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**Photoelectron Spectra of Group 5 Compounds. II.<sup>1</sup>  
Conformational Analysis of Diphosphine (P<sub>2</sub>H<sub>4</sub>)**

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The photoelectron spectra of certain hydrazines,<sup>2-4</sup> disulfides,<sup>5</sup> peroxides,<sup>6</sup> and aminophosphines<sup>7,8</sup> have been assigned to a unique conformer, being present under normal PE spectroscopic conditions. In contrast, different rotamers could be detected in the PE spectra of hexahydropyridazines<sup>3b</sup> and tetrasubstituted diphosphines and diarsines<sup>9</sup> and were assumed for polysilanes.<sup>10</sup> The composition of the rotameric mixture (trans:gauche) obtained for tetramethyldiphosphine from the relative PE peak areas<sup>9</sup> had to be revised.<sup>11</sup>

For the simplest diphosphine P<sub>2</sub>H<sub>4</sub> structural data<sup>12,13</sup> and the results from ab initio<sup>14</sup> and semiempirical<sup>15</sup> methods are available which are consistent with preponderant gauche conformation. However, some discrepancies remain in the reported equilibrium dihedral angles, barrier magnitudes, or the amount of trans isomers. Therefore, it was of interest to elucidate the structure of P<sub>2</sub>H<sub>4</sub> by PE spectroscopy.<sup>16</sup> To gain some insight into its conformational composition we tried to simulate the experimental PE spectrum of P<sub>2</sub>H<sub>4</sub> with EHMO, CNDO, and the reported ab initio orbital energies.<sup>14,17a</sup>

**Experimental Section and Computational Details**

The He I (584-Å) PE spectra were recorded with a Perkin-Elmer PS 16 spectrometer and calibrated with argon (resolution 35-40 meV).

Diphosphine was prepared as described by Baudier and Schmidt,<sup>18</sup> by treating calcium phosphide (Riedel de Haen AG, Seelze) with water in a high-vacuum line, followed by purification by trap to trap distillation.

To retard decomposition, giving PH<sub>3</sub> and solid polymers P<sub>n</sub>H<sub>n</sub>, catalyzed by traces of acids, a continuous flow of ammonia was passed through the PE spectrometer and the inlet equipment over a period of 24 h before the actual measurements. To maintain a constant

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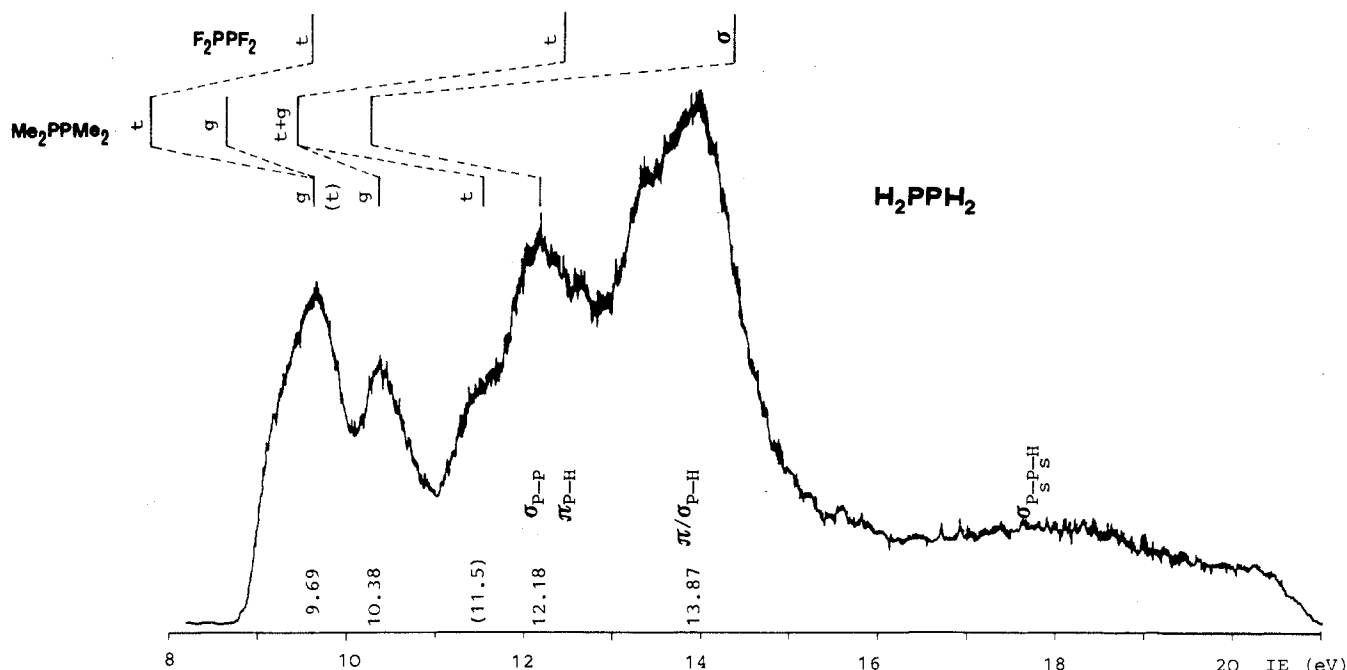


