

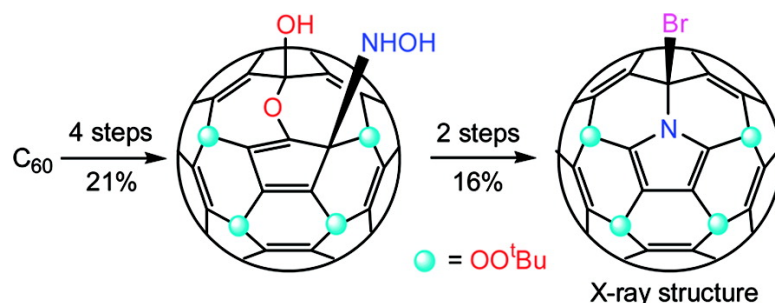
Communication

Preparation of Azafullerene Derivatives from Fullerene-Mixed Peroxides and Single Crystal X-ray Structures of Azafulleroid and Azafullerene

Gaihong Zhang, Shaohua Huang, Zuo Xiao, Quan Chen, Liangbing Gan, and Zheming Wang

J. Am. Chem. Soc., **2008**, 130 (38), 12614-12615 • DOI: 10.1021/ja805072h • Publication Date (Web): 29 August 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Preparation of Azafullerene Derivatives from Fullerene-Mixed Peroxides and Single Crystal X-ray Structures of Azafulleroid and Azafullerene

Gaihong Zhang,[†] Shaohua Huang,[†] Zuo Xiao,[†] Quan Chen, Liangbing Gan,^{*,†,‡} and Zheming Wang^{*,†}

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

Received July 2, 2008; E-mail: gan@pku.edu.cn; zmw@pku.edu.cn

Heterofullerenes are formed by replacing fullerene cage carbons with other noncarbon atoms. The chemistry of heterofullerenes is still a very young discipline within synthetic organic chemistry.¹ So far, it is still restricted to azafullerene. In 1992, a number of C_nN_m clusters were reported by contact-arc vaporization in a partial N_2 or NH_3 atmosphere and by reactive collision scattering of N^+ with C_{60} .² However, none of these species have been isolated or structurally characterized. In 1995 Mattay³ and Hirsch⁴ discovered independently that certain nitrogen containing fullerene derivatives generate azafullerenium such as $C_{59}N^+$ and $C_{69}N^+$ in the gas phase. In the same year, Wudl⁵ accomplished the first synthesis of azafullerene $RC_{59}N$ and the dimer $(C_{59}N)_2$ in bulk quantities using a ketolactam fullerene derivative. Shortly afterward, Hirsch⁶ also succeeded in the bulk preparation of $RC_{59}N$ and $(C_{59}N)_2$ using a bisazafulleroid precursor. The methods have been used widely to prepare azafullerene derivatives for various purposes.⁷

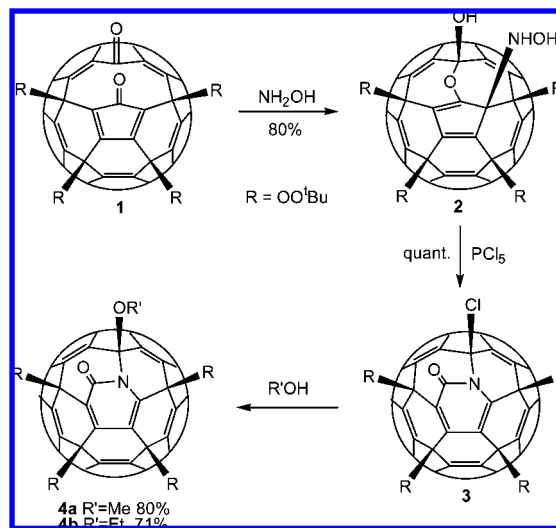
We have reported the synthesis of a number of fullerene mixed peroxides⁸ through the addition of *tert*-butylperoxy radicals to C_{60} . Recently several oxahomofullerenes and cage-opened oxafulleroids⁹ such as **1** were prepared starting from these fullerene-mixed peroxides. Here we report the preparation of azafullerene derivatives.

Compound **1** was prepared from C_{60} in three steps as previously reported.^{9b} Treatment of **1** with aqueous NH_2OH solution resulted in coupling of the carbonyl groups and formation of compound **2** with a hemiacetal moiety (Scheme 1). The hydroxylamino adduct **2** reacted with commercial PCl_5 to give azafulleroid **3** under anhydrous conditions. The purity of PCl_5 greatly effects the yield of compound **3**. Freshly sublimed PCl_5 was too reactive and resulted in other byproduct. In an effort to grow crystals of **3**, the added alcohol replaced the chlorine atom efficiently to form the analogous compounds **4**.

