

Capturing the Labile Fullerene[50] as $C_{50}Cl_{10}$

Su-Yuan Xie,^{1*} Fei Gao,¹ Xin Lu,¹ Rong-Bin Huang,¹
Chun-Ru Wang,² Xu Zhang,³ Mai-Li Liu,³ Shun-Liu Deng,¹
Lan-Sun Zheng¹

All carbon cages (fullerenes) synthesized so far, such as C_{60} and its larger homologs, faithfully satisfy the isolated pentagon rule (IPR) (1), which governs the stability of fullerenes comprising hexagons and exactly 12 pentagons. The smaller non-IPR fullerenes (2–9), which are predicted to have unusual properties because of their adjacent pentagons and high curvature (2–8), are so labile that their properties and reactivity have only been studied in the gas phase (1–3). Experimental efforts directed at their bulk synthesis have produced some results (4–6), but complete structural characterization is still under way (7). Here we report the synthesis in milligram quantity of a small non-IPR fullerene C_{50} , a long-sought little sister of C_{60} (1, 3, 8, 9), through the introduction of chlorine in the form of carbon tetrachloride (CCl_4) during synthesis from graphite.

C_{50} -containing soot (~90 g) was synthesized in a modified graphite arc-discharge process (10) in which 0.013 atm of CCl_4 was added to 0.395 atm of helium. The products in the toluene extract from the soot were isolated with multistage high-performance liquid chromatography (11), and ~2 mg of $C_{50}Cl_{10}$ with 99.5% purity was obtained. The $C_{50}Cl_{10}$ thus obtained is moderately soluble in some organic solvents, e.g., carbon disulfide, toluene, and benzene, as a lemon yellow-colored solution.

The comparable mass spectra from the experiment and a simulation prove the molecular formula of the isolated substance to be $C_{50}Cl_{10}$ (Fig. 1, A and B). ^{13}C nuclear magnetic resonance (NMR) measured in deuterated benzene shows four distinct signals located at 161.5, 146.6, 143.0, and 88.7 parts per million (Fig. 1C) (11). The former three signals are characteristic of sp^2 -hybridized carbons, whereas the latter one is typical of sp^3 -hybridized carbons bonded to chlorine. Among numerous possible structures in the C_{50} isomer family (3, 9), only the D_{5h} fullerene[50] has four unique types of carbon atoms (I to IV, as illustrated in Fig. 1D). The 10 Cl atoms should add to the most reactive C_{IV} sites (that is, to pentagon-pentagon vertex fusions), producing a decachlorofullerene[50] molecule (Fig. 1D). Indeed, the simulated ^{13}C NMR spectrum (Fig. 1C, inset) of this

Saturn-shaped $C_{50}Cl_{10}$ structure agrees well with the experimental one (table S1) (11). Additionally, the D_{5h} fullerene[50] structure has been further cocharacterized by a variety of techniques, including multiple staged mass spectrometry and infrared, Raman, ultraviolet-visible, and fluorescence spectroscopies (figs. S1 to S6 and tables S2 and S3) (11).

Fullerenes smaller than C_{60} are predicted to have unusual electronic, magnetic, and mechanical properties that arise mainly from the high curvature of their molecular surface (1–9). Hindered by the synthetic difficulty, however, experimental investigation of these properties is scarce. Our successful capture of

C_{50} not only brings into reality a long-sought member of the fullerene family but also reveals that small non-IPR fullerenes can be obtained in macroscopic quantities through passivation of the highly active sites of an otherwise extremely unstable cage. We have chromatographic evidence that stable derivatives of other small fullerenes, such as C_{54} and C_{56} , are also formed in the CCl_4 graphite arc-discharge process (fig. S7) (11). The chlorinated small fullerenes thus obtained have their curved cage surfaces maintained (11) and are ready for further chemical manipulations. For example, up to four Cl groups of $C_{50}Cl_{10}$ can be replaced by solvolysis reactions with methanol under mild conditions (fig. S8) (11). These results imply that some of the curvature-related atypical properties of small fullerenes are retained in their chlorinated forms and that new avenues for routine experimental investigations of the properties and applications of small fullerenes and their derivatives are now open.

