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Theoretical Study of the Linear Short-Chain Phosphazene-Na^+ Complexes

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Abstract: In this work, we study simples phosphazenes models, such as R-$[R_2P=N]_n$-X, with (X = H, F, OH), (R= H, F) and (n = 1, 2 and 3) with an attempt to answer the type of Natural Hybrid Orbital (NHO) able to form this π-bond in the phosphazene-Na^+ complex and the Na^+ effect on the geometry and the electronic distribution of the studied molecules by using the HF and DFT studies of electronics, molecular structures and Natural Bond Orbital (NBO) analysis. The substituent effect of the fluorine atom acceptor and the OH group donor is studied. The phosphazene polymers doped by Na^+ cation, linearize all the PNP bond angles.

Keywords: Short-linear phosphazenes, Phosphazene-Na^+ complexes, HF, DFT and NBO analysis.

1. INTRODUCTION

Phosphazenes can be linear short-chain molecules, cyclic molecules or high molecular weight polymers. They possess special properties and play a predominant role in the inorganic chemistry [1, 2]. Several authors [3-5] have studied many types of polyphosphazenes. These polyphosphazenes are applied as biomaterials [6, 7], solid polymer electrolytes [8, 9], membranes [10-12], lubricants and fire-resistant materials [13-15]. Polyphosphazenes also a novel class of polymers that are potential candidates for bone tissue engineering due to their tailorability, biocompatibility and high osteo-compatibility [7].

Among the several bonding theories presented to explain the observed structural properties in cyclopolyphosphazenes, the d_π-p_π bonding model is the most widely adopted one [16, 17]. This model, developed simultaneously by Craig *et al.* [18] and by Dewar *et al.* [19] describes the P=N bonding in terms of σ and π-bonding arising from the overlap of 3d orbital of the phosphorus atom with the 2Pz orbital of the nitrogen one [17]. Allcock *et al.* [20] have elaborated and studied a series of short-chain linear phosphazenes. The structure of $OP(Cl_2)NP(Cl_2)NPCl_3$ displays a significant planarity of the phosphazene skeleton and corresponds to a *cis-trans* planar conformation [21].

Exhaustive experimental and theoretical studies carried out by many authors have been recently reported on the Li^+, Na^+ and K^+ interaction with some organic compounds [22, 23]. It has been shown that in polyphosphazenes membranes, nitrogen atoms interact more strongly with lithium ions than oxygen's do [24]. The abundant Na^+ cation participate in many functions of living systems [25, 26]. Because of its low tendency to form covalent bond, this letter should be considered as a nonspecific binder in many organic compound-Na^+ complexes [22]. The polyphosphazenes form a significant class in the production of the biomaterials. The understanding of the mechanisms of ionic and molecular transport in polymer electrolyte phases is crucial for the development of improved powder sources. Because of the strongly polarized PN bond, it is of significant interest to investigate their electronic and structural behavior in presence of the Na^+ cation.

The aim of this work is an attempt to investigate the nature of Natural Hybrid Orbital (NHO) that may form this π-bond in the phosphazene-Na^+ complex, the Na^+ effect on the geometry and the electronic distribution of the studied molecules and the type of coordination established by Na^+ in the phosphazene-Na^+ complex, using the HF and DFT studies of electronics, molecular structures and Natural Bond Orbital analysis (NBO) [22]. The NBO analysis of Weinhold [22, 27-28] quantifies the electron delocalization in terms of intra-molecular donor-acceptor interactions.

2. COMPUTATIONAL DETAILS

The calculations discussed in this work have been done at the Hartree-Fock (HF), post-HF (MP2) and DFT/B3LYP levels using a standard Gaussian 03 program package [29] with 6-31G* and 6-311++G** basis sets. The computations are carried out at the DFT level [30-32] using the hybrid method B3LYP which includes a mixture of HF exchange with DFT exchange correlation. Becke's three parameters functional where the non local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used and this is implemented in Gaussian 03.

The geometries of all the systems were optimized using Berny algorithm [33] within higher accuracy (keyword opt=

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tight). A vibrational analysis has been performed on the HF and DFT/B3LYP optimized structures using the same basis sets. The results, obtained from this analysis, characterized all of the optimized structures as minima on the potential energy surfaces without any negative mode.

