IPR-Violating Fullerenes

DOI: 10.1002/anie.200800338

Crystal Structures of Saturn-Like $C_{50}Cl_{10}$ and Pineapple-Shaped $C_{64}Cl_4$: Geometric Implications of Double- and Triple-Pentagon-Fused Chlorofullerenes**

Xiao Han, Sheng-Jun Zhou, Yuan-Zhi Tan, Xin Wu, Fei Gao, Zhao-Jiang Liao, Rong-Bin Huang, Yu-Qi Feng, Xin Lu, Su-Yuan Xie, and Lan-Sun Zheng*

Fullerenes are spherical cage carbon molecules constructed from hexagons and exactly 12 pentagons.[1,2] Theoretically, according to the so-called Isolated Pentagon Rule (IPR),[3] fullerenes with isolated pentagons are relatively stable and synthesizable. This same rule predicts that fullerenes with fused pentagons are too reactive to be isolated. IPR-violating fullerenes, however, have been reported to be stabilized by either encapsulation with metal atoms (or their carbide/nitride clusters)[4,5] or external derivatization.[6a,7] Fullerenes featuring fused pentagons have been characterized by computationally corroborated ^{13}C NMR spectroscopy.[6–8] Detailed information regarding their geometries and intermolecular interactions, however, requires single-crystal X-ray characterization, as in the case of $Sc_3N@C_{68}$.[9] The crystal structures of two double-fused-pentagon endohedral metallofullerenes, namely $La@C_{72}(C_6H_3Cl_2)$[10] and $Tb_3N@C_{84}$,[11] have also been determined. Highly accurate structural parameters established by X-ray crystallography are rare for exohedral derivatives of IPR-violating fullerenes. Prinzbach et al., for example, have recently reported the crystal structures of polybrominated dodecahedrane,[12] which is the smallest IPR-violating fullerene derivative known to date. Herein we report two crystal structures of IPR-violating fullerenes (C_{50} (no. 271) and C_{64} (no. 1911))[2,13] stabilized by exohedral chlorination. The former is the smallest fullerene for which a cage can be constructed without triplets of directly or sequentially fused pentagons,[3,6,14] while the latter is a triple-fused-pentagon fullerene.[7] The crystallographic data reported herein provide unequivocal structural information for these IPR-violating fullerene derivatives (e.g., detailed geometric parameters, molecular curvature, pyramidalization angles,[15] aromaticity, intermolecular interactions) and the property implications thereof.

The X-ray structures[16] of $C_{50}Cl_{10}$ (**1**) and $C_{64}Cl_4$ (**2**) are shown in Figure 1. The symmetries of these IPR-violating chlorofullerenes are identical to those of their carbon cage parents, in other words D_{5h}-C_{50} (**1a**) for **1** and C_{3v}-C_{64} (**2a**) for **2**. The former is a Saturn-like chlorofullerene molecule constructed symmetrically from five pairs of two fused pentagons whose fused edges are covalently bound by ten chlorines in a manner that resembles the rings around Saturn (another Saturn-like halogenated molecule is $C_{60}F_{20}$, which was synthesized by Taylor[17]). In contrast, **2** has a pineapple-shaped structure with four chlorine atoms covalently attached

