

DFT Study of the effects of counter ions on bonding, molecular and spectral properties of pentafluorophenyl xenonium difluoride cation

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Abstract. The structures and properties of pentafluorophenyl xenonium difluoride cation (PFF) have been studied in their salts with 12 different counter ions using DFT calculations. The results demonstrated the huge effect of counter ion on all properties. The hybridization values, obtained from the NBO calculations, showed that xenon mostly used pure p orbital in their bonds, especially in Xe-F bond. Calculated binding energies (ΔH_b) and ΔG_b) indicated that the best anions for PFF are OH^- , F^- , BH_4^- and OAc^- . Moreover, the variations of HOMO and LUMO energies and the reactivity parameters have been investigated for all structures. The results of QTAIM calculations confirmed the covalent nature of Xe-C bond and the electrostatic nature of other xenon bonds. Finally, IR frequencies, NMR chemical shifts and NMR coupling constants were calculated to examine the effect of counter ion on the spectral properties of studied structures.

Keywords. Organoxenon; DFT; counter ion; xenonium difluoride; bonding.

1. Introduction

Despite the opinion of pioneer chemists about the unreactivity of noble gases, since 1962¹ (based on the report of Bartlett), it has been accepted that they could react and make stable molecules. After the first synthesis of a compound from the noble gas, a large number of chemists have been interested on this subject and many studies have been performed on the experimental and theoretical investigation of noble gas compounds.^{2,3} Among various noble gases, less attention has been made on the first two noble gases, helium and neon and some studies have been focused on the chemistry of argon^{4–6} and krypton.^{7–10} Since preparation, isolation and study of noble gas compounds are difficult, theoretical methods have been mostly used to anticipate the bonding,^{11,12} formation¹³ and properties^{14,15} of these compounds. Some investigations have been focused on the theoretical study of all noble gases without considering a special noble gas.^{16–23} However, xenon-containing molecules have been mostly studied using theoretical and experimental methods because xenon has more reactivity than the other noble gases and its compounds are more stable than compounds of other noble gases.²⁴ Theoretical studies have also been of interest because many aspects of these materials can-

not be studied by experimental tools. Therefore, some reports have been published on the theoretical study of HXeOX ,²⁵ XeH_2 ,²⁶ xenon-nitrogen compounds,²⁷ HXeBr ,²⁸ and halogenated xenon cyanides.²⁹

Among various xenon compounds, organoxenons have been attracted more attentions after the preparation of the first organoxenon, pentafluorophenylxenon ($\text{C}_6\text{F}_5\text{Xe}^+$) salts by the reaction of $(\text{C}_6\text{F}_5)_3\text{B}$ with XeF_2 in 1989.^{30,31} In this category, some organoxenons have been prepared such as diarylxenon,³² polyfluoroalk-1-enylxenon salts ($\text{RCF}=\text{CRXe}^+$),^{33–35} trifluoropropynyl xenon (II) tetrafluoroborate ($\text{CF}_3\text{CCXe}.\text{BF}_4$)^{36,37} and $[\text{C}_6\text{F}_5\text{XeF}_2][\text{BF}_4]$, which has been fully investigated recently.³⁸ In addition, the preparation and reactivity of compounds containing a carbon-xenon bond have been reviewed by Frohn.³⁹ Contrary to the large number of experimental and theoretical studies on organoxenons,^{40–49} many potential molecules and their properties in this area are also unknown and research on the new organoxenon compounds seems to be interesting. One of them is the effect of counter ions on the stabilities and properties of organoxenon cations. Therefore, to pursue our recent studies on computational chemistry of chemical structures^{50–52} and study of noble gas compounds,⁵³ we have decided to focus on the bonding, spectral and molecular properties of new organoxenon compounds.

In this work, pentafluorophenyl xenonium difluoride ($\text{C}_6\text{F}_5\text{-XeF}_2^+$, PFF) cation and their salts with various

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counter ion have been selected to study their properties. This cation was similar to pentafluorophenylxenon cation ($C_6F_5Xe^+$),^{30,31} the first prepared organoxenon. Pentafluorophenyl xenonium could be prepared from XeF_2 while PFF could be prepared from XeF_4 and the preparation of this compound with BF_4^- as counter ion has been reported by Frohn.^{38,54} This compound could be considered as a potential organoxenon molecule in future. Therefore, the structures of PFF alone and in the presence of 12 different anions (F^- , Cl^- , Br^- , I^- , AsF_6^- , BF_4^- , BH_4^- , CH_3COO^- , CF_3COO^- , NO_3^- , OH^- , PF_6^-) have been optimized. Then, the bonding properties, structural parameters and vibrational frequencies of these molecules have been calculated. The atomic charges, hybridizations and second order perturbation energies of them were obtained using NBO calculations. Finally, AIM and NMR calculations were done to obtain their bonding properties and chemical shifts. The details of computations and the results are presented in the following sections.

2. Computational

Gaussian 09 program package⁵⁵ has been employed to perform all calculations. The calculations have been carried out using density functional theory by employing B3LYP method.^{56,57} The B3LYP method has been validated to give results similar to those of the more computationally expensive methods for molecular geometry and frequency calculations.^{58,59} In combination with this method, triple-zeta Dunning's correlation consistent basis set⁶⁰ augmented with diffuse function (aug-cc-pVTZ) was used for all atom except xenon and iodine. This basis set is usually used for high precision calculations and its redundant functions have been removed and rotated in order to increase computational efficiency.⁶¹ For xenon and iodine, 3-21G and LanL2DZ basis sets were employed because aug-cc-pVTZ basis set could not be used on the atoms in 5th row of periodic table. However, LanL2DZ basis set calculations produced odd results and very strange adsorption energies. Therefore, the results of calculations with LanL2DZ (for xenon and iodine) have not been considered in this manuscript and in all cases, 3-21G basis set has been employed for xenon and iodine. In addition, one series of single point calculations were performed using the same basis set at M062X method as a modern and more reliable DFT method and the results were employed in the calculation of bonding energies.

