AM1 study of photoelectron spectra. 9.* 2,2,4,6-Tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine

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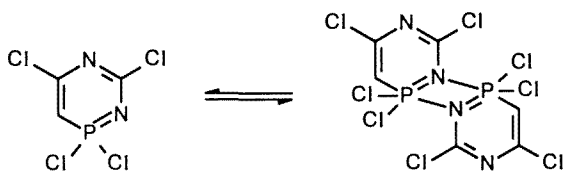
The π-orbital structure of the monomeric form of the 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine has been studied by photoelectron spectroscopy and using quantum-chemical calculations by the semiempirical AM1 method. It has been concluded that the electronic and energy characteristics of four higher π-MOs (frontier and three next orbitals) of this compound may be interpreted in terms of semipolar bonds formed by three atoms (C, P, and N). For describing two low-lying π-MOs of the σ^4,λ^5-phosphorine studied, it is necessary to take into account the π—σ-interaction.

Key words: photoelectron spectrum, semiempirical quantum-chemical calculations, 1,5,2-diazaphosphorinine.

Analysis of the IR spectra of a melt, solution, and suspension of σ^4,λ^5-phosphorine demonstrated that the phase state exerts a pronounced effect on these spectra. The difference in the stretching frequencies of the heteroring of this compound in the liquid and solid states was explained using the concept of transition-induced dimerization of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine[2] (Scheme 1).

Scheme 1



(solution and melt) (Nujol mulls)

The assumption of the dimeric form of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine in the crystalline state is supported by the data of ^{35}Cl NQR according to which the halogen atoms of the PCl_2 fragment are nonequivalent.[2]

An increase in the C=C and C=N stretching frequencies observed upon dissociation makes it possible to conclude that a more delocalized π-system appears (see Scheme 1) and to postulate that the monomeric form is similar to the aromatic form in its properties.[2] The conclusion about the aromaticity of the σ^4,λ^5-phosphorine studied should not be taken literally, because rigorous criteria for describing this property of cyclic conjugated heterosystems are not stated yet.[3] The views on the aromaticity of λ^5-phosphorines are controversial, as demonstrated in a moderate number of selected modern works. Thus, according to Ref. 4, λ^5-phosphabenzenes have high indices of aromaticity. However, the photoelectron spectra of nonaromatic λ^5,λ^5-1,3-diphosphacyclobutadiene and of potentially aromatic $\lambda^5,\lambda^5,\lambda^5$-1,3,5-triphosphabenzene are virtually identical.[5] This indicates that there are no orbital interactions in the latter, which are necessary for the aromatic system.

Apparently,[5] despite the equalization of the P—C bonds, these compounds should be considered as phosphorus di- and triylides. More recently,[6] stabilization of these compounds relative to the fragments was revealed by the analysis of heats of isodesmic reactions. Therefore, it was concluded[6] that the σ^4,λ^5-phosphorines under consideration are "conjugated but not 'classical aromatic' compounds." In this work, based on the results of a study of the orbital structure of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine, a theoretical model was proposed; this model makes it possible to understand qualitatively the mechanism of formation of the π-electron system of this derivative of pentavalent phosphorus.

Experimental

The photoelectron spectrum of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine was obtained on an

* For Part 8, see Ref. 1.

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Table 1. Heats of formations ($\Delta_f H°$) and dipole moments (μ) of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine

Method	Monomer		Dimer	
	$\Delta_f H°$ /kcal mol^{-1}	μ/D	$\Delta_f H°$ /kcal mol^{-1}	μ/D
MNDO	−2.8	2.11	39.7	0.00
AM1	−25.5	1.12	−12.6	0.07
PM3	−33.1	1.84		
CNDO/S (sp)	−12.3	4.59		
CNDO/S (spd)	−12.8	4.78		
Experiment		4.25		

ES-3201 electronic spectrometer. The He(I) resonance irradiation (21.21 eV) was used for exciting the spectrum. The energy scale was calibrated against the Ar (15.76 eV) and chlorobenzene (9.06 eV) ionization potentials. The errors in determination of ionization potentials are no more than 0.05 eV.