The NBO analysis was carried out with 3.1 version [34] that is included in Gaussian 03W program at the HF/6-31+G* level. In the NBO analysis [27, 34], the electronic wave functions are interpreted, in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. NBOs correspond to the picture of localized bonds and lone pairs as basic units of molecular structure. The interactions due to electron delocalization are generally analyzed by selecting a number of bonding and anti bonding NBOs, namely, those relevant to the analysis of donor and acceptor properties. This delocalization of electron density between occupied Lewis-orbital (bond or lone pair) and non-Lewis unoccupied (anti bonding or Rydberg) orbital, corresponds to a stabilizing donor-acceptor interaction. The evaluation of their energies is given by the second-order perturbation theory. For each donor NBO (i) and acceptor (j), the stabilization energy, $E^{(2)}$, associated with $i \rightarrow j$ delocalization, is estimated by the following equation:

$$E^{(2)} = \Delta E_{ij} = q_i * F^2(i,j) /(\varepsilon_i - \varepsilon_j)$$

Where q_i is the ith donor orbital occupancy, ε_i, ε_j are the diagonal elements (orbital energies) and F(i, j) of-diagonal elements respectively, associated with NBO Fock matrix.

3. RESULTS AND DISCUSSIONS

3-1 Substituent Effect in $R[R_2P=N]_1$-X with (R=H, F) and (X=H, F and OH)

The influence of substituents on the P-N interaction have been estimated to be true calculations performed on the H_3PNX and F_3PNX (X= H, F and OH) short phosphazene molecules.

3-1-a Geometry

The obtained results on the optimal geometries of the systems under study, at B3LYP/6-31G*(6-311++G**) and HF levels with the same basis sets, are illustrated in Fig. (**1**).

The PN bond length in H_3PNH is 1.571 Å at B3LYP/ 6-311++G** and 1.546 Å at HF/6-311++G*. This bond is shorter than the one in the NH_2-PO_3^{2-} ion (1.77 Å), which corresponds to a simple PN bond [35] and that of the $O=P(Cl)_2$-$N=P(Cl)_3$ (1.580 Å), attributed to a double P=N bond determined by the X-ray diffraction [36] respectively. When we substitute the hydrogen atom linked to the nitrogen one by OH and F, the P-N bond length increases to 1.606 and to 1.626 Å respectively in the H_3PNOH molecules, from the same theoretical point of view. Similar conclusions are drawn at all other theoretical levels with the same basis sets (see Fig. **1**). These bond lengths are in a good agreement whit those obtained by X-ray diffraction in the $Ph_3P=NMe$ (1.641 Å) molecule [37]. The HF level which does not take into account the electronic correlation, underestimates this bond length as compared to DFT level. This P=N bond length depends strongly on the substituent groups linked to the phosphorus atom. The P=N bond length obtained by X-ray diffraction data in $Ph_3P=NMe$ and in $O=P(Cl)_2$-$N=P(Cl)_3$ are of 1.641 [36], 1.58 Å respectively [36]. The same type P=N bond length in the H_2PN compounds is equal to 1.499 Å at the HF/6-31G* level for a singlet species [38].

The obtained results at the MP2//6-31G* level agree with those of B3LYP/6-31G* with errors varying between 0.002 and 0.039 Å.

H. Sabzyan *et al.* have reported that the P-N bond lengths in the six-member rings decrease with increasing the

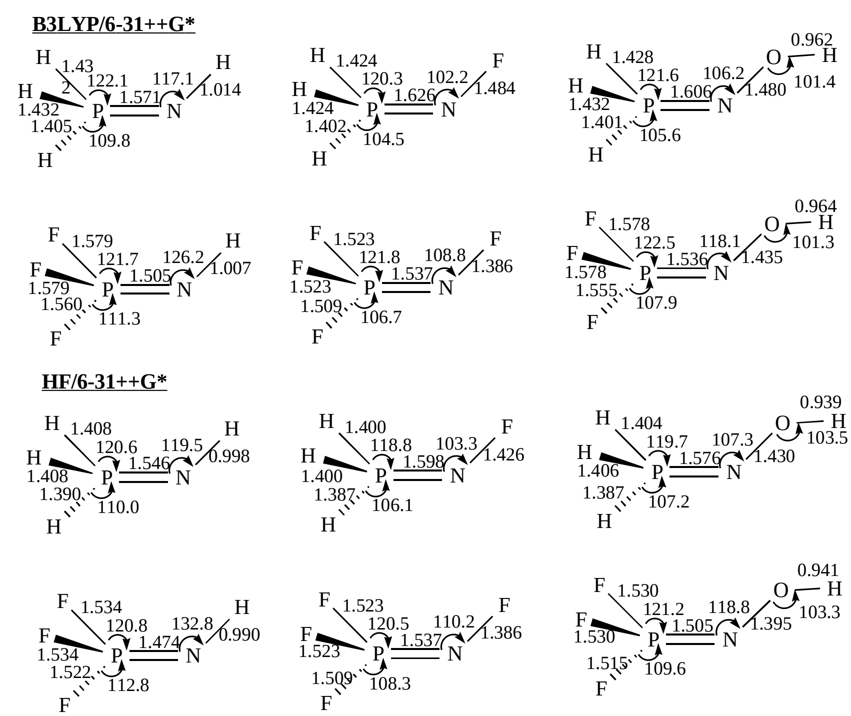


Fig. (1). Geometry of the $Y_3P=N-X$ with Y = H, F and X = H, F and OH.

