Phosphorus nanoclusters and insight into the formation of phosphorus allotropes†

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Elemental phosphorus has a striking variety of allotropes, which we analyze by looking at stable phosphorus clusters. We determine the ground-state structures of \( \text{P}_n \) clusters in a wide range of compositions \((n = 2–50)\) using density functional calculations and global optimization techniques. We explain why the high-energy white phosphorus is so easily formed, compared to the much more stable allotropes – the tetrahedral \( \text{P}_4 \) cluster is so much more stable than nearby compositions that only by increasing the size to \( \text{P}_{10} \) one can get a more stable non-\( \text{P}_4 \)-based structure. Starting from 17 atoms, phosphorus clusters have a single-stranded structure, consisting of a set of well-resolved structural units connected by \( \text{P}_2 \) linking fragments. The investigation of relative stability has revealed even-odd alternations and structural magic numbers. The former are caused by the higher stability of clusters with even numbers of atoms due to closed electronic shells. The structural magic numbers are associated with the presence of particular stable structural units and lead to enhanced stability of \( \text{P}_{18+12k} \) \((k = 0, 1, 2)\) clusters. We also compare the energies of the obtained ground-state structures with clusters of different phosphorus allotropes. Clusters of fibrous phosphorus are energetically the closest to the ground states, while phosphorus clusters are found to be less stable, and the least stable allotrope at the nanocluster scale is black phosphorene.

1. Introduction

Phosphorus, along with carbon, sulfur and boron, has one of the most diverse bonding patterns with each of its three traditional forms, white, black and red, existing in different structural sub-types. This diversity covers structures with 0D (white), 1D (fibrous and Hittorf’s types of red phosphorus), and 2D (black) motifs, resulting in a wide range of band gaps from 0.34 eV (black) to 1.5 eV (Hittorf’s) to 2.1 eV (white) and tremendously varied chemical activity — from highly reactive white phosphorus (which self-ignites in air and is extremely toxic) to the virtually inert black form. The first discovered allotrope was white phosphorus, and it was obtained in 1669 by alchemist H. Brand, followed by red phosphorus in 1847, Hittorf’s in 1865 and black in 1914.

Interestingly, the least energetically stable forms were discovered first, and the most stable ones (still, it is debated whether black or Hittorf’s allotrope is the most stable one) were discovered last, and with special procedures. For example, black phosphorus was first obtained at a high pressure.

Such structural diversity is further multiplied at the nanoscale due to the surface effects and lifting of periodicity constraints. In the recent decade, various low-dimensional structures have drawn attention in light of possible strong competition to graphene, notably phosphorene and blue phosphorus.

A very fruitful way to rationalize allotropy is to systematically study the structure of nanoclusters of increasing size, as they bridge all characteristic scales, from small molecules to bulk. Such information may complement the existing structural rules for phosphorus, developed by von Schnering, Baudler and Haeser, and can shed new light on the structural competition between various forms of phosphorus.

Phosphorus nanoclusters are also of interest as building blocks of various polyphosphides and amorphous red phosphorus (a-P), which emerges now as a promising battery material. Earlier studies suggested that a-P consists of small planar fragments of black phosphorus, but then linear structures were proposed, starting from a theoretical description of a-P as a chain of \( \text{P}_4 \) tetrahedra. Further studies, using
neutron diffraction, showed the presence of $P_8$ and $P_9$ cages, which makes a-P a disordered relative of Hittorf’s and fibrous phosphorus. $P_7$–$P_9$ cages were also pointed out by Raman measurements. In contrast, there are experimental works that claim the dominance of smaller $P_3$ and $P_4$ fragments. This kaleidoscope of views was made even broader by a recent result of combined microscopy, chromatography and methodological measurements describing a-P as a zigzag $\cdot [P_3] \cdot$ polymer. The essential agreement in these results is that a-P consists of various clusters, connected into a most likely linear structure (yet a disordered arrangement has been proposed recently). Experimentally, phosphorus nanoclusters are obtained via laser ablation or evaporation with subsequent mass-spectrum analysis. Since neutral particles cannot be detected by mass spectrometry, clusters are charged – and it is for positively or negatively charged clusters that stability versus size relationship, collision-induced dissociation mass-spectra and electron-detachment energies are studied. Thus, the principal source of information about neutral nanoclusters is theoretical modeling. Among early works in this direction, we note a study on $P_2$–$P_8$ clusters. The $P_8$ block, appearing in many phosphorus-rich compounds including red phosphorus, was first shown to be of a cuneane shape. This was later confirmed in the work by Haeser, who used extensive NMR data on phosphanes to model structures of bare $P_{2n}$ clusters up to $P_{28}$. To model larger clusters some researchers used fullerenelike geometries though they are hardly optimal due to lone-pair interactions at low cage curvatures (see the fundamental work on structural rules in phosphorus). There is important evidence on the difference between structures of charged and neutral clusters – see, for example, systematic calculations, where anionic, cationic and neutral cluster structures for up to $P_{15}$ were selected from earlier publications (a similar work on neutral particles was done in a more recent paper).

