Semiempirical Study of the Molecular Structure of Cyclic $(NPX_2)_n$ Phosphazenes ($n = 2, 3, 4, 5$ and $X = H, F, Cl$)

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The results of a theoretical study of the title compounds on the basis of employing the semiempirical AM1 method are presented. The main features studied are the structural geometrical parameters in order to complement the previous structural analysis made with the molecular mechanics technique. Data are compared with the previous results derived from other methods as well as with available experimental data. The remarkable discrepancies among theoretical values and available experimental data do not allow to state definite conclusions.

The term π-electron-rich heterocycle refers to a planar ring system in which the number of π-electrons exceeds the number of atomic centres in the ring, e.g. $S_3N_3^-$ (1). By contrast cyclophosphazenes, e.g. $R_6P_3N_3$, (2) are π-electron precise molecules, i.e. the number of π-electrons is equal to the number of atomic centres in the ring [1, 2]. The cyclic phosphazenes are of interest to both theoretical and experimental chemists. For example, a new class of thermosensitive cyclotriphosphazenes has been first synthesized recently by stepwise substitution of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with alkoxypoly(ethylene glycol) and amino acid esters [3]. Although the physical and chemical properties of these compounds have been extensively studied [4], the bonding in the rings has been an object of many controversies [5—20].
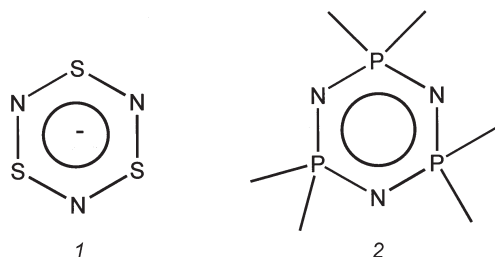
The phosphazene backbone formally consists of alternating single and double P—N bonds and the generally accepted "island model" [8] supposes that the σ-bonds are formed by sp^3 hybrid orbitals of P. Concerning molecular π-orbitals there have been several different interpretations dealing with the role of the

atomic d-orbitals of the central atoms and up to now there is not a general agreement about them [20, 21].

Regarding the geometry of this sort of molecules, the predictions are not similar and different results for the bond lengths and bond angles have been reported in the standard literature [8, 14, 16, 20—25]. Thus, we have considered suitable to start a systematic effort trying to arrive at more definite conclusions and in the previous paper [25] the results of a molecular mechanics study of the title compounds to determine their main geometrical features and characteristic parameters are presented.

In this paper the analysis of the geometrical issues and electronic properties of the same set of chemical compounds determined on the basis of the semiempirical AM1 method is presented and the results are compared with previous data.

The first set of phosphazene derivatives to be studied is that comprising the nine title compounds. However, there have been reported cyclic systems comprising up to at least 17 PNX_2 units (i.e. $n = 1, 2, \ldots, 17$). The most common subjects of theoretical studies are small cyclic phosphazenes (Formula 1) and different sets of geometrical structures have been published [26—30].

The initial central issue regarding molecular structure of phosphazenes is the geometrical nature of the ring. In fact, although several theoretical studies assume a D_{nh} symmetry for the phosphazene rings [20], IR spectra in vapour phase and in solution indicate nonvanishing deviations from ring planarity for $n > 3$ [31]. Even X-ray structural studies on the trimeric halides have firmly established the existence of a pla-

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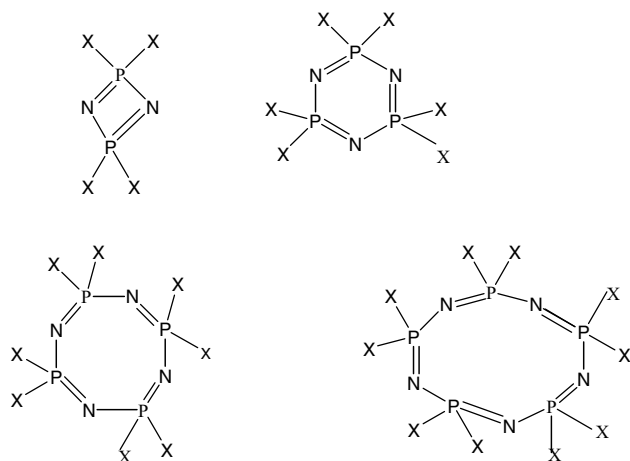
Formula 1. Molecular structure of cyclo-$(NPX_2)_n$, $n = 2, 3, 4,$ 5, phosphazenes.

nar or almost planar six-membered ring of alternating P and N atoms [32, 33].

