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HF, DFT Studies and NBO Analysis of Phosphazenes and Its-Na^+ Complex

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In this work, we study simple phosphazenes models, such as H_3PNX and F_3PNX (X = H, F and OH). Several bonding theories have been presented to explain the observed structural properties in polyphosphazenes of which the d_π-p_π bonding model is most widely adopted. But there is no report on the degree of participation of the 3d and 2p orbital of phosphorus and nitrogen atom respectively, at the d_π-p_π bond, type of natural orbital hybrid (NOH) to form this π-bond in the phosphazenes compounds and in the phosphazene-Na^+ complex. The aim of this work is to attempt to investigate these aspects by means of HF and DFT studies of electronics, molecular structures and natural bond orbital (NBO) analysis.

Key Words: Phosphazenes, HF, DFT and NBO analysis.

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]. Linear polyphosphazenes are a unique class of polymers with an inorganic backbone of repeated -[PR_2 =N]- units with various organic substituents (R) at the phosphorus atom. There are many types of polyphosphazenes, studied by several authors[3-5]. These polyphosphazenes could be applied as biomaterials[6,7], solid polymer electrolytes[8,9], membranes[10-12], lubricants and fire-resistant materials[13-15].

Several bonding theories have been presented to explain the observed structural properties in cyclopolyphosphazenes of which the d_π-p_π bonding model is most widely adopted[16,17].

This model developed by Craig and Paddock[18] and by Dewar, Lucken and Whitehead[19] describes the bonding P=N in terms of σ-bonding and π-bonding arising from the overlap of 3d orbital of the phosphorus atom with the 2pz orbital of the nitrogen[17]. Allcock *et al.*[20] have developed 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].

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The alkali cation (Na^+) participates in many functions of living systems[22,23] and important inside the living beings. It have low tendency to form covalent bonds, so they should be considered nonspecific binders in many organic compounds-Na^+ complex[24]. In most recent experimental and theoretical studies, many authors are reported to have led exhaustive studies on the Li^+, Na^+ and K^+ interaction with some organic compounds[24,25]. On the one hand, the P-N bond being strongly polarized and on the other hand, the polyphosphazenes to forming a significant class in the producing of the biomaterials and understanding of the mechanisms of ionic and molecular transport in polymer electrolyte phases which is crucial for the development of improved power sources. It is shown that in polyphosphazenes membranes, nitrogen atoms interact more strongly with lithium ions than ether oxygen[26]. In this case, it would be important to examine their electronic and structural behaviour in the presence of the Na^+ cation.

Unresolved questions are: (a) What is the degree of participation of the 3d orbital of phosphorus and 2p orbital of nitrogen atom at the d_π-p_π bond? (b) What is the type of natural orbital hybrid (NOH) to form this π-bond in the phosphazenes compounds and in the phosphazene-Na^+ complex? (c) What is the Na^+ effect on, the geometry and the electronic distribution of the studied molecules? (d) What is the type of coordination established by Na^+ in the phosphazene-Na^+ complex?

The aim of this work is to attempt to answer these questions by means of HF and DFT studies of electronics, molecular structures and natural bond orbital analysis (NBO)[27]. The NBO analysis of Weinhold[27,28] offers a way to quantify electron delocalization in terms of intra-molecular donor-acceptor interactions. In accordance with the simple bond picture[29] each bonding NBO π_{PN} can be written in terms of two directed valence hybrids h^π_P, h^π_N on atoms P and N, with corresponding polarization coefficients C_P, C_N:

$$\pi_{PN} = C_P \cdot h^\pi_P + C_N \cdot h^\pi_N$$

Each valence bonding must in turn be paired with a corresponding valence anti bonding NBO

$$p^*_{PN} = C^*_P \cdot h^\pi_P + C^*_N \cdot h^\pi_N$$

In this work, we study simple phosphazenes models, such as H_3PNX and F_3PNX (X = H, F and OH). The substituent effect of the fluorine atom acceptor and the OH group donor is studied.

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[30] with 6-31G*, 6-311++G** and cc-pVTZ basis sets. The computations carried at DFT level[31-33] 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[34] within higher accuracy (keyword opt = tight).

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

The NBO analysis was carried out with 3.1 version[35] included in Gaussian 03W program at the HF/6-31+G* level. In the NBO analysis[28,35], the electronic wave functions are interpreted, in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbital. 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, correspond to a stabilizing donor-acceptor interaction. The evaluation of their energies is done by second-order perturbation theory. For each donor NBO (i) and acceptor (j), the stabilization energy, $E^{(2)}$, associated with i → j delocalization, is estimated by the following equation:

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

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.

RESULTS AND DISCUSSION

Substituent effect: H_3PNX and $F_3P=N-X$, (X = H, F, OH)

Geometry: To estimate the influence of substituents on the P-N interaction, calculations have been performed on the H_3PNX and F_3PNX (X = H, F and OH) short phosphazene molecules. The structural data corresponding to these structures, obtained at B3LYP/6-31G*, 6-311++G**, cc-pVTZ and HF levels with the same basis sets, are given 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 level with the same basis sets. It is much shorter than that of the NH_2-PO_3^{2-} ion (1.77 Å), which corresponds to a simple bond PN[36] and it is shorter than that of the $O=P(Cl)_2-N=P(Cl)_3$ (1.580 Å), which corresponds to a double bond P=N determined by the X-ray diffraction[37].

When we substitute the hydrogen atom legated to the nitrogen one by OH and F, the bond length P-N lengthens to 1.606 and 1.626 Å, respectively for H_3PNOH at the same level of theory. Same conclusions are obtained at all the other levels of theory and the same basis sets (Fig. 1). These bond lengths are very similar to those

