

# Quantum-chemical study of octafluoro-spirobi[triphosphazene]

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Dedicated to Professor Vladimir Kvasnička in honor of his 80<sup>th</sup> birthday.

## Abstract

The geometries of monocharged and neutral octafluoro-spirobi[triphosphazene] in singlet, doublet and/or triplet ground spin states were optimized. Their electronic structures are investigated in terms of Quantum Theory of Atoms-in-Molecules and compared with neutral hexafluorocyclotriphosphazene. The change of the total molecular charge implies mainly the change of the properties of the nitrogen atoms which are bonded to the central spiro-phosphorus atom. The charged systems in singlet spin states have stable structures of  $D_{2d}$  symmetry only unlike the remaining ones of  $C_2$  symmetry within two geometry types. The existence of the less symmetric structures can be fully explained as a consequence of the (pseudo-) Jahn-Teller effect.

Keywords: B3LYP hybrid functional; MP2 calculations; spirobiphosphazenes; Jahn-Teller symmetry descent; group theory;

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## 1. Introduction

The phosphazene backbone formally consists of alternating single and double P–N bonds. Bonding in phosphazenes has been originally explained by Dewar's island model<sup>[1, 2]</sup> of delocalization based on out-of-plane and in-plane  $d_P-p_N$  overlapping  $\pi$  systems resulting in "islands" of electron density over P-N-P units. The break in conjugation at each phosphorus atom implies that adjacent three-centre  $\pi$  bonds need not be coplanar and that the cyclic phosphazenes are not aromatic. However, it has been shown that these  $\pi$  bonds in phosphazenes are dominated by p orbitals, although the bonding interaction between p orbitals on N atoms and d orbitals on P atoms is symmetrically forbidden in rings of  $D_{nh}$  symmetry with odd  $n$ .<sup>[3]</sup> Although the incorporation of d-orbital-type basis functions is necessary for the accurate representation of molecular orbitals, they primarily serve as computationally convenient polarization functions. According to Chaplin et al.<sup>[4]</sup> P-N ionic bonding is the dominant bonding feature in phosphazenes, although contributions from negative hyperconjugation are necessary for a more complete bonding description.

In last years, an increasing number of studies related to spirane compounds of cyclic phosphazenes may be observed in the Web of Knowledge database (8 hits in 1980-1989, 50 hits in 1990-1999, 89 hits in 2000-2009, 133 hits in 2010-2019). In these compounds the cyclophosphazene ring is bonded through its phosphorus as the central spiro atom to two atoms (usually oxygen or nitrogen) of another ring. Both rings are (nearly) perpendicular and so their  $\pi$ -electron systems are practically orthogonal. Nevertheless, no spirane compound consisting of two cyclophosphazene rings is known till now. The existence and possible synthesis of this type compounds is questionable. The composition of spirane molecules consisting of two phosphazene rings is  $N_mP_{m-1}X_{2m-4}$ , where X is a simple substituent,  $m > 2$  and in the case of spirobi[phosphazenes] the m value is even. For neutral molecules it implies an unpaired electron in the ground state (spin doublet) which indicates increased reactivity of this type compounds. On the other hand, they can serve as interesting model systems for the study of phosphazenes structure and bonding.

The aim of our study is a quantum-chemical study of the optimal geometries and corresponding electron structures of neutral and single charged octafluoro-spirobi[triphosphazene] as well as their comparison with neutral hexafluorocyclotriphosphazene. Their electron structure is compared in terms of Quantum Theory of Atoms-in-Molecules (QTAIM) topological analysis of electron density.<sup>[5]</sup>

## 2. Method

Geometries of neutral, cationic and anionic octafluoro-spirobi[triphosphazene] in singlet, doublet and/or triplet ground spin states and of neutral hexafluorocyclotriphosphazene in singlet spin state were optimized at B3LYP<sup>[6]</sup> and MP2<sup>[7-10]</sup> levels of theory using cc-pVDZ basis sets for all atoms.<sup>[11]</sup> Their stability was tested by vibrational analysis (no imaginary vibrations). Gaussian03 software<sup>[12]</sup> was used for quantum-chemical calculations. QTAIM<sup>[5]</sup> atomic volumes and charges of individual atoms were calculated by integration over their atomic basins up to 0.001 a.u. level. QTAIM bond characteristics were evaluated in terms of electron density,  $\rho$ , its Laplacian,  $\nabla^2\rho$ , given by Eq.(1)

$$\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3 \quad (1)$$

and bond ellipticity,  $\varepsilon$ , given by Eq.(2)

$$\varepsilon = \lambda_1/\lambda_2 - 1 \quad (2)$$

each calculated at bond critical points (BCP), which are defined using zero gradients and the eigenvalues  $\lambda_i$  of the Hessian of the BCP electron density within the sequence  $\lambda_1 < \lambda_2 < 0 < \lambda_3$ . The BCP electron density,  $\rho_{\text{BCP}}$ , is proportional to the bond strength; the value and sign of its BCP Laplacian,  $\nabla^2\rho_{\text{BCP}}$ , describes the relative electron density contribution of the bonded atoms to the bond (covalent vs dative bonding); its BCP bond ellipticity,  $\varepsilon_{\text{BCP}}$ , describes its deviation from cylindrical symmetry (such as in ideal single or triple bonds) due to its double-bond character, mechanical strain, and other perturbations. QTAIM analysis was performed using AIM2000 software.<sup>[13]</sup>

