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Helical Structures

Inorganic Double-Helix Structures of Unusually Simple Lithium–Phosphorus Species**

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The double helix represents one of the most fascinating geometric structures in nature. Helical structures can be either right-handed or left-handed depending on the direction of the rotation. In other words they possess the chirality property, which is vital for every living organism. Chiral molecules lack an internal plane of symmetry and thus have a nonsuperposable mirror image. It turns out that for organic compounds nature decides by itself whether the most preferable structure will be right-handed or left-handed, but questions regarding such differentiation in the inorganic world have not yet been answered.

In chemistry and biology, the term double helix usually refers to the structure formed by double-stranded molecules of nucleic acids such as DNA, discovered by Watson and Crick,[1] and RNA. Watson and Crick stressed: "It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material." There are many other organic polymers with helical structures and proteins which have substructures known as α -helices. In spite of the diversity and significance of the role of double-helix structures in evolution and metabolism, they are very rare in inorganic chemistry. In 1993 V. Soghomonian et al. showed that very complicated inorganic solids can be self-assembled from structurally simple precursors by the hydrothermal synthesis of vanadium phosphate and $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$, which contains chiral double helices formed from interpenetrating spirals of vanadium oxo pentamers bonded together by P_5^+ ions.[2] After that, there were also many successful syntheses of inorganic compounds with helical structures.[3,4] Thus, while some advances have been achieved for inorganic materials with a single-helical geometry, reports of counterparts with the double-helix structure are deficient. Recently, double-helical silicon microtubes and double-helical carbon nanotube (CNT) arrays were prepared.[5,6] However, there is no structural model at the atomic level to explain the Si and C tubular double helices.

Here we report the theoretical prediction of the existence of double-helix structures in the series of Li_xP_x ($x = 5$–9) clusters and in an infinite LiP chain and compare them with bulk phases of LiP. It was surprising to discover the double-helix structures in rather simple species consisting of only two elements: lithium and phosphorus. Our initial goal was to probe electronic transmutation for Li_xP_x clusters by making bonded structures[7,8] which obey the Zintl-rule (where the less electronegative lithium atom donates an electron to the more electronegative phosphorus atom, resulting in each phosphorus bearing a negative charge) with the anticipation that structures similar to sulfur compounds would be formed.[8] However, the unexpected double helices were found to be either global minimum structures or low-lying isomers.

We performed an unbiased quantum-chemical search for Li_xP_x ($x = 5$–9) clusters using a Coalescence Kick[9] program written by B. B. Averkiev initially at the B3LYP/3-21G level of theory. The Coalescence Kick method subjects large populations of randomly generated structures to a coalescence procedure in which all atoms are pushed gradually to the molecular center of mass to avoid the generation of fragmented structures and then optimizes them to the nearest local minima. All low-lying isomers found by this method were reoptimized with follow-up frequency calculations at the B3LYP level of theory using the 6-311+G* basis set. The total energies of the lowest isomers of Li_5P_5, Li_6P_6, and Li_7P_7 stoichiometries were calculated at the CCSD(T)/CBS//B3LYP/6-311+G* level of theory by extrapolating CCSD(T)/cc-pvDZ//B3LYP/6-311+G* and CCSD(T)/cc-pvTZ//B3LYP/6-311+G* to the infinite basis set using the Truhlar formula.[10] Additional calculations of the three lowest isomers for each stoichiometry were also performed (see the Theoretical Section).

In Figure 1 we present the right- and left-handed double helices for the Li_5P_5, Li_6P_6, Li_7P_7, Li_8P_8, and Li_9P_9 species.

