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## Structures and magnetic properties of mono-doped fullerenes $C_{59}X^n$ and $C_{59}X^{(6-n)-}$ ( $X=B^-, N^+, P^+, As^+, Si$ ): isoelectronic analogues of $C_{60}$ and $C_{60}^{6-}$

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**Abstract** Structures of mono-doped fullerenes,  $C_{59}X^n$  and  $C_{59}X^{(6-n)-}$  ( $X=B^-, N^+, P^+, As^+, Si$ ), the isoelectronic analogues to  $C_{60}$  and  $C_{60}^{6-}$  with 60 and 66  $\pi$ -electrons, have been investigated at the B3LYP/6-31G\* level of density functional theory. On the basis of the computed nucleus independent chemical shifts (NICS) at the cage center and also at the center of individual rings as magnetic criteria, heterofullerenes with 60  $\pi$ -electrons are as aromatic as the parent  $C_{60}$ , while those with 66  $\pi$ -electrons are much less aromatic than  $C_{60}^{6-}$ . The very distinct endohedral chemical shifts of the 66  $\pi$ -electron systems may be useful to identify the heterofullerenes through their endohedral  $^3He$  NMR chemical shifts.

**Electronic Supplementary Material.** Supplementary material is available for this article if you access the article at <http://dx.doi.org/10.1007/s00894-002-0108-7>. A link in the frame on the left on that page takes you directly to the supplementary material.

**Keywords** Heterofullerene · Structure · Aromaticity · NICS

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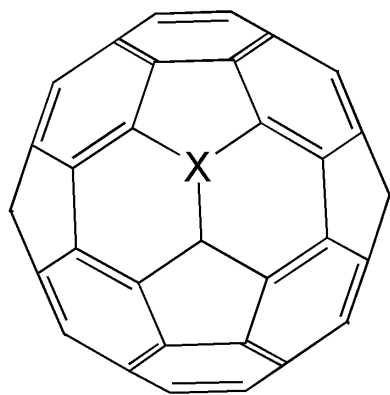
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### Introduction

Heterofullerenes in which one or more cage carbons are substituted by heteroatoms represent the third fundamental group of modified fullerenes besides exo- [1] and endohedral [2] derivatives. They have attracted much interest due to their tunable chemical and physical properties in materials science. [3, 4, 5, 6] Synthesis and isolation of heterofullerenes have been reported, and experimental techniques such as laser ablation, arc-discharge and fragmentation are used for their generation. Until now, heterofullerenes, such as  $C_{60-x}B_x/C_{70-x}B_x$  ( $x=1-2$ ), [7, 8, 9, 10, 11]  $C_{59}N/C_{69}N$ , [12, 13, 14, 15, 16, 17]  $C_{58}BN$ , [11, 18, 19, 20]  $C_{59}O$ , [21, 22]  $C_{60-x}Si_x$ , [23, 24, 25, 26, 27, 28, 29, 30, 31]  $C_{59}Ge/C_{59}As/C_{69}As$ , [32]  $C_{59}P/C_{69}P$ , [33] and transition-metal doped  $C_{59}M/C_{69}M$  ( $M=Pt, Fe, Co, Ni, Rh, Ir$ ), [34, 35] have been generated successfully. In addition,  $C_{59}N$  and  $C_{69}N$  have been identified as dimers in solution by chemical modification of the parent fullerenes. [36, 37, 38]

Apart from the extensive experimental work, theoretical investigations into the mono-doped  $C_{59}B/C_{59}N$ , [39, 40, 41, 42, 43]  $C_{59}O$ , [44, 45, 46]  $C_{59}S$ , [39]  $C_{59}Be$ , [46]  $C_{59}Si$ , [30, 31, 46, 47, 48]  $C_{59}P$ , [49]  $C_{59}M$  ( $M=Fe, Co, Ni, Rh$ ), [50, 51]  $C_{69}M$  ( $M=Co, Rh, Ir$ ), [52]  $C_{58}(BN)$ , [40, 53, 54, 55, 56, 57, 58, 59] and  $C_{59}B/C_{59}N$  dimer [59, 60] have been performed. Moreover, the substitution patterns of poly-doped fullerenes  $C_{58}X_2$  ( $X=N, B, P$ ), [61, 62]  $C_{68}X_2$  ( $X=N, B$ ), [63]  $C_{60-x}N_x/C_{60-x}B_x$  ( $x=2-8$ ), [64]  $C_{70-x}N_x/C_{70-x}B_x/C_{70-x}P_x$  ( $x=2-10$ ), [65]  $C_{60-2x}(BN)_x$  ( $x=1-24$ ) [58, 66, 67] and  $C_{70-2x}(BN)_x$  ( $x=1-3$ ) [68] have been studied and the electronic properties have been calculated based on the most stable isomers.

