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Icosahedral and Ring-Shaped Allotropes of Phosphorus

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Abstract: The existence of two new allotropic forms of phosphorus, icosahedral cages and ring-shaped chains, is predicted. The cages and rings are nanostructural modifications of the black and the red phosphorus, respectively. The icosahedral and ring-shaped allotropes are compared with the experimentally known allotropic forms of phosphorus by quantum chemical methods. Both the cages and the rings are thermodynamically favored over the white phosphorus, the rings being comparable to the Hittorf's violet phosphorus and to the recently discovered fibrous red phosphorus. The stabilities of the icosahedral cages increase as a function of their size, having structural resemblance with the rhombohedral black phosphorus. The high thermodynamic stability of the phosphorus nanostructures suggests their experimental synthesis to be viable.

Keywords: ab initio calculations • allotropy • nanostructures • phosphorus • structure elucidation

Introduction

Phosphorus is known to appear in diverse allotropic forms, making it a promising source for elemental nanostructures. The allotropes of phosphorus are typically divided into three main classes: white, red, and black phosphorus.[1] The white phosphorus has a crystal structure consisting of tetrahedral P_4 molecules.[2,3] The crystal structure of the black phosphorus is orthorhombic at atmospheric pressure.[4,5] Increasing the pressure changes the structure, first into rhombohedral, arsenic-like, form and then into a simple cubic form.[6,7] Characterization of the red phosphorus is less straightforward due to its tendency to form amorphous polymeric networks. Until recently, the only structurally characterized form of the red phosphorus was the Hittorf's violet phosphorus.[8] In 2005 Ruck et al. obtained the crystal structure of a fibrous red phosphorus, which has close structural relations with the violet phosphorus.[9]

Both violet and fibrous red allotropes of phosphorus are composed of layered pentagonal tubes, arranged either perpendicular (violet) or parallel (fibrous red) to each other. The parallel arrangement was first postulated by Thurn and Krebs in conjunction with the structural characterization of the violet phosphorus.[8] These forms were predicted by Böcker and Häser to be energetically the most favorable phosphorus chains.[10] Theoretical predictions have turned out to be helpful in the interpretation of experimental results, thus assisting in the structural characterization of the red phosphorus. The comprehensive theoretical studies by Häser, Böcker and co-workers on phosphorus clusters[11–13] and covalent phosphorus structures,[10] have introduced a systematic classification of various building blocks of the red phosphorus. Böcker and Häser also devised a naming convention for the description of the red phosphorus structures using structural rules derived from the Baudler's rules for covalently bound phosphorus compounds.[14] Böcker and Häser studied several tubular chains of red phosphorus, three of which have been obtained embedded in a copper halide matrix:[15] The chain denoted as]P4(4)[P8][16] was known earlier;]P2[P10][17] and [P2[P12(4)][18] were found soon after the predictions. Recently, the]P4(4)[P8] and]P2[P10] chains were isolated from the copper halide matrix, resulting in phosphorus nanorods.[19,20] The nanorods show parallel arrangement in HRTEM images, crystal structure thus far being unavailable.

Experimental and theoretical studies have been carried out on various other forms of phosphorus. The tendency of phosphorus to form tubular structures has been demonstrated by simulated annealing DFT calculations for P_9, P_{10}, and P_{11} clusters.[21] Furthermore, there is experimental evidence of the existence of a neutral P_6 cluster allotrope.[22] Larger, polyhedral phosphorus cages with size varying from P_{14} to P_{60}, have been predicted to be unstable with respect to dissociation into P_4 molecules.[23] Folding a sheet of the black

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phosphorus into a cylinder has been predicted to yield stable, semiconducting phosphorus nanotubes.[24,25] In addition, a P_{16} macrocycle within an organic compound has also been experimentally prepared.[26]

In theoretical study reported herein, we introduce two nanoscale allotropes of phosphorus: icosahedral cages and ring-shaped chains. The stabilities and electronic properties of the allotropes are determined on the basis of quantum chemical calculations, comparing them with periodic studies on the crystallographically characterized allotropic forms.