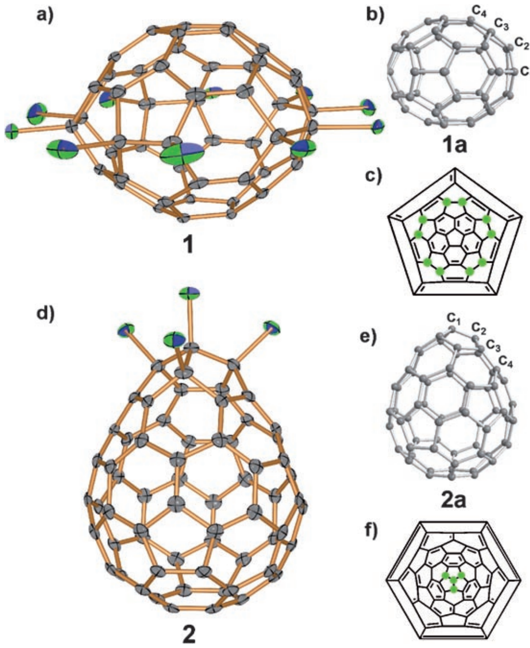

Figure 1. ORTEP structures (a, d) and Schlegel diagrams (c, f) of $C_{50}Cl_{10}$ (**1**) and $C_{64}Cl_4$ (**2**), and theoretically optimized structures (b, e) of C_{50} and C_{64}. The ORTEP structures are plotted with thermal ellipsoids at 50% probability. The chlorine atoms in the Schlegel diagrams (c, f) are indicated as green dots.

---

[*] X. Han,[+] S. J. Zhou,[+] Y. Z. Tan, X. Wu, Dr. F. Gao, Dr. Z. J. Liao, Prof. R.-B. Huang, Prof. Dr. X. Lu, Prof. Dr. S. Y. Xie, Prof. Dr. L.-S. Zheng
State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, Xiamen University, Xiamen 361005 (China)
Fax: (+86) 592-218-3047
E-mail: syxie@xmu.edu.cn
Homepage: http://chem.xmu.edu.cn/person/syxie/index.html
Prof. Dr. Y.-Q. Feng
Department of Chemistry, Wuhan University, Wuhan 430072 (China)

[+] These authors contributed equally to this work.

[**] The authors thank Prof. Quan-Ming Wang, Xiang-Jian Kong, Jun Zhao, and Gui-Lin Zhuang for their kind help with determining the crystal structures, and Prof. G. Michael Blackburn from the University of Sheffield and Dr. Hua-Ping Li from the University of California, Santa Barbara, for revising the manuscript. This work was supported financially by the NNSFC (grant nos. 20525103, 20531050, 20721001, 20625516, and 20425312) and the 973 Program (grant no. 2007CB815301).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

to the fused edges of three fused pentagons like "pineapple leaves". These crystallographic studies confirm our previously reported structure for $C_{50}Cl_{10}$, which was deduced mainly by ^{13}C NMR spectroscopy and theoretical calculations,[6a] and support the structural identification of the recently isolated $C_{64}H_4$.[7]

The most notable feature of these IPR-violating fullerenes is the existence of fused pentagons (two in **1a** and three in **2a**), which lead to enhanced strain of the cage surfaces. The degree of strain is reflected in terms of the pyramidalization angles (θ_p)[15] at the relevant carbon atoms. θ_p for an sp^2-hybridized carbon is defined as the angle of $\theta_{\sigma\pi}$ minus 90.0°, where $\theta_{\sigma\pi}$ is the angle between the π-orbital and its three adjacent C−C bonds (Figure 2a). This θ_p concept can be extended to a single sp^3 carbon in chlorofullerenes by subtracting 109.47°, the regular tetrahedral angle, from the average angle of the three adjoining Cl−C−C bonds (Figure 2b). θ_p for the I_h-symmetric fullerene C_{60}, which lacks a fused pentagon, is approximately 11.64°. The θ_p values of the carbon atoms at the edges of the fused pentagons for these IPR-violating fullerenes are calculated to be 15.58° for C_1 in **1a**, 16.41° for C_2 in **2a**, and 22.23° for C_1 in **2a** (Figures 1b and 1e). The curvature-induced pyramidalization therefore apparently depends on the multiplicity of pentagon fusions while the relative reactivity dramatically increases progressively from I_h-C_{60} (no pentagon fusion) to **1a** (two fused pentagons) and **2a** (three fused pentagons).

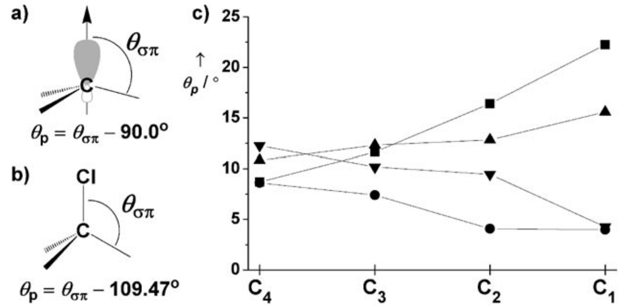

Figure 2. Pyramidalization angles (θ_p) for a) sp^2 and b) sp^3 carbon atoms in chlorofullerenes. c) The θ_p values of the first four carbon atoms in C_{50}, $C_{50}Cl_{10}$, C_{64}, and $C_{64}Cl_4$. ■ C_{64}, ● $C_{64}Cl_4$, ▲ C_{50}, ▼ $C_{50}Cl_{10}$. The carbon labels are defined in Figure 1.

