

# Peculiar Transformations in the $C_xH_xP_{4-x}$ ( $x = 0-4$ ) Series

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 Supporting Information

**ABSTRACT:** In the current work, we performed a systematic study of the  $C_xH_xP_{4-x}$  ( $x = 0-4$ ) series using an unbiased CK global minimum and low-lying isomers search for the singlet and triplet  $P_4-C_4H_4$  species at the B3LYP/6-31G\*\* level of theory. The selected lowest isomers were recalculated at the CCSD(T)/CBS//B3LYP/6-311++G\*\* level of theory. We found that the transition from a three-dimensional tetrahedron-like structure to a planar structure occurs at  $x = 3$ , where planar isomers become much more stable than the tetrahedral structures due to significantly stronger  $\pi$  bonds between carbon atoms in addition to increasing strain energy at the carbon atom in the tetrahedral environment.

## 1. INTRODUCTION

Benzene is by far the most stable isomer for  $C_6H_6$  stoichiometry, with benzvalene and prismane being more than 70 kcal/mol higher in energy.<sup>1</sup> A valence isoelectronic hexaphosphabenzene, on the other hand, is not planar in its most stable benzvalene-like structure. It was recently shown that the transition from the three-dimensional benzvalene-like structure to the planar benzene-like structure in the  $C_xH_xP_{6-x}$  ( $x = 0-6$ ) series occurs at  $x = 4$ .<sup>2</sup> In our current investigation, we analyze structural transformations in the  $C_xH_xP_{4-x}$  ( $x = 0-4$ ) series upon the substitution of a phosphorus atom by the valence isoelectronic C–H group. We demonstrated that  $P_4$  and  $CHP_3$  possess the tetrahedron-like global minimum structures. For the  $C_2H_2P_2$  stoichiometry, we found the two most stable structures: derivative of triafulvene and tetrahedron-like, being almost degenerate. For the  $C_3H_3P$  and  $C_4H_4$  stoichiometries, we determined that the global minimum structures are vinylacetylene-like. Thus, the 3D–2D transition in the considered series occurs at  $x = 3$ . We believe that stronger  $\pi$  bonds between carbon atoms as well as increasing strain energy are responsible for this 3D–2D transition.

## 2. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

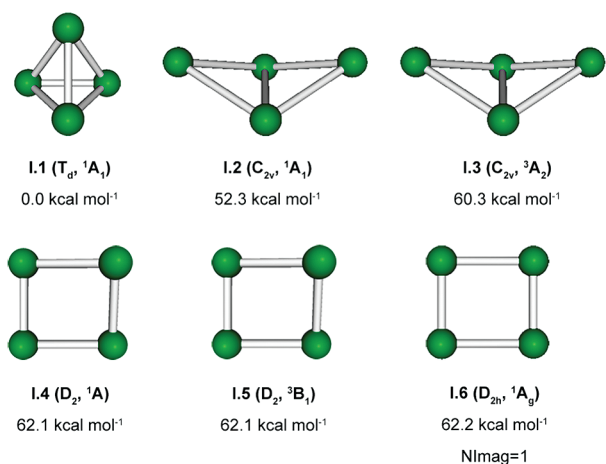
A computational search for the global minima structures of  $P_4$ ,  $CHP_3$ ,  $C_2H_2P_2$ ,  $C_3H_3P$ , and  $C_4H_4$  stoichiometries with singlet and triplet electronic states was performed using the Coalescence Kick (CK) program written by Averkiev.<sup>3</sup> In the CK method, a random structure is first checked for connectivity: if all atoms in the structure belong to one fragment, then the structure is considered as connected, and the Berny algorithm<sup>4</sup> for geometry optimization procedure is applied to it. However, in most cases, a randomly generated structure is fragmented; that is, the structure contains several fragments nonbonded with each other including cases with just one atom not being connected. In these cases, the coalescence procedure is applied to the fragmented structure—all of the fragments are pushed to the center of mass simultaneously. The magnitude