A more extensive set of alternative isomers found in our global minimum search is summarized in the Supporting information (Figures S1–S5). For the Li_5P_5 stoichiometry the double-helix structure is the second lowest isomer, which is

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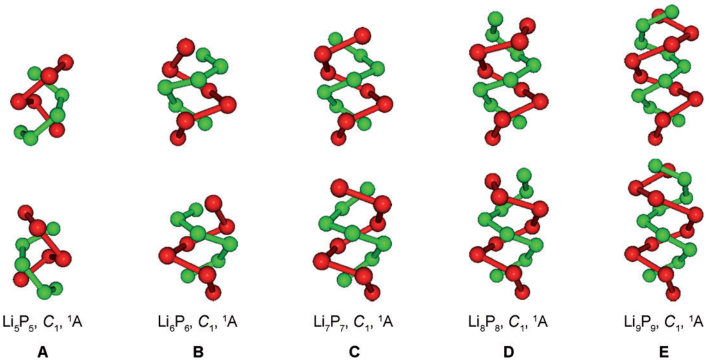

Figure 1. Optimized structures of Li_5P_5, Li_6P_6, Li_7P_7, Li_8P_8, and Li_9P_9 double helices. a) Li_5P_5 (C_1, ^1A), b) Li_6P_6 (C_1, ^1A), c) Li_7P_7 (C_1, ^1A), d) Li_8P_8 (C_1, ^1A), and e) Li_9P_9 (C_1, ^1A).

5.6 kcal mol^{-1} higher than the global minimum (Figure S1). For the Li_6P_6 stoichiometry, the helical structure is the third isomer and is 12.6 kcal mol^{-1} higher than the global minimum structure (Figure S2). Our search for the global minimum in the Li_7P_7 stoichiometry revealed that the double-helix structure (Figure 2 and Figure S3) is the global minimum with the second isomer containing a seven-membered ring similar to sulfur clusters.[11]

We also performed a search for the global minimum S_7 cluster and found two low-lying isomers: *exo* and *endo* isomers with the second one being 3.4 kcal mol^{-1} higher in energy than the global minimum *exo* isomer (Figure S4 in the Supporting Information). Our search also revealed a helical isomer of S_7 which is 34.1 kcal mol^{-1} higher in energy than the global minimum. The helical structure of the S_7 isomer is very similar to the helical phosphorus strand in the double-helix structure of Li_7P_7. The double helices were found to be the global minimum structures for both the Li_8P_8 and Li_9P_9 stoichiometries (Figures S5 and S6).

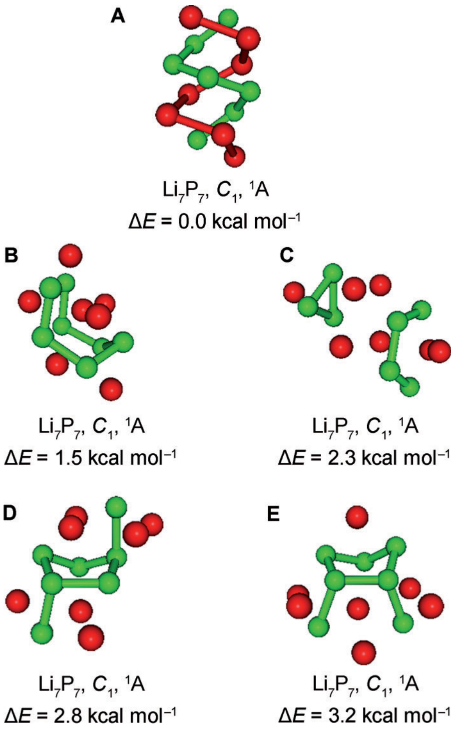

Figure 2. Representative optimized structures of Li_7P_7, their point group symmetries, spectroscopic states, and ZPE-corrected (B3LYP/6-311+G*) relative energies at the CCSD(T)/CBS//B3LYP/6-311+G* level of theory (ZPE = zero-point corrected).

n-Membered rings are the most stable structures for sulfur clusters. It was recently reported, however, that there are two phases having helical structures with triangular and squared chains of sulfur, which are stable at 1.5 GPa and temperatures from 300 K to 1100 K.[12] The same authors also showed that selenium can form the helix squared chain structures similar to sulfur.[12] Another representative of group VI-A elements, oxygen, is able to form analogous helical structures under the pressure of metallization according to the latest theoretical reports.[13,14]

