BN-Doped Fullerenes: An NICS Characterization

Zhongfang Chen,[†,‡] Haijun Jiao,[†,§] Andreas Hirsch,*,[†] and Walter Thiel*,[‡]

Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42,
91054 Erlangen, Germany, Max-Planck-Institut für Kohlenforschung,
45466 Mülheim an der Ruhr, Germany, and Laboratoire de Chimie du Solide et Inorganique Moléculaire,
UMR CNRS 6511, Université de Rennes 1, 35042 Rennes Cedex, France

thiel@mpi-muelheim.mpg.de

Received November 28, 2000

Heterofullerenes $C_{58}(BN)$, $C_{54}(BN)_3$, $C_{48}(BN)_6$, and $C_{12}(BN)_{24}$ and their hexaanions as well as the $C_{58}(BN)$ dimer have been investigated by ab initio calculations. On the basis of the computed nucleus independent chemical shifts (NICS) at the cage center and also at the center of individual rings, BN-doped fullerenes $C_{58}(BN)$, $C_{54}(BN)_3$, and $C_{48}(BN)_6$ are slightly more aromatic than C_{60}, whereas the corresponding hexaanions are significantly less aromatic than $C_{60}{}^{6-}$. The predicted NICS values may be useful for the identification of the heterofullerenes through their endohedral ^{3}He NMR chemical shifts. Compared to C_{60}, the dimerization of $C_{58}(BN)$ is calculated to be more exothermic by 16 kcal/mol.

Introduction

Heterofullerenes are fullerenes in which one or more cage carbon atoms are replaced by heteroatoms. The recent synthesis and characterization of such cages have attracted much interest, since their chemical and physical properties are expected to be tunable for potential application as new materials.[1−3] The boron- and nitrogen-substituted fullerenes, such as $C_{58}(BN)$ and $C_{56}(BN)_2$, are especially intriguing due to their isoelectronic relationship to C_{60}. Theoretical studies have been carried out for selected $C_{58}BN$ isomers[4−12] and for the most stable isomers of the $C_{58}(BN)$, $C_{56}(BN)_2$, and $C_{54}(BN)_3$ cages.[13] There is experimental evidence for the possible formation of such cages, [9,14,15] but an unambiguous identification of $C_{58}(BN)$ or other analogues has not yet been reported. This may be due to the fact that these heterofullerenes have the same mass as C_{60}, and their determination in mass spectra is therefore problematic.

Endohedral ^{3}He NMR chemical shifts have proven to be a useful tool for characterizing fullerenes and their derivatives; i.e., different fullerenes with an encapsulated ^{3}He nucleus have very distinct ^{3}He NMR chemical shifts.[16] For example, the range of endohedral $\delta(^3\mathrm{He})$ values extends from −6.3 (He@C_{60}) to −28.8 (He@C_{70}) for neutral fullerenes[16] and from −49 (He@$C_{60}{}^{6-}$) to 8.3 (He@$C_{70}{}^{6-}$) for hexaanions.[17] Derivatives normally show an increase in ^{3}He shielding with increasing number of addends.[18,19] Thus, it should also be possible to characterize heterofullerenes through their endohedral $\delta(^3\mathrm{He})$ values. Experimental ^{3}He NMR chemical shifts have been reproduced well by quantum chemical methods [18−20] so that computed $\delta(^3\mathrm{He})$ values may be useful to identify heterofullerenes.

In this paper, we present theoretical studies on the heterofullerenes $C_{58}(BN)$ (**1**), $C_{54}(BN)_3$ (**2**), $C_{48}(BN)_6$ (**3**), and $C_{12}(BN)_{24}$ (**4**) without B−B or N−N connections and their hexaanions (**1**$^{6-}$−**4**$^{6-}$) as well as the $C_{58}(BN)$ dimer (**5**) (Figure 1). Nucleus-independent chemical shifts (NICS),[21,22] calculated at the centers of the cage and of the individual rings, have been employed to evaluate the mobility of electrons on the cage surfaces. The NICS values at the cage center serve as predictions for the corresponding endohedral ^{3}He NMR chemical shifts.[20,23]

---

* To whom correspondence should be addressed (A.H., Universität Erlangen-Nürnberg) (W.T., Max-Planck-Institut für Kohlenforschung, Fax: +49 208 306 2996).