electronegativity of the halogen substituents on the phosphorus atom [17]. Our study shows a similar behavior as far as the electronegativity effect is concerned with the short phosphazenes (R_3PNH, R_3PNF and R_3PNOH with R = H, F) (Fig. **1**). Our calculation led to the following results: the PNH angle in H_3PNH is 117.1 degrees at B3LYP/ 6-311++G** and 119.5 degrees at HF level with the same basis sets as the B3LYP level. The HF level, overestimates this angle in comparison with the DFT level.

When the hydrogen atom is substituted by the fluorine ones, the PNF valence angle becomes 102.2 degrees at B3LYP/6-311++G** level and 103.3 at HF/6-311++G* level of theory. When the OH is the substituent, the same valence bond angle becomes 106.2 degrees at B3LYP and 107.3 degrees at HF. In F_3PNX, when X = H, this PNH angle is about 9.1 degrees larger at the B3LYP and 13.3 degrees at the HF level in comparison with the same angle in the H_3PNX (X= H, F and OH) compounds. The substitution effect narrowed the PN bond length and increased the PNX valence angle. Indeed, these results confirm that the effect of the fluorine donor group narrowed strongly the PNX angle by about 14.9 at B3LYP and 16.2 degrees at the HF level of theory with the 6-311++G** while the effect of the OH acceptor group diminished the same angle by 27% at B3LYP and 28% at HF level of theory with the 6-311++G**. The same conclusions are obtained at the same level of theory with the 6-31G* and cc-pVTZ basis sets, respectively.

3-1-b NBO Analysis

The obtained HOMO by SCF Molecular orbital calculations at the B3LYP/6-31G* level, corresponds to a π bond above the plan containing the atoms $H_1P_2N_3H_4$. This π bond is highly polarized with charge essentially localized and maximized at the nitrogen center. It is polarized towards the nitrogen atom and would correspond to an ionic π bond type. This result is in accordance with those reported by Chaplin *et al*. [39].

The HOMO corresponds, in any way, to a π bonding ($\pi_{(P-N)}$) for the three studied molecules (H_3PNX, X = H, F and OH). The fluorine attractor and -OH donor effect stabilizes this π bond (HOMO) by about 0.03309 and 0.07657 eV respectively at the HF/6-31G* level.

The (-OH) group effect, raises the degeneration of the bonding ($\sigma_{P2\text{-}H5}$ and $\sigma_{P2\text{-}H6}$) and anti bonding ($\sigma^*_{P2\text{-}H5}$ and $\sigma^*_{P2\text{-}H6}$) molecular orbital by 0.042 and 1.14 eV respectively. This is due to the small steric effect generated by the hydrogen atom of this group. Moreover, the LUMO corresponds to an σ anti bonding molecular orbital ($\sigma^*_{P2\text{-}H1}$) in the H_3PNH and H_3PNOH molecules. The considered energy gap ($|E_{HOMO} - E_{LUMO}|$) being respectively 0.83104 and 0.89832 eV. The LUMO corresponds to an σ anti bonding molecular orbital ($\sigma^*_{N3\text{-}F4}$), the $\sigma^*_{P2\text{-}H1}$ becomes the (LUMO + 1) ones In the H_3PNF molecule. The energy gap is equal to 0.78161 eV and is lower than that of the H_3PNH and H_3PNOH molecules. The substitution of the Hydrogen atom carried out by the nitrogen one by a fluorine attractor group, increases the HOMO and (LUMO+2) electronic population which corresponds to the binding $\pi_{(P-N)}$ and anti binding $\pi^*_{(P-N)}$ molecular orbital, respectively. Whereas, the donor group effect such as (OH), decreases the electronic populations of the same levels as previously. In addition to this, the two, donor and acceptor groups substitution effect, stabilize the whole of the NBO molecular orbital with a stronger stabilization due to the donor group compared to the acceptor one. The same conclusions can be to drawn in the case of the F_3 PNX (X=H, F and OH) compounds.