Containing a conjugated  $\pi$ -system, fullerenes form a unique class of spherical molecules. It is interesting to know how substitution will affect their aromaticity or the degree of electron delocalization in the cage network. Experimentally, the measured endohedral  $^3He$  NMR chemical shift is an effective method for characterizing fullerene structures and their aromaticity [69, 70, 71, 72, 73] and the experimental helium chemical shifts can be



**Scheme 1** Heterofullerenes,  $C_{59}X^n$  and  $C_{59}X^{(6-n)-}$  ( $X=B, N, P, As, Si$ )

reproduced well using modern quantum mechanical calculations. [74, 75, 76, 77] Theoretically, the calculated nucleus independent chemical shift (NICS) [78] has proved to be a simple and sufficient criterion of aromaticity. Since the endohedral  $^3\text{He}$  NMR chemical shifts normally agree well with the calculated NICS values at the cage centers, the easily computed NICS values instead of  $\delta^3\text{He}$  have been employed to characterize fullerenes, which enables the so-called NICS characterization. [74, 76, 77] For example, the previously unassigned  $C_{82}$  and  $C_{86}$  isomers have been theoretically identified using this method, [77] which is confirmed by theoretical  $^{13}\text{C}$  NMR spectra. [79]

In this paper, we present theoretical studies on the mono-doped fullerenes and their charged analogues,  $C_{59}X^n$  and  $C_{59}X^{(6-n)-}$  ( $X=B, N, P, As, Si$ ), with 60 and 66  $\pi$ -electrons, which are isoelectronic equivalents to  $C_{60}$  and  $C_{60}^{6-}$ , respectively (Scheme 1). Due to their novel structural properties, the oxa and thia ( $X=O, S$ ) analogues have been reported separately. [80] Special attention has been paid to the NICS values at the cage centers and the individual rings adjacent to the heteroatoms to evaluate the mobility of electrons on the cage surfaces.

## Computational details

Geometries were fully optimized in the given symmetry at the B3LYP/6-31G\* density functional level of theory. NICS [78] at the weighted geometrical center of cage and center of individual rings were calculated by using the GIAO-SCF/3-21G method with the B3LYP/6-31G\* geometries. All calculations were done with the Gaussian 98 program. [81] The total electronic energies and the optimized Cartesian coordinates are given in the Supporting Information.

**Table 1** The C–X bond lengths, the differences ( $\text{\AA}$ ) between 6–6 and 6–5 C–X bonds and the sum of bond angles ( $2\alpha+\beta$ ) surrounding the heteroatom in  $C_{59}X^n$  and  $C_{59}X^{(6-n)-}$

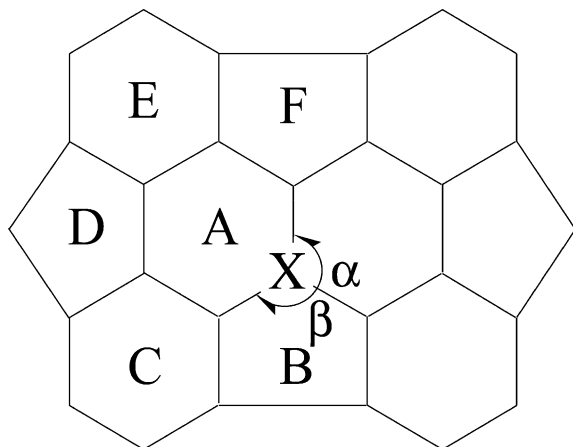
	C–X (6–6)	C–X (6–5)	$\Delta(\text{C–X})$	$2\alpha+\beta$
$C_{60}$	1.395	1.454	0.059	348.0
$C_{59}N^+$	1.369	1.426	0.057	348.4
$C_{59}P^+$	1.791	1.824	0.033	284.6
$C_{59}As^+$	1.908	1.940	0.032	268.9
$C_{59}B^-$	1.496	1.554	0.058	342.3
$C_{59}Si$	1.795	1.848	0.053	291.0
$C_{60}^{6-}$	1.435	1.452	0.017	348.0
$C_{59}N^{5-}$	1.447	1.428	–0.019 <sup>a</sup>	343.6
$C_{59}P^{5-}$	1.834	1.860	0.026	286.3
$C_{59}As^{5-}$	1.922	1.958	0.036	276.7
$C_{59}B^{7-}$	1.516	1.556	0.040	344.6
$C_{59}Si^{6-}$	1.916	1.940	0.024	272.1

