

with the known spectra<sup>1,2</sup> of other  $\text{NF}_4^+$  salts clearly demonstrates the presence of tetrahedral  $\text{NF}_4^+$  cations, and the bands due to  $\text{NF}_4^+$  can be easily assigned. The observation of small splittings for the degenerate modes of  $\text{NF}_4^+$  and the observation of the ideally infrared-inactive  $\nu_1(\text{A}_1)$  mode as a very weak band in the infrared spectra indicate that the site symmetry of  $\text{NF}_4^+$  in these solids is lower than  $T_d$ . This is not surprising in view of the above given x-ray powder data and has previously been also observed<sup>1,2</sup> for other  $\text{NF}_4^+$  salts.

The assignments for the anion bands in  $(\text{NF}_4)_2\text{SnF}_6$  are also straightforward. The vibrational spectra of octahedral  $\text{SnF}_6^{2-}$  are well-known<sup>19,21-24</sup> and establish the presence of  $\text{SnF}_6^{2-}$  in  $(\text{NF}_4)_2\text{SnF}_6$  (see Table II).

The anion spectrum in  $\text{NF}_4\text{SnF}_5$  shows a pattern very similar to that of the anion in  $\text{NF}_4\text{GeF}_5$ . Furthermore, the general appearance of these anion spectra closely resembles the spectrum previously reported<sup>25</sup> for solid  $\text{TaF}_5$ . The structure of the latter has been established by x-ray diffraction data<sup>26</sup> as a cis-fluorine-bridged tetramer. Consequently, the observed vibrational spectra indicate a value of 4 for  $n$  in these  $(\text{MF}_3)_n^{n-}$  polyanions. A thorough vibrational analysis has been carried out<sup>25</sup> for tetrameric  $\text{NbF}_5$  and  $\text{TaF}_5$  by Beattie and co-workers. Using their data, we have made tentative assignments for the stretching modes of  $\text{SnF}_5^-$  and  $\text{GeF}_5^-$  based on tetrameric anions, which are given in Table III. The assumption of a low degree of polymerization, such as a cyclic tetramer, for the anions in these  $\text{NF}_4\text{MF}_5$  salts is not unreasonable in view of their appreciable solubility in solvents, such as HF or  $\text{BrF}_5$ . However, a crystal structure determination is desirable to confirm the above conclusions.

### Summary

The successful syntheses of  $\text{NF}_4\text{SnF}_5$  and  $(\text{NF}_4)_2\text{SnF}_6$  demonstrate the possibility of preparing  $\text{NF}_4^+$  salts derived from nonvolatile and unreactive polymeric Lewis acids. Such salts are important for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators for chemical HF-DF lasers, because they do not require the addition of a clinker-forming reagent. The synthesis of  $\text{NF}_4\text{SnF}_5$  was achieved by depolymerizing  $\text{SnF}_4$  in anhydrous HF and displacing  $\text{BF}_4^-$  from  $\text{NF}_4\text{BF}_4$  as  $\text{BF}_3$  gas. For the synthesis of  $(\text{NF}_4)_2\text{SnF}_6$  a metathetical process was required. Both  $\text{NF}_4^+$  salts were characterized by material balance, elemental analysis, infrared, Raman, and <sup>19</sup>F NMR spectroscopy, x-ray powder diffraction data, and DSC. Whereas  $(\text{NF}_4)_2\text{SnF}_6$  contains monomeric  $\text{SnF}_6^{2-}$  anions,  $\text{NF}_4\text{SnF}_5$  contains polymeric, cis-fluorine-bridged, hexacoordinated anions. The vibrational spectra indicate that in solid  $\text{NF}_4\text{SnF}_5$

the anion is probably present as a cyclic tetramer.

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**Registry No.**  $(\text{NF}_4)_2\text{SnF}_6$ , 61587-66-4;  $(\text{NF}_4)_4(\text{SnF}_5)_4$ , 61587-68-6;  $\text{NF}_4\text{SnF}_5$ , 61587-75-5;  $\text{Cs}_2\text{SnF}_6$ , 16919-25-8;  $\text{SnF}_4$ , 7783-62-2.

**Supplementary Material Available:** Tables IV and V, showing x-ray powder data (2 pages). Ordering information is given on any current masthead page.

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## Molecular Photoelectron Spectroscopic Investigation of Some Caged Phosphorus Compounds and Related Acyclic Species

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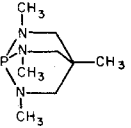
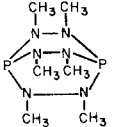
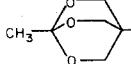
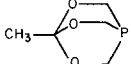
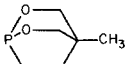
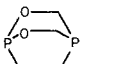
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He I molecular photoelectron (PE) spectra have been obtained for the caged compounds  $\text{P}[\text{N}(\text{CH}_3)\text{CH}_2]_3\text{CCH}_3$  (**1**),  $\text{P}[\text{N}(\text{CH}_3)\text{N}(\text{CH}_3)]_3\text{P}$  (**4**),  $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{CCH}_3$  (**5**),  $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{P}$  (**6**),  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$  (**8**), and  $\text{P}(\text{OCH}_2)_3\text{P}$  (**9**) and the related acyclic species  $[(\text{CH}_3)_2\text{N}]_3\text{PF}_2$  (**2**),  $[(\text{CH}_3)_2\text{N}]_3\text{P}$  (**3**),  $(\text{C}_2\text{H}_5)_3\text{P}$  (**7**), and  $(\text{CH}_3\text{O})_3\text{P}$  (**10**). Some He II PE spectra are also reported. The interpretation of the PE spectrum of **1** fully supports our earlier interpretation of the PE spectrum of **2**. Likewise, the various lone-pair interactions in **4**, **5**, **6**, **8**, and **9** are consistent with the available structural data. However, it is not possible to interpret the PE spectra of **3** and **10** unequivocally because the ground-state structures of these molecules have not been established. The phosphorus lone-pair ionization energies of the caged phosphorus compounds are appreciably different from those of their acyclic analogues. Possible origins of these differences are discussed.