[†] Universität Erlangen-Nürnberg.

[‡] Max-Planck-Institut für Kohlenforschung.

[§] Université de Rennes 1.

(1) Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 1.

(2) Hirsch, A.; Nuber, B. *Acc. Chem. Res.* **1999**, *32*, 795.

(3) Reuther, U.; Hirsch, A. *Carbon* **2000**, *38*, 1539.

(4) Xia, X.; Jelski, D. A.; Bowser, J. R.; George, T. F. *J. Am. Chem. Soc.* **1992**, *114*, 6493.

(5) Bowser, J. R.; Jelski, D. A.; George, T. F. *Inorg. Chem.* **1992**, *31*, 154.

(6) Liu, J.; Gu, B.; Han, R. *Solid State Commun.* **1992**, *84*, 807.

(7) Rustagi, K. C.; Ramaniah, L. M.; Nair, S. V. *Int. J. Mol. Phys. B* **1992**, *6*, 3941.

(8) Kurita, N.; Kobayashi, K.; Kumabora, H.; Tago, K. *Phys. Rev. B.* **1993**, *48*, 4850.

(9) Piechota, J.; Byszewshi, P.; Jablonski, R.; Antonova, K. *Fullerene Sci. Technol.* **1996**, *4*, 491.

(10) Chen, Z.; Ma, K.; Chen, L.; Zhao, H.; Pan, Y.; Zhao, X.; Tang, A.; Feng, J. *THEOCHEM* **1998**, *452*, 219.

(11) Piechota, J.; Byszewski, P. *Z. Phys. Chem.* **1997**, *200*, 147.

(12) Esfarjani, K.; Ohno, K.; Kawazoe, Y. *Phys. Rev. B* **1994**, *50*, 17830.

(13) Chen, Z.; Ma, K.; Zhao, H.; Pan, Y.; Zhao, X.; Tang, A.; Feng, J. *THEOCHEM* **1999**, *466*, 127.

(14) Nakamura, T.; Ishikawa, K.; Yamamoto, K.; Ohana, T.; Fujiwara, S.; Koga, Y. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2631.

(15) Antonova, K.; Byshewski, P.; Zhizhin, G.; Piechota, J.; Marhevka, M. *Microchim. Acta* **1997**, *14*, 271.

(16) Saunders, M.; Cross, R. J.; Jimenez-Vazuez, H. A.; Schimshi, R.; Khong, A. *Science* **1996**, *271*, 1693.

(17) Shabtai, E.; Weitz, A.; Haddon, R. C.; Hoffman, R. E.; Rabinovitz, M.; Khong, A.; Cross, R. J.; Saunders, M.; Cheng, P. C.; Scott, L. T. *J. Am. Chem. Soc.* **1998**, *120*, 6389.

(18) Birkett, P. R.; Bühl, M.; Khong, A.; Saunders, M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2037.

(19) Bühl, M. *Chem. Eur. J.* **1998**, *4*, 734.

