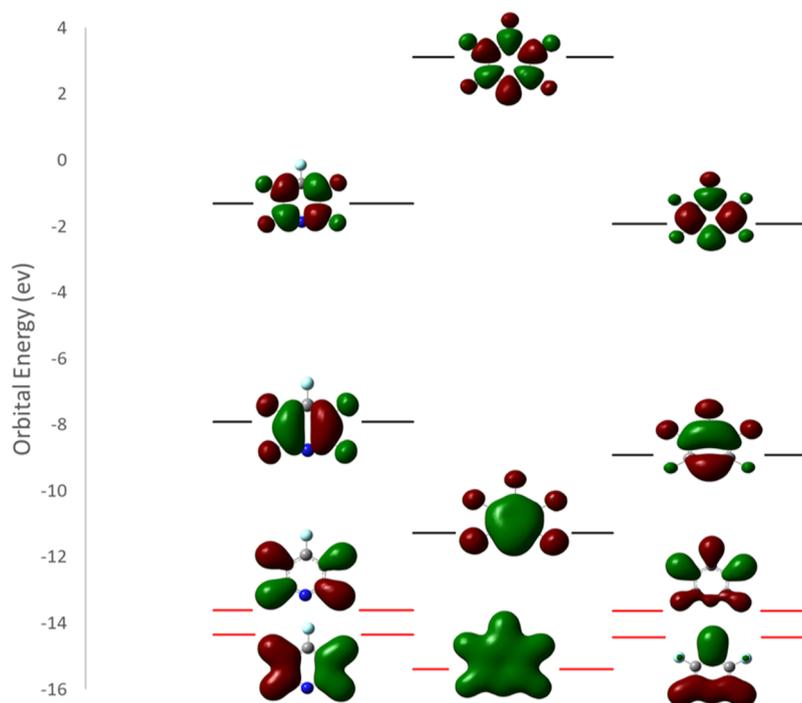


Figure 4. π -system molecular orbitals for pentafluoropyridine (highest three orbitals are unoccupied). Conventional aromatic orbitals are shown in black while additional π -orbitals formed by the conjugation of substituents to the ring are shown in red.

Table 7. Parameters Related to Aromaticity Including HOMA (Harmonic Oscillator Model of Aromaticity), Polarizability, and Band Gap for all of the Fluoropyridines (Most Energetically Stable for Each Isomeric Set Shown in Bold Print)

molecule	HOMA	polarizability (\AA^3)	band gap
pyridine	0.7254	9.4610	6.0847
2-fluoropyridine	0.5745	9.5009	6.0975
3-fluoropyridine	0.7024	9.5187	6.0510
4-fluoropyridine	0.7125	9.5069	6.4311
2,3-difluoropyridine	0.5378	9.6297	5.9734
2,4-difluoropyridine	0.5729	9.5720	6.3743
2,5-difluoropyridine	0.5607	9.5542	5.7465
2,6-difluoropyridine	0.4726	9.5794	6.0382
3,4-difluoropyridine	0.6977	9.6001	6.3283
3,5-difluoropyridine	0.6837	9.6001	5.9296
2,3,4-trifluoropyridine	0.5479	9.7260	6.3133
2,3,5-trifluoropyridine	0.5193	9.7112	5.7261
2,3,6-trifluoropyridine	0.4461	9.6978	5.7699
2,4,5-trifluoropyridine	0.5554	9.6667	5.9960
2,4,6-trifluoropyridine	0.4696	9.6697	6.4379
3,4,5-trifluoropyridine	0.8405	9.7141	6.2779
2,3,4,5-tetrafluoropyridine	0.5255	9.8473	6.0507
2,3,4,6-tetrafluoropyridine	0.4479	9.8237	6.1228
2,3,5,6-tetrafluoropyridine	0.4153	9.8503	5.6143
pentafluoropyridine	0.4205	10.0057	5.9955

fluorobenzene case, the carbon–fluorine bonds become shorter as more fluorine atoms are added to the pyridine ring. When the fluorine atoms are as close together as possible, as in the case of 2,3,4-trifluoropyridine compared to 2,4,6-trifluoropyridine, the carbon to fluorine bonds lengthen and the carbon to carbon bonds shorten. Therefore, to put it another way, the more spread out the fluorine atoms are within