In each compound the P—N ring bonds are of equal length within experimental error, and exocyclic halogen atoms complete an approximate tetrahedral arrangement of bonds around the P atoms. A quite interesting feature of phosphazene rings is their intimate electronic structures and the aromatic character of the out-of-plane π-electron bonds [4, 5, 20, 34, 35]. This feature is studied here because the previous study

[25] made with molecular mechanics technique did not allow to draw any conclusion about it.

If the exocyclic X atoms in phosphazenes are replaced by other atoms or groups, a considerable range of compounds can be prepared. Some examples of substituents are NH_2, CH_3, SCN, C_6H_5, OH, and OR, in addition to halogen atoms. Taking into account the existence of derivatives containing two or three different substituents, the number of possible phosphazenes increases markedly.

Four kinds of isomerism are possible for substituted cyclic derivatives (cyclo-$(NPX_2)_n$ phosphazenes, $n = 2, 3, 4, 5$ and X = H, F, Cl) [32]:

1. **Positional isomerism.** This arises because a given substituent may have a choice of P atom to which it may be attached, such as structures *b* and *c* (see Formula 2).

2. ***Cis-trans*** **isomerism.** This can arise if geometrically different forms can be obtained by placing a substituent alternatively above or below the plane of the ring when attached to the same P atom, such as structures *h* and *i*.

3. **Optical isomerism.** This should arise whenever the particular isomer is unsymmetrical and cannot be superimposed on its mirror image, such as structures *d* and *e*.

4. **Ring (or conformational) isomerism.** Each of the isomers arising from *1* and *2* could, in principle, be associated with different ring geometries, *e.g.* planar, chair, boat, *etc.*
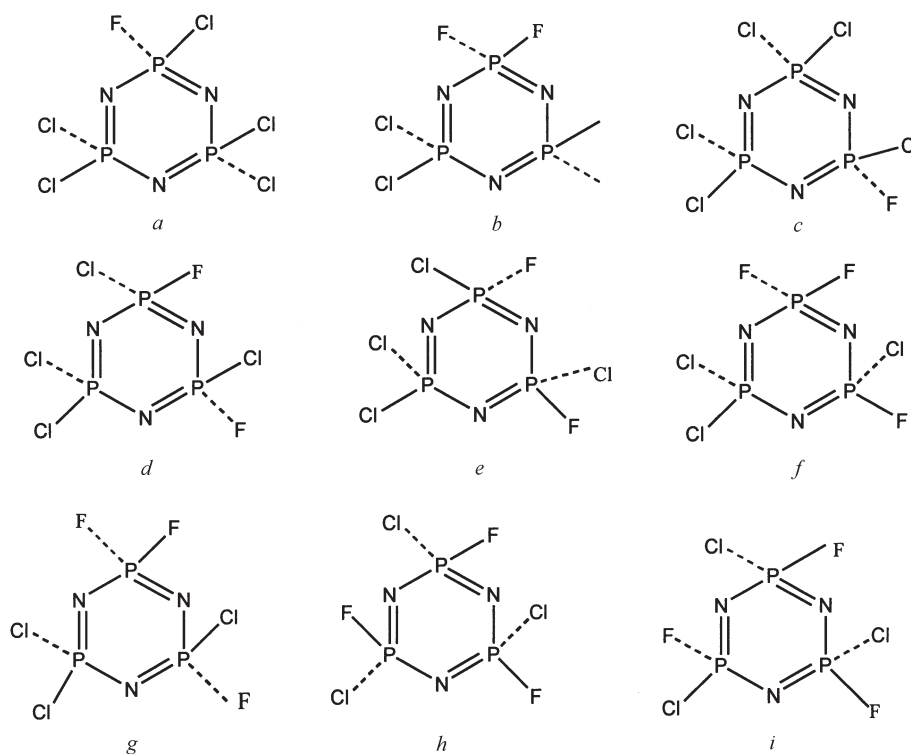
Formula 2. Isomers of phosphazene substituted cyclic derivatives.

Obviously, when all exocyclic groups are identical, only ring isomerism is to be expected (which is the case of the present study).

COMPUTATIONAL METHOD

In 1959, when discussing the status and potential of quantum chemistry, Professor *C. A. Coulson* noted that theoretical chemists were divided into two fundamentally different groups [36]. One group was concerned with purely nonempirical methods, the so-called *ab initio* methods, while the second was concerned with semiempirical methods. After the passage of more than forty years, this division still exists although the boundary between the two procedures is less well-defined, mainly due to improvements in semiempirical techniques. The development of semiempirical methods often parallels that of other methods and their semiempirical parameters may be given a clear physical interpretation.

