DOI: 10.1002/anie.200702632

Halogenated Fullerenes

Connectivity of the Chiral D_2-Symmetric Isomer of C_{76} through a Crystal-Structure Determination of $C_{76}Cl_{18}\cdot TiCl_4$**

*Kalin S. Simeonov, Konstantin Yu. Amsharov, and Martin Jansen**

By considering the isolated pentagon rule (IPR), the molecular structures of all stable fullerenes up to C_{100} have been predicted by mathematical enumeration.[1] Although the combination of this geometric contrivance with NMR spectroscopic studies has allowed the molecular structures of diverse fullerene species to be confirmed, a direct method of structure determination, such as X-ray crystallography, is expected to be necessary for the recognition of single isomers. In fact, a structure determination of an ordered, monoconstituent fullerene crystal has not yet been reported. This situation is due to the virtually spherical shape of all fullerenes, which gives rise to dynamic and orientational disorder even at low temperatures. Two different approaches have been followed to overcome this problem. In the first approach, cocrystals of fullerenes with many other molecular species have been investigated.[2] The second approach has focused on fullerene derivatives.[2,3] In particular, halogenation has proven to be a versatile and efficient method for obtaining well-crystallized fullerene species. Notwithstanding that halogenation partially removes the conjugation of the π electrons, the overall connectivities of the fullerenes persist. Both approaches have been applied almost exclusively to C_{60} and C_{70} thus far.[4–6] The next accessible fullerene is D_2-symmetric C_{76}, the smallest chiral IPR fullerene. Although C_{76} is of great interest in fullerene chemistry,[7] an ordered crystal structure of C_{76} has not yet been presented.

Herein, we report the synthesis of the first halogenated derivative of the D_2-symmetric C_{76} fullerene, $C_{76}Cl_{18}$, and the analysis of its structure by X-ray crystallography.[8] The quality of the crystals allowed a structure determination of high accuracy with all atoms in ordered and fixed positions (Figure 1). The crystal structure consists of two enantiomers of $C_{76}Cl_{18}$, the carbon skeletons of which are as proposed for the enantiomers of pristine D_2-symmetric C_{76},[9] and $TiCl_4$. The two fullerene molecules are assigned the descriptors ^{f,s}C (clockwise) and ^{f,s}A (anticlockwise).[10] The crystal packing appears to be dominated by the different polarities and by the optimization of space filling. The fullerene molecules form 2D arrays extending parallel to the (001) plane. The more densely

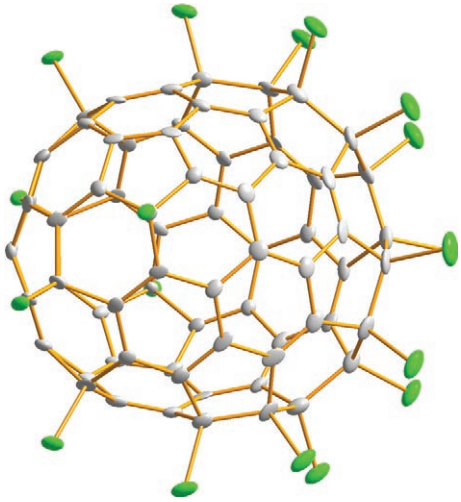

Figure 1. ORTEP projection of the molecular structure of $C_{76}Cl_{18}$ in the crystal at 173 K. Thermal ellipsoids are set at 50% probability. C gray, Cl green.

chlorinated parts of the fullerene cages approach $TiCl_4$ moieties, whereas the less polar, less halogenated parts of the fullerene cages are directed towards one another, as can be seen in Figure 2.

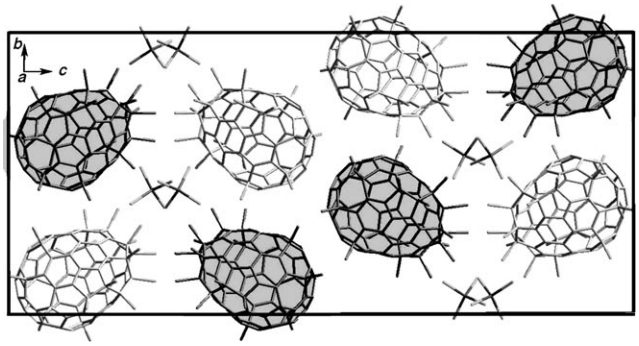

Figure 2. Projection of the structure of $C_{76}Cl_{18}\cdot TiCl_4$ onto the (100) plane. Shaded: ^{f,s}C isomer, unshaded: ^{f,s}A isomer.