The dipole moment of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine in a solution in carbon tetrachloride at 25 °C was measured on a Tangent instrument. The concentration range of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine used was $3.0 \cdot 10^{-3}$—$4.3 \cdot 10^{-2}$ mol L^{-1}.

Quantum-chemical calculations were carried out by the semiempirical AM1, MNDO, and PM3 methods (using the MOPAC-6.0 program) and the CNDO/S method;[7] all bond lengths, bond angles, and dihedral angles were optimized. The equilibrium geometry calculated by the AM1 method was used in calculations in the CNDO/S approximation. For the dimer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine, the most favorable conformation proved to be the conformation shown in Scheme 1. According to the heats of formation ($\Delta_f H°$) and the calculated and experimental values of dipole moments (μ), 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine in the gaseous state and in a nonpolar liquid exists in the monomeric form (Table 1). The photoelectron spectrum of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine is also inconsistent with the orbital energies of the dimer.

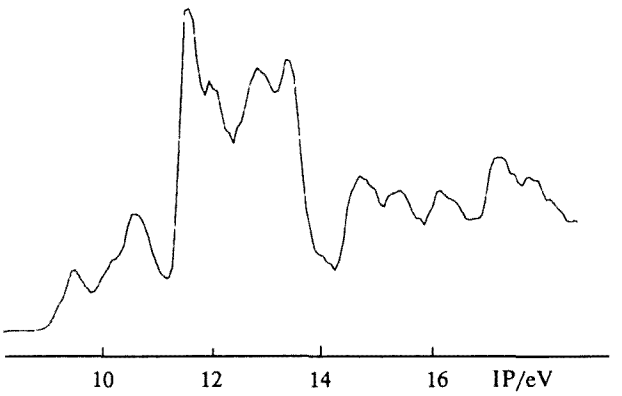


Fig. 1. Photoelectron spectrum of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine.

Results and Discussion

The photoelectron spectrum of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine is shown in Fig. 1. The highest intensity bands are in the range 11.5—13.5 eV. This energy range is typical of nonbonding electron pairs of chlorine atoms (n(Cl)). High intensities of spectral lines are also typical of n-MOs of the halogen atom. The three rather low-intensity bands with maxima at ~9.5, 10.1, and 10.6 eV correspond, apparently, to the π- and n(N) levels of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine. A more detailed empirical analysis of the photoelectron spectrum is difficult because of the large number and variety of MOs of σ^4,λ^5-phosphorine studied. Note only that the first three

Table 2. Theoretical and experimental ionization potentials (eV) of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine

AM1		Photo-electron spectrum, IP_i	MNDO		Photo-electron spectrum, IP_i	PM3		Photo-electron spectrum, IP_i	CNDO/S (spd)		Photo-electron spectrum, IP_i
MO	$-\varepsilon_i$[a]		MO	$-\varepsilon_i$[b]		MO	$-\varepsilon_i$[c]		MO	$-\varepsilon_i$[d]	
π	10.64	9.42	π	10.28	9.42	π	9.90	9.42	π	8.54	9.42
n(N)	11.60	10.12	n(N)	11.89	10.12	π	10.65	10.12	n(N)	10.75	10.12
π	11.94	10.62	π	11.98	10.62	n(N)	10.77	10.62	π	10.88	10.62
π	12.59	11.52	π	13.01	11.52	π	10.84	10.62	n(N)	11.85	11.52
n(ClC)	12.60	11.52	n(N)	13.08	11.52	n(ClC)	10.85	10.62	π	12.39	12.02
n(ClC)	12.77	11.52	n(ClC)	13.25	11.52	n(ClC)	11.07	10.62	n(ClC)	12.82	12.90
n(N)	13.18	12.02	n(ClC)	13.25	12.02	n(N)	11.53	11.52	n(ClC)	13.03	13.08
π(ClP)	13.47	12.02	π(ClP)	13.68	12.02	π(ClP)	12.00	12.02	π(ClP)	13.80	13.40
n(ClP)	13.83	12.90	n(ClP)	14.07	12.90	n(ClP)	12.27	12.02	n(ClP)	13.85	13.40
n(ClP)	14.00	13.08	n(ClP)	14.14	13.08	n(ClP)	12.35	12.02	π	13.93	13.40
n(ClP)	14.22	13.40	π	14.52	13.40	n(ClP)	12.61	12.90	n(ClP)	14.26	14.56
π	14.53	13.40	n(ClP)	14.59	13.40	π	13.03	13.08	σ	14.48	14.56
π	15.72	14.56	π	15.77	14.56	π	13.70	13.40	n(ClP)	14.52	14.56
σ	15.95	15.16	σ	16.29	15.16	σ	14.25	14.56	π	14.80	15.16
σ	16.91	15.50	σ	16.92	15.50	σ	14.83	15.16	σ	15.56	15.50

