

coupled with transfer of scale constants between related molecules can serve as a practical and highly reliable tool for the accurate prediction of infrared spectra.

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## Phosphorus-Nitrogen Multiple Bonds. A Theoretical Investigation of Structure and Bonding in (NH)<sub>2</sub>PNH<sub>2</sub>, (NH<sub>2</sub>)<sub>2</sub>PN, and the (Cyclic) Dimer P<sub>2</sub>N<sub>6</sub>H<sub>8</sub>

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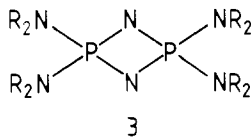
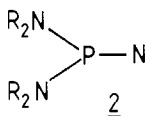
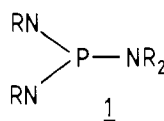
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**Abstract:** Results of extended basis set treatments on the SCF level and with inclusion of correlation effects are reported for various geometries of (NH)<sub>2</sub>PNH<sub>2</sub>, (NH<sub>2</sub>)<sub>2</sub>PN, and the dimer P<sub>2</sub>N<sub>6</sub>H<sub>8</sub>. These molecules are considered as models for recently investigated compounds containing SiMe<sub>3</sub> or isopropyl instead of H. Computed geometric structure constants are in excellent agreement with experiment as far as a comparison is possible. On the highest level of theory, (NH)<sub>2</sub>PNH<sub>2</sub> is found to be 22 kcal/mol lower in energy than the isomer (NH<sub>2</sub>)<sub>2</sub>PN, but dimerization to P<sub>2</sub>N<sub>6</sub>H<sub>8</sub> is exothermic by 45 kcal/mol. A detailed investigation of the electronic structures reveals that phosphorus is best considered as a tetravalent P<sup>+</sup> in all compounds considered. The present results indicate (NH<sub>2</sub>)<sub>2</sub>PN to be a highly reactive molecule, quite different from (NH)<sub>2</sub>PNH<sub>2</sub>.

### 1. Introduction

Phosphorus(V) compounds usually show coordination numbers 4 to 6. The first planar, threefold coordinated phosphorus compound, PN<sub>3</sub>R<sub>4</sub> (**1**, R = SiMe<sub>3</sub>), was obtained<sup>1,2</sup> and investigated<sup>3,4</sup> a decade ago. The existence of the isomer **2** (for R = *i*-Pr, isopropyl) has recently been postulated as a short-lived intermediate<sup>5</sup> which undergoes, e.g., a head-to-tail cycloaddition<sup>6</sup> to



form the PN four-ring system P<sub>2</sub>N<sub>6</sub>R<sub>8</sub> (**3**). Molecule **1** is valence isoelectronic to PO<sub>2</sub>Cl which according to recent experimental and theoretical investigations<sup>7</sup> is also planar.

The electronic structure in compounds **1-3** is so far not well understood (see, e.g., ref 4), and the basic question is: are stable double or triple PN bonds (e.g., RN=P in **1** and P≡N in **2**) formed in **1,2** or dominates the ionic character which would imply high reactivity. In order to answer this question we have performed extended ab initio calculations which will be reported in this paper. For this purpose we treated only the simplest possible case, R = H. This is a simplification, but since R serves mainly to saturate the valences of N, this should have no appreciable effect on the electronic structure of the PN<sub>3</sub> system in **1** or **2**, or the P<sub>2</sub>N<sub>6</sub> system in **3**. The large groups R = SiMe<sub>3</sub> or R = *i*-Pr serve mainly to protect the PN bonds sterically and lead to some stabilization due to their appreciable polarizability.

A thorough investigation of possible PN double and triple bonds has been published by Trinquier<sup>8</sup> for the simplest possible cases: H<sub>2</sub>NP, NPH<sub>2</sub>, and HPNH. It was found that the electronic structure of singlet H<sub>2</sub>PN is best described as H<sub>2</sub>P=N, rather than H<sub>2</sub>P≡N, and that H<sub>2</sub>PN has only "somewhat triple-bond character". However, H<sub>2</sub>PN and its isomers constitute rather simplified model cases for **1** and **2**, and a treatment of the more realistic molecules **1** to **3** (for R = H) appeared appropriate.

