Contribution from the Chimie Théorique et Chimie Organique Physique Equipe de Recherche Associée
au CNRS No. 895 IURS, 6400 Pau, France, and ER No. 82 associée à l'Université Paul Sabatier Laboratoire
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Electronic Structure of Tris(dialkylamino)phosphines and 1,3-Dimethyl-1,3,2-diazaphospholanes. A Novel and Critical Study

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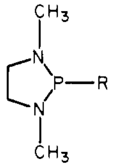
Received May 14, 1980

The electronic structures of three tris(dialkylamino)phosphines (I) (**1–3**) and four 2-organyl-1,3-dimethyl-1,3,2-diazaphospholanes (II) (**4–7**) have been studied by PES with use of He I and He II excitations and orbital energy calculations. In comparison with precedent works, we take into account the pyramidalization of nitrogen atoms when the dihedral angle between the lone pair of phosphorus and those of nitrogen is not strictly 90°. For diazaphospholanes (II) our interpretation of the PES spectra based on orbital energy calculations leads us to assign three possible conformations for the five-membered ring; the first two are envelopes with the flap on either the P atom ($E_P{}^6$) or the N (endocyclic) atom ($E_N{}^1$); the third is a half-chair (H^1).

The structural study of organophosphorus derivatives containing a tricoordinated phosphorus–nitrogen bond, whether they are acyclic as tris(dialkylamino)phosphines (I) or cyclic as 2-organyl-1,3,2-diazaphospholanes (II), has been extensively pursued at both the experimental[2–15] and theoretical[16,17] levels.

$P(NR_2)_3$

I



II

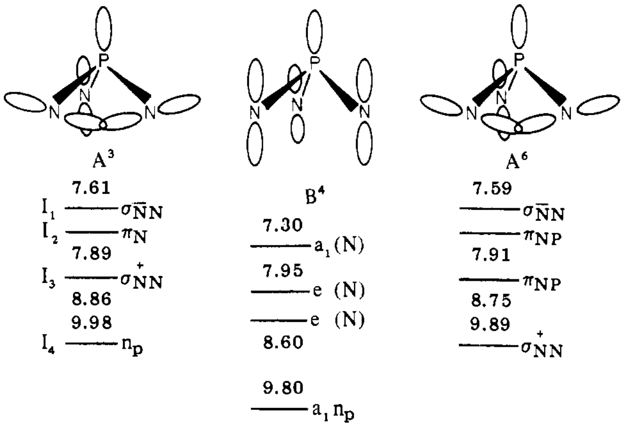
Two important points remain unresolved in these works, one of which is that of preferred conformations: the relative orientations of the lone pairs on phosphorus and nitrogen in I and the conformation of the pentagonal cycle in II. The second point is the hybrid state of the nitrogen atoms bonded to phosphorus.

The present paper is our contribution to the study of these problems with the use of photoelectron spectroscopy, a valuable method for determining preferred structures in the gaseous state. A previous study in this direction has been performed by Worley and co-workers.[6,18]

Our interpretation, based on an analysis of photoelectron spectra obtained with excitation by the He I and He II resonance lines combined with semiempirical calculations, is sufficiently different from that of the authors cited above: the discussion includes the points of similarity and difference between the two sets of results.

Tris(dialkylamino)phosphines (I)

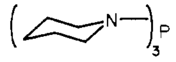
Among this family of derivatives, tris(dimethylamino)phosphine (**1**) has uncontestably been studied to the greatest extent by photoelectron spectroscopy; however, the interpretation of the resulting spectra has been shown to be contradictory. Thus, in the structure (A) advanced by Cowley and co-workers,[3] the lone pairs of two of the nitrogens interact in a pseudo-σ manner and that of the third interacts in a pseudo-π manner with the lone pair of phosphorus. Lappert[4] proposed a structure (B) with C_{3v} symmetry, a hypothesis which was subsequently criticized by Cowley.[5] Hargis and Worley[6] analyzed the spectra of this compound and proposed the same structure as Cowley (A) but with a totally different attribution of photoelectron spectral bands.



The recent publication of the X-ray structure of tripiperidinophosphine (**2**) and trimorpholinophosphine (**3**) was the basis for our undertaking the photoelectron spectroscopic study of derivatives **1**, **2**, and **3**.

$P(NMe_2)_3$

1



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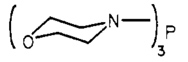

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(1) (a) Chimie Théorique et Chimie Organique Physique Equipe de Recherche Associée au CNRS No. 895. (b) ER du CNRS No. 82 associée à l'Université Paul Sabatier Laboratoire des Hétérocycles de l'Azote et du Phosphore.

(2) Vilkov, L. V.; Khaikin, L. S.; Evdokimov, V. V. *Zh. Strukt. Khim.* **1969**, *10*, 1101.

(3) Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Schweiger, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 6506.

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(7) Cowley, A. H. *Phosphorus Sulfur* **1976**, *2*, 283.

(8) Yarbrough, L. W.; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269.

(9) (a) Romming, C.; Songstad, J. *Acta Chem. Scand. Ser. A* **1978**, *A32*, 689. (b) Romming, C.; Songstad, J. *Acta Chem. Scand., Ser. A* **1978**, *A33*, 187.

(10) Naumov, V. A.; Gulyaeva, N. A.; Pudovik, M. A. *Dokl. Akad. Nauk.* SSSR **1972**, *203*, 590.

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(12) Albrand, J. P.; Cogne, A.; Gagnaire, D.; Robert, J. B. *Tetrahedron* **1972**, *28*, 819.

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(14) Gray, G. A.; Albright, T. A. *J. Am. Chem. Soc.* **1976**, *98*, 3857.

(15) Hargis, J. H.; Worley, S. D.; Jennings, W. B.; Tolley, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 8090.

(16) Cowley, A. H.; Davis, R. E.; Lattman, M.; McKee, M.; Remadna, K. *J. Am. Chem. Soc.* **1979**, *101*, 5090.

(17) Cowley, A. H.; Mitchell, D. J.; Whangbo, M. H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224.

(18) Worley, S. D.; Hargis, J. H.; Chang, L.; Mattson, G. A.; Jennings, W. B. *Inorg. Chem.* **1979**, *18*, 3581.

(19) Hargis, J. H.; Jennings, W. B.; Worley, S. D.; Tolley, M. S.; *J. Am. Chem. Soc.* **1980**, *102*, 13.

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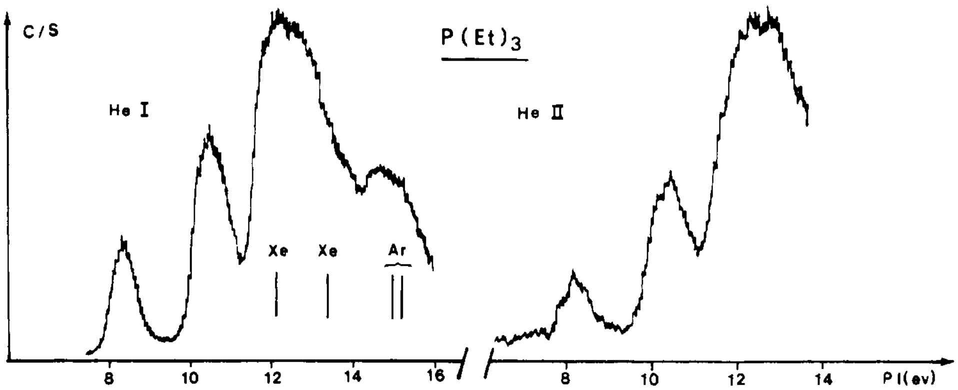

Figure 1. Photoelectron spectra (He I, He II) of triethylphosphine.