The molecular orbital involved in the largest energy stabilization $E^{(2)}$ by delocalization of the H_3PNX and F_3PNX molecules when X = H, F and OH groups obtained at the NBO analysis with the HF/6-31G* level show that the HOMO of H_3PNOH is lower than that of H_3PNH of 0.07656 eV and its population decreases by 0.01877 e^- compared to that of H_3PNH. The OM $\pi^*_{(P_2\text{-}N_3)}$ occupation passes from 0.26145 e^- to 0.24949 e^- whereas that of $\sigma^*_{(P_2\text{-}N_3)}$ increases by 0.04975e^-. This proves that the $\pi_{(P_2\text{-}N_3)} \rightarrow \sigma^*_{(P_2\text{-}N_3)}$ interaction is strongly stabilizing, indeed E^2 ($\pi_{(P_2\text{-}N_3)} \rightarrow \sigma^*_{(P_2\text{-}N_3)}$) is equal to, 15.03 in H_3PNOH, 0.67 kcal/mol in H_3PNF and not found in H_3PNH. In the three cases, stabilization by hyperconjugaison, between the $\pi_{(P_2\text{-}N_3)}$ on the one hand and ($\sigma^*_{(P_2\text{-}H_5)}$ et $\sigma^*_{(P_2\text{-}H_6)}$) on the other, is significant. The two interactions energies are degenerated and are respectively worth 20.80, 18.86 kcal/mol in the case of H_3PNH and H_3PNF molecules and the same interactions are not degenerated and are equal to 16.87 kcal/mol for the $\pi_{(P_2\text{-}N_3)} \rightarrow \sigma^*_{(P_2\text{-}H_5)}$ interaction and 19.65 kcal/mol for the $\pi_{(P_2\text{-}N_3)} \rightarrow \sigma^*_{(P_2\text{-}H_6)}$ interaction in the case of H_3PNOH. The anti bonding $\pi^*_{(P_2\text{-}N_3)}$ occupation is primarily due to the interaction of this one with the $\sigma_{(P_2\text{-}H_5)}$ and $\sigma_{(P_2\text{-}H_6)}$. In these cases, energies of interactions are most important and are equal to 112.47 kcal/mol in H_3PNF, 106.86 kcal/mol in H_3PNH and (70.76 kcal/mol for $\sigma_{(P_2\text{-}H_5)} \rightarrow \pi^*_{(P_2\text{-}N_3)}$ and 106.61 kcal/mol for $\sigma_{(P_2\text{-}H_6)} \rightarrow . \pi^*_{(P_2\text{-}N_3)}$) in H_3PNOH. We notice that the delocalization energy of π ($P_2.N_3$) $\rightarrow \sigma^*$ ($P_2.F_5$) and π ($P_2.N_3$) $\rightarrow \sigma^*$ ($P_2.F_6$) are different in F_3PNOH. This difference, is about 16.50 kcal/mol, at HF/6-31G* and does not appear for the F_3PNF and F_3PNH molecules. This is due to the presence of the OH group; this one implies that the F_5 and F_6 environment is not the same.

3-2 Complex R_3P=N-X ….Na^+ with (R=H, F) and (X=H, F, OH)

During the past decade, the importance of compounds-M^+ interaction has been clearly demonstrated in the biological process such as the regulation of enzymes, stabilization and function nucleic acids [40-43]. In addition, this unusual interaction plays significant role in many designing new materials [44]. The formation of a cation-bonded complex implies that a certain amount of electronic charges is transferred in the formed complex. In addition, there is a rearrangement of molecular structure and electron density of the phosphazene in the phosphazene-cation complex. In the current work, the NBO analysis was performed to discus these aspects.

3-2-a Geometry and Energy

In Table **1**, we give the bond length in Å, the valence and dihedral angles in degrees, of the most stable phosphazenes-Na^+ complexes. All calculations were found at the HF levels of theory with the 6-31G* and 6-31++G** basis sets. The results obtained from these calculations characterized all of the optimized structure as, minima on the potential energy surface without any negative mode.

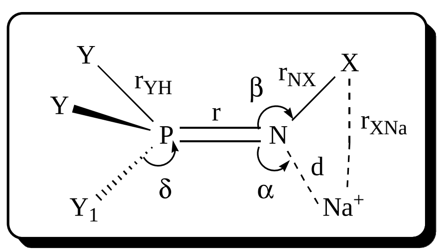
For the $H_3PNH....Na^+$ structure, the PN bond length increases by 0.0373 Å, the PNH bond angle decrease by 6.7 degrees in comparison with the same bond length and the same bond angle in the H_3PNH molecule. The Na^+ ion is located at 2.24Å of the nitrogen atom and at 2.74Å of the hydrogen atom carried by the nitrogen. The four atoms H_1, P_2, N_3, H_4 and Na are coplanar, thus the $N...Na^+$ interaction is done on the sigma level. This proves that the Na^+ ion cannot form the π coupling complex with short chain phosphazene.