### 2. Details of Computation

The calculations were performed with the Karlsruhe version<sup>9</sup> of the "Columbus system of programs".<sup>10</sup> Geometry optimizations were carried out on the SCF level by means of a gradient program.<sup>11</sup>

The following CGTO basis sets were employed:

P:	(11,7,1)/[6,4,1]	η(d) = 0.4
N:	(9,5,1)/[5,3,1]	η(d) = 0.8
H:	(4)/[2]	

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**Table I.** Computed Energies and Assignment of High-Lying MOs for Molecules Considered in This Work

molecule <sup>a</sup>	$E(\text{au})^b$	IPs (eV) <sup>c</sup>	assignment
<b>1a</b>	$E_{\text{SCF}} = -506.36743$	$1a_2$ (10.3)	$\pi$ -type, N(2)–N(3) antibonding
	$E_{\text{CI(SD)}} = -506.92570$	$6b_1$ (11.2)	$\sigma$ -type, lone pairs
	$E_{\text{CPF}} = -507.02585$	$3b_2$ (11.5)	N(2),N(3) antibonding $\pi$ -type, lone pair N(1)
<b>1b</b>	$E_{\text{SCF}} = -506.35162$		
<b>2a</b>	$E_{\text{SCF}} = -506.32343$	$3b_2$ (9.4)	$\pi$ -type, PN(1) bonding
	$E_{\text{CI(SD)}} = -506.88590$	$6b_1$ (9.7)	$\sigma$ -type, lone pair N(1) $\perp$ to PN(1) axis
<b>2b</b>	$E_{\text{SCF}} = -506.30457$	$10a_1$ (12.2)	$\sigma$ -type, lone pair N(1)
		$1a_2$ (12.4)	$\pi$ -type, lone pairs, N(2),N(3) antibonding
		$6b_1$ (10.0)	$\sigma$ -type, lone pair N(1), $\perp$ to PN(1) axis
		$3b_2$ (10.6)	$\pi$ -type, PN(1) bonding
		$10a_1$ (12.1)	$\sigma$ -type, lone pair N(1)
$5b_1$ (13.2)	$\sigma$ -type, lone pairs, N(2),N(3) antibonding		
<b>2b'</b>	$E_{\text{SCF}} = -506.29598$		
<b>2c</b>	$E_{\text{SCF}} = -506.34548$		
	$E_{\text{CI(SD)}} = -506.86567$		
	$E_{\text{CPF}} = -506.95797$		
	$E_{\text{SCF}} = -1012.80668$	$2b_{3g}$ (9.85)	$\pi$ for ring, N(1), N(2) antibonding
<b>3a</b>		$6b_{1u}$ (10.1)	as $2b_{3g}$ , but weakly N(1), N(2) bonding
		$5b_{2u}$ (10.3)	$\sigma$ -MO of ring, N(1), N(2) antibonding P(1), N(1) bond
<b>3b</b>	$E_{\text{SCF}} = -1012.80289$		

<sup>a</sup> Notation as in Figure 1 and text. <sup>b</sup> Total electronic energies, obtained at the SCF, CI(SD), and CPF level as described in section 2. <sup>c</sup> Ionization potentials according to Koopmanns' theorem.

The primitive GTOs were taken from Huzinaga's tables. The basis set is of DZP quality or better, except for H, and should give molecular and electronic structures very close to the SCF limit.

The above basis set is much too small to provide a reliable description of electron correlation effects.<sup>12</sup> Therefore, only a few calculations were performed beyond the SCF level in order to correct the well-known deficiencies of the SCF method to describe singlet–triplet separations. These calculations were done by means of the recently developed coupled pair functional (CPF) method, which is basically a size extensive modification of a CI(SD).<sup>13</sup> Only valence MOs were correlated. One high-lying MO per P and/or N atom, which is of 1s character, was kept frozen.

In order to visualize electronic structures, we further carried out population analyses based on occupation numbers<sup>14,15</sup> in using modified AOs.<sup>16</sup> Details of the present program will be published elsewhere.<sup>17</sup> Within this method the electronic structure is characterized by means of atomic net charges  $Q(A)$ , for atom A, and shared electron numbers SEN (AB) for the AB bond. The SEN provide a reliable measure of covalent bond strength.<sup>17</sup> Typical values for the SEN are as follows: strong  $\sigma$ -bonds (C–H, C–C), SEN  $\approx$  1.4; double bonds (C=C), SEN  $\approx$  2.2; triple bonds (C $\equiv$ C, N $\equiv$ N), SEN  $\approx$  3.0. The SEN is reduced in polar bonds (NaF, SEN = 0.3) and in weak bonds, such as Cl<sub>2</sub> (SEN = 0.9) and F<sub>2</sub> (SEN = 0.7).

