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Aromatic stabilization in heterofullerenes $C_{48}X_{12}$ ($X = N, P, B, Si$)[†]

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ABSTRACT: B3LYP density functional calculations were performed on two S_6 symmetrical isomers (**I** and **II**) of $C_{48}X_{12}$ ($X = N$, B, P, Si) heterofullerenes, and their global and local aromaticity were evaluated by nucleus-independent chemical shifts (NICS). Despite the unfavorable heteroatom repulsive interactions, isomer **II** is more stable than **I** owing to the combination of global and local aromaticity. The latter arises from the presence of triphenylene units in isomer **II**. The aromatic stabilization effects found in this study should be taken into account when predicting the most stable isomers of heterofullerenes. The same is true for predictions of the isomers of fullerene adducts such as $C_{60}Cl_{12}$. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: heterofullerenes; isomerism; stability; NICS; aromaticity

INTRODUCTION

Heterofullenenes (for reviews, see Ref. 1) have received attention both experimentally and theoretically because of the possibility of fine-tuning the physical and chemical properties of the fullerene cages. (for reviews, see Ref. 2) Among others, the synthesis of $C_{48}N_{12}$ as the core shell in cross-linked carbon nitride nano-onions is an exciting achievement.[3] Since the number of possible isomers increases rapidly as more heteroatoms are incorporated, the isomerism of heterofullerenes, which is difficult to address experimentally, has only been investigated theoretically.[4] In $C_{58}X_2$ ($X = N$, B, P), for example, the 1,4-substitution pattern in hexagonal rings is preferred energetically.[4a,b] The most stable isomers of $C_{58}Si_2$ have the two silicon atoms in a pentagon at the 1,3-positions, or in a hexagon at the 1,4-positions[5,6] and at the HF/6–31G* level both isomers are very similar in energy [within 0.9 kcal mol^{-1} (1 kcal = 4.184 kJ)] (Z. Chen, H. Jiao, A. Hirsch and W. Thiel, unpublished results). Accordingly, the S_6 symmetric structure (**I**) shown in Fig. 1, containing evenly spaced nitrogen atoms, i.e. one in each pentagon, has been proposed as the most likely isomer of $C_{48}N_{12}$ because the repulsive nitrogen–nitrogen interactions are minimized.[3,7] The same isomerism pattern may be expected for its B, P and Si analogues. Recently, however, a more stable S_6 symmetrical $C_{48}N_{12}$ structure (**II**) has been proposed, in which repulsive nitrogen–nitrogen interactions are outweighed by the presence of aromatic triphenylene units with extended stabilizing influences.[8] Owing to the considerable interest in $C_{48}N_{12}$, the IR spectrum, dipole moments, polarizabilities, hyperpolarizabilities[9a] and NMR spectra[9] of the less stable isomer **I** have been computed.

In this paper, we present theoretical calculations on the structures, electronic properties and local and global aromaticity of heterofullerenes $C_{48}X_{12}$ ($X = N$, P, B, Si). Our results show that the aromatic stabilization found in $C_{48}N_{12}$ also exists in other doped fullerenes, and thus needs to be considered when predicting the most stable isomers of heterofullerenes.

COMPUTATIONAL DETAILS

The two S_6 isomers (**I** and **II**) of $C_{48}X_{12}$ ($X = N$, P, B, Si) were fully optimized at the density-functional B3LYP/6–31G* level. Nucleus-independent chemical shift (NICS) values[10] at the ring and cage centers, which are a simple and effective local and global aromaticity probe, were

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[†]Dedicated to Professor Tadeusz Marek Krygowski on the occasion of his 65th birthday.

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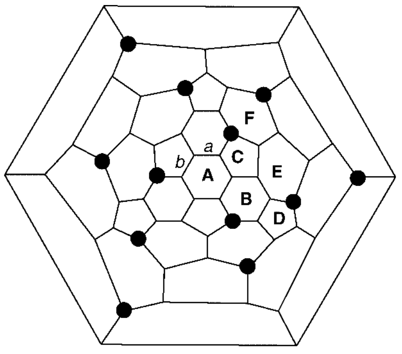
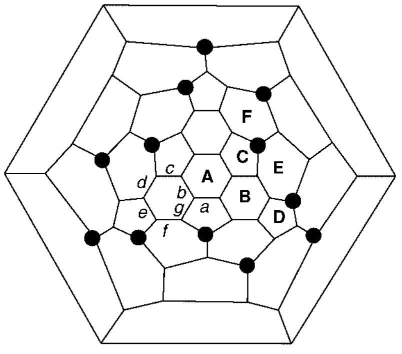