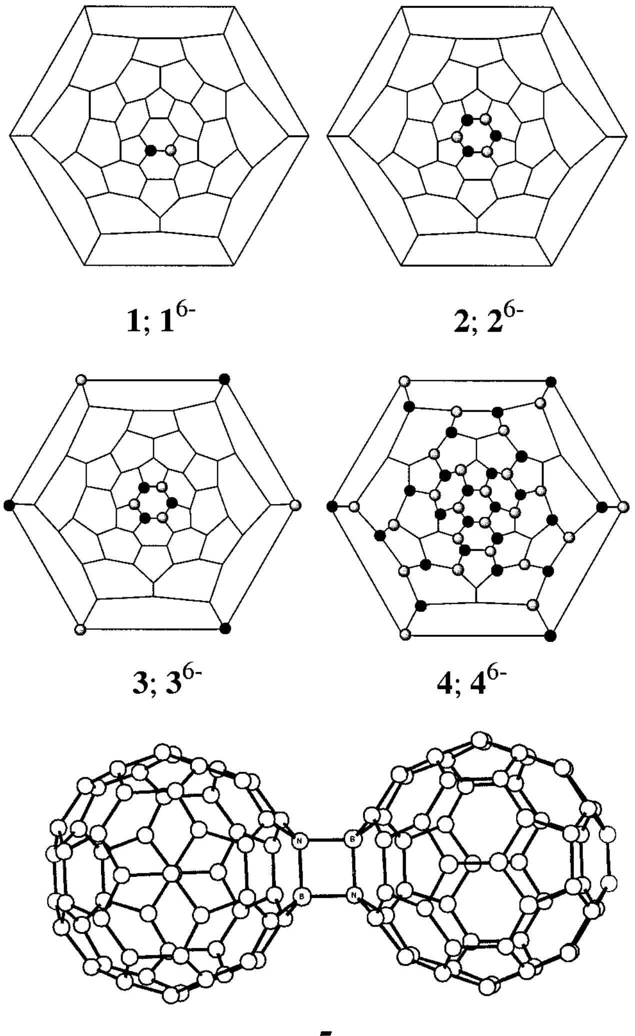
(20) Bühl, M.; Thiel, W.; Jiao, H.; Schleyer, P. v. R.; Saunders, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6005.

(21) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(22) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.

(23) Saunders, M.; Jimenez-Vazquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256.

10.1021/jo001672a CCC: $20.00



1; 1^{6-} **2; 2**$^{6-}$

3; 3^{6-} **4; 4**$^{6-}$

5

Figure 1. Structure of BN-doped fullerenes studied in this paper: solid circle, N; shaded circle, B.

2. Computational Details

Geometries were fully optimized in the given symmetry at the HF/6-31G* level (HF/3-21G for C_{60} and $C_{58}(BN)$ dimers to limit the computational costs). Nucleus independent chemical shifts (NICS, in ppm) were calculated by using the GIAO-SCF/3-21G method on the optimized structures. All calculations were done with the Gaussian 98 program.[24]

3. Results and Discussion

According to semiempirical AM1 and MNDO calculations,[13] cage **1** is the most stable structural isomer of $C_{58}BN$. The stability of the $C_{60-2x}(BN)_x$ heterofullerenes decreases with the increasing x ($x = 1-3$),[13] and thus, **1** may be the predominant species in the product mixture from the contact-arc method assuming that the reaction is controlled thermodynamically. Cage **2** is the most likely $C_{54}(BN)_3$ isomer in which the six carbon atoms of one hexagon are substituted by three alternating BN units to form the borazine-like ($B_3N_3H_6$) substructure. In cage **3**, there are two such substructures at opposite sides. Finally, cage **4** has as many as C_2 units replaced by BN as is possible without generating B−B and N−N connections.

Table 1. Computed NICS Values (ppm) at the Cage Centers

compd	symmetry	NICS[a,b]
C_{60}	I_h	−9.6 (−6.3)
$C_{58}(BN)$ (**1**)	C_s	−10.9
$C_{54}(BN)_3$ (**2**)	C_3	−12.0
$C_{48}(BN)_6$ (**3**)	S_6	−12.3
$C_{12}(BN)_{24}$ (**4**)	S_6	−7.8
$C_{60}{}^{6-}$	I_h	−56.7 (−48.7)
$C_{58}(BN)^{6-}$ (**1**$^{6-}$)	C_s	−25.3
$C_{54}(BN)_3{}^{6-}$ (**2**$^{6-}$)	C_3	−13.1
$C_{48}(BN)_6{}^{6-}$ (**3**$^{6-}$)	S_6	−44.1
$C_{12}(BN)_{24}{}^{6-}$ (**4**$^{6-}$)	S_6	−9.0
$(C_{60})_2$	D_{2h}	−11.4 (−8.8)
$(C_{58}(BN))_2$	C_{2h}	−11.6

[a] At GIAO-SCF/3-21G (in ppm). [b] Experimental ^{3}He NMR chemical shifts are given in parentheses.