$C_{76}Cl_{18}$ possesses C_2 point-group symmetry. The chlorine atoms build two belts around the C_{76} cage, both of which form clockwise helices in the case of the ^{f,s}C isomer or anticlockwise helices in the case of the ^{f,s}A isomer (Figure 3). Adding halogen atoms to the fullerene cage leads to a change in the hybridization of some carbon atoms from sp^2 to sp^3. This alteration significantly modifies the π system of the fullerene molecule. The main factor contributing to the stability of

[*] K. S. Simeonov, Dr. K. Yu. Amsharov, Prof. Dr. M. Jansen
Max Planck Institute for Solid State Research
Heisenbergstrasse 1, 70569 Stuttgart (Germany)
Fax: (+49) 711-689-1502
E-mail: m.jansen@fkf.mpg.de

[**] We gratefully acknowledge generous support by the Fonds der Chemischen Industrie and thank Dr. J. Nuss for collecting the X-ray data.

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

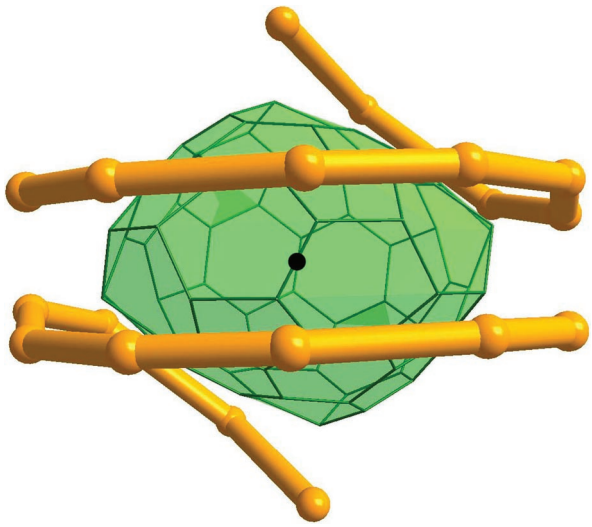

Figure 3. Two belts of chlorine atoms in the ^{f,s}C isomer of $C_{76}Cl_{18}$. The chlorine atoms are linked together for clarity. The black dot corresponds to the C_2 axis. C green, Cl orange.

highly halogenated fullerenes is the formation of a number of isolated aromatic systems.[5,6,11] As can be seen in the Schlegel diagram in Figure 4, the sp^2-hybridized carbon atoms in $C_{76}Cl_{18}$ form a rather extended "aromatic" system. In contrast to all other known π systems of halogenated fullerenes, that of $C_{76}Cl_{18}$ is not composed of isolated fragments, but extends over the whole molecule. The "aromatic girdle", which consists of 14 six-membered cycles, forms a helix in the same direction as the chlorine atoms. Comparison of the theoretically calculated bond lengths in pristine C_{76}[12] and the experimentally determined bond lengths in $C_{76}Cl_{18}$ underlines the tendency of decreasing alternation in the π system of the aromatic girdle (see Supporting Information). Despite the apparent conjugation, the nonplanar character of the helix leads to partial localization of the electron density. The formation of two 14-electron anthracene fragments (B), two six-electron benzene rings (C), and one 10-electron naphthalene ring (A) can be distinguished. The presence of four double bonds (1.33–1.35 Å) is obvious as well (Figure 4). Nevertheless, the bonds between the aromatic moieties are relatively short (1.42–1.43 Å), which substantiates the presence of a comparatively strong interaction between the p orbitals of the aromatic fragments. Despite their nonplanar character, all of these moieties are conjugated.

The trend towards "planarity" exerted by the π system and the strong repulsion of vicinal chlorine atoms lead to considerable distortion of the fullerene cage. This situation explains the formation of extremely long $C(sp^3)$–$C(sp^3)$ bonds, which reach values of up to 1.71 Å. Quantum-chemical calculations also indicate the presence of such long bonds, as can be concluded from Figure 5. C–C single bonds of similar length are known only for extremely strained cyclobutenes substituted with bulky additives. The longest $C(sp^3)$–$C(sp^3)$ bonds of 1.72–1.733 Å are found in naphthocyclobutene derivatives.[13] Among highly deformed fullerenes, a comparable elongation of a $C(sp^3)$–$C(sp^3)$ bond was found in $C_{60}F_{18}$ (1.682 Å)[5c] and in $C_{60}Cl_{30}$ (1.70 Å).[6c]