Because of their small size and unique properties, clusters could become good samples for describing a structural model of the double helix at the atomic level. Therefore, to gain additional insight into the structure and chemical bonding of the double-helix structure of Li_xP_x species, we performed natural bond orbital analysis (NBO).[15] According to NBO analysis for the Li_5P_5 double helix, the bonding between lithium and phosphorus atoms is quite ionic with effective atomic charges for Li ranging from $+0.4$ to $+0.7\,|e|$. Additionally, NBO analysis revealed the presence of two P–Li σ-bonds with occupation numbers (ON) equal to 1.84–1.86 $|e|$, four P–P σ bonds with ON ranging from 1.92–1.96 $|e|$, one double bond with ON = 1.83 $|e|$ for the π bond, and one triple bond with ON = 1.80 $|e|$ and ON = 1.30 $|e|$ for two π bonds, respectively (Figure S7 in the Supporting Information). For the Li_6P_6 double-helix structure, we found the following bonding picture: the effective atomic charges on Li range from $+0.5$ to $+0.8\,|e|$; four Li–P σ bonds with ON = 1.63–1.68 $|e|$; five P–P σ bonds with ON = 1.94–1.96 $|e|$; one double bond with ON = 1.86 $|e|$ for the P–P π bond. Starting from Li_7P_7 and up to Li_9P_9 double helices have a similar chemical bonding pattern: effective charges on Li range from $+0.8$ to $+0.9\,|e|$; there are no more Li–P σ bonds, there are six (Li_7P_7), seven (Li_8P_8), and eight (Li_9P_9) P–P σ bonds with ON = 1.95–1.98 $|e|$; there is one double bond at the end of phosphorus chain with ON = 1.93–1.94 $|e|$ for the π bond (see Figures S8–S11). We see from this data that when the bonding between the Li and P atoms is ionic, beginning from Li_7P_7 to Li_9P_9, the double-helix structures are much more favourable relative to other isomers. We believe that for the smaller clusters, termination effects are responsible for the double-helix structures being less stable. Thus, the electronic transmutation takes place in the case of Li_xP_x ($x = 5$–9) clusters, but in a rather strange way. The presence of lithium cations seems to be working similar to high pressure and high temperature in the helix phases of sulfur and selenium. Though NBO analysis does not show any significant direct Li–Li covalent bonding, in our graphical representation of double-helix structures, we connected adjacent Li atoms to make the double-helix structure more apparent. From our point of view, the helix structure formed by lithium cations because of favourable electrostatic interactions with neighboring phosphorus anions.

To further test the viability[16] of our double-helix structures we checked their lowest frequencies and the HOMO–LUMO gaps. The lowest frequencies for Li_5P_5, Li_6P_6, Li_7P_7, Li_8P_8, and Li_9P_9 are 102, 89, 61, 82, and 75 cm^{-1}, respectively, which are comparable to the lowest theoretically calculated frequency at the same level of theory (102 cm^{-1}) in the $Li_3Al_4^-$ anion observed in a molecular beam.[17] The HOMO–LUMO gap for the clusters are as follows: Li_5P_5 (2.27 eV), Li_6P_6 (2.14 eV), Li_7P_7 (2.24 eV), Li_8P_8 (1.90 eV), and Li_9P_9 (1.71 eV) (HOMO/LUMO = highest occupied/lowest unoccupied molecular orbital). All data presented (calculated at the B3LYP/6-311+G* level of theory) are comparable to the HOMO–LUMO gap (2.02 eV, B3LYP/cc-pvTZ/Ta/Stuttgart/B/aug-cc-pVTZ) in the TaB_{10}^- wheel-type Ta-centered anionic cluster, which was recently prepared in a molecular beam.[18]

