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# Inorganic nanotubes and fullerenes

## Structure and properties of hypothetical phosphorus fullerenes

G. Seifert[1,a], T. Heine[2], and P.W. Fowler[3]

[1] Theoretische Physik, Universität-GH Paderborn, 33098 Paderborn, Germany
[2] Department of Physical Chemistry, University of Geneva, 1211 Genève, Switzerland
[3] University of Exeter, School of Chemistry, Exeter, EX4 4QD, UK

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**Abstract.** The possibility of stable non-carbon fullerenes is discussed for the case of phosphorus fullerene-like cage structures. On the basis of Density Functional Tight Binding calculations it is shown that many such cages correspond to metastable structures, but with increasing nuclearity become less stable with respect to separate molecular $P_4$ units. Stability rules, known for carbon fullerenes, such as the "isolated pentagon rule", do not reflect the different electronic and steric requirements of the phosphorus atom. The computational results tend to rule out phosphorus fullerenes.

**PACS.** 36.40.-c Atomic and molecular clusters – 61.48+c Fullerenes and fullerene-related materials

The discoveries of fullerenes [1] and carbon nanotubes [2] as new forms of carbon in the nanoscale region have opened new horizons in solid state physics, chemistry and materials science with a wide spectrum of possible applications. Moreover, the generation of nanostructures from layered materials is not restricted to carbon: boron nitride (BN) is capable of forming nanotubes and nanocages, and their synthesis and properties have been studied (see [3] and references therein). Tenne *et al.* have successfully produced inorganic fullerene-like and tubular structures from more complex layered compounds such as tungsten disulphide ($WS_2$) [4] and molybdenum disulphide ($MoS_2$) [5]. The structure, stability and electronic properties of such nanotubes, and of non-carbon nanotubes in general, are discussed in [7] and [8], respectively.

In the present paper we describe results of a theoretical study concerning the possible existence of phosphorus based fullerenes. The results were obtained using atomistic simulations based on self-consistent Density Functional (DFT) and non-orthogonal Density Functional based Tight Binding (DFTB) [9] schemes.

Phosphorus shows a great variety of structures in the solid state [10,11]. The most well known forms are orthorhombic black (**b-P**), cubic white (**w-P**), monoclinic violet (Hittorf phosphorus – **H-P**) and amorphous red phosphorus (**a-P**). In all these forms the phosphorus atom is threefold coordinated. Trivalent P is characterized by three $\sigma$ bonds and a lone electron pair. Sixfold puckered rings characterize the orthorhombic black phosphorus (**b-P**). Using considerations based on the topological similarity of the puckered honeycomb network of threefold coordinated P atoms in **b-P** with the planar graphene sheets, we were recently able to show computationally that tubular structures of phosphorus, similar to carbon nanotubes, are stable and we suggested that they might be synthesized [12]. Considering that fivefold rings exist in the **H-P** allotrope, one may also speculate about the possible existence of phosphorus-based "fullerenes", *i.e.* geometrically closed molecular cages made up of hexagons and 12 pentagons.

There exist already a series of theoretical studies of the structure of phosphorus clusters $P_N$ [13,14,16]. However, systematic investigations are restricted to small sizes ($N \leq 11$). Häser [14] also performed some Hartree-Fock and MP2 calculations in the size range $10 \leq N \leq 28$. Recently, Chen *et al.* [18] presented structural predictions for large cationic phosphorus clusters, based on semiempirical PM3 and DFT-GGA calculations, considering only a few selected cluster sizes ($N = 8$, 25, 41, 49, 89), and taking cage-like structures into account only for $N = 25$. Several authors have studied specifically the dodecahedral $P_{20}$ cluster [14,15,17]. Häser [14] already noted the relatively high stability of the dodecahedral $P_{20}$ ($I_h$-symmetry – see Fig. 1), which corresponds to the smallest fullerene structure, consisting only of twelve pentagons, as forced by Euler's theorem. Although $I_h$ $P_{20}$ was found to be a local minimum it was calculated to be less stable than $5 \times P_4$. The stability of $P_{20}$ with respect to $5 \times P_4$ is however very sensitive to the level of approximation in the calculation. In our own DFT-based calculations we find for $E(I_h - P_{20}) - 5E(P_4) - 187.4$ kcal/mol (DFTB), $-52.5$ kcal/mol (LDA-VWN) and $+6.2$ kcal/mol