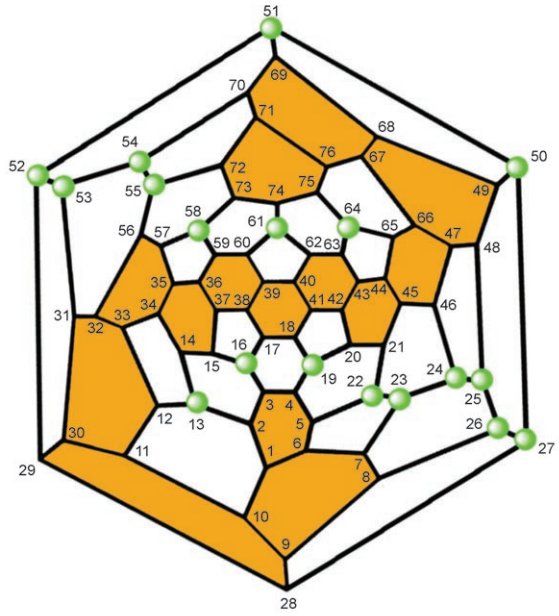

Figure 4. Top: Schlegel diagram of the experimentally observed C_2-symmetric ^{f,s}C isomer of $C_{76}Cl_{18}$ with the numbering scheme for the carbon atoms. All interatomic distances are given in the Supporting Information. Bottom: Schematic representation of the π system. See text for details. C black, Cl green.

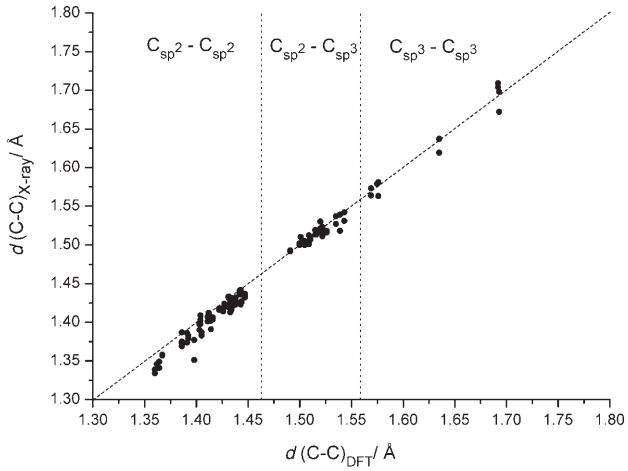

Figure 5. Correlation of the C–C distances determined by experiment (d(C–C)$_{X\text{-ray}}$) and by DFT calculation (d(C–C)$_{DFT}$). The extreme spread of the C–C bond lengths is clearly visible.

Analysis of the C–Cl bond lengths reveals some unexpected trends: those of vicinal chlorine atoms, which endure strong mutual repulsion, are characterized by insignificant

elongation, while those not strained by repulsion are substantially elongated. The same bond-length distribution was predicted by a DFT calculation and can be explained by considering the interaction between the chlorine-bearing carbon atoms and the aromatic system. The longest C–Cl distances (1.815–1.846 Å) are encountered where chlorine-bearing carbon atoms connect directly to three sp^2-hybridized carbon atoms, whereas the intermediate (1.804–1.812 Å) and shortest (1.773–1.796 Å) distances are present where chlorine-bearing carbon atoms bind with two and one sp^2-hybridized partners, respectively.

Within the crystal, the chlorine atoms form a 2D network with rather short intermolecular Cl···Cl distances (3.148, 3.170, 3.213 Å), which are about 0.45 Å shorter than the sum of the van der Waals radii. Taking into account that long C–Cl bonds are characterized by high polarity and by localization of negative charge on the chlorine atom, the short distances between chlorine atoms are unexpected. Moreover, such short Cl···Cl contacts cannot be explained by the close packing of anisotropic building units.[14] We regard the short contacts as evidence of unconventional attractive interaction between the chlorine atoms.

In summary, the connectivity pattern of the chiral D_2-symmetric C_{76} isomer has been confirmed by single-crystal X-ray analysis of $C_{76}Cl_{18}{\cdot}TiCl_4$. As the structure-determining factor, we identify the tendency of halogen-free carbon atoms to develop conjugated subunits. The long C–C bonds of 1.71 Å, which marks the longest distance reported for a fullerene derivative, could serve as hyphenation points in attempts to break down the cage in a controlled manner, while the polarized chlorine atoms could allow for specific substitutions along the cage. Thus, halogenation offers opportunities for the selective modification of fullerenes, which otherwise show rather unspecific reactivities.