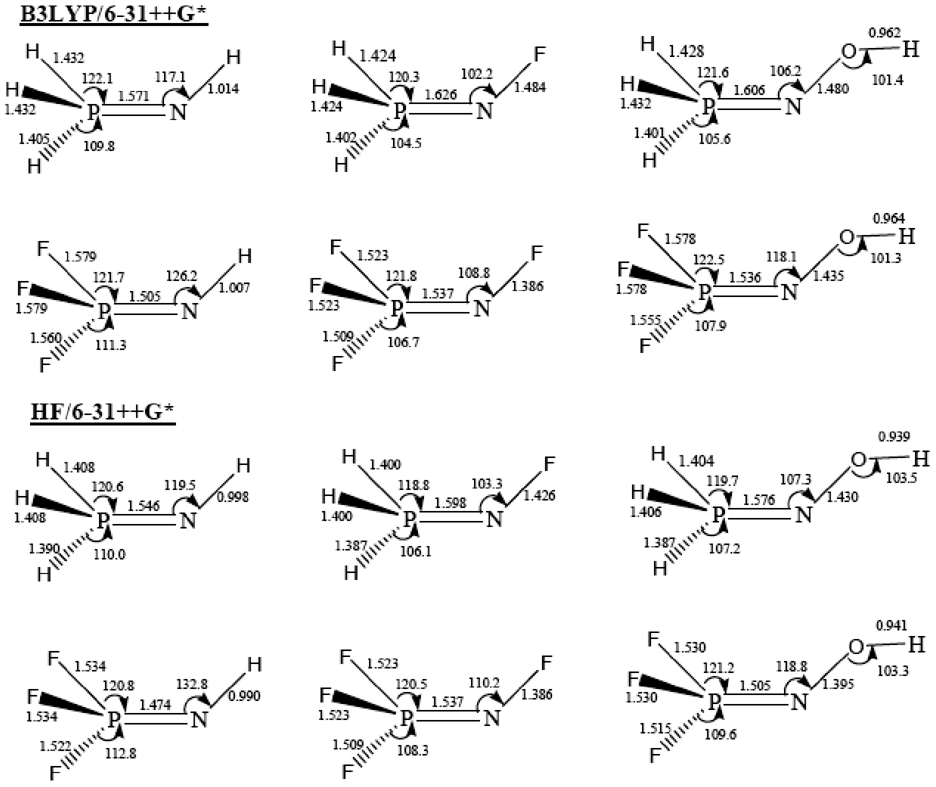


Fig. 1. Geometry of all the molecules

obtained by X-ray diffraction in the $Ph_3P = NMe$ (1.641 Å) molecule[38]. The HF level which not takes into account the electronic correlation, under estimates this bond in comparison with the DFT level.

This bond length P=N depends strongly on the substituents group bridged to the phosphorus atom. The X-ray diffraction data in $Ph_3P = NMe$ gives the bond length P=N equal to 1.641 Å[38] and 1.58 Å in $O=P(Cl)_2-N=P(Cl)_3$[37]. The same 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[39].

The complete geometry optimization, of the all molecules at the MP2//6-31G * level, gives results comparable with those obtained at the B3LYP/6-31G* level. The errors made over the bond lengths PN vary between 0.002 and 0.039 Å.

The P-N bond lengths in the six-member rings are shortened with an increasing of the electronegativity of the halogen substituents on the phosphorus atom[40]. Again, in the short phosphazenes (X_3PNH, X_3PNF and X_3PNOH with X = H, F), the P-N bond lengths are shortened with an increasing of the electronegativity of the X substituents on the phosphorus atom (Fig. 1).

The P-N-H angle in H_3PNH is 117.1° at B3LYP/ 6-311++G** and 119.5° at HF level with the same basis sets than the B3LYP level. The HF level, which does not take into account the electron correlation, over-estimates this angle in comparison with the DFT level.

After including the fluorine substituent, the valence angle P-N-F becomes 102.2° at B3LYP level 6-311++G** and 103.3 at HF level of theory at the same basis sets and when we include the OH substituent, the same valence bond angle becomes 106.2° at B3LYP and 107.3° at HF with the same basis sets. In F_3PNX, when X = H, this angle PNX is about 9.1° larger at B3LYP and 13.3° at the HF level in comparison with the same angle in the H_3PNX (X= H, F and OH) compounds. The effect of the passage from H_3PNX to F_3PNX narrowed the PN bond length and opens the valence bond angle PNX.

These results prove that the effect of the fluorine donor group narrowed strongly the PNX angle about 14.9 at B3LYP and 16.2° at the HF level of theory with the 6-311++G**. The effect of the OH acceptor group diminishes the same angle by 27 % at B3LYP 28 % at HF level of theory with the 6-311++G**. The same conclusions are obtained respectively at the same level of theory with the 6-31G* and cc-pVTZ basis sets.

NBO analysis of the H_3PNX molecules with X = H, F and OH: Fig. 2 shows that the HOMO, obtained by SCF molecular orbital at the B3LYP/6-31G* level, corresponds to a π bond above the plan containing the atoms $H_1P_2N_3H_4$. The 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.

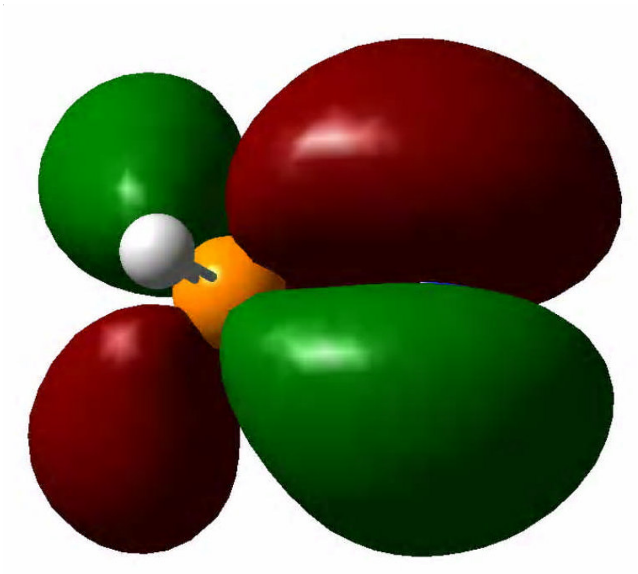
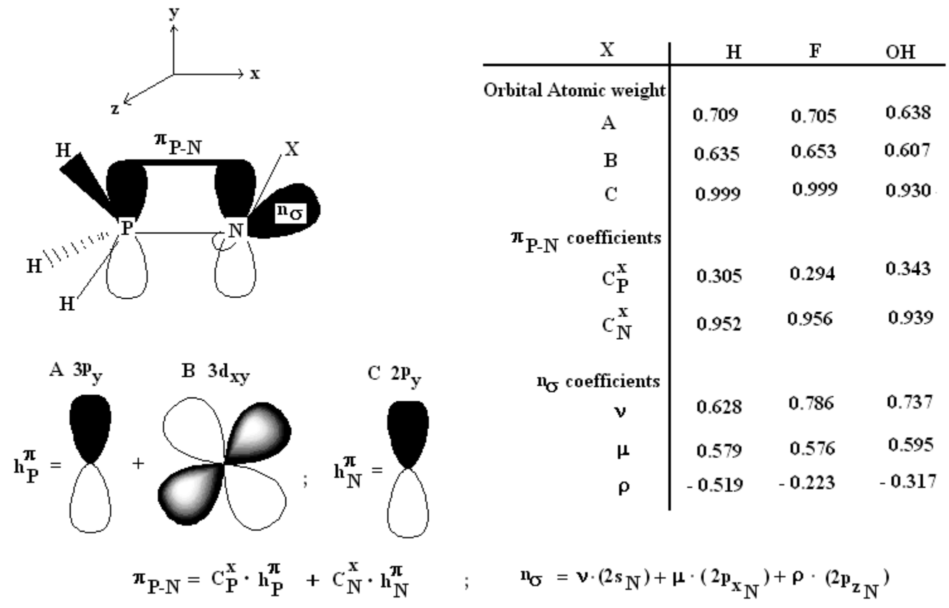


Fig. 2. HOMO energies obtained by SCF molecular orbital at B3LYP/6-31G*levels

Fig. 3 shows the Lewis structure obtained by NBO analysis at the HF/6-31G* level for the H_3PNX molecules with X = H, F and OH. This is corresponding to, six bonds ($3\sigma_{P\text{-}H}$, $1\sigma_{P\text{-}N}$, $1\pi_{P\text{-}N}$ and $1\sigma_{N\text{-}X}$) and one electronic doublet localized at the nitrogen atom and formed by a σ_{sp^2} hybrid (Fig. 3).