In each optimization process, the absence of imaginary frequency verified that structure was a true minimum. The results of frequency calculations were used

after applying an appropriate scaling factor (0.971 for the employed method).⁶² NMR chemical shifts were obtained from the Gauge-Independent Atomic Orbital (GIAO) method.⁶³ NBO analysis of all structures have been done using NBO⁶⁴ program as implemented in the Gaussian program package. NBO calculations are useful tools to calculate molecular properties such as atomic charges, atomic hybridizations and the interactions between orbitals (second-order perturbation energies) with high precision. QTAIM analyses were performed using AIM2000 program.⁶⁵ Finally, the chemical potentials (μ), chemical hardnesses (η), global softnesses (S) and electrophilicity indexes (ω) of all compounds have been calculated as defined in equations 1–4 according to Koopman's theorem.^{66,67}

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad (1)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (2)$$

$$S = 1/\eta \quad (3)$$

$$\omega = \mu^2/2\eta \quad (4)$$

3. Results and Discussions

3.1 Structural parameters and dipole moments

All structures have been optimized to extract their parameters and used in subsequent calculations. It should be mentioned that the structural study of these molecules is an important topic in chemistry, where the cation is fixed and the anion is changed to study the effect of anion on its structure.

In this report, the only structural parameters (other data to be discussed in subsequent sections) consisting of xenon atom have been reported. It is accepted that by changing the anion from fluoride to iodide, the shape of the crystal, symmetry group, density, electrostatic interactions, hydrogen bonding, melting point, color, solubility and many other specifications of salts could be changed. The optimized structures of all PFF-anions are depicted in figure 1, the most important structural parameters of all molecules are listed in table 1 and the general numbering scheme for all structures are shown in figure 2. In table 1, the experimental values of PFF- BF_4 that have also been reported³⁸ that showed small differences with our calculated values.

Xenon is connected to two fluorine atoms in cation (PFF). The deviated T-shape of PFF- XeF_2 have been proven by previous reports.^{38,54} The lengths of these

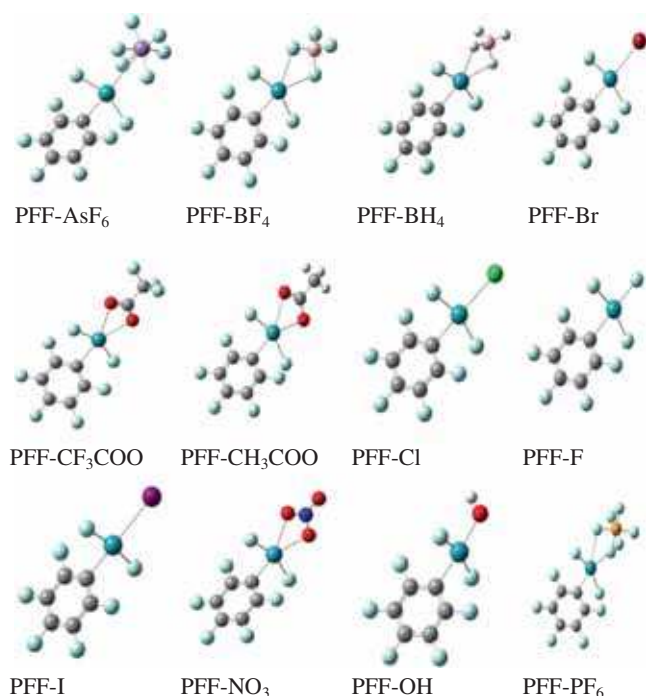


Figure 1. Graphical representation of optimized structures of all molecules.

two bonds in each molecule except PFF-OH and PFF-PF₆ are the same. In PFF-PF₆, the difference was small (only 0.003 Å) while in PFF-OH, the Xe-F bond, which was closer to OH group, was 0.066 Å smaller than the other Xe-F bond, probably because of a weak intramolecular hydrogen bonding. More importantly, the lengths of Xe-F bonds were affected by

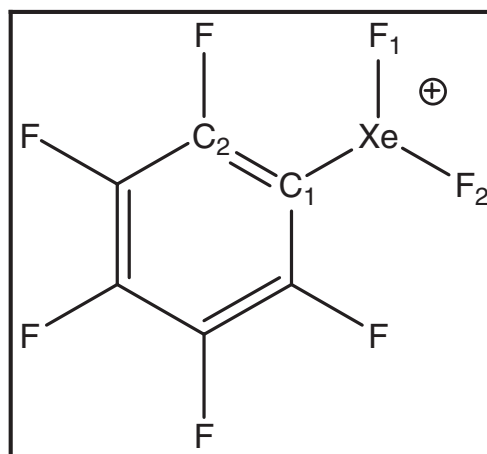


Figure 2. The numbering scheme for all structures.

the anion and their values lied between 1.982–2.118 Å. The length of Xe-F bond in PFF alone (1.944 Å) is smaller than that in all molecules, showing that the interaction of xenon with anion was a motive to decrease the strength and increase the length of Xe-F bonds. The order of Xe-F bond lengths in various counter ions in these molecules was found to be: F⁻ > CH₃COO⁻ > CF₃COO⁻ > BF₄⁻ > AsF₆⁻, PF₆⁻ > BH₄⁻ > I⁻ > NO₃⁻ > OH⁻ > Br⁻ > Cl⁻. This order has direct relation to the strength of the interaction between PFF and counter ion. These variations showed that different anions have different interactions with PFF and the amount of these interactions are related to the electronic and spatial effects of counter ion. The first rank of fluoride showed the strongest interaction

Table 1. Optimized structural parameters and dipole moments for all structures. Bond lengths (R) are in Å and bond angles (A) and dihedral angles (D) are in degrees.