Experimental Section

The pristine C_{76} fullerene was produced by evaporation of graphite along the radio-frequency furnace route, the details of which have been reported elsewhere.[15] The soot collected was Soxhlet extracted and separated by two-step high-performance liquid chromatography using the Buckyprep column. The new fullerene halide was obtained through chlorination of C_{76} (0.2 mg) in a mixture of $Br_2/TiCl_4$ (1:100 v/v, 1 mL) in a closed glass ampoule. The ampoule was frozen, evacuated, and sealed. Orange crystals of $C_{76}Cl_{18}{\cdot}TiCl_4$ formed directly on the glass wall after heating the mixture at 150 °C for 1 week. Subsequently, the ampoule was opened, and the excess solvent was decanted. The product was found to be stable in air for at least 1 month. X-ray diffraction data were collected using a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator). The crystal structure was solved and all atoms refined in the anisotropic approximation using SHELTXL.[16] Quantum-chemical calculations were performed with Gaussian 03 using the DFT method B3LYP/6-31G.[17]

Received: June 15, 2007
Revised: July 27, 2007
Published online: September 26, 2007

Keywords: C_{76} · fullerenes · halogenation · structure elucidation · X-ray diffraction

[1] P. W. Fowler, D. E. Manolopoulous, *An Atlas of Fullerenes*, Clarendon, Oxford, **1995**.
[2] I. S. Neretin, Yu. L. Slovokhotov, *Russ. Chem. Rev.* **2004**, *73*, 455 – 486.
[3] A. Hirsch, M. Brettreich, *Fullerenes Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**.
[4] M. Schulz-Dobrick, M. Panthöfer, M. Jansen, *Eur. J. Inorg. Chem.* **2005**, 4064 – 4069.
[5] a) P. B. Hitchcock, R. Taylor, *Chem. Commun.* **2002**, 2078 – 2079; b) A. G. Avent, B. W. Clare, P. B. Hitchcock, D. L. Kepert, R. Taylor, *Chem. Commun.* **2002**, 2370 – 2371; c) I. V. Goldt, O. V. Boltalina, L. N. Sidorov, E. Kemnitz, S. I. Troyanov, *Solid State Sci.* **2002**, *4*, 1395 – 1401.
[6] a) P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. M. Walton, *Nature* **1992**, *357*, 479 – 481; b) F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Thorn, G. C. Campbell, J. C. Calabrese, N. Herron, R. J. Young, E. Wasserman, *Science* **1992**, *256*, 822 – 825; c) 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; d) S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov, E. Kemnitz, *Angew. Chem.* **2005**, *117*, 436 – 0439; *Angew. Chem. Int. Ed.* **2005**, *44*, 432 – 435; e) S. I. Troyanov, A. A. Popov, *Angew. Chem.* **2005**, *117*, 4287 – 4290; *Angew. Chem. Int. Ed.* **2005**, *44*, 4215 – 4218; f) N. B. Shustova, A. A. Popov, L. N. Sidorov, A. P. Turnbull, E. Kemnitz, S. I. Troyanov, *Chem. Commun.* **2005**, 1411 – 1413.
[7] C. Thilgen, F. Diederich, *Chem. Rev.* **2006**, *106*, 5049 – 5135.
[8] Crystals of C_2-symmetric $C_{76}Cl_{18}{\cdot}TiCl_4$: $0.03 \times 0.02 \times 0.01$ mm; orthorhombic; space group *Pbca*; $a = 11.5543(9)$, $b = 21.2875(17)$, $c = 47.168(4)$ Å; $V = 11601.5(16)$ Å^3; $Z = 8$; $2\theta_{max} = 47.65°$; $-13 < h < 13$, $-24 < k < 24$, $-53 < l < 53$; $\lambda = 0.71073$ Å; $T = 100(2)$ K; no. reflections = 105007; no. independent reflections = 8909; data/restraints/parameters = 8909/0/892; full-matrix least-squares refinement on F^2; semiempirical absorption correction from equivalents; $\mu = 1.217$ mm^{-1} (transmission min/max = 0.964/0.988); final R indices ($F_o > 4\sigma(F_o)$) are $R_1 = 0.0478$ and $wR_2 = 0.087$ (R_1(all data) = 0.0972 and wR_2(all data) = 0.1036). CCDC-650718 contains 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.
[9] C. Thilgen, F. Diederich, *Nature* **1991**, *353*, 149 – 153.
[10] F. Cozzi, W. H. Powell, C. Thilgen, *Pure Appl. Chem.* **2005**, *77*, 843 – 923.
[11] S. I. Troyanov, E. Kemnitz, *Eur. J. Org. Chem.* **2003**, 3916 – 3919.
[12] J. R. Colt, G. E. Scuseria, *J. Phys. Chem.* **1992**, *96*, 10265 – 10268.
[13] F. Toda, *Eur. J. Org. Chem.* **2000**, 1377 – 1386.
[14] A. Dunand, R. Gerdil, *Acta Crystallogr.* **1982**, 570 – 575.
[15] M. Jansen, G. Peters, N. Wagner, *Z. Anorg. Allg. Chem.* **1995**, *621*, 689 – 693.
[16] G. M. Sheldrick, SHELXTL v. 6.14, Bruker AXS.
[17] M. J. Frisch et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, **2004**.