## 3. Results and discussion

The highest possible symmetry of octafluoro-spirobi[triphosphazene] is  $D_{2d}$ . Geometry optimization of its cation (model A1) and anion (model C) in  $^1A_1$  ground spin states lead to stable structures of this symmetry group. However, for the neutral molecule (model B1) in a  $^2A_2$  ground spin state an analogous DFT optimized structure is unstable with the e-type imaginary vibration unlike the stable MP2 one. We found a stable structure of  $C_2$  symmetry (model B2) in a  $^2B$  ground spin state at both levels of theory (Figure 1, Table 1). We were not successful in geometry optimization of an analogous cationic molecule in

a triplet ground spin state within the  $D_{2d}$  symmetry group in a  $^3E$  ground spin state and we obtained only two different stable structures of  $C_2$  symmetry (models A2 and A3) in  $^3B$  ground spin states (Figure 1, Table1). In all the above structures both cyclophosphazene rings are symmetry related (by  $C_2$  rotation) and a simplified atom notation according Figure 1 can be used whereby for the atoms in another ring a dashed notation is used. The structures of all the above model systems under study are described in Tables 2 - 4. The corresponding electron structure data in terms of QTAIM analysis is presented in Table 5.

The most electron rich anionic model C is most similar to hexafluorocyclotriphosphazene (Table 6). The central spiro phosphorus atom is unable to bind four phosphazene nitrogens so effectively and the  $P_1-N_1$  bond is longer than in hexafluorocyclotriphosphazene. On the other hand the  $N_1-P_2$  bonds in the C model are shorter than in hexafluorocyclotriphosphazene. The  $N_1$  atom is bonded to  $P_2$  more strongly than to the spiro  $P_1$  atom which is binds four nitrogens unlike the  $P_1$  one which binds only two nitrogens.

Neutral models containing one electron less have three possibilities how to bind four nitrogens to the central spiro phosphorus atom. All four P-N bonds might be equivalent as in model B1 where the single electron deficiency is uniformly distributed among four P-N bonds or alternatively one pair of P-N bonds is shorter than the remaining one. If these two shorter bonds are distributed among both phosphazene rings then the planarity of both rings is disturbed (model B2). If these two shorter bonds were on one phosphazene ring only, then the planarity of both rings would be preserved within a structure of a  $C_{4v}$  symmetry. However, this type structure was not found at neither DFT nor MP2 levels.

The model B1 geometry is very similar to the C one and the same holds for their electron structures as well. The missing electron in the B1 model is reflected in the decrease of negative  $N_1$  ( $N_2$ ) charges by 0.2 whereas the charges of remaining atoms are practically unchanged in comparison with the C model.  $N_1-P_2$  bond elongation may be ascribed to the  $N_1$  charge decrease. On the other hand, this bond ellipticity significantly decreased which indicates a lower mechanical strain in comparison with the C model. The electron depletion is reflected in little  $P_1-N_1$  bond strengthening in agreement with the theory of ionic bonding with back donation of Chaplin et al.<sup>[4]</sup> This bond is shorter with a little bit higher BCP electron density and significantly higher BCP Laplacian than in the C model.

In the B2 model the electron depletion is reflected in a single pair of  $P_1-N_1$  bonds only, this bond is substantially elongated and weakened as documented by its BCP electron density in comparison with the  $P_1-N_2$  one which almost agrees in character with the P-N bond in

hexafluorocyclotriphosphazene at both DFT and MP2 levels of theory. This change is expressed by the  $N_1$  atomic volume and charge in comparison with the  $N_2$  ones. The total energy of this conformation is lower than of the B1 model at both DFT and MP2 levels of theory. As the B1 model was unstable at the DFT level (single negative frequency) we can suppose that the B1 model of  $D_{2d}$  symmetry corresponds to a transition state between two stable B2 model configurations of  $C_2$  symmetry.

For cationic octafluoro-spirobi[triphosphazene] we have found only one stable configuration of  $D_{2d}$  symmetry in the singlet state (model A1) and two stable configurations of  $C_2$  symmetry in the triplet state (models A2 and A3). From the energetical point of view the singlet state is more stable than the triplet ones at the MP2 level whereas at the DFT level the reverse relation is valid. At the DFT level the models C, B1 and A1 of similar geometries and of the same symmetry differ in charges only and some trends in  $P_1-N_1$ ,  $P_2-N_3$  and  $P_2-F_{1a}$  bond length decrease,  $N_1-P_2$  bond length increase and other bond characteristics (BCP electron density, its Laplacian and ellipticity). These trends are not observed at MP2 level, especially in the case of the  $P_1-N_1$  bond which is elongated in the A1 model (unlike DFT) and is even longer than in the C model (Tables 3 and 4).

In triplet models A2 and A3 no such substantial trend differences between DFT and MP2 levels are observed. The A2 model represents the geometry where all  $P_1-N_1$  bond lengths are equivalent but its symmetry is lower ( $C_2$  symmetry group) as the phosphazene rings are non-planar.  $P_1-N_1$  and  $N_1-P_2$  bond lengths are practically equal as in the A1 model as well as all other characteristics except the BCP electron density Laplacian which is in the case of the  $P_1-N_1$  bond higher at MP2 level.