	Xe-F1	Xe-F2	Xe-C1	Xe-A ^a	Xe-A ^b	F1-Xe-F2	F1-Xe-C1	C1-Xe-F2	F1-Xe-C1-C2	dipole
PFF	1.944	1.944	1.973	–	–	176.6	88.3	88.3	79.0	2.16
PFF-AsF ₆	2.064	2.064	2.128	2.568	3.486	154.1	77.0	77.1	52.1	10.28
PFF-BF ₄	2.071	2.071	2.138	2.522	3.203	153.7	76.9	76.8	51.0	9.92
PFF-BF ₄ (exp) ^c	1.948	1.925	2.058	2.937	3.073	170.2	84.0	86.3	–	–
PFF-BH ₄	2.004	2.004	2.060	2.185	2.655	160.2	80.1	80.1	90.2	4.45
PFF-Br	1.968	1.968	2.147	2.948	2.948	161.0	80.5	80.5	52.3	5.11
PFF-CF ₃ COO	2.078	2.078	2.192	2.575	2.915	153.2	76.6	76.6	50.5	4.44
PFF-CH ₃ COO	2.099	2.099	2.206	2.519	2.897	151.6	75.8	75.8	52.1	0.81
PFF-Cl	1.963	1.963	2.125	2.830	2.830	159.9	80.0	80.0	52.8	5.89
PFF-F	2.118	2.118	2.214	2.163	2.163	164.5	82.3	82.3	62.3	3.80
PFF-I	1.999	1.999	2.086	3.063	3.063	169.0	84.5	84.5	78.4	4.49
PFF-NO ₃	1.992	1.992	2.027	2.484	2.920	157.9	79.0	79.0	79.4	6.16
PFF-OH	1.982	2.048	2.075	2.097	2.097	163.4	80.0	73.5	77.7	1.87
PFF-PF ₆	2.064	2.067	2.127	2.586	3.440	154.0	77.1	77.0	52.8	10.66

^a The distance to the Closest atom of anion

^b The distance to the central atom of anion

^c According to reference ³⁸

between PFF and counter ion and it could be related to the highest electronegativity of fluorine; while the chloride (also has high electronegativity) had the weakest interaction with PFF. This showed that electrostatic interactions were not the sole interaction between ions and other possibilities such as polarizability (of electron clouds) and the size of anion should be considered. The order of Xe-C1 bond length, despite some similarity with that for the Xe-F bond, showed some differences, thereby confirming the complexity of the nature of these interactions. This order of Xe-C bond was found to be: $F^- > CH_3COO^- > CF_3COO^- > Br^- > BF_4^- > AsF_6^- > PF_6^- > Cl^- > I^- > OH^- > BH_4^- > NO_3^-$. This order is more logical because the Xe-C bond was placed exactly in the opposite side of the counter ion. In the next column, the distances between xenon and the closest atom of anion (Xe-A) and the central atom of anion (Xe-A) were reported. These values are mostly dependent on the size of counter ion. The largest Xe-A value belonged to PFF-I and the largest Xe—A values were related to PFF-AsF₆ and PFF-PF₆. In bond angles (columns 7–9), the values of F1-Xe-F2, C1-Xe-F and C1-Xe-F2 angles tended to be smaller in salts versus the PFF alone because of the existence of counter ions and the value of this difference were directly related to the size of counter ion. The F1-Xe-C1-C2 dihedral angle showed the amount of deviation from the planar structure of PFF. These values for PFF are equal to 79.0 degrees and in salts, they are between 50.0–90.2 degrees. Therefore, by changing the counter ion, the interaction of Xe-F bonds with benzene ring and related dihedral angle will be changed.

In the last column, the dipole moment of the molecules (in Debye) was reported. Since the large positive bar (2.136, according to table 2) was placed on xenon atom, the dipole moment of PFF was directed toward the benzene ring. Therefore, when the electronegativity of the counter ion increases, it attracted the electron density from the ring and decreases the dipole moment (PFF-OH: 1.87, PFF-OAc: 0.81). However, when the anion consisted of many electronegative atoms (PF₆⁻ and AsF₆⁻), the high dipole moment toward the anion could be observed. This means that the directions of dipole moments in different molecules are not the same.

3.2 NBO analyses

Atomic charges and hybridizations, obtained from the NBO calculations, are listed in table 2. The values of xenon positive charges were decreased in salts versus the cation. It seems that the amount of this decrease

was directly related to the softness of the anion and inversely related to its electronegativity. The smallest xenon charges were respectively related to PFF-I, PFF-CH₃COO, PFF-CF₃COO and PFF-Br while the highest xenon positive charges belonged to PFF-OH and PFF-NO₃. A different relation could be observed in the charges of fluorine atoms connected to the xenon. The maximum negative charges on fluorines belonged to PFF-BH₄, PFF-NO₃, PFF-I and PFF-OH.