### 3. Results

The SCF results obtained for the molecular and electronic structures of the most stable molecular states are presented in Figure 1 and the corresponding electronic energies on the SCF, CI(SD), and CPF level in Table I. The computed relative stabilities are displayed in Table II. (The CI(SD) energies are listed for the sake of completeness. The following discussion is based on CPF energies—besides the SCF energies—since they are considered to be more reliable.) Some additional results will be listed below. All bond distances are given in pm, angles in deg, and atomic net charges in units of  $e$ . For high-lying MOs we list the IPs, in eV, obtained according to Koopmanns' theorem together with a shorthand description of their character in Table I. Some contour diagrams will be displayed and discussed in the next section.

**a. (NH)<sub>2</sub>PNH<sub>2</sub> (1).** The most stable geometry is shown as **1a** in Figure 1, with imino protons in cis position to each other. A secondary minimum **1b** was found with imino protons flapped

**Table II.** Computed Relative Energies (kcal/mol) on Various Levels of Approximation

molecule <sup>a</sup>	SCF	CI(SD)	CPF
<b>1a</b>	0.0	0.0	0.0
<b>1b</b>	9.9		
<b>2a</b>	27.6	25.0	22.3
<b>2b</b>	39.4		
<b>2b'</b>	44.8		
<b>2c</b>	13.8	37.7	42.6
<b>3a<sup>b</sup></b>	-45.1		
<b>3b<sup>b</sup></b>	-42.7		

<sup>a</sup> The notation is the same as in Table I. <sup>b</sup> With respect to 2 (N–H)<sub>2</sub>PNH<sub>2</sub> (**1a**)

toward the NH<sub>2</sub> group and with the following structure constants (compare **1a** in Figure 1): PN(1) = 165.0, PN(2) = 152.4, N(1)H(1) = 100.5, N(2)H(3) = 100.7, N(2)PN(3) = 125.8°, H(1)N(1)H(2) = 116°, PN(2)H(3) = 240°.

The results of the population analysis and the SCF orbital energies are virtually identical with those for the cis conformer. The secondary minimum is 9.9 kcal/mol higher in energy than the cis form on the SCF level.

**b. (NH)<sub>2</sub>PN (2).** Three local minima were found for singlet states, all with C<sub>2v</sub> molecular symmetry. The most stable of these is planar, shown as **2a** in Figure 1. The secondary minimum, **2b** in Figure 1, is 11.8 kcal/mol higher in energy than **2a**. The third configuration **2b'** is smaller to **2b** but with NH<sub>2</sub> groups inverted, i.e., protons in cis position. The structure constants of **2b'** are virtually identical with those of **2b** (Figure 1) except for the following angles: N(4)PN(3) = 110°, H(5)N(3)H(7) = 109.2°, H(5)N(3)P = 114.9°. The cis isomer **2b'** is 5.4 kcal/mol higher in energy than **2b** on the SCF level.

Since nitrenes usually have a low-lying triplet state—with just one of the 2p electrons of N involved in bonding, the others being unpaired—we further investigated the triplet state, which is a <sup>3</sup>A'' state in C<sub>s</sub> molecular symmetry, **2c** in Figure 1.

The <sup>3</sup>A'' state is 13.8 kcal/mol lower in energy than the planar singlet state **2a** on the SCF level (but still higher than **1a**). This order is reversed if correlation effects are included. The planar singlet **2a** is now 20.3 kcal/mol lower than the <sup>3</sup>A'' state on the CPF level (see Table II).

**c. P<sub>2</sub>N<sub>6</sub>H<sub>8</sub> (3).** Only the <sup>1</sup>A<sub>g</sub> state in D<sub>2h</sub> molecular symmetry was investigated. The lowest energy was obtained for the configuration shown as **3a** in Figure 1, where the amino protons point away from each other and the nitrogen lone pairs are directed toward each other. A secondary minimum, **3b**, was obtained if the NH<sub>2</sub> groups were flapped away from the ring such that the

(12) K. Jankowski, R. Becherer, P. Scharf, H. Schiffer, and R. Ahlrichs, *J. Chem. Phys.*, **82**, 1413 (1985).