Compound **3** is an excellent precursor for the preparation of azafullerenes. Silica gel purification could partially convert **3** into the azafullerene **5**. Later we found that basic alumina gave complete conversion. Treating **5** with Br_2 led to the bromo analogue **6**. The bromo adduct **6** could be changed to the hydroxyl adduct **7** by silver perchlorate. Amines such as benzyl amine and *n*-butyl amine converted **3** directly to the hydroxyl azafullerene **7**.

Spectroscopic data are in agreement with the structures depicted in Schemes 1 and 2. The 1H NMR spectrum of **5** showed a singlet signal corresponding to the fullerenyl hydrogen at 6.59 ppm. There are 28 peaks for the sp^2 fullerene skeleton carbons ranging from 129.22 to 150.64 ppm in the ^{13}C NMR spectrum, which is consistent with the C_s symmetry. The DEPT spectrum confirmed that the peak

Scheme 1. Formation of Azafulleroids



at 60.33 ppm corresponds to the sp^3 carbon atom connected to the hydrogen. In the ^{13}C NMR of the C_1 symmetric **3**, there are 55 peaks for the sp^2 carbons ranging from 110.52 to 168.45 ppm and five sp^3 peaks ranging from 79.30 to 94.21 ppm. The FTIR spectrum of **3** shows a strong peak at 1773 cm^{-1} due to the lactam carbonyl group. This is much bigger than the $C=O$ stretching band (1727 cm^{-1}) for the first cage-opened keto-lactam fullerene derivative reported by Wudl et al.¹⁰ ESI-MS of the new compounds showed expected molecular signals.

Single crystals were obtained for both **4b** and **6** by slow evaporation of a CS_2 /ethanol solution at $5\text{ }^\circ\text{C}$. The X-ray structures at 200 K are in agreement with the NMR derived assignments (Figure 1). The carbonyl group in **4b** is located above the cage surface and tilted toward the seven-membered ring. The local structure of the carbonyl group is reminiscent of the ring-opened 5,6-methano-bridged fullerene derivatives (homofullerenes). The seven-membered ring shows a great amount of strain as indicated by its relatively long bond distances.

Similar to the solution phase structure, a mirror plane is present bisecting the molecule in the X-ray structure of **6**. The *tert*-butylperoxy groups were frozen at their most favored configuration. The pyrrole moiety is not completely planar. The dihedral angle of the pyrrole plane ($N-C-C$) is 0.8° , and the bonding distances range from 1.363 to 1.424 \AA within the pyrrole ring. The shortest double bonds (1.350 \AA) are those located on the outer perimeter of the azacorannulene subunit. The structure of **6** is analogous to the azafullerene derivative $Cl_4ArC_{59}N$ reported by Hirsch et al.⁷ An

[†] Peking University.

[‡] Chinese Academy of Sciences.

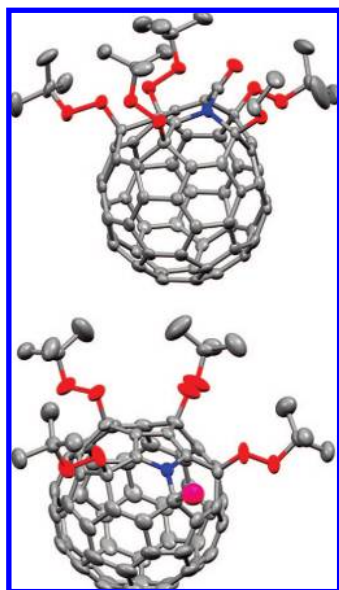
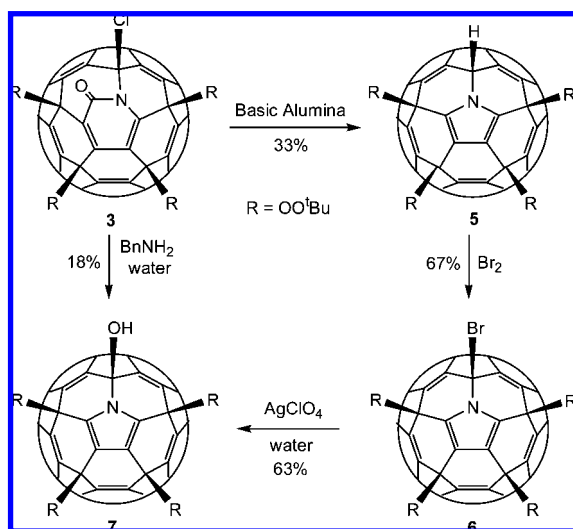


Figure 1. Single crystal structures of **4b** (above) and **6** (below). Ellipsoids were drawn at 50% level. For clarity hydrogen atoms were omitted. Color scheme: gray = C; red = O; blue = N; magenta = Br.