of shift should be small enough so that atoms do not approach each other too closely but large enough so that the procedure converges in a reasonable amount of time. In the current version of the CK program, a 0.2 Å shift is used. The obtained structure is checked for connectivity again, and the procedure repeats. When two fragments approach each other close enough, they “coalesce” to form a new fragment, which will be pushed as a whole in the following steps. Obviously, at some point, all fragments are coalesced. This method does not deal with cases when, in a randomly generated structure, two atoms are too close to each other. To avoid this problem, the initial structures are generated in a very large box with all three linear dimensions being 4\* (the sum of atomic covalent radii). Hence, usually an initially generated random structure consists of separated atoms as initial fragments. The current version of the program is designed for the global minimum searches of both single molecules of desired composition and complexes of molecules like solvated anions (e.g.,  $SO_4^{2-} \cdot 4H_2O$ ),<sup>5,6</sup> where the initial geometry of each molecular unit is specified in the input file. In the latter case, the two molecular units of the complex are considered as connected in a fragment if the distances between two of their atoms are less than the sum of the corresponding van der Waals radii.

The CK calculations were performed at the B3LYP level of theory<sup>7–9</sup> using the 6-31G\*\* split-valence basis set.<sup>10</sup> Low-lying isomers were reoptimized with followup frequency calculations at the B3LYP level of theory using the 6-311++G\*\* basis set.<sup>11–14</sup> Tetrahedron-like and cyclobutadiene-like structures for every stoichiometry were also reoptimized using the CCSD(T) method<sup>15–17</sup> and the 6-311++G\*\* basis set. The final relative energies of the found low-lying isomers were calculated at the CCSD(T)/CBS level by extrapolating CCSD(T)/cc-pvDZ and CCSD(T)/cc-pvTZ<sup>18–22</sup> to the infinite basis set using the Truhlar formula.<sup>23,24</sup> We also calculated relative energies of the two lowest-lying isomers for every stoichiometry at the CCSD(T)/cc-pvQZ level of theory.

Received: October 14, 2011

Published: November 17, 2011



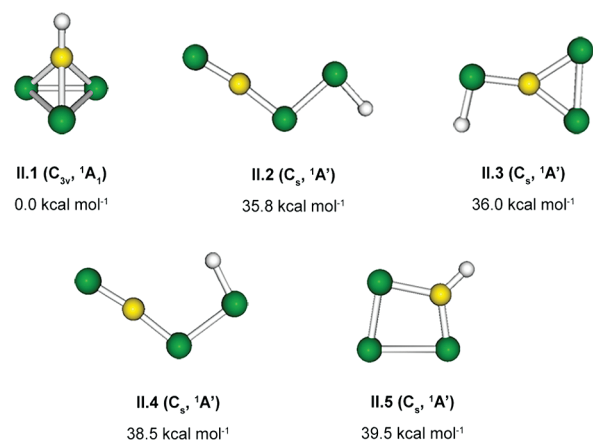
**Figure 1.** Representative optimized structures of  $P_4$ , their point group symmetries, spectroscopic states, and ZPE-corrected (CCSD(T)/6-311+ $G^*$ ) relative energies (CCSD(T)/CBS//CCSD(T)/6-311+ $G^*$ ).

A chemical bonding analysis was performed using Adaptive Natural Density Partitioning (AdNDP)<sup>25,26</sup> and Natural Bond Orbital (NBO) analysis.<sup>27,28</sup> The AdNDP approach leads to partitioning of the charge density into elements with the lowest possible number of atomic centers per electron pair:  $n$ -center–two-electron (nc–2e) bonds, including core electrons, lone pairs, 2c–2e bonds, etc. If some part of the density cannot be localized in this manner, it is represented using completely delocalized objects, similar to canonical MOs, naturally incorporating the idea of the completely delocalized bonding. Thus, AdNDP achieves a seamless description of different types of chemical bonds. The density matrix in the basis of the natural atomic orbitals as well as the transformation between atomic orbital and natural atomic orbital basis sets was generated at the B3LYP/6-31 $G^{**}$  level of theory by means of the NBO 3.1 code<sup>29</sup> incorporated into Gaussian 09. It is known that the results of the NBO analysis do not generally depend on the quality of the basis set, so the choice of the level of theory for the AdNDP analysis is adequate. All *ab initio* calculations were done using the Gaussian 09 program.<sup>30</sup> Molecular structure visualization was performed with the Molden 3.4<sup>31</sup> and Molekel 5.4.0.8<sup>32</sup> programs.