Table 8. Comparison of Average Carbon–Fluorine Bond Lengths for the Fluoropyridines (Most Energetically Stable for Each Isomeric Set Shown in Bold Print)

molecule	average C–F bond length (\AA)
2-fluoropyridine	1.34431
3-fluoropyridine	1.34824
4-fluoropyridine	1.34439
2,3-difluoropyridine	1.338525
2,4-difluoropyridine	1.340705
2,5-difluoropyridine	1.345565
2,6-difluoropyridine	1.33868
3,4-difluoropyridine	1.33827
3,5-difluoropyridine	1.34493
2,3,4-trifluoropyridine	1.333593
2,3,5-trifluoropyridine	1.33915
2,3,6-trifluoropyridine	1.336613
2,4,5-trifluoropyridine	1.337403
2,4,6-trifluoropyridine	1.335737
3,4,5-trifluoropyridine	1.335007
2,3,4,5-tetrafluoropyridine	1.332195
2,3,4,6-tetrafluoropyridine	1.332203
2,3,5,6-tetrafluoropyridine	1.334413
pentafluoropyridine	1.329102

a given isomeric set, the more the fluorine atoms contribute to the aromatic behavior of the ring.

This effect is caused by the unique ability of fluorine atoms to draw negative charge out of the ring through their sigma bond to it, and then return some of that charge through the π -molecular orbitals it shares with the ring system. This ability to return charge to the ring is enhanced at the positions ortho and para to the nitrogen atom of the pyridine (see Figure 5 below).

Other Halogens. Chlorine, bromine, and iodine will each interact with the π -system of an aromatic ring in a fashion similar to fluorine but not nearly as efficiently or effectively

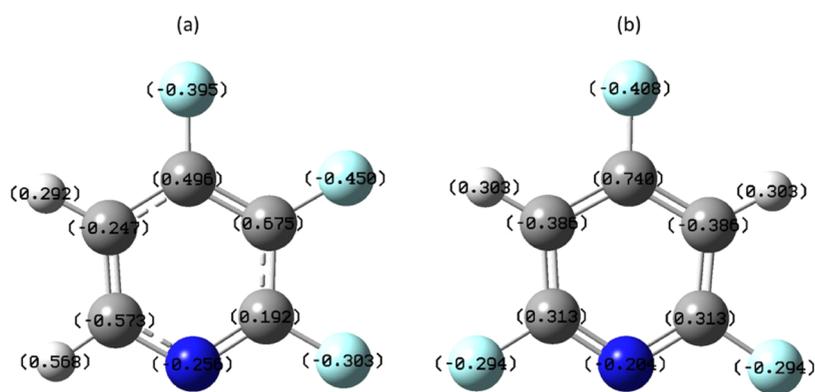


Figure 5. Millikan charges for (a) 2,3,4-trifluoropyridine and (b) 2,4,6-trifluoropyridine.

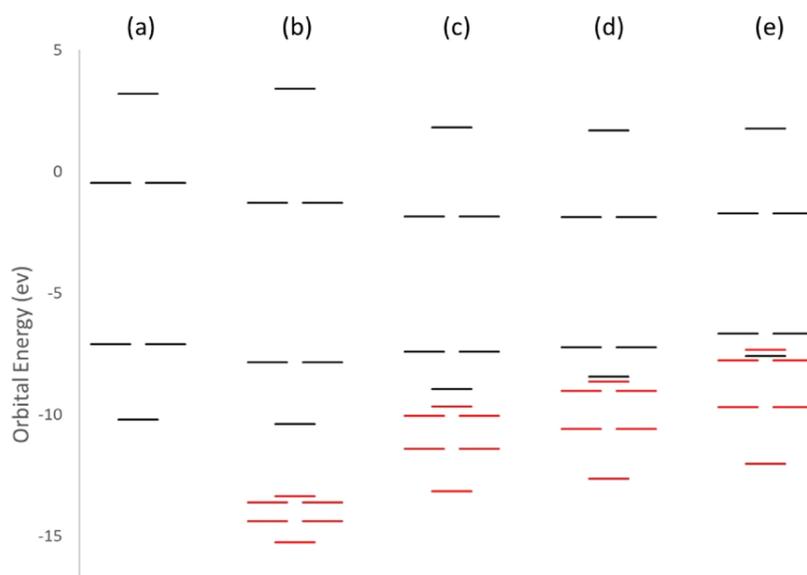


Figure 6. π -molecular orbital diagrams for (a) benzene, (b) hexafluorobenzene, (c) hexachlorobenzene, (d) hexabromobenzene, and (e) hexaiodobenzene. Conventional aromatic orbitals are shown in black while additional π -orbitals formed by the conjugation of substituents to the ring are shown in red.