Scheme 2. Formation of Azafullerenes



AM1 calculation on the tetrachlorinated azafullerene^{7a} revealed bonding distances similar to those of **6**. To our knowledge, the structure of **6** appears to be the first well-resolved single crystal structure of azafullerene.¹¹

Mechanisms for the formation of azafulleroid **3** and azafullerenes are not clear at present. In the reaction of **2** with PCl_5 , a nitronium ion is probably formed from heterolysis of the hydroxylamino N–OH bond, which initiates the rearrangement leading to the lactam moiety of **3**. The main driving force for the loss of lactam

CO from **3** should be steric strain, as indicated by the above X-ray structure of the analogue **4b**. The process is reminiscent of the mechanism proposed by Wudl et al. for their azafullerene formation reaction.⁵ In the Wudl mechanism, a fullerene ketolactam precursor is converted to an azafullerene ion C_{59}N^+ by loss of the lactam CO group.

In summary, azafullerene was prepared by addition of hydroxylamine to cage-opened fullerene derivatives and subsequent PCl_5 induced rearrangement. The new method reported here produces azafullerene derivatives with peroxide addends, which may be used for further skeleton modification. Work is in progress to study mechanisms of the reactions and to prepare other heterofullerenes such as diazafullerenes.

Acknowledgment. Financial support is provided by NNSFC Grants 20632010, 20521202, and 20472003), the Ministry of Education of China, and the Major State Basic Research Development Program (2006CB806201).

Supporting Information Available: Experimental procedure and spectroscopic data for new compounds and cif files for compounds **4b** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191. (b) Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 93.
- (2) (a) Pradeep, T.; Vijayakrishnan, V.; Santra, A. K.; Rao, C. N. R. *J. Phys. Chem.* **1991**, *95*, 10564. (b) Christian, J. F.; Wan, Z.; Anderson, S. L. *J. Phys. Chem.* **1992**, *96*, 10597.
- (3) (a) Averdung, J.; Luftmann, H.; Schlachter, I.; Mattay, J. *Tetrahedron* **1995**, *51*, 6977. (b) Mattay, J.; Torres-Garcia, G.; Averdung, J.; Wolff, C.; Schlachter, I.; Luftmann, H.; Siedschlag, C.; Luger, P.; Ramm, M. *J. Phys. Chem. Solids* **1997**, *58*, 1929.
- (4) Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grosser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257.
- (5) (a) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554. (b) Keshavarz, K. M.; Gonzalez, R.; Hicks, R. G.; Srdanov, G.; Collins, T. G.; Hummelen, J. C.; Bellavia-Lund, C.; Pavlovich, J.; Wudl, F.; Holczler, K. *Nature* **1996**, *383*, 147.
- (6) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421.
- (7) (a) Reuther, U.; Hirsch, A. *Chem. Commun.* **1998**, 1401. (b) Tagmatarchis, N.; Shinohara, H.; Pichler, T.; Krause, M.; Kuzmany, H. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2361. (c) Vougioukalakis, G. C.; Orfanopoulos, M. *J. Am. Chem. Soc.* **2004**, *126*, 15956. (d) Hauke, F.; Vostrowsky, O.; Hirsch, A.; Quaranta, A.; Leibl, W.; Leach, S.; Edge, R.; Navaratnam, S.; Bensasson, R. V. *Chem.—Eur. J.* **2006**, *12*, 4813.
- (8) (a) Gan, L. B.; Huang, S. H.; Zhang, X.; Zhang, A. X.; Cheng, B. C.; Cheng, H.; Li, X. L.; Shang, G. *J. Am. Chem. Soc.* **2002**, *124*, 13384. (b) Gan, L. B. *Pure Appl. Chem.* **2006**, *784*, 841. (c) Gan, L. B. *Chimie* **2006**, *9*, 1001.
- (9) (a) Huang, S. H.; Xiao, Z.; Wang, F. D.; Zhou, J.; Yuan, G.; Zhang, S. W.; Chen, Z. F.; Thiel, W.; Schleyer, P. R.; Zhang, X.; Hu, X. Q.; Chen, B. C.; Gan, L. B. *Chem.—Eur. J.* **2005**, *11*, 5449. (b) Huang, S. H.; Wang, F. D.; Gan, L. B.; Yuan, G.; Zhou, J.; Zhang, S. W. *Org. Lett.* **2006**, *8*, 277. (c) Xiao, Z.; Yao, J. Y.; Yang, D. Z.; Wang, F. D.; Huang, S. H.; Gan, L. B.; Jia, Z. S.; Jiang, Z. P.; Yang, X. B.; Zheng, B.; Yuan, G.; Zhang, S. W.; Wang, Z. M. *J. Am. Chem. Soc.* **2007**, *129*, 16149.
- (10) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003.
- (11) Disorder in the single crystal X-ray structure of the azafullerene cation $[\text{C}_{59}\text{N}^+][\text{Ag}(\text{CB}_{11}\text{H}_6\text{Cl}_6)^2]^-$ prevented accurate bond length data from being obtained for C_{59}N^+ ; see: Kim, K.-C.; Hauke, F.; Hirsch, A.; Boyd, P. D. W.; Carter, E.; Armstrong, R. S.; Lay, P. A.; Reed, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 4024.

JA805072H