### 3. RESULTS AND DISCUSSION

**$P_4$  Isomers.** The  $P_4$  tetrahedron is known to be a very stable form of phosphorus, and vapor up to 800 °C over phosphorus is completely composed of tetrahedrons.<sup>33</sup> According to our calculations for singlet and triplet states, the singlet  $P_4$  tetrahedral structure is indeed the global minimum structure I.1 (Figure 1) with the butterfly structure I.2 being 52.3 kcal/mol higher (for  $P_4$  structures, relative energies are given at CCSD(T)/CBS//CCSD(T)/6-311+ $G^*$ ). The lowest triplet state isomer I.3 is 60.3 kcal/mol higher than the global minimum. Quasi-planar rectangular tetrphosphacyclobutadiene I.4 was found to be 62.1 kcal/mol higher in energy than the tetrahedral  $P_4$  (Figure 1).

The planar structure I.6 was found to be a minimum at B3LYP/6-311+ $G^*$  but is a first-order saddle point at CCSD(T)/6-311+ $G^*$ . Geometry optimization following an imaginary frequency mode leads to the slightly nonplanar structure I.4. Our results are in agreement with calculations reported by Sherer.<sup>34</sup>



**Figure 2.** Representative optimized structures of  $CHP_3$ , their point group symmetries, spectroscopic states, and ZPE-corrected (B3LYP/6-311+ $G^{**}$ ) relative energies (CCSD(T)/CBS//B3LYP/6-311+ $G^{**}$ ).

The only difference is that the planar structure I.6 is not a minimum in our calculations. The distortion of the structure I.6 into the structure I.4 along the  $a_u$  imaginary mode occurs due to the pseudo-Jahn–Teller effect (PJT),<sup>35,36</sup> resulting from vibronic coupling of HOMO–2 ( $2b_{1u}$ ) and LUMO ( $1b_{1g}$ ). Indeed, the direct product of their symmetries is the symmetry of the imaginary mode:

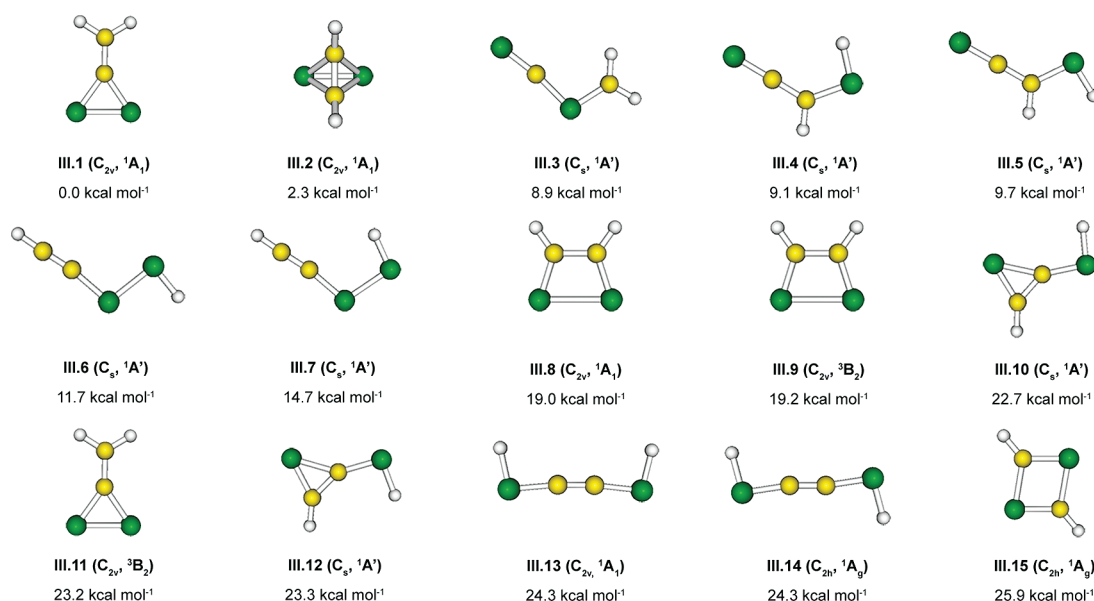
$$b_{1u} \otimes b_{1g} = a_u \quad (1)$$

Thus, the symmetry rule<sup>37</sup> for the PJT effect is satisfied, as is the second condition:<sup>37</sup> the symmetry of the imaginary mode ( $a_u$ ) of the  $D_{2h}$  structure corresponds to the totally symmetric ( $a$ ) mode in the distorted  $D_2$  isomer. The HOMO–2 and LUMO gap is 8.48 eV (HF/cc-pvTZ//B3LYP/6-311+ $G^*$ ).