The reactive carbon atoms at the fused pentagon edges can be stabilized by exohedral addends, in the present case chlorines, which change the carbon hybridization from sp^2 to sp^3 and thus relieve strain.[6,7] The θ_ps values for the carbon atoms at, and adjacent to, the fusion sites in parent and chlorinated C_{50} and C_{64} are shown in Figure 2c. These data highlight the extraordinary stabilities of the chlorinated fullerenes in comparison to all-carbon cages.

Another prominent structural feature is the aromaticity of the sp^2-hybridized carbon framework of **1** and **2**. Ten equatorial sp^3 C−Cl bonds split molecule **1** into two distinct sp^2 C_{20} fragments (Figure 1c) which are similar to the carbon skeleton seen in corannulene $C_{20}H_{10}$.[18] Although the C_{20} fragments in **1** are necessarily more curved than in the bowl-shaped $C_{20}H_{10}$ in order to maintain a closed cage structure (θ_p at C_4 is 12.27° in the C_{20} fragments of **1** vs. 8.39° in $C_{20}H_{10}$), X-ray structure analyses reveal that the alternations of C−C/C=C single/double bonds in the C_{20} fragments of **1** are much less prominent than those in $C_{20}H_{10}$ (average C−C/C=C bond lengths are 1.423/1.397 Å in the C_{20} caps of **1** and 1.433/1.379 Å in $C_{20}H_{10}$,[18] respectively). These geometric properties are linked to the electron delocalization and aromaticity of these C_{20} components and undoubtedly contribute to the stability of **1**. For species **2**, removal of the chlorine and carbon atoms from the three fused pentagons gives an open-cage C_{60} species containing a 15-membered-ring orifice (Figure 1f). This enlarged C_{60} cluster is analogous to the previously synthesized complex $[(C_5H_5)Co(C_{64}H_4)]$,[19] and is aromatic with I_h-C_{60} symmetry and alternate single/double bond lengths of 1.445/1.385 Å, on average. Such aromaticity retention in the remaining non-pentagon-fused fragments may be another essential requirement for stabilization of IPR-violating fullerenes by exohedral derivatization.

Among isomers containing only hexagons and pentagons, both **1a** and **2a** have the minimum number of carbon atoms at their pentagon-fused edges,[2] that is, 10 for **1a** and 4 for **2a**. A single C_{50} (no. 271) isomer with ten reactive pentagon-fused carbon atoms is the theoretical precursor for $C_{50}Cl_{10}$. In the case of $C_{64}Cl_4$, however, there are four possible C_{64} candidates with four active carbons, namely C_{64} nos. 1911, 3451, 3452, and 3457. Although C_{64} (no. 1911) is not itself the energetically most favorable species among C_{64} fullerenes, quantum chemical computations predict that the other three $C_{64}Cl_4$ isomers are low band-gap species with HOMO–LUMO gaps of less than 0.9 eV and are at least 31.9 kcal mol^{-1} less stable than **2** (see Supporting Information). These values explain why none of the other $C_{64}Cl_4$ isomers, which are thermodynamically and kinetically unstable, have been detected experimentally.[20]

The sp^2-hybridized portions of **2** are close to each other in the crystal packing cell of **2** (Figure 3), whereas the chlorinated parts are remotely orientated. The intermolecular interactions in **2** are dominated by π-π stacking. There are 16 C···C distances shorter than 3.27 Å around the surfaces of each $C_{64}Cl_4$ cage. The four shortest intermolecular C···C distances are 3.107 Å, which is about 0.24 Å shorter than the usual π-π stacking distance (3.35 Å) seen in layered graphite or multiwall carbon nanotubes.[4,21] Such strong C···C interactions have potential implications for applications in molecular electronics because of the easier electron transfer between neighboring fullerene cages in the crystal.