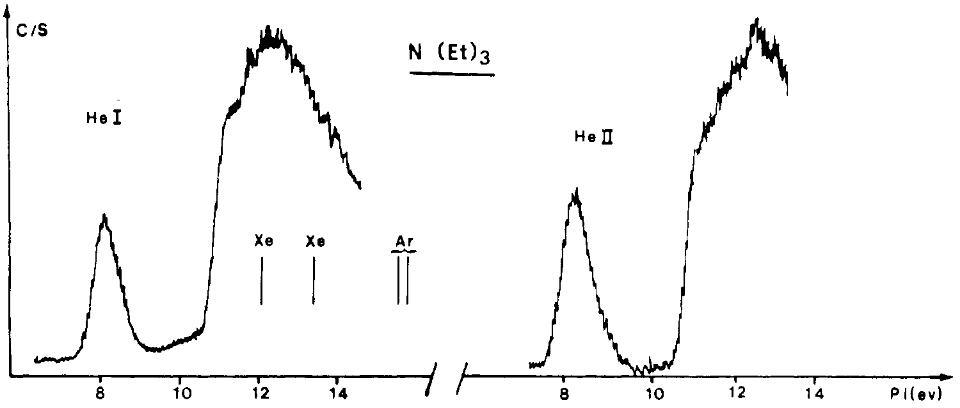

Figure 2. Photoelectron spectra (He I, He II) of triethylamine.

Results and Discussion. We recorded the spectra of tris(alkylamino)phosphines **1–3** and followed the changes in band intensity when excitation was switched from the He I line to the He II line in order to alternatively identify the potentials corresponding to the ionization of electrons which are more or less localized on phosphorus.

It is seen, for example, as observed by Schweig,[20] that for the $P(C_2H_5)_3$ and $N(C_2H_5)_3$ spectra the intensity of the band associated with the lone pair decreases for phosphine and increases for the amine in relation to that of the ionization of σ electrons of the C–H bonds (Figures 1 and 2).

The spectra of compounds **1** (7.59, 7.91, 8.75, 9,89 eV) and **2** (7.4, 7.8, 8.6, 9.7 eV) are very similar; that of compound **3**, however, exhibits slight differences in the positions of the respective bands (7.82, 8.6, 9.55 eV). A relative decrease in the intensity of the second and fourth band is demonstrated by comparing the spectra obtained with the He I and He II lines (Figure 3). We thus confirm the interpretation of Cowley which is the only one which agrees with the observed modificatons of intensity, a conclusion which also agrees with the findings of Yarbrough and Hall.[8]

This observation is apparently inconsistent with the substituent effects discussed by Worley.[3] It should nonetheless be noted that Lappert[4] observed that increasing the alkyl chain length in R_2NPF_2 was reflected by a greater effect on the ionization potential of the lone pair of phosphorus (0.25 eV) than on that of the nitrogen lone pair (0.15 eV). The effectiveness of the alkyl group as an electron donor to stabilize the ionic state involves not only a mechanism lengthwise along the bonds acting on the ionization of the nitrogen lone pair but also, and nonnegligibly, a spatial mechanism (notable overlapping during chain elongation) acting on the ionization of the phosphorus lone pair.

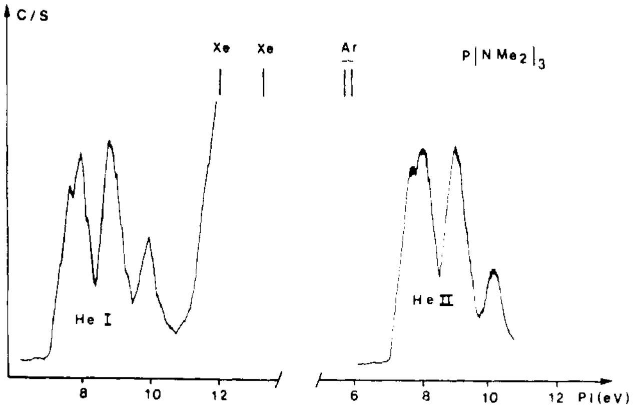

Figure 3. Photoelectron spectra (He I, He II) of tris(dimethylamino)phosphine (**1**).

A conformation of C_s symmetry with a "pseudo-σ" orientation of the lone pairs of two nitrogen atoms and a "pseudo-π" orientation of the lone pair of the third thus appears to be privileged in the gaseous state. We cannot, however, arrive at a formal conclusion on the respective geometries of the nitrogen atoms based on photoelectron spectroscopy data alone.

Crystallographic studies on tris(dimethylamino)phosphine complexed to $Fe(CO)_3$[16] and especially tripiperidinophosphine **2**,[9] for which we observed a spectrum similar to that of **1**, demonstrated a pyrimidalization of the "pseudo-π" nitrogen. The lone pairs of phosphorus and nitrogen are in trans configuration, and there is a slight deviation of the trigonal-plane geometry of the "pseudo-σ" nitrogen when the dihedral angle between the lone pairs of phosphorus and nitrogen is no longer 90°. These experimental results are to be considered in the

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(20) Schweig, A.; Thiel, W. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *3*, 27.

light of data in the literature[21] on the critical points of the surface potential of aminophosphine (PH_2NH_2). Using a double-ζ base with polarization functions, Csizmadia[21] proposed a preferred conformation of aminophosphine which corresponded to a dihedral angle of 90° between the two lone pairs, with nitrogen being in a trigonal-plane geometry. The inversion barrier leading to the trans form with a pyrimidal nitrogen $\sum\angle N = 330.6°$ was estimated to be 3.25 kcal/mol. We employed a 4-31G base minimization process (simultaneous optimization of all geometric parameters) with introduction of a polarization function (d on N and P; p on H) and reached slightly different conclusions:[22] the preferred conformation would correspond to a gauche form ($\sum\angle N = 353°$), with the dihedral angle θ between the "lone pairs" of phosphorus and nitrogen being approximately 80°. This conformation is nonetheless preferred in relation to the form for which $\theta = 90°$ and $\sum\angle N = 360°$ of 0.6 kcal/mol. The energetically unfavorable trans form with 6.1 kcal/mol barrier exhibits a pyrimidalization close to that obtained by Csizmadia ($\sum\angle N = 335°$).

