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## Isomerism and aromaticity of heterofullerene $C_{70-n}P_n$ ( $n=2-10$ )

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**Abstract** A systematic investigation on possible structures of heterofullerenes  $C_{70-n}P_n$  ( $n=2-10$ ) has been performed employing semiempirical MNDO and ab initio methods. The stabilities decrease with increasing number of heteroatoms. The structures whose carbon atoms are substituted in the *para* pattern across the equatorial hexagons correspond to the most stable isomers. The isomeric pattern of P-doped  $C_{70}$  systems follows our previously proposed correlation between the isomerism of the fullerene adducts  $C_{60}X_n/C_{70}X_n$  and those of the heterofullerenes  $C_{60-n}N_n$  or  $C_{60-n}B_n/C_{70-n}N_n$  or  $C_{70-n}B_n$ . The aromaticity of the most stable structures of heterofullerenes is studied to investigate the heteroatom doping effect on the electron delocalization of the fullerene cage.

**Keywords** Heterofullerenes · P-doped fullerenes · Isomerism · Aromaticity

### Introduction

Heterofullerenes are fullerene molecules in which one or more carbon atoms are replaced by heteroatoms such as boron or nitrogen, whose formation is a kind of “on-ball” doping of the fullerene cage. Apart from exohedral and endohedral fullerene derivatives, heterofullerenes represent the third fundamental group of modified fullerenes, and are mainly of interest for the possibility of fine-tuning the electronic properties of the cage structures and their ability to be assembled into materials with specific physical and chemical properties.

In experiments great progress has been achieved in the last decade in the synthesis of heterofullerenes by

chemical modification of isocyclic fullerenes or by the laser ablation technique or the contact-arc method. [1, 2, 3, 4, 5] Up to now, heterofullerenes, such as  $C_{60-x}B_x/C_{70-x}B_x$  ( $x=1-2$ ), [6, 7, 8, 9, 10]  $C_{59}N/C_{69}N$ , [11, 12, 13, 14, 15, 16]  $C_{58}BN$ , [10, 17, 18, 19]  $C_{59}O$ , [20, 21]  $C_{60-x}Si_x$ , [22, 23, 24, 25, 26, 27, 28, 29, 30]  $C_{59}Ge/C_{59}As/C_{69}As$ , [31]  $C_{59}P/C_{69}P$ , [32], and transition metal-doped  $C_{59}M/C_{69}M$ , ( $M=Pt, Fe, Co, Ni, Rh, Ir$ ) [33, 34] have been generated successfully. In addition,  $C_{59}N$  and  $C_{69}N$  have been identified in dimeric form in solution by chemical modification of the parent fullerenes. [35, 36, 37] However, except for nitrogen-doped fullerenes, the macroscopic syntheses and purification of the heterofullerenes mentioned above have not been successful.

Only if macroscopic amounts of materials are available will the chemistry of heterofullerenes develop well. The contact-arc method may be the most convenient way to obtain macroscopic amounts of heterofullerenes. However, many experimental problems with respect to purification and characterization of heterofullerenes generated by this method exist, and the structures of multi-substituted fullerenes have not been clarified so far.

On the theoretical side, although the stabilities, electronic properties, band structures and the third-order polarizability of the heterohedral fullerenes have been studied, mostly these studies are based on the arbitrarily assigned geometries which often give ambiguous and contradictory results. [38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53] Until recently, systematic theoretical studies on isomerism of heterofullerenes  $C_{60-n}X_n$  ( $n=2-6$ ) [54, 55] and  $C_{70-n}X_n$  ( $n=2-10$ ) ( $X=N, B$ ), [56, 57]  $C_{60-2n}(BN)_n$  [58] and  $C_{70-2n}(BN)_n$  ( $n=1-3$ ), [59]  $C_{58}P_2$  [60] and  $C_{69}Si$  [61] have been reported by our group. The isomeric pattern of BN-doped fullerenes has been extended to  $C_{60-2n}(BN)_n$  ( $n=7-24$ ) by Kar and co-workers [62, 63]. The theoretical studies on the isomerism of heterofullerenes may assist in the further experimental synthesis and characterization since the computationally lowest energy isomers would be the experimen-

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tally observed structures when the contact-arc method is used to generate heterofullerenes, providing that the reaction products obtained in the contact-arc method are thermodynamically controlled.