One of the more exciting developments in the field of phosphorus chemistry has been the application of molecular

photoelectron spectroscopy (PES) to questions of conformation and bonding.<sup>2,3</sup> The stereochemical information in the PES

Table I. Lone-Pair Ionization Energies (IE) and Interaction Parameters ( $\beta$ )

| Compd  | No. | Ionization energies <sup>a</sup> |                        |                      |                                     |                                     | Interaction parameters <sup>c</sup> |   |
|--|-----|----------------------------------|------------------------|----------------------|-------------------------------------|-------------------------------------|-------------------------------------|---|
|  |     | IE <sub>N</sub>                  | IE <sub>O</sub>        | IE <sub>P</sub>      | $\overline{\text{IE}}_{\text{N}}^b$ | $\overline{\text{IE}}_{\text{O}}^b$ |                                     | $\overline{\text{IE}}_{\text{P}}^b$                                 |
|   | 1   | 7.71<br>8.59                     |                        | 9.03 sh <sup>d</sup> | 8.30                                |                                     | 9.03                                | $\beta_{\text{NN}}^{\sigma} = 0.30$                                 |
| $[(\text{CH}_3)_2\text{N}]_3\text{PF}_2$   | 2   | 8.04<br>9.03<br>9.31             |                        |                      | 8.79                                |                                     |                                     | $\beta_{\text{NN}}^{\sigma} = 0.38$                                 |
| $[(\text{CH}_3)_2\text{N}]_3\text{P}$  | 3   | 7.61<br>7.89<br>8.86             |                        | 9.98                 |                                     |                                     |                                     | $\beta_{\text{NN}}^{\sigma} = 0.63; \beta_{\text{NP}}^{\pi} = 0.35$ |
|   | 4   | 7.21<br>8.24<br>9.26<br>9.64     |                        | 9.48<br>10.48        |                                     |                                     |                                     |   |
|   | 5   |                                  | 9.45<br>10.00          |                      |                                     | 9.82                                |                                     | $\beta_{\text{OO}}^{\sigma} = 0.18$                                 |
|   | 6   |                                  | 9.14<br>9.97           | 10.34 sh             |                                     | 9.69                                | 10.34                               | $\beta_{\text{OO}}^{\sigma} = 0.28$                                 |
| $(\text{CH}_3\text{CH}_2)_3\text{P}$   | 7   |                                  |                        | 8.40                 |                                     |                                     | 8.40                                |   |
|   | 8   |                                  | 9.95<br>10.43          | $\sim 10.6^e$        |                                     | 10.27                               | $\sim 10.6^e$                       | $\beta_{\text{OO}}^{\sigma} = 0.16$                                 |
|  | 9   |                                  | 9.40<br>10.50          | 10.50                |                                     | 10.13                               | 10.50                               | $\beta_{\text{OO}}^{\sigma} = 0.37$                                 |
| $(\text{CH}_3\text{O})_3\text{P}$  | 10  |                                  | 9.40<br>10.65<br>11.15 | 11.35                |                                     |                                     |                                     | $\beta_{\text{OO}}^{\sigma} = 0.25; \beta_{\text{OP}}^{\pi} = 0.45$ |

<sup>a</sup> Vertical IE's in eV. <sup>b</sup> MO degeneracies taken into account when computing mean ionization energies,  $\overline{\text{IE}}$ . <sup>c</sup> In eV. The superscript  $\sigma$  indicates a primarily  $\sigma$ -type interaction between the lone pairs; the superscript  $\pi$  indicates a primarily  $\pi$ -type interaction between the lone pairs. <sup>d</sup> sh = shoulder. <sup>e</sup> Estimated value. Phosphorus lone-pair ionization obscured beneath the oxygen lone pair ionization.

experiment stems principally from the nature of the lone pair-lone pair interactions.<sup>4</sup> However, some of the PES stereochemical studies which have been executed have been open to question.<sup>2j,k,q,s</sup> The ambiguities in interpretation have arisen in regard to acyclic structures with incompletely defined conformational preferences. As the next stage in the development of PES as a structural tool in this area of chemistry, it seemed advantageous to investigate some rigid, polycyclic phosphorus compounds which possess either known structures or geometries that can be confidently inferred. This article describes a PES study of the caged compounds 1, 4-6, 8, and 9. In turn it was realized that the empirical lone pair-lone

$[(\text{CH}_3)_2\text{N}]_3\text{P}$  (3),  $(\text{C}_2\text{H}_5)_3\text{P}$  (7), and  $(\text{CH}_3\text{O})_3\text{P}$  (10).

### Experimental Section

The compounds 1,<sup>5</sup> 2,<sup>6</sup> 3,<sup>7</sup> 4,<sup>8</sup> 5,<sup>9</sup> 6,<sup>10</sup> 7,<sup>11</sup> 8,<sup>12</sup> and 9<sup>13</sup> were prepared and purified according to literature methods. Trimethyl phosphite, 10, was procured commercially and fractionally distilled in vacuo prior to use.

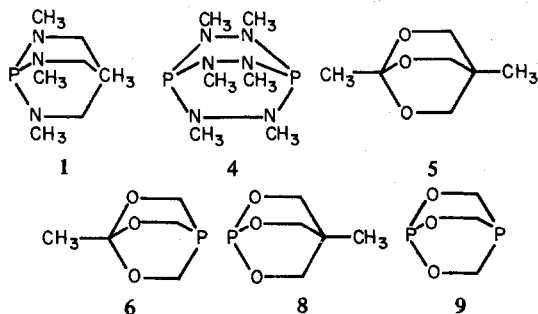
All PE spectra were run on a Perkin-Elmer Model PS 18 spectrometer.