Bearing these considerations in mind, it is logical to propose a conformation for tris(dimethylamino)phosphine in the vapor phase which corresponds to the orientations suggested by Cowley but one must take into account the pyrimidalization of the nitrogen atom when the dihedral angle between the lone pair of phosphorus and that of the nitrogens is no longer 90°. We attempted to verify these hypotheses by using the CNDO/S method to calculate the orbital energies corresponding to "limiting conformations" possible based on crystallographic data. We thus adopted a pyrimidalizaton of the pseudo-π nitrogen, $\sum\angle N = 340°$, with trans orientation of the lone pairs in agreement with the X-ray structure of **2**[9] and theoretical data on aminophosphine.[22]

We also considered a possible pyrimidalization of the "pseudo-σ" nitrogens when the dihedral angle between the lone pair of phosphorus and those of nitrogen(s) is not strictly 90°.

The following six conformations were studied.

Conformation a: the dihedral angle θ between the lone pair of phosphorus and those of the two "pseudo-σ" nitrogens is 90°; consistent with experimental and theoretical studies, the two nitrogens are "trigonal plane".

Conformation b: one of the dihedral angles θ_1 is 90° (trigonal-plane nitrogen) and the other dihedral angle, θ_2, is defined at 70° in the same direction of rotation. We adopted a slight pyrimidalization of the nitrogen in this configuration ($\sum\angle N = 350°$). This conformation corresponds to that observed by Romming and Songstad[9] for **2**.

Conformation c: same parameters as for conformation b, but angle θ_2 corresponds to a 70° rotation in the opposite direction.

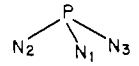
Conformation d: the two nitrogens are slightly pyramidal $\sum\angle N = 350°$ with 70° torsion angles in the same direction.

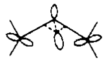
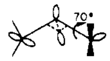
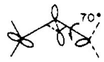
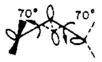
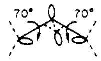
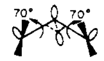
Conformation e: pyrimidalization is identical to that in conformation d, but the 70° torsion angles are in the opposite direction, with the lone pairs of nitrogen directed toward each other.

Conformation f: same conformation as that in conformation e, but with the lone pairs of nitrogen in opposite directions.

The geometric data defining lengths and angles adapted to phosphorus and nitrogen are shown in the Experimental Section.

Table I. Orbital Energies Calculated for Compound 1



conformation *a*		conformation *b*		conformation *c*	
$E_t = -36.1848$ eV		$E_t = -36.3270$ eV		$E_t = -35.9133$ eV	
					
orbital E, eV	localization	orbital E, eV	localization	orbital E, eV	localization
10.03	$\sigma_{N_2N_3}^-$	10.07	$\sigma_{N_2N_3}^-$	10.23	$\pi_{N_1} - n_p$
10.27	$\pi_{N_1} - n_p$	10.31	$\pi_{N_1} - n_p$	10.38	$\sigma_{N_2N_3}^+$
10.70	$\sigma_{N_2N_3}^+$	10.98	$\sigma_{N_2N_3}^+$	10.61	$\sigma_{N_2N_3}^-$
11.98	$\pi_{N_1} + n_p$	12.10	$\pi_{N_1} + n_p$	12.11	$\pi_{N_1} + n_p$
conformation *d*		conformation *e*		conformation *f*	
$E_t = -36.0032$ eV		$E_t = -35.6913$ eV		$E_t = -36.2481$ eV	
					
orbital E, eV	localization	orbital E, eV	localization	orbital E, eV	localization
10.25	$\pi_{N_1} - n_p$	10.27	$\pi_{N_1} - n_p$	10.01	$\sigma_{N_2N_3}^-$
10.47	$\sigma_{N_2N_3}^-$	10.43	$\sigma_{N_2N_3}^+$	10.29	$\pi_{N_1} - n_p$
10.72	$\sigma_{N_2N_3}^+$	10.60	$\sigma_{N_2N_3}^-$	11.34	$\sigma_{N_2N_3}^+$
12.12	$\pi_{N_1} + n_p$	12.14	$\pi_{N_1} + n_p$	12.12	$\pi_{N_1} + n_p$

The data shown in Table I demonstrate a satisfying agreement between the experimental spectrum of tris(dimethylamino)phosphine and calculated values for conformation a and especially conformation b; furthermore, the calculations of these conformations with the CNDO/S method are energetically favored.

Thus, in the vapor phase, only two dimethylamino groups of tris(dimethylamino)phosphine adopt conformations which are theoretically determined as preferential: a hybridation of nitrogen such that $\sum\angle N \approx 350°$ (or $\sum\angle N = 360°$) with an orientation of the lone pair forming an angle $\theta = 70°$ (or $\theta = 90°$) with the lone pair of phosphorus. There is a minimization of the effects of doublet–doublet interactions and steric factors, however, as the third group presents an energetically unfavorable disposition corresponding to the trans form of aminophosphine.

2-Organyl-1,3-dimethyl-1,3,2-diazaphospholane (II)

In spite of considerable work in this field, the conformation of the diazaphospholane ring has not been definitively established. With the exception of Navech and co-workers,[13] who described a twisted conformation of various diazaphospholanes based on proton NMR studies, most authors agree on an envelope conformation for this ring. Thus, this form was proven by X-ray studies of 1,2,3-triphenyl-1,3,2-diazaphospholane.[11]

The phosphorus atom is in the flap position, and the dihedral angle is approximately 28°. On the basis of electron diffraction studies of 2-chloro-1,3,2-diazaphospholane, Naumov and co-workers[10] proposed an envelope configuration with the Cl substituent in the axial position. Finally, contradictory suggestions were recently advanced by Gray and co-workers[14] and by Hargis and co-workers[15,19] after NMR studies of the ^{15}N and ^{13}C nuclei. The former proposed that the envelope with the phosphorus atom in flap position exhibited a trans configuration between the lone pairs of the phosphorus atom and the exocyclic nitrogen. The latter group suggested that these doublets would be oriented in a gauche form,[15] and after a more extensive study of dynamic NMR spectra of ^{15}N and

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[21] (a) Csizmadia, I. G.; Cowley, A. H.; Taylor, M. W.; Tel, L. M.; Wolfe, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1147. (b) Cowley, A. H.; Taylor, M. W.; Whangbo, M. H.; Wolfe, S. *Ibid.* **1976**, 838. (c) Csizmadia, I. G.; Cowley, A. H.; Taylor, M. W.; Wolfe, S. *Ibid.* **1974**, 432.

[22] Gonbeau, D.; Liotard, D.; Pfister-Guillouzo, G. *Nouv. J. Chim.* **1980**, *4*, 227.

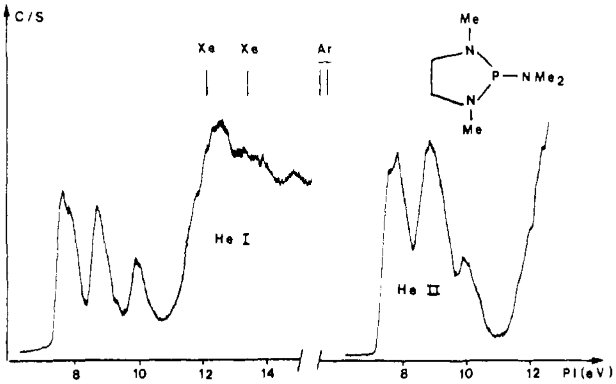


Figure 4. Photoelectron spectra (He I, He II) of 2-(dimethylamino)-1,3,2-diazaphospholane (**4**).