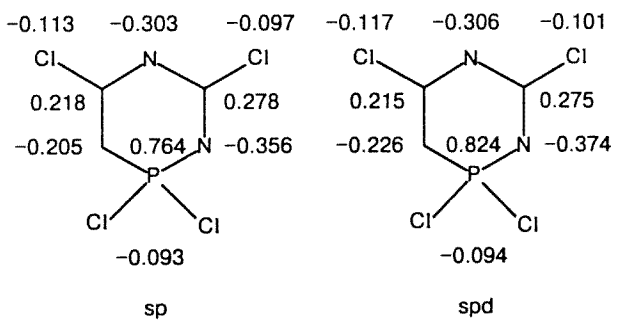
[a] $-\varepsilon_i = 1.74 + 0.952IP_i$, $r = 0.993$. [b] $-\varepsilon_i = 1.82 + 0.962IP_i$, $r = 0.989$. [c] $-\varepsilon_i = 1.75 + 0.863IP_i$, $r = 0.993$.
[d] $-\varepsilon_i = 0.29 + 0.983IP_i$, $r = 0.977$.

ionization potentials determined are substantially higher than those typical of six-membered λ^5-phosphorine compounds studied previously.[5,6,8]

The theoretical analysis of the photoelectron spectrum of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine was carried out using the results of calculations of its monomer by several semiempirical methods. Both the number of bands in the first two groups and their relative intensities are best represented in the AM1 and MNDO approximations (Table 2). Hereinafter, we shall use the results obtained by the AM1 method because of a lower error in the reproduction of the ionization energy.

We begin the consideration of the orbital structure of the monomer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine with the following assumption: its PCl_2 group has a purely electrostatic effect on the π orbitals of the remaining heterofragment. In essence, this is equivalent to the concept that the monomer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine is the ylide of four-coordinate phosphorus. This concept is based on the characteristic features of the electron distribution over the heavy atoms of the free molecule of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine found by the CNDO/S method; the dipole moment of the monomer is most readily calculated by this method (see Table 1).

As can be seen from the charge distribution chart given below, an almost entire electron is transferred from the phosphorus atom to the heterofragment. Besides, it is seen that qualitatively analogous and quantitatively close results were obtained with the sp and spd basis sets; hence, there is no need to use d orbitals for describing the electron distribution in the ground state. Therefore, calculations by the CNDO/S method confirm once again this familiar fact (see, for example, Ref. 9).



Therefore, the ionic pair consisting of the carbanion and the proton (Fig. 2, the proton occupies the position of the phosphorus atom in the equilibrium structure of the free monomer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine) can serve as a model of the ylide. The orbital characteristics (the order in which occupied π-MOs are arranged and the electron densities corresponding to these MOs) appear to be the same for the ionic pair and the monomer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine, with the exception of two features, which we shall consider below. The calculated orbital energies of the occupied π-MOs of the ionic pair (Table 3) correlate with the energies of π-MOs of the modeled molecule and with the experimental data with a high degree of accuracy. Therefore, the characteristics of four lower ionic π-states of the monomer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine in the gaseous phase are determined by the polar nature of the bonds formed by the phosphorus, nitrogen, and carbon atoms.