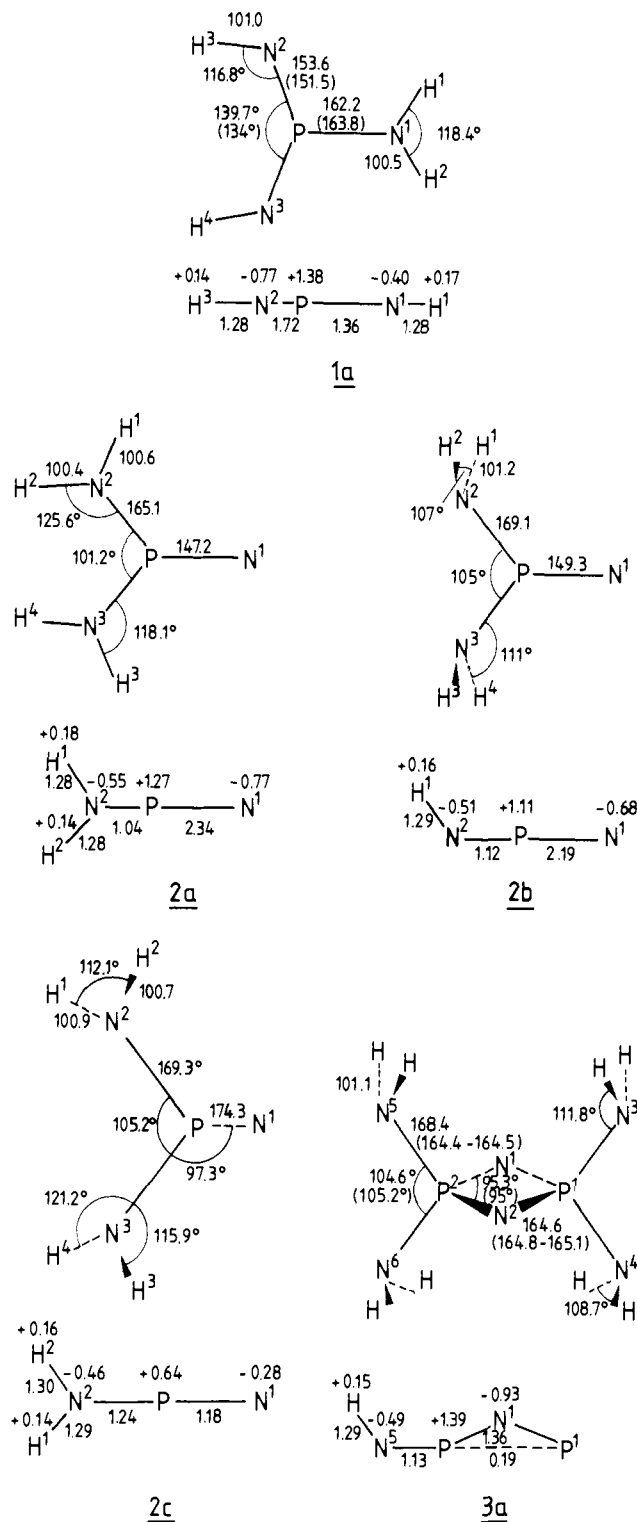
(13) R. Ahlrichs, P. Scharf, and C. Ehrhardt, *J. Chem. Phys.*, **82**, 890 (1985).

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**Figure 1.** Structure constants and results of the population analysis for molecules treated in this work. Distances are given in pm, angles in deg. Results of the population analysis are sketched schematically, charges above and SEN (as described in the text) below the atoms. Experimental structure constants are given in parentheses for **1a** as obtained for  $((\text{SiMe}_3)_2\text{N})_2\text{PN}(\text{SiMe}_3)_2$ ,<sup>4</sup> and for **3a** as obtained for H replaced by isopropyl.<sup>6</sup>

$\text{NH}_2$  planes are almost parallel. For the structure constants of **3b** we found the following values (compare **3a** in Figure 1):  $\text{P}(1)\text{N}(3) = 163.7$ ,  $\text{P}(1)\text{N}(5) = 168.2$ ,  $\text{N}(5)\text{H}(9) = 101.1$ ,  $\text{N}(3)\text{P}(1)\text{N}(4) = 96.1^\circ$ ,  $\text{N}(5)\text{P}(1)\text{N}(7) = 109.8^\circ$ ,  $\text{H}(9)\text{N}(5)\text{H}(11) = 110.6^\circ$ ,  $\text{P}(1)\text{N}(5)\text{H}(9) = 114.6^\circ$ .