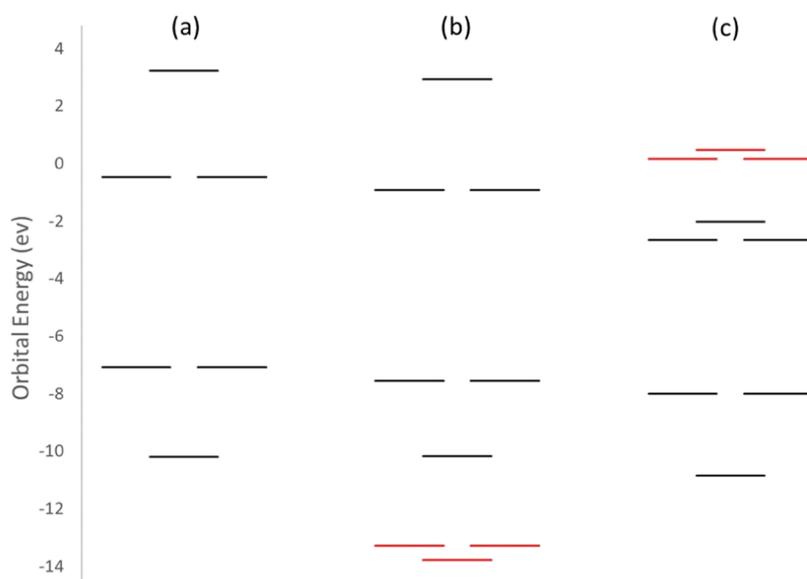


Figure 7. π -molecular orbital diagrams for (a) benzene, (b) 1,3,5-trifluorobenzene, and (c) 1,3,5-triborylbenzene. Conventional aromatic orbitals are shown in black while additional π -orbitals formed by the conjugation of substituents to the ring are shown in red.

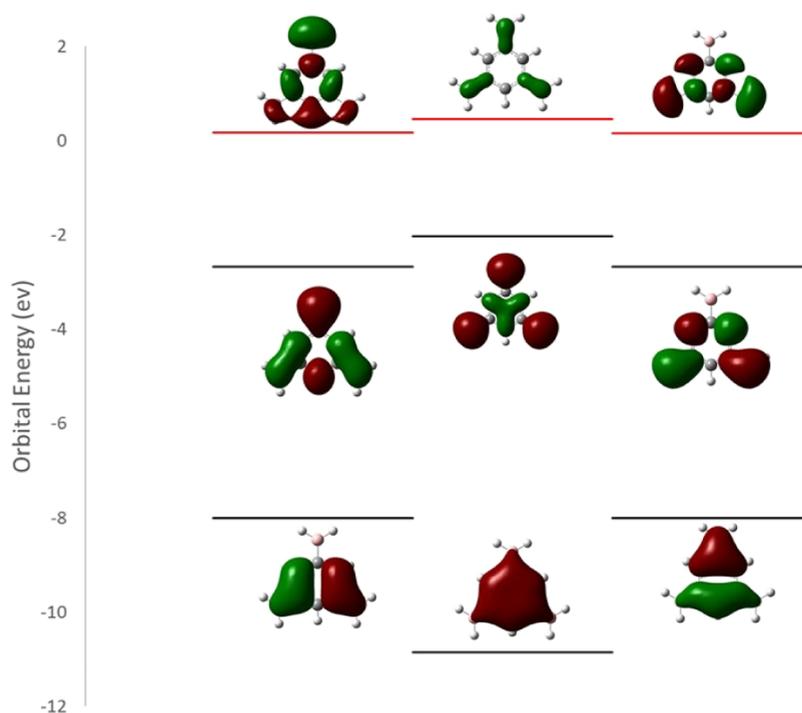


Figure 8. π -system molecular orbitals for 1,3,5-triborylbenzene (highest six orbitals are unoccupied). Conventional aromatic orbitals are shown in black, while additional π -orbitals are formed by the conjugation of substituents to the ring are shown in red.

(see Figure 5 below). While the substitution of the six fluorine atoms onto the benzene lowered the energies of the occupied aromatic orbitals and had little effect on the band gap, the introduction of other halogens to the same positions increases the energy of the occupied π -orbitals and significantly reduces the band gap (Figure 6). Additionally, the energies of the new π -orbitals generated by the larger halogens are significantly higher than those generated by fluorine atoms, to the point that their energies begin to surpass those of the originally occupied orbitals by the time we reach iodine.