### Results

The PES data for compounds 1-10 are displayed in Table I. Only the lone-pair ionization energies (IE's) are indicated since, to a first approximation, stereochemical preferences are determined by interactions among the various lone-pair molecular orbitals (MO's). Furthermore, the  $\sigma$ -bonding MO's of 1-10 are generally very complex and overlapped, thereby rendering spectral assignment difficult.

### Discussion

The molecular geometry of 1 has not been established by x-ray crystallography. However, the corresponding phosphine oxide and phosphine-borane, i.e.,  $\text{XP}[\text{N}(\text{CH}_3)\text{CH}_2]_3\text{CCH}_3$ ,  $\text{X} = \text{O}, \text{BH}_3$ , have been characterized structurally.<sup>14</sup> Collectively, the significant features of these x-ray crystal structures are (i) the skeletal geometry of the  $\text{PN}_3$  moiety is  $\text{C}_{3v}$  and (ii) the nitrogen atoms adopt an essentially trigonal-planar geometry. Due to the constraints of the cage system, it is safe to assume that these structural features are



pair interaction schemes that were derived for the caged compounds might be pertinent to the interpretation of the PE spectra of the related acyclic compounds  $[(\text{CH}_3)_2\text{N}]_3\text{PF}_2$  (2),

Scheme I

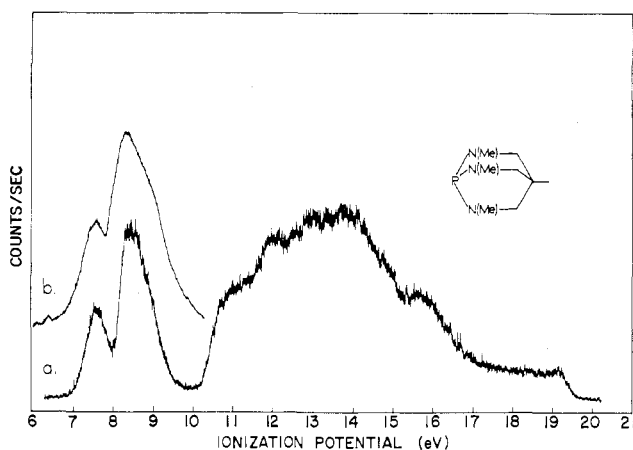
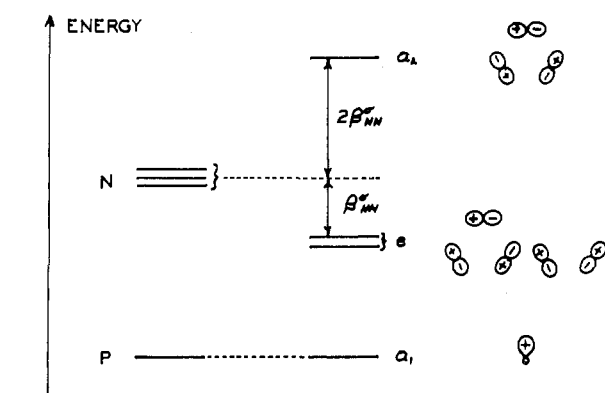
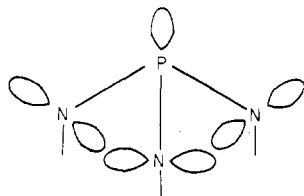


Figure 1. PE spectra of  $P[N(CH_3)CH_2]_3CCH_3$  (1): (a) He I; (b) He II.

extant in 1. In turn, this implies that the phosphorus lone pair is orthogonal to the nitrogen lone pairs, viz.



The three locally co-planar nitrogen lone pairs can interact according to the  $C_{3v}$  point group of the  $PN_3$  moiety to afford combinations of symmetry  $a_2$  and  $e$  with a separation  $3\beta_{NN}^r$  as indicated in Scheme I.<sup>15</sup> The ionization energy sequencing  $e > a_2$  follows from consideration of the nodal properties of the MO's.<sup>4</sup>

The He I PE spectrum of 1 (Figure 1a) is in good agreement with Scheme I. The first band is attributed to the nitrogen lone-pair combination of symmetry  $a_2$  while the second band is assigned to correspond to the combination of symmetry  $e$ . The  $\sim 0.17$ -eV splitting of the  $e$  combination is attributed to a Jahn–Teller distortion of the radical cation. The assignment of the shoulder of the second band to the phosphorus lone pair is supported by the He II PE spectrum of 1 (Figure 1b). The ionization cross sections for 3s and 3p atomic orbitals (AO's) are appreciably less than those of 2s and 2p AO's, and the diminution of intensity of bands in He II PES compared to He I PES is considered to be indicative of the ionization of electrons from, e.g., P 3s and P 3p orbitals.<sup>16</sup> When He II radiation is applied to 1, it is evident that the shoulder of the second band in the He I PE spectrum is somewhat diminished.

The foregoing assignment for the PE spectrum of 1 supports our original interpretation<sup>21</sup> that the nitrogen lone pairs of 2

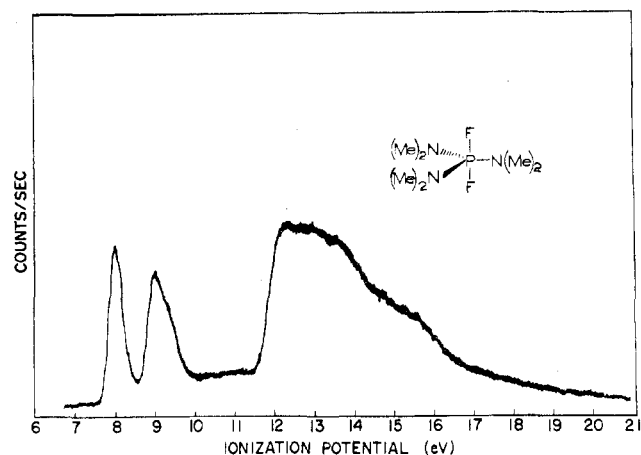


Figure 2. He I PE spectrum of  $[(CH_3)_2N]_3PF_2$  (2).

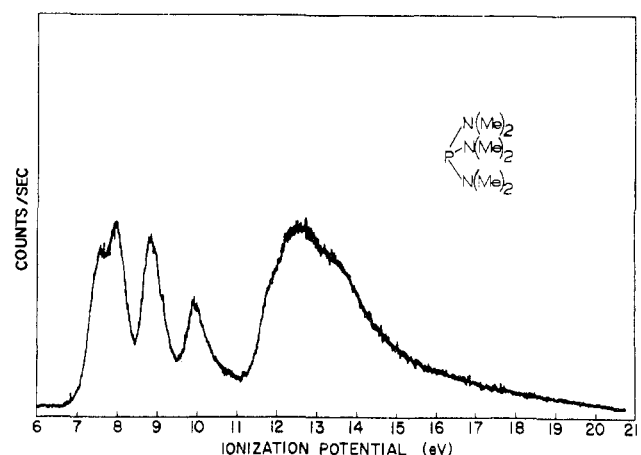
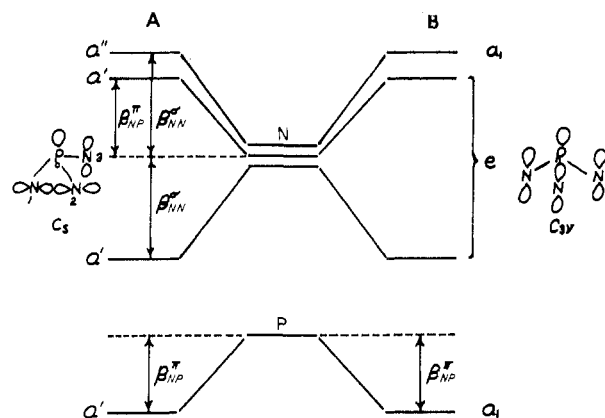
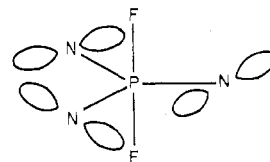


Figure 3. He I PE spectrum of  $[(CH_3)_2N]_3P$  (3).

Scheme II



reside in the equatorial plane of a trigonal bipyramid, i.e.



The first three peaks in the He I PE spectrum of 2 (Figure 2) are very similar to those in the He I PE spectrum of 1 and can, therefore, be assigned to the nitrogen lone-pair combinations of symmetry  $a_2$  and  $e$ . Furthermore, the nitrogen lone-pair interaction parameters,  $\beta_{NN}^r$ , of 1 and 2 (Table I), are quite similar. This is anticipated because 2 does not possess

a phosphorus lone pair and in **1** phosphorus and nitrogen lone pairs are orthogonal. The fact that the mean nitrogen lone pair ionization energy,  $\bar{IE}_N$ , is slightly larger for **2** than for **1** (Table I) is due to the inductive effect of replacing a phosphorus lone pair by two fluorine ligands. The proposed structure for **2** is consistent with the minimization of nitrogen lone pair–bond pair repulsions and with a recent x-ray crystal of a dimethylamino-substituted oxyphosphorane which shows an equatorial planar disposition of the nitrogen lone pair.<sup>17</sup>

The interpretation of the PES of the acyclic aminophosphine **3** (Figure 3) has been somewhat more controversial. In our original interpretation<sup>2j</sup> we postulated that, as indicated in Scheme IIA, the molecule is distorted to  $C_s$  symmetry such that two of the nitrogen lone pairs, 1 and 2, interact in the  $\sigma$  manner to afford combinations of symmetry  $a'$  and  $a''$ , and the third lone pair, 3, experiences a  $\pi$ -type interaction with the phosphorus lone pair. The interpretation offered a number of advantages. First, it was consistent with the x-ray crystal structure of  $(C_6H_5O)_3PO$  which exhibits a  $C_s$  skeletal symmetry,<sup>18</sup> second, it avoided the necessity of postulating a large Jahn–Teller effect (vide infra), and, third, it explained the trends<sup>2j</sup> in the phosphorus lone pair IE's in the series  $[(CH_3)_2N]_xPF_{3-x}$ ,  $x = 0, 1, 2$ .

The model did, however, require that the molecular structure of **3** be reexamined since the electron diffraction data<sup>19</sup> were interpreted on the explicit assumption of a  $C_3$  skeletal geometry. More recently Lappert and co-workers<sup>25</sup> have presented an alternative interpretation of the PE spectrum of **3**. If, in fact, **3** adopts a  $C_{3v}$  structure, the nitrogen lone-pair combinations transform as the irreducible representations  $a_1$  and  $e$ , the IE ordering being  $a_1 > e$ .<sup>15</sup> However, the  $a_1$  nitrogen lone-pair combination could interact strongly with the phosphorus lone pair, thereby increasing the IE of the latter and reversing the ordering of the  $a_1$  and  $e$  MO's of the nitrogen lone pairs. The final feature of Scheme IIB is a Jahn–Teller splitting of the doubly degenerate nitrogen lone-pair combination. The interpretation of Lappert et al.<sup>25</sup> possesses a number of disadvantages. First, the assignment of PES peaks according to Scheme IIB would imply an unusually small  $\pi$ -type interaction between the nitrogen lone pairs ( $\beta_{NN}^r = 0.14$  eV). While lone pair orbital overlap considerations would suggest that  $\sigma$ -type interactions are larger than  $\pi$ -type interactions, the reduction from  $\beta_{NN}^r = 0.30$  eV in **1** to  $\beta_{NN}^r = 0.14$  eV in **3** seems to be unreasonably large. Second, the Jahn–Teller splitting of 0.97 eV for the doubly degenerate nitrogen lone-pair MO in **3** is considerably greater than the corresponding splittings in **1** (<0.2 eV) and **2** (0.28 eV). Finally, a  $C_{3v}$  structure for **3** would necessarily imply considerable steric hindrance among the  $(CH_3)_2N$  groups. It is of interest to note that Scheme IIB would also accommodate a  $C_3$  structural model in which the three nitrogen lone pairs are at the "crossover angle" between a horizontal ( $\sigma$ -type) and vertical ( $\pi$ -type) interaction, the degeneracy of the  $e$  MO being lifted by Jahn–Teller splitting. If the phosphorus and nitrogen lone pairs interact according to a cosine  $\phi$  relationship,<sup>4</sup> then the P...N inter-lone-pair angles,  $\phi$ , would be 30°. This interpretation would be consistent with the electron diffraction of **3**<sup>19</sup> (in which threefold symmetry was tacitly assumed); however, it suffers the disadvantage of necessitating a very large Jahn–Teller splitting of the doubly degenerate MO (vide supra).

Clearly, additional structural data for **3** would be very desirable since PES is incapable of effecting an unequivocal discrimination among the various models. In fact, the Jahn–Teller distortion that is postulated to accompany the photoionization of **3** in the  $C_{3v}$  model (Scheme IIB) may well yield a radical cation that is isostructural with  $C_s$  ground state conformation (Scheme IIA).

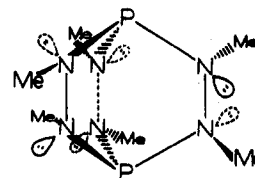


Figure 4. Structure of  $P[N(CH_3)N(CH_3)]_3P$  (**4**).

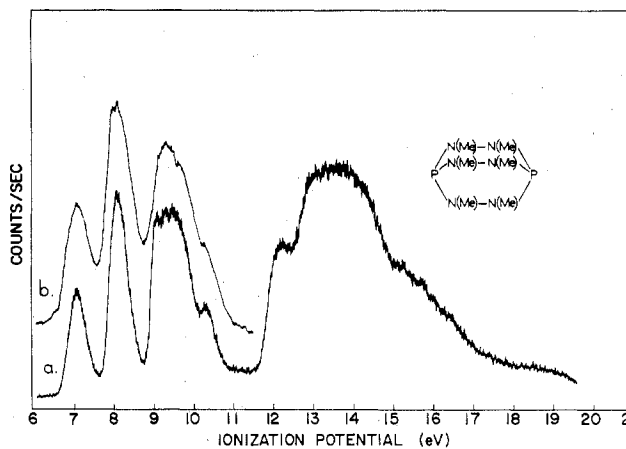
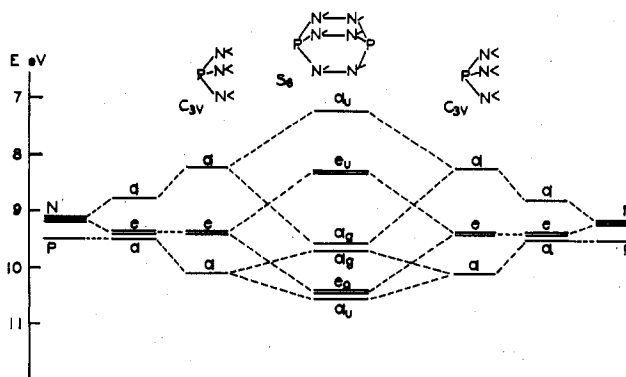


Figure 5. PE spectra of  $P[N(CH_3)N(CH_3)]_3P$  (**4**): (a) He I; (b) He II.

#### Scheme III



The essential features of the x-ray crystal structure<sup>20</sup> of the hydrazino-bridged cage, **4**, are displayed in Figure 4. The He I PES of **4** can be interpreted satisfactorily according to Scheme III in which two  $\sigma$ -type  $PN_3$  moieties of  $C_{3v}$  symmetry interact to form the hydrazino-bridged cage of  $S_6$  skeletal symmetry. The phosphorus–nitrogen inter-lone-pair angles,  $\phi$ , have been assumed to be 90° as indicated in Scheme I. Furthermore, the initial energies for the nitrogen lone pairs in **4** have been adjusted by adding 0.8 eV to the average nitrogen lone-pair ionization energy,  $\bar{IE}_N$ , of **1**. This figure was arrived at by considering the nitrogen lone-pair ionization energies of  $(CH_3)_3N$  (7.82 eV)<sup>21</sup> and  $(CH_3)_4N_2$  (8.63 eV)<sup>22</sup> and thereby estimating the inductive change of replacing a  $CH_3$  by a  $(CH_3)_2N$  group on a given nitrogen lone pair. The inductive stabilization of the phosphorus lone pair in proceeding from **1** to **4** was estimated to be 0.4 eV. The only other aspect of Scheme III which is worthy of comment is the final sequence of MO energies. In general, nodal rule considerations would place the  $u$  species at lower IE than the corresponding  $g$  combinations. However, in the case of the interaction between the phosphorus lone pairs this ordering is inverted because the interaction takes place through the  $\sigma$  framework.<sup>4</sup> A similar situation has been found to obtain in the case of 1,4 bicyclic diamines such as diazabicyclo[2.2.2]octane (Dabco).<sup>23</sup>

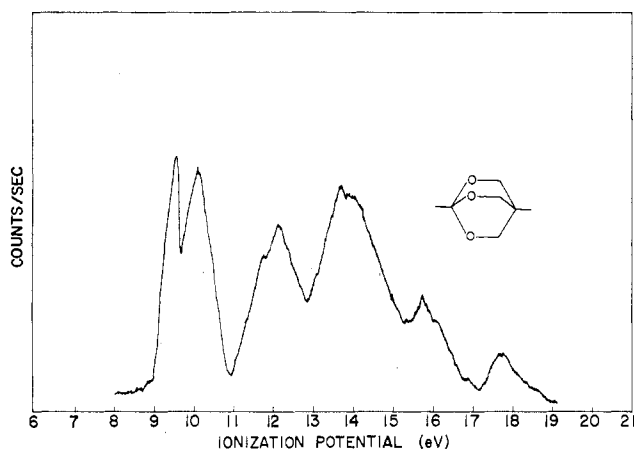
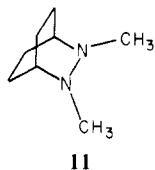


Figure 6. He I PE spectrum of  $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{CCH}_3$  (**5**).

The first band in the He I PE spectrum of **4** (Figure 5a) is assigned to the nitrogen lone-pair combination of symmetry  $a_u$ , and the second is attributed to the  $e$  species nitrogen lone-pair MO, the slight splitting (0.2 eV) arising by virtue of the Jahn–Teller effect. The next four ionizations are overlapping and it is difficult to arrive at a unique assignment. However, the most satisfactory approach is to assign the first portion of the third band to the  $a_g$  species of the nitrogen and phosphorus lone-pair combinations, respectively, while the latter portion likely corresponds to the Jahn–Teller split nitrogen lone-pair MO of symmetry  $e_g$ . The assignment of the fourth band to the phosphorus lone-pair combination of symmetry  $a_u$  is confirmed by the He II PE spectrum of **4** (Figure 5b) which exhibits a significant diminution of intensity of this band compared to the other ionizations. The  $\beta_{\text{NN}}^{\text{N}}$  of  $\sim 1.6$  eV which is derived for **4** is in good agreement with the value reported for the cyclic hydrazine **11**.<sup>24</sup> The  $\beta_{\text{PP}}^{\text{P}}$  value



of 1.0 eV in **4** is somewhat smaller than the nitrogen lone-pair interaction parameter,  $\beta_{\text{NN}}^{\text{N}}$ , in 1,4 cyclic diamines such as Dabco.<sup>23</sup> This likely is a result of poorer overlap of the phosphorus lone pair, which is predominantly of  $s$  type, compared with the nitrogen lone pair of the diamines, with the appropriate higher lying  $\sigma^*$  orbitals.

Attention is now turned to the oxygen-substituted cage molecules **5**, **6**, **8**, and **9** and their acyclic analogues **7** and **10**. At the outset it is important to point out that, despite the fact that bicoordinate oxygen possesses two lone pairs, their energies are substantially different.<sup>25</sup> In fact, only the lone pair which is perpendicular to the oxygen  $\sigma$  bonds will fall in the 9–12-eV IE region; the other “lone pair” is admixed with O–P and O–C  $\sigma$ -bonding orbitals and appears at much higher energy. In turn, this implies that the bona fide oxygen lone pair can be treated in an analogous fashion to the nitrogen lone pair from the standpoint of the various interaction schemes.

Consider first compound **5** in which the only heteroatoms are oxygen. The molecule is expected to possess a  $C_{3v}$  skeletal geometry; hence the three oxygen lone pairs interact to afford MO's of symmetry  $a$  and  $e$  in the IE sequence  $a < e$  (cf. Scheme I). In the He I PE spectrum of **5** (Figure 6) the first two bands are clearly due to the  $a$  and  $e$  oxygen lone-pair combinations, respectively, and the interaction parameter,  $\beta_{\text{OO}}^{\text{O}}$ , is 0.18 eV. Compound **6**, in which a phosphorus atom has been substituted at the bridgehead position opposite to the  $\text{CO}_3$

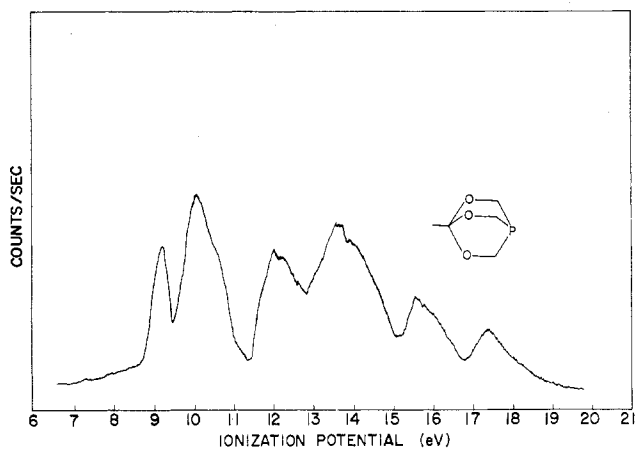


Figure 7. He I PE spectrum of  $\text{CH}_3\text{C}(\text{OCH}_2)_3\text{P}$  (**6**).

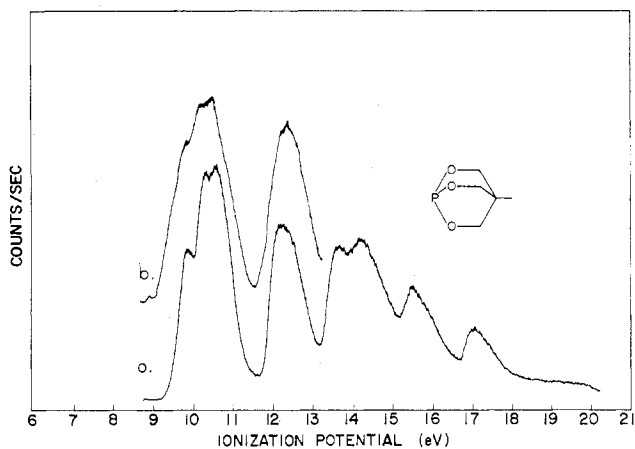


Figure 8. PE spectra of  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$  (**8**): (a) He I; (b) He II.

moiety, can be regarded as being isostructural with **5** from the standpoint of oxygen lone-pair stereochemical interrelationships. Thus, in the He I PE spectrum of **6** (Figure 7) the first two bands correspond to the ionization of oxygen lone-pair combinations of symmetry  $a_2$  and  $e$ , respectively, leaving the shoulder of the second band to be assigned to the phosphorus lone pair of symmetry  $a_1$ . Unfortunately, He II irradiation of **6** is not very definitive since the peaks comprising the second band are overlapping.

It is particularly noteworthy that the phosphorus lone pair in **6** is stabilized by  $\sim 2.0$  eV compared to that in the acyclic tertiary phosphine **7**. This effect seems too large to be attributable to the  $\beta$  inductive effect of oxygen atoms. Furthermore, oxygen–phosphorus  $p_x$ – $d_\pi$  bonding cannot be responsible for such a large effect because a saturated carbon atom intervenes between the oxygen and phosphorus atoms. It is therefore postulated that the phosphorus lone pair in **6** is stabilized by interaction with the  $\sigma^*$  orbitals of the C–O bonds. This net transfer of charge from phosphorus to oxygen is presumably responsible for the fact that the oxygen–oxygen interaction parameter,  $\beta_{\text{OO}}^{\text{O}}$ , is larger in **6** (0.28 eV) than in **5** (0.18 eV).

The x-ray crystal structures of **8** and **9** have not been determined. However, the related compounds **12**,<sup>26</sup> **13**,<sup>27</sup> **14**,<sup>28</sup> and **15**<sup>29a</sup> have been characterized structurally. Compounds **12**–**15** possess  $C_{3v}$  skeletal geometries for the  $\text{PO}_3$  moieties, the POC bond angles ranging between 115 and 122 °C. The same stereochemical features can be safely assumed to exist in **8** and **9**; hence the PE spectra of both molecules are interpretable according to Scheme I. Thus, for **8**, the first ionization in the He I spectrum (Figure 8a) is assigned to the  $a_2$  oxygen lone-pair combination while the second band is

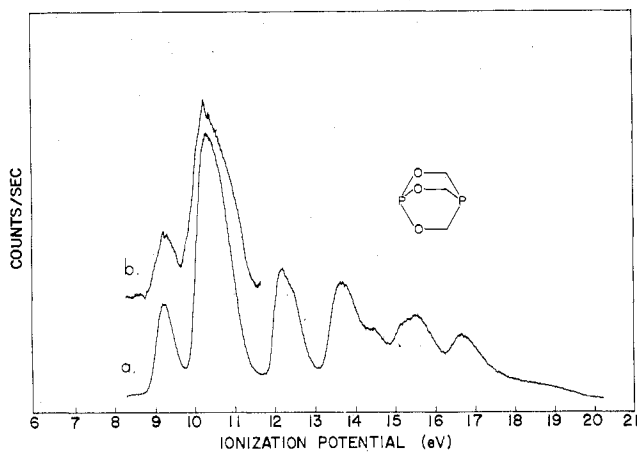
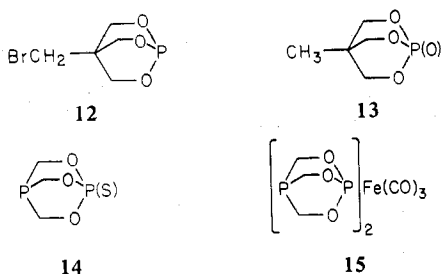


Figure 9. PE spectra of  $P(OCH_2)_3P$  (9): (a) He I; (b) He II.



ascribed to the oxygen lone-pair MO of symmetry  $e$ , the splitting of the doubly degenerate orbital arising because of the Jahn-Teller effect. One of the peaks in the second band could conceivably be due to ionization of the phosphorus lone pair; however, there is an imperceptible change in the intensities of the first two bands upon He II irradiation of **8** (Figure 8b), thus implying that the phosphorus lone-pair ionization is obscured beneath the oxygen lone-pair ionizations. The increase in the mean oxygen lone-pair ionization energy,  $\bar{I}E_O$ , in going from **5** to **8** is interesting. Hybridization changes at oxygen are unlikely to be responsible for this observation because the orthogonality of the higher lying (i.e., lower IE) oxygen lone pair to the oxygen  $\sigma$  bonds should render it insensitive to hybridization changes in the P-O-C framework. It is therefore tempting to attribute the stabilization of  $\bar{I}E_O$  in **8** (compared to **5**) to a conjugative interaction between the oxygen lone pairs and vacant phosphorus orbitals of  $\pi$  symmetry. This is consistent with the conclusion drawn from dipole moment studies that the  $PO_3$  group moment of 0.8 D in **8** is in the direction of phosphorus rather than the more electronegative oxygens.<sup>29b</sup>

In compound **9**, as with **8**, the first two bands in the He I PE spectrum (Figure 9a) are assigned to the  $a_2$  and  $e$  combinations of oxygen lone-pair orbitals, respectively. The most satisfactory assignment for both phosphorus lone-pair ionizations is to place them in band 2 since comparison of the He I and He II PE spectra of **9** (Figure 9b) indicates that little change of intensity takes place when He II photons are employed. Thus, despite the observation that Lewis basicity measurements<sup>30</sup> indicate differing reactivities for the P(O) and P(C) sites, the present PES study implies that the energies of the two phosphorus lone pairs in **9** are rather close. This result further substantiates the idea that the strong molecular dipole in **9** directed toward the P(O) end is responsible for the preference of this phosphorus for Lewis acids.<sup>30</sup> Presumably the near equivalence of the phosphorus lone-pair energies in the  $PC_3$  and  $PO_3$  moieties arises because of the stabilizing interaction of the P(C) lone pair with the  $\sigma^*$  orbitals of the C-O bonds as suggested above for **6**. Note that, as expected,

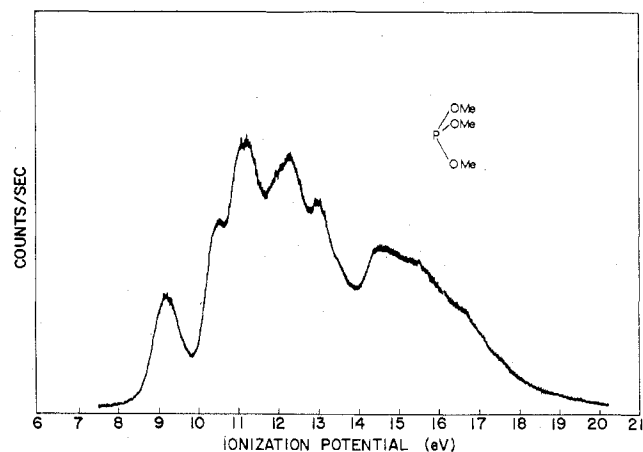


Figure 10. He I PE spectrum of  $(CH_3O)_3P$  (10).

the  $\beta_{PO}^*$  in **9** is somewhat larger than that in **8** (cf. **5** and **6** above) due to the transfer of electronic charge from P(C) to the oxygen atoms. This  $\sigma^*$  argument predicts the C-O bond distances in **6** and **9** to be somewhat larger than those in **5** and **8**. Unfortunately, structural data are not available to test this prediction; however, it is of interest to note that (S) $P(OC_2H_5)_3$ , **13**,<sup>28</sup> exhibits a larger C-O bond distance than (O) $P(OCH_2)_3CCH_3$ .<sup>27</sup>

As expected, the arguments which were presented earlier regarding the PE spectrum and molecular structure of **3** are very pertinent to the oxygen analogue **10**. Unfortunately, no structural data are available for **10** and it is not possible to be unequivocal regarding a structural assignment from the PES experiment. However, since  $(C_6H_5O)_3P(O)$  has been found to possess a distorted structure<sup>18</sup> it seems reasonable to assign the PE spectrum of **10** in terms of the  $C_s$  point group (Figure 10). As in the case of **3** the vertical lone pair of symmetry  $a'$  (in this case oxygen) is strongly admixed with the phosphorus lone pair.

It has been found experimentally that acyclic phosphites and phosphate esters<sup>31a</sup> as well as aminophosphines<sup>31b</sup> exhibit higher Lewis basicities and nucleophilicities than their cyclic analogues.<sup>31</sup> Comprehension of the decreasing Lewis basicity from **3** to **1** and from **10** to **8**, for example, solely from the standpoint of the phosphorus lone-pair ionization energies in Table I is impossible. Furthermore, toward the  $BH_3$  unit the order of Lewis basicity of simple phosphines is<sup>32</sup>  $PF_2H > PF_3 > PF_2Cl > PF_2Br > PF_2I > PH_3$ , yet the lone-pair IE's are 11.0,<sup>28</sup> 12.23,<sup>28</sup> 12.8,<sup>28</sup> 11.8,<sup>28</sup> 11.2,<sup>28</sup> and 10.6 eV,<sup>2a</sup> respectively. Other factors in the sequencing of Lewis basicity such as the nature of the Lewis acid,<sup>33</sup> solvation,<sup>34</sup> and kinetic considerations must be considered. Accordingly, we are currently engaged in a PES study of phosphorus basicity in which the trends in all of the valence-shell electrons are monitored prior to and after adduct formation. Regarding the present compounds the only discernible difference between the acyclic species **3** and **10** and their cyclic counterparts **1**, **8**, and **9** is that the molecular symmetry permits extensive mixing of the phosphorus lone-pair MO with the nitrogen and oxygen lone-pair MO's in **3** and **10**, respectively. Possibly this lone-pair admixture is responsible for the superior Lewis basicity of acyclic phosphites and aminophosphines.

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## Synthesis and Characterization of Straight-Chain Oligomers of Methylene-diphosphonic Acid

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A mixture of predominantly linear oligomers was produced by condensing an equimolar mixture of methylenediphosphonic acid with its tetrachloride. This mixture was separated by eluting a long cellulose-ether column with a proportional gradient of aqueous triethylammonium bicarbonate. From comparison with the data obtained on a polyphosphate mixture in the same column using the same eluate, as well as from the  $^{31}\text{P}$  NMR spectra of the various aqueous fractions, it was found that the linear bis- through the octakis(methylenediphosphonate) anions were separated. The  $^{31}\text{P}$  NMR spectra exhibited a natural subdivision into groups of resonances which for these oligomers corresponded to the monomer, the terminal phosphorus atoms of the chains, the next nearest phosphorus atoms, and the remaining middle-position phosphorus atoms. In these spectra the small amounts of simple-ring molecules exhibited sharp single resonances as expected.

### Introduction

In a previous study by our group<sup>1</sup> it was shown that methylenediphosphonic acid,  $(\text{HO})_2(\text{O})\text{PCH}_2\text{P}(\text{O})(\text{OH})_2$ , may be condensed by dicyclohexylcarbodiimide to give oxygen-bridged linear and cyclic bis(methylenediphosphonic) acids as well as several more condensed cyclic species including the un-ionized birdcage anhydride  $\text{P}_4\text{O}_8(\text{CH}_2)_2$  which is the doubly

methylene-bridged analogue of phosphorus pentoxide. Unfortunately, methylenediphosphonic acid and its acid salts are found to undergo decomposition upon heating, rather than condensing in a manner similar to that found for the analogous phosphates. Therefore, we decided to look more carefully into an alternative method for condensing methylenediphosphonate anions in order to see whether it would be possible to make