The heterofullerenes $C_{58}(BN)$ (**1**), $C_{54}(BN)_3$ (**2**), and $C_{48}(BN)_6$ (**3**) are slightly more aromatic than C_{60} itself, and only $C_{12}(BN)_{24}$ (**4**) is less aromatic, as indicated by the calculated NICS values at the cage center (Table 1). For example, the NICS value in **2** (−12.0) is more diatropic than in C_{60} (−9.6). At first sight, this finding is counterintuitive, since the electrons in the BN unit are mainly localized on nitrogen as lone pair: borazine ($B_3N_3H_6$), which is often called "inorganic benzene", has a localized electronic structure and is nonaromatic,[25] and one may thus expect to get "localized" or "nonaromatic" fullerenes through stepwise B−N substitutions.

This issue can be resolved by considering the entire cage rather than only the substituted ring. It is well-known that C_{60} contains diatropic hexagons and paratropic pentagons,[26] with NICS values (SCF/3-21G) of −6.6 and +6.1 at the ring centers, respectively, and the corresponding ring currents combine to produce a relatively small NICS (−9.6) at the center of the C_{60} cage. As shown in Figure 2, the substitution of C_2 units by BN lowers the local NICS values as expected. For example, the borazine ring in $C_{54}(BN)_3$ (**2**) is indeed nonaromatic (+0.2), but the NICS values of the adjacent pentagons (+1.2) and hexagons (−4.6) are also decreased compared to C_{60}, especially for the pentagons. Thus, the borazine region in **2** has both reduced aromatic and anti-aromatic character. Moreover, the other six-membered rings in **2** without doping are slightly more aromatic than in C_{60}, while the other five-membered rings are slightly less anti-aromatic than in C_{60} (Figure 2). Therefore, BN-doping affects the whole cage, and the compensation between diatropic and paratropic ring currents yields a more negative NICS value in **2** than in C_{60}. Similar NICS patterns occur in the fullerene adduct $C_{60}H_2$.[19]

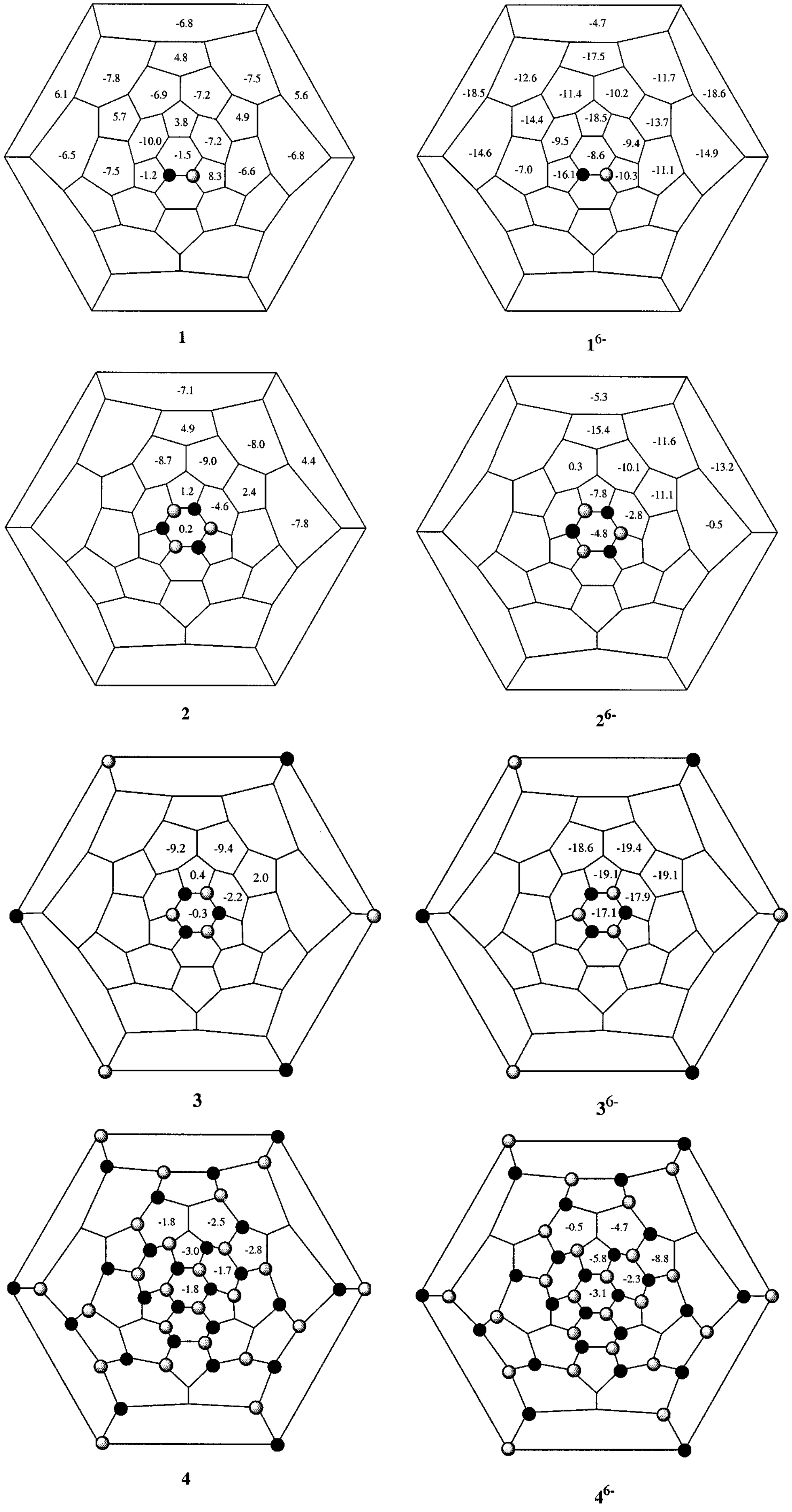
To analyze the effects of BN-doping further, a set of small reference molecules **6**−**20** have been calculated with the same approach. For some of these molecules (e.g., **6**, **7**, and **16**), similar NICS values at different theoretical levels have been reported previously.[21] As shown in Figure 3, borol **6** is less antiaromatic with NH_2