Many factors should be considered to explain these charges. In the fifth column of the data, the net charges of the anions did not exceed -0.867 and in many cases, these charges were less than -0.685 . These values demonstrated that a sizable amount of the electron density of anion sank toward PFF cation. This electron transfer obviously has direct effect on the properties of the cation. The other proof for this claim is related to changing the hybridization of xenon atom in its bond with C1 in different molecules (columns 6,7). It should be first explained that our calculations confirmed that xenon mostly used its p orbital (without hybridization) in the bond with fluorine atoms (99.82–100 percent of its orbitals in Xe-F bonds were pure p orbital). Therefore, xenon only used hybridized orbitals in bonding with C1. The value of p orbital percentage that xenon atom used in Xe-C1 bonds varied from 82.17% (in PFF) to 97.19% (in PFF-F). In PFF cation, xenon was mostly hybridized because it lost one electron and tended to make a more effective bond. These values will be confirmed by the Xe-C1 bond lengths. According to our data, the least value (and the most bond strength) belonged to PFF cation. In other molecules (PFF and anion), the p orbital percentages were larger than 90.27%. The highest p orbital percentages belonged to PFF-F and PFF-OH, which consisted of the most electron-withdrawing anions. Since the increase of p orbital contribution was related to the decrease of the bond strength, it could be concluded that electron-withdrawing anions made the Xe-C bond weaker because this bond was placed in the opposite side of Xe-anion connection.

3.3 Energies and stabilities

It is important to obtain energy and stability information, especially when we encounter noble gas molecules. In this line, the effect of counter ion on the stability of salts seems to be important. Table 3 shows calculated binding energies (in kcal/mol) between PFF and various anions obtained from both B3LYP and M062X methods using 3-21G basis set for xenon and iodine and aug-cc-pVTZ basis set for other atoms. The

Table 2. Atomic charges (in atomic units) and hybridizations (in percent) obtained from NBO calculations.

charges	Atomic charges					Hybridizations ^a	
	Xe	F1	F2	C1	A	Xe in Xe-C1	Xe in Xe-F
PFF	2.136	-0.588	-0.588	-0.432		82.17	
PFF-AsF ₆	2.062	-0.560	-0.560	-0.290	-0.865	90.41	99.82
PFF-BF ₄	2.045	-0.562	-0.562	-0.293	-0.829	91.18	99.84
PFF-BH ₄	2.050	-0.620	-0.620	-0.391	-0.578	93.62	
PFF-Br	1.982	-0.604	-0.604	-0.357	-0.538	92.38	
PFF-CF ₃ COO	1.936	-0.580	-0.580	-0.279	-0.632	93.23	99.82
PFF-CH ₃ COO	1.920	-0.593	-0.593	-0.278	-0.547	94.51	99.83
PFF-Cl	2.035	-0.603	-0.603	-0.363	-0.605	91.91	
PFF-F	2.010	-0.567	-0.567	-0.333	-0.652	97.19	99.87
PFF-I	1.911	-0.614	-0.614	-0.424	-0.409	92.26	
PFF-NO ₃	2.130	-0.619	-0.619	-0.401	-0.685	90.57	
PFF-OH	2.135	-0.612	-0.648	-0.433	-0.566	96.17	
PFF-PF ₆	2.059	-0.559	-0.558	-0.289	-0.867	90.27	99.82

^aHybridizations were expressed by the percent of p orbital in the defined bond

results of both methods are similar and only M062X bonding energies have tended to be more positive (between 2–8 kcal/mol). Both heats of binding (ΔH_b) and Gibbs free energies of binding (ΔG_b) at standard conditions were calculated for all the molecules. Except in PFF-I, all binding energies are negative by large amounts. These values showed that counter anion made organoxenon molecules more stable (except iodide). They also proposed that in terms of interaction energies, the best anions for PFF were OH⁻, F⁻, BH₄⁻, OAc⁻, Cl⁻, Br⁻, NO₃⁻, CF₃COO⁻, BF₄⁻, PF₆⁻, AsF₆⁻ and I⁻, respectively. It is obvious that by increasing electronegativity and decreasing the size of the anion, its stabilizing effect on PFF will be increased. Therefore, it could be concluded that the electron-withdrawing

anions attract the extra electron density placed on xenon atom and stabilize it while large anions increase the electron repulsion and destabilize PFF.

The other important energy entries are frontier molecular orbitals (FMOs, i.e., HOMO and LUMO) energies. The shapes of these orbitals are shown in figure 3. The HOMO and LUMO energy values could be related to the reactivity parameters, softness and hardness. Therefore, HOMO and LUMO energies, the energy gaps (E_g), chemical potentials (μ), chemical hardnesses (η), global softnesses (S) and electrophilicity indexes (ω) have been calculated and the results are listed in table 4. Because of the cationic nature of PFF, it was expected that the HOMO and LUMO energies of PFF would be lower than those in all neutral molecules,

Table 3. Calculated binding energies between PFF and various anions defined by heats of binding (ΔH_b) and Gibbs free energies of binding (ΔG_b , both in kcal/mol) at standard condition using 3-21G basis set for xenon and iodine and aug-cc-pVTZ basis set for other atoms.