Taking into account the $2p_z$ atomic orbital weight (Fig. 3), the angle formed by the σ_N doublet and the P-N bond ($PN\sigma_N$) varies as follows: ($PN\sigma_N$) X = F > ($PN\sigma_N$) X = OH > ($PN\sigma_N$) X = H.

In all cases, the $\pi_{P\text{-}N}$ bond formed by the combination of the h^{π}_P and h^{π}_N hybrids with the h^{π}_N weight is larger than that of the h^{π}_P hybrid (Fig. 3). This proves that the π_{PN} bond is strongly polarized towards the nitrogen atom. This is in accordance with the result obtained at the SCF level (Fig. 2).



X	H	F	OH
Orbital Atomic weight			
A	0.709	0.705	0.638
B	0.635	0.653	0.607
C	0.999	0.999	0.930
$\pi_{P\text{-}N}$ coefficients			
C^x_P	0.305	0.294	0.343
C^x_N	0.952	0.956	0.939
n_σ coefficients			
ν	0.628	0.786	0.737
μ	0.579	0.576	0.595
ρ	- 0.519	- 0.223	- 0.317

$$\pi_{P\text{-}N} = C^x_P \cdot h^{\pi}_P + C^x_N \cdot h^{\pi}_N \quad ; \quad n_\sigma = \nu \cdot (2s_N) + \mu \cdot (2p_{x_N}) + \rho \cdot (2p_{z_N})$$

Fig. 3. Atomic orbital involved in the $\pi_{P\text{-}N}$ bond in the H_3PNX (X = H, F and OH) with NBO analysis at HF/6-31G*. n_σ is a doublet located in the nitrogen atom

In Table-1, the energy and the character of selected molecular orbital (occupied and unoccupied) with the NBO analysis at the HF/6-31G * level of the H_3PNX with X= (H, F and OH) are reported.

For the three studied molecules, the HOMO corresponds to a bonding $\pi(\pi_{(P\text{-}N)})$. The fluorine attractor and -OH donor effect stabilizes this π bond (HOMO) about 0.03309 and 0.07657 eV, respectively at the HF/6-31G* level.

In addition to this, the presence of the (-OH) group raises the degeneration of the bonding ($\sigma_{P2\text{-}H5}$ and $\sigma_{P2\text{-}H6}$) and antibonding ($\sigma^*_{P2\text{-}H5}$ and $\sigma^*_{P2\text{-}H6}$) molecular orbital by 0.042 and 1.14 kcal, respectively. This is due to the small steric effects generated by the presence of the hydrogen atom of this group.

In the H_3PNH and H_3PNOH molecules, the LUMO correspond to an σ antibonding molecular orbital ($\sigma^*_{P2\text{-}H1}$). The energy gap ($E_{HOMO} - E_{LUMO}$) being respectively: 0.83104 and 0.89832 eV.

In the H_3PNF molecule, the LUMO correspond to an σ antibonding molecular orbital ($\sigma^*_{N3\text{-}F4}$), the $\sigma^*_{P2\text{-}H1}$ becomes the (LUMO + 1) ones. The energy gap is equal to 0.78161 eV and is lower than that of the H_3PNH and H_3PNOH molecules.

Table-1 shows that the substitution of the hydrogen atom carried by the nitrogen one by an attractor group (F), increases the HOMO and (LUMO + 2) electronic population which correspond respectively to the binding $\pi_{(P\text{-}N)}$ and antibonding $\pi^*_{(P\text{-}N)}$ molecular orbital. Whereas, the effect of a donor group such as (OH), decreases the electronic populations of the same levels as previously. In addition to this, the substitution effect, by the two donor and acceptor groups, stabilizes 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_3PNX (X = H, F and OH) compounds (Table-2).

F_3P=N-X, (X = H, F, OH): In Table-2, the energy and the character of selected molecular orbital (occupied and unoccupied) with the NBO analysis at the HF/6-31G* level of the F_3PNX with X = (H, F and OH) are reported.

For the studied molecules, the HOMO corresponds to a bonding π ($\pi_{(P\text{-}N)}$) except when X = OH where the HOMO corresponds to a free doublet $n_{1(O4)}$ (Table-2). The $\pi_{(P\text{-}N)}$ molecular orbital becomes a HOMO-1; the presence of the OH group stabilizes it.

The fluorine acceptor and -OH donor effect stabilizes this π bond (HOMO) between 0.02544 and 0.12986 eV, respectively at the HF/6-31G* level.

The presence of the (-OH) group raises the degeneration of the bonding ($\sigma_{P2\text{-}F5}$ and $\sigma_{P2\text{-}F6}$) and antibonding ($\sigma^*_{P2\text{-}F5}$ and $\sigma^*_{P2\text{-}F6}$) molecular orbital respectively by 0.098 and 0.040 kcal. The steric effect of the hydrogen atom, in this case, is smaller than in the case of the H_3PNOH compound.

In the F_3PNH and F_3PNOH molecules, the LUMO correspond to an σ antibonding molecular orbital ($\sigma^*_{P2\text{-}F1}$) (Table-2). The energy gap becomes respectively 0.93835 and 0.99027 eV. These gaps are greater than those obtained for the H_3PNH and H_3PNOH molecules.

In the F_3PNF molecule (Table-2), the LUMO correspond to an σ antibonding molecular orbital ($\sigma^*_{N3\text{-}F4}$), the $\sigma^*_{P2\text{-}H1}$ becomes the (LUMO + 1) ones. The energy gap is equal to 0.82540 eV. This gap is greater than that of the H_3PNF and lower than that of the F_3PNH and F_3PNOH molecules.

The NBO analysis shows that the Lewis structure of F_3PNH is formed by one π bond (Fig. 4a1). It is formed by the following combination:

$$\pi_{(P\text{-}N)} = 0.3296\ (h^{\pi}_{P}) + 0.9441\ (h^{\pi}_{N})$$

with h^{π}_{P} and h^{π}_{N} which are hybrids carried respectively by the phosphorus and the nitrogen atoms (Fig. 4). These orbital hybrids are defined within framework NBO as follows:

TABLE-1
SOME OCCUPIED (H-i) AND VIRTUAL MOLECULAR ORBITAL (L + i), OCCUPATION (in e$^-$) AND ENERGY (in eV)
OBTAINED BY THE NBO ANALYSIS FOR H_3PNH (REFERENCE), H_3PNF AND H_3PNOH AT THE HF/6-31G* LEVEL OF THEORY