<sup>a</sup> The negative value indicates that 6–6 bond is longer than 6–5 bond

## Results and discussion

Not only synthesis and generation, but also characterization are important in fullerene chemistry. In addition to structures, stability and reactivity on the cage surface, the endohedral chemical shifts, especially those of the encapsulated  $^3\text{He}$  nucleus, reflect the substantial differences between fullerenes in different oxidation states. For example, weakly aromatic  $C_{60}$  has a moderate upfield shifted  $\delta^3\text{He}$  of  $-6.3$  ppm, [69] while the corresponding hexaanion  $C_{60}^{6-}$  is highly aromatic with  $\delta^3\text{He}=-48.7$  ppm. [72] In contrast, from  $C_{70}$  to  $C_{70}^{6-}$ , the helium chemical shift changes from  $-28.8$  ppm to  $8.3$  ppm. [69, 72] On this basis, one may expect that  $\delta^3\text{He}$  might be used to identify new (hetero) fullerenes. [77, 82]

As in  $C_{60}$ , the B3LYP/6-31G\* method favors trivalent heteroatoms and therefore closed cage configurations, although some deformation around the hetero-doped position has been observed. The degree of such deformation can be characterized by the sum of the three CXC bond angles (Table 1 and Fig. 1).  $C_{59}B^-$ ,  $C_{59}N^+$ ,  $C_{59}B^{7-}$  and  $C_{59}N^{5-}$  are isoelectronic to  $C_{60}$  and  $C_{60}^{6-}$ , and contain a heteroatom with a covalent radius comparable with that of carbon. It is thus not surprising that they are ball-like as is  $C_{60}$ , and have nearly equal sums of CXC angles. Furthermore, the difference between the two C–X bond lengths of the 60  $\pi$ -electron species ( $C_{59}B^-$ ,  $C_{59}N^+$ ) is nearly the same as in  $C_{60}$ . However, considerable cage deformation has been found upon substitution by  $X=Si, P, As$ , and instead of the ideal cage form, the structures are like water drops with the heteroatom as the peak. This is clearly due to the larger covalent radius of these heteroatoms. Moreover, all the bonds in the heterofullerenes with 66  $\pi$ -electrons are somewhat longer than the corresponding bonds in their 60  $\pi$ -electron analogues, just as found in  $C_{60}^{6-}$ . [83, 84] As in  $C_{60}$  and  $C_{60}^{6-}$ , all 6–6 C–X bonds (shared by two six-membered rings) are shorter than the 6–5 C–X bonds, except for  $C_{59}N^{5-}$ , where the 6–6 C–N bond is slightly longer (1.447 versus 1.428  $\text{\AA}$ ).  $C_{59}N^{5-}$  with such unusual bond lengths has



**Fig. 1** Fragment showing neighboring rings and bond angles around the heteroatom (X)

been confirmed as the true minimum at the HF/STO-3G level (1.540 and 1.489 Å for 6–6 and 6–5 C–N bonds, respectively). This is the second such example (the first one being  $C_{59}O$  [80]).