Molecule	B3LYP calculations		M062X calculations	
	ΔH_b^a	ΔG_b^b	ΔH_b^a	ΔG_b^b
PFF-AsF ₆	-80.60	-68.89	-78.62	-66.81
PFF-BF ₄	-91.46	-80.50	-86.40	-75.55
PFF-BH ₄	-132.32	-124.44	-124.26	-116.30
PFF-Br	-124.28	-116.23	-120.41	-112.46
PFF-CF ₃ COO	-109.44	-96.90	-106.32	-93.68
PFF-CH ₃ COO	-134.33	-120.66	-128.78	-115.20
PFF-Cl	-127.61	-119.22	-122.98	-114.49
PFF-F	-150.06	-142.21	-142.56	-134.78
PFF-I	205.46	211.61	213.20	218.54
PFF-NO ₃	-126.98	-115.95	-121.23	-110.31
PFF-OH	-177.27	-168.56	-168.22	-159.62
PFF-PF ₆	-80.81	-69.71	-77.84	-66.84

^a $\Delta H_b = H(\text{PFF-Anion}) - H(\text{PFF}) - H(\text{anion})$

^b $\Delta G_b = G(\text{PFF-Anion}) - G(\text{PFF}) - G(\text{anion})$

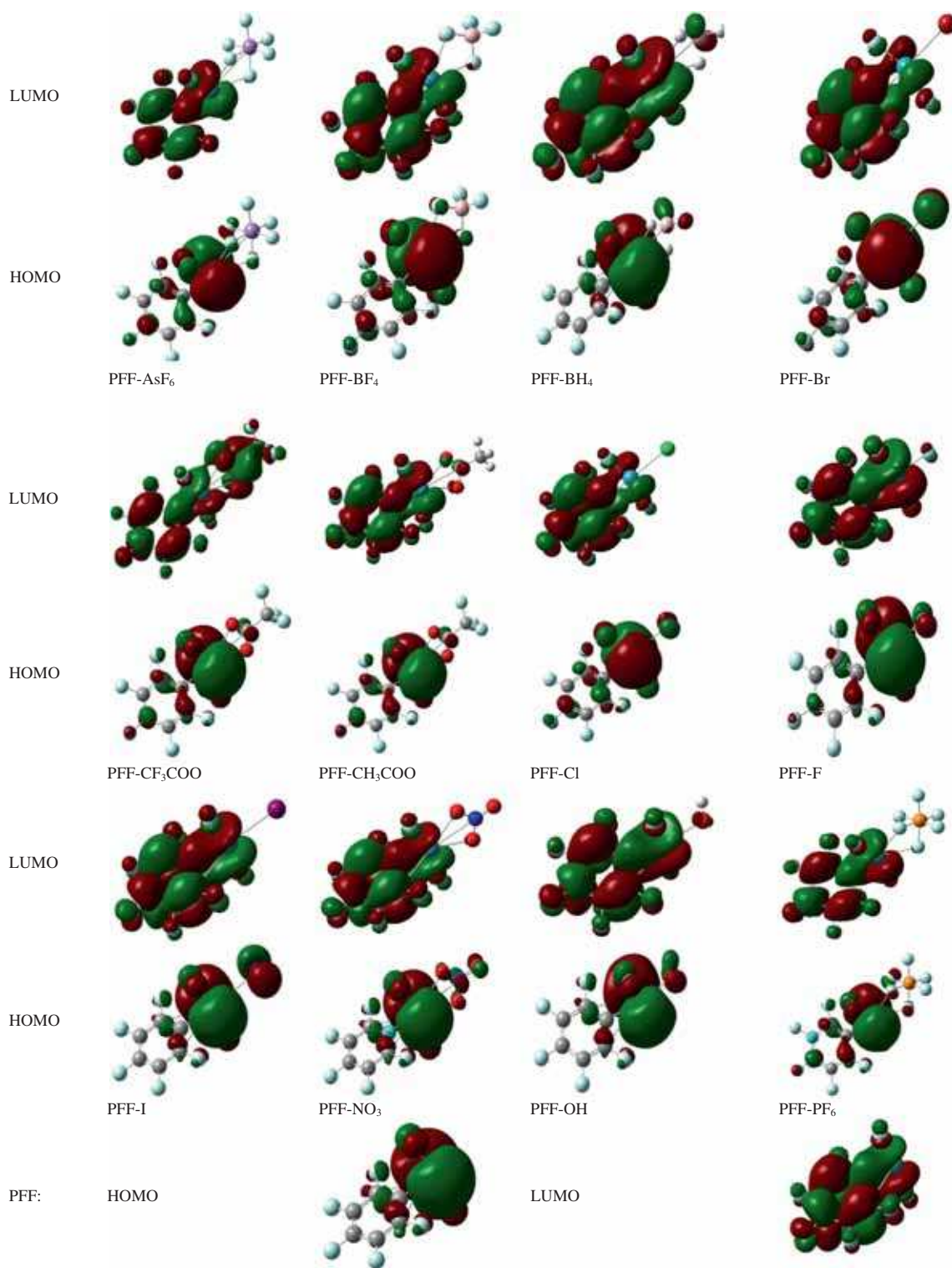


Figure 3. The graphical representation of HOMO and LUMO for all molecules.

but its energy gap was placed almost in the middle of E_g for other molecules. Moreover, fluorine-containing substituents (F, CF_3COO , BF_4 , AsF_6 and PF_6) obviously decreased the HOMO energy. This decrease was followed by decrease in LUMO energy and therefore, no specific change in E_g could be observed. In other

columns, chemical potentials, softness, hardness and electrophilicity indexes show changes with variation of the counter ion. The chemical potentials of fluorine-containing anions have the smallest values (the highest absolute values) while PPF-I had the highest chemical potential (-0.206). Moreover, softness and hardness

Table 4. The energies of HOMO, LUMO, band gap (E_g) and reactivity parameters from population analyses.