OM Type	H_3PNH			H_3PNF			H_3PNOH		
	Occupation	Energy	OM character	Occupation	Energy	OM character	Occupation	Energy	OM character
$\sigma^*_{(P2\text{-}H5)}$	0.07832	0.5942	L+3	0.06374	0.57451	L+4	0.07318	0.57745	L+4
$\sigma^*_{(P2\text{-}H6)}$	0.07832	0.5942	L+3	0.06374	0.57451	L+4	0.06836	0.58239	L+5
$\sigma^*_{(P2\text{-}N3)}$	0.00667	0.58091	L+2	0.01264	0.50329	L+3	0.05642	0.52150	L+3
$\pi^*_{(P2\text{-}N3)}$	0.26145	0.48656	L+1	0.27480	0.44891	L+2	0.24949	0.47577	L+1
$\sigma^*_{(H1\text{-}P2)}$	0.05109	0.47284	LUMO	0.02296	0.44144	L+1	0.02349	0.46355	LUMO
$\sigma_{(N3\text{-}F4)}$	-	-	-	0.00904	0.39032	LUMO	-	-	-
$\pi_{(P2\text{-}N3)}$	1.93774	-0.35820	HOMO	1.94146	-0.39129	HOMO	1.91897	-0.43477	HOMO
$\sigma_{(P2\text{-}H5)}$	1.83746	-0.58063	H-1	1.83265	-0.61513	H-3	1.84678	-0.60443	H-3
$\sigma_{(P2\text{-}H6)}$	1.83746	-0.58063	H-1	1.83265	-0.61513	H-3	1.84949	-0.60263	H-2
$n_{1(N3)}$	1.90460	-0.51946	H-2	1.97731	-0.68583	H-4	1.96526	-0.62419	H-4
$\sigma_{(P2\text{-}N3)}$	1.99608	-1.01194	H-5	1.99177	-0.99154	H-7	1.95257	-0.87836	H-7

TABLE-2
SOME OCCUPIED (H-i) AND VIRTUAL MOLECULAR ORBITAL (L+i), OCCUPATION (in e$^-$) AND ENERGY (in eV)
OBTAINED BY THE NBO ANALYSIS FOR F_3PNH (REFERENCE), F_3PNF AND F_3PNOH AT THE HF/6-31G* LEVEL OF THEORY

OM Type	F_3PNH			F_3PNF			F_3PNOH		
	Occupation	Energy	OM character	Occupation	Energy	OM character	Occupation	Energy	OM character
$\sigma^*_{(N3\text{-}X4)}$	0.00924	0.80297	L+5	0.01029	0.37285	LUMO	0.00734	0.48844	L+1
$\sigma^*_{(P2\text{-}F5)}$	0.08487	0.77206	L+4	0.09794	0.64056	L+5	0.11119	0.63547	L+4
$\sigma^*_{(P2\text{-}F6)}$	0.08487	0.77205	L+4	0.09793	0.64068	L+4	0.10642	0.63970	L+5
$\sigma^*_{(P2\text{-}N3)}$	0.06118	0.71901	L+3	0.05833	0.58900	L+3	0.09477	0.58560	L+3
$\sigma^*_{(F1\text{-}P2)}$	0.08040	0.68730	L+2	0.09276	0.41417	L+1	0.09531	0.43330	LUMO
$\pi^*_{(P2\text{-}N3)}$ (1)	0.10173	0.52885	L+1	0.10646	0.47901	L+2	0.11278	0.55512	L+2
$\pi^*_{(P2\text{-}N3)}$ (2)	0.12302	0.51124	LUMO	not found	not found	not found	not found	not found	not found
$\pi_{(P2\text{-}N3)}$ (2)	1.94979	-0.42711	HOMO	not found	not found	not found	not found	not found	not found
$n_{1(O4)}$	–	–	–	–	–	–	1.98697	-0.55697	HOMO
$\pi_{(P2\text{-}N3)}$ (1)	1.94950	-0.46302	H-1	1.95015	-0.45255	HOMO	1.92542	-0.61746	H-1
$\sigma_{(N3\text{-}X4)}$	1.99171	- 0.94131	H-6	1.98519	-1.07185	H-9	1.98619	-1.03622	H-12

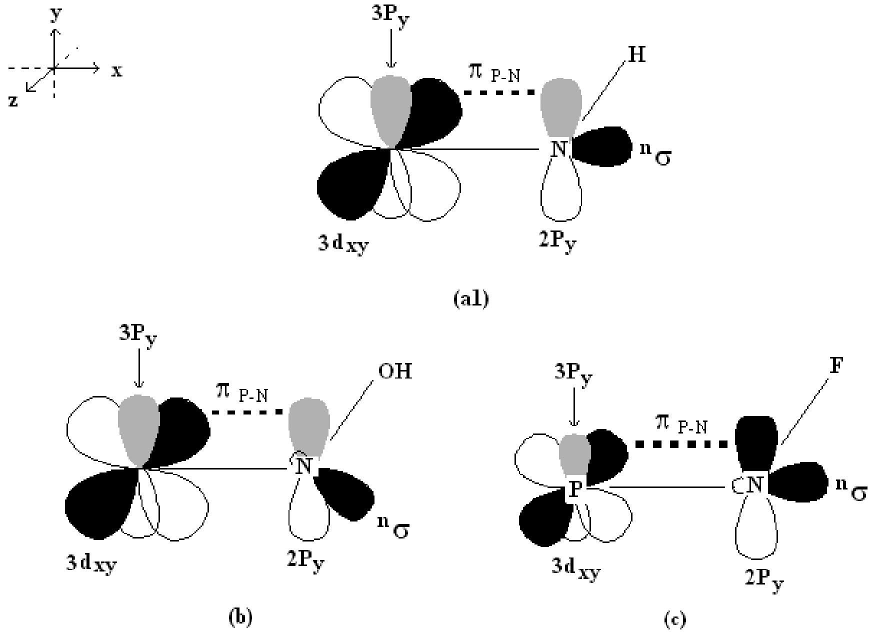


Fig. 4. Atomic orbital involved in the π_{P-N} bond, (a1) in F3PNH; (b) in F3PNOH and (c) in F3PNF with NBO analysis at HF/6-31G*. n_σ is a doublet located in the nitrogen atom

$$h^{\pi}_{P} = 0.7301\ (3P_{y(P)}) + 0.6616\ (3d_{xy\ (P)})$$
$$h^{\pi}_{N} = 0.9984\ (3P_{y(N)})$$

Thus the NBO analysis, considers a doublet σ located on the nitrogen atom and predict respectively five and three valences bond for the phosphorus and nitrogen atoms.

For the F_3PNOH and F_3PNF molecules, NBO analysis envisages the same π bonds type.

For F_3PNOH (Fig. 4b): $\pi_{(P-N)} = 0.4092\ (h^{\pi}_{P}) + 0.9125\ (h^{\pi}_{N})$ and

For F_3PNF (Fig. 4c): $\pi_{(P-N)} = 0.3314\ (h^{\pi}_{P}) + 0.9435\ (h^{\pi}_{N})$.

It is noticed that the h^{π}_{P} hybrid contribution is more significant in F_3PNOH and that the h^{π}_{N} is more important in F_3PNF.