The deep gap between molecular mechanics and the *ab initio* calculations is occupied by the semiempirical molecular orbital methods. They are basically quantum mechanical in nature but the main difference to *ab initio* methods is the introduction of semiempirical parameters in order to reduce the high costs of computer time necessary for explicit evaluation of all integrals. One-centre repulsion integrals and resonance integrals are substituted by parameters fitted as closely as possible to experimental data. Another basic idea of the semiempirical approach is the consideration of the fact that most of the interesting molecular properties are mainly influenced by the valence electrons of the corresponding atoms. Therefore only the valence electrons are taken into account, leading to a further reduction in computer time.

All the semiempirical methods apply the same theoretical assumptions, they only differ in the approximations being made [37, 38]. Semiempirical methods like AM1 [39] and PM3 [40—42] provide a quite effective compromise between the accuracy of the results and the expense of computer time required. A calculation performed with these methods is able to express the experiment as effectively as an *ab initio* calculation using a small basis set. The advantage of semiempirical methods over *ab initio* calculations is not only that they are several orders of magnitude faster, but also calculations for systems up to 200 atoms are possible with the semiempirical methods only. The quality of semiempirical methods for a wide range of molecules and the calculation of different properties has been subject of several reviews [39—42].

Thus, we have deemed suitable to perform the calculations *via* the AM1 method contained in the HYPERCHEM® package [43], resorting to the aromatic character of the ring through the corresponding option and also applying the "model building" choice at the calculation start to speed up the computational

rates. We have also employed the conjugate gradient algorithm due to Polak—Ribiére as the minimization technique and a RMS gradient of 0.042 kJ mol^{-1} to define the termination condition in the iterative process.

Polak—Ribiére procedure is a conjugate gradient method using one-dimensional searches and it improves other similar methods (such as Fletcher—Reeves algorithm) by also considering the previous conjugate direction. This technique does not require resetting the conjugate direction and it demands slightly more memory but tends to converge more quickly than the Fletcher—Reeves method.

The geometry optimizations were made without any restriction at all, which is a very significative point in this study since there are possibilities of existing of planar and nonplanar $(N—P)_n$ cyclic structures.

RESULTS AND DISCUSSION

The energy results corresponding to the most stable conformations are given in Table 1, while in Table 2 the selected structural data for $(NPX_2)_n$ are presented together with other theoretical and experimental results for comparative purposes.

The first important structural feature to be noted is the high symmetry of all structures, which present a planar cyclic arrangement, with rather small deviations from perfect planarity. This property is clearly revealed by the zero or nearly null dipole moment for all the molecules (see Table 1). In Figs. 1 and 2 the theoretically determined molecular structures at the equilibrium positions of the two phosphazenes having a nonnull dipole moment, *i.e.* $(NPF_2)_4$ (0.002 *D* and 0.006 *D*, respectively) are displayed. It can be seen clearly that they are nearly planar, as stated before.
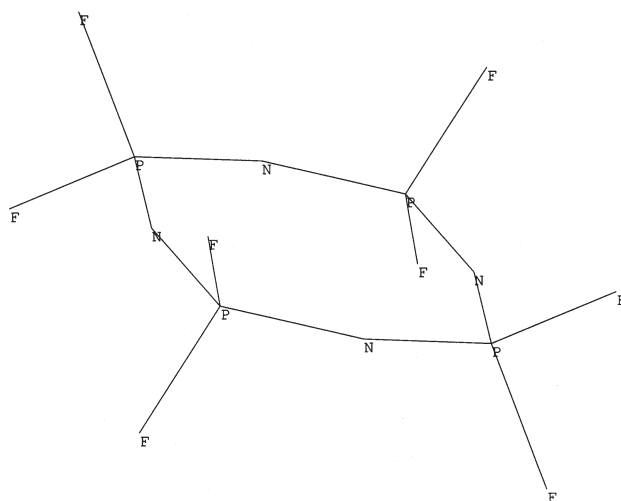

Fig. 1. Theoretical $(NPF_2)_4$ molecular structure.