(a) isomer **I**



(b) isomer **II**

Figure 1. $C_{48}X_{12}$ and $C_{60}Cl_{12}$ positional isomers **I** and **II**

computed at the GIAO-B3LYP/3–21G and GIAO-HF/3–21G levels using the B3LYP/6–31G* optimized geometries. Note that the NICS values used in the discussion are GIAO-B3LYP unless otherwise stated. The ^{13}C chemical shifts at the GAIO-B3LYP/3–21G//B3LYP/6–31G* level, referenced to the C_{60} experimental value (143.15 ppm),[11] also are reported. The Gaussian 98 program package was used throughout.[12]

Table 1. $C_{48}X_{12}$ B3LYP/6–31G* total energies (E_{tot}), relative energies (E_{rel}, kcal mol^{-1}) and HOMO–LUMO gaps

	E_{tot}(au)	E_{rel}(kcal mol^{-1})	Gap(eV)
$C_{48}N_{12}$ (**I**)	−2485.67615	13.2	1.78
$C_{48}N_{12}$ (**II**)	−2485.69722	0.0	2.74
$C_{48}P_{12}$ (**I**)	−5925.01444	78.7	2.08
$C_{48}P_{12}$ (**II**)	−5925.13990	0.0	3.50
$C_{48}B_{12}$ (**I**)	−2127.03368	25.9	1.34
$C_{48}B_{12}$ (**II**)	−2127.07491	0.0	1.60
$C_{48}Si_{12}$ (**I**)	−5302.36899	81.3	1.23
$C_{48}Si_{12}$ (**II**)	−5302.49856	0.0	1.28

RESULTS AND DISCUSSION

Table 1 summarizes the relative energies for the two sets of $C_{48}X_{12}$ isomers and clearly shows that independent of the heteroatom, X, isomer **II** is more stable than isomer **I**. The smallest energy difference between these two isomers (13.2 kcal mol^{-1}) is found for $C_{48}N_{12}$, which agrees with the literature data.[8] Much larger differences are found for $C_{48}P_{12}$ (78.7 kcal mol^{-1}) and $C_{48}Si_{12}$ (81.3 kcal mol^{-1}), while $C_{48}B_{12}$ has a relative isomer energy (25.9 kcal mol^{-1}) intermediate between nitrogen- and silicon-doped systems. The higher chemical stability of isomer **II** than isomer **I** is in line with the larger HOMO–LUMO of **II**. Thus isomer **II** is both thermodynamically and kinetically more stable than isomer **I**, despite the greater repulsive interactions among the heteroatoms.

Manaa *et al.*[8] proposed that the higher stability of $C_{48}N_{12}$ (**II**) is due to the extended local aromaticity of the eight all-carbon hexagon rings in the triphenylene units. This suggestion is confirmed by the NICS values of −11.8 and −1.2 ppm (Table 2) at the centers of the peripheral and central hexagonal rings (Fig. 1). The values for triphenylene are −10.8 and −3.0 ppm at the GIAO-HF/6–31+G*//B3LYP/6–31G* level[10a] (−8.7 and −2.8 ppm at GIAO-B3LYP/3–21G//B3LYP/6–31G*; −9.5 and −2.9 ppm at GIAO-HF/3–21G//B3LYP/6–31G*). The strong aromaticity in the peripheral rings and the weak aromaticity in the central ring indicated by NICS values are also supported by the structural data as given in Table 3. The harmonic oscillator model of aromaticity (HOMA),[13] a reliable quantitative aromaticity measure based on geometric criteria, also was employed to analyze the aromaticity of the benzene-like subunits. The HOMA values, listed in Table 2, correlate strongly with the NICS results. Thus, the 18 π-electrons in each triphenylene unit are distributed to give the outer rings a benzene-like

Table 2. B3LYP/3–21G and HF/3–21G (in parentheses) NICS values at the cage and ring centers, including benzene-like ring HOMA indices (*italics*) (geometries B3LYP/6–31G* optimized)