The cation metal attachment to the Nitrogen favoured site of phosphazene rises to the coordinated complexes as depicted in Table **1**. The PNNa angle (α in Table **1**) is 138.7 degrees, thus the P, N and Na atoms are not collinear. The α angle (Table **1**) varies proportionally with the weight of the 2Pz orbital with the hybrid n_σ which corresponds to the free doublet localised on the nitrogen atom.

The substitution of the hydrogen atom, carried by the nitrogen one in the $H_3P{=}N{-}H$, by the fluorine atom, increases the PN bonds (r in Table **1**) by 0.036 Å and closes the bond angle PNH (β in Table **1**) of 10.4 degrees. The Na^+ ion is located at 2.28Å of the nitrogen atom and at only 2.22Å of the fluorine one. The distance (r_{FNa}) is shorter than $H....Na^+$ in $H_3PNH...Na^+$ complex with 0.42Å; this is due to the strong electronegativity of the fluorine atom. The NaNF angle becomes 68.7 degrees while it was equal to 109.3 degrees to NaNH in H_3PNH. In this case, these H_1, P_2, N_3, H_4 and Na are coplanar, thus the $N...Na^+$ interaction is always done on the sigma level. The PNNa angle is equal to 189.7 degrees, thus the P, N and Na atoms approach the co-linearity.

The bond length PN decreases by 0.052Å compared to the same distance in $H_3PNH...Na^+$. The bond angle PNH narrowed by 10.5 degrees in the $F_3PNH...Na^+$ complex. The Na^+ cation is located at 2.31 and 2.87 Å to the nitrogen atom and the hydrogen carried by that nitrogen, respectively. The H_1, P_2, N_3, H_4 and Na are coplanar and the $N...Na^+$ interaction is always done on the sigma level. The PNNa angle is equal to 128.2 degrees, thus the P, N and Na^+ atoms are not collinear. The substitutions of the hydrogen atoms

Table 1. Bond Lengths in Å, Valence and Torsional Angles in Degrees in the $Y_3PNX...Na^+$ Complex with (X=H, F, OH) and (Y=H, F) Obtained at the HF/6-31G* Level



X(Y)	H(F)	F(F)	OH(F)
Bond lengths in Å			
d	2.240 (2.309)	2.276 (2.329)	2.259 (2.315)
r	1.585 (1.523)	1.621 (1.569)	1.611 (1.554)
rPH	1.380 (1.519)	1.379 (1.504)	1.379 (1.507)
rNX	1.006 (1.004)	1.474 (1.436)	1.453 (1.437)
rXNa	2.744 (2.872)	2.217 (2.297)	2.310 (2.351)
rOH	/	/	0.952 (0.953)
rHNa	/	/	2.889
Valence angles in degrees			
α	138.7 (128.2)	189.7 (184.6)	183.3 (-)
β	112.0 (117.0)	101.6 (104.7)	107.1 (110.4)
δ	109.5 (109.7)	105.6(107.4)	107.0 (108.9)
Torsional angles in degrees			
H1PNX	180.0 (180.0)	180.0 (180.0)	180.0 (180.0)
H1PNNa	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)

carried by the phosphorus ones do not assign in anything the conclusions drawn in the case from the passage H_3PNH to H_3PNF. The only significant remark is that the PNNa angle is, in this case, equal to 184.6 degrees while it was 189.7 degrees in $H_3PNF... Na^+$. Thus, the P, N and Na atoms are quasi collinear. The presence of the Na^+ cation in $H_3PNOH…Na^+$ generates a preferential orientation with the OH group in the complex (see Table **1**). The sodium is located at 2.26 Å of the N atoms and at 2.31 Å of the oxygen ones thus forming a stable structure with a light increase of the bond length O-H about 0.009Å. The NaNO angle is equal to 69.6 degrees. The substitution of the hydrogen atoms, carried by the phosphorus atom, increase the distance $N…Na^+$ and $O…Na^+$ from 0.056 and 0.041 Å respectively. The attachment, of the metal cation to the favoured sites of each molecules, rise to the bi-coordinated complexes as depicted in Table **1**, in the all cases. The X_1, P_2, N_3, X_4 and Na atoms are coplanar in the X_3PNX molecules with X= H and F, whereas, in the case of $X_3PN(OH)$, the X_1, P_2, N_3, O_4 are coplanar and Na is out of this plan and bi-coordinated to the N_3 and O_4 atoms.