Figure 1. PE spectrum and vertical IP's of diphosphine as well as vertical lone-pair ionization energies of  $P_2Me_4$  and  $P_2F_4$ .

pressure during the recordings  $P_2H_4$  was immersed in a  $CO_2$ -ether cooling mixture and was stirred magnetically. The more volatile  $PH_3$  which was clearly distinguishable by its characteristic first band exhibiting vibrational fine structure could be completely removed in this way after 2 h. Several spectra were then run within a period of 12 h. No changes in band shapes could be detected. (This contrasts  $P_2Me_4$  where contaminating  $PMe_3$  discernible by changes in band intensities could not be removed entirely within 12 h despite repeated fractional distillation. The first PE band of  $PMe_3$  (8.6 eV<sup>1</sup>) coincides with the second band of  $P_2Me_4$  obscuring its real intensity!)

CNDO (with and without d orbitals) and EHMO calculations (without d orbitals) were performed on the Univac 1108 computer of the University Computing Center at Frankfurt/M.

Phosphorus 3p and 3s valence ionization potentials were parametrized in the EHMO computations of  $PH_3$  in order to reproduce the experimental  $n/\sigma$  energy gap (ca. 3 eV) within the corresponding eigenvalues. The parameters thus obtained ( $P_{3p}$ , 11.0 eV;  $P_{3s}$ , 19.0 eV) were employed in EHMO calculations of  $P_2H_4$  to gain a reasonable energy separation  $\Delta E(n \leftrightarrow \sigma)$ .

Ab initio eigenvalues were estimated from the orbital energy plot presented by Van Wazer et al.<sup>14</sup> Their ab initio and CNDO total energy equations have been used too.

The simulation of the PE spectrum of  $P_2H_4$  was carried out using our "Boltzmann" program previously described.<sup>10</sup> Lorentz curves instead of Gaussians were chosen since they fitted slightly better experimental band contours. No significant changes in the simulated spectra have been detected on varying  $T$  from  $-30$  to  $+30$  °C in the Boltzmann expression, considering possible Joule-Thompson effects. The different bonding characters of the  $\sigma_{P-H}$  and  $n_P$  lone-pair orbitals were taken into account reducing the half-widths of  $n_P$  bands by a factor of 0.67 with respect to  $\sigma$  bands (half-width 0.7 eV). s-Type orbitals (1a, 1b) and the instrumental decrease in intensity occurring at higher energies were neglected.

The orbital and total energies of  $P_2H_4$  were calculated by varying only the twist angle  $\phi$  from  $0^\circ$  (cis, eclipsed) to  $180^\circ$  (trans, staggered) at intervals of  $10^\circ$ .

## Results and Discussion

The He I PE spectrum of diphosphine is given in Figure 1. Six of seven bands due to valence orbitals are expected according to corresponding ab initio<sup>14</sup> and semiempirical calculations. Weak bands beyond 15.5 eV (ca. 18 and 20.3 eV) should be due to  $P_s-H$  (1b) and  $(H)P_s-P_s(H)$  (1a)  $\sigma$ -bonding levels. Between 12 and 15.5 eV two partly overlapping bands of different intensity due to  $\sigma_{P-P}$  (3a) and  $\sigma/\pi_{P-H}$  (2a, 2b) levels occur. The low-energy shoulder at 11.5 eV is attributed

to the trans lone-pair orbital combination  $n_+$  if analogy with  $P_2Me_4$ <sup>9,16</sup> and  $P_2F_4$ <sup>19</sup> PE data is assumed (Figure 1). Below 11 eV the  $P_2H_4$  spectrum contains two lone-pair bands centered at 9.69 and 10.38 eV. The first one is assigned mainly to the gauche combination  $n_-$  (4a). It exhibits a shoulder on its low-energy side indicating another conformational ratio than in perfluoro- and permethylidiphosphine. Their lone-pair bands are nearly symmetrical and were assigned to only one or two fixed molecular geometries, respectively. The second band is attributed to the gauche combination  $n_+$  (3b) and should not be confused with the first band of  $PH_3$  (10.59 eV)<sup>20</sup> (see Experimental Section).

