Computational study on molecular structure, vibrational spectrum analysis and acidity strength of \( \text{P}_4\text{O}_{n} \) (\( n = 6-10 \)) phosphorus oxides with cage structure

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Abstract

In this study, molecular structure, IR spectra and acidity strength of \( \text{P}_4\text{O}_{n} \) (\( n = 6-10 \)) type phosphorus oxides with cage structure were investigated at the PBE1PBE/6-311+G(2d) level. Structural parameters and IR spectra of oxides were obtained from optimized structures. From the structural parameters and IR spectra, \( \text{P}_4\text{O}_6 \) and \( \text{P}_4\text{O}_{10} \) molecules were found in \( T_d \) symmetry, \( \text{P}_5\text{O}_7 \) and \( \text{P}_5\text{O}_{10} \) molecules in \( C_{3v} \) symmetry and \( \text{P}_6\text{O}_8 \) molecule in \( C_{2v} \) symmetry. Symmetry labeling of the peaks in the IR spectra of oxides was performed. To predict the acidity strength of the oxides in the gas phase, the protonated species were optimized at the PBE1PBE/6-311+G(2d) level. Proton affinity values were calculated using the total energies of neutral and protonated species. Acidity strength ranking according to proton affinity values was obtained as \( \text{P}_4\text{O}_6 < \text{P}_5\text{O}_7 < \text{P}_5\text{O}_{10} < \text{P}_6\text{O}_8 < \text{P}_4\text{O}_{10} \).

1. Introduction

Tetraphosphorus hexaoxide (\( \text{P}_4\text{O}_6 \)) is obtained from the reaction of white phosphorus (\( \text{P}_4 \)) in tetrahedral geometry with a limited amount of oxygen, and tetraphosphorus decoxide (\( \text{P}_4\text{O}_{10} \)) from its reaction with excessive oxygen. It has been reported that intermediate compounds such as \( \text{P}_5\text{O}_7 \), \( \text{P}_5\text{O}_{10} \) and \( \text{P}_6\text{O}_8 \) can also be synthesized under controlled conditions [1,2].

The molecular structures of \( \text{P}_4\text{O}_6 \) and \( \text{P}_4\text{O}_{10} \) compounds have been determined in previous studies and have been found to have a white phosphorus structure [3,4]. \( \text{P}_4\text{O}_6 \) molecule is formed by the introduction of oxygen atoms between adjacent phosphor atoms in the white phosphorus structure. The difference of \( \text{P}_4\text{O}_{10} \) molecule from \( \text{P}_4\text{O}_6 \) is that each phosphorus atom contains a terminal oxygen atom. In \( \text{P}_5\text{O}_7 \), \( \text{P}_5\text{O}_{10} \) and \( \text{P}_6\text{O}_8 \) compounds, one, two, and three of the phosphorus atoms have terminal oxygen atoms, respectively [5].

Phosphorus compounds and oxygen atoms give chemiluminescence reactions and form the basis of laser systems [6,7]. Therefore, \( \text{P}_4\text{O}_{10} \) is used in the development of high energy laser lenses [8]. Also, since these compounds contain cages, they are used as host materials for the vitrification of nuclear waste [9].

\( \text{P}_4\text{O}_{10} \) is a powerful dehydrating agent and is used in desiccators as desiccant. \( \text{H}_3\text{PO}_4 \) is formed as a result of the hydrolysis reaction of \( \text{P}_4\text{O}_{10} \). Phosphoric acid is used in the pharmaceutical industry, oil industry, insecticide production and for various cleaning purposes. It is used in cola and baking powders in the food industry. It participates in the structure of DNA and RNA. It is found in the structure of all nucleotides. Phosphoric acid, an inorganic compound, is the group that imparts acidic properties to nucleic acids [10].

The acidity strength of a chemical species depends on two main factors: itself and its environment. The acidity force arising from the species itself is obtained from the proton affinity values measured in the gas phase. The higher the value of the proton affinity, the higher the basicity of the species, the weaker the conjugate acid [11].

Molecular orbital theory can also be used to predict acidity or basicity of chemical species. According to the molecular orbital theory, the acidity of a molecule depends on LUMO energy and its basicity depends on HOMO energy. The species with low LUMO energy are acidic. The species with high HOMO energy and with non-binding molecular orbitals act as bases [12]. In this study, we aimed to predict the molecular structure and acidity strength of \( \text{P}_4\text{O}_{n} \) (\( n = 6-10 \)) type oxides. For this purpose, neutral phosphorus oxides...
and their protonated species were optimized at the PBE1PBE/6-311+G(2d) level. Bond lengths, bond angles, IR spectra of neutral oxides were obtained from the optimized structures. Proton affinity of the oxides was calculated from the total energies of neutral and protonated species and acidity strength sequences were estimated.