	LUMO	HOMO	E_g	μ	H	S	ω
PFF	-0.318	-0.456	0.138	-0.387	0.069	14.491	5.18E-03
PFF-AsF ₆	-0.216	-0.341	0.124	-0.278	0.062	16.069	2.41E-03
PFF-BF ₄	-0.215	-0.338	0.124	-0.277	0.062	16.172	2.37E-03
PFF-BH ₄	-0.156	-0.308	0.152	-0.232	0.076	13.158	2.05E-03
PFF-Br	-0.163	-0.272	0.109	-0.218	0.054	18.350	1.29E-03
PFF-CF ₃ COO	-0.192	-0.319	0.127	-0.256	0.063	15.769	2.07E-03
PFF-CH ₃ COO	-0.173	-0.304	0.131	-0.238	0.065	15.298	1.85E-03
PFF-Cl	-0.164	-0.283	0.118	-0.223	0.059	16.929	1.48E-03
PFF-F	-0.205	-0.320	0.115	-0.262	0.058	17.370	1.98E-03
PFF-I	-0.163	-0.250	0.087	-0.206	0.044	22.885	9.30E-04
PFF-NO ₃	-0.154	-0.306	0.152	-0.230	0.076	13.160	2.02E-03
PFF-OH	-0.144	-0.299	0.155	-0.221	0.078	12.891	1.90E-03
PFF-PF ₆	-0.219	-0.342	0.123	-0.281	0.062	16.256	2.42E-03

All parameters (except S) have been reported in eV. S values are in eV⁻¹

are directly related to the size of the anion. For example, PFF-I had the minimum hardness and the maximum softness while PFF-OH had maximum hardness and minimum softness. In the last column, the order of electrophilicity indexes by various anions is shown as, $PF_6^- > AsF_6^- > BF_4^- > CF_3COO^- > BH_4^- > NO_3^- > F^- > OH^- > OAc^- > Cl^- > Br^- > I^-$, showing the special effect of fluorine-containing anions on the electrophilicity indexes of molecules. All of these values demonstrated that counter ions changed the reactivity parameters of molecules. In this line, fluorine-containing anions and electron-withdrawing anions have more intense effects.

3.4 Bonding properties from the QTAIM

QTAIM analysis is a valuable tool to define the quality and quantity of inter- and intramolecular bonding interactions. In table 5, the ρ (electronic density in e³/a₀³) and the Laplacian of ρ (in e/a₀⁵) at the bond critical points (BCPs) have been listed for Xe-C1, Xe-F1, Xe-F2 and Xe-anion interactions.

Because of the large electron density placed on xenon atom, all ρ values are large for the Xe-C1, Xe-F1 and Xe-F2 bonds. For Xe-C1 bond (columns 2–4), ρ values are placed between 0.117–0.160 for salts and 0.170 for PFF. It was found that the counter ion decreased the electron density of the Xe-C1 bond. The smallest ρ values were observed for fluoride and acetate anions. The ρ values in Xe-F1 and X3-F2 (columns 5 and 8) were almost the same and generally smaller than those in Xe-C1 bonds. These values are in the range of 0.0995–0.131 for salts and 0.137 for PFF. In addition, in these bonds, the minimum ρ value was observed in fluoride and acetate anions. All ρ values confirmed that electron-withdrawing anions

attract the electron density of xenon and reduced the corresponding ρ values. The ρ values between PFF and different anions (the second part of table 5) are between 0.036 (in PFF-AsF₆) and 0.113 (in PFF-OH). The order of ρ values between PFF and different anions is $OH^- > F^- > BH_4^- > NO_3^- > OAc^- > CF_3COO^- > PF_6^- > Cl^- > Br^- > BF_4^- > I^- > AsF_6^-$. This order confirmed the tendency of electron density towards more electron-withdrawing groups. The next parameter, Laplacian of ρ ($L(\rho) = -1/42 \nabla^2 \rho$), showed the nature of each bond between two atoms.

The Laplacian of ρ is positive for Xe-C1 bond and negative for Xe-F1, Xe-F2 and Xe-A bonds. This means that Xe-C1 is a covalent bond while Xe-F1, Xe-F2 and Xe-A are non-covalent and they have closed shell or electrostatic interaction in their bonds. These observations confirmed the NBO results regarding the electrostatic nature of Xe-F bonds. Moreover, the value of Laplacian of ρ in PFF is larger than those in other molecules. The least absolute values of Laplacian of ρ have been observed in electron-withdrawing and fluorine-containing anions.

3.5 Harmonic vibrations

The harmonic vibrational modes for all molecules were calculated using frequency calculations. The results for Xe-F (symmetric and asymmetric), Xe-C1 and Xe-A stretching vibrations are listed in table 6 in addition to the reported experimental values³⁸ for PFF-BF₄. These experimental values are in agreement with our data showing the reliability of our calculated frequencies. From the data listed in this table, it was found that PFF has the maximum value in each entry of frequency tables, showing that all these bonds in PFF were stronger than those in other molecules. The

Table 5. The electron densities (ρ) and the Laplacian of the electron densities ($L(\rho) = -1/4\nabla^2\rho$) obtained from AIM calculations.