Computational Methods

The structures, stabilities and electronic properties of the icosahedral and ring-shaped phosphorus allotropes were investigated with hybrid density functional B3LYP and ab initio MP2 methods. All the structures were fully optimized by the B3LYP method within their respective point group symmetries. Single-point MP2 calculations were performed at the B3LYP-optimized geometries. The stabilities of the phosphorus molecules were compared with white phosphorus, P_4, together with periodic B3LYP calculations on other experimentally characterized allotropes. For the violet,[8] the fibrous red,[9] and the orthorhombic black phosphorus,[5] the experimental cell parameters were retained, while the atomic coordinates within the cell were optimized. Additionally, monolayers of the orthorhombic and rhombohedral black phosphorus together with infinite red phosphorus chains, [P2[P8],]P4(4)[P8],[16] [P2[P10],[17] and [P2[P12(4)],[18] were fully optimized for reference purposes. The periodic calculations were carried out with the CRYSTAL software (versions 2003 and 06).[27] All the other calculations were performed with TURBOMOLE 5.8.[28] To enable the comparisons between periodic and molecular calculations at the B3LYP level, an optimized basis set was necessary. As a starting point we used the 85-21G(d) basis set originally developed by Zicovich-Wilson et al.[29] for phosphorus in $AlPO_4$. We re-optimized the outermost sp exponent (α_{sp} 0.1350 → 0.1627) and the d polarization exponent (α_d 0.74583 → 0.41660) for the orthorhombic black phosphorus. The MP2 calculations were performed using the resolution-of-identity (RI) approximation as implemented in TURBOMOLE.[30] Together with the MP2 method a triple-valence-zeta basis set with polarization functions[31] and the corresponding RI auxiliary basis set[32] were applied. Icosahedral structures up to P_{180} and ring-shaped structures up to P_{280} were verified as true minima by vibrational frequency calculations.[33] Zero-point vibrational energy scaling factor of 0.9806 was adopted for the calculation of Gibbs free energies.[34]

Results and Discussion

Icosahedral allotropes of phosphorus: The I_h-symmetric polyhedral phosphorus cages P_{20} and P_{60} have been previously found to be unstable with respect to decomposition into P_4.[11,23] The dodecahedral P_{20} cage is composed of 12 pentagons, while P_{60} is a topological analogue of C_{60} fullerene with 12 pentagons and 20 hexagons. The instability of P_{20} and P_{60} can be understood in terms of structural strain. While the lone pairs of the P_4 tetrahedron are directed away from each other, the increasing planarity of the I_h-symmetric P_{20} and P_{60} gives rise to lone pair repulsions.[11] We studied larger icosahedral phosphorus cages, where the repulsion between the lone pairs is significantly decreased by placing a portion of the lone pairs inside the cage. The smallest icosahedral cage applicable for this "in–out" isomerism is P_{80}, where 20 phosphorus atoms connect the 20 sets of three pentagons (Figure 1). The lone pairs of the 20 interconnecting atoms point inwards, resulting in puckering of the cage and significantly reduced structural strain. The "in–out" isomerism has been previously shown to stabilize the analogous tetrahedrally coordinated fulleranes,[35] polysilanes[36] and Group 13–15 binary hydrides.[37] P_{80} is the smallest icosahedral cage that is stable with respect to the P_4 tetrahedron. At the B3LYP level of theory it is favored in total energy over P_4 by 6.72 kJ mol^{-1} per phosphorus atom (Table 1). With the MP2 method the difference increases to 10.4 kJ mol^{-1} per phoshorus atom, in favor of P_{80}.