2. Methods and techniques

Molecular structures of P$_4$O$_n$ (n = 6-10) phosphorus oxides with cage type were drawn in GaussView 6.0.16 program [13]. Phosphorus oxides were optimized at PBE1PBE/6-311G(2d) level with the Gaussian 09: AS64L-G09RevD.01 program [14]. PBE1PBE is a pure functional of density functional theory (DFT) developed in 1996 by Perdew, Burke and Ernzerhof [15]. This functional was transformed into a hybrid functional by Adamo [16] and shown with the PBE1PBE keyword. This hybrid functional uses 25% exact exchange and 75% DFT exchange. It is known in the literature as PBE0 [16] and PBE hybrid [17]. 6-311+G(2d) level was found as the best level [1].

Bond lengths, bond angles and vibrational spectrum analysis were performed from the optimized structures of neutral phosphorus oxides. To calculate the proton affinity of phosphorus oxides, a proton was added to the atom with the most negative charge and the total energy was calculated. As shown in Equation (1), the proton affinity in the energies of neutral and protonated species was determined [18].

P$_4$O$_n$(g) + H$^+$ (g) → P$_4$O$_n$H$^+$ (g)

PA=E(P$_4$O$_n$)-E(P$_4$O$_n$H$^+$)  

\[ \text{(1)} \]

3. Findings and Discussion

3.1. Optimized structures of phosphorus oxides

The structures of P$_4$O$_n$ (n = 6-10) type phosphorus oxides drawn in GaussView 6.0.16 program were optimized in the gas phase at the level of PBE1PBE/6-311+G(2d) in Gaussian 09 calculation program. Optimized structures are given in Fig. 1 with atomic labeling. Bond lengths and bond angles obtained from the optimized structures in Fig. 1 are given in Table 1.

Experimental values in Table 1 are taken from reference [1]. Only one of the equivalent bond lengths and bond angles was shown.

As seen in Fig. 1, P1-O11, P5-O12, P8-O13 and P9-O14 bonds show the bonding of terminal oxygen with phosphorus. These bonds are equivalent length and are shown in Table 1 as P1-O11 and their length is given as approximately 1.44 Å. Other P-O bonds belong to bridge oxygen. P-Ob bond lengths vary between 1.60-1.66 Å. This difference between P-Ot and P-Ob lengths is explained by the formation of $\pi$-bonds. $\pi$-bond is formed between terminal oxygen p$\pi$-orbital and phosphor atom d$\pi$-orbital. $\pi$-bond formation causes the P-Ob bond to be shorter.

The change of P-Ob bond lengths between 1.60-1.66 Å in P4O7 and P4O8 is due to their distance from terminal oxygen. It can be seen from Table 1 and Figure 1 that the P-Ob bond, which is farther away from the terminal oxygen atom, is longer than the closer one.

As can be seen from Table 1, there are three types of bond angles for phosphorus oxides ranging from about 100, 115 and 122-127 degrees. Ob-P-Ob bond angles are approximately 100 degrees, Ob-P-Ot bond angles are about 115 degrees and P-Ob-P bond angles range from 122-127 degrees. These angles neither belong to the ideal tetrahedral geometry nor the ideal triangular plane. Therefore, the geometries of oxides are given by symmetry point groups. Considering the symmetry operation of the molecules, it was found that P$_4$O$_6$ and P$_4$O$_{10}$ are in the T$_d$ symmetry point group, P$_4$O$_7$ and P$_4$O$_9$ are in the C$_{3v}$ symmetry point group and P$_4$O$_8$ in the C$_{2v}$ symmetry point group.
of the molecules in the Tₐ point group. In the Tₐ point group, only T₂ symmetry modes is IR active. Since the T₂ symmetry species is triple degenerate, four peaks are expected in the IR spectrum of the P₄O₉ molecule and six peaks in the IR spectrum of the P₄O₁₀ molecule.