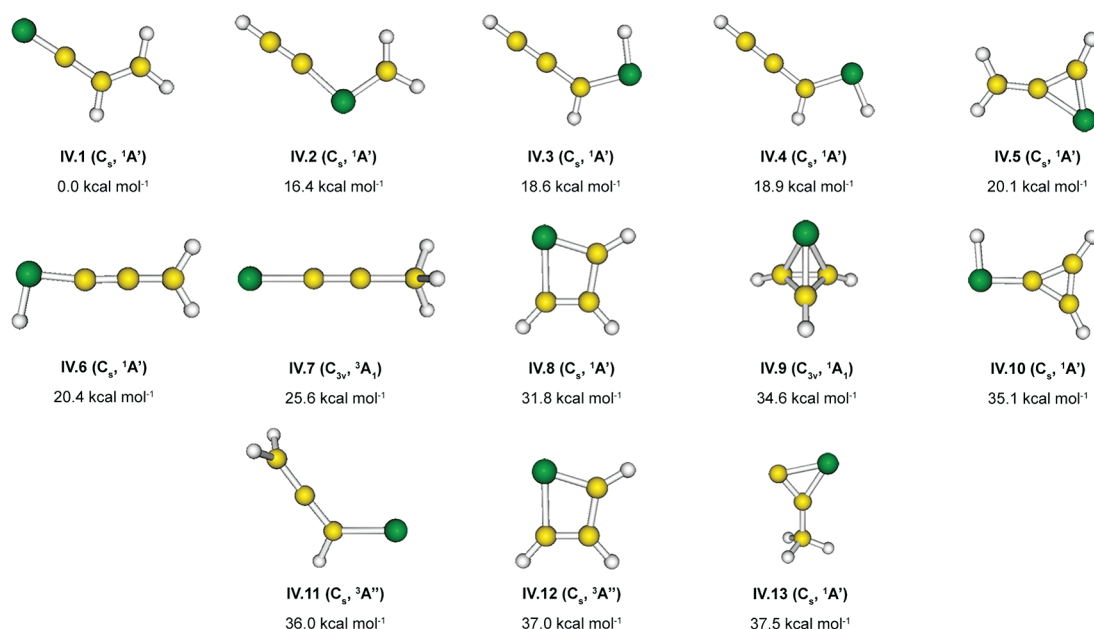
**$CHP_3$  Isomers.** Our CK global minimum search for the singlet and triplet  $CHP_3$  stoichiometries revealed that the tetrahedral structure II.1 (Figure 2) is the global minimum, and it is significantly more stable than the alternative singlet and triplet structures.

The second lowest isomer, a phosphorus derivative of vinylacetylene (structure II.2), is 35.8 kcal/mol higher in energy than the global minimum structure. The cyclobutadiene-like structure II.5 is 39.5 kcal/mol (here and elsewhere, relative energies of the isomers are given at CCSD(T)/CBS//B3LYP/6-311+ $G^{**}$ ) higher in energy (Figure 2), but it is now a minimum at both B3LYP/6-311+ $G^{**}$  and CCSD(T)/6-311+ $G^{**}$ . Apparently, the substitution of one P atom by the C–H group in tetrphosphacyclobutadiene completely quenched the PJT effect. Surprisingly, the UMO–OMO gap in the lowest isomer of  $CHP_3$  that is responsible for out-of-plane distortion is actually slightly smaller (8.34 eV) than the corresponding gap in  $P_4$ . Therefore, the simple consideration of PJT may not be always applicable. However, we found in our previous works that the simple PJT consideration worked rather well.<sup>2,38,39</sup> We were not able to find any theoretical or experimental data regarding  $CHP_3$  isomers in the literature.