Our previous work showed that the 1,4-substitution pattern is thermodynamically preferred for  $C_{60-n}X_n$  ( $X=N$  or  $B$ ,  $n=2-6$ ) and  $C_{70-n}X_n$  ( $X=N$  or  $B$ ,  $n=2-10$ ), and that there is a fair correlation between the isomerism of heterofullerenes and the regioisomerism of fullerene adducts with sterically demanding and segregated addends, i.e. the isomerism of heterofullerenes  $C_{60-n}N_n$  or  $C_{60-n}B_n/C_{70-n}N_n$  or  $C_{70-n}B_n$  follows the isomerism of fullerene adducts  $C_{60}X_n/C_{70}X_n$  ( $X$  is the sterically demanding addend). [54, 55, 56, 57] This correlation also holds true for  $C_{58}P_2$ . [60] These findings build a bridge to connect these two groups and allow us to deduce the most stable isomers based on the knowledge of the relatively well-studied fullerene adducts.

In this paper we extend our investigation on isomerism of heterofullerenes to phosphorus-substituted  $C_{70}$  systems,  $C_{70-n}P_n$  ( $n=2-10$ ). First, a systematic investigation on the possible energetically favored isomers of  $C_{68}P_2$  will be presented using semiempirical MNDO and ab initio methods. Then carefully chosen most likely isomers of multi-substituted species will be calculated. We will show that the relative energies of  $C_{70-n}P_n$  systems correlate with those of the regioisomeric fullerene adducts  $C_{70}X_n$  ( $X$  is the sterically demanding addend), which follows the former established correlation between the isomerism of the fullerene adducts  $C_{60}X_n/C_{70}X_n$  and those of heterofullerenes  $C_{60-n}N_n$  or  $C_{60-n}B_n/C_{70-n}N_n$  or  $C_{70-n}B_n$ . The degree of electron-delocalization is evaluated by using the computed NICS (nucleus independent chemical shift) [64] at the cage centers of the most stable isomers of  $C_{70-n}P_n$ . NICS has been demonstrated to be a useful criterion for aromaticity or anti-aromaticity. [64, 65, 66, 67] The NICS at the cage center has essentially the same value as the  $^3\text{He}$  endohedral shift, which is a valuable experimental tool for characterizing fullerenes and their derivatives [68, 69, 70, 71, 72] and can be reproduced computationally reasonably well, [73, 74, 75, 76] and is also a promising tool to characterize heterofullerenes. [77]

### Computational details

Given the large number and the size of the isomers studied, we have mostly applied semiempirical MNDO-type methods to assess the relative stability of heterofullerenes. [54, 55, 56, 57, 58, 59, 60, 61] These methods generally provide reasonable results for pure fullerenes and their derivatives (see [78] for a brief review). Their good performance in predicting the relative energies of various isomers of specific fullerenes has been tested recently using B3LYP/6-31G\* results for 150 fullerene structures as reference data. [79] We believe that common trends obtained at the semiempirical level are unlikely to change at higher levels.