### 3.2. IR spectra of phosphorus oxides and symmetry labeling of peaks

IR spectra were calculated at the optimization level and symmetry labeling of the peaks was performed to test the correctness of the molecular structure of phosphorus oxides. Symmetry species of the basic vibrational modes of molecules, IR active modes and expected peak numbers in the IR spectrum were obtained by symmetry application [19] and are given in Table 2.

As seen in Table 2, the vibration modes A₂, E and T₁ of the molecules in the Tₐ point group and A₂ vibration modes of the molecules in the C₃ᵥ and C₂ᵥ point group are IR inactive. Peak intensities of vibration modes with IR inactive are zero. Therefore, IR inactive modes do not generate peaks. When the peak intensities of the vibration modes with IR active below a certain value, they do not generate peaks. Therefore, fewer peaks are observed in the IR spectrum than expected. P₄O₆ and P₄O₁₀ molecules are in the Tₐ point group. In the Tₐ point group, only T₂ symmetry modes is IR active. Since the T₂ symmetry species is triple degenerate, four peaks are expected in the IR spectrum of the P₄O₆ molecule and six peaks in the IR spectrum of the P₄O₁₀ molecule.

| Molecule | Bond | Length (Å) | Exp. [1] | Bond | Angle (°) | Exp. [1] |
|----------|------|------------|----------|------|-----------|----------|
| P₄O₆     | P1-O2 | 1.654      | 1.638    | O2-P1-O3 | 100.0     | 99.8     |
|          | -     | -          | -        | P1-O2-P5 | 126.1     | 126.7    |
| P₄O₇     | P1-O2 | 1.602      | 1.644    | O2-P1-O3 | 103.0     | -        |
| P5-O2    | 1.668 | 1.684      | O2-P5-O6 | 99.3     |
| P5-O6    | 1.651 | 1.595      | O2-P1-O11| 115.3    |
| P1-O11   | 1.443 | 1.450      | P1-O4-P8 | 124.1    |
|          | -     | -          | P5-O7-P9 | 126.6    |
| P₄O₈     | P1-O2 | 1.612      | 1.633    | O2-P1-O3 | 102.3     | -        |
| P1-O3    | 1.601 | 1.668      | O3-P1-O4 | 103.1    |
| P8-O4    | 1.665 | 1.576      | O2-P1-O11| 115.2    |
| P8-O10   | 1.649 | 1.596      | O3-P1-O11| 115.9    |
| P1-O11   | 1.440 | 1.414      | P1-O2-P5 | 122.7    |
|          | -     | -          | P1-O4-P8 | 124.4    |
|          | -     | -          | P8-O10-P9| 127.1    |
| P₄O₉     | P1-O2 | 1.611      | 1.661    | O2-P1-O3 | 102.3     | -        |
| P1-O3    | 1.602 | 1.605      | O2-P1-O4 | 102.1    |
| P1-O11   | 1.438 | 1.418      | O2-P1-O11| 115.6    |
|          | -     | -          | O3-P1-O11| 116.7    |
|          | -     | -          | O3-P9-O7 | 99.2     |
|          | -     | -          | P1-O2-P5 | 122.9    |
|          | -     | -          | P1-O3-P9 | 124.5    |
| P₄O₁₀    | P1-O2 | 1.610      | 1.604    | O2-P1-O11| 116.1     | 116.5    |
| P1-O11   | 1.436 | 1.429      | O2-P1-O3 | 102.0    | 101.6    |
|          | -     | -          | P1-O2-P5 | 122.8    | 123.5    |

Table 2 Basic vibration modes of phosphorus oxides and IR active modes.

| Molecule | Point group | Fundamental modes | IR active modes | Peak number |
|----------|-------------|-------------------|-----------------|-------------|
| P₄O₆     | Tₐ          | 1A₁+2E+2T₁+4T₂    | 4T₂             | 4           |
| P₄O₇     | C₃ᵥ         | 7A₁+2A₂+9E        | 7A₁+9E         | 16          |
| P₄O₈     | C₂ᵥ         | 10A₁+5A₂+7B₁+8B₂ | 10A₁+7B₁+8B₂   | 25          |
| P₄O₉     | C₃ᵥ         | 7A₁+4A₂+11E       | 7A₁+11E        | 18          |
| P₄O₁₀    | Tₐ          | 3A₁+3E+3T₁+6T₂   | 6T₂            | 6           |
P\textsubscript{4}O\textsubscript{7} and P\textsubscript{4}O\textsubscript{9} molecules are in the C\textsubscript{3v} point group. A\textsubscript{2} modes of molecules in C\textsubscript{3v} point group are IR inactive, A\textsubscript{1} and E modes are IR active. E is a double degenerate symmetry type. Sixteen peaks are expected in the IR spectrum of P\textsubscript{4}O\textsubscript{7} molecule and eighteen peaks in P\textsubscript{4}O\textsubscript{9} molecule is in the C\textsubscript{3v} point group. A\textsubscript{2} modes of molecules in the C\textsubscript{2v} point group are IR inactive and other vibration modes are IR active. Therefore, 25 peaks are expected in the IR spectrum.