Despite the vast number of insightful studies, a systematic unbiased ab initio prediction of the structure of phosphorus nanoclusters larger than 15 atoms is still missing. This is hampered by the extremely complex potential energy surface and the high cost of ab initio calculations. In the present study we use our recently developed powerful global optimization techniques to determine the ground-state structures of $P_n$ clusters with $n \leq 50$. We also compare the relative stabilities of clusters of different phosphorus allotropes to obtain a complete picture of the structural peculiarities of this material at the nanoscale.

2. Computational methods

The ground-state structure determination of phosphorus nanoclusters was performed in two steps. First, we used the unbiased evolutionary variable-composition global optimization algorithm USPEX, extended to molecules and nanoparticles. This technique allows one to simultaneously optimize structures in a wide range of compositions and demonstrates significant speedup compared to previously used approaches, which perform global optimization for each cluster composition independently. The method was successfully used for the global optimization of various systems.

Next, after the inspection of the evolutionary global optimization results, we performed an additional structure search. It consisted in identifying structural fragments, frequently appearing in the USPEX search, and connecting them in all possible ways, as described in Section 3.

The local geometry optimization was performed using the density functional theory using the projector augmented wave method and Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional as implemented in the VASP code. The $s^2$ and $p^3$ electrons of phosphorus have been treated as valence electrons. In these cases we used a 255 eV plane wave energy cutoff and the periodic images of a cluster were separated by 10 Å vacuum in all dimensions. All these calculations were done in the spin-polarized mode of the VASP code.

The energies of 20 best structures for each composition were then refined using the GAUSSIAN code with the B3LYP hybrid functional and the Def2TZVP basis set. Since some of the investigated phosphorus structures have the form of separate fragments, held together by dispersion interactions, van der Waals correction has been applied in the D3 (zero damping) form proposed by Grimme.

The minimal possible spin multiplicity ($M = 1$ for even-electron clusters and $M = 2$ for odd-electron clusters) was chosen for the refinement step. For the low-energy structures, higher multiplicities have been considered as well. The results confirmed that for the ground-state structures the minimal multiplicity is energetically more favorable.

3. Optimal structures of $P_n$ clusters

In the first step of structure determination, we predicted the structures of phosphorus nanoclusters between $P_2$ and $P_{45}$ using the evolutionary algorithm USPEX. During the USPEX search, ~150,000 candidate structures were constructed and locally optimized. The inspection of the resulting low-energy structures revealed that, starting from a certain size, many of the clusters can be described as a sequence of well-resolved structural units linked by $P_2$ fragments. Such a structural pattern is common for the 1D-like phosphorus allotropes such as fibrous or Hittorf’s phosphorus and nanorod systems, chemically isolated from (CuI)$_n$P$_y$ crystals. Fig. 1a shows the internal structural units of the clusters found in our search ($P_2$, $P_3$, $P_8$, $P_{10}$) together with other units ($P_9$, $P_{13}$) taken from phosphorus structures described in the literature. The $P_2$ unit is common for most clusters and serves as a link between other units. The $P_3$ unit appeared in a few structures and further consideration pointed to its high instability due to the dangling bond and a two-coordinated phosphorus atom, which violates the octet rule (the requirement that each phosphorus atom is bonded to three other atoms). The $P_8$ unit is well-known and appears in fibrous and Hittorf’s phosphorus. It also appears in many 1D phosphorus systems, synthesized...
We start the discussion of the ground-state structures of $P_n$ clusters by considering the compositions with $n$ up to 15, as these systems have been extensively studied in other theoretical works.\textsuperscript{34,35,37,38,64–66} The available literature data show some controversy, as different works suggest different ground-state geometries for some compositions. To verify that the structures, discovered with our global optimization, are indeed energetically the most favorable, we reconstructed the lowest energy structures reported in the literature and recalculated their energies at the theoretical level, used in the present study, including geometry optimization. We found that the ground-state structures of $P_4$ and $P_{14}$ clusters, obtained in our calculations, are lower in energy by 0.47 and 0.66 eV than the corresponding structures reported in the literature.\textsuperscript{66} The ground states of $P_2$-$P_7$, $P_8$-$P_{12}$, $P_{14}$, and $P_{15}$ clusters are found to coincide with those reported earlier.