**$C_2H_2P_2$  Isomers.** The CK search for the global minima of the singlet and triplet  $C_2H_2P_2$  species revealed that the potential energy surface has more low-lying structures than that of  $P_4$  and  $CHP_3$  with the lowest structure III.1 (Figure 3), which can be considered as derivative of triafulvene.



**Figure 3.** Representative optimized structures of  $C_2H_2P_2$ , their point group symmetries, spectroscopic states, and ZPE-corrected (B3LYP/6-311++G\*\*) relative energies (CCSD(T)/CBS//B3LYP/6-311++G\*\*).



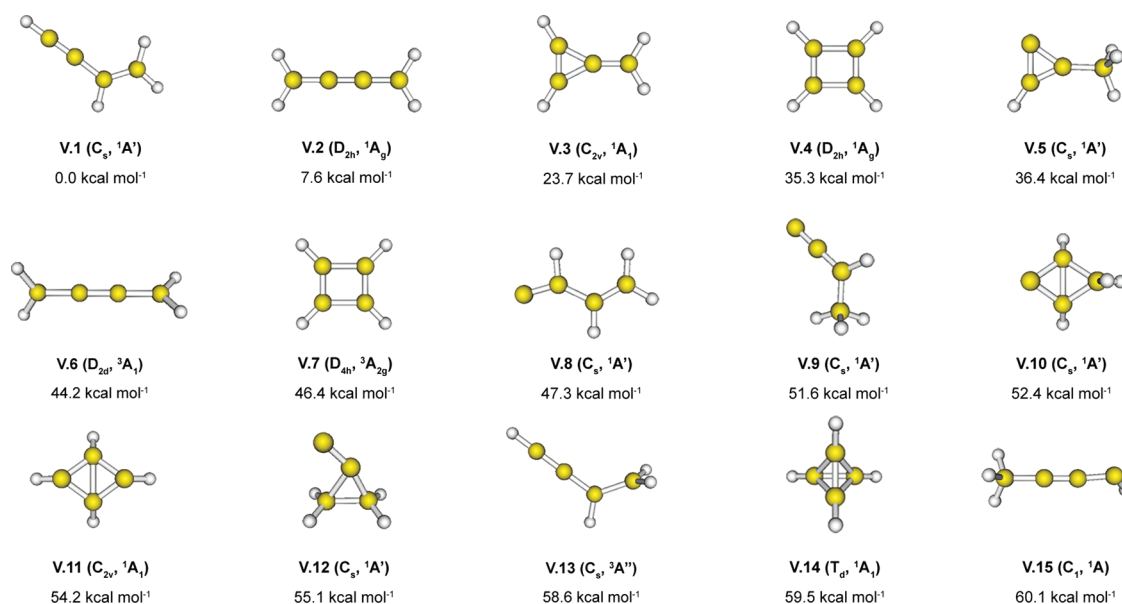
**Figure 4.** Representative optimized structures of  $C_3H_3P$ , their point group symmetries, spectroscopic states, and ZPE-corrected (B3LYP/6-311++G\*\*) relative energies (CCSD(T)/CBS//B3LYP/6-311++G\*\*).

The tetrahedron-like structure III.2 is the second lowest isomer, being just 2.3 kcal/mol higher in energy, and this energy difference is too small to make a definite decision of which of these two structures is the true global minimum. The vinylacetylene-like structures III.3–III.7 are the next set of low-lying isomers, with the relative energies being 8.9–14.7 kcal/mol above the global minimum structure. The *cis*-diphosphacyclobutadiene isomer III.8 is 19.0 kcal/mol higher than isomer III.1 and 16.7 kcal/mol higher in energy than isomer III.2 (Figure 3). The *trans*-diphosphacyclobutadiene isomer III.15 is 25.9 kcal/mol higher than isomer III.1 and 23.6 kcal/mol higher than isomer III.2. The lowest triplet isomer III.9 was found to be 19.2 kcal/mol

higher in energy than the global minimum. Our results are in agreement with previously reported computational data.<sup>40</sup>

**$C_3H_3P$  Isomers.** From our CK search for the global minimum structure of the singlet and triplet  $C_3H_3P$  stoichiometries, we found that the derivative of vinylacetylene (IV.1) is the global minimum (Figure 4), with its other derivatives being the second (IV.2), third (IV.3), and fourth (IV.4) lowest isomers.