Although the gauche configuration is predicted to be the most stable one of diphosphine,<sup>12,14,15</sup> it is known that barriers to rotation around P-P bonds are much smaller than in hydrazines (e.g., see ref 17), and should favor the population of different rotamers. Our simulation includes total energy curves ( $\phi = 0 \rightarrow 180^\circ$ ) with a Boltzmann distribution at 25 °C using the calculations cited above.

Barrier curves and eigenvalue plots are compared in Figure 2. Corresponding simulated PE spectra are obviously governed by energy sets at their equilibrium dihedral angles.

Graphs of EHMO eigenfunctions for the eclipsed ( $0^\circ$ ,  $C_{2v}$ ) and staggered ( $180^\circ$ ,  $C_{2h}$ ) rotamers of  $P_2H_4$  are displayed in Figure 3 to illustrate  $n$ ,  $\sigma$ , and  $\pi$  symbols used here to characterize the main orbital contributions.

Although the experimental band contours are badly reproduced by all calculations employed here, the best agreement between experimental and simulated PE spectra is provided by the ab initio method.<sup>14</sup> The spectrum in Figure 2 A clearly shows that the main component of both separated lone pairs found experimentally (9.69 and 10.38 eV) originates from the gauche split. The trans rotamer is calculated to be present with  $\sim 10\%$  only. The conclusion of Ames and Turner that  $n_{\pm}$  orbital energies of the gauche conformation of  $P_2Me_4$  are separated<sup>11</sup> is substantiated by our observation. The  $\Delta n_P$  energy gap (Figure 1, 0.69 eV) is similar to that in hydrazine (0.73 eV);<sup>2-4</sup> this is unexpected since orbital interactions should be comparatively smaller with longer bonds.

The unsuccessful simulation by semiempirical techniques can be understood from Figure 2. Although the overall eigenvalue plots are rather similar, the  $\phi$ -dependent total energy