It is worth noting that the ground-state structure of the $P_8$ cluster is a van der Waals bonded $P_4$ dimer structure. The monomer $P_8$ cluster, reported in earlier works (similar to an isolated $P_8$ unit, shown in Fig. 1), is significantly less favorable in energy (by 0.47 eV). In this case, the question on the most energetically stable cluster depends on the definition of a cluster as either a covalently bonded monomer, or the lowest energy solution, irrespective of the number of fragments. The $P_{10}$, $P_{11}$, $P_{13}$ and $P_{14}$ clusters can be described as two terminal structural units (Fig. 1b), linked together via the intermediate $P_4$ unit. The $P_{15}$ and $P_{16}$ clusters consist of two terminal units ($P_8^*P_2^*$ and $P_8P_8^*$), directly bonded to each other without the $P_2$ linking fragment.

Starting from $n = 17$ all the ground-state structures of $P_n$ clusters are characterized by the presence of intermediate $P_2$ units, which serve as a link between more complex units. The addition of new atoms leads to the reorganization of the cluster structure to construct the combination of structural units with the lowest energy among all other possible combinations. We find that among all internal units considered, besides the linking $P_2$ fragment, only the $P_8$ and $P_10$ appear in the ground states, which points to their higher stability. The terminal units show a higher diversity: $P_1^*$, $P_4^*$, $P_7^*$ and $P_8^*$ are found in the lowest energy clusters. To get a deeper insight into the relative stability of the phosphorus clusters with different numbers of atoms, we analyze the energetic characteristics of the calculated ground states.

### 4. Energetics and stability

The energies per atom of $P_n$ clusters ($n = 2$–50), relative to an isolated $P$ atom, are shown in Fig. 3. This important graph has the following main features: (1) it decreases overall as the size of the cluster increases and will approach the energy of the bulk crystal in the limit of an infinite number of atoms. (2) It oscillates in a remarkably strict way, such that clusters with even numbers of atoms have a lower energy than their neighboring odd clusters. Such oscillations signify the local stability of the clusters compared to the neighboring ones, which can
then be related to the relative frequency of their occurrence in experiments. Even clusters should be much more abundant than odd ones, as we discuss below. (3) A very large drop in the energy due to the formation of the \( P_4 \) cluster has profound consequences. This tetrahedral cluster is the first one where all atoms satisfy the octet rule, see Fig. 2. Moreover, the next cluster satisfying the octet rule is \( P_{10} \). This means the easy formation of the \( P_4 \) cluster, but its further growth is strongly hin-

Fig. 2 Ground-state structures of \( P_n \) clusters with \( n = 3 \)–30. The \( P_2 \) units serving as a linking fragment between other units are marked with a darker color.
Fig. 3 Energies per atom for \( P_n \) clusters relative to an isolated P atom. The black solid line connects the ground-state systems. The blue and pink symbols are related to clusters with and without the \( P_2 \) structural unit, respectively. The black, white and red symbols depict the clusters obtained from black phosphorene, white phosphorus and fibrous phosphorus, respectively. The black arrows depict the magic clusters, consisting of \( P*_{8} \) and \( P*_{10} \) structural units, connected by \( P_2 \) units (structural magic numbers).

