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On non-planarity of cyclotetraphosphazenes

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In the memory of Dr. Imrich Vrábel, PhD (1970–2001)

Abstract

Using MP2/cc-pVDZ treatment, the optimal conformations of simple cyclotetraphosphazenes, cyclo-$(NPX_2)_4$ for X = H, F and Cl, were investigated. The most stable structures correspond to D_{2d} symmetry for all the compounds under study. Their stabilization energies have the same trend as the X electronegativities. Only C_{4v}, D_{2d} and two different C_{2h} stable cyclo-$(NPH_2)_4$ structures have been found. For X = F, the number of stable conformers is reduced to D_{2d} and C_{2h} (II) only. For X = Cl, only C_{4v}, D_{2d} and C_{2h}(I) stable structures have been found. The deviations of electronic structure characteristics from the D_{4h} conformation ones are very small.

Keywords: MP2 method; Geometry optimization; Cyclic phosphazenes; Stable non-planar conformations; Electronic structures

1. Introduction

The most common subjects of ab initio theoretical studies are small cyclic phosphazenes, cyclo-$(NPX_2)_n$ with X = H or halogen [1–11] performed at Hartree–Fock or DFT level of theory (the only exception is the MP2 study on hexachlorocyclotriphosphazene and similar heterocyclic rings [8]). The greatest deal of these studies is restricted to species with planar phosphazene rings [1–8]. This assumption is true for cyclo-$(NPX_2)_n$ with $n = 2$ and 3, but their higher analogues may be non-planar. Really, full geometry optimizations (without any symmetry restrictions) carried out for this series molecules with $n = 4$, 5 and 6 resulted in a variety of non-planar structures [9,11]. Whereas the N–P–N angle remains almost constant, the P–N–P angle opens considerably with increasing ring size, n. The X–P–X angle varies largely depending on the size and electronegativity of X but the ring size appears not to have a significant influence on this angle [10,11].

Nevertheless, some controversy still remains. According to Enlow [11], the symmetry of the optimized geometry of cyclo-$(NPX_2)_4$ is dependent on the identity of X. When X = F, a D_{4h} conformation with a planar P–N backbone is obtained (Fig. 1). Puckering within C_{4v} symmetry (Fig. 2) is not supported. When X = H or Cl, a D_{2d} conformation is obtained (Fig. 3) with nitrogen atoms alternating above and below the four phosphorus atoms plane (ca. 0.4 Å for X = H and ca. 0.2 Å for X = Cl, respectively). On the other hand, Elias et al. [9] have obtained non-planar S_4 geometry for X = F (with nitrogen atoms deviations from the ring plane of ca. 0.2 Å at HF level and ca. 0.4 Å at B3LYP level, respectively).

Early X-ray structure data [12] on room temperature structure of cyclo-$(NPF_2)_4$ propose a perfectly planar structure of this compound. Based on infrared and Raman spectral calculations [13,14], a non-planar structure with a symmetry of C_{2h} or lower has been assigned. This structure has been recently re-determined [9] by using X-ray diffraction, gas electron diffraction (GED) and differential scanning calorimetry. Their results support a puckered S_4 structure that undergoes a phase transition at ca. −74 °C (Table 1). The high temperature phase contains two individual sites related by a center of inversion. The unit cells of the high and low temperature modifications are closely related (doubling the c axis and removing one-half of the symmetry elements under phase transition temperature). In the gas-phase structure, the most probable D_{2d} and S_4

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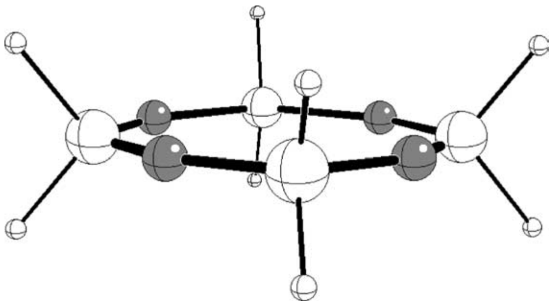

Fig. 1. Structure of planar cyclotetraphosphazenes (D_{4h} symmetry).