The substitution of the hydrogen atom in F_3PNH by a donor and an acceptor group decreases the electronic density between the two atoms of phosphorus and nitrogen.

We have one π bond in F_3PNH, F_3PNOH and F_3PNF with a localization of the doublet σ of nitrogen. In the F_3PNOH molecule, the doublet σ is hybridized in sp^2 (Fig. 4b):

$$n_\sigma = 0.7020\ (2s_{(N)}) + 0.5631\ (2P_{x(N)}) - 0.4331\ (2P_{z(N)})$$

In the F_3PNH and F_3PNF molecule, the doublet σ is hybridized in sp (Fig. 4c): For example, the sp doublet in F_3PNF is given by:

$$n_\sigma = 0.7754\ (2s_{(N)}) + 0.5526\ (2P_{x(N)})$$

This explains the lengthening of the P-N bond of about 0.031 and 0.063 Å, respectively for F_3PNOH and F_3PNF at the HF/6-311++G ** level, the bond length P-N, in F_3PNH is 1.474 Å at the same level of theory. The short bond length of PN, 1.474 Å in F_3PNH, is obtained at the HF/6-311++G** level (Fig. 1). It is important to point out that there exists no evidence either by experiments or theory to prove or disprove the above mentioned modes of bonding in short-chain phosphazenes.

In Tables 3a and 3b, we report 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.

The HOMO of H_3PNOH (Table-2) is lower than that of H_3PNH of 0.07656 eV and its population decreases by $0.01877e^-$ compared to that of H_3PNH. The occupation of the OM $\pi^*_{(P2\text{-}N3)}$ passes from 0.26145 e^- to 0.24949 e^- whereas that of $\sigma^*_{(P2\text{-}N3)}$ increases by 0.04975 e^-. This proves that the $\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}N3)}$ interaction is strongly stabilizing, indeed $E^2\ (\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}N3)})$ is equal to, 15.03 in H_3PNOH, 0.67 kcal/mol in H_3PNF and not found in H_3PNH (Table-3a). In the three cases, stabilization by hyperconjugaison between the $\pi_{(P2\text{-}N3)}$ on the one hand and ($\sigma^*_{(P2\text{-}H5)}$ and $\sigma^*_{(P2\text{-}H6)}$) on the other hand is significant. In the case of H_3PNH and H_3PNF, the two interaction energies are degenerated and are respectively worth 20.80, 18.86 kcal/mol (Table-2). In the case of H_3PNOH, the two interaction energies are not degenerated and are equal to 16.87 kcal/mol for the $\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}H5)}$ interaction and 19.65 kcal/mol for the $\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}H6)}$ interaction. The antibonding $\pi^*_{(P2\text{-}N3)}$ occupation is primarily due to the interaction of this one with the $\sigma_{(P2\text{-}H5)}$ and $\sigma_{(P2\text{-}H6)}$. In these cases, energies of interactions are most significant and are equal to 112.47 kcal/mol in H_3PNF, 106.86 kcal/mol in H_3PNH and (70.76 kcal/mol for $\sigma_{(P2\text{-}H5)} \rightarrow \pi_{(P2\text{-}N3)}$ and 106.61 kcal/mol for $\sigma_{(P2\text{-}H6)} \rightarrow \pi_{(P2\text{-}N3)}$) in H_3PNOH (Table-3a).

It is noticed here that the delocalization energy of $\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}F5)}$ and $\pi_{(P2\text{-}N3)} \rightarrow \sigma^*_{(P2\text{-}F6)}$, in F_3PNOH, are different (Table-3b). This difference, is about 16.50 kcal/mol, at HF/6-31G* and does not appear for the F_3PNF and F_3PNH molecules (Table-3b). This is due to the presence of the OH group, which implies that the F5 and F6 environment is not the same.

Complex $H_3P = N–X\cdots Na^+$ and $F_3P = N–X\cdots Na^+$ with X = H, F and 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[41-44]. In addition, this unusual interaction plays significant role in many designing new materials[45]. 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.

TABLE-3a
RESULTS OF SECOND-ORDER PERTURBATION THEORY ANALYSIS OF THE FOCK MATRIX WITHIN THE NBO BASIS OF H_3PNX (X = H, F and OH)

Type of interaction	H_3PNOH	H_3PNH	H_3PNF
	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol
$\sigma_{(P2-N3)} \rightarrow \pi^*_{(P2-N3)}$	29.76	not found	not found
$\sigma_{(P2-N3)} \rightarrow \sigma^*_{(P2-H5)}$	11.64	1.06	1.22
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-N3)}$	15.03	≤ 0.50	0.67
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-H5)}$	16.87	20.80	18.86
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-H6)}$	19.65	20.80	18.86
$\sigma_{(P2-H5)} \rightarrow \sigma^*_{(P2-N3)}$	22.37	2.53	2.80
$\sigma_{(P2-H5)} \rightarrow \pi^*_{(P2-N3)}$	70.76	106.86	112.47
$\sigma_{(P2-H5)} \rightarrow \sigma^*_{(P2-H6)}$	34.54	37.17	37.64
$\sigma_{(P2-H6)} \rightarrow \pi^*_{(P2-N3)}$	106.61	106.86	112.47
$\sigma_{(P2-H6)} \rightarrow \sigma^*_{(P2-H5)}$	34.78	37.17	37.64

TABLE-3b
RESULTS OF SECOND-ORDER PERTURBATION THEORY ANALYSIS OF THE FOCK MATRIX WITHIN THE NBO BASIS OF F_3PNX (X = F and OH)

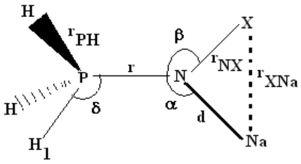
Type of interaction	F_3PNOH	F_3PNF
	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol
$\sigma_{(P2-N3)} \rightarrow \pi^*_{(P2-N3)}$	37.11	≤ 0.50
$\sigma_{(P2-N3)} \rightarrow \sigma^*_{(P2-F5)}$	29.28	4.13
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-N3)}$	26.73	≤ 0.50
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-F5)}$	14.82	26.38
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-F6)}$	31.32	26.38
$\sigma_{(P2-F5)} \rightarrow \sigma^*_{(P2-N3)}$	21.64	1.39
$\sigma_{(P2-F5)} \rightarrow \pi^*_{(P2-N3)}$	18.95	50.94
$\sigma_{(P2-F5)} \rightarrow \sigma^*_{(P2-F6)}$	27.10	30.90
$\sigma_{(P2-F6)} \rightarrow \pi^*_{(P2-N3)}$	39.31	50.94
$\sigma_{(P2-F6)} \rightarrow \sigma^*_{(P2-F5)}$	26.80	30.90
$\sigma_{(P2-N3)} \rightarrow \sigma^*_{(P2-F6)}$	6.11	4.13

Geometry and energy: In Fig. 5, the bond lengths are given 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 $H_3PNH\cdots Na^+$ structure, the PN bond length increases by 0.0373 Å, the PNH bond angle decrease by 6.7° in comparison with the same bond length and the same bond angle in the H_3PNH molecule. The Na^+ ion is located at 2.24 Å of the nitrogen atom and at 2.74 Å 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 $N\cdots Na^+$ interaction is done on the σ level. This proves that the Na^+ ion cannot form the π coupling complex with short chain phosphazene.