Full geometry optimizations were carried out at the MNDO semiempirical level utilizing the VAMP 7.0 program. [80] The full optimizations were carried out without any symmetry constraints in Cartesian coordinates and initial input geometries were based on the optimized  $C_{70}$  with specific carbon atoms displaced by phosphorus atoms. For the key structures, single-point ab initio Hartree-Fock (HF) energy calculations were performed at the MNDO-optimized geometries employing the 3-21G basis set (HF/3-21G//MNDO) using the Gaussian-98 program. [81] NICS values [64] were computed at the cage centers of interest at the GIAO-SCF/3-21G level with the MNDO geometries utilizing the Gaussian-98 suite of programs. [81]

### Results and discussion

There are 143 structurally distinct isomers for  $C_{68}P_2$ . Our previous studies on  $C_{58}X_2$  ( $X=B, N, P$ ) [54, 60] and  $C_{68}X_2$  ( $X=N, B$ ) [56] indicate that the isomer corresponding to 1,4-substitution to the cyclohexatriene unit is the most stable isomer and the stabilities decrease with increasing distance between the heteroatoms. Thus, instead of calculating all the 143 possible isomers, only the isomers resulting from 1,2-substitution across the 6,6-fusion and from 1,4-substitution across 6-rings, as well as other selected isomers in which the heteroatoms are located in the same pentagon or hexagon, will be calculated. These isomers are listed in Table 1 and the numbering system used in this work is given in Fig. 1. Similar to previous studies, [54, 55, 56, 57, 58, 59, 60] the isomers

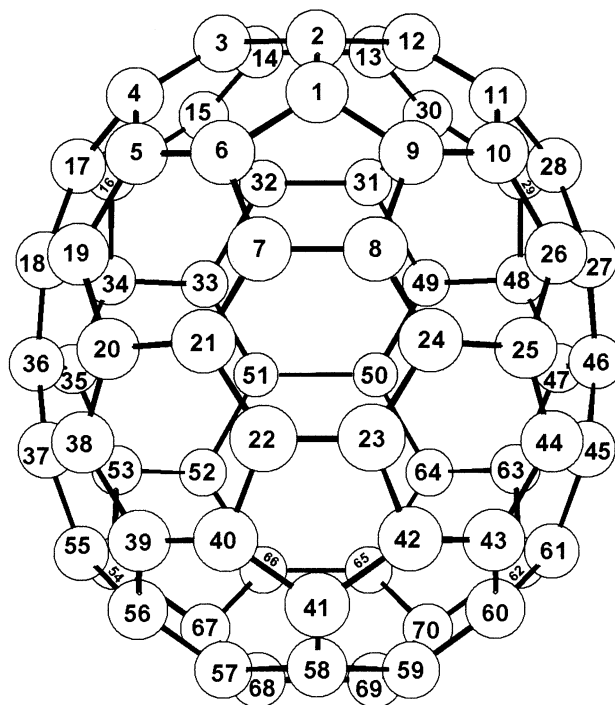
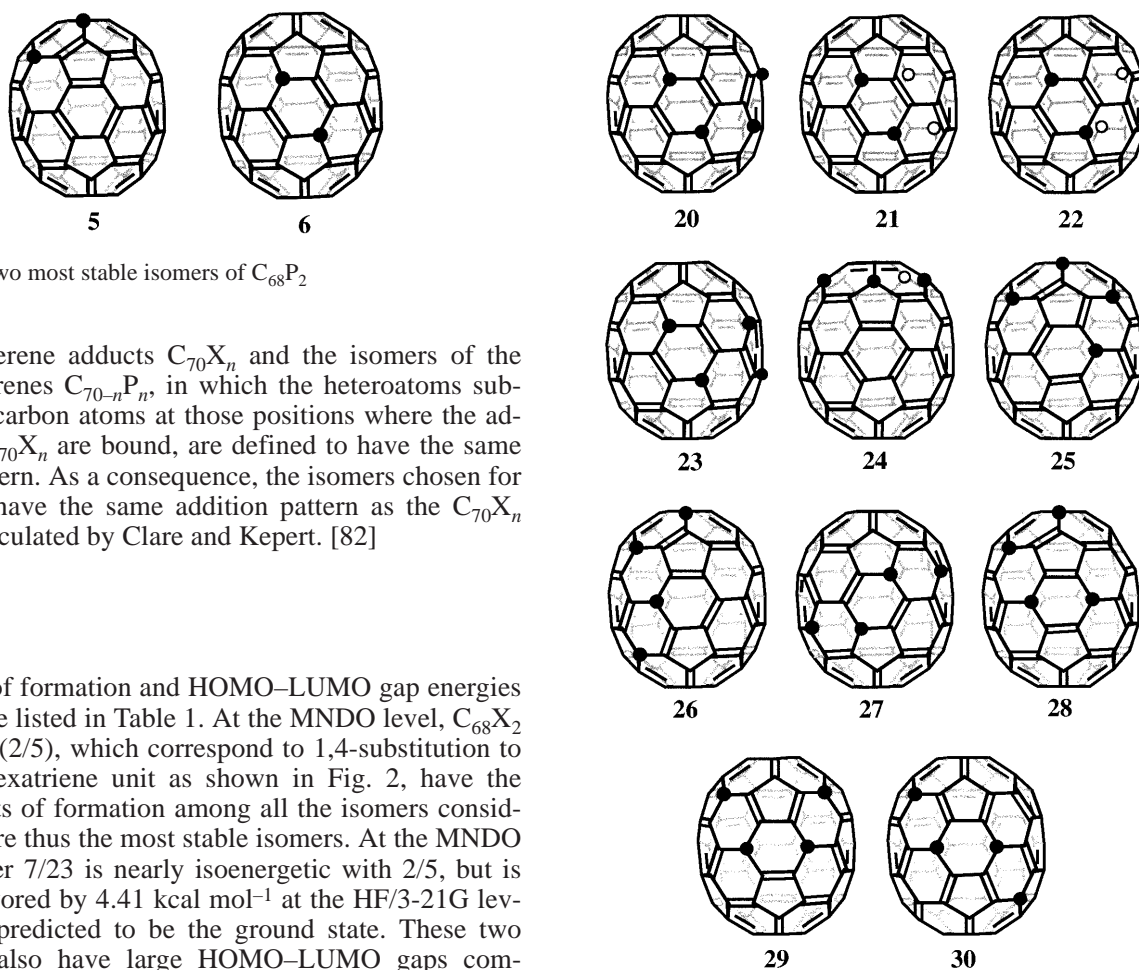