The A3 model comprises the B2 one without a single electron which reflects in increasing differences between  $P_1-N_1$  and  $P_1-N_2$  bond lengths, in an increased non-planarity of phosphazene rings (the torsion angle  $P_1-P_3-P_2-N_1$  is of ca  $16^\circ$  at DFT and of ca  $19^\circ$  at MP2 levels), in overall lengthening of the bonds between the central spiro-phosphorus atom and neighboring nitrogens, in their weakening (BCP electron density decrease) and in lowered polarity of these bonds. On the other hand, the bonds between phosphorus and fluorine atoms are shortened, their strength and polarity increase (increasing BCP electron density and of its Laplacian).

Model geometries obtained at DFT and MP2 levels exhibit, in general, similar trends. The bond lengths in model C are practically equal at both levels (Tables 3 and 4) unlike

remaining models (A1 – A3, B1 – B2). The greatest differences can be observed especially in the bond lengths between the central spiro-phosphorus atom and neighboring nitrogens where the effects of unpaired electrons are concentrated as the spin density is located exclusively at N<sub>1</sub> and N<sub>2</sub> atoms. This is the case of A3 and B2 models of C<sub>2</sub> symmetry where the P<sub>1</sub>-N<sub>1</sub> bonds are longer than the P<sub>1</sub>-N<sub>2</sub> ones. This difference is much higher at MP2 than at DFT level withal the P<sub>1</sub>-N<sub>1</sub> bonds are longer and the P<sub>1</sub>-N<sub>2</sub> ones shorter at the MP2 level.

QTAIM topological analysis of electron density confirmed the differences between DFT and MP2 treatments as well. BCP electron density was very similar at both levels of theory except the above mentioned differences in A3 and B2 model geometries where the P<sub>1</sub>-N<sub>1</sub> bond elongation at MP2 level causes its BCP electron density decrease and, on the contrary, the P<sub>1</sub>-N<sub>2</sub> bond shortening at MP2 level causes its BCP electron density increase. Generally much higher bond polarity may be observed, especially between N and P atoms, as indicated by increasing BCP electron density Laplacians and higher charge differences between atoms at MP2 level. If focussing on bond angles in the optimized structures, some trends might be noticed. Bond angles N<sub>1</sub>-P<sub>1</sub>-N<sub>2</sub> and F-P-F decrease with the increasing negative charge of spirobi[phosphazene]. The F-P-F bond angle decrease might be explained by increasing P-F bond lengths with the increasing negative charge (due to electrostatic repulsion) which spacially enables the F-P-N angle to be lower. Similarly the N<sub>3</sub>-P-F angle decrease with increasing negative charge of the whole molecule might be explained as well.

An alternative explanation of the above non-planarity and of the lower symmetry of the systems under study in general is based on the Jahn-Teller effect.<sup>[14]</sup> Cationic A1 and anionic C model systems with electron configurations ...(*e*)<sup>4</sup>(*a*<sub>2</sub>)<sup>0</sup> and ...(*e*)<sup>4</sup>(*a*<sub>2</sub>)<sup>2</sup>, respectively, which correspond to the non-degenerate <sup>1</sup>A<sub>1</sub> electron state (Table 1), are Jahn-Teller stable. An analogous cationic system of D<sub>2d</sub> symmetry in the triplet spin state with the electron configuration ...(*e*)<sup>3</sup>(*a*<sub>2</sub>)<sup>1</sup> corresponds to the degenerate <sup>3</sup>E electron state which is Jahn-Teller unstable and implies a symmetry decrease.

The method of epikernel principle<sup>[15-17]</sup> predicts the symmetry descent to Jahn-Teller stable structures using Jahn-Teller active coordinates. Their symmetries are determined by the symmetric direct product

$$[E \otimes E]^+ = A_1 \oplus B_1 \oplus B_2 \quad (3)$$

The full-symmetric *a*<sub>1</sub> coordinate does not change the parent D<sub>2d</sub> symmetry whereas the non-degenerate *b*<sub>1</sub> and *b*<sub>2</sub> coordinates cause the symmetry descent to the kernel groups  $K(D_{2d}, b_1) =$

$D_2$  and  $K(D_{2d}, b_2) = C_{2v}$ , respectively, which are Jahn-Teller stable as they contain no two-dimensional irreducible representations. Unfortunately, this method does not explain the existence of stable A2 and A3 model systems of  $C_2$  symmetry (Table 1).

The method of step-by-step symmetry descent<sup>[18-25]</sup> is based on consecutive splitting of degenerate electron states. Two-dimensional E representation (electron state) of  $D_{2d}$  group is split by symmetry descent to its immediate subgroups  $D_2$  and  $C_{2v}$  into  $B_2 \oplus B_3$  and  $B_1 \oplus B_2$  non-degenerate representations, respectively, which are Jahn-Teller stable, or remains degenerate in its immediate subgroup  $S_4$ . Therefore the  $S_4$  group is Jahn-Teller unstable and the symmetry descent continues to its immediate subgroup  $C_2$  which is Jahn-Teller stable as the original E electron state is split into two non-degenerate B electron states in agreement with our results of the geometry optimization (Table 1). During this symmetry descent either  $C_2(z)$  or  $C_2'$  rotation axes may be preserved which implies two various stable structures of the  $C_2$  symmetry.