Two sets of disordered $C_{50}Cl_{10}$ molecules share approximately identical chlorine positions in the crystal structure of **1**. In addition to the much shorter intermolecular C···C distances, which indicates stronger π–π stacking, a short intermolecular Cl···Cl contact (3.167 Å) is also observed in the $C_{50}Cl_{10}$ crystal (Figure 4). This Cl···Cl distance, which is comparable to those observed in polychlorinated IPR fullerenes such as $C_{60}Cl_{30}$, $C_{60}Cl_{28}$, $C_{70}Cl_{16}$, and $C_{76}Cl_{18}$,[22] can be explained in terms of both n-type Cl···Cl−C halogen bonding and π-type aromatic-C_{20}···Cl−C bonding.[23] These intriguing intermolecular interactions, together with the short and

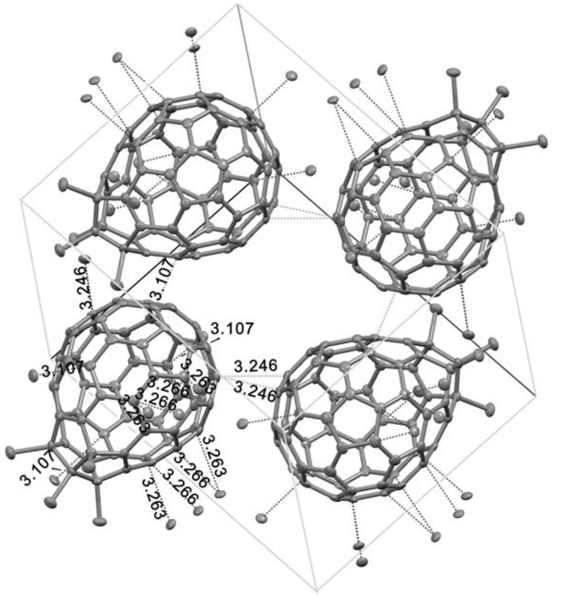

Figure 3. The crystal packing motif of $C_{64}Cl_4$. Short intermolecular C⋯C contacts (less than 3.27 Å) inside and outside the crystal cell are indicated by dashed lines. The C⋯C distances around a representative molecule are given in angstroms.

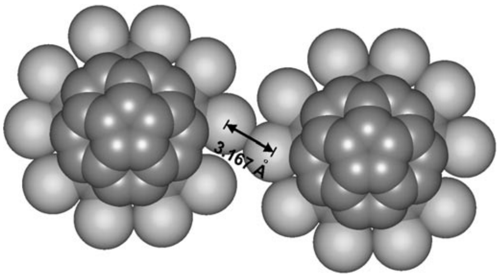

Figure 4. Two adjacent $C_{50}Cl_{10}$ molecules (CPK model) in the crystal structure of **1**. Carbon atoms and chlorine atoms are in dark gray and light gray, respectively.

equidistant intramolecular Cl⋯Cl contacts, imply that the smaller chlorinated fullerene $C_{50}Cl_{10}$ might be an ideal nanoscale "molecular gear" with promising applications.[24]

In conclusion, the detailed geometries of D_{5h}-$C_{50}Cl_{10}$ and C_{3v}-$C_{64}Cl_4$ have been reported. The highly reactive double- or triple-pentagon-fusion sites in these IPR-violating fullerenes can be stabilized by exohedral derivatization. The resulting stability is additionally enhanced by the aromaticity of the residual sp^2-hybridized carbon skeletons. Hence, the difficulties in synthesizing IPR-violating fullerenes can be overcome by means of external functionalization, and additional fullerenes with fused pentagon may be realized in the future. The X-ray crystallographic data of these molecules also reveal strong π-π stacking in $C_{64}Cl_4$ and short Cl⋯Cl contacts in $C_{50}Cl_{10}$, thereby suggesting potential applications in molecular electronics and nano-devices.