Fig. 1 Numbering of atoms in  $C_{70}$

**Table 1** Heats of formation, relative heats of formation (kcal mol<sup>-1</sup>) and frontier orbital energies (eV) of possible stable isomers of C<sub>68</sub>P<sub>2</sub>

C <sub>68</sub> P <sub>2</sub>	ΔH <sub>f</sub>	E <sub>rel</sub>	HOMO (eV)	LUMO (eV)	Gap (eV)	E <sub>rel</sub> <sup>a</sup>
<b>1</b> (2,1)	843.54	5.61	-8.702	-2.942	5.760	
<b>2</b> (5,6)	849.03	11.10	-8.814	-2.923	5.891	
<b>3</b> (7,21)	859.23	21.30	-8.809	-2.940	5.869	
<b>4</b> (20,21)	876.32	38.39	-8.691	-3.028	5.663	
<b>5</b> (2/5)	837.77	-0.16	-8.795	-2.949	5.846	4.41
<b>6</b> (7/23)	837.93	0.00	-8.749	-2.935	5.814	0.00
<b>7</b> (6/20)	853.86	15.93	-8.756	-2.899	5.857	
<b>8</b> (1/4)	840.78	2.85	-8.486	-2.927	5.559	
<b>9</b> (7/19)	856.51	18.58	-8.425	-3.125	5.300	
<b>10</b> (21/24)	856.71	18.78	-8.814	-2.888	5.926	
<b>11</b> (2;12)	854.61	16.68	-8.854	-3.112	5.742	
<b>12</b> (2;6)	881.67	43.74	-7.706	-4.070	3.636	
<b>13</b> (2;4)	873.15	35.22	-8.318	-3.439	4.879	
<b>14</b> (6;19)	867.54	29.61	-8.336	-3.335	5.001	
<b>15</b> (6;21)	893.80	55.87	-7.672	-4.010	3.662	
<b>16</b> (6;7)	874.31	36.38	-8.412	-3.350	5.062	
<b>17</b> (7;8)	851.50	13.57	-8.830	-2.909	5.921	
<b>18</b> (7;24)	891.15	53.22	-7.732	-3.818	3.914	
<b>19</b> (7;22)	886.61	48.68	-7.674	-3.955	3.719	