Boron. As a negative test of our hypothesis, we modeled 1,3,5-triborylbenzene (terminated with hydrogen atoms) and compared the π -molecular orbital system to those of benzene and of 1,3,5-trifluorobenzene (see Figure 7 below). The empty p-orbital on each sp^3 hybridized boron atom on 1,3,5-triborylbenzene conjugates to the ring in a similar way to the way fluorine conjugates to the ring in 1,3,5-trifluorobenzene with the exception that because the p-orbitals from the boron are empty, virtual orbitals, they conjugate with the aromatic π -system to form unoccupied orbitals higher in energy than the three unoccupied aromatic orbitals (see Figure 8).

These additional orbitals push the conventional unoccupied orbitals down in energy reducing the band gap. The occupied aromatic orbitals are also slightly lowered in energy such that the highest occupied π -bonding orbital is not the highest occupied molecular orbital (HOMO) of the molecule but rather than HOMO – 2 as two occupied sigma orbitals now lie between the highest occupied π -orbital and the lowest unoccupied molecular orbital, which is the lowest unoccupied orbital in the π -system.

This also produces the opposite effect on the ring geometry from what we saw in 1,3,5-trifluoropyridine. The conjugation of the empty boron p-orbitals to the π -system of the ring pulls electron density out of the π -bonding orbitals in the ring

reducing the stability of the ring and increasing the average carbon–carbon bond length to 1.405 Å.

CONCLUSIONS

The examination of the π -systems on fluoroaromatic molecules and the effect that they have on the structure and aromatic behavior of the ring have shown that fluorine substituent atoms have a special effect on aromaticity compared to other halogens. This effect stems from fluorine's unique ability to draw out electron density through its sigma bonding orbitals and then donate some of it back into the ring through the interaction of its nonbonding electrons with the π -system of the ring. This π -system interaction generates a new set of π -orbitals that mimic the original aromatic system but at lower energy and with π -bonding between the ring and the fluorine atoms as opposed to the antibonding seen between fluorine and the original π -system. A special case of this is when three fluorine atoms are placed symmetrically around the ring at every other carbon atom. This generates three new π -orbitals that are lower energy mimics of the three occupied aromatic π -orbitals that are of the bonding character both between the ring and the fluorine atoms and around the ring creating a smaller tighter and arguably more “aromatic” molecule, as demonstrated by its increased activation energy of hydrogenation.

We refer to this effect as “fluoromaticity”. We believe it gives a theoretical explanation to the desirable thermodynamic and chemical resistance properties that are found in polymers that have fluoroaromatics as part of their architecture. Undergraduate institutions would be well served in adding a discussion of this effect to their undergraduate organic curriculum.

■ COMPUTATIONAL METHODS

All models for this work were computed using the Gaussian 09 suite of programs, including use of Gaussview 5 to generate three-dimensional figures.^{46,47} Each molecule to be modeled was constructed in the Arguslab⁴⁸ environment and had its geometry optimized first with molecular mechanics and then with the PM3 semiempirical method. These structures were then used as starting structures for optimization using the B3LYP density functional and the AUG-cc-pVTZ basis set for all atoms except iodine, for which the MidiX basis set was used. Augmented basis sets allow for a more accurate treatment of long-range interactions like those seen in extensively conjugated systems. The B3LYP/AUG-cc-pVTZ model chemistry has been used extensively in recent years to model the aromaticity and its causes.^{49–58} Geometries optimized with DFT were verified with frequency analysis at the same level of theory as the optimization to assure no imaginary vibrational frequencies. Orbital population analysis was also conducted at the same level of theory.

In computing the activation energies of hydrogenation for benzene, 1,3,5-trifluorobenzene, and hexafluorobenzene, transition states were modeled using the synchronous transit-guided quasi-Newton (STQN) method⁵⁹ to find the transition state between the previously optimized structures of the product of hydrogenation and the reactants. These three molecules were chosen as representative cases because of their high symmetry and difference in number of fluorine atoms. Each transition state model was then treated with frequency analysis to assure there was exactly one imaginary frequency and that imaginary frequency corresponded to movement between the two intermediates. After this, lower energy conformations for each of the reactants and products were discovered by performing an intrinsic reaction coordinate⁶⁰ analysis on the transition state model structures at the same level of theory as the other models were performed. Initially, hydrogenation across one double bond, leading to the 1,3-cyclohexadiene product was assumed. However, the addition of the two atoms from H₂ across the ring at sites para to one another, following the geometry of the Birch reduction^{61–67} yielded much lower activation energies, so those will be reported in this paper.

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Notes

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