The local stability of clusters can be explored in more detail using the second-order difference of energy, \( \Delta^2 E(n) \):

\[
\Delta^2 E(n) = E(n+1) + E(n-1) - 2E(n)
\]

where \( E(n) \) is the total energy of a cluster containing \( n \) atoms. This quantity characterizes the resistance towards the transfer of one atom between two identical clusters, for example, during their collision. Clusters with a positive \( \Delta^2 E(n) \) are called magic clusters and the corresponding numbers of atoms are called magic numbers. Such magic clusters appear more often in experimental mass spectra. The \( \Delta^2 E(n) \) function (Fig. 4a) exhibits even-odd alternations: \( \Delta^2 E(n) \) is positive for even \( n \) and negative for odd \( n \), which is a direct consequence of the oscillations in the energy per atom (Fig. 3). These oscillations are easily explained by the fact that \( P_2 \) clusters with odd \( n \) have an odd total number of electrons and therefore open-shell electronic structure, which leads to their instability compared to clusters with an even number of atoms. The stability alternations also correlate with atomic coordination numbers and the hybridization type. Whereas most of the atoms in the ground-state clusters are in their three-coordinated \( sp^3 \)-hybridized form, the appearance of two-coordinated \( sp^2 \)-atoms lowers the stability of their corresponding clusters. Starting from \( n = 5 \), each odd-numbered system contains one two-coordinated P atom, which results in their negative \( \Delta^2 E(n) \) values. In larger clusters, represented by a sequence of structural units, such an atom appears as part of terminal \( P*_{i} \) and \( P*_{j} \) blocks. In these terms, the higher stability of even-numbered clusters arises from the absence of two-coordinated atoms (all atoms are three-coordinated with \( sp^3 \) hybridization). The exception is the \( P_8 \) cluster, which contains two two-coordinated \( sp^3 \)-hybridized atoms, resulting in the lowest \( \Delta^2 E(n) \) value among other even-numbered clusters.

To investigate the relative stability of clusters with an even number of atoms, we extended the criterion (1) to consider the exchange of 2 phosphorus atoms: \( \Delta^2_{ext} E(n) = E(n+2) + E(n-2) - 2E(n) \):

\[
\Delta^2_{ext} E(n) = \min \{ \Delta^2 E(n), \Delta^2_{2p} E(n) \},
\]

One can see (Fig. 4b) that the clusters \( P_{4s}, P_{8s}, P_{14s}, P_{18s}, P_{30} \) and \( P_{42} \) stand out most strongly. \( P_4 \) and \( P_8 \) clusters are minimal fragments of white (molecular) phosphorus. The \( P_{14} \) cluster consists of two stable terminal units, \( P*_{8} \) and \( P*_{6} \). We want to draw attention to the \( P_{18s}, P_{30} \) and \( P_{42} \) clusters, whose compositions obey the rule

\[
n = 18 + 12k \quad (k = 0, 1, 2)
\]

The structures of these clusters are formed according to the following principle: they consist of two terminal \( P*_{8} \) units and \( k \)
intermediate $P_{10}$ units, connected by the $P_2$ linking fragments (see, for example, the atomic structures for $P_{18}$ and $P_{30}$ in Fig. 2). This sequence of compositions, differing by the number of $P_{10}P_2$ groups, gives structural magic numbers.

Interestingly, the mass spectra of charged phosphorus clusters $P_n^-$ also show periodic magic numbers ($n = 8k + 1$, where $k = 3, 4, \ldots$)\textsuperscript{29,69} – note that these are odd numbers (for singly charged phosphorus clusters $P_n^-$ or $P_n^+$ only odd clusters will have even numbers of electrons). Despite the difference in exact values, one expects that the nature of this phenomenon is the same: 1D-clusters are formed from certain terminal units and a variable number of identical internal units. However, the exact structure of such structural units should be a topic for a separate study, since charging can strongly affect the structure of the low-energy clusters.