To further investigate the existence of double-helix structures we performed a solid-state study using plane-wave density functional theory (see the Theoretical Section), on the LiP infinite double-helix chain and two bulk phases of LiP of different symmetry. The LiP infinite double-helix chain was found to be stable (Figure 3). The structure comprises four functional units (FU) of Li_1P_1 per turn and is 6.00 kcal mol^{-1} lower in energy than Li_9P_9. Atomic chained helices of this kind were first found by Cromer in the Zintl phases, LiAs and NaSb[19,20] and exist in XY (X = Li,Na,K,Rb,Cs, Y = P,As,Sb).[21] Using ab initio random structure searching (AIRSS)[22,23] we recovered the *P*21/*c* symmetric Li_1P_1 bulk phase comprising of packed double helices[24] where adjacent helices are of opposite sense and 9.69 kcal mol^{-1} lower in energy than the infinite double-helix chain (Figure 4). Using AIRSS a metastable bulk phase of $P2_12_12_1$ symmetry, in which all helices have the same sense, similar to Na_1P_1[25] was also uncovered which was 0.24 kcal mol^{-1} higher in energy than the *P*21/*c* symmetric phase.

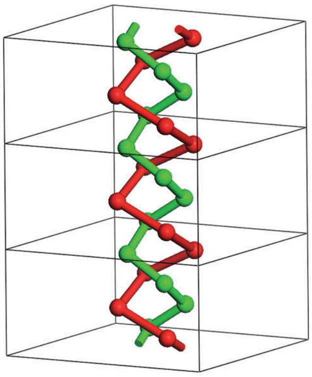

Figure 3. Three periodic repetitions of the LiP infinite double-helix chain geometry optimized at the DFT-PBE level of theory.

The structures presented for Li_xP_x ($x = 5$–9) are simple molecules which possess a double-helix structure comprising only two kinds of atoms. From solid-state calculations the LiP infinite double-helix chain was also found to be stable. Our solid-state calculations showed that the *P*21/*c* symmetric Li_1P_1 bulk phase comprising of packed double helices has an energy that is lower than the infinite double-helix chain. We believe that although the Li atoms are not connected by chemical bonding it is the positions of the Li atoms in space that make the structures double helical. The structures of XY (X = Li,Na,K,Rb,Cs, Y = P,As,Sb) Zintl phase compounds[21] may then also be interpreted as double helical. Our results extended the family of double-helical solids and we hope that other inorganic double-helix structures which obey the Zintl rule may be found.

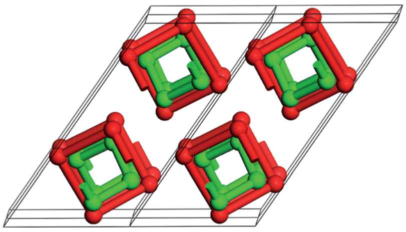

Figure 4. A 2×2 supercell containing a *P*21/*c* symmetric Li_1P_1 bulk phase comprising of packed double helices.

Theoretical Section

Calculations: Additional calculations including geometry optimization and frequency calculations for the lowest three isomers of Li_5P_5, Li_6P_6, Li_7P_7, Li_8P_8, and Li_9P_9 stoichiometries were performed at the PBE1PBE/6-311+G* and M06/6-311+G* levels of theory. The results of these two levels of theory are generally consistent with the results at the B3LYP/6-311+G* level of theory. To test the applicability of the CCSD(T) and B3LYP methods for our systems we performed single-point calculations of the Li_7P_7 double-helix structure at the CASSCF(10,12)/6-311+G* level of theory. According to these calculations the Hartree–Fock coefficient in the CASSCF expansion (314028 configurations) is 0.973. Thus, both B3LYP and CCSD(T) methods are valid. Chemical bonding analysis was performed using the natural bond orbital (NBO) analysis. All quantum-chemical calculations were performed using the Gaussian 09 program.[26] Molecular visualization was performed using the Molekel 4.3 program.[26]

The solid-state study was performed using the plane-wave density functional theory code CASTEP[28] and the PBE exchange-correlation functional, ultrasoft pseudopotentials, and a Brillouin zone sampling finer than $2\pi \times 0.05$ Å^{-1}. The valence states were described by a basis set containing plane waves with energies up to 400 eV. The infinite chain was relaxed in a supercell which had 10 Å between each periodic repetition. The structure was fully geometry-optimized and phonon calculations were performed to demonstrate its stability (see the Supporting Information).