	Xe-C1		Xe-F1		Xe-F2		Xe-A: CP1		Xe-A: CP2	
	ρ	$L(\rho)$	ρ	$L(\rho)$	ρ	$L(\rho)$	ρ	$L(\rho)$	ρ	$L(\rho)$
PFF	0.170	5.05E-02	0.137	-7.92E-02	0.137	-7.92E-02				
PFF-AsF ₆	0.135	3.28E-02	0.110	-5.07E-02	0.110	-5.07E-02	0.036	-3.33E-02	0.035	-3.28E-02
PFF-BF ₄	0.133	3.16E-02	0.109	-5.01E-02	0.109	-5.01E-02	0.040	-3.64E-02	0.040	-3.64E-02
PFF-BH ₄	0.151	3.07E-02	0.122	-6.46E-02	0.122	-6.47E-02	0.054	-2.08E-02	0.054	-2.09E-02
PFF-Br	0.130	2.14E-02	0.130	-7.26E-02	0.130	-7.25E-02	0.041	-1.70E-02		
PFF-CF ₃ CO ₂	0.122	2.19E-02	0.105	-4.97E-02	0.105	-4.97E-02	0.044	-3.01E-02	0.045	-3.02E-02
PFF-CH ₃ CO ₂	0.119	1.99E-02	0.103	-5.04E-02	0.103	-5.04E-02	0.051	-3.03E-02	0.050	-3.01E-02
PFF-Cl	0.136	2.55E-02	0.131	-7.35E-02	0.131	-7.35E-02	0.043	-2.09E-02		
PFF-F	0.117	1.72E-02	0.100	-4.72E-02	0.099	-4.72E-02	0.090	-6.06E-02		
PFF-I	0.142	2.13E-02	0.123	-6.60E-02	0.123	-6.61E-02	0.040	-1.47E-02		
PFF-NO ₃	0.160	3.93E-02	0.125	-6.67E-02	0.125	-6.67E-02	0.053	-3.49E-02	0.439	-1.72E-01
PFF-OH	0.147	2.35E-02	0.112	-6.29E-02	0.127	-6.67E-02	0.113	-4.91E-02		
PFF-PF ₆	0.136	3.27E-02	0.110	-4.97E-02	0.110	-4.93E-02	0.035	-3.24E-02	0.017	-1.75E-02

Table 6. Calculated harmonic vibrational frequencies (in cm⁻¹).

corrected	Xe-F1,2 (Asym)	Xe-F1,2 (Sym)	Xe-C1	Xe-A
PFF	571	516	829	
PFF-AsF ₆	372	366	739	96
PFF-BF ₄	401	360	736	128
PFF-BF ₄ (exp) ³⁸	535	530	789	127
PFF-BH ₄	519	447	808	159
PFF-Br	510	475	763	112
PFF-CF ₃ COO	384	347	717	186
PFF-CH ₃ COO	377	334	722	188
PFF-Cl	519	489	773	151
PFF-F	356	307	710	351
PFF-I	480	431	793	113
PFF-NO ₃	498	455	825	205
PFF-OH	494	430	813	451
PFF-PF ₆	386	368	735	98

values of Xe-F for asymmetric vibration were between 356–519 cm⁻¹ and for symmetric vibrations, they were between 307–489 cm⁻¹. Since many factors can affect the frequencies, no meaningful order could be observed for these vibrations. However, the least frequency value for both cases was related to PFF-F. It is demonstrated that by increasing the strength of interaction between PFF and the counter ion, the values of xenon-related stretching vibrations were decreased. In the next column, the Xe-C stretching modes were in the range of 717–825 cm⁻¹. These values are larger than the frequency of Xe-F bond because this bond is covalent in nature, unlike the electrostatic nature of Xe-F bond. Moreover, this frequency was useful for determining the existence of organoxenon compounds. Like Xe-F frequencies, no meaningful relation between Xe-C1 frequencies and the nature of counter ion could be observed.

The last frequency, Xe-A, was linked to the stretching between PFF cation and counter ion. The existence of this frequency proved the remarkable interaction between these ions and more importantly, the direct relation between the strength of this interaction and the value of stretching frequency between ions. We examined the linearity of this relation (between frequency and ΔH_b in all molecules except PFF-I) and a line ($\Delta H_b = -0.225 \times \nu(\text{PFF-A}) - 77.852$) with $R^2 = 0.727$ was observed. Therefore, this was not a linear relation, but it could be considered as a qualitative relation.

3.6 NMR chemical shifts

In the final part of this study, NMR chemical shifts (in ppm) and coupling constants (in Hz) were calculated for all the molecules. The results are listed in

table 7 and the experimental values⁵⁴ for PFF-BF₄ are also added to the table. We focused on ¹²⁹Xe, ¹⁹F (F1 and F2) and C1 chemical shifts in these calculations. The ¹²⁹Xe chemical shift is an interesting topic in NMR studies of xenon-containing molecules. Xenon chemical shifts were determined versus the chemical shift of XeOF₄ and fluorine chemical shifts were determined versus the chemical shift of CFCI₃. For ¹²⁹Xe and ¹³C chemical shifts and Xe-F coupling constants, the differences between experimental and theoretical values are small. However, for ¹⁹F chemical shifts, large differences were observed. The range of xenon chemical shifts was varied from 847 ppm in PFF-I to 2220 ppm in PFF-NO₃ and the chemical shift of xenon in PFF was placed in the middle of this range (1559 ppm). Oxygen-containing anions increased the xenon chemical shift evidently, while halogen-containing anions (including fluoride) decreased its chemical shift versus the PFF ($\delta = 1559$ ppm). It seems that the strong interaction between PFF and counter ion, like the interaction observed in fluoride and fluorine-containing substituents, increases the electron density around xenon and shields it in NMR experiment.