Fig. 4c shows another measure of stability, the so-called fragmentation energy ($E_{\text{frag}}$) – the lowest energy of fission of a given cluster into smaller clusters. $E_{\text{frag}}$ has a large value for the $P_4$ cluster; in addition, one can note that $E_{\text{frag}}$ drops after magic clusters $P_8$, $P_{16}$, $P_{30}$, and $P_{14}$ – by adding just one atom to these magic clusters, one obtains more easily fission clusters (analogous to the drop of ionization potential going from closed-shell noble gases to alkali metals with one more electron). It is even more interesting to consider the lowest-energy fission paths: for all $P_n$ clusters with $n \geq 6$ the fission products are $P_4 + P_{n-4}$. A complete set of fragmentation energies and fission products is given in Table S1 of the ESL.\textsuperscript{†} This means that sublimation of solid phosphorus is most likely to produce $P_4$ clusters in the vapor, the condensation of which should produce white phosphorus. Indeed, it is a well-known experiment: condensation of vapor obtained by sublimation of red phosphorus does produce white phosphorus.

We also calculated the HOMO–LUMO gaps for the obtained clusters (Fig. 4d) which have shown a notable correlation with the $\Delta E(n)$ behavior. The largest gaps are found for tetrahedral $P_4$ and $P_8$ clusters, whereas the smallest values correspond to odd-numbered clusters.

5. Clusters of phosphorus allotropes

With an increasing number of atoms in a cluster, the structure and energies of the lowest-energy cluster will converge to those of the most stable crystalline allotrope. It is well known that phosphorus exhibits rich structural diversity with multiple allotropes known to date. It has been shown previously that the question of the stable phosphorus allotrope is not yet resolved and is not trivial.\textsuperscript{7} The lowest-energy allotropes – black and Hittorf’s phosphorus – are very close in energy and their calculated relative energy is very sensitive, for example, to the description of van der Waals interactions. Accurate computations within the random-phase approximation revealed that the Hittorf’s allotrope is slightly more stable than black phosphorus.\textsuperscript{7} In order to investigate the relative stability of different phosphorus allotropes at the nanoscale, we performed additional computations of phosphorus clusters constructed from periodic phosphorus structures and compared the resulting energies with the ground-state structures found during our global optimization.

Black phosphorus is described as a stack of 2D-sheets held together by van der Waals forces. The largest clusters, considered in our study, contain 50 atoms, a number which is not enough to consider a stack of multiple phosphorus layers. Therefore, to obtain clusters with the structural features of black phosphorus, we used its 2D counterpart – a single isolated layer, often called black phosphorene. To construct the atomic structure of the corresponding clusters, we used different ways to cut finite fragments from the 2D lattice of black phosphorene with the number of atoms from 15 to 50.

White phosphorus consists of tetrahedral $P_4$ molecules, held together by van der Waals interactions. Depending on the temperature, various packings of the $P_4$ molecules exist. The atomic geometries of white phosphorus clusters were obtained by extracting spherical fragments from the $\gamma$- and $\beta$-modifications of bulk white phosphorus.

The fibrous and Hittorf’s allotropes of phosphorus are structurally similar. They are both composed of 1D nanorods, which are described as a sequence of $P_4P_2P_9P_2$ fragments and are connected pairwise with a crosslink between the $P_9$ structural units. The difference between these two allotropes is related to the mutual orientation of the nanorods. In the fibrous modification, the nanorods are oriented parallel to each other, forming double-stranded chains, whereas in the case of Hittorf’s phosphorus, they are oriented perpendicular to each other. To construct the atomic structure of such connected nanorods, we used an algorithm similar to the one we used for building single-stranded clusters from different structural units. We started by considering a pair of crosslinked $P_9$ units and increased the cluster size by attaching other possible phosphorus units to it. As a result, we considered all possible unique combinations of structural units to construct $P_n$ clusters with $n = 18–50$ with the inclusion of the crosslinked $P_9$ pair. It is worth noting that the two strands, forming these clusters, are connected with only a single bond between the $P_9$ units. This leads to a very high rotational flexibility of such strands. As a result, the obtained clusters can be close to both fibrous and Hittorf’s modifications due to different possible orientations of the strands.