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[a] e-mail: `seifert@phys.uni-paderborn.de`

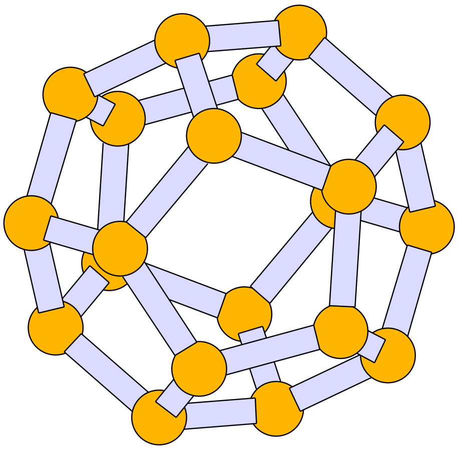

**Fig. 1.** Dodecahedral $P_{20}$ fullerene-like cluster.

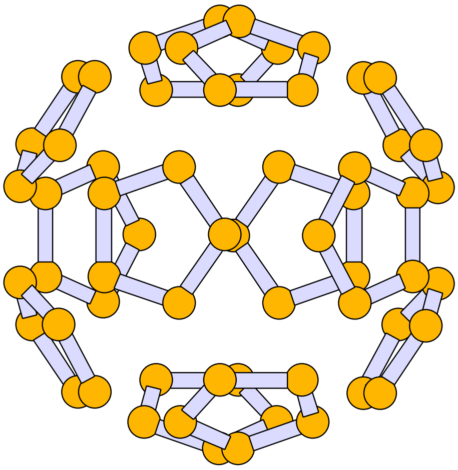

**Fig. 2.** $P_{60}$ fullerene-like cluster. The long P-P bonds between the pentagons ($R(\mathrm{PP}) = 2.69$ Å) are not drawn.