In this study, IR spectra of the phosphorus oxides were calculated in gas phase at PBE1PBE/6-311+G(2d) level. Peaks with intensity greater than 10 km/mol [20] are given with their labels in Figure 2.

![IR spectra of phosphorus oxides calculated at PBE1PBE/6-311+G(2d) level.](image1)

As seen in Figure 2, while four peaks are expected in the IR spectrum of P\textsubscript{4}O\textsubscript{6} molecule, three peaks are calculated. This is because the peak intensity of one of the vibration modes in the T\textsubscript{2} symmetry is greater than zero but less than 10 km/mol. The same is true for other molecules except P\textsubscript{4}O\textsubscript{10}. In P\textsubscript{4}O\textsubscript{10}, the expected peak number was equal to the calculated peak number. The vibration modes, frequencies and symmetry labeling of the peaks in Figure 2 are given in Table 3.

As seen in Table 3, around 1400 cm\textsuperscript{-1} peaks were obtained for P\textsubscript{4}O\textsubscript{7}, P\textsubscript{4}O\textsubscript{8}, P\textsubscript{4}O\textsubscript{9} and P\textsubscript{4}O\textsubscript{10} molecules. This peak belongs to the P-Ot stretching vibration. For P\textsubscript{4}O\textsubscript{10}, this peak was calculated comparatively at 1418 cm\textsuperscript{-1} and experimentally observed at 1406 cm\textsuperscript{-1} [21]. These results are quite compatible with each other. Since this bond is not in the P\textsubscript{4}O\textsubscript{6} molecule, no IR peak around 1400 cm\textsuperscript{-1} was observed. Since the P-Ot bond has a double bond character, it occurs at high frequency, that is, in the double bond stretching region. Other P-Ob bonds have a single bond character. Therefore, it appeared at low frequency, that is, in the single bond stretching region.

Both the compatibility of molecular structure parameters with experimental values and IR spectrum analyzes show that the point groups and structures of molecules are determined correctly.

### 3.3 Proton affinities and acidity strengths of phosphorus oxides

Proton affinity was calculated for prediction the acidity strength of oxides. To calculate proton affinity, a proton was connected to the atom with the most negative charge, it was optimized and the total energy was calculated. The most negative formal charged atom was determined by considering Mulliken charges. Mulliken charges of atoms are given in Fig. 3.

![Mulliken charges of atoms calculated at PBE1PBE/6-311+G(2d) level in gas phase.](image2)

As seen in Figure 3, P\textsubscript{4}O\textsubscript{6} can be protonated from any oxygen atom and P\textsubscript{4}O\textsubscript{10} any of the bridge oxygen atoms. P\textsubscript{4}O\textsubscript{7} can be protonated from one of the oxygen atoms.
atoms numbered with 2, 3 or 4, $\text{P}_4\text{O}_8$ oxygen atom numbered with 2, and $\text{P}_4\text{O}_9$ any of the oxygen atoms numbered with 2, 4 and 6. According to the Equation (1), the proton affinity were calculated from the total energies of the neutral and protonated species and given in Table 4.

### Table 3
Vibration modes, frequencies and symmetry labeling of phosphorus oxides computed at PBE1PBE/6-311+G(2d) level