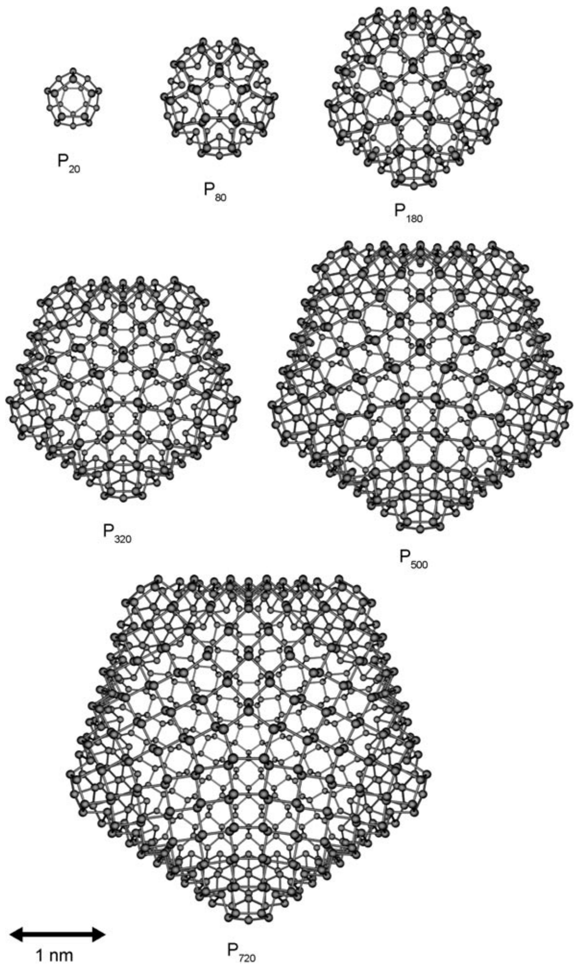

Figure 1. Optimized structures of the icosahedral allotropes of phosphorus.

The structural principles described for P_{80} apply for larger phosphorus cages, as well. In the next largest I_h-symmetric cage, P_{180}, there are 60 phosphorus atoms pointing towards the interior of the cage, resulting in a structure even more stable than the P_{80}. Further enlargement of the icosahedral cages produces molecular structures that can be considered as monolayers of rhombohedral black phosphorus sewed up to a cage. The I_h-symmetric allotropes of phosphorus can be grouped into two series: P_x cages with $x = 20$, 80, 180, 320,

Table 1. Relative[a] total energies and Gibbs free energies ($T=298.15$ K), HOMO–LUMO gaps, and diameters of the icosahedral cages and the ring-shaped chains of phosphorus together with other forms of phosphorus.[b]

	Point group	ΔE_{B3LYP}	ΔG_{B3LYP}	ΔE_{MP2}	ΔG_{MP2}[c]	Gap_{B3LYP} [eV]	Diameter [nm]
P_4	T_d	0.0	0.0	0.0	0.0	6.48	
P_{20}	I_h	2.26	13.5	4.10	15.3	2.93	0.6
P_{80}	I_h	−6.72	6.95	−10.4	3.20	2.79	1.2
P_{180}	I_h	−9.65	4.60	−14.1	0.15	2.53	1.8
P_{320}	I_h	−11.3		−15.9		2.77	2.4
P_{500}	I_h	−12.4				2.83	3.1
P_{720}	I_h	−13.2				2.75	3.7
P_{80}	C_{4v}	−13.3	0.25	−17.3	−3.61	3.13	1.9
P_{120}	D_{12h}	−17.9	−4.00	−21.1	−7.17	3.53	2.7
P_{160}	D_{16h}	−18.7	−4.66	−21.6	−7.61	3.58	3.5
P_{200}	D_{20h}	−18.8	−4.73	−21.6	−7.57	3.60	4.4
P_{240}	D_{24h}	−18.7	−4.68	−21.5	−7.45	3.62	5.2
P_{280}	D_{28h}	−18.6	−4.59	−21.3	−7.33	3.64	6.0
P_{320}	D_{32h}	−18.5		−21.2		3.65	6.9
P_{360}	D_{36h}	−18.4				3.66	7.7
$P_{o\text{-}sheet}$		−16.1				2.16	
$P_{r\text{-}sheet}$		−16.6				3.41	
$P_{]P2[P8]}$		−17.2				3.63	
$P_{]P4(4)[P8]}$		−17.0				3.67	
$P_{]P2[P10]}$		−16.9				3.43	
$P_{]P2[P12(4)]}$		−16.4				3.65	
$P_{fibrous}$		−18.7				2.73	
P_{violet}		−19.1				2.56	