In order to determine the position of the Na^+ ion in the phosphazene-Na^+ complex, several initial geometries were investigated. The Na^+ ion bending to the N terminal atom of the phophazene and the X one position are considered. Though the situation of the cation-π coupling complex has been taken into account, these results prove that the Na^+ ion cannot form the π coupling complex with phosphazene. When we neglected the basis set superposition error (BSSE) and corrected by the zero-point vibrational energy (ZPVE), the bending energies in the complex are calculated, in the B3LYP/6-31G* level, by the relation:

$$\Delta E_{\text{(binding energy)}} = E_{\text{(phosphazene…Na+)}} - (E_{\text{(phosphazene)}} + E_{\text{(Na+)}})$$

These binding energies are equal to -30.54, -31.51 and -34.54 kcal/mol for the F_3PNH, F_3PNF and F_3PNOH compounds, respectively. These are larger of about 12.7, 13.5 and 13.8 kcal/mol. in favour to H_3PNH, H_3PNOH and H_3PNF respectively. These energies are three times larger than those which we find in the Guanine-Na^+ complex [24].

In this species, the distances N-Na^+, on the one hand, are 2.24, 2.28 and 2.26 Å respectively for the H_3PNH, H_3PNF and H_3PNOH and 2.31, 2.33 and 2.32 Å for the F_3PNH, F_3PNF and F_3PNOH molecules. These distances are very similar to those located in the Guanine-Na^+ complex [24] and the distances X-Na^+, on other hand, are 2.74, 2.21 and 2.31 Å for the H_3PNH, H_3PNF and H_3PNOH and 2.87, 2.30 and 2.35 Å for the F_3PNH, F_3PNF and F_3PNOH (Table **1**).

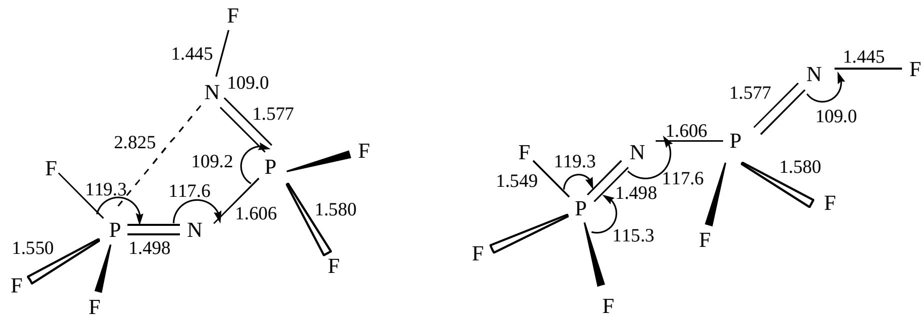
3-2-b NBO Analysis

In Table **2**, we report the molecular orbital involved in the largest energy stabilization $E^{(2)}$ by delocalization for the $H_3PNX…Na^+$ and $F_3PNX…Na^+$ complex when X = OH, H and F obtained at the NBO analysis with the HF/6-31G* level.

All the interactions using the bonding and anti bonding OM π do not appear in the H_3PNX molecules when X = H, F and OH. This is due to the fact that the π doublet is located on the nitrogen atoms. The stabilization energy by delocalization $E^{(2)}$, between the doublet σ of N atoms and the 3s valence orbital of Na ones, is 5.72, 2.07 and 2.98 kcal/mol for H_3PNH, H_3PNF and H_3PNOH, respectively. It is only 3.58, 1.30 and 1.79kcal/mol for the F_3PNH, F_3PNF and F_3PNOH molecules, respectively. In addition, the presence of the Na^+ cation locates the doublet π on the nitrogen atom and the only stabilizing interactions energies correspond to the hyperconjugaison between the doublet πand the anti bonding molecular orbital $\sigma^*_{(P_2\text{-}H_5)}$ and $\sigma^*_{(P_2\text{-}H_6)}$ which are about 19.36, 17.07 and 17.61 kcal/mol,

Table 2. The Molecular Orbital Involved in the Largest Energy Stabilization $E^{(2)}$ by Delocalization for the $Y_3PNX…Na^+$ with (X=OH, H, F) and (a): Y=H and (b): Y=F, Obtained by the NBO Analysis