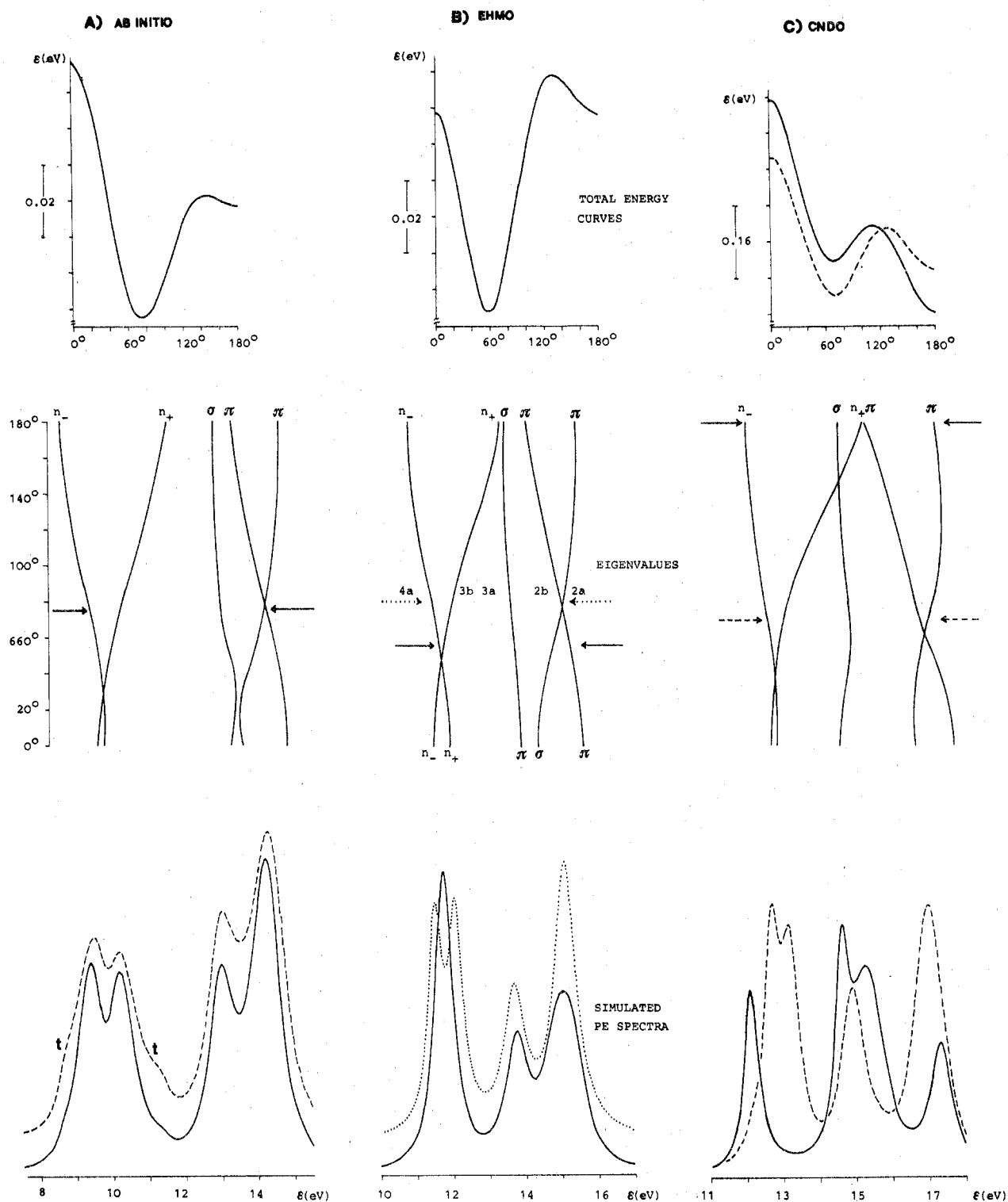


Figure 2. Comparison of total energy curves, eigenvalue plots, and simulated PE spectra of  $P_2H_4$  from (A) ab initio,<sup>14</sup> (B) EHMO (-d), and (C) CNDO (+d) calculations. Equilibrium angles are indicated by arrows within the eigenvalue plots. The dotted lines refer (A) to an ab initio barrier curve compressed by an energy scale factor of 0.6, (B) to simulation with  $\phi = 80^\circ$ , and (C) to simulation based on Van Wazer's CNDO (+d) total energy equation.

curves disagree either in minimum angles or in the barrier heights. While the ab initio equilibrium angle ( $75.2^\circ$ <sup>14</sup> ( $75^\circ$ ),  $180^\circ$ <sup>17a</sup>) is close to the experimental one ( $74^\circ$ ,<sup>12</sup>  $81^\circ$ <sup>13</sup>), EHMO calculations favor a total energy minimum with  $\phi$  approximately  $58^\circ$ , here  $n_p$  energies being almost degenerate. Better simulation from EHMO data is obtained using the experimental  $\phi$  angle (Figure 2B, dotted line,  $80^\circ$ ). The CNDO total energy curve (Figure 2C, solid line) favors staggered rotamers similar to Wagner's ab initio barrier curve

and is therefore unrealistic. Van Wazer's CNDO (+d) total energy equation referring to another set of parameters gives a much better fit (Figure 2C, broken line) confirming the assumption of predominant gauche rotamers.

Comparing the vertical  $n_p$  IP's of  $P_2Me_4$ <sup>9</sup> and  $P_2F_4$ <sup>19</sup> with those of  $P_2H_4$  (Figure 1) and especially analyzing the shapes of the first and the third bands there is good reason for trans conformers being present to a larger extent as is suggested by the "arrest" at  $180^\circ$  of the ab initio barrier curve (Figure 2A).

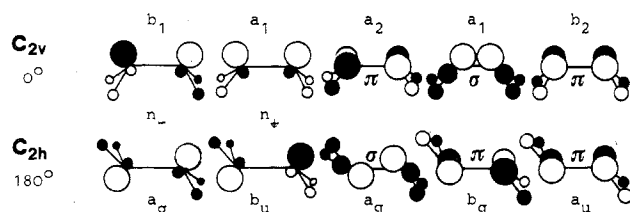


Figure 3. EHMO orbital diagrams and their irreducible representations in  $C_{2v}$  (eclipsed) and  $C_{2h}$  (staggered) of  $P_2H_4$ .

Therefore we artificially compressed this curve with an energy scale factor of 0.6 to increase the population of trans species. The resulting simulated spectrum is shown in Figure 2A as a broken line, and bands attributed to the trans isomers are indicated "t".

Assuming an approximately parallel shift of lone-pair energies upon replacement of H by methyl groups (compare to  $N_2H_4$ ,  $N_2Me_4^{2-4}$ ) or by F atoms (the perfluoro effect should equalize  $\Delta n_p$  gaps of "trans-only"  $P_2H_4$  and  $P_2F_4$  molecules due to pseudo- $\pi$  symmetry,  $C_{2h}$ ), the  $n_+(t)$  combination of *trans*-diphosphine is assigned to the band at 11.5 eV overlapped by  $\sigma$ - and  $\pi$ -orbital ionizations. The  $n_-(t)$  combination is then responsible for the low-energy asymmetry of the first band (Figure 1).

It seems that the sufficient separation of lone-pair ionization energies of different rotamers makes diphosphine a good example for making PE studies of temperature-dependent changes in conformer populations as well as for checking the quality of computed rotational barriers.

Registry No.  $P_2H_4$ , 13445-50-6.

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