[a] The energies in kJ mol^{-1} per phosphorus atom are given relative to the white phosphorus P_4. [b] The following forms of phosphorus are included: $P_{o\text{-}sheet}$: a monolayer sheet of orthorhombic black phosphorus; $P_{r\text{-}sheet}$: a monolayer sheet of rhombohedral black phosphorus; $P_{]P2[P8]}$, $P_{]P4(4)[P8]}$, $P_{]P2[P10]}$, $P_{]P2[P12(4)]}$: infinite chains of red phosphorus; $P_{fibrous}$: fibrous red phosphorus; P_{violet}: violet phosphorus. [c] Gibbs corrections to the total energies are obtained from the B3LYP calculations.

500, …, $20n^2$ and $x=60$, 240, 540, 960, 1500, …, $60n^2$. The $20n^2$ series approaches the monolayer sheet of rhombohedral black phosphorus both in structure and stability (Table 1). The Gibbs corrections to the total energy do not change the order of stability, but make the smaller cages less favorable than P_4 at 298.15 K. At the MP2 level the difference in Gibbs free energies between P_4 and P_{180} is only 0.15 kJ mol^{-1} per phosphorus atom, indicating the P_{320} to be favored over P_4. Three first members of the series, P_{20}, P_{80}, and P_{180} were verified as true minima by vibrational frequency calculations.

The series with $x=60n^2$ is an extension of P_{60}. The main structural difference to the $20n^2$ series is the presence of 20 planar hexagons with all the lone pairs pointing outside the cage, giving rise to increased lone pair repulsion. As a consequence, the $60n^2$ series is less stable than the $20n^2$ series. The B3LYP energies for the P_{60}, P_{240} and P_{540} cages in comparison to the P_4 are 26.3, 5.44, and −3.37 kJ mol^{-1} per phosphorus atom, respectively. We have calculated the vibrational frequencies for the first two members of the series, P_{60} and P_{240}. They are not true minima, having several imaginary vibrational modes. In addition to the icosahedral cage structures with five- and six-membered phosphorus rings, we have also studied octahedral cages with four- and six-membered rings, and tetrahedral cages with three- and six-membered rings. They are, however, far less stable than the icosahedral cages.

The HOMO–LUMO gaps of the icosahedral cages vary between 2.53 and 2.93 eV. For comparison, the calculated band gaps for the monolayers of the orthorhombic and rhombohedral black phosphorus are 2.16 and 3.41 eV, respectively. For the bulk structure of the orthorhombic black phosphorus the calculated band gap is 0.54 eV, the large difference between the monolayered structures and the bulk structure being due to the interlayer interactions.[24,25,38] The experimental band gap for the orthorhombic black phosphorus is 0.33 eV.[39]

Ring-shaped allotropes of phosphorus: The C_{2v}-symmetric P_{18} and P_{28} have been reported by Häser et al.[11,13] as stable clusters of red phosphorus. They are also short chains, where P_8 and P_2 structural units are sequentially repeated. We studied longer phosphorus chains by increments of P_8 + P_2 structural units. Optimization of the linear chains produced clearly bent structures (Figure 2). These chains are energetically favorable over P_4

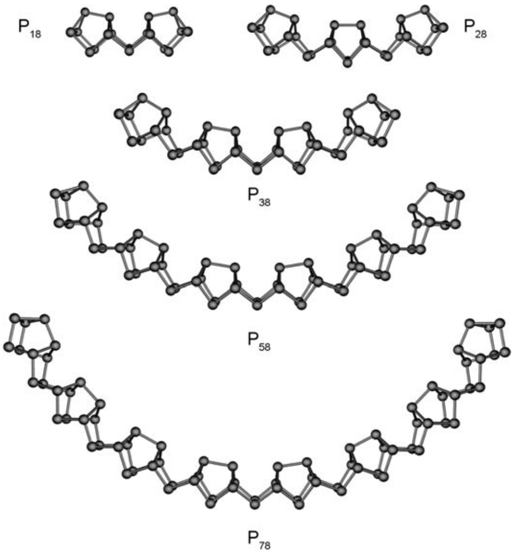

Figure 2. Optimized structures of the C_{2v}-symmetric phosphorus chains composed of P_8 and P_2 structural units.