The phosphacyclobutadiene isomer IV.8 is more stable than the tetrahedron-like isomer IV.9 by 2.8 kcal/mol (Figure 4). Substitution of three P atoms by three C–H groups in tetraphosphacyclobutadiene switched the relative stabilities of planar and tetrahedron-like isomers. The tetrahedron-like isomer is much



**Figure 5.** Representative optimized structures of C<sub>4</sub>H<sub>4</sub>, their point group symmetries, spectroscopic states, and ZPE-corrected (B3LYP/6-311++G\*\*) relative energies (CCSD(T)/CBS//B3LYP/6-311++G\*\*).

higher (by 34.6 kcal/mol) in energy than the global minimum structure. The lowest triplet isomer IV.7 is 25.6 kcal/mol above the global minimum. Hence, the 3D–2D transition occurs between C<sub>2</sub>H<sub>2</sub>P<sub>2</sub> and C<sub>3</sub>H<sub>3</sub>P. We are not aware of any experimental or theoretical data for this system.

An opposite 2D–3D transition was observed in the series of mixed boron–aluminum cluster ions, B<sub>6–n</sub>Al<sub>n</sub><sup>2–</sup> (*n* = 0–6), and their lithium salts.<sup>41</sup> It was shown that the transition occurs late in the series, at BAl<sub>5</sub><sup>2–</sup>, and that covalent bonding has an extraordinarily resilient effect that governs the cluster shape more than delocalized bonding does.

**C<sub>4</sub>H<sub>4</sub> Isomers.** The CK search for the global minima revealed that there are a lot of interesting structures on the potential surface of C<sub>4</sub>H<sub>4</sub>. The global minimum is well-known vinylacetylene (V.1, Figure 5).

Butatriene and methylenecyclopropene (V.2 and V.3, Figure 5) are 7.6 and 23.7 kcal/mol higher in energy. Our calculations at the CCSD(T)/CBS//B3LYP/6-311++G\*\* level show that cyclobutadiene (V.4) is the fourth lowest isomer and is 24.2 kcal/mol more stable than the tetrahedral structure (V.14). The lowest triplet isomer V.6 was found to be 44.2 kcal/mol higher than vinylacetylene. The triplet aromatic structure V.7 is 11.1 kcal/mol less stable than antiaromatic structure V.4. Our highest-level relative energy values of C<sub>4</sub>H<sub>4</sub> isomers are in a good agreement with previous calculations.<sup>42,43</sup>

**Chemical Bonding Pictures Revealed by AdNDP.** In order to interpret our results from the chemical bonding point of view, we performed the AdNDP analysis for the global minimum structures. The results of our analysis for these structures are shown in Figure 6.

For the tetrahedral P<sub>4</sub> molecule (I.1), the AdNDP analysis revealed the expected six two-center, two-electron (2c–2e) P–P σ bonds and a lone pair located on each phosphorus atom (not shown in Figure 6), all with occupation numbers (ON) being close to ideal values of 2.00 |e|. The tetrahedron-like structures (II.1 and III.2) have seven 2c–2e (ON = 1.96–2.00 |e|) and eight 2c–2e (ON = 1.97–2.00 |e|)