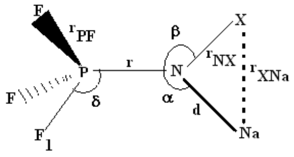
The attachment of metal cation to the N favoured site of phosphazene rises to the coordinated complexes as depicted in Fig. 5.

The PNNa angle, α in Fig. 5a, is 138.6º, thus the P, N and Na atoms are not collinear. The angle α (Fig. 5a and 5b) varies proportionally with the weight of the $2p_z$ orbital with the hybrid $n_σ$ which corresponds to the free doublet localized on the nitrogen atom (Fig. 6a and 6b).



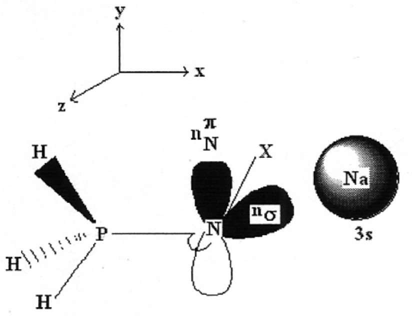
X	H	F	OH
bond lengths in Å			
d	2.240	2.276	2.259
r	1.585	1.621	1.611
r_{PH}	1.380	1.379	1.379
r_{NX}	1.006	1.472	1.453
r_{XNa}	2.744	2.217	2.310
r_{OH_2}	/	/	0.952
r_{H_2Na}	/	/	2.889
valence angles in degrees			
α	138.7	189.7	183.3
β	112.0	101.6	107.1
δ	109.5	105.6	107.0
torsional angles in degrees			
∠ H_1PNX	180.0	180.0	180.0
∠ H_1PNNa	0.0	0.0	0.0

Fig. 5a. Bond lengths in Å, valence and torsional angles in degrees of the H_3PNX (X = H, F, OH) obtained at the HF/6-31G*



X	H	F	OH
bond lengths in Å			
d	2.309	2.329	2.315
r	1.523	1.569	1.554
r_{PF}	1.519	1.504	1.507
r_{NX}	1.004	1.436	1.437
r_{XNa}	2.872	2.297	2.351
r_{OH_2}	/	/	0.953
r_{H_2Na}	/	/	x
valence angles in degrees			
α	128.2	184.6	x
β	117.1	104.7	110.4
δ	109.7	107.4	108.9
torsional angles in degrees			
∠ F_1PNX	180.0	180.0	180.0
∠ F_1PNNa	0.0	0.0	0.0

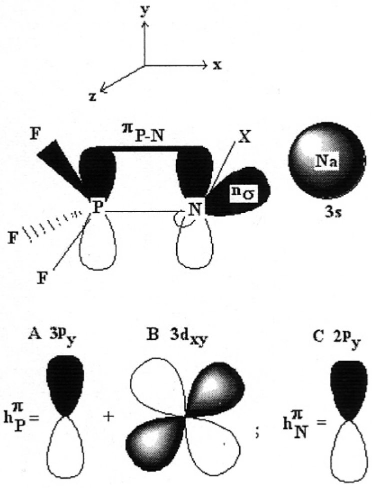
Fig. 5b. Bond lengths in Å, valence and torsional angles in degrees of the F_3PNX (X = H, F, OH) obtained at the HF/6-31G*



X	H	F	OH
$2p_{y_N}$ weight			
A	0.9994	0.9994	0.9990
n_{σ} coefficients			
ν	0.618	0.775	0.733
μ	0.635	0.602	0.608
ρ	- 0.462	- 0.192	- 0.305

$$n^{\pi}_{N} = A \cdot 2p_{y_N} \quad ; \quad n_{\sigma} = \nu \cdot (2s_N) + \mu \cdot (2p_{x_N}) + \rho \cdot (2p_{z_N})$$

Fig. 6a. Natural bond orbital of the H_3PNX with X = H, F and OH at the HF/6-31G* level



X	H	F	OH
Orbital Atomic weight			
A	0.724	0.712	0.711
B	0.672	0.695	0.675
C	0.999	0.999	0.991
$\pi_{P\text{-}N}$ coefficients			
C^{x}_{P}	0.291	0.278	0.288
C^{x}_{N}	0.957	0.961	0.958
n_{σ} coefficients			
ν	0.595	0.775	0.726
μ	0.603	0.582	0.589
ρ	- 0.530	- 0.244	- 0.353

$$\pi_{P\text{-}N} = C^{x}_{P} \cdot h^{\pi}_{P} + C^{x}_{N} \cdot h^{\pi}_{N} \qquad n_{\sigma} = \nu \cdot (2s_N) + \mu \cdot (2p_{x_N}) + \rho \cdot (2p_{z_N})$$

Fig. 6b. Natural bond orbital of the F_3PNX with X = H, F and OH at the HF/6-31G* level

The substitution of the hydrogen atom carried by the nitrogen one and by the fluorine atom, increases the P-N bonds by 0.0238 Å and opens the bond angle P-N-F (β in Fig. 5b) of 1.5°. The Na^+ ion is located at 2.28 Å of the nitrogen atom and at only 2.22 Å of the fluorine atom. This distance is shorter than that $H \cdots Na^+$ in $H_3PNH \cdots Na^+$ complex with 0.46 Å. This is due to the strong electronegativity of the fluorine atom.

The NaNF angle becomes 68.7° whereas it was equal to 109.4° to NaNH in H_3PNH. In this case, these H_1, P_2, N_3, H_4 and Na are coplanar, thus the $N \cdots Na^+$

interaction is always done on the σ level. The PNNa angle is equal to 170.3º, thus the P, N and Na atoms approach the co-linearity.

In the $F_3PNH\cdots Na^+$ complex, the bond length P-N increases by 0.0427 Å that is to say an additional lengthening of 14.5 % compared to the same distance in $H_3PNH\cdots Na^+$. The bond angle PNH narrowed only of 3º. The Na^+ cation is located at 2.31 and 2.87 Å, respectively to the nitrogen atom and the hydrogen carried by this nitrogen one. The H_1, P_2, N_3, H_4 and Na are coplanar and the $N\cdots Na^+$ interaction is always done on the σ level. The PNNa angle is equal to 128.2º, thus the P, N and Na^+ atoms are not collinear.

The substitutions of the hydrogen atoms 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 175.4º whereas it was 170.3º in $H_3PNF\cdots Na^+$. Thus, the P, N and Na atoms are quasi collinear.