<sup>a</sup> HF/3-21G//MNDO level



**Fig. 2** The two most stable isomers of C<sub>68</sub>P<sub>2</sub>

of the fullerene adducts C<sub>70</sub>X<sub>n</sub> and the isomers of the heterofullerenes C<sub>70-n</sub>P<sub>n</sub>, in which the heteroatoms substitute the carbon atoms at those positions where the addends of C<sub>70</sub>X<sub>n</sub> are bound, are defined to have the same isomer pattern. As a consequence, the isomers chosen for this work have the same addition pattern as the C<sub>70</sub>X<sub>n</sub> adducts calculated by Clare and Kepert. [82]

### Isomerism

The heats of formation and HOMO–LUMO gap energies of C<sub>68</sub>P<sub>2</sub> are listed in Table 1. At the MNDO level, C<sub>68</sub>X<sub>2</sub> (7/23) and (2/5), which correspond to 1,4-substitution to the cyclohexatriene unit as shown in Fig. 2, have the lowest heats of formation among all the isomers considered, and are thus the most stable isomers. At the MNDO level isomer 7/23 is nearly isoenergetic with 2/5, but is slightly favored by 4.41 kcal mol<sup>-1</sup> at the HF/3-21G level, and is predicted to be the ground state. These two structures also have large HOMO–LUMO gaps compared to others. They conform to the same rule we found for other heterofullerenes, [54, 55, 56, 57, 60] and the lowest energy isomer has the 1,4-substitution across the *para* positions of an equatorial hexagon.

If further substitution follows the same pattern of this most stable isomer, i.e. with *para* substitution only across two equatorial C<sub>6</sub> rings, four possible isomers

**Fig. 3** Calculated isomers of C<sub>66</sub>P<sub>4</sub>

**20–23** for C<sub>66</sub>P<sub>4</sub> would result, as shown in Fig. 3. Figure 3 also shows seven other possible structures **24–30** with *para–para–para* substitutions. All these isomers and their energies are summarized in Table 2.

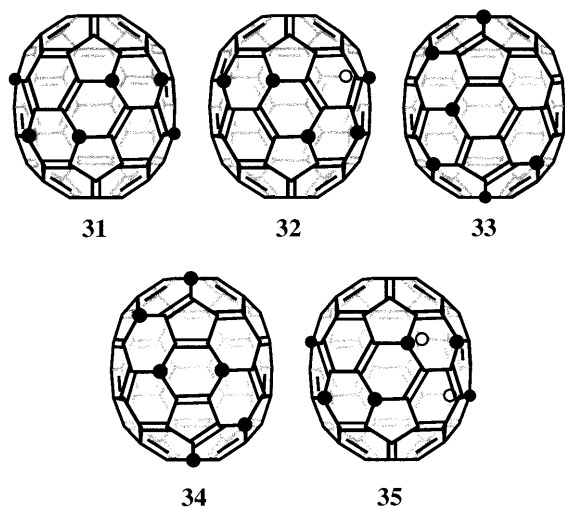
**Table 2** Heats of formation, relative heats of formation ( $\text{kcal mol}^{-1}$ ) and frontier orbital energies (eV) of possible stable isomers of  $\text{C}_{66}\text{P}_4$