More complex problem of neutral spirobi[triphosphazene], where the  $D_{2d}$  structure with the electron configuration  $...(e)^4(a_2)^1$  corresponding to the  ${}^2A_2$  electron state is stable at the MP2 level only, can be explained by the pseudo-Jahn-Teller effect. The 1<sup>st</sup> excited state with the electron configuration  $...(e)^3(a_2)^2$  corresponds to the degenerate  ${}^2E$  electron state. Its interaction with the ground state, which might be stronger at the DFT level than at the MP2 one, destabilizes the  $D_{2d}$  structure (B1 model). According to Bersuker<sup>[26]</sup> this interaction must be sufficiently strong to destabilize the high symmetric structure. The above mentioned method of epikernel principle can be used for pseudo-Jahn-Teller systems as well.<sup>[27]</sup> The symmetry of the Jahn-Teller active coordinates in this case can be determined by the symmetric direct product

$$[(A_2 \oplus E) \otimes (A_2 \oplus E)]^+ = 2 A_1 \oplus B_1 \oplus B_2 \oplus E \quad (4)$$

As mentioned above, the Jahn-Teller active coordinates of  $b_1$  and  $b_2$  symmetries imply Jahn-Teller stable  $D_2$  and  $C_{2v}$  structures, respectively. The epikernel groups  $E(D_{2d}, e)$  of  $C_2$  (with preserved  $C_2'$  axis) or  $C_s$  symmetries explain the existence of the B2 structure. The Jahn-Teller active coordinate of the e symmetry coincides with the e-type imaginary vibration of the B1 model at the DFT level. Alternatively, the B2 structure might be explained by the hidden Jahn-Teller effect<sup>[28, 29]</sup>, i.e. a huge Jahn-Teller effect in the excited E state which is formally equal as in the case of the above mentioned cationic triplet models.

The obtained results of DFT and MP2 calculations of spirobi[phosphazene] qualitatively confirm the recent conception of the electron structure of phosphazenes, especially the model of ionic bonding with back donation.<sup>[4]</sup> Perturbed planarity of the phosphazene ring was observed in the systems with unpaired electrons which might be caused by hyperconjugation weakening in electron-depleted orbitals forming P-N bonds. Subsequent weakening and elongation of this bond caused the phosphazene ring nonplanarity.

#### 4. Conclusions

Our results on the electronic structure of spirobi[phosphazenes] confirmed the theory of ionic bonding with back donation of Chaplin et al.<sup>[4]</sup> The QTAIM analysis implies that the change of the total spirobi[phosphazene] charge becomes evident mainly in the change of the properties of the nitrogen atoms which are bonded to the central spiro-phosphorus atom (see bold data in Tables 4 - 5). High symmetric  $D_{2d}$  structures are stable for the charged systems in full symmetric singlet state only. The electron structure of other octafluoro-spirobi[phosphazene] systems makes suppositions for the stable structures of lower symmetries despite we have found the  $C_2$  ones only. Their existence can be fully explained as a consequence of the (pseudo-) Jahn-Teller effect.

It might be expected that our results are of more general validity. Further theoretical studies including the investigation of spirobiphosphazenes with other substituents as well as the use of other quantum-chemical methods are necessary to fully explain the spirobiphosphazenes bonding as well.

Declarations of interest

None.

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Table 1. Total charges, symmetries, spin states and total energies at DFT and MP2 levels of theory of optimized geometries of various models of octafluoro-spirobi[triphosphazene] under study.

Model	Total charge	Symmetry	Spin state	Total energy [Hartree]	
				DFT	MP2
A1	+1	$D_{2d}$	$^1A_1$	-2833.96161	-2828.85171
A2	+1	$C_2$	$^3B$	-2833.97839	-2828.80231
A3	+1	$C_2$	$^3B$	-2833.98000	-2828.80484
B1	0	$D_{2d}$	$^2A_2$	-2834.33487	-2829.17235
B2	0	$C_2$	$^2B$	-2834.34128	-2829.17937
C	-1	$D_{2d}$	$^1A_1$	-2834.52930	-2829.15747

Table 2. Bond lengths  $d$ , BCP electron densities  $\rho_{\text{BCP}}$ , their Laplacians  $\nabla^2\rho_{\text{BCP}}$  and ellipticities  $\epsilon_{\text{BCP}}$  of the octafluoro-spirobi[triphosphazene] systems under study evaluated at the DFT level of theory.