The presence of the Na^+ cation in $H_3PNOH\cdots Na^+$ causes a preferential orientation with the OH group in the complex (Fig. 5). The sodium is located at 2.26 Å of N and at 2.31 Å of the oxygen atom thus forming a stable structure with a light increase of the bond length O-H about 0.009 Å. The bond angle NaNO is equal to 69.6º. The substitution of the hydrogen atoms carried by the phosphorus atom, increase the distance $N\cdots Na^+$ and $O\cdots Na^+$ from 0.056 and 0.041 Å, respectively. In all cases, the attachment of the metal cation to the favoured sites of each molecules rise to the bi-coordinated complexes as depicted in Fig. 5. For the X_3PNX molecules with X = H and F, the X_1, P_2, N_3, X_4 and Na atoms are coplanar, 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 plane and bi coordinated to the N_3 and O_4 atoms.

To determine the position of the Na^+ ion in the phosphazene-Na^+ complex, several initial geometries were investigated. The Na^+ ion bridging the N terminal of the phophazene and the X one position are considered. Though the situation of the cation-π coupling complex has been taken into account, this proves 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:

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

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.

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$^+$, in 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 (Fig. 5a and 5b).

NBO Analysis: In the Tables 4a and 4b, the molecular orbital involved in the largest energy stabilization $E^{(2)}$ by delocalization for the $H_3PNX\cdots Na^+$ and $F_3PNX\cdots Na^+$ complex when X = H, F and OH is obtained at the NBO analysis with the HF/6-31G* level were reported.

Because of the fact that the doublet π is localized on the nitrogen atom, all the interactions using the bonding and anti bonding OMπ, do not appear for H_3PNX when X = H, F and OH.

The stabilization energy by delocalization $E^{(2)}$, between the doublet σ of N and the 3s orbital of valence of Na (Table-4a) is 5.72, 2.07 and 2.98 kcal/mol for H_3PNH, H_3PNF and H_3PNOH, it is only 3.58, 1.30 and 1.79 kcal/mol for the F_3PNH, F_3PNF and F_3PNOH molecules, respectively.

TABLE-4a
RESULTS OF SECOND-ORDER PERTURBATION THEORY ANALYSIS OF THE FOCK MATRIX WITHIN THE NBO BASIS OF $H_3PNX\cdots Na^+$, WITH X = OH, H and F

Type of interaction	$H_3PN(OH)\cdots Na^+$	$H_3PN(H)\cdots Na^+$	$H_3PN(F)\cdots Na^+$
	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol
$\sigma_{(P2-N3)} \rightarrow \pi^*_{(P2-N3)}$	≤ 0.5	≤ 0.5	≤ 0.5
$\sigma_{(P2-N3)} \rightarrow \sigma^*_{(P2-H5)}$	1.01	0.94	1.08
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-N3)}$	≤ 0.5	≤ 0.5	≤ 0.5
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-H5)}$	≤ 0.5	≤ 0.5	≤ 0.5
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-H6)}$	≤ 0.5	≤ 0.5	≤ 0.5
$\sigma_{(P2-H5)} \rightarrow \sigma^*_{(P2-N3)}$	3.50	2.73	3.44
$\sigma_{(P2-H5)} \rightarrow \pi^*_{(P2-N3)}$	≤ 0.5	≤ 0.5	≤ 0.5
$\sigma_{(P2-H5)} \rightarrow \sigma^*_{(P2-H6)}$	2.96	2.92	3.01
$\sigma_{(P2-H6)} \rightarrow \pi^*_{(P2-N3)}$	≤ 0.5	≤ 0.5	≤ 0.5
$\sigma_{(P2-H6)} \rightarrow \sigma^*_{(P2-H5)}$	2.95	2.92	3.01
$N_{\sigma N} \rightarrow 3s^*_{Na}$	2.98	5.72	2.07
$N_{\pi N} \rightarrow \sigma^*_{(P2-H5)}$	17.61	19.36	17.07
$N_{\pi N} \rightarrow \sigma^*_{(P2-H6)}$	17.61	19.36	17.07
$N_{\sigma F} \rightarrow 3s^*_{Na}$	X	X	1.84
$N^{(1)}_{\sigma O} \rightarrow 3s^*_{Na}$	0.46	X	X
$N^{(2)}_{\sigma O} \rightarrow 3s^*_{Na}$	0.58	X	X

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 π and the antibonding molecular orbital $\sigma^*_{(P2-H5)}$ and $\sigma^*_{(P2-H6)}$ which are about 19.36, 17.07 and 17.61 kcal/mol, when X is H, F or OH, respectively.

TABLE-4b
RESULTS OF SECOND-ORDER PERTURBATION THEORY ANALYSIS OF THE FOCK MATRIX WITHIN THE NBO BASIS OF $F_3PNX\cdots Na^+$ (X = OH, H and F)

Type of interaction	$F_3PN(OH)\cdots Na^+$	$F_3PN(H)\cdots Na^+$	$F_3PN(F)\cdots Na^+$
	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol	$E^{(2)}$ in kcal/mol
$\sigma_{(P2-N3)} \rightarrow \pi^*_{(P2-N3)}$	5.56	≤ 0.5	≤ 0.5
$\sigma_{(P2-N3)} \rightarrow \sigma^*_{(P2-F5)}$	0.63	3.59	4.02
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-N3)}$	1.99	≤ 0.5	1.06
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-F5)}$	22.88	21.79	18.79
$\pi_{(P2-N3)} \rightarrow \sigma^*_{(P2-F6)}$	18.05	21.80	18.96
$\sigma_{(P2-F5)} \rightarrow \sigma^*_{(P2-N3)}$	≤ 0.5	1.19	1.43
$\sigma_{(P2-F5)} \rightarrow \pi^*_{(P2-N3)}$	60.02	54.51	52.64
$\sigma_{(P2-F5)} \rightarrow \sigma^*_{(P2-F6)}$	29.15	29.86	29.03
$\sigma_{(P2-F6)} \rightarrow \pi^*_{(P2-N3)}$	45.01	54.52	53.22
$\sigma_{(P2-F6)} \rightarrow \sigma^*_{(P2-F5)}$	29.45	29.86	29.02
$\sigma_{(P2-N3)} \rightarrow \sigma^*_{(P2-F6)}$	9.73	3.59	3.99
$n_{\sigma N} \rightarrow 3s^*_{Na}$	1.79	3.58	1.30
$\sigma_{(P2-N3)} \rightarrow 3s^*_{Na}$	0.17	≤ 0.5	0.21
$n_{\sigma F} \rightarrow 3s^*_{Na}$	X	X	1.25
$n^{(1)}_{\sigma O} \rightarrow 3s^*_{Na}$	0.57	X	X

For some X, in H_3PNX, the HOMO corresponds to a doublet π located on $2p_y$ atomic orbital of the nitrogen atom. Its NBO electronic population is 1.8484 e^-, 1.8693 e^- and 1.8514 e^-, respectively for X = H, F and OH. The HOMO is strongly depopulated for the profit of the NBO molecular orbital acceptors of electrons.

The doublet σ 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 atom.

The substitution of the hydrogen's carried by the phosphorus atom by fluorine ones, increases the electronic populations of the HOMO which corresponds for X = H, F and OH to the $\pi_{(P2-N3)}$ of 0.1104 e^-, 0.0948 e^- and 0.1008 e^-. Thus the population, of the doublet σ_N for X = F and OH and $\pi_{(P2-N3)}$ for X = H, F and OH, increases.