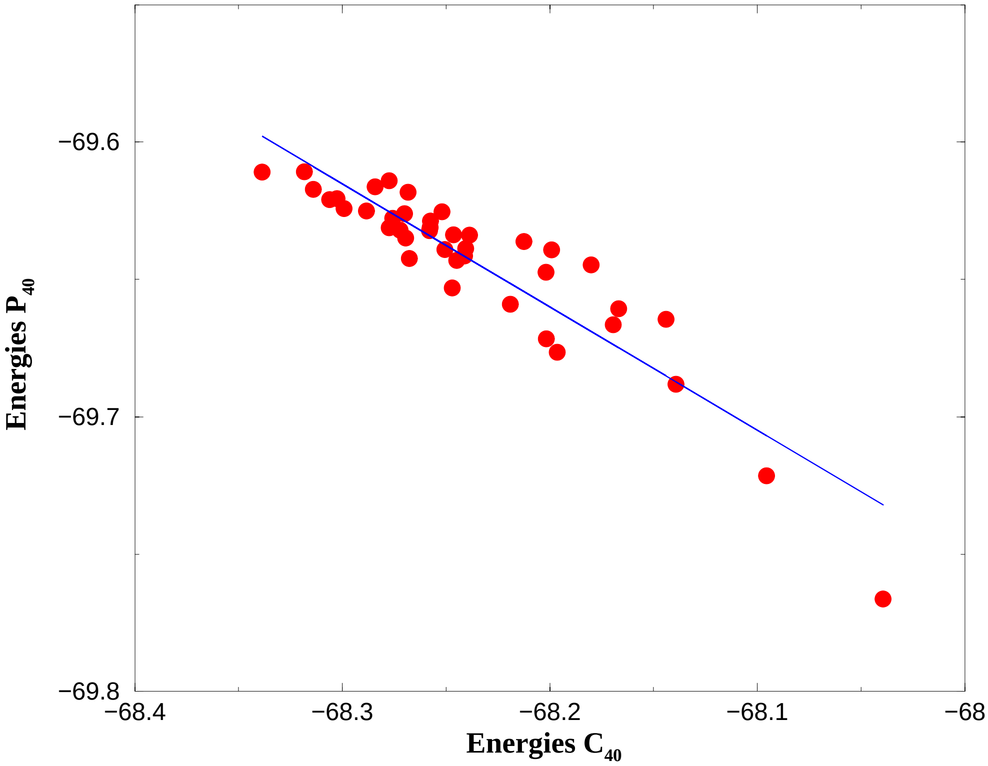

**Fig. 3.** Calculated binding energies of $C_{40}$ fullerene-like clusters *versus* energies of $P_{40}$ fullerene-like clusters. Energies in atomic units (1 a.u. = 626.82 kcal/mol).

(GGA – BLYP). Thus, the gradient-corrected DFT-LDA calculation (GGA – BLYP) supports the conclusion of Häser, but only narrowly, as a result of a nearly isoenergetic balance. The DFTB model probably favours the cage too much, and the LDA calculation gives a result in between. Nevertheless, all calculations give the $I_h$-$P_{20}$ cage as a rather stable local minimum. We have now investigated the evolution of the stability of fullerene P-cages as a function of cluster size and shape. In the first part of the study we established that $I_h$-$P_{20}$ is not only a locally stable cage in itself, but that it is the best possible trivalent cage of 20 P-atoms. The full set of 7595 mathematically conceivable 20-vertex trivalent polyhedra was used to start optimizations with the DFTB model Hamiltonian. Most of them preserved the starting topology and converged to local minima as closed polyhedral structures. The dodecahedral cage emerged as the clear winner, with an energy 14 kcal/mol below its nearest rival. In the case of carbon [19], the preference amongst 20-vertex cages for the fullerene form may be ascribed to its low curvature and consequent ability to support a degree of $\pi$ bonding over the whole cage. In the case of phosphorus, $\pi$ bonding is a much less important factor, and the stability may be attributable to the suitability of the pyramidal vertices for trivalent, lone pair-bearing P centres. Next we considered the cage structures of the so called carbon "fullerene road" [20] for $P_N$, $24 \leq N \leq 60$, taking the carbon fullerene structures, rescaling the bond lengths and optimizing these structures within the DFTB model. Although we could obtain a stable structure for each cluster size within the fullerene topology, the stability with respect to $P_4$ ($P_N \longrightarrow N/4\ P_4$) decreased monotonically with increasing cluster size. Hence, even within the DFTB model, $P_{60}$ is only metastable and is of significantly higher energy than $15 \times P_4$. Interestingly, the optimized structure of $P_{60}$ gives shorter bonds within the pentagons (2.42 Å) than between them (2.69 Å). This is illustrated in Fig. 2. It shows clearly the difference from carbon, where the pentagons are the "defects" in an ideal hexagon network, and is a natural consequence of the different electron count. The unoccupied $\pi$ molecular orbitals of $C_{60}$ are antibonding along hexagon-hexagon edges, and ions such as $C_{60}^{6-}$ already show the tendency for these bonds to lengthen [22]; in $P_{60}$, all 30 such orbitals are formally occupied. To explore further this difference from carbon, we took as a specific example all the fullerene isomers of $C_{40}$, which we have studied in detail before [21], and optimized these structures as phosphorus instead of carbon cages. The calculated energies of the optimized structures for $P_{40}$ are plotted against the corresponding energies of $C_{40}$ in Fig. 3. As one can see from this figure, there exists a near anticorrelation. The most stable carbon structure corresponds to the least stable phosphorus structure and *vice versa*. This opposite behaviour in carbon and phosphorus implies that unlike the carbon fullerenes, which obey a minimal-pentagon-adjacency rule, small phosphorus cages actually favour pentagon fusion, exhibiting a drive to pyramidal P sites rather than the planar $\pi$-stabilised C sites of the fullerenes. Thus there is no isolated-pentagon rule for phosphorus cages and no evidence of special stability for phosphorus fullerenes. Where phosphorus forms polyhedral arrays it favours puckered-hexagon **H-P**-like tubes, extended networks (**a-P**, **b-P**) or dissociation to $P_4$ tetrahedra over $P_N$ fullerene formation.

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