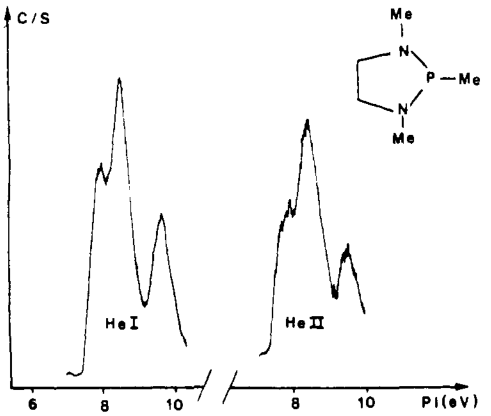


Figure 5. Photoelectron spectra (He I, He II) of 2-methyl-1,3,2-diazaphospholane (**5**).

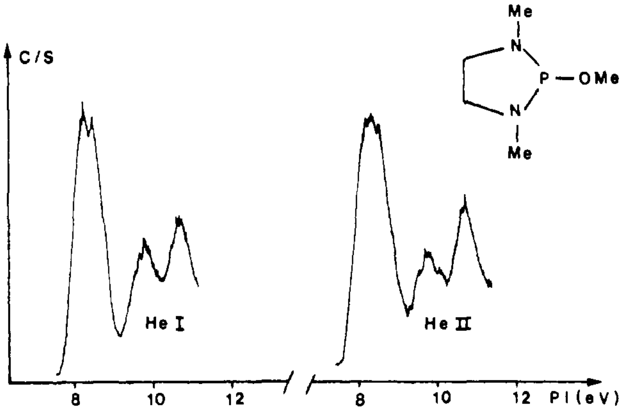
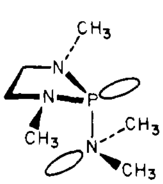


Figure 6. Photoelectron spectra (He I, He II) of 2-methoxy-1,3,2-diazaphospholane (**6**).

^{13}C,[19] they concluded to an envelope conformation with endocyclic nitrogen in flap position.



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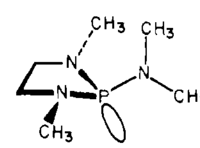

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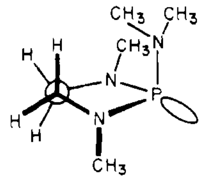

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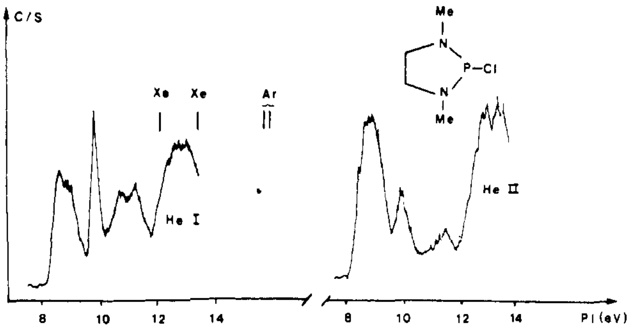

Figure 7. Photoelectron spectra (He I, He II) of 2-chloro-1,3,2-diazaphospholane (**7**).

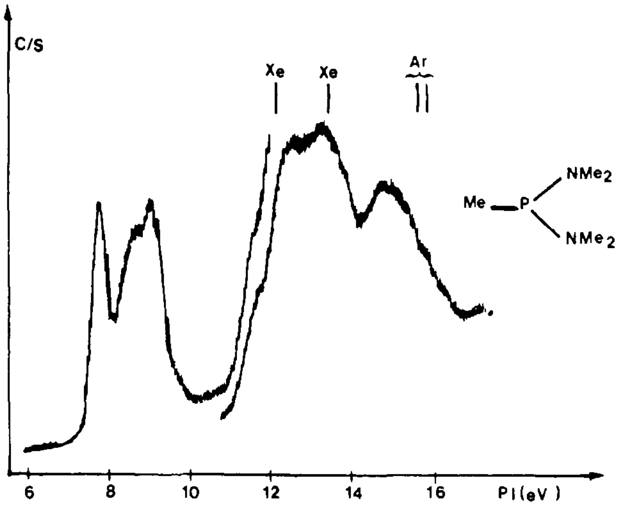

Figure 8. Photoelectron spectra of methylbis(dimethylamino)phosphine.

Table II. Orbital Energies Calculated for Compound **4**[a]

conformation $E_P{}^1$	conformation $E_P{}^2$	conformation $E_P{}^3$
9.86 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.77 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.64 $\mathrm{N}_1, \mathrm{N}_2, N_3$
10.09 P, N_1, N_2	10.15 $\mathrm{P}, \mathrm{N}_1, N_2$	10.34 P, N_1, N_2
10.74 $\mathrm{N}_1, \mathrm{N}_2, \mathrm{N}_3$	10.90 N_1, N_2, N_3	10.94 $\mathrm{N}_1, \mathrm{N}_2, N_3$
12.10 $P, \mathrm{N}_1, \mathrm{N}_2$	11.82 $P, \mathrm{N}_1, \mathrm{N}_2$	11.57 $P, \mathrm{N}_1, \mathrm{N}_2$
$E_t = -35.6151$ eV	$E_t = -34.9971$ eV	$E_t = -34.3608$ eV
conformation $E_P{}^4$	conformation $E_P{}^5$	conformation $E_P{}^6$
9.72 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.81 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.82 $\mathrm{N}_1, \mathrm{N}_2, N_3$
10.33 $\mathrm{P}, N_1, N_2, N_3$	10.16 $\mathrm{P}, \mathrm{N}_1, N_2$	10.14 $\mathrm{P}, \mathrm{N}_1, \mathrm{N}_2$
10.89 $\mathrm{N}_1, \mathrm{N}_2, N_3$	10.77 $\mathrm{N}_1, \mathrm{N}_2, N_3$	10.52 $\mathrm{N}_1, \mathrm{N}_2, N_3$
11.04 $P, \mathrm{N}_1, \mathrm{N}_2$	11.27 $P, \mathrm{N}_1, \mathrm{N}_2$	11.59 $P, \mathrm{N}_1, \mathrm{N}_2$
$E_t = -35.8260$ eV	$E_t = -36.0811$ eV	$E_t = -36.3178$ eV
conformation H^1	conformation H^2	conformation H^3
9.77 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.74 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.63 $\mathrm{N}_1, \mathrm{N}_2, N_3$
10.06 $\mathrm{P}, \mathrm{N}_1, \mathrm{N}_2$	10.0 P, N_1, N_2	10.17 P, N_1, N_2
10.53 $\mathrm{N}_1, \mathrm{N}_2, \mathrm{N}_3$	10.70 N_1, N_2, N_3	10.82 $\mathrm{N}_1, \mathrm{N}_2, N_3$
11.75 $P, \mathrm{N}_1, \mathrm{N}_2$	11.47 $P, \mathrm{N}_1, \mathrm{N}_2$	11.30 $P, \mathrm{N}_1, \mathrm{N}_2$
$E_t = -35.8586$ eV	$E_t = -35.3290$ eV	$E_t = -34.9987$ eV
conformation $E_N{}^1$	conformation $E_N{}^2$	conformation $E_N{}^3$
9.98 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.94 $\mathrm{N}_1, \mathrm{N}_2, N_3$	9.92 $P, \mathrm{N}_1, \mathrm{N}_2$
10.15 $P, \mathrm{N}_1, \mathrm{N}_2$	10.19 $\mathrm{P}, \mathrm{N}_1, \mathrm{N}_2$	10.01 $\mathrm{N}_1, \mathrm{N}_2, N_3$
10.65 $\mathrm{N}_1, \mathrm{N}_2, N_3$	10.91 $\mathrm{N}_2, \mathrm{N}_3$	10.69 $\mathrm{N}_1, \mathrm{N}_2, \mathrm{N}_3$
11.68 $P, \mathrm{N}_1, \mathrm{N}_2$	11.38 $P, \mathrm{N}_1, \mathrm{N}_2$	12.06 $P, \mathrm{N}_1, \mathrm{N}_2$
$E_t = -35.9999$ eV	$E_t = -35.6992$ eV	$E_t = -36.1918$ eV