Model	Symmetry	Bond	$d$ [Å]	$\rho_{\text{BCP}}$ [e/bohr <sup>3</sup> ]	$\nabla^2\rho_{\text{BCP}}$ [e/bohr <sup>5</sup> ]	$\epsilon_{\text{BCP}}$
A1	$D_{2d}$	P <sub>1</sub> –N <sub>1</sub>	1.646	0.172	0.712	0.004
		N <sub>1</sub> –P <sub>2</sub>	1.663	0.174	0.579	0.015
		P <sub>2</sub> –N <sub>3</sub>	1.592	0.191	0.866	0.044
		P <sub>2</sub> –F <sub>1a</sub>	1.573	0.156	0.931	0.028
A2	$C_2$	P <sub>1</sub> –N <sub>1</sub>	1.654	0.171	0.656	0.037
		N <sub>1</sub> –P <sub>2</sub>	1.650	0.177	0.632	0.009
		P <sub>2</sub> –N <sub>3</sub>	1.600	0.188	0.835	0.043
		P <sub>2</sub> –F <sub>1a</sub>	1.576	0.155	0.909	0.028
		P <sub>2</sub> –F <sub>1b</sub>	1.569	0.157	0.954	0.024
A3	$C_2$	P <sub>1</sub> –N <sub>1</sub>	1.704	0.159	0.496	0.044
		P <sub>1</sub> –N <sub>2</sub>	1.618	0.181	0.782	0.030
		N <sub>1</sub> –P <sub>2</sub>	1.674	0.170	0.551	0.026
		N <sub>2</sub> –P <sub>3</sub>	1.616	0.185	0.767	0.038
		P <sub>2</sub> –N <sub>3</sub>	1.582	0.194	0.916	0.062
		P <sub>3</sub> –N <sub>3</sub>	1.622	0.181	0.742	0.034
		P <sub>2</sub> –F <sub>1a</sub>	1.578	0.155	0.896	0.022
		P <sub>2</sub> –F <sub>1b</sub>	1.566	0.158	0.971	0.019
		P <sub>3</sub> –F <sub>2a</sub>	1.573	0.156	0.930	0.028
		P <sub>3</sub> –F <sub>2b</sub>	1.575	0.155	0.918	0.030
B1	$D_{2d}$	P <sub>1</sub> –N <sub>1</sub>	1.654	0.170	0.659	0.001
		N <sub>1</sub> –P <sub>2</sub>	1.614	0.187	0.763	0.033
		P <sub>2</sub> –N <sub>3</sub>	1.603	0.188	0.816	0.061
		P <sub>2</sub> –F <sub>1a</sub>	1.592	0.149	0.833	0.030
B2	$C_2$	P <sub>1</sub> –N <sub>1</sub>	1.699	0.158	0.513	0.048
		P <sub>1</sub> –N <sub>2</sub>	1.623	0.180	0.747	0.054
		N <sub>1</sub> –P <sub>2</sub>	1.644	0.181	0.634	0.009
		N <sub>2</sub> –P <sub>3</sub>	1.590	0.193	0.865	0.068
		P <sub>2</sub> –N <sub>3</sub>	1.590	0.192	0.876	0.071
		P <sub>3</sub> –N <sub>3</sub>	1.619	0.183	0.758	0.049
		P <sub>2</sub> –F <sub>1a</sub>	1.592	0.149	0.832	0.029
		P <sub>2</sub> –F <sub>1b</sub>	1.591	0.149	0.838	0.026
		P <sub>3</sub> –F <sub>2a</sub>	1.594	0.149	0.822	0.031
		P <sub>3</sub> –F <sub>2b</sub>	1.592	0.149	0.836	0.032
C	$D_{2d}$	P <sub>1</sub> –N <sub>1</sub>	1.665	0.167	0.597	0.003
		N <sub>1</sub> –P <sub>2</sub>	1.574	0.198	0.944	0.112
		P <sub>2</sub> –N <sub>3</sub>	1.616	0.185	0.766	0.080
		P <sub>2</sub> –F <sub>1a</sub>	1.617	0.141	0.715	0.035

Table 3. Bond lengths  $d$ , BCP electron densities  $\rho_{\text{BCP}}$ , their Laplacians  $\nabla^2\rho_{\text{BCP}}$  and ellipticities  $\epsilon_{\text{BCP}}$  of the octafluoro-spirobi[triphosphazene] systems under study evaluated at the MP2 level of theory.