Type of Interaction	$Y_3PN(OH)…Na^+$ $E^{(2)}$ in kcal/mol.	$Y_3PN(H)…Na^+$ $E^{(2)}$ in kcal/mol.	$Y_3PN(F)…Na^+$ $E^{(2)}$ in kcal/mol.
$\sigma_{(P2\text{-}N3)} \rightarrow \pi^*_{(P2\text{-}N3)}$	≤ 0.5[a] (5.56)[b]	≤ 0.5 (≤ 0.5)	≤ 0.5(≤ 0.5)
$\sigma_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}Y5)}$	1.01 (0.63)	0.94(3.59)	1.08(4.02)
$\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}N3)}$	≤ 0.5(1.99)	≤ 0.5(≤ 0.5)	≤ 0.5(1.06)
$\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}Y5)}$	≤ 0.5(22.88)	≤ 0.5(21.79)	≤ 0.518.79)
$\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}Y6)}$	≤ 0.5(18.05)	≤ 0.5(21.80)	≤ 0.5(18.96)
$\sigma_{(P2\text{-}Y5)} \rightarrow \sigma^*_{(P2\text{-}N3)}$	3.50(≤ 0.5)	2.73(1.19)	3.44(1.43)
$\sigma_{(P2\text{-}Y5)} \rightarrow \pi^*_{(P2\text{-}N3)}$	≤ 0.5(60.02)	≤ 0.5(54.51)	≤ 0.5(52.64)
$\sigma_{(P2\text{-}Y5)} \rightarrow \sigma^*_{(P2\text{-}Y6)}$	2.96(21.15)	2.92 (29.86)	3.01(29.03)
$\sigma_{(P2\text{-}Y6)} \rightarrow \pi^*_{(P2\text{-}N3)}$	≤ 0.5(45.01)	≤ 0.5(54.52)	≤ 0.5(53.22)
$\sigma_{(P2\text{-}Y6)} \rightarrow \sigma^*_{(P2\text{-}Y5)}$	2.95(29.45)	2.92(29.86)	3.01(29.02)
$n_{\sigma(N)} \rightarrow 3s^*_{Na}$	2.98(1.79)	5.72(3.58)	2.07(1.30)
$n_{\pi(N)} \rightarrow \sigma^*_{(P2\text{-}Y5)}$	17.61(/)	19.36(/)	17.07(/)
$n_{\pi(N)} \rightarrow \sigma^*_{(P2\text{-}Y6)}$	17.61(/)	19.36(/)	17.07(/)



cis-trans *trans-trans*

Fig. (2). Structures of the most stable configuration of F-$[PF_2{=}N]_2$-F obtained at the DFT(B3LYP/6-31G*) level. The sum of the electronics and zero point energy of the most stable configuration is – 1391.548412 u.a.

when X is H, F or OH, respectively. For all X, in H_3PNX, the HOMO corresponds to a doublet π located on $2P_y$ orbital atomic of the nitrogen atoms. Its NBO electronic population is 1.8484 e^-, 1.8693 e^- and 1.8514 e^- for X = H, F and OH respectively. The HOMO is strongly depopulated. The σ doublet of N, in interaction with the Na^+ cation, corresponds to the (HOMO – 1) for X=H, the (HOMO-2) for X=OH and the (HOMO-5) for X=F, thus the electronegativity of X stabilizes the doublet σ of the nitrogen atoms.

If the hydrogen's atoms, carried by the phosphorus ones, are substituted by fluorine ones:

* The stabilizing interaction $n_{\sigma(N)} \longrightarrow 3s^*_{(Na)}$ decrease,
* The interactions, implying the OM $\sigma_{(P2\text{-}N3)}$ and $\sigma^*_{(P2\text{-}N3)}$, are largely decreased by the Na^+ approach,
* The $\sigma_{(P2\text{-}F5)} \longrightarrow \pi^*_{(P2\text{-}N3)}$ interaction (60.02 instead of 18.95 kcal/mol) is largely increased for $F_3PN(OH)...Na^+$ and quasi-constant for the two other complexes whereas the $\sigma_{(P2\text{-}F6)} \longrightarrow \pi^*_{(P2\text{-}N3)}$ interaction remains almost constant in all the cases.

4. PHOSPHAZENE CHAIN EXTENSION

The phosphazene Chain extensions to two unit leads to the structures showed in Fig. (**2**). The *cis-trans* configuration is more stable than the *trans-trans* one about 15.97 kcal/mol at the DFT (B3LYP/6-31G*) level. The large energy difference between the conformations *cis-trans* and *trans-trans* should be originated from the hypercoordination of phosphorus atom.

In the most stable configuration (*cis-trans*), the $P_2{=}N_3$ bond length is longer than that in the *trans-trans* one by 0.003 Å, whereas that corresponding to N_3-P_4 it longer by 0.008 Å. The greatest structural differences appear at the bond angles. In fact, the $P_2N_3P_4$ are 138.6 and 117.6 degrees in the *cis-trans* and *trans-trans* configuration respectively, whereas, the $N_3P_4N_5$ angle is practically the same in both cases.