	Center	A	B	C	D	E	F
$C_{48}N_{12}$ (**I**)	0.6 (−4.5)	−8.2 (−12.0) *0.860*	3.1 (1.3)	−8.1 (−10.1)	−12.0 (−14.4)	−1.6 (−4.3)	1.3 (−1.0)
$C_{48}N_{12}$ (**II**)	−5.8 (−10.4)	−1.2 (−3.1) *0.374*	−11.8 (−15.8) *0.853*	−9.2 (−10.5)	−10.9 (−12.8)	0.8 (−0.9)	−1.4 (−3.3)
$C_{48}P_{12}$ (**I**)	−3.8 (−5.6)	−6.2 (−8.1) *0.904*	−1.3 (−1.2)	−2.2 (−3.0)	−1.3 (−2.6)	−0.9 (−1.4)	−3.8 (−4.3)
$C_{48}P_{12}$ (**II**)	−8.6 (−10.9)	−6.9 (−8.5) *0.403*	−9.6 (−11.5) *0.715*	0.2 (−0.3)	−1.9 (−2.5)	−2.7 (−3.6)	−1.1 (−1.5)
$C_{48}B_{12}$ (**I**)[a]	12.1	7.7 *0.723*	8.8	11.4	5.0	10.3	9.9
$C_{48}B_{12}$ (**II**)	−0.9 (−5.9)	−5.9 (−8.3) *0.202*	−0.9 (−4.7) *0.540*	6.8 (5.0)	7.3 (6.3)	5.5 (4.1)	4.1 (2.0)
$C_{48}Si_{12}$ (**I**)	0.2 (−6.6)	1.9 (−3.0) *0.565*	−0.7 (−2.6)	10.4 (7.1)	6.6 (4.5)	−1.5 (−3.4)	−0.1 (−1.6)
$C_{48}Si_{12}$ (**II**)	−4.6 (−8.8)	−2.9 (−4.7) *0.074*	−4.0 (−6.2) *0.493*	8.9 (7.5)	2.4 (1.6)	0.3 (−0.8)	−4.1 (−5.2)

[a] The HF wavefunction is unstable.

Table 3. B3LYP/6–31G* optimized bond lengths (Å) (see Fig. 1)

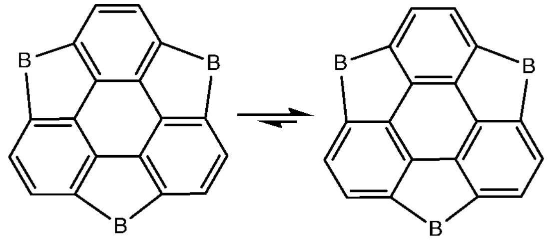
	a	*b*	*c*	*d*	*e*	*f*	*g*
$C_{48}N_{12}$ (**I**)	1.406	1.416					
$C_{48}N_{12}$ (**II**)	1.448	1.424	1.401	1.402	1.418	1.403	1.413
$C_{48}P_{12}$ (**I**)	1.402	1.412					
$C_{48}P_{12}$ (**II**)	1.454	1.405	1.432	1.395	1.441	1.376	1.426
$C_{48}B_{12}$ (**I**)	1.401	1.433					
$C_{48}B_{12}$ (**II**)	1.466	1.401	1.454	1.399	1.441	1.387	1.445
$C_{48}Si_{12}$ (**I**)	1.401	1.445					
$C_{48}Si_{12}$ (**II**)	1.472	1.402	1.457	1.417	1.449	1.389	1.436

sextet, and the number of the π sextets is maximized. Such an aromaticity pattern in the triphenylene unit is consistent with the well-known Clar rule for polycyclic aromatic hydrocarbons.[14]

$C_{48}N_{12}$ (**I**) also has all-carbon and heterocyclic [A, C and D in Fig. 1(a)] rings which are aromatic on the basis of NICS (−8.2, −8.1 and −12.0 ppm, respectively) and structural data (Tables 2 and 3). However, $C_{48}N_{12}$ (**II**) has much stronger global aromaticity than $C_{48}N_{12}$ (**I**), as assessed by the NICS value at the cage center of −5.8 and 0.6 ppm, respectively. Thus, the decisive factor for the higher stability of **II** is not only the local aromaticity in the triphenylene units, but also the global aromaticity in the whole system.