$\text{C}_{66}\text{P}_4$	$\Delta H_f$	$E_{\text{rel}}$	HOMO (eV)	LUMO (eV)	Gap (eV)	$E_{\text{rel}}^a$
<b>20</b> (7,23;44,27)	732.30	0.00	-8.860	-2.964	5.896	0.00
<b>21</b> (7,23;63,49)	735.33	3.03	-8.778	-3.037	5.741	8.33
<b>22</b> (7,23;48,64)	737.50	5.20	-8.665	-3.096	5.569	
<b>23</b> (7,23;26,45)	743.85	11.55	-8.768	-2.990	5.778	
<b>24</b> (1,4;15,30)	738.39	6.09	-8.459	-2.994	5.465	
<b>25</b> (5,2;10,24)	750.82	18.52	-8.900	-2.975	5.925	
<b>26</b> (2,5;21,39)	750.50	18.20	-8.877	-3.073	5.804	
<b>27</b> (7,19;37,53)	759.59	27.29	-8.198	-3.716	4.482	
<b>28</b> (2,5;21,24)	754.76	22.46	-8.896	-2.972	5.924	
<b>29</b> (5,21;24,10)	758.84	26.54	-8.874	-2.984	5.890	
<b>30</b> (5,21;24,43)	802.84	70.54	-7.656	-4.301	3.355	

<sup>a</sup> HF/3-21G//MNDO level

**Table 3** Heats of formation, relative heats of formation ( $\text{kcal mol}^{-1}$ ) and frontier orbital energies (eV) of possible stable isomers of  $\text{C}_{64}\text{P}_6$  and  $\text{C}_{62}\text{P}_8$

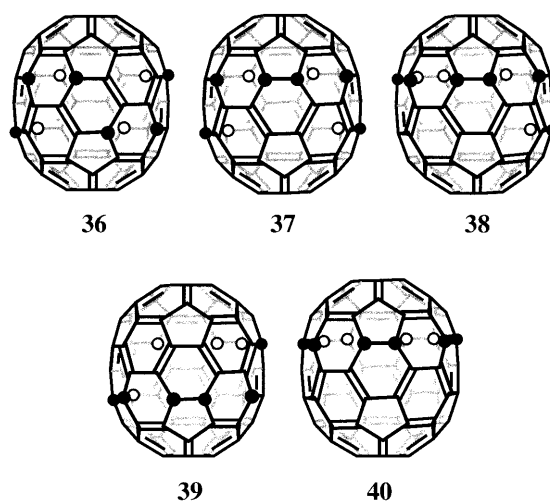
$\text{C}_{66}\text{P}_4$	$\Delta H_f$	$E_{\text{rel}}$	HOMO (eV)	LUMO (eV)	Gap (eV)
$\text{C}_{64}\text{P}_6$ <b>31</b> (7,23;44,27;48,64)	626.57	0.00	-8.871	-3.041	5.830
$\text{C}_{64}\text{P}_6$ <b>32</b> (7,19;37,53;33,49)	642.36	15.79	-8.532	-3.509	5.023
$\text{C}_{64}\text{P}_6$ <b>33</b> (2,5;21,39;58,43)	647.10	20.53	-8.984	-3.136	5.848
$\text{C}_{64}\text{P}_6$ <b>34</b> (2,5;21,24;43,58)	652.41	25.84	-8.981	-3.051	5.930
$\text{C}_{62}\text{P}_8$ <b>35</b> (7,23;44,27;48,64;52,34)	519.31	-	-9.205	-2.859	6.346



**Fig. 4** Calculated isomers of  $\text{C}_{64}\text{P}_6$  and the most stable structure of  $\text{C}_{62}\text{P}_8$

The isomer (7,23; 44,27) is computed to be the lowest energy structure by both MNDO and ab initio calculations. This structure corresponds to the *ra-para-para* substitution pattern across the equatorial area. This is thermodynamically favorable not only because the unfavorable P-P interaction is avoided but also because no [5, 6] double bonds must be introduced in the polar region and [5, 6] double bonds in the equator are removed.