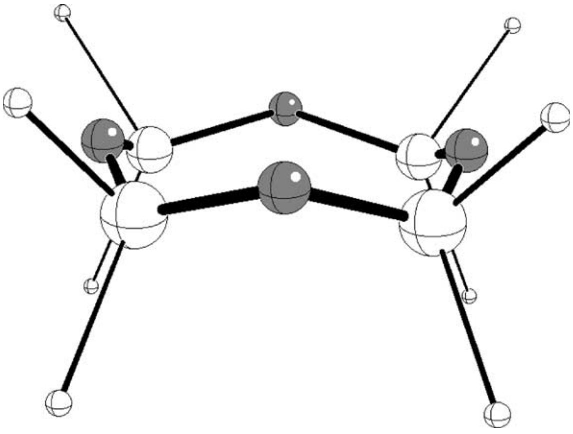

Fig. 2. Structure of the crown form of cyclotetraphosphazenes (C_{4v} symmetry).

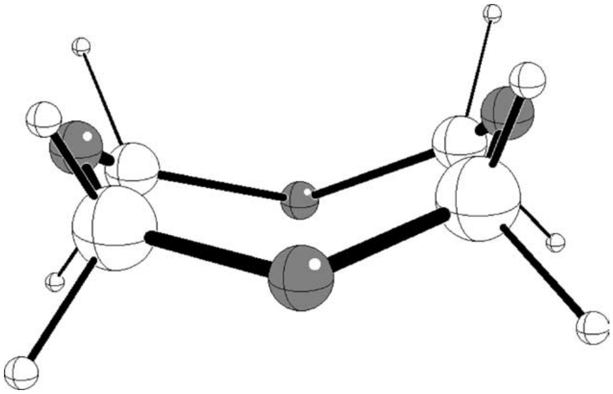

Fig. 3. Structure of the boat form of cyclotetraphosphazenes (D_{2d} symmetry).

structures are indistinguishable within the experimental uncertainty (see Table 1).

Two crystal modifications of cyclo-$(NPCl_2)_4$, generally called the K and the T form, are known (Table 1). At room temperature, the chair-shaped T form of C_i symmetry (approximated to C_{2h}, Fig. 4) is the stable modification [15]. Its unit cell is twice as large as that of the K form [16] with boat-shaped molecules of S_4 symmetry (approximated to D_{2d}, Fig. 3).

The aim of this study is a systematic search for possible non-planar conformations of the simplest cyclic tetraphosphazenes, cyclo-$(NPX_2)_4$ with X = H, F and Cl, using quantum-chemistry treatment. It is probable

Table 1
Selected experimental structure data on cyclo-$(NPX_2)_4$

X	F			Cl	
Symmetry	X-ray [9] S_4	GED [9] S_4 or D_{2d}	X-ray [9] Chair/saddle	X-ray [15] C_i (T form)	X-ray [16] S_4 (K form)
Temperature (K)	172(2)	RT	232(2)	RT	RT
Distances (10^{-10} m)					
P–N	1.543(2)	1.520(5)	1.591(6)/1.490(7)	1.56(1)	1.570(9)
			1.470(5)/1.623(7)		1.569(9)
			1.530(5)/1.557(7)		
			1.610(6)/1.460(6)		
P–X	1.524(1)	1.554(5)	1.508(2)	1.989(4)	1.985(4)
			1.518(2)	1.988(4)	1.993(4)
			1.508(2)	1.990(4)	
			1.508(2)	2.002(4)	
Δ_{plane}	0.170	0.23(7)	0.202/0.187	0.218	0.447
Angles (°)					
N–P–N	123.2(2)	122.9(10)	125.5(3)/121.8(3)	119.3(7)	121.2(5)
			121.3(3)/119.3(4)	121.7(7)	
P–N–P	140.4(1)	141.2(9)	136.8(5)/144.4(5)	133.6(8)	131.3(6)
			143.1(5)/142.8(6)	137.6(8)	
X–P–X	99.3(7)	98.0(6)	98.1(13)	103.3(2)	102.8(2)
			98.58(16)	102.9(2)	
P–N–P–N	27.5	30.4(22)	?	19.8	57.3
	28.7	26.6(48)		59.4	15.6
				75.8	
				45.3	

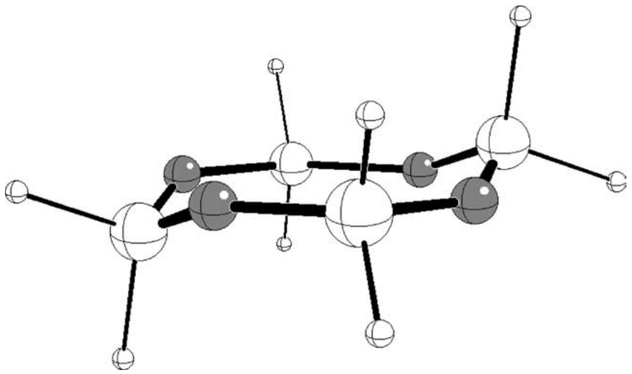

Fig. 4. Structure of the chair form (I) of cyclotetraphosphazenes (C_{2h} symmetry).

that some authors [9–11] have it done for particular cases but their results have not been published until now.

2. Method of calculation

Ab initio MP2 calculations of cyclo-$(NPX_2)_4$ molecules with X = H, F and Cl were performed using a standard Gaussian 94 program package [17] with Dunning's correlation consistent cc-pVDZ basis sets [18–20]. The geometries of all the systems were optimized using Berny algorithm [21] within higher accuracy (keyword Opt = Tight). Electronic structure was evaluated in terms of Mulliken population analysis (gross atomic charges for atoms and overlap populations for bonds).

3. Results and discussion

Cyclooctane, the most known compound with eight-membered ring, has over 10 stable conformers originating in chair–chair, boat–boat and chair–boat families, respectively. The situation in phosphazenes is complicated by non-equivalence of P and N atoms, which may cause doubling the number of the conformers. On the other hand, high P–N–P angles flexibility should significantly reduce this number. Our study started with all possible out-of-plane deformations of the optimized D_{4h} geometry of the P_4N_4 ring (ca. ± 1 Bohr) and continued with geometry optimizations within C_{4v}, D_{2d} or C_{2h} symmetry groups and/or within their C_{2v}, S_4, C_2, C_i and C_s subgroups. In this way obtained structures were compared from the energetic as well as geometric point of view. The structures with difference in energy under 10^{-5} hartree, in bond lengths under 10^{-12} m and in bond/torsion angles under 1° were declared to be identical. Our results on energies, geometries and electronic structure characteristics are collected in Tables 2–4. For stable conformers, only the deviations from high-symmetric D_{4h} structure are presented. Nevertheless, the average root-mean-square distances of P and N atoms from the P_4N_4 ring plane, Δ_{plane}, as well as N–P–N–P torsion angles are equivalent to their absolute values, too.

Table 2
Selected characteristics of cyclo-$(NPH_2)_4$ and their deviations from the reference D_{4h} symmetry

	Reference	Deviations			
Symmetry	D_{4h}	C_{4v}	D_{2d}	C_{2h}(I)	C_{2h}(II)
E_{tot} (a.u.)	−1586.49656	−0.01630	−0.02151	−0.01853	−0.01836
Distances (10^{-10} m)					
N–P	1.608	0.023	0.025	0.024/0.029	0.021/0.027
P–H	1.418	0.018/−0.013	0.000	0.014/−0.013/−0.002	−0.009/0.010
N–N	2.873	0.003	0.001	−0.001/−0.016	−0.017
Δ_{plane}	0.000	0.266	0.528	0.394	0.316
Angles (°)					
N–P–N	126.6	−2.9	−3.4	−3.7/−4.7	−4.6
P–N–P	143.4	−20.7	−20.2	−22.6	−21.9
H–P–H	100.6	2.0	0.8	2.8/0.7	1.1
H–P–N	106.7	2.6/−1.8	−4.0/+5.7	0.6/−1.8/2.7/−0.3	−1.9/0.3/2.3/3.5
H–P–N–P	126.6	−68.7/+40.7	−49.2/47.6	41.0/61.3/24.0/−48.6	28.7/−30.7/19.1/−90.2
N–P–N–P	0.0	72.9	46.2	51.5/73.0	93.8/33.9
Gross charges					
P	0.710	−0.061	−0.039	−0.057/−0.066	−0.039
N	−0.629	0.031	0.010	0.018	0.016/0.000
H	−0.040	−0.023/0.052	0.014	0.048/−0.006	0.042/−0.008
d population on P	0.600	−0.024	−0.029	−0.028	−0.029
Overlap population					
N–P	0.514	−0.035	−0.181	−0.034/−0.047	−0.028/−0.043
P–H	0.326	−0.031/0.042	0.007	−0.019/0.036	−0.016/0.031
N–N	−0.028	−0.000	−0.002	−0.002	−0.002

Table 3
Selected characteristics of cyclo-$(NPF_2)_4$ and their deviations from the reference D_{4h} symmetry

	Reference	Deviations	
Symmetry	D_{4h}	D_{2d}	C_{2h}(II)
E_{tot} (a.u.)	−2379.15658	−0.01044	−0.00662
Distances (10^{-10} m)			
N–P	1.577	0.017	0.018/0.010
P–F	1.593	−0.002	0.006/−0.006
N–N	2.808	0.005	−0.030
Δ_{plane}	0.000	0.327	0.241
Angles (°)			
N–P–N	125.9	−2.1	−4.2
P–N–P	144.1	−17.3	−21.7/−8.2
F–P–F	98.8	0.7	0.5
F–P–N	107.2	−2.3/+3.3	−1.0/0.0/2.0/3.6
F–P–N–P	127.4	44.0/−45.3	20.6/−21.7/−80.6/21.3
N–P–N–P	0.0	43.5	25.3/89.0
Gross charges			
P	1.151	−0.009	0.002
N	−0.611	0.002	0.023/−0.037
F	−0.270	0.000	0.008/−0.008
d population on P	0.860	−0.009	−0.011
Overlap population			
N–P	0.514	−0.019	−0.009/−0.015
P–F	0.353	0.000	0.008/−0.008
N–N	−0.027	−0.002	−0.001

Our results (Tables 2–4) imply that the most stable structure corresponds to D_{2d} symmetry for all the compounds under study in agreement with [9]. Their stabilization energy (as the energy related to the D_{4h} one) has the same trend as the X electronegativities (analogously as the majority of geometric and electronic structure data). Only C_{4v} (Fig. 2), D_{2d} (Fig. 3) and two different C_{2h} (Figs. 4 and 5) stable cyclo-$(NPH_2)_4$ structures are found. The alternative D_{2d} structure with interchanged PH_2 and N sites is unstable (analogous interchange for C_{4v} structure leads to the same optimized geometry). For $X = F$, the number of stable conformers is reduced (to D_{2d} and

Table 4
Selected characteristics of cyclo-$(NPCl_2)_4$ and their deviations from the reference D_{4h} symmetry

	Reference	Deviations		
Symmetry	D_{4h}	C_{4v}	D_{2d}	C_{2h}(I)
E_{tot} (a.u.)	−5259.14569	−0.01014	−0.01799	−0.01286
Distances (10^{-10} m)				
N–P	1.590	0.016	0.024	0.020
P–Cl	2.040	0.015/−0.019	−0.004	−0.004/0.000
N–N	2.827	0.001	0.011	−0.034/0.016
Δ_{plane}	0.000	0.202	0.499	0.278
Angles (°)				
N–P–N	125.6	−2.1	−2.5	−1.7/−5.3
P–N–P	144.4	−12.4	−19.3	−16.7
Cl–P–Cl	102.3	0.7	0.6	0.3/1.4
Cl–P–N	106.7	3.0/−2.3	−3.3/+4.5	−3.0/3.8/4.2/−2.0
Cl–P–N–P	125.6	52.6/−53.6	−47.7/+46.7	35.1/−35.6/−75.3/36.0
N–P–N–P	0.0	59.7	45.4	33.9/81.2
Gross charges				
P	0.785	−0.022	−0.026	−0.018/−0.029
N	−0.529	−0.006	0.004	0.004
Cl	−0.128	−0.010/+0.025	0.011	0.012/−0.013/−0.003
d population on P	0.768	−0.016	−0.025	−0.019/−0.026
Overlap population				
N–P	0.504	−0.018	−0.028	−0.022/−0.024
P–Cl	0.285	0.016/−0.011	0.007	0.006/−0.002/0.021
N–N	−0.025	0.000	−0.002	−0.003/0.001

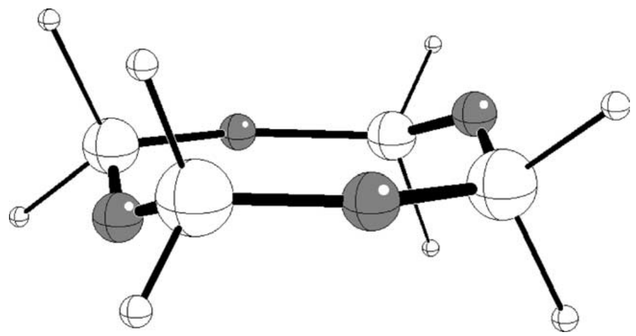

Fig. 5. Structure of the alternative chair form (II) of cyclotetraphosphazenes (C_{2h} symmetry).

C_{2h}(II) only) and the remaining ones are indistinguishable from the D_{4h} one. Analogously, only C_{4v}, D_{2d} and C_{2h}(I) stable structures have been found for X = Cl. The X-ray structures of K [16] and T [15] form of $N_4P_4Cl_8$ originate in D_{2d} and C_{2h}(I) structures deformed by solid state influences, respectively (Table 1). Their relative stability is in agreement with our results, too.

The deviations of electronic characteristics from the D_{4h} conformation (Tables 1–3) are very small. It implies that the electronic structure in planar D_{4h} and non-planar stable conformers are practically equal. Thus the conclusions on vanishing d(P)–N(p) bonding for D_{nh} planar rings [7,8] should be valid also for these stable conformers. As indicated by negative values of N–N bond indices, the interaction between the neighboring nitrogen atoms is

Table 5
Calculated harmonic frequencies (cm^{-1}) and IR intensities (km/mol, in parentheses) of cyclo-$(NPH_2)_4$ vibrations

Symmetry	C_{4v}	D_{2d}	C_{2h}(I)	C_{2h}(II)
1	45(0)	−12(0)	−22(23)	−37(7)
2	73(0)	143(9)	52(2)	72(1)
3	162(0)	143(9)	60(0)	105(1)
4	165(1)	147(4)	132(0)	131(6)
5	165(1)	156(0)	196(7)	169(2)
6	176(11)	179(7)	212(0)	184(4)
7	232(0)	195(0)	286(0)	314(18)
8	398(65)	422(84)	342(58)	388(46)
9	398(65)	422(84)	439(38)	422(35)
10	482(22)	564(0)	457(0)	458(27)
11	639(51)	633(0)	636(0)	638(3)
12	715(3)	696(0)	702(0)	705(5)
13	715(3)	696(0)	727(2)	723(1)
14	731(0)	750(44)	730(0)	734(3)
15	758(14)	756(0)	754(48)	759(34)
16	758(14)	772(6)	790(0)	772(44)
17	789(13)	772(6)	793(162)	792(112)
18	834(0)	823(120)	838(0)	833(2)
19	868(0)	888(0)	872(0)	869(2)
20	944(0)	913(0)	926(0)	922(3)
21	959(14)	928(30)	929(76)	926(9)
22	959(14)	928(30)	951(11)	959(8)
23	975(0)	942(0)	965(0)	970(0)
24	1091(592)	1093(67)	1078(569)	1084(525)
25	1091(592)	1093(67)	1108(534)	1087(563)
26	1116(0)	1140(54)	1123(0)	1119(14)
27	1135(0)	1167(0)	1158(0)	1133(29)
28	1142(43)	1177(0)	1164(320)	1137(45)
29	1142(43)	1181(170)	1172(124)	1166(156)
30	1145(25)	1181(170)	1172(0)	1174(268)
31	1178(0)	1189(0)	1181(0)	1185(64)
32	1225(0)	1232(0)	1226(757)	1208(258)
33	1233(780)	1233(665)	1236(0)	1222(526)
34	1233(780)	1233(665)	1244(577)	1235(290)
35	2350(0)	2475(0)	2403(0)	2373(55)
36	2358(46)	2477(0)	2405(6)	2399(11)
37	2358(46)	2477(0)	2416(0)	2407(327)
38	2374(475)	2481(349)	2417(0)	2461(88)
38	2580(0)	2487(0)	2549(0)	2546(197)
40	2581(127)	2492(329)	2549(0)	2548(0)
41	2581(127)	2492(329)	2550(204)	2583(72)
42	2583(9)	2501(0)	2553(0)	2588(54)

repulsive. This repulsive interaction may increase in some stable conformers what should reduce their stabilization energies.

Our data on bond lengths and bond angles are in agreement with other authors [9–11] within the above mentioned numerical errors (experimental structure data are significantly influenced by solid state effects – see Table 1). Nevertheless, the attempt to confirm definitely the stability of our conformers by vibration data failed due to the presence of small imaginary frequencies related to out-of-ring plane movement of P and N atoms (see Table 5 for cyclo-$(NPH_2)_4$ vibration data, the calculations for its halogen analogs failed due to enormous disk space demands) despite the corresponding energy hypersurface mapping exhibits the energy increase. Similar problem is known in the case of very precise post-SCF calculations on hydration of dianions of dicarboxyl acids [22,23]. The vibrational modes corresponding to internal rotation of the carboxylate groups, with the low frequency were found to be imaginary. The authors performed single point calculations in both directions along the normal mode eigenvector associated with the imaginary frequency, and found the energy to increase in both directions, concluding that a harmonic description is inadequate for the mode. The same conclusion might hold for cyclotetraphosphazenes. Nevertheless, the vibrational analysis of such systems is outside the scope of this article. Precise systematic studies in this field are desirable.

Acknowledgements

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