In both cases, when the two structures are doped by Na^+ cation, we lead the same stable complex represented in Fig. (**3**), which gives a quasi covalent bond between the terminal nitrogen atoms with the Na^+ cation. The N….Na^+ bond length is equal to 2.272 Å. The distance is in agreement with that obtained in the smallest phosphazene…Na^+ complex (see Table **1**); it is also in the same order with that established in the guanidine-Na^+ complex [24]. The most important results are the opening bond length $P_2N_3P_4$, which passes from 138.6 (117.6) in the *cis-trans* (*trans-trans*) to the 169 degrees. The $P_2N_3P_4$ angle becomes quasi linear even when the chain of the phosphazene polymer increases (see Figs. **3** and **4**). Thus, the doping phosphazene polymers by Na^+ cation linearize all the PNP bond angles, which confer to them rather important properties of π electron transmitter, therefore remarkable linear and non linear optical properties. Indeed, calculation on the DFT (B3LYP/6-31G*) level of the dipole moment, the electric polarizability and the hyperpolarisabilty, led to values which are multiplied by 10

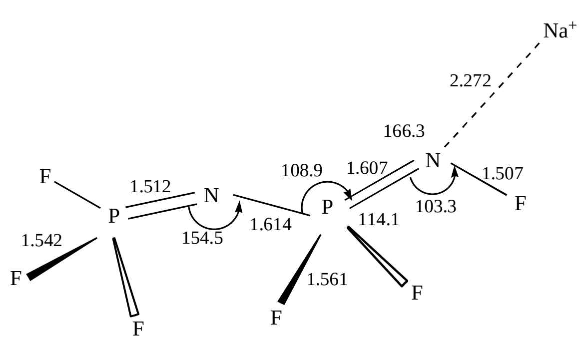


Fig. (3). Geometry of the F-$[PF_2{=}N]_2$-F…Na^+ complexes, obtained at the DFT(B3LYP/6-31G*) level.

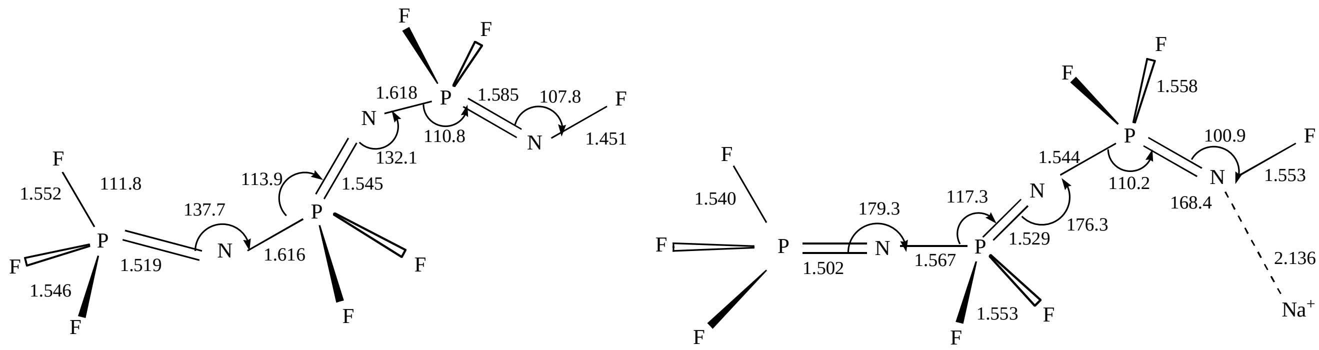


Fig. (4). Geometry of the F-$[PF_2=N]_3$-F…Na^+ complexes, obtained at the DFT(B3LYP/6-31G*) level.

to see even by 100 when we holds in account the solvent effect in the dielectric continuum (PCM) approximation.

5. CONCLUSION

In conclusion, this structural analysis conduces at the P-N bond lengths are shortened with increasing the electronegativity of the X substituents on the phosphorus atom; the effect of the passage from H_3PNX to F_3PNX narrowed the PN bond length and opens the valence bond angle PNX; the PN bond is highly polarized with charge essentially localized and maximized at the nitrogen atom, and this NBO analysis conduces to three significant remarks:

(i) The PN bond length (1.513 Å) obtained at B3LYP/6-31G* for the F_3PNH molecules is short of about 0.257 Å compared to the σ bond that we found in $NH_2 – PO_3^{2-}$ [35] and shorter of about 0.067 Å compared to a double bound PN than we found in $(Cl_2)NP(Cl_2)NPCl_3$ [21].

(ii) In all cases, the doublet sigma is localized in the nitrogen atom.

(iii) The phosphazene polymers doped by Na^+ cation, linearize all the PNP bond angles, which confer to them rather important properties of π electron transmitter, therefore remarkable linear and non linear optical properties.

SUPPLEMENTARY MATERIAL

Supplementary material can be viewed at www.bentham.org/open/tosbj.

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