[a] Italic values correspond to the highest localizations (contributions from atomic orbitals, %). **IP**$_{\mathbf{exptl}}$: 7.59, 7.78, 8.72, 9.88 eV.

These diverse and contradictory data led us to perform photoelectron studies on the diazaphospholane ring conformation in a series of type II compounds, with $N(CH_3)_2$ (**4**), CH_3 (**5**), Cl (**6**) and OCH_3 (**7**) as exocyclic substituents. Considering the strain imposed by cyclization, this technique should a priori enable us to define the preferred orientations of the two lone pairs of the endocyclic nitrogens and to de-

Table III. Orbital Energies Calculated for Compounds 5–7[a]

$\mathrm{IP}_{\mathrm{exptl}}$, eV	conformation $\mathrm{E_P}^{1}$ [b]	conformation $\mathrm{E_P}^{6}$ [b]	conformation H^{1} [b]	conformation $\mathrm{E_N}^{1}$ [b]	conformation $\mathrm{E_N}^{3}$ [b]
Compound 5					
7.89	9.82 P, N_1, N_2	9.86 P, N_1, N_2, C	9.78 P, N_1, N_2, C	9.90 *P*, N_1, N_2, C	9.71 P, N_1, N_2, C
8.50	10.49 N_1, N_2	10.19 N_1, N_2	10.27 N_1, N_2	10.34 N_1, N_2	10.50 N_1, N_2
9.68	12.17 *P*, N_1, N_2	11.71 *P*, N_1, N_2	11.84 *P*, N_1, N_2	11.78 *P*, N_1, N_2	12.14 P, N_1, N_2
11.5–12	13.19 P, C	13.24 P, C	13.11 P, N_1, C	13.24 P, C	13.17 P, C
	$E_t = -30.0139$ eV	$E_t = -30.2311$ eV	$E_t = -30.0148$ eV	$E_t = -30.0838$ eV	$E_t = -30.1592$ eV
Compound 6					
8.14	10.28 P, N_1, N_2	10.08 N_1, N_2	10.14 N_1, N_2	10.23 N_1, N_2	10.08 P, N_1, N_2
8.40	10.31 N_1, N_2	10.35 P, N_1, N_2	10.26 P, N_1	10.34 P, N_1, N_2	10.40 N_1, N_2
9.70	12.19 *P*, N_1, N_2	11.64 P, N_1, N_2	11.79 *P*, N_1, N_2	11.73 P, N_1, N_2	12.11 *P*, N_1, N_2
10.63	12.31 *O*	12.48 *O*, N_1, N_2	12.34 *O*	12.59 *O*	12.59 *O*
	$E_t = -38.1232$ eV	$E_t = -40.0043$ eV	$E_t = -39.7265$ u.a.	$E_t = -38.2951$ u.a.	$E_t = -38.3268$ eV
Compound 7					
8.63	10.39 P, N_1, N_2	10.46 N_1, N_2	10.38 P, N_1, N_2	10.49 P, N_1, N_2	10.25 P, N_1, N_2
8.92	10.67 N_1, N_2	10.52 P, N_1, N_2	10.52 N_1, N_2	10.57 N_1, N_2	10.74 N_1, N_2
9.98	11.93 P, N_1, N_2, C1	11.76 P, N_1, N_2, C1	11.76 P, N_1, N_2, C1	11.81 P, N_1, N_2, C1	12.06 P, N_1, N_2, *Cl*
10.77	12.67 *Cl*	12.79 *Cl*	12.73 *Cl*	12.85 *Cl*	12.86 *Cl*
11.25	14.06	13.56	13.78	13.62	13.82
	$E_t = -36.1596$ eV	$E_t = -37.7050$ eV	$E_t = -37.4752$ eV	$E_t = -36.3984$ eV	$E_t = -36.4899$ eV

[a] Only localizations >10 have been reported. [b] Italic values correspond to the highest localizations.

termine the predominant conformer(s) in the vapor phase.

Results and Discussion. The spectra of the four diazaphospholanes studied (**4**–**7**) are shown in Figures 4–7. The values of the different ionization potentials are shown in Tables II and III. It should be noted that passing from the He I to He II lines caused a decrease of intensity of the band from 9.7 to 10 eV for all the compounds. We attribute this decrease to the ionization of electrons which are localized primarily on the lone pair of phosphorus. Concerning the other bands of the He I spectrum, we can only conclude that there is a change in the shape of the first large peak of compounds **4**, **6**, and **7**, while a clear and reproducible reduction of the first band is observed for compound **5**. If we compare the ionization potentials of this compound with those observed for the corresponding acyclic derivative[23] $CH_3P(NMe_2)_2$ (Figure 8) (7.73, 8.57 and 9.03 eV), a significant shift of the third band toward higher energies is noted (ΔIP = 0.65 eV), which is attributed to the ionization of the lone pair of phosphorus.

These two considerations suggest the existence of a phosphorus lone pair–nitrogen lone pair(s) interaction.

The same conclusion is reached if we examine the ionization potential of the lone pair of phosphorus in compound **4** (9.88 eV). This value is quite comparable to that of compound **1** (9.89 eV) for which a phosphorus lone pair–"pseudo-π" nitrogen lone pair interaction was concluded.

The substituent effect of *o*-methylated and -chlorinated derivatives should induce a clear stabilization of the ionization potential of the phosphorus lone pair. In this case it is more difficult to determine if such an interaction exists since oxygen (or chlorine) lone pair–phosphorus lone pair interactions would compensate for the inductive effect. As in the case of derivative **5**, a 0.5-eV shift of the phosphorus ionization potential[24] is noted in compound **7** in relation to the acyclic compound (8.25, 8.95, and 9.50 eV).

These observations suggest that the diazaphospholane ring adopts a conformation in the vapor phase in which the lone pair of phosphorus interacts with one or both lone pairs of the endocyclic nitrogens.

This conclusion is similar to that of Worley but does not at all predict the type of interaction involved (reciprocal orientation of the pairs).

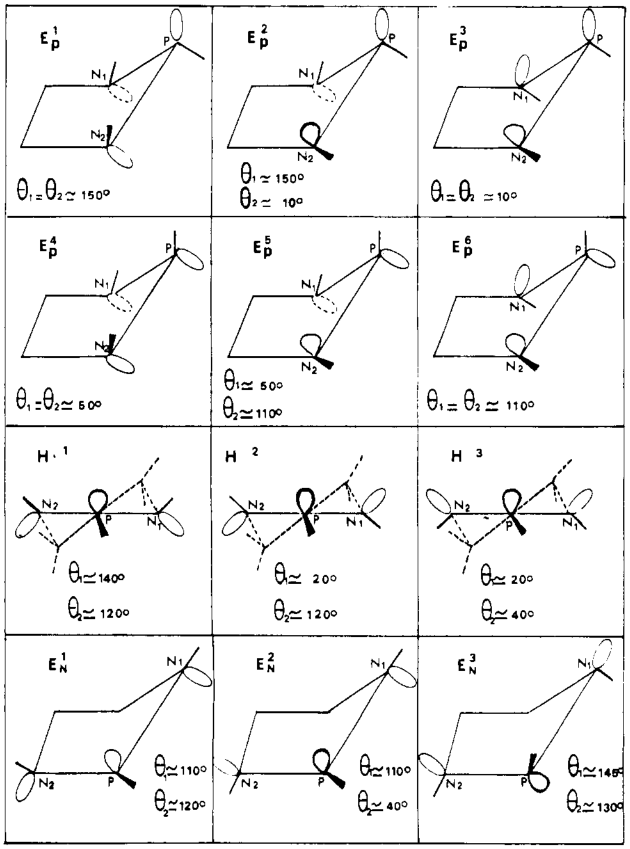

Figure 9. Envelope and half-chair forms envisaged.

If among all the possible envelope and half-chair forms we retain only those generally invoked, i.e., envelope with phosphorus flap ($\mathrm{E_p}$), half-chair with a C_2 pseudo-axis (*H*) or envelope with nitrogen flap ($\mathrm{E_N}$) as recently proposed,[19] a certain number of other forms nonetheless remain possible in the vapor phase. These forms are shown in Figure 9, where a slightly pyrimidal geometry ($\sum\angle\mathrm{N} = 355°$) is adopted for the endocyclic nitrogens. This hypothesis is justified a posteriori since the dihedral angle between the phosphorus lone pair and the lone pairs of the endocyclic nitrogens is never close

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(23) It is generally admitted that the orientation of the lone pairs of the nitrogen atoms in this compound is pseudo-σ in relation to the lone pair of phosphorus, as for chlorobis(dimethylamino)phosphine.

(24) Lappert, M. F.; Pedley, J. B.; Wilkins, B. T.; Stelzer, O.; Unger, E. *J. Chem. Soc., Dalton Trans.* **1975**, 1207.

Table IV. Orbital Energies and Localizations Calculated for Compounds 4–7

IP_{exptl}, eV	conformation H^1 [b]		conformation $E_N{}^1$ [b]		conformation $E_p{}^6$ [b]	
Compound 4						
7.59	9.77	N_1 10, N_2 27, N_3 44	9.98	N_1 28, N_2 18, N_3 24	9.82	N_1 24, N_2 24, N_3 34
7.78	10.06	*P 26*, N_1 37, N_2 19	10.15	*P 35*, N_1 18, N_2 27	10.14	*P 35*, N_1 23, N_2 23
8.72	10.53	P 7, N_1 20, N_2 24, N_3 29	10.65	N_1 17, N_2 18, N_3 39	10.52	N_1 17, N_2 17, N_3 40
9.88[a]	11.75	*P 45*, N_1 18, N_2 18	11.68	*P 38*, N_1 24, N_2 21	11.59	*P 39*, N_1 22, N_2 22
Compound 5						
7.89[a]	9.78	*P 28*, N_1 26, N_2 27, C 10	9.90	*P 36*, N_1 23, N_2 21, C 10	9.86	*P* 36, N_1 21, N_2 21, C 11
8.50	10.27	N_1 37, N_2 38	10.34	N_1 36, N_2 40	10.19	N_1 39, N_2 39
9.68[a]	11.84	*P 45*, N_1 18, N_2 18	11.78	*P 39*, N_1 23, N_2 20	11.71	*P 40*, N_1 21, N_2 21
11.5–12	13.11	P 27, N_1 15, C 22	13.24	P 25, N_1 7, C 20	13.24	P 24, N_1 7, N_2 7, C 20
Compound 6						
8.14	10.14	N_1 15, N_2 59	10.23	N_1 44, N_2 30	10.08	N_1 39, N_2 39
8.40	10.26	*P 25*, N_1 50, N_2 8	10.34	*P 35*, N_1 14, N_2 30, O 5	10.35	*P 38*, N_1 22, N_2 22
9.70[a]	11.79	*P 42*, N_1 18, N_2 18	11.73	*P 35*, N_1 23, N_2 22	11.64	*P 36*, N_1 22, N_2 22
10.63	12.34	N_1 9, N_2 8, O 48	12.59	N_1 8, N_2 8, O 49	12.48	P 10, N_1 12, N_2 12, O 48
Compound 7						
8.63	10.38	P 25, N_1 17, N_2 39	10.49	P 35, N_1 30, N_2 14	10.46	N_1 39, N_2 39
8.92	10.52	N_1 46, N_2 26	10.57	N_1 28, N_2 45	10.52	P 36, N_1 21, N_2 21
9.98[a]	11.76	P 29, N_1 14, N_2 14, *Cl 32*	11.81	*P 25*, N_1 20, N_2 17, *Cl 23*	11.76	*P 26*, N_1 19, N_2 19, *Cl 24*
10.77	12.73	Cl 69, N_1 7, N_2 7	12.85	Cl 74	12.79	Cl 74
11.25	13.78		13.62		13.56	

[a] The intensity of the band decreases when going from the He I to the He II spectrum. [b] Italic values correspond to the highest localization.

to 90° in all the models advanced.[25]

It would appear impossible and totally arbitrary to determine the preferred form from ionization potential values and a qualitative estimation of interactions between phosphorus and nitrogen lone pairs. Even for models such as $E_P{}^1$ (trans orientation of lone pairs) and $E_P{}^3$ (cis orientation), it is difficult to a priori evaluate the difference between a cis interaction and a trans interaction which is known to be greater (principle of maximum negative overlapping[26]). STO-3G calculations[22] on minimized cis, gauche, and trans forms of aminophosphine enabled us to estimate the nonnegligible influence of the reciprocal orientation of lone pairs on the associated splitting of molecular orbitals. These data are visualized in Figure 10.

In order to more rigorously determine the nature and importance of the interactions occurring in the different models under consideration, we calculated the corresponding orbital energies. The magnitude of the problem led us to choose the semiempirical CNDO/S method.