These conclusions hold true for other heterofullerenes studied in this work, although subtle differences do exist. For example, with Si atoms located above the average surface, optimized $C_{48}Si_{12}$ isomers are severely distorted from the ideal spherical shape and the aromaticity of the hexagonal carbon rings is extinguished or significantly diminished. Because of the inherently pyramidal phosphorus systems which result in much higher stability of heterofullerene $P_8(C{=}C)_6$ than $N_8(C{=}C)_6$,[15] $C_{48}P_{12}$ has an even more serious distortion than $C_{48}N_{12}$. However, the aromatic pattern found in $C_{48}N_{12}$ survives in $C_{48}P_{12}$. Another point of interest is the NICS patterns in the A and B rings of the $C_{48}B_{12}$ heterofullerenes. The all-carbon hexagonal isomer **I** central A ring is weakly paratropic (7.7 ppm) owing to the electron deficiency of the neighboring boron atoms. In contrast, isomer **II**, which has the A ring at the center of a triphenylene unit, has unexpectedly weakly diatropic central hexagon and non-aromatic peripheral rings. Hence, in contrast to the case in other heterofullerenes with maximal (three) π sextets per unit, the triphenylene moiety in $C_{48}B_{12}$ (**II**) has only one π sextet, and can be designated as an '*anti*-Clar' moiety, with *peri*-fused anti-aromatic four-electron five-membered heterocyclic rings (Fig. 2). The parent $C_{18}B_3H_9$ system (C_{3v}, Fig. 3), a bowl-shaped structure at the B3LYP/6–31G* level, is a local minimum. The NICS results in Fig. 3 show that such an *anti*-Clar pattern persists, suggesting that the Clar structure can be modified, or even reversed, by annelating *anti*-aromatic rings.

The NICS values at the Hartree–Fock (HF) level were also computed and are included in Table 2. Chemical shift values at fullerene cage centers also can be assessed by endohedral ^{3}He NMR.[16] Previous experience indicates that the experimental endohedral helium chemical shifts of neutral fullerenes can be reproduced reasonably well (within ca 2–3 ppm) at the GIAO-HF/3–21G level[17] (systematic DFT level computations have not been reported yet). Therefore, the NICS values at the cage centers reported in Table 2 may be useful guides for future experimental probes of the internal electronic environment of $C_{48}X_{12}$ heterofullerenes using endohedral



(**A**) (**B**)

Figure 2. Clar and *anti*-Clar Kekulé substructure in $C_{48}B_{12}$ (**II**)

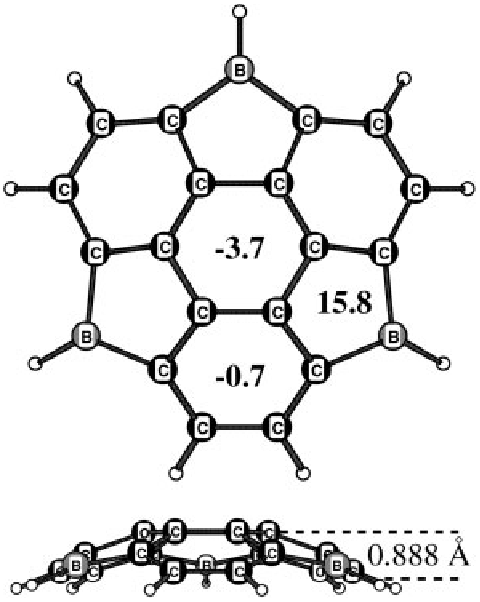


Figure 3. The $C_{18}B_3H_9$ (C_{3v}) B3LYP/6–31G* geometry and NICS values

chemical shifts. As in smaller fullerenes[18] (for statistical analysis, see Ref. 23), the NICS values at the center of $C_{48}X_{12}$ cages tend to be more positive at the B3LYP than at the HF level. Further theoretical work is still required to elucidate electron correlation effects on such endohedral chemical shifts.[19]

A correlation has been found between the isomeric preferences of heterofullerene and fullerene additions with sterically hindered addends.[4a–e] Does the aromatic stabilization in heterofullerenes, as deduced above, also exist in fullerene adducts? Fullerene adducts with large addends, such as $C_{60}Cl_{12}$,[20a] $C_{60}Ph_{12}$[20b] and $C_{60}Me_{12}$,[20c] have been synthesized, but the structures have not been characterized. Theoretically, an essentially kinetic sequential π-electronic model has been developed by Rogers and Fowler[21] to predict radical additions to fullerenes, and the structure of $C_{60}Cl_{12}$ (**III**) has been predicted. Clare and Kepert[23] found that the two most stable $C_{60}Cl_{12}$ isomers follow thermodynamic sequences and either have two opposite skew pentagonal pyramids (**IV**, C_{2h} symmetry) or have the same pattern as in isomer **I** of heterofullerenes.

We performed semiempirical MNDO computations on **I** and **II** (based on the positions shown in Fig. 1) and on the $C_{60}Cl_{12}$ isomers in Fig. 4: the kinetically preferred **III** and the thermodynamically favored structure **IV**, discussed above, and also the two C_2 symmetrical isomers (**V** and **VI**) with two antipodal pentagonal pyramid moieties. Both **V** and **VI** are based on the most stable $C_{60}Me_{12}$ structures computed semiempirically.[20c] The satisfactory performance of semiempirical methods (MNDO, AM1 and PM3) in computational fullerene chemistry has been validated recently.[23] Our MNDO results show that isomer **II** has the lowest energy: it is not only 34.4 kcal mol^{-1} more stable than **I** but also it is more favorable by ca 6 kcal mol^{-1} than structure **IV**, claimed to have the lowest energy earlier.[22] Isomers **V** and **VI** are ca 6 kcal mol^{-1} less stable than **II**, as is the kinetically preferred isomer **III** (by 14 kcal mol^{-1}). Thus, $C_{60}Cl_{12}$ (**II**), which preserves the extended aromaticity as in the heterofullerenes, is more favorable thermodynamically than the best structural candidates proposed formerly.

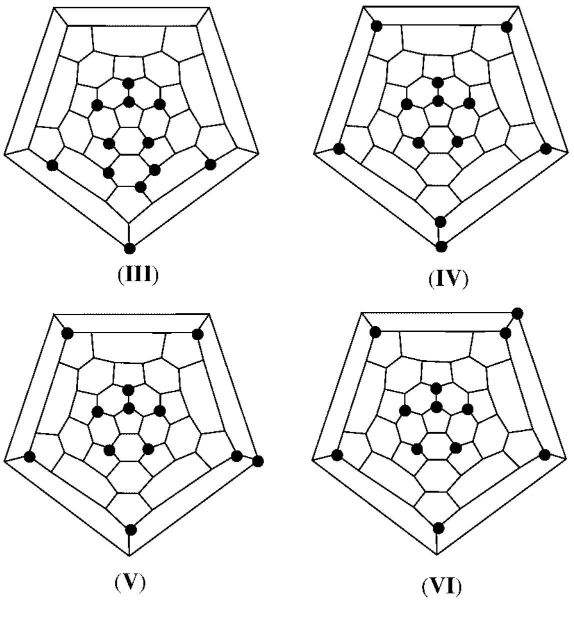

(III) (IV)
(V) (VI)

Figure 4. $C_{60}Cl_{12}$ isomers (also see Fig. 1)

Table 4. ^{13}C NMR spectra of $C_{48}X_{12}$ (X = N, P, B, Si) isomers computed at the GIAO-B3LYP/3–21G//B3LYP/6–31G* level (ppm)

$C_{48}N_{12}$ (**I**)	$C_{48}N_{12}$ (**II**)	$C_{48}P_{12}$ (**I**)	$C_{48}P_{12}$ (**II**)
113.9	115.4	100.1	139.0
116.6	126.2	124.0	139.7
119.6	131.6	131.6	140.2
128.2	138.1	132.4	142.8
131.5	139.5	141.0	146.0
131.6	141.8	145.2	148.9
136.1	150.4	150.0	155.7
140.8	150.0	150.4	153.3
NMR span—			
26.9	34.6	50.3	14.3

$C_{48}B_{12}$ (**I**)	$C_{48}B_{12}$ (**II**)	$C_{48}Si_{12}$ (**I**)	$C_{48}Si_{12}$ (**II**)
151.7	149.6	150.9	131.5
161.1	151.9	153.2	138.9
161.7	155.5	155.1	145.1
165.8	156.5	159.2	158.6
167.0	161.4	160.6	161.4
168.3	162.0	166.5	165.2
173.5	164.7	187.3	170.7
189.8	185.7	188.7	191.8
NMR span—			
38.1	36.1	37.8	60.3

NMR spectroscopy is a powerful technique for structure elucidation. Table 4 summarizes the computed ^{13}C NMR spectra at the GIAO-B3LYP/3–21G//B3LY/6–31G* level. Both isomers have eight independent carbon atoms and there are eight ^{13}C NMR peaks with equal intensities. These computed NMR spectra, and especially the span of NMR chemical shifts, may be useful for the characterization of these heterofullerenes.

CONCLUSION

Although aromaticity does not necessarily parallel energy (since other factors such as strain and topological charge stabilization also can be important),[10b,24] aromaticity stabilizes $C_{48}X_{12}$ (X = N, B, P, Si) heterofullerenes significantly. The aromatic stabilization in isomer **II**, which is due not only to the aromatic triphenylene units, but also to the global aromaticity in the whole heterofullerene system, preponderates over the unfavorable repulsive interactions between heteroatoms. In addition to the principle that the repulsive interactions between heteroatoms should be minimized, this study shows that aromatic stabilization must be taken into account to predict the most stable isomers of heterofullerenes. The same is true for the isomers of fullerene adducts such as $C_{60}Cl_{12}$.

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