Experimental Section

$C_{50}Cl_{10}$ (**1**) and $C_{64}Cl_4$ (**2**) were produced under 0.1974 atm of helium and 0.0395 atm of carbon tetrachloride (or 0.0263 atm of chlorine gas) in a modified Krätschmer–Huffman arc-discharge reactor. The soot was extracted with toluene in a supersonic bath and separated by multi-step high-performance liquid chromatography. About 2 mg of $C_{50}Cl_{10}$ and 1 mg of $C_{64}Cl_4$ was collected in high purity (about 99%). Red $C_{50}Cl_{10}$ crystals and black $C_{64}Cl_4$ crystals were obtained by evaporation of toluene solutions containing chloroform or acetone, respectively. X-ray diffraction data were collected with an Oxford CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator). The structures were solved and refined in the anisotropic approximation using SHELTXL.[25] Quantum chemical calculations were performed at the PBE/DNP level of theory using the $DMol^3$ package.[26]

Received: January 22, 2008
Published online: June 11, 2008

Keywords: aromaticity · cage compounds · density functional calculations · fullerenes · X-ray diffraction

---

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163.
[2] P. W. Fowler, D. E. Manoloupoulos, *An Atlas of Fullerenes*, Oxford University Press, Oxford, **1995**.
[3] H. W. Kroto, *Nature* **1987**, *329*, 529–531.
[4] X. Lu, Z. F. Chen, *Chem. Rev.* **2005**, *105*, 3643–3696, and references therein.
[5] H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843–892.
[6] a) S. Y. Xie, F. Gao, X. Lu, R. B. Huang, C. R. Wang, X. Zhang, M. L. Liu, S. L. Deng, L. S. Zheng, *Science* **2004**, *304*, 699; b) X. Lu, Z. Chen, W. Thiel, P. von R. Schleyer, R. B. Huang, L. S. Zheng, *J. Am. Chem. Soc.* **2004**, *126*, 14871–14878; c) Z. F. Chen, *Angew. Chem.* **2004**, *116*, 4794–4796; *Angew. Chem. Int. Ed.* **2004**, *43*, 4690–4691.
[7] C. R. Wang, Z. Q. Shi, L. J. Wan, X. Lu, L. Dunsch, C. Y. Shu, Y. L. Tang, H. Shinohara, *J. Am. Chem. Soc.* **2006**, *128*, 11352–11353.
[8] Z. Q. Shi, X. Wu, C. R. Wang, X. Lu, H. Shinohara, *Angew. Chem.* **2006**, *118*, 2161–2165; *Angew. Chem. Int. Ed.* **2006**, *45*, 2107–2111.
[9] a) S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H. C. Dorn, *Nature* **2000**, *408*, 427–428; b) M. M. Olmstead, H. M. Lee, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn, A. L. Balch, *Angew. Chem.* **2003**, *115*, 928–931; *Angew. Chem. Int. Ed.* **2003**, *42*, 900–903.
[10] H. Nikawa, T. Kikuchi, T. Wakahara, T. Nakahodo, T. Tsuchiya, G. M. A. Rahman, T. Akasaka, Y. Maeda, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 9684–9685.
[11] C. M. Beavers, T. Zuo, J. C. Duchamp, K. Harich, H. C. Dorn, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2006**, *128*, 11352–11353.
[12] a) E. Sackers, T. Obwald, K. Weber, M. Keller, D. Hunkler, J. Worth, L. Knothe, H. Prinzbach, *Chem. Eur. J.* **2006**, *12*, 6242–6254; b) F. Wahl, A. Weiler, P. Landenberger, E. Sackers, T. Voss, A. Haas, M. Lieb, D. Hunkler, J. Wörth, L. Knothe, H. Prinzbach, *Chem. Eur. J.* **2006**, *12*, 6255–6267.
[13] The fullerene isomers are numbered according to the spiral codes, see Ref. [2] for detailed information. The molecular formulae of C_{50} and C_{64} in this article refer to C_{50} (no. 271) and C_{64} (no. 1911), respectively, if there is no other specific notation.
[14] H. W. Kroto, D. R. M. Walton, *Chem. Phys. Lett.* **1993**, *214*, 353–356.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[15] a) R. C. Haddon, L. Scott, *Pure Appl. Chem.* **1986**, *58*, 137 – 142; b) R. C. Haddon, *Acc. Chem. Res.* **1988**, *21*, 243 – 249; c) R. C. Haddon, *Science* **1993**, *261*, 1545 – 1550.