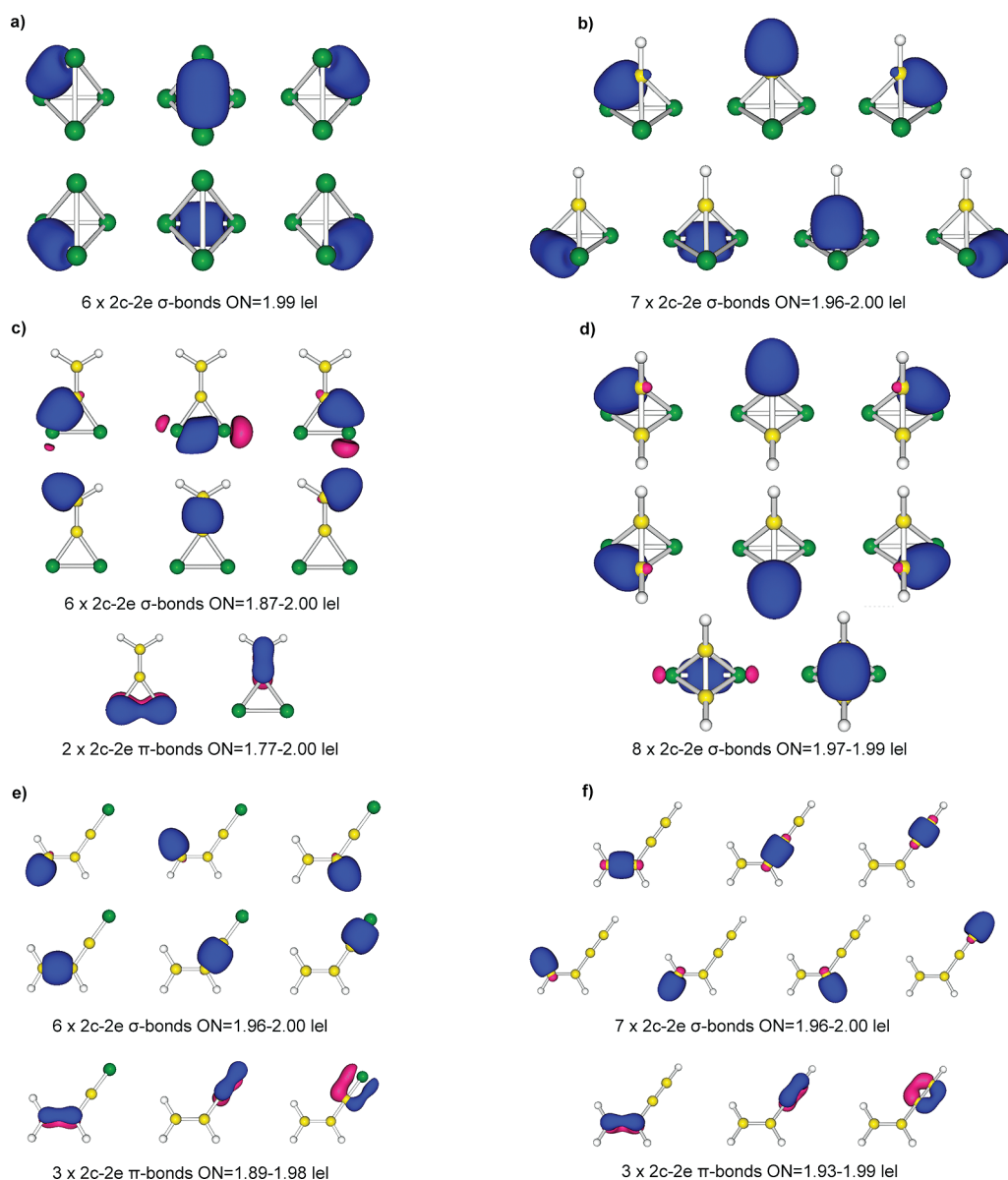
σ bonds, respectively, as well as a lone pair on each P atom (not shown in Figure 6). For the planar triafulvene-like structure (III.1), we found six 2c–2e (ON = 1.87–2.00 |e|) σ bonds and two 2c–2e (ON = 1.77–2.00 |e|) π bonds. The results of our AdNDP analysis show that the number of π bonds is increasing upon the substitution of P atoms by C–H groups. This has a big influence on the stability of corresponding structures (IV.1, V.1).

According to our systematic computational study, if we consider the relative energies between tetrahedral-like and planar structures along the C<sub>x</sub>H<sub>x</sub>P<sub>4–x</sub> (*x* = 0–4) series upon substitution of P atoms by the C–H groups, a transition from the three-dimensional tetrahedron-like structures to the planar structures occurs at *x* = 3. In this case, the increase in relative stability of the planar structure is not related to aromaticity as it was in the C<sub>x</sub>H<sub>x</sub>P<sub>6–x</sub> (*x* = 0–6) series, since in our case the planar structures are not aromatic.