Model	Symmetry	Bond	$d$ [Å]	$\rho_{\text{BCP}}$ [e/bohr <sup>3</sup> ]	$\nabla^2\rho_{\text{BCP}}$ [e/bohr <sup>5</sup> ]	$\epsilon_{\text{BCP}}$
A1	$D_{2d}$	P <sub>1</sub> –N <sub>1</sub>	1.675	0.166	0.683	0.041
		N <sub>1</sub> –P <sub>2</sub>	1.676	0.173	0.622	0.005
		P <sub>2</sub> –N <sub>3</sub>	1.593	0.193	0.919	0.040
		P <sub>2</sub> –F <sub>1a</sub>	1.572	0.154	1.017	0.016
A2	$C_2$	P <sub>1</sub> –N <sub>1</sub>	1.651	0.173	0.754	0.071
		N <sub>1</sub> –P <sub>2</sub>	1.658	0.177	0.678	0.016
		P <sub>2</sub> –N <sub>3</sub>	1.597	0.192	0.909	0.048
		P <sub>2</sub> –F <sub>1a</sub>	1.575	0.153	1.001	0.015
		P <sub>2</sub> –F <sub>1b</sub>	1.566	0.156	1.045	0.012
A3	$C_2$	P <sub>1</sub> –N <sub>1</sub>	1.735	0.151	0.500	0.056
		P <sub>1</sub> –N <sub>2</sub>	1.605	0.188	0.884	0.029
		N <sub>1</sub> –P <sub>2</sub>	1.705	0.165	0.538	0.053
		N <sub>2</sub> –P <sub>3</sub>	1.609	0.188	0.861	0.050
		P <sub>2</sub> –N <sub>3</sub>	1.569	0.202	1.019	0.074
		P <sub>3</sub> –N <sub>3</sub>	1.621	0.182	0.823	0.030
		P <sub>2</sub> –F <sub>1a</sub>	1.574	0.153	1.002	0.012
		P <sub>2</sub> –F <sub>1b</sub>	1.564	0.157	1.057	0.009
		P <sub>3</sub> –F <sub>2a</sub>	1.574	0.153	1.006	0.016
		P <sub>3</sub> –F <sub>2b</sub>	1.572	0.153	1.021	0.017
B1	$D_{2d}$	P <sub>1</sub> –N <sub>1</sub>	1.656	0.169	0.746	0.024
		N <sub>1</sub> –P <sub>2</sub>	1.618	0.189	0.816	0.031
		P <sub>2</sub> –N <sub>3</sub>	1.603	0.191	0.877	0.057
		P <sub>2</sub> –F <sub>1a</sub>	1.590	0.146	0.929	0.016
B2	$C_2$	P <sub>1</sub> –N <sub>1</sub>	1.704	0.155	0.590	0.099
		P <sub>1</sub> –N <sub>2</sub>	1.619	0.184	0.821	0.067
		N <sub>1</sub> –P <sub>2</sub>	1.649	0.183	0.690	0.024
		N <sub>2</sub> –P <sub>3</sub>	1.596	0.196	0.888	0.065
		P <sub>2</sub> –N <sub>3</sub>	1.589	0.196	0.933	0.068
		P <sub>3</sub> –N <sub>3</sub>	1.617	0.185	0.834	0.047
		P <sub>2</sub> –F <sub>1a</sub>	1.589	0.147	0.933	0.013
		P <sub>2</sub> –F <sub>1b</sub>	1.589	0.147	0.935	0.011
		P <sub>3</sub> –F <sub>2a</sub>	1.592	0.146	0.922	0.016
		P <sub>3</sub> –F <sub>2b</sub>	1.589	0.146	0.936	0.017
C	$D_{2d}$	P <sub>1</sub> –N <sub>1</sub>	1.662	0.168	0.694	0.002
		N <sub>1</sub> –P <sub>2</sub>	1.575	0.201	0.985	0.113
		P <sub>2</sub> –N <sub>3</sub>	1.615	0.188	0.833	0.073
		P <sub>2</sub> –F <sub>1a</sub>	1.614	0.137	0.821	0.017

Table 4. Bond angles (in degrees) in the octafluoro-spirobi[triphosphazene] systems under study.