Four possible *para-para-para-para-para* structures **31–34** exist, as shown in Fig. 4 for  $\text{C}_{64}\text{P}_6$ . The most stable structure **31** has oblique *para* substitution across three connected equatorial six-membered rings. Further substitution in the same way yields  $\text{C}_{62}\text{P}_8$  **35**. The energy data of  $\text{C}_{64}\text{P}_6$  and  $\text{C}_{62}\text{P}_8$  are summarized in Table 3.



**Fig. 5** Calculated isomers of  $\text{C}_{60}\text{P}_{10}$

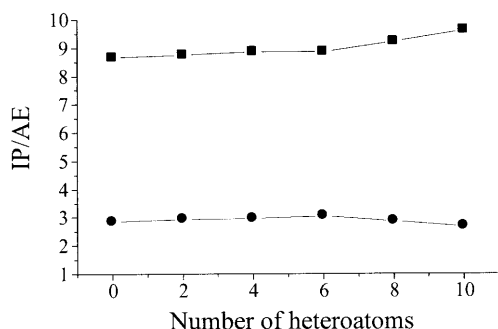
Following the same pattern for further substitution, we cannot obtain a continuous *para* equatorial belt in all five equatorial six-membered rings, only the structures **36** shown in Fig. 5 can be obtained. On the other hand, a complete belt can be obtained if one or more *ortho* equatorial rings are introduced. Thus, we can obtain four such isomers **37–40**, as also summarized in Fig. 5 and Table 4, among which the isomers **37** (7,23;44,27;48,64;52,34; 18,19) correspond to the experimental structure of  $\text{C}_{70}\text{Cl}_{10}$  [83]. At the MNDO level, **36** and **37** are the two most stable isomers with **36** slightly preferred by 1.10  $\text{kcal mol}^{-1}$ , while ab initio calculations reverse the energy order and indicate **37** to be more stable by 6.98  $\text{kcal mol}^{-1}$ .

As in other heterofullerenes, [54, 55, 56, 57, 58, 59, 60, 61] the cluster geometry is seriously affected by the



**Table 4** Heats of formation, relative heats of formation (kcal mol<sup>-1</sup>) and frontier orbital energies (eV) of possible stable isomers of C<sub>60</sub>P<sub>10</sub>

C <sub>60</sub> P <sub>10</sub>	$\Delta H_f$	$E_{rel}$	HOMO (eV)	LUMO (eV)	Gap (eV)	$E_{rel}^a$
<b>36</b> (7,23;44,27;48,64;52,34;18,38)	421.78	-1.10	-9.280	-2.709	6.571	6.98
<b>37</b> (7,23;44,27;48,64;52,34;18,19)	422.88	0.00	-9.633	-2.678	6.955	0.00
<b>38</b> (7,23;44,27;48,49;33,34;18,19)	450.37	28.59	-9.607	-2.956	6.651	
<b>39</b> (7,23;44,45;63,64;52,34;18,19)	450.68	28.90	-9.639	-2.880	6.759	
<b>40</b> (7,8;26,27;48,49;33,34;18,19)	477.37	55.59	-9.455	-3.181	6.274	

<sup>a</sup> HF/3-21G//MNDO level**Fig. 6** Ionization potentials and affinity energies of the most stable isomers of C<sub>70-n</sub>P<sub>n</sub> (n=2–10)

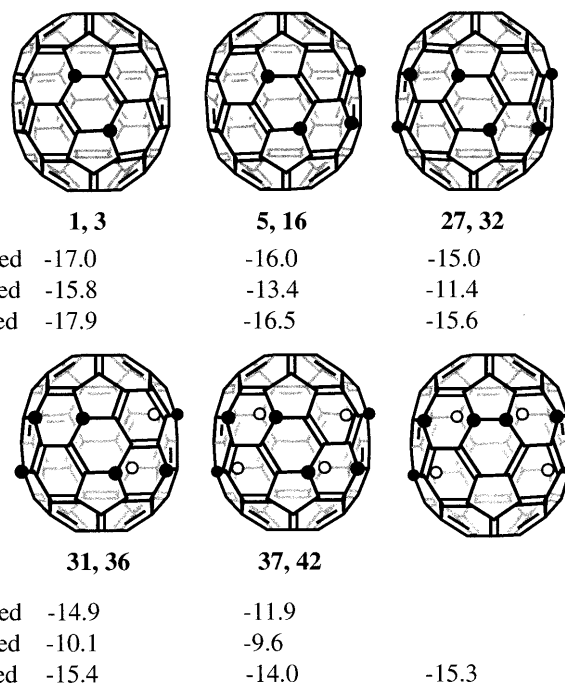
substitution. Significant distortion occurs at the heteroatom site for all the heterofullerene structures. Generally the phosphorus atoms pop out of the mean surface of the fullerene cage, showing its characteristic sp<sup>3</sup> hybridization with its lone pair electrons.

The MNDO calculated ionization potentials (IP) and affinity energies (AE) from Koopmans' theorem for the most stable C<sub>70-n</sub>P<sub>n</sub> isomers are summarized in Fig. 6. For the most stable species, C<sub>70-n</sub>P<sub>n</sub> (n=2–6) has both bigger IP and AE compared to C<sub>70</sub>, C<sub>62</sub>P<sub>8</sub> and C<sub>60</sub>P<sub>10</sub> have much larger IPs, while C<sub>62</sub>P<sub>8</sub> has nearly the same EA as C<sub>70</sub> and C<sub>60</sub>P<sub>10</sub> has smaller EA relative to C<sub>70</sub>. The changes of IP and EA indicate that the redox characteristics of C<sub>70</sub> can be modified by substitution of phosphorus atoms.

### Aromaticity of heterofullerenes

Containing a conjugated  $\pi$ -system, fullerenes form a unique class of spherical molecules. The question arises naturally, how will the heteroatom substitution affect its aromaticity or electron delocalization? To evaluate the mobility of electrons on the cage surfaces, NICSs [64] were calculated at the cage-centers of the heterofullerenes.

Figure 7 shows the most stable isomers of heterofullerenes and their endohedral chemical shifts. For comparison, the endohedral chemical shifts of N- and B-doped C<sub>70</sub> species are also summarized in Fig. 7. Compared with the endohedral chemical shift of C<sub>70</sub> at the same level, -20.9 ppm (exp. -28.8 ppm [68]), generally the

**Fig. 7** The most stable isomers of C<sub>70-n</sub>X<sub>n</sub> (X=N, B, P) and their endohedral NICSs (ppm)

aromaticity decreases with increasing number of heteroatoms in the system. P-doped species are the most aromatic ones among N-, B- and P-doped fullerenes, and B-doped fullerenes exhibit the least electron delocalization. Since NICSs at the cage centers have essentially the same values as the endohedral helium chemical shifts, these computed values also provide a basis for the possible characterization of these heterofullerenes.

### Conclusion

The most stable structures of the heterofullerenes C<sub>70-n</sub>P<sub>n</sub> (n=2–10) have been calculated. Our previously proposed correlation between the isomerism of the fullerene adducts C<sub>60</sub>X<sub>n</sub>/C<sub>70</sub>X<sub>n</sub> and that of the heterofullerenes C<sub>60-n</sub>N<sub>n</sub> or C<sub>60-n</sub>B<sub>n</sub>/C<sub>70-n</sub>N<sub>n</sub> or C<sub>70-n</sub>B<sub>n</sub> holds true for C<sub>70</sub> adducts and phosphorus-doped C<sub>70</sub> systems, thus we can deduce the stability of the doped C<sub>70</sub> fullerenes on the basis of the regioselectivity of [70] fullerene adducts. The endohedral NICSs of the most stable isomers of

$C_{70-n}P_n$  have been computed to assess the aromaticity and provide a basis for further characterization of these doped fullerenes.

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