---

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(25) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669.

(26) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Science* **1992**, *257*, 1660.



1 $\mathbf{1}^{6-}$

2 $\mathbf{2}^{6-}$

3 $\mathbf{3}^{6-}$

4 $\mathbf{4}^{6-}$

Figure 2. NICS values of individual rings (values not shown are determined by symmetry) for BN-doped fullerenes and their hexaanions.

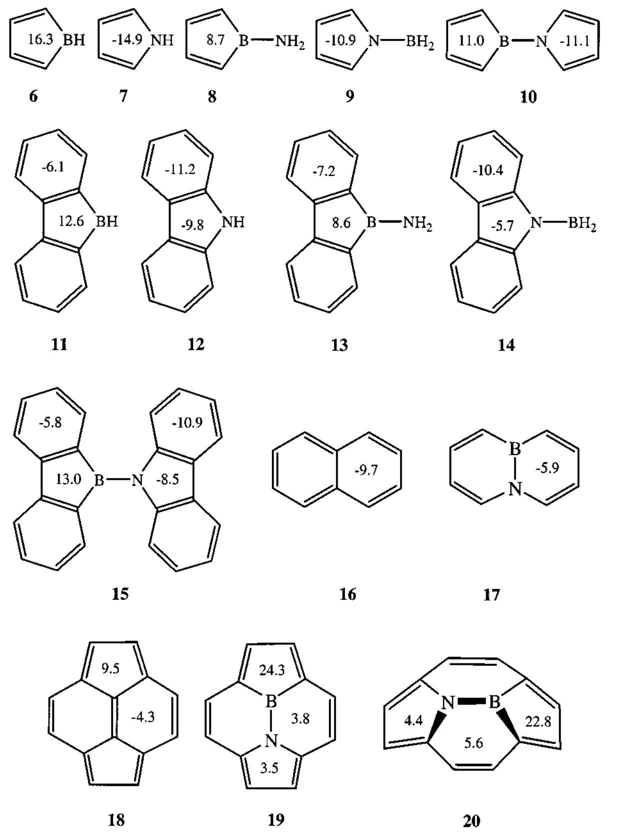


Figure 3. Small reference molecules and their NICS values at the ring centers (in ppm).

substitution (**8**), while pyrrole **7** is less aromatic under BH_2 substitution (**9**). The five-membered rings in **10** resemble those in **8** and **9** in character. Similar effects are found in the series (**11**−**15**) in which the five-membered rings are annelated with six-membered aromatic rings. The five-membered rings in **11** and **12** are less paratropic and diatropic than those in **6** and **7**. With BH_2 and NH_2 substitutions, the NICS values of the five-membered rings in **13** and **14** are reduced further in magnitude. However, the NICS values in **15** are closer to those in **11** and **12** than **13** and **14**. This indicates the less pronounced electronic coupling across the B−N linkage in **15** than in **10**.

