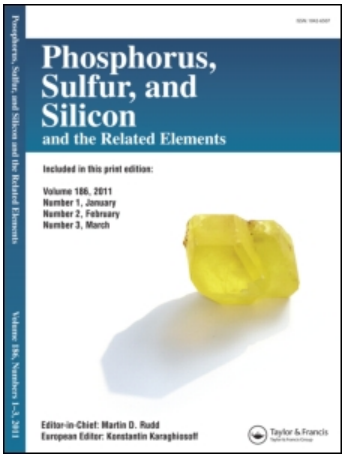

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Cyclic Delocalization Effects in Substituted λ⁵-Diaza- and Triazaphosphorines

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CYCLIC DELOCALIZATION EFFECTS IN SUBSTITUTED λ^5-DIAZA- AND TRIAZAPHOSPHORINES

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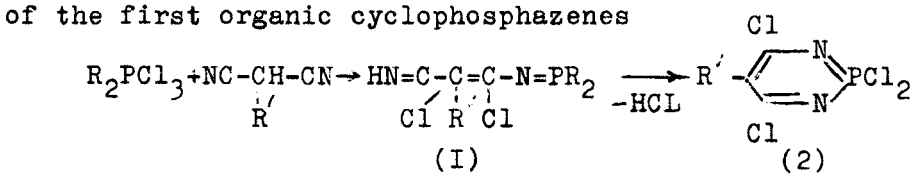
Abstract Six-membered cyclophosphazenes, I,3-diaza- and I,3,5-triaza-2-phosphorines are characterized by a dipolar structure of ylide type with a positive charge on phosphorus atom and negative one, delokalized in an azine fragment. In n-donor substituents at a phosphorus atom, as well as in electron-acceptor substituents in 4,6 heterocycle position this leads to an anomalous ratio of length of formally ordinary exocyclic and double endocyclic bonds PNexo > PNendo. Quantum chemical analysis of the situation performed by means of SCF method in CNDO/2 approximation reveals more pronounced s-character of nitrogen atoms in exocyclic bonds in comparison to endocycli ones.

INTRODUCTION

Chemistry of cyclophosphazenes with one or more P=N bonds differs from that of traditiomal heterocycles, thus drawing constant attention.[1] The least studied among them are phosphorus-containing analogues of uncondensed azines, derivatives of pyrimidine and s-triazine, which combine the phosphazene fragment and an ordinary π-system.

Principles of these substances synthesis were developed in the 70s by the authors of the review[2] and also by A.Schmidpeter, as well as by O.Glemser with coworkers (see refrences in[1,2]) after A.Kirsanov and others[3] received one of the first organic cyclophosphazenes



(I) (2)

The cyclization of (I) to (2) proceeds readily in the

presence of catalytic amounts of hydrogen chlorides. Its mechanism was theoretically studied by us earlier[4,5] by means of SCF method in CNDO/2 approximation. Our calculations are in good agreement with the spectral studies.[2] However the pattern of the electron structure of the heterocycles thus obtained seems not very accurate because of the lack of experimental geometrical parameters which became only lately available.[6]

RESULTS AND DISCUSSION

Delocalization effects on a phosphorine cycle geometry are well observed on 2,2,4-tris(dimethylamino)-5-cyano-6-trichlormethyl-I,3-diaza-2-phosphorine (3), the central fragment of which is given in the figure.[6]

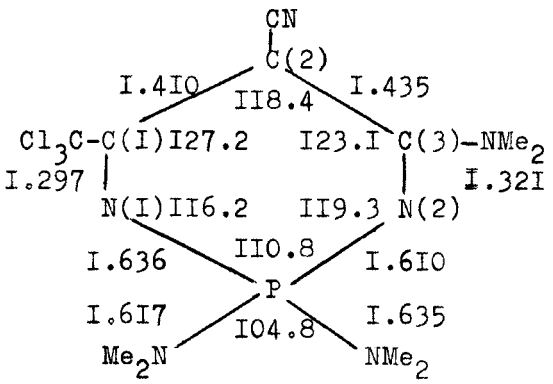


FIGURE I Geometry of the central fragment of molecule (3), bond lengths (Å outside) and bond angles (deg. inside the ring).

The heterocycle appears asymmetric: i. e. endocyclic bonds C(2)-C(3) and C(3)-N(2) adjacent to π-donor substituent dimethylamino group are longer than C(2)-C(I) and C(I)-N(I) bonds near elektronwithdrawing CCl_3 group. Contrary to this, endocyclic PN(2) bond is shorter than similar P-N(I) bond, although their mean values (I.623 Å and I.626 Å, respectively) are practically the same. A phosphorus atom configuration is very close to tetrahedral, thus indicating its phosphonium character.

Interatomic distances are similarly distributed in the molecules of symmetrical I,3,5-triaza-2 ^{5}-phosphorines (4, 7) (see Table I)[7-9], where the substituents effect is more pronounced, since the substitution of carbon atom C(2) by more electronegative nitrogen atom increases heterocycle polarization and the excess of electron density in azine fragment. This is revealed structurally in the non-equivalence of endocyclic bond lengths PN endo $<$PNexo on transition from molecule (4) to (6-8). Their difference increases with increase of a donor character of the substituents near the phosphorus atom, whose electron effect is likely to play an important role.

TABLE I Endocyclic distances (Å) and angles (deg) at phosphorus atom in triazaphosphorines $\overset{\frown}{N{=}C(R')-N{=}C(R')-N{=}}PR_2$

compound	R′	R	PN endo	PN exo	NC	CN	NPN endo	NPN exo
4	Me_2N	Me_2N	I.583	I.668	I.354	I.344	II3.2	I0I.7
5	CF_3	Cl	I.6I6	-	I.308	I.339	III.6	I05.0
6	CF_3	N	I.635	I.6I9	I.295	I.338	I09.3	I02.9
7	CCl_3	Me_2N	I.64I	I.6I4	I.305	I.33I	I08.9	I05.I
8	CCl_3	$Ph_3P{=}N$	I.658	I.585	I.292	I.336	I07.I	II3.4

Nevertheless, this does not explain completely the observed effects: according to the above values of valent angle at the phosphorus atom its σ-constituent must be characterized by greater s-contribution into the endocyclic bond. This contribution,however, decreases in the sequence (4→8) and in the latter case endocyclic angle appears even smaller than exocyclic one, due to greater steric effect of triphenylphosphazogroup. Taking into consideration small changes in other endocyclic angles it might be suggested that the main factor determining difference in bond lengths PNendo and PNexo is the difference in the hybridization of corresponding nitrogen atoms.

Quantum chemical calculations of partial Wiberg indices between each AO of nitrogen and all the phosphorus orbitals[10] allowed to establish s-characters of N atoms in phosphorus bonds (Table 2).

TABLE 2 Atomic charge Q , Wiberg indices W and s-character of nitrogen atoms $X_s(N)$ (in %)

compound	Q(P)	Q(N) endo	Q(N) exo	W(PN) endo	W(PN) exo	$X_s(N)$ endo	$X_s(N)$ exo
4	0.34	-0.36	-0.17	I.62	I.23	I9.5	25.8
6	0.35	-0.28	-0.16	I.45	I.53	I9.4	26.0
7	0.30	-0.30	-0.15	I.47	I.37	I9.0	26.2
8	0.36	-0.32	-0.23	I.40	I.34	I9.5	28.7

s-Characters appeared to have greater value in exocyclic bonds what corresponds to interatomic distances. It was also found that polar bond length of phosphorus-nitrogen in (4-8) is determined primarily by s-character of the two atoms,

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