All the data obtained for compound **4** are shown in Table II, and when these data are compared with experimental values, the following five forms were retained for each type of conformation: (i) envelope with phosphorus flap, equatorial substituent $E_P{}^1$ and $E_P{}^2$; axial substituent $E_P{}^6$; (ii) half-chair H^1; (iii) envelope with nitrogen flap, axial substituent $E_N{}^1$; equatorial substituent $E_N{}^3$.

Without attributing too much reliability to the total energies calculated by this method as applied to the model conformations, it is satisfying to observe that notably the $E_P{}^6$, H^1, $E_N{}^1$ and $E_N{}^3$ conformations are energetically the most favored.

For these conformations ($E_P{}^6$, H^1, $E_N{}^1$, and$E_N{}^3$), Table III shows the orbital energies calculated for compounds **5–7**. The values calculated for conformation $E_P{}^1$ are also reported as an indication.

It is to be noted that for all the compounds, the envelope form with phosphorus flap and the substituent in an equatorial position is definitively excluded, since the calculated spread between the third and fourth bands in this conformation of compounds **5–7** is too small. Since this fourth band is characteristic of the substituent R, it may be deduced that the interactions between the lone pairs of the endocyclic nitrogens and the lone pairs of oxygen, of chlorine, or of the "π" orbitals of CH_3 are poorly shown by this model. It appears equally reasonable to reject for these compounds the $E_N{}^3$ conformation, for which the notable interaction between the phosphorus lone pair and the lone pairs of the endocyclic nitrogens would lead to too great a splitting between the first and third bands: $\Delta E_{calcd} \simeq 2$ eV, 1.3 eV $< \Delta E_{exptl} <$ 1.6 eV.

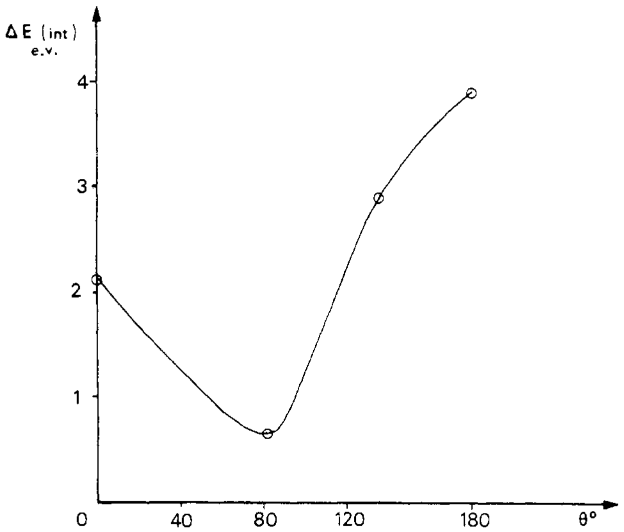

Figure 10. Calculated splitting between molecular orbitals associated with the lone pairs of phosphorus and nitrogen atoms vs. the dihedral angle between these lone pairs.

On the other hand, a fairly satisfying agreement is observed between experimental values and orbital energies calculated for conformations $E_P{}^6$, H^1, and $E_N{}^1$. These energies are very close since the dihedral angles between the phosphorus lone pair and that of the nitrogens is on the same order: $E_P{}^6$, $\theta_1 = \theta_2 = 110°$; H^1, $\theta_1 = 140°$, $\theta_2 = 120°$; $E_N{}^1$, $\theta_1 = 110°$, $\theta_2 = 120°$. Only the dihedral angle α between the lone pairs of the

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(25) Geometric parameters are reported in the experimental section. The direction of the lone pair is defined as the perpendicular to the base of the pyramid with N at the apex and whose edges along bond directions have a unit length.

(26) Weinhold, F.; Brunck, K. *J. Am. Chem. Soc.* **1976**, *98*, 3745.

endocyclic nitrogens is slightly different: $E_P{}^6(\alpha) \simeq 0°$; $H^1(\alpha) \simeq 20°$; $E_N{}^1(\alpha) \simeq 10°$. A more pronounced N–N interaction results for the first form. This is seen especially in the case of compound **5**: the energy of the second ionization potential associated with the antisymmetric combination of the endocyclic atoms (not perturbed by R) increases in the order $E_P{}^6 < H^1 \simeq E_N{}^1$. Even though the destabilization calculated for the envelope form does not correspond to experimental observation, this conformation cannot be eliminated by this argument alone.

After considering the above data, we believe the preferred form in the vapor phase to be an $E_P{}^6$ envelope with phosphorus flap; the substituent in this atom is axial and trans in relation to the methyl substituents on the endocyclic nitrogens. Alternatively, we invoke a half-chair with either the NPN (H^1) system or the PNC ($E_N{}^1$) system in the median plane where, as above, the substituent on the phosphorus is axial and trans in relation to the methyl groups.

The first conformer corresponds to that determined by Naumov for 2-chloro-1,3,2-diazaphospholane;[9] the third conformation is that recently suggested in solution.[19,27]

It does not, however, seem possible to determine the preference of one or another of these conformations which are very close, especially since there is the possibility of a rapid pseudo-rotation of the nucleus around the C–C bond and the presence of one and/or another form is not excluded, as is the eventuality of a preferred conformer which could vary as a function of the nature of the substituent.

Regardless of the preferred conformation, it should be noted that the diazaphospholane ring in the vapor phase presents an orientation of the nitrogen lone pairs which is relatively "pseudo-σ"[28] in relation to the orientation of phosphorus. Our interpretation differs from that of Worley and co-workers[18] on this point: these authors proposed a model in which the interactions between the lone pairs of the endocyclic nitrogens and the phosphorus atom are "pseudo-π". We believe that the photoelectron spectra cannot be interpreted on the basis of the simple "pseudo-π" interaction model but rather on the basis of more complex interactions (the P–N interaction for a "pseudo-σ" interaction of 110–130° is notable, in spite of all considerations cf. Figure 10). Table IV shows the localizations calculated for the four compounds and for the H^1, $E_N{}^1$, and $E_P{}^6$ conformations. These localizations are clearly quite close and correspond to experimental observations.

For compounds **5**–**7**, the molecular orbital resulting from the interaction between the phosphorus lone pair and the lone pairs of the endocyclic nitrogens with notable weight on the phosphorus is associated with the third band.

When passing from He I to He II excitation, we observed a considerable decrease of intensity in the third band of these compounds, which indeed corresponds to the ionization of electrons which are partially localized on the phosphorus atom.