In the case or the hydrogen atoms, carried by the phosphorus ones, they are substituted by fluorine atoms: • the doublet π remains to delocalize on the two centers knowing that the phosphorus, the nitrogen and the doublet σ of the nitrogen which interacts with the Na^+ cation form a N-Na covalent bond. • decreases the stabilizing interaction $n_{\sigma N} \rightarrow 3s^*_{Na}$ (Tables 6a and 6b). • the interactions implying the OM $\sigma_{(P2-N3)}$ and $\sigma^*_{(P2-N3)}$ are largely decreased by the approach of the Na^+ cation. Whereas, the $\sigma_{(P2-F5)} \rightarrow \pi^*_{(P2-N3)}$ interaction (60.02 instead of 18.95 kcal/mol) is largely increased for $F_3PN(OH)\cdots Na^+$ and quasi-constant for the two other complexes, whereas the $\sigma_{(P2-F6)} \rightarrow \pi^*_{(P2-N3)}$ interaction remains almost constant in all the cases.

Charges analysis

Table-5 give the Mulliken obtained at the HF/6-31G*(6-311++G**) level and shows that the P-N bond is strongly polarized towards the nitrogen atom. The NBO analysis consolidates this tendency with a complete displacement of an electron of phosphorus towards nitrogen.

TABLE-5
MULLIKEN'S AND NBO CHARGES ON THE HF/6-31G* LEVEL FOR
THE X_3PNX AND $X_3PNX\cdots Na^+$ SPECIES WITH X = H, F and OH

Atoms	H_3PNH	H_3PNF	H_3PNOH	F_3PNH	F_3PNF	F_3PNOH
P	757.9 (1301.0)	772.1 (1234.2)	780.9 (1266.7)	1652.4	1696.0 (2799.9)	1685.6 (2812.7)
N	-918.8 (-1397.7)	-326.6 (-688.5)	-470.1 (-851.1)	-876.5	-263.9 (-746.9)	-416.8 (-916.6)
μ	3.373	5.553	3.745	1.515	2.892	1.124
Atoms	$H_3PNH\cdots Na^+$	$H_3PNF\cdots Na^+$	$H_3PNOH\cdots Na^+$	$F_3PNH\cdots Na^+$	$F_3PNF\cdots Na^+$	$F_3PNOH\cdots Na^+$
P	808.9 (739.1)* (1294.0)	813.4 (1231.1)	810.7 (1251.1)	1788.7 (1240.6)* (2886.5)	1812.0 (1225.0)* (2875.1)	1803.9 (1042.5)* (2885.3)
N	-1075.4 (-1001.0)* (-1551.5)	-427.2 (-784.5)	-572.7 (-949.4)	-1046.1 (-1046.4)* (-1581.5)	-381.1 (-765.6)* (-837.3)	-537.1 (-716.4)* (-1007.4)
Na	875.0 (992.0)* (982.0)	874.8 (987.6)	872.5 (984.0)	897.6 (964.9)* (989.1)	894.3 (927.9)* (991.1)	897.1 (967.9)* (989.3)
μ	12.12 (12.17)*	13.66	13.87	13.81 (14.49)*	16.66 (16.30)*	16.86 (22.91)*

(-)*Mulliken charges at the HF/6-311++G** level; (–) NBO charges.

The substitution effect of H by F and OH in H_3PNH at the HF/6-31G* level, involves a modification of the charge carried by the nitrogen atom, which causes an evident increase in the dipole moment of H_3PNF (5.55 Debye) against 3.73 D for H_3PNH and 3.75 D for H_3PNOH. The same conclusions are observed when we proceed to the same substitutions in the F_3PNH.

The passage of H_3PNX to the F_3PNX one decreases the electronic density of the phosphorus atom to the detriment of the fluorine ones more than on the nitrogen atom, thus decreasing, in all cases, the dipole moment of more than half. The charges NBO analysis leads to the same observations with a multiplication by 1.5 of all the charges.

The complexation effect of H_3PNX and F_3PNX by the Na^+ cation, does not lead, in the case of H_3PNX to a strong modification of the phosphorus charge. On the other hand, in the case of F_3PNX, the charges of P increases about 6.8 to 8.3 % and that of N of 19.4 to 44.4 %.

It is important to point out that in this case which the nitrogen atom acquires a more significant negative charge when it is connected to the Na^+ cation. The NBO charges lead to the same conclusions with a clear increase in the charge of P and N in comparison to the Mulliken charges. In addition, let us announce, that calculations, fact at the HF/6-311++G ** level, for some complexes (Table-5), lead to the same conclusions with a reduction in the charge of P and an increase in that of N. On the other hand, the effect of the Na^+ cation, multiplies by 2.5 to 3.7 the value of the dipole moment of $H_3PNX\cdots Na^+$ and about 5.8 to 15.1 that of $F_3PNX\cdots Na^+$.

Conclusion

In conclusion, this structural analysis conduces at: (a) the P-N bond lengths are shortened with increasing the electronegativity of the X substituents on the phosphorus atom, (b) the effect of the passage from H_3PNX to F_3PNX narrowed the PN bond length and opens the valence bond angle PNX, (c) the P-N bond is highly polarized with charge essentially localized and maximized at the nitrogen atom and this NBO analysis conduces to four significant remarks: (i) The P-N 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 same bond[36] in NH_2-PO_3^{2-} and shorter of about 0.067 Å compared to a double bond[21] P-N in $(Cl_2)NP(Cl_2)NPCl_3$. (ii) In all cases, for F_3PNOH, F_3PNF and F_3PNH, the h^{π}_P hybrid is formed by the linear combination of the 3d orbital of the phosphorus atom, as found in all theoretical studies[16-20] and of the 3p orbital of the same phosphorus atom. In this case, it is clear that the linear combination of the $3p_y$ and $3d_{xy}$ atomic orbital of the phosphorus atom led to an hybrid orbital of p_y symmetry which form with the $2p_y$ atomic orbital of the nitrogen atom the π bonds. (iii) In all cases, the doublet σ is localized in the nitrogen atom. These doublets are hybridized sp^2 in F_3PNOH and F_3PNH and sp in F_3PNF molecules. This justifies the values of the angles P-N-X (X = O, F) respectively in F_3PNOH and F_3PNH which are about (118.0, 108.8º) on the B3LYP/ 6-311++G** level and (117.6, 92.5º) on the HF/cc-pVTZ level. These variations are interpreted in terms of electron-pair repulsion. The doublet σ orientation in these molecules could explain the cation M^+ complexation with these molecules. (iv) It appears, in all the cases, that the 3p and 3d orbital of the phosphorus atom are combined linearly to form the π_{PN} bond, whereas this one (phosphorus) is connected to three another atoms (H or F). The natural orbital hybrids, of the phosphorus atom, given by the NBO analysis, prove that the 3d orbital is implied with the 3p and the 3s ones in $\sigma_{P\text{-}H}$ or $\sigma_{P\text{-}F}$ bonds.

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