There are two main reasons for the switch in the relative stabilities in the considered series along the substitution of phosphorus atoms by the C–H groups. The first one is the strain energy in the tetrahedron structure due to the smaller valence angle at the vertex of the tetrahedron. It is much easier to deform the angle at the phosphorus atom than at the carbon atom. The reported strain energy in tetrahedron C<sub>4</sub>H<sub>4</sub> (~119.5 kcal/mol)<sup>44</sup> is significantly larger than that in tetrahedral P<sub>4</sub> (~14.34 kcal/mol).<sup>45</sup> Hence, phosphorus structures with acute bonding angles are less strained than carbon analogous structures.

The second factor for the 3D–2D transition is that π-bonding between two carbons is stronger than P–P π-bonding due to a larger overlap of atomic orbitals. The consideration of the C<sub>x</sub>H<sub>x</sub>P<sub>4–x</sub> (*x* = 0–4) series proves this statement, because the increase in relative stability of the planar structure is not related to aromaticity as it was in the C<sub>x</sub>H<sub>x</sub>P<sub>6–x</sub> (*x* = 0–6) series, since in our case the planar global minimum structures are not aromatic. In the planar vinylacetylene-like molecules, there are two σ bonds less and three π bonds more compared to the tetrahedron-like structures.





**Figure 6.** Chemical bonding patterns of the (a) I.1, (b) II.1, (c) III.1, (d) III.2, (e) IV.1, and (f) V.1 global minimum structures revealed by AdNDP.

## 4. CONCLUSIONS

We presented a systematic study of the  $C_xH_xP_{4-x}$  ( $x = 0-4$ ) series. We performed an unbiased CK global minimum and low-lying isomers search for the singlet and triplet  $P_4-C_4H_4$  species at the B3LYP/6-31G\*\* level of theory. The selected lowest isomers were recalculated at the CCSD(T)/CBS//B3LYP/6-311++G\*\* level of theory. In addition to that, we calculated relative energies of two isomers at CCSD(T)/cc-pvQZ//B3LYP/6-311++G\*\*. Results at this level of theory are consistent with CCSD(T)/CBS//B3LYP/6-311++G\*\* extrapolations. We found that the global minimum structures and low-lying isomers always have the singlet electronic ground state. The transition from a 3D structure to a 2D structure occurs at  $x = 3$  ( $C_3H_3P$ ), where tetrahedron-like isomers become significantly more unstable than the planar structures.

From the discussion, one can see that six P–P  $\sigma$  bonds in the tetrahedral structure I.1 are much more favorable than four P–P

$\sigma$  bonds and two P–P  $\pi$  bonds in the quasi-planar structure I.4. Along the series, upon substitution of P atoms by CH groups, the relative stability of tetrahedron-like structures is diminishing, and in  $C_3H_3P$ , the planar structure is now more stable than the tetrahedral one, even though the planar molecules are not aromatic. This analysis clearly demonstrates that the 3D–2D transition in the discussed series occurs due to significantly stronger  $\pi$  bonds between carbon atoms in addition to increasing strain energy at the carbon atom in the tetrahedral environment. The importance of  $\pi$  bonding and high strain energy in carbon-rich molecules can also be seen from the global minimum structure IV.1 and structure IV.9, where in the last one the number of  $\sigma$  bonds is increased to three and the number of  $\pi$  bonds is reduced to three. Thus, in evaluating relative stabilities of structures composed of carbon atoms and valence isoelectronic species having phosphorus and silicon, one should keep in mind that carbon-containing molecules would prefer to

maximize the number of  $\pi$  bonds and decrease their bonding strain, whereas in the molecules containing third-row elements, the acute bond angle at the vertex of the tetrahedral structure is the most preferable, and weak  $\pi$  bonds would yield to stronger  $\sigma$  bonds.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Geometry of low-lying structures and their relative energies (CCSD(T)/CBS, CCSD(T)/cc-pvTZ, CCSD(T)/cc-pvDZ and B3LYP/6-311++G\*\*). Relative energies of two low-lying isomers for every stoichiometry at CCSD(T)/cc-pvQZ. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENT

This work was supported by the National Science Foundation (CHE-1057746). The computational resource, the Uinta cluster supercomputer, was provided through the National Science Foundation under Grant CTS-0321170 with matching funds provided by Utah State University.

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