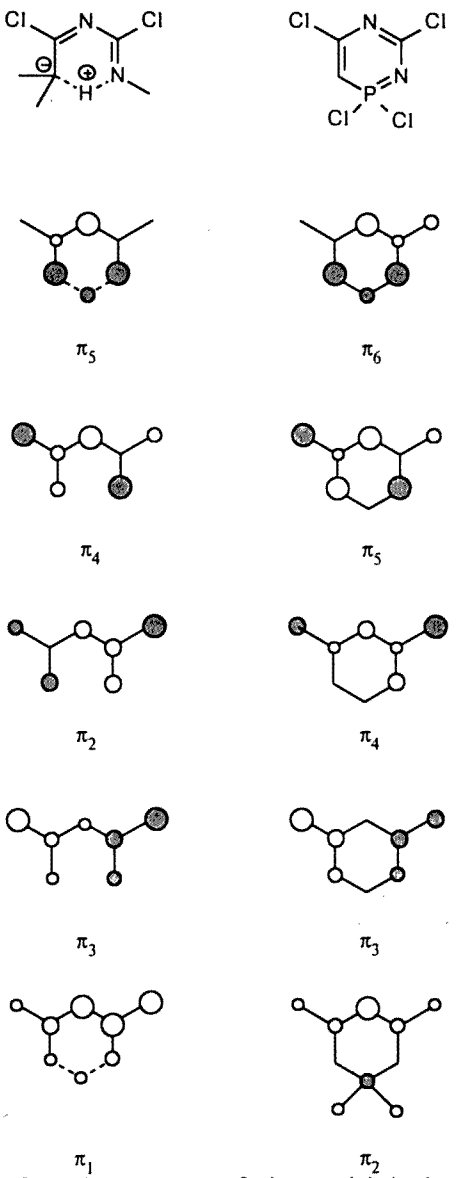


Fig. 2. Orbital structures of the model ionic pair and 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine (the AM1 method).

The above-mentioned slight differences are as follows: 1) the ionic pair has one occupied π-MO less than the monomer of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine and 2) the lowest π-MO of

