Inorganic nanotubes and fullerenes

Structure and properties of hypothetical phosphorus fullerenes

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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 P4 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.

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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 (WS2) [4] and molybdenum disulphide (MoS2) [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 σ 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 ≤ 11). Häsler [14] also performed some Hartree-Fock and MP2 calculations in the size range 10 ≤ N ≤ 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 P20 cluster [14,15,17]. Häsler [14] already noted the relatively high stability of the dodecahedral P20 (Ih-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 P20 was found to be a local minimum it was calculated to be less stable than 5 × P4. The stability of P20 with respect to 5 × P4 is however very sensitive to the level of approximation in the calculation. In our own DFT-based calculations we find for E(I h – P20) – 5E(P4) = 187.4 kcal/mol (DFTB), −52.5 kcal/mol (LDA-VWN) and +6.2 kcal/mol.
Fig. 1. Dodecahedral \( P_{20} \) fullerene-like cluster.

Fig. 2. \( P_{40} \) fullerene-like cluster. The long P-P bonds between the pentagons \((R(PP) = 2.69 \, \text{Å})\) are not drawn.

Fig. 3. Calculated binding energies of \( C_{40} \) fullerene-like clusters \textit{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 isoequigradient 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