**3b** is 2.4 kcal/mol higher in energy than **3a**. This energetic ordering may be reversed for other groups (than  $\text{R} = \text{H}$ ) or as

a result of solid-state packing effects.

#### 4. Discussion

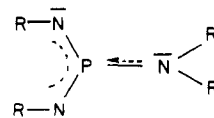
Let us first note the excellent agreement found between SCF and X-ray structure constants for **1a** and **3a** (Figure 1) as far as a comparison is possible. This is expected since the SCF method usually is accurate to  $\sim 1$  pm or  $\sim 1^\circ$  for this kind of compound. Slight further deviations may be caused by the different ligands,  $\text{R} = \text{H}$  vs.  $\text{R} = \text{SiMe}_3$  or *i*-Pr, and by solid-state packing effects.

The next immediate observation concerns the relative stability of the molecules investigated, as listed in Table II. The cyclic dimers **3a** and **3b** are by far the lowest in energy, followed by  $(\text{NH})_2\text{PNH}_2$  (**1a**, and **1b**). The phosphonitriles **2a-c** are highest in energy and are expected, as will be discussed below, to dimerize readily to form the ring systems **3a** or **3b**. In order to get a better understanding, let us now discuss some of the results which are of relevance for the chemical behavior of the various molecules.

**a.  $(\text{RN})_2\text{PNR}_2$  (**1**).** The chemical behavior of **1** is clearly determined by the high-lying  $\pi$  MOs: the  $3b_2$  MO, dominantly lone pair  $\text{N}(1)$ , and the  $1a_2$ ,  $2b_2$  MOs which form a four-electron, three-center  $\pi$ -system for  $\text{N}(2)\text{PN}(3)$  isoelectronic to the one found in the allyl anion. The  $3b_2$  and  $1a_2$  MOs are essentially nonbonding, but the  $2b_2$  MO is  $\text{PN}(2)$  and  $\text{PN}(3)$  bonding. It is one of the well-known peculiarities of quantum mechanics that such a doubly occupied three-center MO leads to a bond order of  $\sim 0.7$  for both bonds  $\text{PN}(2)$  and  $\text{PN}(3)$ , thus causing an appreciable stabilization. This is also reflected by the SEN of 1.72, which is in-between single and double bonds and rather close to a polar double bond. Another characteristic of four-electron, three-center bonds is the uneven charge distribution: roughly one electron is on the central atom P (which contributes two  $\pi$  electrons) and 1.5 on either ligand (which contribute one each). This allows one to rationalize the net charges  $Q(\text{N}1) = -0.77$  and  $Q(\text{P}) = 1.39$ . Four-electron, three-center bonds prefer a collinear arrangement of the atoms involved,  $\text{N}(2)\text{PN}(3)$ , since the corresponding nonbonding  $1a_2$  MO is  $\text{N}(2)\text{N}(3)$  antibonding and strongly prefers this geometry (compare the Walsh diagrams for  $\text{AB}_2$  molecules, especially  $\text{CO}_2$  as the classical example<sup>18</sup>). We note in passing that a similar angle such as  $\text{N}(2)\text{PN}(3)$  is found in  $\text{PO}_2\text{Cl}:\text{ZOPO} = 135^\circ$ .<sup>7</sup> The large  $\text{N}(2)\text{PN}(3)$  angle ( $139.7^\circ$  from our calculation and  $134^\circ$  for  $\text{R} = \text{SiMe}_3$ ) is clearly not caused by steric effects; it is natural for four-electron, three-center bonds.

There are appreciable stabilizing contributions of phosphorus 3d AOs to the nonbonding  $\pi$  MOs  $1a_2$  and  $3b_2$ , and the HOMO ( $1a_2$ ) in **1** has a larger IP than those in **2**. This  $p\pi-d\pi$  back-bonding is also expressed by the SEN ( $\text{PN}(1)$ ) of 1.36, which is relatively large for a polar bond and considerably larger than the value SEN ( $\text{PN}(2)$ ) = 1.04 found in **2a** (Figure 1).