Table 1. Total Energies, Heats of Formation, and Dipole Moments of the Title Compounds Corresponding to the Most Stable Conformations

Molecule	Total energy/a.u.	Heat of formation/(kJ mol^{-1})	Dipole moment/D
$(NPH_2)_2$	−26.53520	251.54	0.000
$(NPH_2)_3$	−39.99215	−120.16	0.001
$(NPH_2)_4$	−53.4622	−510.54	0.001
$(NPH_2)_5$	−66.86767	−762.75	0.000
$(NPCl_2)_2$	−79.60765	−228.93	0.001
$(NPCl_2)_3$	−119.60007	−840.54	0.000
$(NPCl_2)_4$	−159.60798	−1489.50	0.006
$(NPCl_2)_5$	−199.56138	−1996.94	0.000
$(NPF_2)_2$	−99.07845	−1153.25	0.000
$(NPF_2)_3$	−144.29492	−2195.52	0.000
$(NPF_2)_4$	−192.52153	−3264.45	0.002
$(NPF_2)_5$	−240.69020	−4181.15	0.001

Table 2. Structural Data for the Cyclo-$(NPX_2)_n$ Phosphazenes (n = 2, 3, 4, 5; X = H, F, Cl)

Molecule	Distance/Å		Angle/°			Comments
	P—N	P—X	P—N—P	N—P—N	X—P—X	
$(NPH_2)_2$	1.750	1.380	97.6	82.0	117.0	[25]
	1.840	1.420	86.8	93.2	103.1	DZ basis set[a] [16]
	1.540	1.286	98.6	81.4	96.2	Present calculation
$(NPH_2)_3$	1.730	1.380	118.0	107.5	109.6	[25]
	1.724	1.419	119.8	120.2	103.1	DZ basis set[a] [16]
	1.497	1.288	134.6	105.7	97.8	Present calculation
$(NPH_2)_4$	1.720	1.380	123.0	111.0	107.8	[25]
	1.576	1.392	148.3	121.7	101.6	DZP basis set [20]
	1.490	1.292	156.8	113.2	97.9	Present calculation
$(NPH_2)_5$	1.730	1.380	121.0	109.7	108.4	[25]
	1.480	1.297	170.3	117.7	97.6	Present calculation
$(NPCl_2)_2$	1.700	2.000	97.4	82.6	119.0	[25]
	1.623	1.996	84.3	95.7	102.7	DZ basis set[a]
	1.549	1.921	97.1	82.9	103.4	Present calculation
$(NPCl_2)_3$	1.690	2.010	120.0	108.2	109.8	[25]
	1.580	1.990	121.4	118.4	101.4	[27]
	1.490	1.944	134.6	105.5	102.6	Present calculation
$(NPCl_2)_4$	1.690	2.020	128.0	113.0	105.0	[25]
	1.559	1.992	133.6	120.5	103.1	[30]
	1.489	1.955	157.3	112.7	102.4	Present calculation
$(NPCl_2)_5$	1.770	1.380	121.0	110.0	108.0	[25]
	1.482	1.963	170.9	117.1	102.5	Present calculation
$(NPF_2)_2$	1.720	1.730	97.3	82.7	119.0	[25]
	1.608	1.526	83.7	96.3	98.9	DZP basis set [20]
	1.550	1.535	99.2	80.8	94.0	Present calculation
$(NPF_2)_3$	1.700	1.740	118.0	107.0	110.0	[25]
	1.570	1.529	120.4	119.6	99.1	[26]
	1.510	1.544	135.5	104.6	94.5	Present calculation
$(NPF_2)_4$	1.700	1.740	122.0	110.0	109.0	[25]
	1.507	1.514	147.2	122.7	99.9	[28]
	1.510	1.550	158.6	111.4	94.4	Present calculation
$(NPF_2)_5$	1.690	1.740	122.5	112.0	108.0	[25]
	1.500	1.550	172.2	115.8	94.2	Present calculation

a) Pseudopotential calculation [16].