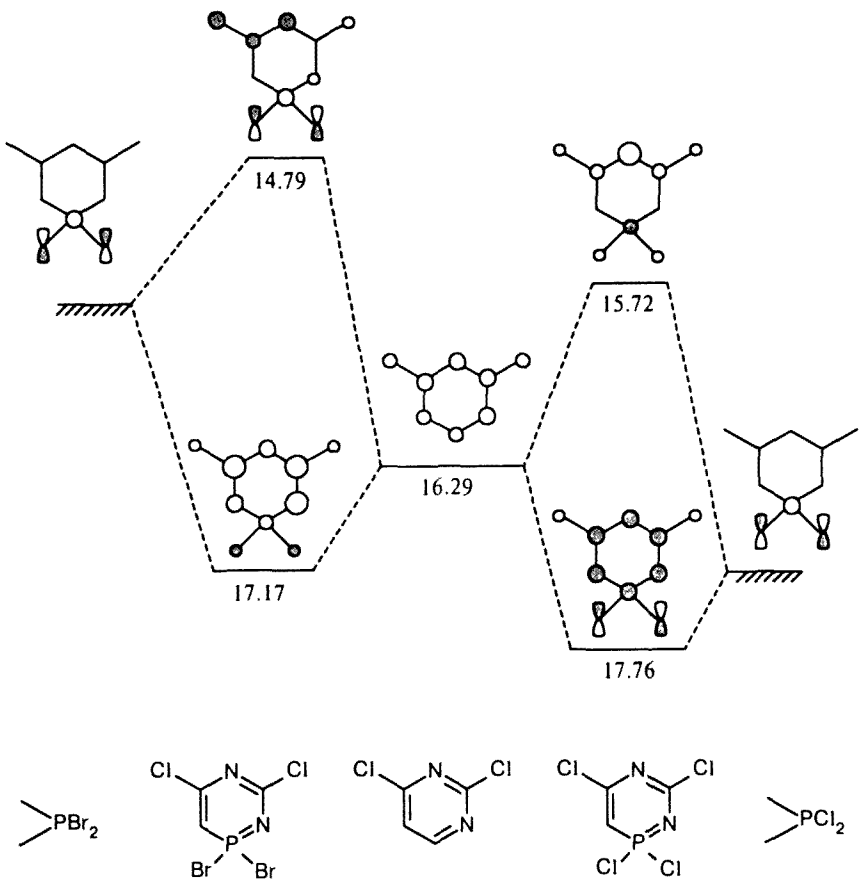


Fig. 3. Correlation diagram of the lowest-lying π-MOs of σ^4,λ^5-phosphorines and 2,4-dichloropyrimidine. When PCl_2 is replaced by PF_2, the diagram is qualitatively analogous.

the ionic pair is destabilized to a lesser degree than the corresponding occupied π-MO of σ^4,λ^5-phosphorine (see Table 3). Undoubtedly, this characteristic feature of the orbital structure of the model ionic pair is a reflection of the fact that the molecule of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine contains the PCl_2 group, whose s orbitals can be mixed with the fragment MOs of the π-system due to superconjugation.

Table 3. Ionization potentials (eV) of π-MOs of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine and model ionic pair calculated by the AM1 method (using the Koopmans theorem)

MO	Ionic pair, IP_i (the Koopmans theorem)	2,2,4,6-Tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine	
		ΔIP_i[a] (AM1)	ΔIP_i[a] (Photoelectron spectrum)
π_6	9.98	−0.66	0.46
π_5	11.16	−0.78	0.54
π_4	11.96	−0.63	0.42
π_3	13.84	−0.69	0.40
π_2	15.46	−0.26	0.90
π_1	—	(17.76)[b]	(16.6)[b]

[a] Deviations of ionization potential of ionic pairs from the theoretical and experimental values for the neutral molecule of 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2-diazaphosphorinine. [b] Ionization potentials.

The orbital correlation diagram in Fig. 3 clearly illustrates the π—σ mixing; in this diagram, the fully bonding π-MO of 2,4-dichloropyrimidine and σ-orbitals of the P—Cl or P—Br bonds are shown as unperturbed orbitals (their energy positions are calculated based on the effect of perturbation; overlapping was ignored). When the =CH group was replaced by the PX_2 group in 2,4-dichloropyrimidine, it is the fully bonding MO (among the occupied π-MOs) that significantly interacts with the σ-bond orbitals. As a result of this mixing, two low-lying common π_1- and π_2-MOs appear in σ^4,λ^5-phosphorine: the antibonding and bonding combinations of the fragment orbitals. Because these π-MOs are generally located in the spectral region of the σ-core, it is difficult to observe their perturbations from the photoelectron spectra. Besides, the orbital π—σ interaction in the σ^4,λ^5-phosphorine under consideration has a weak effect on the higher occupied π-orbitals because of the node properties of π-MOs (see Fig. 2) and large energy gaps.

Therefore, the orbital effect is difficult to observe directly, but under certain conditions (π—σ^* interaction) this effect may strongly affect the heats of fragmentation processes and the chemical reactions with the participation of the PX_2 group. Because orbital π—σ interactions substantially vary even in the halogen series (see Fig. 3), it is believed that these interactions depend on the nature of other atoms forming PX σ-bonds. Note that the particular model obtained principally correlates with the view of the role of the π—σ interactions in organophosphorus compounds summarized in Ref. 9.

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