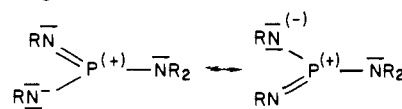
The electronic structure of **1** is best characterized as



where the dashed line indicates the four-electron, three-center bond (like that for the allyl anion) and the dotted arrow weak  $p\pi-d\pi$  back-bonding.

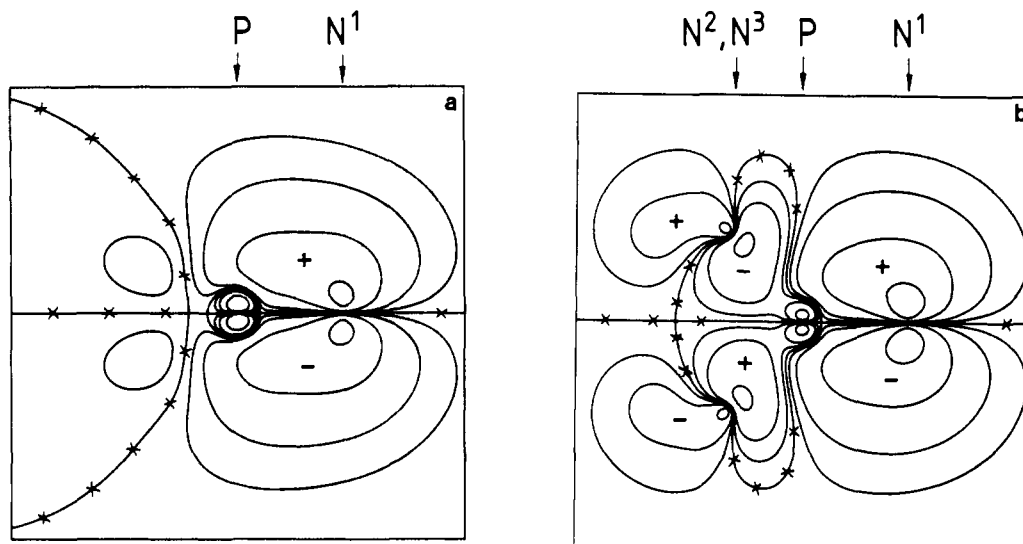
The present results indicate **1** to be a relatively stable molecule, although the polarity of PN bonds requires protection and some stabilization, which is easily achieved by large groups like  $\text{SiMe}_3$  to prevent oligomerization.

The electronic structure could also be described as a resonance of the following VB structures:

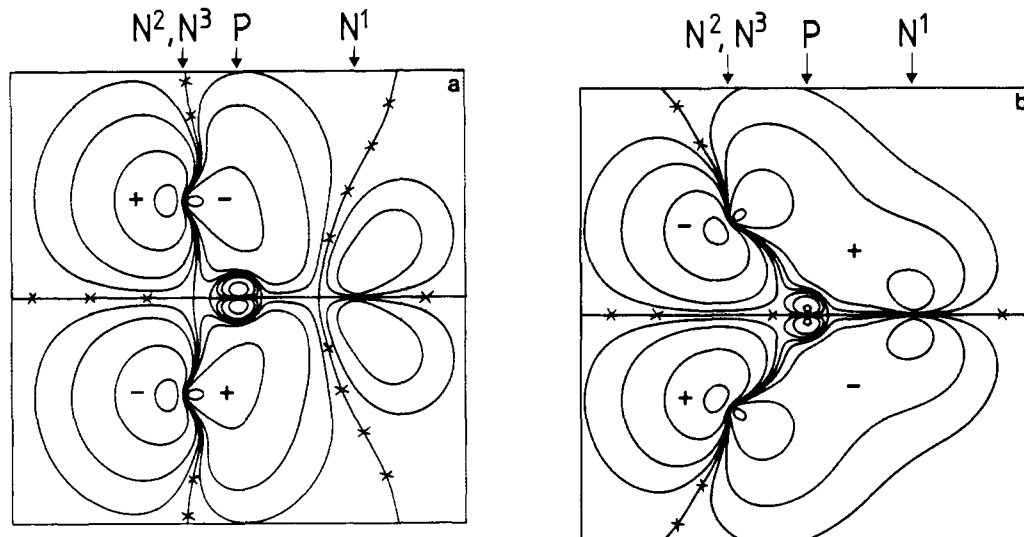


However, one has to keep in mind that the appreciable resonance stabilization leads here to a PN bond order larger than 1.5. This