These findings are coincident with previous experimental and theoretical studies [16, 25, 26, 28] which seem to state definitively the planar structure of the phosphazene rings. Experimental studies on these compounds show that in each molecule the P—N ring bonds are of equal lengths within experimental errors, and the exocyclic X atoms complete an approximate tetrahedral arrangement of bonds around the P atoms. Regarding ring planarity, X-ray structural studies reveal that in certain cases (n = 2, 3) they are planar
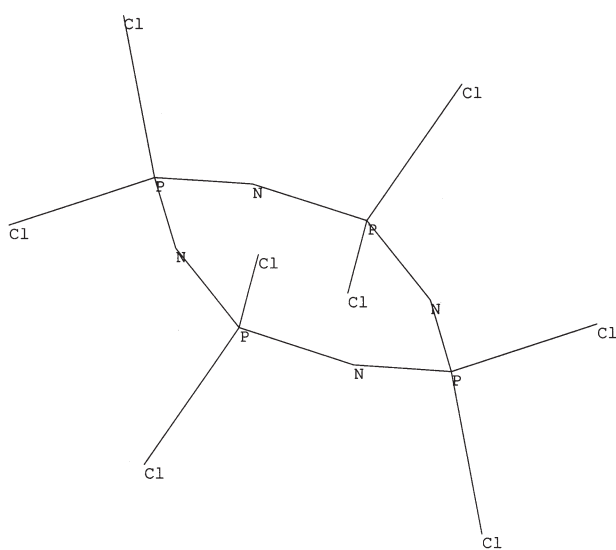
Fig. 2. Theoretical $(NPCl_2)_4$ molecular structure.

while the remaining ones are not ($n = 4, 5$). However, the deviations from planarity are rather small [20].

With respect to bond length and bond angles, some trends can be noted. First, P—N distances are rather low regarding experimental data and other theoretical calculations (see column 2 in Table 2). Deviations are large when compared with previous determinations [25] performed with the molecular mechanics method. A similar situation takes place with PN bond distances, although differences are not so great. A special case is the PX bond distance in the $(NPCl_2)_5$ molecule, since previous calculations predicted a 1.380 A value [25], which is somewhat low, while present calculation yields 1.963 A and it is in line with other similar data for these molecules (see column 3 in Table 2).

Predicted P—N—P angles are rather larger than data determined with other theoretical methods and experimental findings (see column 4 in Table 2), but deviations are not very large. N—P—N angles do not present a well defined tendency with respect to other data, but there is a good agreement with molecular mechanics predictions (see column 5 in Table 2). Regarding X—P—X bond angles, predicted values are smaller than other theoretical and experimental data in a marked degree (see column 6 in Table 2). Since available experimental data show some remarkable variations (for example P—N distances in $(NPH_2)_2$ and $(NPCl_2)_4$, P—N—P angle in $(NPH_2)_3$ and $(NPCl_2)_3$, N—P—N angle in $(NPH_2)_3$, P—N—P angle in $(NPH_2)_3$, *etc.*), it is difficult to establish some definite conclusions about well defined values of bond distances and bond angles. This feature for this molecular set is not new. In fact, in a very recent paper on electronic structure of planar phosphazene rings [20] dealing with the same molecular set as the chosen one in this work, the comparison of different theoretical

predictions showed somewhat notorious disagreement among some molecules (see Table 1 in Ref. [20]).

Enthalpies of formation are presented in Table 1 (column 3) and we note a regular increase of molecular stability when considering the series $(NPX_2)_n$, $n = 2$, 3, 4, 5 for a given X (*cf.* data for the three series, *i.e.* X = H, Cl, F). These results are important to apply the group additivity method which has provided a powerful means for studying chemical reactions on the basis of thermochemistry [44—46]. The method assumes that the properties of a chemical substance are the sum of the contributions from each polyvalent atom (central atoms) in the molecule.

CONCLUSION

The application of the molecular orbital theory through the semiempirical AM1 method has allowed us to determine the main geometrical features and characteristic structural parameters of the cyclo-$(NPX_2)_n$ ($n = 2$, 3, 4, 5 and X = H, F, Cl) phosphazenes. Practically all the molecules are planar and those nonplanar deviate slightly from complete planarity. Theoretical dipole moments calculated at this semiempirical level are zero or practically null for the whole molecular set. The predicted bond distances and bond angles are quite reasonable when compared with available experimental data, standard values, and other theoretical calculations. However, the discrepancies existing among different data sources do not permit to draw definite conclusions. The analysis of heats of formation presents a regular stability increase when the members of a given series are compared (*i.e.* $n = 2$, 3, 4, and 5 for a given X), and these results are in line with the basic assumption in the group additivity scheme devised by *Benson et al.* [44—46].

Naturally, these results together with those previously reported [43] make up an initial step in the analysis of the molecular structure of phosphazene rings. Now it should be necessary to resort to more elaborated molecular orbital methods and even to post-Hartree—Fock methods and Density Functional Theory and to extend the study for other members of the phosphazenes family to get a more general and encompassing perspective about the main geometrical features and bonding properties of these molecules. Research along these lines is actually under development in our laboratory and results will be presented elsewhere in the forthcoming future.

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