Model	A1	A2	A3	B1	B2	C
DFT method						
N <sub>1</sub> -P <sub>1</sub> -N <sub>2</sub>	115.9	116.5	113.6	114.4	114.9	113.0
P <sub>1</sub> -N <sub>2</sub> -P <sub>3</sub>	121.7	119.1	122.3	122.1	120.6	122.5
N <sub>2</sub> -P <sub>3</sub> -N <sub>3</sub>	119.9	117.0	119.1	122.0	121.5	123.6
P <sub>3</sub> -N <sub>3</sub> -P <sub>2</sub>	120.9	122.0	121.4	117.4	118.7	114.8
N <sub>3</sub> -P <sub>2</sub> -N <sub>1</sub>	119.9	116.9	113.4	122.0	121.2	123.6
P <sub>2</sub> -N <sub>1</sub> -P <sub>1</sub>	121.7	119.1	118.2	122.1	117.6	122.5
N <sub>1</sub> -P <sub>1</sub> -N <sub>1</sub> '	<b>106.4</b>	<b>109.5</b>	<b>102.5</b>	<b>107.1</b>	<b>93.5</b>	<b>107.7</b>
N <sub>1</sub> -P <sub>1</sub> -N <sub>2</sub> '	<b>106.4</b>	<b>102.8</b>	<b>104.9</b>	<b>107.1</b>	<b>111.1</b>	<b>107.7</b>
N <sub>2</sub> -P <sub>1</sub> -N <sub>1</sub> '	<b>106.4</b>	<b>109.5</b>	<b>116.5</b>	<b>107.1</b>	<b>110.5</b>	<b>107.7</b>
N <sub>2</sub> -P <sub>1</sub> -N <sub>2</sub> '	<b>106.4</b>	<b>102.8</b>	<b>104.9</b>	<b>107.1</b>	<b>111.1</b>	<b>107.7</b>
F <sub>1a</sub> -P <sub>2</sub> -F <sub>1b</sub>	101.8	101.4	101.3	98.3	98.5	94.7
F <sub>2b</sub> -P <sub>23</sub> -F <sub>2b</sub>	101.8	101.4	101.1	98.3	97.5	94.7
F <sub>1a</sub> -P <sub>2</sub> -N <sub>3</sub>	110.9	111.4	115.2	108.8	110.2	106.8
F <sub>1b</sub> -P <sub>2</sub> -N <sub>3</sub>	110.9	109.9	111.1	108.8	110.3	106.8
F <sub>2a</sub> -P <sub>3</sub> -N <sub>3</sub>	110.9	109.9	108.0	108.8	107.0	106.8
F <sub>2b</sub> -P <sub>3</sub> -N <sub>3</sub>	110.9	111.4	108.6	108.8	107.7	106.8
MP2 method						
N <sub>1</sub> -P <sub>1</sub> -N <sub>2</sub>	120.0	118.9	110.4	115.9	116.3	113.8
P <sub>1</sub> -N <sub>2</sub> -P <sub>3</sub>	118.1	116.5	122.4	120.8	117.2	121.9
N <sub>2</sub> -P <sub>3</sub> -N <sub>3</sub>	120.6	116.5	119.1	122.4	121.8	124.0
P <sub>3</sub> -N <sub>3</sub> -P <sub>2</sub>	122.6	122.2	122.0	117.5	119.1	114.5
N <sub>3</sub> -P <sub>2</sub> -N <sub>1</sub>	120.6	116.5	114.7	122.4	121.2	124.0
P <sub>2</sub> -N <sub>1</sub> -P <sub>1</sub>	118.1	116.5	114.9	120.8	114.5	121.9
N <sub>1</sub> -P <sub>1</sub> -N <sub>1</sub> '	<b>104.5</b>	<b>111.1</b>	<b>101.8</b>	<b>106.4</b>	<b>88.2</b>	<b>107.4</b>
N <sub>1</sub> -P <sub>1</sub> -N <sub>2</sub> '	<b>104.5</b>	<b>99.0</b>	<b>104.4</b>	<b>106.4</b>	<b>112.0</b>	<b>107.4</b>
N <sub>2</sub> -P <sub>1</sub> -N <sub>1</sub> '	<b>104.5</b>	<b>111.1</b>	<b>123.5</b>	<b>106.4</b>	<b>110.6</b>	<b>107.4</b>
N <sub>2</sub> -P <sub>1</sub> -N <sub>2</sub> '	<b>104.5</b>	<b>99.0</b>	<b>104.4</b>	<b>106.4</b>	<b>112.0</b>	<b>107.4</b>
F <sub>1a</sub> -P <sub>2</sub> -F <sub>1b</sub>	102.1	101.5	101.5	98.5	98.7	94.8
F <sub>2b</sub> -P <sub>23</sub> -F <sub>2b</sub>	102.1	101.5	100.9	98.5	98.1	94.8
F <sub>1a</sub> -P <sub>2</sub> -N <sub>3</sub>	110.7	111.8	116.3	108.6	110.2	106.7
F <sub>1b</sub> -P <sub>2</sub> -N <sub>3</sub>	110.7	110.3	112.4	108.6	110.4	106.7
F <sub>2a</sub> -P <sub>3</sub> -N <sub>3</sub>	110.7	110.3	108.1	108.6	106.8	106.7
F <sub>2b</sub> -P <sub>3</sub> -N <sub>3</sub>	110.7	111.9	108.0	108.6	107.8	106.7



Table 5. QTAIM atomic volumes  $V$  [bohr<sup>3</sup>] and charges  $q$  of the octafluoro-spirobi[triposphazene] systems under study.

Model	A1		A2		A3		B1		B2		C	
	V	q	V	q	V	q	V	q	V	q	V	q
DFT method												
P <sub>1</sub>	31.6	3.49	31.8	3.45	32.3	3.44	34.6	3.46	31.7	3.45	32.1	3.46
N <sub>1</sub>	<b>125.7</b>	<b>-1.70</b>	<b>125.7</b>	<b>-1.72</b>	<b>121.6</b>	<b>-1.51</b>	<b>129.0</b>	<b>-1.88</b>	<b>124.3</b>	<b>-1.71</b>	<b>132.9</b>	<b>-2.06</b>
P <sub>2</sub>	31.5	3.52	31.1	3.52	31.5	3.51	31.4	3.52	31.2	3.53	32.8	3.49
N <sub>2</sub>	<b>125.7</b>	<b>-1.70</b>	<b>125.7</b>	<b>-1.72</b>	<b>130.0</b>	<b>-1.94</b>	<b>129.0</b>	<b>-1.88</b>	<b>131.8</b>	<b>-2.04</b>	<b>132.9</b>	<b>-2.06</b>
P <sub>3</sub>	31.5	3.52	31.1	3.52	30.9	3.54	31.4	3.52	32.2	3.49	32.8	3.49
N <sub>3</sub>	130.7	-2.02	129.2	-1.97	129.2	-1.96	131.1	-2.03	130.7	-2.02	131.5	-2.04
F <sub>1a</sub>	102.2	-0.71	102.1	-0.72	103.1	-0.71	103.6	-0.74	103.4	-0.74	104.3	-0.77
F <sub>1b</sub>	102.2	-0.71	102.8	-0.72	103.0	-0.72	103.6	-0.74	103.7	-0.75	104.3	-0.77
F <sub>2a</sub>	102.2	-0.71	102.1	-0.72	103.1	-0.71	103.6	-0.74	103.4	-0.74	104.3	-0.77
F <sub>2b</sub>	102.2	-0.71	102.8	-0.72	103.0	-0.72	103.6	-0.74	103.7	-0.75	104.3	-0.77
MP2 method												
P <sub>1</sub>	27.7	3.66	24.5	3.72	26.0	3.72	25.0	3.75	24.5	3.73	23.9	3.77
N <sub>1</sub>	132.6	-1.81	128.9	-1.84	121.6	-1.46	133.8	-2.04	124.9	-1.85	138.7	-2.24
P <sub>2</sub>	23.9	3.82	23.7	3.83	24.0	3.81	23.7	3.82	23.8	3.83	24.2	3.82
N <sub>2</sub>	132.6	-1.81	128.9	-1.84	137.8	-2.22	133.8	-2.04	137.4	-2.21	138.7	-2.24
P <sub>3</sub>	23.9	3.82	23.7	3.83	23.2	3.85	23.7	3.82	23.8	3.81	24.2	3.82
N <sub>3</sub>	136.5	-2.20	136.1	-2.19	136.3	-2.19	136.6	-2.21	136.5	-2.21	137.1	-2.22
F <sub>1a</sub>	102.1	-0.79	102.1	-0.78	103.9	-0.78	103.9	-0.81	103.8	-0.80	103.8	-0.83
F <sub>1b</sub>	102.1	-0.79	102.8	-0.79	102.3	-0.79	103.9	-0.81	104.2	-0.81	103.8	-0.83
F <sub>2a</sub>	102.1	-0.79	102.1	-0.78	102.1	-0.78	103.9	-0.81	103.7	-0.80	103.8	-0.83
F <sub>2b</sub>	102.1	-0.79	102.8	-0.79	103.3	-0.79	103.9	-0.81	104.0	-0.81	103.8	-0.83