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**Figure 2.** Contour lines of high-lying MOs of  $(\text{NH}_2)_2\text{PN}$  (**2a**) (see Figure 1): (a) the  $3b_2$  MO describing the  $\text{PN}(1)$   $3p\pi-2p\pi$  bond in a plane perpendicular the molecular plane; (b) the  $6b_1$  MO in the molecular plane. Although  $6b_1$  is dominantly lone pair  $\text{N}(1)$ , a marked phosphorus  $3d\pi$  contribution is visible describing  $2p\pi-3d\pi$  back-bonding. Lines plotted correspond to 0 (crossed),  $\pm 0.01$ ,  $\pm 0.03$ ,  $\pm 0.1$ , and  $\pm 0.3$  in a.u. Atomic positions are indicated on the margins.



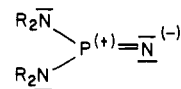
**Figure 3.** Contour lines of MOs describing the antibonding combination of nitrogen lone pairs: (a) the  $6b_1$  MO of  $(\text{NH}_2)_2\text{PNH}_2$  (**1b**), as described in section 3a; (b) the  $5b_1$  MO of  $(\text{NH}_2)_2\text{PN}$  (**2b**) (see Figure 1). Both diagrams show appreciable stabilizing phosphorus  $3d$  contributions; lines plotted as in Figure 2.

fact is easily overlooked and may then lead to the conclusion that because of the relatively short bond distances the "ionic" contributions should be of little importance.<sup>4</sup>

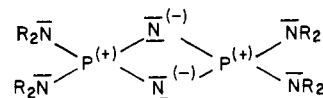
**b.**  $(\text{R}_2\text{N})_2\text{PN}$  (**2**). The electronic structure of **2** is easily rationalized. In the  $^3\text{A}'$  state one just has a trivalent P atom with bond angles of  $97.3$  and  $105.2^\circ$ , and two unpaired electrons on  $\text{N}(1)$ .

The singlet states also show clear-cut polarized single bonds between P and the amino groups, as is obvious from the bond distance and the corresponding SEN of 1.04–1.12. The SENs ( $\text{PN}(1)$ ) of 2.34 (planar **2a**) and 2.19 (**2b**) are larger than that for a polar double bond and indicates some triple-bond character. The  $\pi$ -type lone pair of P, the  $3b_2$  HOMO, is almost completely delocalized over  $\text{PN}(1)$  as shown in Figure 2a. The next MO,  $6b_1$ , is a lone pair of  $\text{N}(1)$  (in-plane, perpendicular to the  $\text{PN}(1)$  axis), with slight back-transfer to P as may be seen from Figure 2b. The  $\text{PN}(1)$  bond in **2a** is the strongest one found in this study, according to the short bond distance and the large SEN. However, the molecule is expected to be highly reactive because of the appreciable charge at the unprotected  $\text{N}1$  atom. **2** should readily form "adducts" with other polar molecules and especially undergo a cycloaddition.<sup>6</sup> The instability of **2** is also indicated by the high energy as compared to **1** or **3**; see Table II.

All our results are consistent with the following shorthand description of the electronic structure:



**c.** Cyclic  $\text{P}_2\text{N}_6\text{R}_8$  (**3**). The electronic structure is clear-cut:



This electronic structure emerges from the results of the population analysis: the charge on the ring N's,  $Q(\text{N}) = -0.93$ , is the largest found for any N in this work. The positivity of P,  $Q(\text{P}) = +1.39$ , causes slight back-bonding from ring N into  $3d$  AOs of P. This stabilization of ring bonds is expressed by the SEN of 1.35, which may be compared to the P-amino bonds of 1.13.

The pronounced ionic character could have been inferred from the X-ray structure constants; the  $\text{PNP}$  angle ( $85^\circ$ ) is smaller than the  $\text{NPN}$  angle ( $95^\circ$ ) in the ring. This would be hard to understand for dominantly covalent bonds for which the larger angle is expected at N. The repulsion between nitrogen atoms in the

ring is also expressed by a small negative SEN of  $-0.02$ . A detailed description of the electronic structure appears to be complicated. We find a slight PP bonding effect,  $SEN = 0.19$  (which is in line with the short PP distance of 221.8 pm, well below the sum of van der Waals radii of 360 pm<sup>19</sup>), and rather pronounced three-center effects,  $SEN (PNP) = 0.12$ , for ring atoms; for the other molecules considered in this paper, we find three-center SENs below 0.05.