In the case of compound **7**, this band appears in the form of a narrow intense peak, unlike the broadened structure observed with compounds **5** and **6**. This aspect is explained by the calculations as a considerable mixing with the hemi-symmetrical chlorine lone pair.[29]

Finally, in the case of compound **4**, whose spectrum is close to that of tris(dimethylamino)phosphine, we assign the fourth

Table V. Geometric Parameters Minimized in the Diazaphospholane Ring by the MNDO Method[a]

	$P\text{-}N_{exo}$	$P\text{-}N_{1,2endo}$	$C\text{-}N_{1,2}$	C–C	$\angle N_1\text{-}PN_2$	$\angle PN_{1,2endo}C$	$\angle N_{exo}PN_{1,2}$	$\angle PN_{1,2exo}C$	$\angle CN_{1,2exo}C$	$\angle N_{1,2}CC$	$\angle PN_{exo}C$	NCCN	CCNP	CNPN	NPNC	PNCC
A[b]	1.670	1.660 1.663	1.475 1.476	1.573	94.2	115.9 115.7	107.3 105.7	122.8 121.5	121. 120.	106.8 107.	128. 113.5	3.99	0.97	2.04	4.79	5.82
B[c]	1.672	1.657 1.66	1.477 1.474	1.572	94.4	115.9 115.6	106.8 105.6	123. 121.5	120.8 120.5	106.9 107.1	127.7 113.8	0.07	0.64	0.83	0.78	0.51

[a] Bond lengths given in Å; angles in deg. Given the large size of the molecules studied, we were obliged to fix all the C–H lengths. It thus remains possible that the two minima reached in fact correspond to one extremely flat minimum. [b] $E_t(A) = -1770.1396$ eV. [c] $E_t(B) = -1770.1646$ eV.

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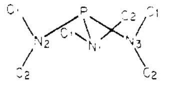
(27) The interpretation of $^2J_{PNC}$ coupling of Hargis and co-workers[19] does not seem unequivocal since the values of J may correpond either to one of the three forms (envelope with nitrogen flap (considered by these authors): half-chair with NPN system in the median plane, envelope with phosphorus flap (axial substituent)), or to a system of rapid exchange among these three conformation.

(28) We define a π orientation, either cis or trans, for an angle between the lone pair of phosphorus and that of nitrogen from 0 to 45° and from 135 to 180°.

(29) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

Table VI. Bond Lengths (Å) and Angles (Deg) for Tris(dimethylamino)phosphine and the Various Diazaphospholanes



A. Tris(dimethylamino)phosphine

P-N	C-N	$\angle N_2PN_3$	$\angle N_2PN_1$-$\angle N_1PN_3$	$\angle N_1PC_1$-$\angle N_1PC_2$	$\angle N_2PC_1$-$\angle N_3PC_1$	$\angle N_2PC_2$-$\angle N_3PC_2$
1.70	1.46	105	98	115	125	115

B. Diazaphospholanes

form	E_P (eq)[a]	E_P (ax)[a]	H^1	E_N
P-N	1.70	1.70	1.70	1.70
C-N(endo)	1.475	1.475	1.475	1.45
C-N(exo)	1.45	1.45	1.45	1.45
P-C	1.84	1.84	1.84	1.84
P-O	1.63	1.63	1.63	1.63
P-Cl	2.10	2.10	2.10	2.10
∠NPN (N endo)	96.5	96.5	96.5	98
∠CNP (N endo)	110	110	109.2	107.8 (N flap) 110
$\angle N_{endo}PX$	96.5	105[b]	100[b]	105[b]
$\angle PN_{exo}C_1$	120	125[b]	125[b]	120
$\angle PN_{exo}C_2$	120	118	118	120
torsional angle	CNNP	CNNP	NCCN	NPCN
angle, deg	20	20	40	20

[a] Equivalent substituent, eq; axial substituent, ax. [b] We were led to adapt these values for the angles since very great steric strain existed in the forms in question, especially for the case of the NMe_2 substituent. Note that the methyl groups were always fixed on the endocyclic nitrogens so as to obtain $\Sigma\angle N = 335°$.

band (only this band exhibits an intensity decrease when excited with He II) to the molecular orbital arising from the interaction between the lone pair of phosphorus and the lone pairs of the nitrogens.

The intensity variations observed for the first band do not enable us to determine the ionization potential which must be associated with the molecular orbital having a lone-pair character on phosphorus. This remark also concerns derivatives **6** and **7**. The calculated localizations also depend on the conformation and, in light of these data, it is not possible to come to an unambiguously conclusion.

We do not believe it is possible to utilize only photoelectron data to unequivocally define the nature of the preferred conformation of the diazaphospholane ring in the vapor phase (envelope with flap phosphorus and axial substituent, half-chair with the NPN system, or the PNC system in the median plane). The present analysis demonstrates that the lone pairs of the endocyclic nitrogens, which can reasonably be admitted as being slightly pyrimidal, are oriented at about 120° from the lone pair of phosphorus. This renders hazardous the definition of interaction parameters which are transposable in the varied series of aminophosphines.

It should be noted that these hypotheses concerning the conformation of the diazaphospholane ring are consistent with our conclusions on the basis of a theoretical study of aminophosphine and the analysis of the spectrum of the acyclic derivative. Considering cyclization-induced strain, the ring would adopt a configuration in which the orientation of the lone pairs of endocyclic nitrogens would be as close to 90° as possible, in other words 120°.

A minimization of the principal parameters by the MNDO method[30] did not enable us to remove this indetermination of the privileged conformation of the diazaphospholane ring in the vapor phase.

Indeed, this method does not satisfactorily account for nonplanar heterocyclic structures and clearly underestimates their folding angle.[31] The different plausible conformations (E_P, E_N, E_C, *H*) converge with minimization toward two quasi-plane forms which are not reasonable to consider (Table V).

Experimental Section

Photoelectron spectra were recorded with a Perkin-Elmer PS 18 and calibrated with the ${}^2P_{1/2}$ and ${}^3P_{3/2}$ peaks of xenon (12.127 and 13.433 eV) and of argon (15.755 and 15.93 eV). Precision of measurements was 20 mV in the case of well-resolved bands.

Calculations were performed with the CNDO/S method extended to the third period,[32] by adopting the following parameters for phosphorus: $\beta^\circ_s = \beta^\circ_p = -22$ eV (value close to that adopted by Schweig et al.[33]): $\beta^\circ_d = -4$ eV. Concerning values for γ_{AA}, we have retained $\gamma_{AA}(s) = \gamma_{AA}(p) = 7.88$ eV proposed by Boyd and Whitehead.[34] Since a lower value had to be adopted for $\gamma_{AA}(d)$,[35] we adopted $\gamma_{AA}(d) = 4.42$ eV.

Geometric parameters (bond lengths and angles) used for tris(dimethylamino)phosphine and the various diazaphospholanes are shown in Table VI. The data in the case of tris(dimethylamino)phosphine corresponds to the mean values deduced by the X-ray study of Songstad et al.[9a] on trimorpholinophosphine and tripiperidinophosphine.

Concerning the different diazaphospholanes, we chose standard values deduced from data in the literature[36] and adjusted them in order to close the rings envisaged without creating excessive steric hindrances.

Acknowledgment. We thank Professor J. Songstad from the University of Bergen, Bergen, Norway, for supplying compounds **2** and **3**.

Registry No. **1**, 1608-26-0; **2**, 13954-38-6; **3**, 5815-61-2; **4**, 6069-38-1; **5**, 32294-62-5; **6**, 7137-86-2; **7**, 6069-36-9; $CH_3P(NMe_2)_2$, 14937-39-4; $P(C_2H_5)_3$, 554-70-1; $N(C_2H_5)_3$, 121-44-8.

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(30) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(31) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.
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