The shorter distance between xenon and these anions (table 1) is the other proof for this claim. Unlike the xenon chemical shifts, C1 chemical shifts in all molecules (between 129–152 ppm) are greater than those in PFF alone (118 ppm). The acceptable explanation for this difference is the fact that for xenon chemical shift, anion has two effects; one is inductive electron withdrawing effect to reduce the shielding and the other

is increasing electron density to increase the shielding. However, for C1 chemical shifts, the anion only had the inductive and deshielding effect on C1. Therefore, all electron-withdrawing anions (both oxygen and fluorine-containing anions) increased the chemical shift of C1. The fluorine chemical shifts (F1 and F2) had a large range, between –120 ppm and 117 ppm. The order of these variations for different molecules was Br[–] > Cl[–] > I[–] > NO₃[–] > BH₄[–] > OH[–] > CH₃COO[–] > CF₃COO[–] > F[–] > AsF₆[–] > PF₆[–] > BF₄[–]. This order was also interesting because fluorine- and oxygen-containing anions had the smallest chemical shift and halides (except fluorine) had the highest chemical shifts for F1 and F2. This observation was the same with xenon chemical shifts and therefore, the same argument could be assigned to explain it. In table 7, Xe-F1, Xe-F2, and Xe-C1 coupling constants are also reported.

Interestingly, despite the identical sign of the gyromagnetic ratios of ¹⁹F and ¹³C, Xe-F coupling constants are negative while Xe-C coupling constants are positive. Moreover, Xe-F coupling constants were greater than Xe-C coupling constants. These differences might arise from the different nature or strength of these two bonds. The values of J_{Xe-F} in fluorine containing anions were larger than those in other molecules. However, J_{Xe-C} values were greater in halide and smaller in fluorine containing anions. All of these observations could help us to investigate new organoxenon molecules. However, in addition to the value of xenon chemical shifts, Xe-F or Xe-C coupling constants can give us useful

Table 7. Calculated NMR chemical shifts for all structures.

	Chemical shifts versus reference ^a				Coupling constants ^b		
	Xe	C1	F1	F2	Xe-F1	Xe-F2	Xe-C1
PFF	1559	118	55	55	–2614	–2614	252
PFF-AsF ₆	1608	148	–114	–114	–3395	–3407	152
PFF-BF ₄	1844	148	–120	–120	–3338	–3336	163
PFF-BF ₄ (exp) ^c	1706	122	–29.5	–29.5	–3892	–3892	–
PFF-BH ₄	2040	130	19	19	–2731	–2732	347
PFFBr	1293	138	116	117	–2799	–2800	680
PFF-CF ₃ COO	2136	152	–104	–104	–3133	–3130	283
PFF-CH ₃ COO	2151	151	–99	–99	–3008	–3008	309
PFF-Cl	1270	137	106	106	–2802	–2803	579
PFF-F	1181	145	–110	–110	–3505	–3505	302
PFF-I	847	129	104	104	–2764	–2764	737
PFF-NO ₃	2220	131	22	22	–2538	–2538	290
PFF-OH	1676	131	–11	57	–2440	–3370	339
PFF-PF ₆	1614	149	–118	–115	–3430	–3413	153

^aThe reference molecule for ¹⁹F-NMR is CFCI₃ with chemical shift = 163.4 ppm and for ¹²⁹Xe NMR is XeOF₄ with chemical shift = 1633.8 ppm

^bGyromagnetic ratios: C = 6.73 F = 25.18 Xe = -7.4×10^7 rad/T.Sec

^c According to the reported values in reference⁵⁴

information regarding the nature of the molecule and their binding strength. They can also suggest the best counter ion for each purpose.

4. Conclusions

Novel organoxenon compounds are the subject of interest in both experimental and theoretical studies. Among these molecules, pentafluorophenyl xenonium difluoride ($C_6F_5-XeF_2^+$, PFF) was selected in this study and their molecular properties in presence of different counter ions have been examined. DFT calculations (B3LYP and M062X methods) with aug-cc-pVTZ basis set were used for this purpose. From the calculations, optimized structures, molecular parameters and binding energies between PFF and 12 different counter ions were extracted. The Xe-F and Xe-C bond lengths were different in different molecules. In addition, the molecular dipole moments were more sensitive to the counter ion. NBO calculations were used to investigate the charge and hybridization in these molecules. The hybridization values showed that pure p orbital of xenon mostly involved in the bonds, especially in Xe-F. The heats of binding (ΔH_b) and Gibbs free energies of binding (ΔG_b) at standard conditions were calculated for all molecules. The results indicated that in terms of interaction energies, the best anions for PFF were OH^- , F^- , BH_4^- , OAc^- , Cl^- , Br^- , NO_3^- , CF_3COO^- , BF_4^- , PF_6^- , AsF_6^- and I^- , respectively. Then the variation of HOMO and LUMO energies and the reactivity parameters versus different counter ions were examined. Further, bonding properties have been studied using QTAIM calculations and the results demonstrated the important difference in the electron densities of different salts. In addition, the sign of Laplacian of electron densities confirmed the covalent nature of Xe-C bond and the electrostatic nature of other xenon bonds. Finally, harmonic vibrations, NMR chemical shifts and NMR coupling constants have been calculated. These values could be used as useful tools to prove and examine the existence and nature of new organoxenon molecules.

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