In polycyclic conjugated systems, BN doping makes the hexagon in **17** (NICS = −5.9) less aromatic than in naphthalene **16** (NICS = −9.7), due to the localized nitrogen lone pair on the ring perimeter. Even more pronounced changes are found when going from **18** to **19**, most probably because of the predominant resonance contribution from the antiaromatic[12]annulene perimeter in **19**. The artificially curved molecule $C_{12}BNH_8$ (**20**), which corresponds to a fragment of $C_{58}BN$ (**1**), shows essentially the same NICS pattern as planar **19**.

As expected on the basis of the calculated NICS values (Table 1), the measured chemical shift of encapsulated ^3He changes dramatically when six electrons are added to C_{60} (from −6.3 to −48.7 ppm).[17] The NICS values of the hexaanions $\mathbf{1}^{6-}$−$\mathbf{4}^{6-}$ at the cage center are generally less negative than those computed for C_{60}^{6-} and for the isoelectronic neutral $C_{54}N_6$ isomers.[27]

The NICS value of $\mathbf{1}^{6-}$ is about only half of C_{60}^{6-}, while $\mathbf{2}^{6-}$ and $\mathbf{4}^{6-}$ have nearly the same values as their neutral counterparts. Only $\mathbf{3}^{6-}$ exhibits a highly negative NICS value in this series, which is probably due to a rather even distribution of the negative charges as in the case of C_{60}^{6-}. The detailed differences of $\mathbf{1}^{6-}$−$\mathbf{4}^{6-}$ are also reflected by the local NICS values at the centers of the five- and six-membered rings. While the NICS values at the present level are the same for both types of rings in C_{60}^{6-} (−23.6), they are significantly reduced and quite individual in $\mathbf{1}^{6-}$−$\mathbf{4}^{6-}$. This demonstrates again the localization effects of the nitrogen lone pair around the cage perimeter.

Recently, the [2 + 2]-type C_{60} dimer, $(C_{60})_2$, has been synthesized and characterized.[28] The present ab initio calculations at the HF/3-21G level indicate that the [2 + 2] dimerizations of both C_{60} and $C_{58}(BN)$ are exothermic and that the binding energy (evaluated from the difference ΔE of the corresponding total energies) is larger for the $C_{58}(BN)$ dimer by 16.3 kcal/mol. The decomposition of the dimer into two monomers, which is quite facile in the case of $(C_{60})_2$,[28] should thus require more activation for $(C_{58}(BN))_2$.

$$2C_{60} \rightarrow (C_{60})_2 \quad \Delta E = -10.6 \text{ kcal/mol}$$

$$2C_{58}(BN) \rightarrow (C_{58}(BN))_2 \quad \Delta E = -26.9 \text{ kcal/mol}$$

The computed endohedral helium chemical shift of $(C_{60})_2$, −11.4 ppm, agrees well with the experimental value of −8.8 ppm,[28] and the helium is more shielded in the dimer $(C_{60})_2$ than in the monomer (computed change −1.8 ppm, observed −2.5 ppm). The same trend holds true for $C_{58}(BN)$ but is less pronounced: the endohedral helium chemical shift is computed to be −11.6 ppm for the dimer and −10.9 ppm for the monomer.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (DFG). We thank the Alexander von Humboldt Foundation (Z.C.) and Centre National de la Recherche Scientifique (H.J.) for research fellowships. We also thank Dr. M. Bühl for helpful discussions.

JO001672A

---

[27] Bühl, M. *Chem. Phys. Lett.* **1995**, *242*, 580.

[28] Komatsu, K.; Wang, G. W.; Murata, Y.; Tanaka, T.; Fujiwara, K.; Yamamoto, K.; Saunders, M. *J. Org. Chem.* **1998**, *63*, 9358.