and become increasingly stable as a function of the chain length (Table 2). Insertion of a P_2 fragment between the terminal P_8 units enables the chain closure, resulting in a ring-shaped structure. The smallest ring, which is a true minimum, is P_{80} (Figure 3). At the B3LYP level of theory, it is $13.3\,kJ\,mol^{-1}$ per P atom more stable than P_4 in terms of total energy (Table 1). Due to the small size of the ring, the P_8 units in P_{80} twist slightly out of the plane to avoid the overlap of the lone pairs of the phosphorus atoms inside the ring. The resulting structure has C_{4v} symmetry, optimizations within higher C_{8v} or D_{8h} symmetries yielding several imaginary vibrational modes.

Table 2. Relative[a] total energies and Gibbs free energies ($T=298.15$ K) and HOMO–LUMO gaps of the C_{2v}-symmetric phosphorus chains composed of P_8 and P_2 structural units.

	$\Delta E_{\mathrm{B3LYP}}$	$\Delta G_{\mathrm{B3LYP}}$	ΔE_{MP2}	ΔG_{MP2}[b]	$\mathrm{Gap}_{\mathrm{B3LYP}}$ [eV]
P_{18}	−13.1	−2.3	−13.3	−2.5	3.86
P_{28}	−15.1	−3.2	−16.3	−4.4	3.82
P_{38}	−16.1	−3.6	−17.7	−5.2	3.74
P_{48}	−16.7	−3.8	−18.5	−5.7	3.71
P_{58}	−17.0	−4.0	−19.0	−6.0	3.68
P_{68}	−17.3	−4.1	−19.4	−6.2	3.66
P_{78}	−17.5	−4.2	−19.7	−6.4	3.64

[a] The energies in $kJ\,mol^{-1}$ per phosphorus atom are given relative to the white phosphorus P_4. [b] Gibbs corrections to the total energies are obtained from the B3LYP calculations.

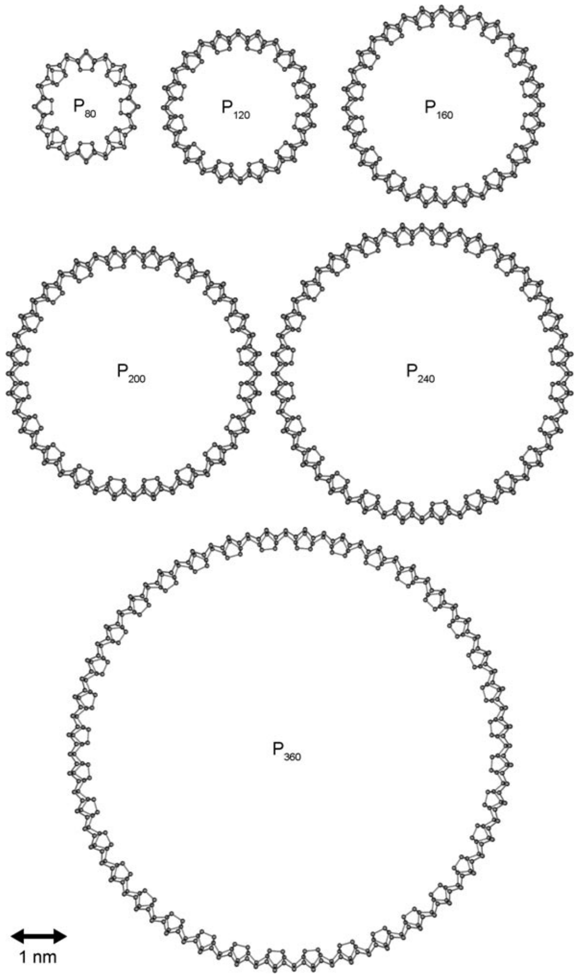

Figure 3. Optimized structures of the ring-shaped allotropes of phosphorus.