On the basis of the calculated NICS values at the cage center, the heterofullerenes with 60  $\pi$ -electrons,  $C_{59}B$ ,  $C_{59}N^+$ ,  $C_{59}P^+$ ,  $C_{59}As^+$ ,  $C_{59}Si$ , are as aromatic as the parent  $C_{60}$  (Table 2). Significant effects upon doping are observed only for the rings neighboring the heteroatom (Fig. 1 and Table 2), and the alternation of aromatic six-membered rings and antiaromatic five-membered rings around the heteroatom center has changed considerably, while the perturbation for other rings is not remarkable. Since the endohedral chemical shifts of the doped fullerenes with 60  $\pi$ -electrons are essentially the same as that of  $C_{60}$ , they are not useful for identification purposes. It is interesting to note that the  $\delta^3He$  values for fulleroids with a largely preserved fullerene  $\pi$ -system are also very similar to those of the parent fullerenes, [85] and therefore of very limited use for characterization.

Since the aromatic character of  $C_{60}$  and  $C_{60}^{6-}$  differs remarkably, one might expect similar changes for the heterofullerenes. The bonds in the 66  $\pi$ -electron systems alternate less than those in their 60  $\pi$ -electron analogues. All rings, including those adjacent to the heteroatoms, exhibit diatropic ring currents, as indicated by the negative NICS values at the ring centers, and thus all the heterofullerenes with 66  $\pi$ -electrons are more aromatic than their 60  $\pi$ -electron analogues, which resembles the case of  $C_{60}$  itself, where the measured chemical shift of encapsulated  $^3He$  changes dramatically when going from neutral  $C_{60}$  to its hexaanion (from  $-6.3$  to  $-48.7$  ppm). [69, 72] The NICS values at the cage center of heterofullerene anions with 66  $\pi$ -electrons are all less negative than that computed for  $C_{60}^{6-}$ , indicating their reduced aromaticity. The endohedral chemical shifts of  $C_{59}N^{5-}$  and  $C_{59}B^{7-}$  are much more shielded than those of  $C_{59}P^{5-}$ ,  $C_{59}Si^{6-}$ ,  $C_{59}As^{5-}$ , which may be attributed to their more spherical geometries as discussed above.

**Table 2** NICS values (ppm) at the cage center and ring centers neighboring the heteroatom

	Cage center	A(6)	B(5)	C(6)	D(5)	E(6)	F(5)
$C_{60}$	-8.0	-5.9	7.2	-5.9	7.2	-5.9	7.2
$C_{59}N^+$	-8.3	-7.5	0.3	-6.9	7.5	-4.4	7.9
$C_{59}P^+$	-8.7	-1.6	0.0	-7.1	6.4	-2.1	8.0
$C_{59}As^+$	-8.9	0.5	0.0	-7.1	5.5	-1.8	8.1
$C_{59}B^-$	-7.6	-1.2	12.3	-6.0	5.8	-6.8	5.2
$C_{59}Si$	-8.1	-2.0	6.4	-5.7	7.0	-5.2	6.5
$C_{60}^{6-}$	-55.6	-23.2	-23.3	-23.2	-23.3	-23.2	-23.3
$C_{59}N^{5-}$	-35.7	-3.6	-31.5	-16.2	-30.6	-14.9	-36.6
$C_{59}P^{5-}$	-14.2	-3.5	-5.1	-7.9	-14.4	-9.5	-8.4
$C_{59}As^{5-}$	-26.0	-9.5	-8.0	-10.9	-15.2	-14.1	-12.7
$C_{59}B^{7-}$	-40.7	-18.2	-22.5	-17.9	-28.0	-13.4	-39.2
$C_{59}Si^{6-}$	-24.6	-7.4	-5.3	-10.9	-13.1	-13.1	-11.4

In  $C_{60}^{6-}$ , both five- and six-membered rings have the same NICS values and therefore the same aromatic character. In  $C_{59}N^{5-}$  and  $C_{59}B^{7-}$ , however, the five-membered rings around the heteroatom center are more aromatic than the corresponding six-membered ring, and also more aromatic than those in  $C_{60}^{6-}$ . The same trend is found for  $C_{59}P^{5-}$ , but less pronounced. In  $C_{59}Si^{6-}$  and  $C_{59}As^{5-}$ , the six-membered rings are somewhat more aromatic than the five-membered rings, but both are much less aromatic than those in  $C_{60}^{6-}$ .