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[1] J. D. Watson, F. H. C. Crick, *Nature* **1953**, *171*, 737.
[2] V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, C. J. O'Connor, *Science* **1993**, *259*, 1596.
[3] M. Yang, N. A. Kotov, *J. Mater. Chem.* **2010**, *21*, 6775.
[4] S.-H. Yu, H. Cölfen, K. Tauer, M. Antonietti, *Nat. Mater.* **2005**, *4*, 51.
[5] H. Morito, H. Yamane, *Angew. Chem.* **2010**, *122*, 3720; *Angew. Chem. Int. Ed.* **2010**, *49*, 3638.
[6] Q. Zhang, M.-Q. Zhao, D.-M. Tang, F. Li, J.-Q. Huang, B. Liu, W.-C. Zhu, Y.-H. Zhang, F. Wei, *Angew. Chem.* **2010**, *122*, 3724; *Angew. Chem. Int. Ed.* **2010**, *49*, 3642.
[7] R. Nesper, *Prog. Solid State Chem.* **1990**, *20*, 1.
[8] J. K. Olson, A. I. Boldyrev, *Chem. Phys. Lett.* **2012**, *523*, 83.
[9] A. P. Sergeeva, B. B. Averkiev, H. J. Zhai, A. I. Boldyrev, L. S. J. Wang, *J. Chem. Phys.* **2011**, *134*, 224304.
[10] D. G. Truhlar, *Chem. Phys. Lett.* **1998**, *294*, 45.
[11] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, *6 ed.*, Wiley, New-York, **1999**, pp. 499–502.
[12] O. Degtyareva, E. Gregoryanz, M. Somayazulu, P. Dera, H. K. Mao, R. J. Hemley, *Nat. Mater.* **2005**, *4*, 152.
[13] Z. Wang, Y. Wang, G. Zou, H.-K. Mao, Y. Ma, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 751.
[14] J. Sun, M. Martinez-Canales, D. D. Klug, C. J. Pickard, R. J. Needs, *Phys. Rev. Lett.* **2012**, *108*, 045503.
[15] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211.
[16] R. Hoffmann, P. v. R. Schleyer, H. F. Schaefer III, *Angew. Chem.* **2008**, *120*, 7276; *Angew. Chem. Int. Ed.* **2008**, *47*, 7164.
[17] A. E. Kuznetsov, K. A. Birch, A. I. Boldyrev, X. Li, H.-J. Zhai, L. S. Wang, *Science* **2003**, *300*, 622.
[18] T. R. Galeev, C. Romanescu, W.-L. Li, L. S. Wang, A. I. Boldyrev, *Angew. Chem. Int. Ed.* **2012**, *51*, 2101.
[19] D. T. Cromer, *Acta Cryst.* **1959**, *12*, 36.
[20] D. T. Cromer, *Acta Cryst.* **1959**, *12*, 41.
[21] C. X. Cui, M. Kertesz, *J. Am. Chem. Soc.* **1989**, *111*, 4216.
[22] C. J. Pickard, R. J. Needs, *Phys. Rev. Lett.* **2006**, *97*, 045504.
[23] C. J. Pickard, R. J. Needs, *J. Phys. Condens. Matter* **2011**, *23*, 053201.
[24] W. Hönle, H. G. von Schnering, *Z. Kristallogr.* **1981**, *155*, 307.
[25] H. G. von Schnering, W. Hoenle, *Z. Anorg. Allg. Chem.* **1979**, *456*, 194.
[26] Gaussian 09 (Rev. B.01), M. J. Frisch, et al., Gaussian, Inc., Wallingford, CT **2009** (see the Supporting Information).
[27] U. Varetto, Molekel 5.4.0.8, Swiss National Supercomputing Centre: Manno, Switzerland, **2009**.
[28] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.* **2005**, *220*, 567.