Encouraged by the significant stability of the P_{80} ring, we extended the studies to larger rings by systematically increasing the length of the phosphorus chain by four $P_8 + P_2$ structural units. Thus, the next ring structure is a P_{120} ring. Here the repulsion of the lone electron pairs inside the ring is less severe. Hence, the P_8 units do not twist as in the case of P_{80}, resulting in D_{12h} symmetry.[40] The P_{120} ring is considerably less strained than the P_{80}, being $-17.9\,kJ\,mol^{-1}$ per atom more stable than the P_4 in terms of total energy. The next two ring-shaped structures in size are P_{160} and P_{200}, which adopt structures similar to P_{120}. (Figure 3). As a consequence, the P_x ring structures studied here generally have point group symmetries of $D_{(x/10)h}$.[40] Using the naming convention postulated by Böcker and Häser[10] the P_x rings can be written as $(]P2[P8])_8$, $(]P2[P8])_{12}$, …, $(]P2[P8])_{x/10}$. At the B3LYP level of theory, the ring structures become increasingly stable until P_{200}, after which the stabilities start slowly to decrease. This applies for both total energies and Gibbs free energies. At the MP2 level the minimum energy is reached at P_{160}, the difference to P_{200} being only $0.04\,kJ\,mol^{-1}$ per atom. Increasing the size of the ring decreases its curvature, the structures approaching a linear chain. We optimized the structures of several infinitely long linear phosphorus chains. All the studied rings except P_{80} are more stable than the favored]P2[P8] chain, the rings beyond 200 atoms approaching the]P2[P8] chain both in structure and stability.

The B3LYP-calculated relative total energies of the phosphorus rings with about 200 atoms are practically equal to the relative total energy of the fibrous allotrope of red phosphorus, while being only about $0.4\,kJ\,mol^{-1}$ above the violet allotrope. The small relative energy difference of the violet and fibrous red phosphorus is in good agreement with the results of Ruck et al. who found the energy difference between violet and fibrous red forms to be less than $0.3\,kJ\,mol^{-1}$ per atom at the density-functional tight-binding level.[9] Practically equal energies for the violet and fibrous red allotropes were also predicted by Böcker and Häser in a comparison of the basic building blocks of the red phosphorus.[10] Since the phosphorus rings are equal in stability to the experimentally known violet and fibrous red allotropes of phosphorus, their preparation might be feasible. It should be noted, however, that the violet and fibrous red phosphorus probably adopt a more compact crystal packing in solid state.

The HOMO–LUMO gaps of the red phosphorus rings increase slowly as a function of the ring size. The gaps are of the same magnitude with the infinite]P2[P8] chain, around 3.6 eV at the B3LYP level. The calculated band gaps of the violet and fibrous red phosphorus are 2.56 and 2.73 eV, respectively. The difference of about 1 eV to the rings and the chain is apparently due to the bonding and interactions between the pentagonal phosphorus tubes. For comparison, the experimental band gap of amorphous red phosphorus is 1.95 eV.[41]

Comparisons between the allotropes of phosphorus: The relative total energies of the icosahedral and the ring-shaped allotropes of phosphorus are compared in Figure 4 at the B3LYP level of theory. The ring-shaped allotropes are favored over the icosahedral ones. In terms of Gibbs free energies, the rings are even more stable with respect to the cages. The difference in stability becomes smaller when the number of phosphorus atoms is increased beyond 200. This is due to the icosahedral cages becoming increasingly stable, while the stabilities of the ring-shaped structures reach a maximum at around 160–200 phosphorus atoms. Moving towards infinitely large systems, the cages approach the monolayer sheet of rhombohedral black phosphorus while the rings approach an infinitely long linear]P2[P8] chain. These two reference structures are separated by only 0.53 kJ mol^{-1} per atom in total energy, in favor of the chain.