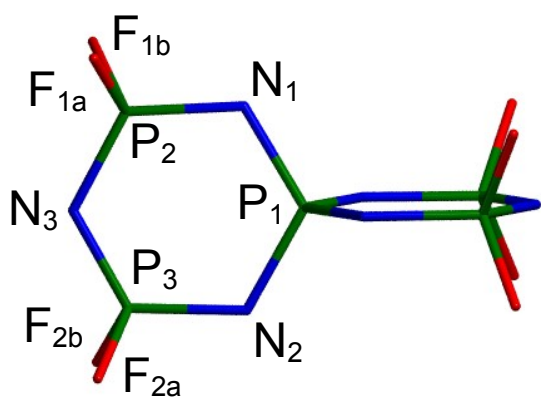
Table 6. QTAIM atomic volumes  $V$  and charges  $q$ , bond lengths  $d$ , BCP electron densities  $\rho_{\text{BCP}}$ , their Laplacians  $\nabla^2\rho_{\text{BCP}}$  and ellipticities  $\epsilon_{\text{BCP}}$  in hexafluorocyclotriphosphazene optimal geometry.

Atóm	$V$ [bohr <sup>3</sup> ]	$q$	Bond	$d$ [Å]	$\rho_{\text{BCP}}$ [e/bohr <sup>3</sup> ]	$\nabla^2\rho_{\text{BCP}}$ [e/bohr <sup>5</sup> ]	$\epsilon_{\text{BCP}}$
DFT method							
P	30.7	3.53	P – N	1.604	0.188	0.817	0.066
N	131.7	-2.04	P – F	1.593	0.149	0.832	0.034
F	103.5	-0.75					
MP2 method							
P	22.6	3.84	P – N	1.602	0.191	0.886	0.061
N	136.5	-2.22	P – F	1.591	0.146	0.927	0.019
F	103.7	-0.81					

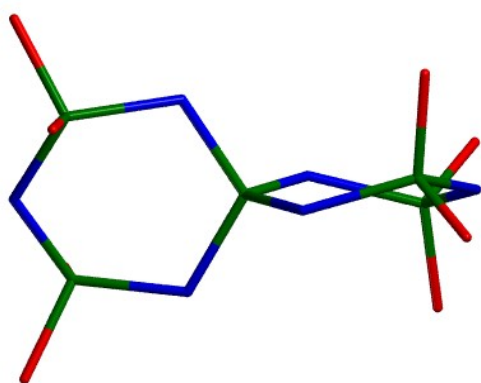
Figure captions:

Figure 1. Optimized structures of octafluoro-spirobi[triphosphazene] systems under study with atom notation.

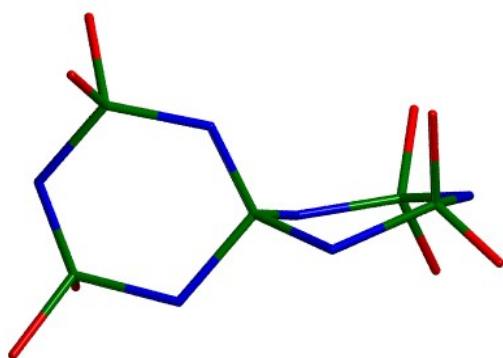
Fig. 1



$D_{2d}$  group (A1, B1, C models)



$C_2$  group (A2 model)



$C_2$  group (A3, B2 models)