**d. Hypervalent Contributions.** We find no indications of truly pentacovalent phosphorus, mainly since P carries a charge  $Q(P) > +1.0$ , which indicates that only four valence electrons remain at P. The population analysis based on occupation numbers provides a measure of hypervalent contributions by means of the hypervalent or unshared population  $u(P)$ . The largest unshared population of P is found for **1** and **3**,  $u(P) = 0.07$ , which has to be compared to  $u \approx 0.2$  found for Cl in  $ClO_4^-$  or S in  $SF_6$ .<sup>17</sup> 3d AOs are important for a reliable description of electronic structures of **1-3**; their contribution is never large enough to justify the term pentacovalent.

**e. Lone-Pair Interactions.** In the structures **2b** and **3a** we find the adjacent amino groups oriented such that the nitrogen lone pairs point toward each other; this may be formally considered as a lone-pair-lone-pair attraction. If the  $NH_2$  group is "inverted" to reduce the lone-pair interactions, one finds a secondary minimum **3b** which is 2.4 kcal/mol higher in energy than **3a** and a secondary minimum **2b'** which is 5.4 kcal/mol higher than **2b**. The situation is somewhat different for **1** where the lone pairs of imino groups avoid each other in the most stable geometry **1a**. However, the  $N(2)PN(3)$  angle is larger in **1a** ( $139.7^\circ$ ) than in **1b** ( $125.8^\circ$ ), contrary to what would be expected by means of lone-pair repulsions.

The just-described state of affairs may be rationalized in the following way. First of all, one cannot just consider the lone pairs of  $NH_2$  and  $NH$  groups but has also to take into account the negatively charged nitrogen atoms  $N(1)$  in **2b** and the ring nitrogen atoms in **3a**. An inversion of the amino groups would lead to an unfavorable strong repulsion of their lone pairs with the negatively charged N atoms. Next, one has to keep in mind that the amino groups are bonded to strongly charged P atoms which have rather low-lying d orbitals. The latter can stabilize the MO representing the antibonding combination of lone-pair orbitals of the  $NH_2$  and  $NH$  groups in question. The stabilizing admixture of phosphorus d AOs is, in fact, visible from the contour lines of the  $5b_1$  MO of **2b** and the  $6b_1$  MO of **1b** displayed in Figure 3. The stabilization of the antibonding combination together with the attractive

interaction of the bonding combination (of localized lone-pair orbitals) may, in fact, lead to a net attraction. The above reasoning is clearly not limited to the molecules treated in this work. Attraction of lone pairs—or at least an appreciable reduction of their repulsion—may occur if unoccupied low-lying orbitals can stabilize the antibonding combination of lone-pair MOs.

## 5. Summary

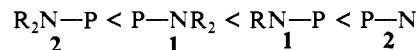
Phosphorus carries a charge larger than  $+1.0$  in compounds **1-3**, and is best described as a tetravalent  $P^+$  ion. No genuine pentacovalent P(V) has been found.

The  $(RN)-P-(NR)$  moiety in **1** is best described by the Rundle model of a four-electron, three-center  $\pi$ -system.<sup>20-23</sup> The accumulation of electronic charge on the corresponding N atoms requires protection and stabilization by spacious polarizable groups. The high-lying and nonbonding  $\pi$  MOs  $1a_2$  and  $3b_2$ , the latter on the  $NH_2$  group, are stabilized by  $2p\pi-3d\pi$  back-bonding, which results in a very strong  $P-NH_2$  single bond.

A strong PN double bond is found in **2**. The large negative charge on the unprotected nitrene N makes this a highly reactive and energetic molecule.

The  $(PN)_2$  ring in **3** is best described as  $(P^+N^-)_2$ , with tetravalent  $P^+$  and divalent  $N^-$ . Lone-pair orbitals of  $N^-$  are stabilized by back-bonding into 3d AOs of  $P^+$ . The PN (ring) bond is a very strong single bond.

The computed bond distances and the SENs allow one to order the PN bonds according to their bond strength in the following way:



which are best designated as a typical PN single bond, a PN single bond with slight double-bond character, a "Rundle-type" double bond, and a strong double bond, respectively.

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**Registry No.**  $(NH)_2PNH_2$ , 61333-04-8;  $(NH_2)_2PN$ , 14902-74-9;  $P_2N_6H_8$ , 98586-79-9.

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