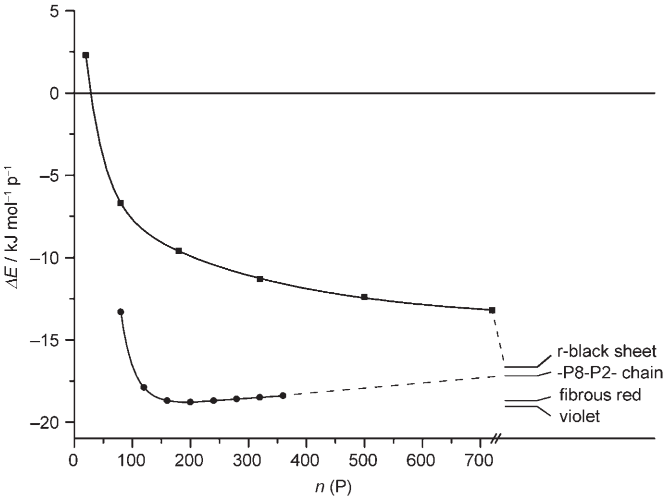

Figure 4. Total energies of the icosahedral cages (■) and the ring-shaped chains (●) of phosphorus relative to the white phosphorus at the B3LYP/85-21G(d) level. Four other forms of phosphorus are included for comparison: a monolayer of rhombohedral black phosphorus, an infinite]P2[P8] chain of red phosphorus, fibrous red phosphorus, and violet phosphorus.

Both the icosahedral cages and the ring-shaped chains are thermodynamically favored over the white phosphorus at low temperatures. However, the calculated Gibbs free energies show that the relative stability of the white phosphorus becomes higher at elevated temperatures. Therefore, a high temperature synthesis is likely to favor the formation of the white phosphorus, the modifications of red phosphorus being obtainable at intermediate temperatures. Alongside with the reaction conditions, the kinetic aspects may play a role, possibly in favor of the white phosphorus.

Several experimental procedures might be applicable for the preparation of the introduced icosahedral and ring-shaped allotropes of phosphorus. The icosahedral cages may require novel synthetic approaches due to their lower relative stabilities. Consisting of black phosphorus sheets, the cages can be considered as the analogues of fullerenes formed from graphene sheets. Thus, the methods used to prepare fullerenes, such as the resistive heating of graphite under an inert atmosphere,[42] could be starting points for the synthesis of the cages. The various modifications of red phosphorus have been synthesized by altering catalysts and conditions of crystallization. For example, the violet allotrope can be crystallized from lead melt,[8] whereas the crystallization of the fibrous red allotrope requires the presence of a iodine catalyst.[9] The quartz glass ampoules have played an important role in the formation of the fibrous red phosphorus tubes, supporting their parallel orientation.[9,20] Alternatively, copper halide matrix techniques have been used for the synthesis of red phosphorus nanorods.[15] These methods could be used as guidelines for the preparation of the ring-shaped allotropes, as well.

Conclusion

We have predicted the molecular structures and stabilities of two new allotropic forms of phosporus: icosahedral cages and ring-shaped chains. The icosahedral cages, where the lone pair repulsion is minimized by placing a portion of the lone pairs inside the cages, resemble the black phosphorus. The ring-shaped chains are derived by concatenation of the building blocks of the red phosphorus.

The stabilities of the icosahedral cages and ring-shaped chains were determined on the basis of comparisons with the experimentally known allotropes of phosphorus. Both the cages and rings are thermodynamically stable with respect to the white phosphorus. The cages become increasingly stable as a function of their size, approaching a monolayer sheet of rhombohedral black phosphorus. The ring-shaped chains are favored over the cages. The stabilities of the rings peak at around 160–200 phosphorus atoms, being comparable to the stabilities of the experimentally known violet and fibrous red allotropes of phosphorus. The synthesis of the icosahedral and ring-shaped allotropes of phosphorus would produce elemental nanostructures with well-defined molecular structures.

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