References and Notes

- K. M. Kadish, R. S. Ruoff, Eds., *Fullerene: Chemistry, Physics and Technology* (Wiley, New York, 2002).
- T. Guo et al., *Science* **257**, 1661 (1992).
- H. W. Kroto, *Nature* **329**, 529 (1987).
- C. Piskoti, J. Yarger, A. Zettl, *Nature* **393**, 771 (1998).
- A. Koshio, M. Inakuma, T. Sugai, H. Shinohara, *J. Am. Chem. Soc.* **122**, 398 (2000).
- A. Koshio, M. Inakuma, Z. W. Wang, T. Sugai, H. Shinohara, *J. Phys. Chem. B* **104**, 7908 (2000).
- P. W. Fowler, T. Heine, *J. Chem. Soc. Perkin Trans.* **2001**, 2487 (2001).
- J. R. Heath, *Nature* **393**, 730 (1998).
- D. Bakowies, W. Thiel, *J. Am. Chem. Soc.* **113**, 3704 (1991).
- F. Gao, S. Y. Xie, R. B. Huang, L. S. Zheng, *Chem. Commun.* **2003**, 2676 (2003).
- Materials and methods are available as supporting material on Science Online.
- We thank R. E. Smalley and X. Xu for reviewing the manuscript and for helpful suggestions; J. L. Ye, Y. Q. Feng, L. J. Yu, W. Z. Weng, D. Y. Wu, Y. B. Jiang, and J. Z. Zhou for technical support; Y. P. Sun, Z. Q. Tian, S. T. Lee, L. Eche-goyen, L. S. Long, Y. L. Chow, J. G. Qian, J. S. Shao, and Z. C. Tang for helpful discussions; and L. E. Eche-goyen for her careful reading and editing of the manuscript. Supported by the National Natural Science Foundation of China, the Ministry of Science and Technology of China, and the Ministry of Education of China.

Supporting Online Material

www.sciencemag.org/cgi/content/full/304/5671/699/DC1
Materials and Methods
Figs. S1 to S8
Tables S1 to S3
References and Notes

12 January 2004; accepted 1 March 2004

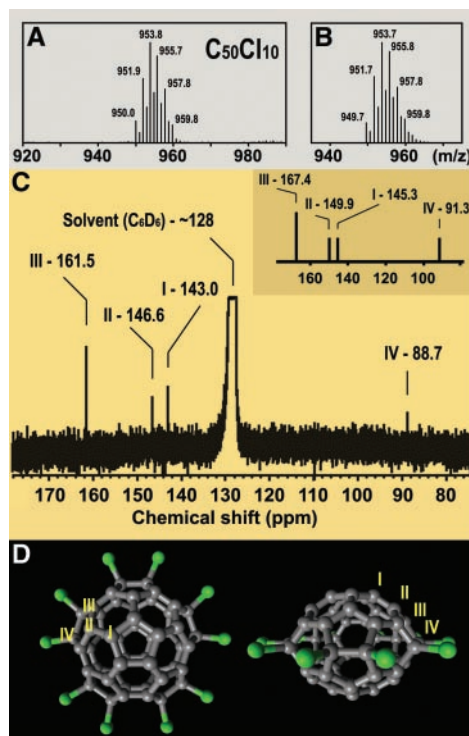


Fig. 1. (A) An atmospheric pressure chemical ionization mass spectrum of the isolated product acquired in the negative-ion mode on a Finnigan LCQ instrument. m/z , mass-to-charge ratio. (B) Simulated mass spectrum for $C_{50}Cl_{10}$. (C) Experimental and theoretical ^{13}C NMR spectra of D_{5h} $C_{50}Cl_{10}$. The theoretical ^{13}C NMR spectrum (inset) was obtained at the B3LYP/6-31G(d) level of theory with Gaussian98 (11). (D) Schematic structure of $C_{50}Cl_{10}$.

¹State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, Xiamen University, Xiamen, 361005, China. ²Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China. ³State Key Laboratory of Magnetic Resonance and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan, 430071, China.

*To whom correspondence should be addressed. E-mail: syxie@jingxian.xmu.edu.cn