The calculated NICS data are useful in fullerene chemistry since they are very close to the observable endohedral  $^3He$  NMR chemical shifts. Several fullerenes and their derivatives have been characterized by their distinct  $^3He$  NMR chemical shifts, [69, 70, 71, 72, 73] and some fullerene structures [77] have been identified by calculated NICS values. Moreover, such a NICS characterization has also been applied to heterofullerenes. [82] The endohedral chemical shifts are generally very sensitive to added electrons. In the present case, the heterofullerenes in the reduced form have distinct endohedral chemical shifts that cover a large range, varying from  $-14.2$  ppm ( $C_{59}P^{5-}$ ) to  $-40.7$  ppm ( $C_{59}B^{7-}$ ) compared to  $-55.6$  ppm of  $C_{60}^{6-}$ . Thus, shifts can aid in the characterization of the heterofullerenes, being influenced by the nature of the heteroatom and the extent of reduction.

The triply degenerate LUMO ( $t_{1u}$ ) of  $C_{60}$  can accommodate six extra electrons. How about its hetero-analogues? As indicated in Table 3, in spite of the reduced symmetry ( $C_s$ ), the gaps between the HOMO and the three LUMOs are close to those of  $C_{60}$ . Therefore, these heterofullerenes should also be able to add six additional electrons. In fact, the cyclic voltammogram of  $(C_{59}N)_2$  shows three overlapping pairs of reversible one-electron reductions within the solvent window, [36] and the alkali metal intercalated compound  $K_6C_{59}N$  contains quasi-spherical monomeric  $(C_{59}N)^{6-}$  ions. [86]

The most promising species to be characterized using the helium NMR technique in this series is the azafulle-

**Table 3** Energy gaps between HOMO and three LUMO (eV)

	Gap	Gap+1	Gap+2
C <sub>60</sub>	2.77	2.77	2.77
C <sub>59</sub> N <sup>+</sup>	2.36	2.62	2.77
C <sub>59</sub> P <sup>+</sup>	1.74	2.69	2.75
C <sub>59</sub> As <sup>+</sup>	1.68	2.72	2.76
C <sub>59</sub> B <sup>-</sup>	2.00	2.03	2.13
C <sub>59</sub> Si	2.17	2.60	2.63

rene C<sub>59</sub>N<sup>+</sup>, which is thought to be a key intermediate, [87] but has not been isolated so far. Upon reduction, the endohedral chemical shifts will change from -8.3 ppm of C<sub>59</sub>N<sup>+</sup> to -35.7 ppm of C<sub>59</sub>N<sup>5-</sup>. The <sup>3</sup>He NMR spectrum of <sup>3</sup>He@(C<sub>59</sub>N)<sub>2</sub> has already been used to follow the shielding effects of the heterofullerene on the endohedral <sup>3</sup>He atom. [88] Thus, it is expected that helium chemical shifts will facilitate the characterization of these species.

## Conclusion

The aromaticity of heterofullerenes C<sub>59</sub>X<sup>n</sup> and their charged analogues C<sub>59</sub>X<sup>(6-n)-</sup> (X=B, N, P, As, Si), iso-electronic to the all-carbon analogues C<sub>60</sub> and C<sub>60</sub><sup>6-</sup>, has been studied systematically. Structural abnormality is found for C<sub>59</sub>N<sup>5-</sup>, the second fullerene network (following C<sub>59</sub>O [80]) with the 6–6 bond longer than the 6–5. On the basis of the computed NICS values at the cage centers, heterofullerenes with 60 π-electrons have essentially the same aromatic character as C<sub>60</sub>, while their 66 π-electron analogues are less aromatic than C<sub>60</sub><sup>6-</sup>. Endohedral chemical shifts, accessible via <sup>3</sup>He NMR of the corresponding endohedral helium compounds, should be a valuable indicator for the extent of reduction and a useful tool for characterizing heterofullerenes since their anions with 66 π-electrons show distinct endohedral chemical shifts, while those of their 60 π-electron analogues have NICS values similar to that of C<sub>60</sub>. Thus, it is possible to use the individual endohedral chemical shifts to distinguish between the different fullerene anions.

## Supporting information available

Total electronic energies and the optimized Cartesian coordinates for all molecules are listed. This material is available free of charge via the internet.

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