| Peak | Modes | Freq. (cm$^{-1}$) | Symmetry | Peak | Modes | Freq. (cm$^{-1}$) | Symmetry |
|------|-------|------------------|----------|------|-------|------------------|----------|
| $\text{P}_4\text{O}_6$ | 1 | 6,7,8 | 391.6 | $\text{T}_2$ | 1 | 6 | 259.9 | $\text{A}_1$ |
| | 2 | 16,17,18 | 646.3 | $\text{T}_2$ | 2 | 11,12 | 392.2 | $\text{E}$ |
| | 3 | 22,23,24 | 942.6 | $\text{T}_2$ | 3 | 14 | 418.9 | $\text{A}_1$ |
| $\text{P}_4\text{O}_7$ | 4 | 15 | 545.8 | $\text{A}_1$ |
| | 1 | 8 | 375.5 | $\text{A}_1$ |
| | 2 | 9,10 | 413.4 | $\text{E}$ |
| | 3 | 16 | 635.8 | $\text{A}_1$ |
| | 4 | 17,18 | 651.6 | $\text{E}$ |
| | 5 | 19,20 | 698.3 | $\text{E}$ |
| | 6 | 21 | 705.7 | $\text{A}_1$ |
| | 7 | 24 | 955.0 | $\text{A}_1$ |
| | 8 | 25,26 | 972.3 | $\text{E}$ |
| | 9 | 27 | 1395.3 | $\text{A}_1$ |
| $\text{P}_4\text{O}_8$ | 1 | 11 | 401.1 | $\text{A}_1$ |
| | 2 | 12 | 428.7 | $\text{B}_1$ |
| | 3 | 14 | 541.2 | $\text{A}_1$ |
| | 4 | 16 | 606.3 | $\text{A}_1$ |
| | 5 | 17 | 649.8 | $\text{A}_1$ |
| | 6 | 18 | 681.3 | $\text{B}_2$ |
| | 7 | 19 | 689.2 | $\text{B}_1$ |
| | 8 | 22 | 740.3 | $\text{B}_1$ |
| | 9 | 25 | 793.9 | $\text{A}_1$ |
| | 10 | 26 | 973.9 | $\text{B}_2$ |
| | 11 | 27 | 986.5 | $\text{A}_1$ |
| | 12 | 28 | 996.3 | $\text{B}_1$ |
| | 13 | 29 | 1398.6 | $\text{B}_2$ |
| | 14 | 30 | 1414.1 | $\text{A}_1$ |

### Table 4
Total energies and proton affinity (PA) of phosphorus oxides calculated at PBE1PBE/6-311+G(2d) level in gas phase

| Molecule | E(neutral) (Hartree) | E(protonated) (Hartree) | PA (eV) |
|----------|---------------------|-------------------------|---------|
| $\text{P}_4\text{O}_6$ | -1816.211019 | -1816.495185 | 7.73 |
| $\text{P}_4\text{O}_7$ | -1891.431078 | -1891.701142 | 7.35 |
| $\text{P}_4\text{O}_8$ | -1966.646769 | -1966.894749 | 6.75 |
| $\text{P}_4\text{O}_9$ | -2041.857303 | -2042.089442 | 6.32 |
| $\text{P}_4\text{O}_{10}$ | -2117.061515 | -2117.277013 | 5.86 |

As can be seen from Table 4, as the number of terminal oxygen atoms increases, the proton affinity decreases. Acidity increases as proton affinity decreases. Because, according to the Lowry-Bronsted acid base definition, the acidity of a species depends on the tendency to give protons. According to this definition, the species that can give proton acts as acid and the species that can take proton acts as base. The tendency to give protons is inversely proportional to the proton interest. According to the proton affinity values, the acidity strength of phosphorus oxides with cage structure is as follows: $\text{P}_4\text{O}_6 < \text{P}_4\text{O}_7 < \text{P}_4\text{O}_8 < \text{P}_4\text{O}_9 < \text{P}_4\text{O}_{10}$.
It can be said that the P$_2$O$_{10}$ molecule is a strong dehydration agent and the formation of H$_3$PO$_4$ as a result of its hydrolysis is related to its acidity strength.

4. Conclusions

As a result of this study, molecular structures, molecular structure parameters and IR spectra of phosphorus oxides were calculated. Calculations were made at the PBE1PBE/6-31+G(2d) level. It was found that P$_2$O$_6$ and P$_2$O$_{10}$ molecules are in the Td point group, P$_2$O$_7$ and P$_2$O$_9$ molecules in the C$_{2v}$ point group and P$_4$O$_8$ molecule in the C$_{2v}$ point group. Symmetry labeling of the peaks in the IR spectra of the studied molecules was performed. Protonated species were also optimized at the computation level. Proton affinity values were calculated using the total energies of neutral and protonated species. Acidity strength ranking according to proton affinity values was obtained as P$_2$O$_6 < P$_2$O$_7 < P$_2$O$_8 < P$_2$O$_9 < P$_2$O$_{10}$.

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