The manually constructed clusters of black phosphorene, white and fibrous $P$ allotropes have been optimized at the same level of theory as other clusters in the present work. The resulting energy values per atom for the corresponding lowest energy structures are shown in Fig. 3. To illustrate the idea, Fig. 5 shows the equilibrium geometries of such different clusters with the same $P_{48}$ composition.

We find that the highest energy allotrope at the size scale considered is black phosphorene. The 2D nature of this material leads to a high fraction of boundary atoms with dangling bonds for clusters with $n \leq 50$, resulting in relatively high energy values. White phosphorus clusters are found to have a lower energy compared to black phosphorene clusters. Moreover, for compositions $P_4$ and $P_8$ they represent the
ground-state solutions, obtained during global optimization. The fibrous phosphorus clusters have relatively high energies for smaller clusters, but starting from $n \sim 24$ their energy starts to drop, approaching the values of the ground-state structures for compositions close to $n = 50$. We can expect that a further increase in the cluster size will lead to the stabilization of black phosphorene relative to white phosphorus, and double-stranded clusters relative to single-stranded ones.

The HOMO–LUMO gaps of the clusters of phosphorus allotropes show trends similar to those of their bulk counterparts. The largest gap values are obtained for the white phosphorus clusters. Clusters of fibrous phosphorus have gap values closest to those of the ground-state structures and have intermediate values. The smallest gaps correspond to the black phosphorene clusters. The calculated values of HOMO–LUMO gaps for nanoclusters of black phosphorene, white and fibrous phosphorus, are given in Fig. S2 of the ESL.$^\dagger$

6. Conclusions

Prediction of stable phosphorus clusters has given us new insights into the formation and stability of bulk allotropes of phosphorus. First, we explain the ease with which high-energy (and hence reactive, pyrophoric and toxic) white phosphorus (made of $P_4$ molecules) is formed from atoms or from the sublimation of other allotropes. Second, we observe that only clusters with an even number of atoms are magic clusters due to electronic effects. Structural effects additionally stabilize single-stranded $P_n$ clusters with $n = 18 + 12k$ ($k = 0, 1, 2$). We have shown that these clusters are made of well-defined sequentially arranged building blocks. For singly charged clusters (which are studied in mass spectrometry) other magic numbers are known (with odd numbers of phosphorus atoms).

Our results reveal a significant difference in the relative stability of phosphorus allotropes at the scale of small clusters as compared to the bulk state. In the bulk, the least stable system is white phosphorus, and the black, fibrous and Hittorf’s modifications have significantly lower energies, the latter being likely the ground state. In the case of $P_n$ clusters with $n \leq 8$, white phosphorus ($P_4$) is the ground state, and for $8 < n \leq 50$ single-stranded fragments are the ground state. The double-stranded fragments have slightly higher energy values, white phosphorus clusters have intermediate energies and clusters derived from the 2D black phosphorene are the highest-energy ones for these cluster sizes due to many dangling bonds. Our results explain why the formation of 2D (black phosphorus) and nearly-1D (fibrous phosphorus and Hittorf’s phosphorus), rather than the 0D allotrope (white phosphorus made of 0D-molecules), will be kinetically much more difficult – their small-to-medium clusters will be destabilized by dangling bonds. Generally, if a substance has bulk modifications of different structural dimensionalities, the kinetic ease of their formation will tend to decrease as the fraction of dangling bonds in the nucleation seed grows, usually in the sequence $0D \rightarrow 1D \rightarrow 2D \rightarrow 3D$. One clear example is CH – molecular (0D) compound benzene $C_6H_6$ was well known since its isolation in 1825 by Michael Faraday. However, it is now well established that graphene, a 2D modification with the same composition CH, is significantly more stable,$^{70}$ and graphene was synthesized only in 2009.$^{71}$

We expect more examples of this rule to emerge in the near future.

Author contributions

D. Rybkovskiy – conceptualization, data curation, validation, visualization, writing – the original draft, and writing – review and editing. V. Baturin – formal analysis, investigation, and writing – the original draft. S. Lepeshkin – global optimization, data curation, validation, methodology and writing – review and editing. A. Mikhailova – global optimization, data curation, methodology, visualization, and writing – the original draft. A. R. Oganov – conceptualization, writing – review and editing, and supervision. All co-authors contributed to the discussion of the data. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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