[16] Crystal data for D_{5h}-symmetric $C_{50}Cl_{10}$: red crystal; monoclinic; space group *C2/c*; $a = 13.665(3)$, $b = 17.852(4)$, $c = 12.977(3)$ Å; $\alpha = 90.00°$, $\beta = 93.616(4)°$, $\gamma = 90.00°$; $V = 3159.4(12)$; $Z = 4$; $T = 100(2)$ K; $R_1 = 0.0310$ $[F_o > 4\sigma(F_o)]$; $wR_2 = 0.0818$ (all data). Crystal data for C_{3v}-symmetric $C_{64}Cl_4$: black crystal; orthorhombic; space group *Pnma*; $a = 16.6815(6)$, $b = 14.5131(5)$, $c = 13.1990(5)$ Å; $V = 3195.5(2)$; $Z = 4$; $T = 100(2)$ K; $R_1 = 0.0378$ $[F_o > 4\sigma(F_o)]$; $wR_2 = 0.0864$ (all data). CCDC 674739 and 674740 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] O. V. Boltalina, V. Y. Markov, P. A. Troshin, A. D. Darwish, J. M. Street, R. Taylor, *Angew. Chem.* **2001**, *113*, 809 – 811; *Angew. Chem. Int. Ed.* **2001**, *40*, 787 – 789.

[18] a) W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380 – 381; b) W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1971**, *93*, 1730 – 1745; c) J. C. Hanson, C. E. Nordman, *Acta Crystallogr. Sect. B* **1976**, *32*, 1147 – 1153; d) M. A. Petrukhina, K. W. Andreini, J. Mack, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 5713 – 5716; e) L. T. Scott, M. M. Hashemi, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1991**, *113*, 7082 – 7084.

[19] M.-J. Arce, A. L. Viado, Y.-Z. An, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **1996**, *118*, 3775 – 3776.

[20] S. Y. Xie, R. B. Huang, S. L. Deng, L. J. Yu, L. S. Zheng, *J. Phys. Chem. B* **2001**, *105*, 1734 – 1738.

[21] F. A. Cotton, G. Wilkinson, A. Murillo, M. Bochmann in *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**.

[22] a) P. A. Troshin, R. N. Lyubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz, S. I. Troyanov, *Angew. Chem.* **2005**, *117*, 238 – 241; *Angew. Chem. Int. Ed.* **2005**, *44*, 234 – 237; b) S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov, E. Kemnitz, *Angew. Chem.* **2005**, *117*, 436 – 439; *Angew. Chem. Int. Ed.* **2005**, *44*, 432 – 435; c) S. I. Troyanov, A. A. Popov, *Angew. Chem.* **2005**, *117*, 4287 – 4290; *Angew. Chem. Int. Ed.* **2005**, *44*, 4215 – 4218; d) K. S. Simeonov, K. Y. Amsharov, M. Jansen, *Angew. Chem.* **2007**, *119*, 8571 – 8573; *Angew. Chem. Int. Ed.* **2007**, *46*, 8419 – 8421.

[23] M. Fourmigué, P. Batail, *Chem. Rev.* **2004**, *104*, 5379 – 5418.

[24] The diameter of an individual $C_{50}Cl_{10}$ molecule is about 11 Å.

[25] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2007**, *64*, 112 – 122.

[26] PBE/DNP refers to the theoretical method employing the Perdew–Burke–Ernzerhof (PBE) density functional with all-electron double numerical plus polarization (DNP) basis sets. See a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865 – 3868; b) B. Delley, *J. Chem. Phys.* **1990**, *92*, 508 – 517; c) B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756 – 7764. The PBE/DNP theoretical method has been proved to be suitable for fullerenes and chlorofullerenes (see refs. [6]–[8]).

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim