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Higher Fullerenes

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Four Isomers of C_{96} Fullerene Structurally Proven as $C_{96}Cl_{22}$ and $C_{96}Cl_{24}$**

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Investigations of higher fullerenes (larger than C_{70}) have been hampered by their low abundance in fullerene soot and by the fact that the number of stable fullerene isomers obeying the isolated pentagon rule (IPR) increases rapidly with the cage size.[1] Structural characterization of higher fullerenes is typically accomplished by means of ^{13}C NMR spectroscopy which provides information on molecular symmetry. However, the identification of higher fullerenes by this conventional method is not unambiguous in many cases since several isomers may exhibit the same molecular symmetry.[2] Theoretical calculations provide information concerning the relative stability and the expected line distribution in the NMR spectra, thus assisting in the cage assignment.[3] The derivatization of higher fullerenes followed by the separation of derivatives and characterization by direct methods appeared to be a rather effective approach, as illustrated by some examples for C_{78}–C_{90} based on their perfluoroalkylated and halogenated derivatives.[4]

Experimental observations on higher fullerenes beyond C_{90} are additionally hindered by the very small amounts of available materials and the large number of possible isomers to be separated. As one of the largest higher fullerenes isolable from fullerene soot, C_{96} is predicted to have 187 possible IPR cage isomers according to the topological analysis.[1] The first chromatographic isolation and ^{13}C NMR characterization of C_{96} fullerenes indicated the presence of as many as ten different isomers in fullerene soot.[5]

Theoretical calculations were performed for C_{96} isomers to predict their relative stabilities. According to the calculations by the tight binding energy method, the four most stable C_{96} isomers possess C_1, C_1, C_s, and D_{6d} symmetry.[6a] Another series of stable isomers was suggested by using MM3 and MNDO calculations with the D_2 isomer as the most stable followed by another D_2 isomer then C_2 and D_{6d} isomers.[6b] More exhaustive computations at the B3LYP/6-31G level predicted isomer 183 (D_2) to be the most stable at low temperatures followed by isomers 181 (C_2), 144 (C_1), and 145 (C_1).[7a] This order of stability was confirmed by PBE1PBE/6-311G* single point energy calculations.[7b]

The first direct experimental proof of the cage connectivity of C_{96} (isomer 145) was achieved by pentafluoroethylation of a C_{76}–C_{96} mixture with C_2F_5I, followed by HPLC separation and a single-crystal X-ray analysis of $C_{96}(C_2F_5)_{12}$.[8] Very recently, the isolation of four pristine C_{96} isomers and X-ray structural characterization of two of them (nos. 3 and 181) have been reported.[9] In the present work we used chlorination as the derivatization method; we isolated and crystallographically characterized C_{96} chlorides containing four different C_{96} cages, three of which were detected for the first time. The results are compared with theoretical predictions for C_{96} IPR isomers and discussed further in terms of cage connectivities, addition patterns, and formation energies.

We isolated three C_{96} fractions from the fullerene soot synthesized from an undoped graphite rod by three-stage HPLC (see the Supporting Information for experimental details). Briefly, in the first stage, the C_{96} fraction with retention times ranging from 35.3 to 39.0 min was collected using a Cosmosil 5PYE column. This fraction was further separated in the second stage by recycling HPLC using a Buckyprep column to afford two major fractions. In the third stage, each of these fractions was further separated by recycling HPLC under similar conditions, resulting in the isolation of three C_{96} subfractions which were labeled C_{96} (I), C_{96} (II), and C_{96} (III). MALDI-TOF MS analysis showed that these fractions are compositionally pure and and differences in their elecronic structures are clearly seen in UV/Vis/NIR spectra (see the Supporting information).

C_{96} fractions (I–III) were used in chlorination experiments with VCl_4 as the chlorinating agent. A small amount of C_{96} (I, II, or III) (0.05–0.1 mg) and an excess of VCl_4 (ca. 0.4 mL) were heated in a glass ampoule at 340–360 °C for 7–30 days. The formation of microcrystals was observed after several days; upon further heating crystals slowly grew with dimensions of up to 0.01–0.03 mm. After the ampoule was opened, the excess VCl_4 was removed by washing the residue with water. The remaining tiny crystals were investigated by X-ray diffraction with the use of synchrotron radiation.[10]

The crystallographic results revealed that the chlorides obtained from fractions C_{96} (I) and C_{96} (III) have the compo-

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sition $C_{96}Cl_{22}$, whereas fraction C_{96} (II) produced $C_{96}Cl_{24}$ (in two modifications). The analysis of cage connectivities in four $C_{96}Cl_n$ molecules revealed the presence of four different C_{96} carbon cages which correspond to C_{96} isomers 145 (C_1),[8] 144 (C_1), 176 (C_2), and 183 (D_2), of which the latter three are reported for the first time (Figure 1).

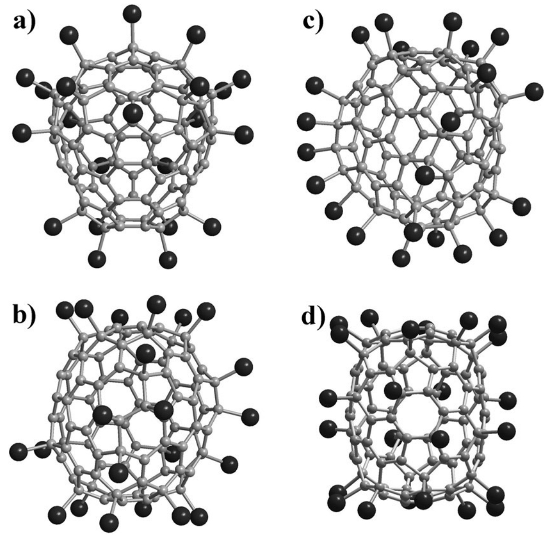
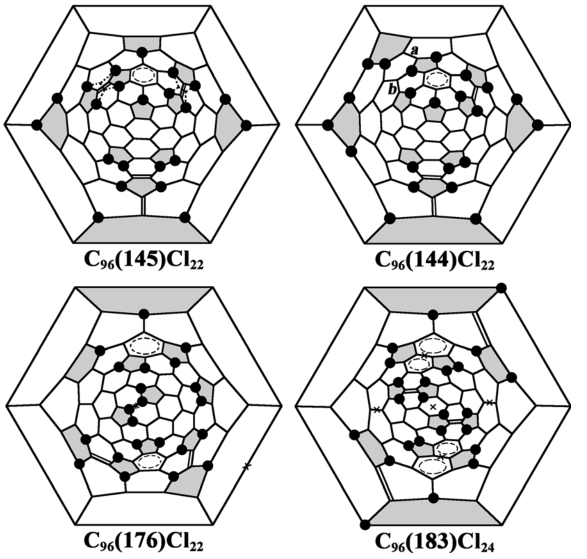


Figure 1. Molecules of a) C_1-C_{96}(145)Cl_{22}, b) C_1-C_{96}(176)Cl_{22}, c) C_1-C_{96}(144)Cl_{22}, and d) D_2-C_{96}(183)Cl_{24}. The projections in (b) and (d) are given along twofold axes of the corresponding pristine cages.

All four C_{96} cages confirmed in the present work belong to the group of low-energy isomers predicted by theoretical calculations of 187 IPR cages.[7] The most stable C_{96} cage in the ground state is isomer 183 (0 $kJ\,mol^{-1}$), followed by the nearly isoenergetic isomers 181, 144, and 145 (less than 10 $kJ\,mol^{-1}$) and some isomers (182, 146, 142, 176, and 130) with slightly higher formation energies (13.7–30.6 $kJ\,mol^{-1}$).[7a] Consideration of enthropy effects showed that the relative populations change at higher temperatures, but C_{96} isomers 183, 144, 145, and 176 retain their high abundance at temperatures up to 3000–4000 K. Our results are also compatible with earlier experimental data on C_{96} based on ^{13}C NMR spectroscopy which suggested the presence of no less than ten isomeric species (in order of decreasing abundance): C_1 (four isomers), C_2 (three isomers), C_s, D_2, and D_{3d}.[5]

Two types of crystals were obtained by chlorination of C_{96} (III) in different chlorination experiments. The first type, in spite of very weak diffraction, gave unambiguously the structure of C_1-C_{96}(144)Cl_{22} with a very asymmetric chlorination pattern (Figure 1 c). In contrast, the second type of crystals displayed a symmetric arrangement of 22 Cl atoms on the C_{96} fullerene cage (Figure 1 a), whereas the cage itself contained two formally disordered C–C bonds (appearing as bond crosses in Figure 2, top left) in both crystallographically independent $C_{96}Cl_{22}$ molecules. The formal disorder can be interpreted as an overlap of either two enantiomeric $C_{96}Cl_{22}$ molecules having the asymmetric cage of C_1-C_{96}(145) or two different molecules with the cages of C_s-C_{96}(146) and C_s-C_{96}(147) in a 1:1 ratio (see the Supporting Information for details). The former assumption seems to be more realistic because the formation energies of both isomers 146 and 147 are much higher than that of isomer 145.[7a] In addition, the presence of isomer C_{96}(145) in a fullerene soot was proved earlier by the isolation and crystallographic study of C_{96}(C_2F_5)$_{12}$.[8]



C_{96}(145)Cl_{22} C_{96}(144)Cl_{22}

C_{96}(176)Cl_{22} C_{96}(183)Cl_{24}

Figure 2. Schlegel diagrams of four $C_{96}Cl_n$ molecules. Cage pentagons are shown in gray. Benzenoid rings and isolated C–C double bonds are indicated. Small crosses denote the positions of twofold axes. For C_1-C_{96}(145)Cl_{22}, the alternative positions of two C–C double bonds in the enantiomeric molecule are indicated by dashed lines.

The chlorination of fractions C_{96} (I) and C_{96} (II) afforded crystals of C_1-C_{96}(176)Cl_{22} and D_2-C_{96}(183)Cl_{24}, respectively (Figure 1 b,d). This is the first experimental confirmation of the C_{96}(176) and C_{96}(183) fullerene cages. It should be noted that four C_{96} isomers were isolated previously by HPLC from the arc-discharge fullerene synthesis with Sm_2O_3-doped graphite rods.[9] Two of them, C_2-C_{96}(181) and D_{3d}-C_{96}(3), were unambiguously characterized by X-ray diffraction of their co-crystals with Ni^{II}OEP (OEP–octaethylporphyrin). While the isomer C_2-C_{96}(181) is expected because of its low formation energy,[7] the presence of high-energy D_{3d}-C_{96}(3) (122 $kJ\,mol^{-1}$[7a]) is surprising and might be attributed to the influence of Sm doping on the distribution of isomers in the fullerene soot.[9] Two other C_{96} isomers isolated from the same soot were characterized by UV/vis/NIR absorption spectroscopy alone. We found relatively close similarities between the spectra of C_{96}(II) and C_{96}(III) in Ref. [9] and the spectra of our fractions II and III, respectively (Figure S3 in the Supporting Information). Therefore, it is very probable that C_{96}(II) and C_{96}(III) in Ref. [9] contain C_{96}(183) and a mixture of C_{96}(144) and C_{96}(145), respectively.

The Schlegel diagrams in Figure 2 allow more detailed discussion of the chlorination patterns in four $C_{96}Cl_n$ chlorides. All structures are characterized by the formation of stabilizing isolated aromatic systems and C–C double bonds on the fullerene cages. The addition of Cl atoms in adjacent positions occurs in all four molecules, whereas the C atoms in the positions of triple hexagon junctions (THJs) are not chlorinated.

The structure of C_1-C_{96}(145)Cl_{22} contains one benzenoid ring and four isolated C−C double bonds. All positions of Cl attachments have counterparts in *para* positions in cage hexagons. The deviation of the carbon cage and the whole $C_{96}Cl_{22}$ molecule from mirror symmetry is due to the orientation of only one C−C double bond (see Figure 2). However, the symmetrical arrangement of 22 Cl atoms defines the outer shape, thus making it possible that both enantiomeric molecules occupy the same crystallographic site.

The carbon cage of C_{96}(144) resembles that of C_{96}(145) in that 9 of 12 pentagon are situated similarly. In fact, C_{96} isomers 144 and 145 are topologically related by two formal Stone–Wales rearrangements of C−C bonds *a* and *b* on the Schlegel diagram of C_{96}(144)Cl_{22} (see the Supporting Information for more details). As a consequence, the chlorination pattern of C_1-C_{96}(144)Cl_{22} resembles that of C_{96}(145)Cl_{22} in that 19 Cl atoms are attached in similar positions on the fullerene cages and as a result one benzenoid ring and three isolated C−C double bonds are in the same positions in the two isomers (see Figure 2). A distinctive feature of the chlorination pattern of C_{96}(144)Cl_{22} is a five-membered chain of Cl atoms attached in adjacent positions.

In the chlorination pattern of C_1-C_{96}(176)Cl_{22} only 18 Cl attachments follow the symmetry of the pristine isomer C_2-C_{96}(176). There are two benzenoid rings, two isolated C−C double bonds, and a four-membered chain of adjacent Cl attachments on the fullerene cage. The latter includes a rare addition to an interpentagonal C−C bond (ICCB),[4c] which connects two cage pentagons. The cages of C_2-C_{96}(176) and C_1-C_{96}(144) isomers are formally related to one another by three successive Stone–Wales rearrangements.

The chlorination pattern of D_2-C_{96}(183)Cl_{24} retains the symmetry of the pristine D_2-C_{96}(183) cage. The whole chlorination pattern can be regarded as consisting of *para* attachments in cage hexagons. In addition to two naphthalene substructures, there are four isolated C−C double bonds on the fullerene cage. D_2-C_{96}(183) as well as isomers 144, 145, and 176 belongs to a large family of 162 C_{96} isomers which can be interconverted by Stone–Wales rearrangements. However, the transformation of C_{96}(183) into the nearest member (isomer 176) requires as many as 14 steps.

According to DFT calculations (see the Supporting Information), the average C−Cl bond energies (the enthalpy of chlorination of the parent fullerene per Cl atom) in $C_{96}Cl_{22}$ and $C_{96}Cl_{24}$ are within 3 kJ mol^{-1}. The respective values for $C_{96}Cl_{22}$ and $C_{96}Cl_{24}$ are 3.3–4.7 and 1.8 kJ mol^{-1} higher than that for D_{3d}-$C_{60}Cl_{30}$ (195 ± 5 kJ mol^{-1}),[11] thus suggesting that C−Cl bond energy decreases with the increasing number of the attached Cl atoms per fullerene cage regardless of its size.

D_2-C_{96}(183)Cl_{24} occurs in two crystalline modifications of monoclinic and orthorhombic symmetry (Figure 3). In fact, the geometrical parameters of the C_{96}(183)Cl_{24} molecules are virtually the same in both structures. The isolated C−C double bonds, the averaged C−C bond of the naphthalene substructures, and single ClC−CCl bonds are 1.32–1.33 Å, 1.40 Å, and 1.59–1.60 Å long, respectively. C−Cl distances lie in a typical range of 1.80–1.84 Å, which was also found in the chloro derivatives of C_{84},[12] C_{88},[13] and C_{90}.[4e]

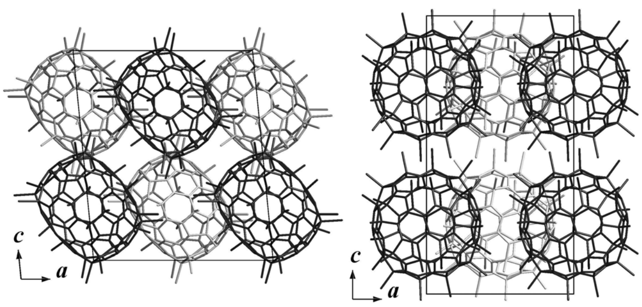


Figure 3. Crystal packing of D_2-C_{96}(183)Cl_{24} molecules in the monoclinic (left) and orthorhombic (right) modifications. The *b* directions coincide with different C_2 axes passing through the centers of opposite hexagons (left) and the centers of C−C bonds (right).

Two twofold axes of the D_2-C_{96}(183)Cl_{24} molecule pass through the centers of opposite C−C bonds, whereas the third axis goes through the centers of opposite hexagons. In the crystal packings, crystallographic twofold (*b*) axes pass through the centers of hexagons in the monoclinic modification and through the centers of C−C bonds in the orthorhombic one (Figure 3).

In conclusion, we have confirmed the structures of four C_{96} isomers (nos. 145, 144, 176, and 183) by the the X-ray crystallographic study of their chlorides $C_{96}Cl_{22}$ and $C_{96}Cl_{24}$, and the latter three isomers have been reported for the first time. Moreover, the elucidation of molecular structures of C_{96} chlorides allows deeper insight into the chemical reactivity of C_{96} fullerenes and a better comparison with other higher fullerenes. Chlorination followed by single-crystal X-ray diffraction analysis proved to be an effective strategy the the investigation of higher fullerenes available only in very small quantities. Further structural study of higher fullerene derivatives is underway in our laboratories.

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Keywords: C_{96} isomers · chlorination · fullerenes · structure elucidation

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[1] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, **1995**.

[2] Y. Achiba, K. Kikuchi, Y. Aihara, T. Wakabayashi, Y. Miyake, M. Kainosho in *Science and Technology of Fullerene Materials*, *Vol. 359* (Eds.: P. Bernier, et al.), MRS Symposia Proceedings, Pittsburgh, **1995**, pp. 3 – 9.

[3] G. Sun, *Chem. Phys.* **2003**, *289*, 371 – 380.

[4] a) K. S. Simeonov, K. Yu. Amsharov, E. Krokos, M. Jansen, *Angew. Chem.* **2008**, *120*, 6379 – 6381; *Angew. Chem. Int. Ed.* **2008**, *47*, 6283 – 6285; b) K. S. Simeonov, K. Yu. Amsharov, M. Jansen, *Chem. Eur. J.* **2009**, *15*, 1812 – 1815; c) I. E. Kareev, A. A. Popov, I. V. Kuvychko, N. B. Shustova, S. F. Lebedkin, V. P. Bubnov, O. P. Anderson, K. Seppelt, S. H. Strauss, O. V. Boltalina, *J. Am. Chem. Soc.* **2008**, *130*, 13471 – 13489; d) N. B. Tamm, L. N. Sidorov, E. Kemnitz, S. I. Troyanov, *Chem. Eur. J.* **2009**, *15*,

10486 – 10492; e) S. I. Troyanov, S. F. Yang, C. Chen, E. Kemnitz, *Chem. Eur. J.* **2011**, *17*, 10662 – 10669.

[5] T. Minami, Y. Miyake, K. Kikuchi, Y. Achiba in *The 18th Fullerene General Symposium*, The Fullerene Research Association of Japan, Okazaki, **2001**, p. 42.

[6] a) X. Q. Wang, C. Z. Wang, B. L. Zhang, K. M. Ho, *Chem. Phys. Lett.* **1993**, *214*, 193 – 196; b) R. L. Murry, G. E. Scuseria, *J. Phys. Chem.* **1994**, *98*, 4212 – 4214.

[7] a) X. Zhao, Z. Slanina, H. Goto, *J. Phys. Chem. A* **2004**, *108*, 4479 – 4484; b) N. Shao, Y. Gao, W. An, X. C. Zeng, *J. Phys. Chem. A* **2006**, *110*, 7672 – 7676.

[8] N. B. Tamm, L. N. Sidorov, E. Kemnitz, S. I. Troyanov, *Angew. Chem.* **2009**, *121*, 9266 – 9268; *Angew. Chem. Int. Ed.* **2009**, *48*, 9102 – 9104.

[9] H. Yang, H. Jin, Y. Che, B. Hong, Z. Liu, J. A. Gharamaleki, M. M. Olmstead, A. L. Balch, *Chem. Eur. J.* **2012**, *18*, 2792 – 2796.

[10] Data collection was performed on a MAR225 CCD detector at 100 K on BL14.2 operated by the Joint Berlin MX-Laboratory at the BESSY II electron storage ring (Berlin-Adlershof, Germany) ($\lambda = 0.886$ or 0.905 Å, BL14.2, PSF of the Free University of Berlin, Germany). Structure solution and refinement with SHELXS97 and SHELXL97, respectively. $C_{96}(145)Cl_{22}$:·triclinic, $P\bar{1}$, $a = 14.603(1)$, $b = 21.495(1)$, $c = 22.902(2)$ Å, $\alpha = 68.233(4)$, $\beta = 89.815(4)$, $\gamma = 86.641(5)°$, $V = 6663.4(8)$ Å^3, $Z = 4$, $R_1/wR_2 = 0.087/0.224$ for 18330/26400 observed/independent reflections and 1770 parameters. Both independent $C_{96}Cl_{22}$ molecules contain two C-C crosses (see text). $C_{96}(144)Cl_{22}·0.6\,Cl_2$: orthorhombic, *Pbca*, $a = 14.618(1)$, $b = 23.107(2)$, $c = 39.910(3)$ Å, $V = 13481(2)$ Å^3, $Z = 8$, $R_1/wR_2 = 0.185/0.429$ for 2524/10394 reflections and 601 parameters. $C_{96}(176)Cl_{22}·0.07\,Cl_2$: monoclinic, $P2_1/n$, $a = 22.912(1)$, $b = 14.155(1)$, $c = 42.819(2)$ Å, $\beta = 102.596(6)°$, $V = 13553(1)$ Å^3, $Z = 8$, $R_1/wR_2 = 0.067/0.184$ for 20917/31276 reflections and 2155 parameters. – $C_{96}(183)Cl_{22}·0.06\,Cl_2$: monoclinic, *C2/c*, $a = 15.6571(8)$, $b = 24.039(1)$, $c = 18.351(1)$ Å, $\beta = 95.605(7)°$, $V = 6873.9(6)$ Å^3, $Z = 4$, $R_1/wR_2 = 0.041/0.107$ for 5737/6956 reflections and 550 parameters. $C_{96}(183)Cl_{22}·0.04\,Cl_2$: orthorhombic, *Pbcn*, $a = 12.8541(8)$, $b = 22.104(1)$, $c = 24.268(1)$ Å, $V = 6895.2(6)$ Å^3, $Z = 4$, $R_1/wR_2 = 0.067/0.176$ for 5219/6833 reflections and 559 parameters. CCDC 866951, 866952, 866953, 866954, 8866955 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.

[11] T. S. Papina, V. A. Luk'yanova, S. I. Troyanov, N. V. Chelovskaya, A. G. Buyanovskaya, L. N. Sidorov, *Russ. J. Phys. Chem. A* **2007**, *81*, 159 – 163.

[12] a) S.-F. Yang, C. Chen, T. Wei, N. B. Tamm, E. Kemnitz, S. I. Troyanov, *Chem. Eur. J.* **2012**, *18*, 2217 – 2220; b) M. A. Lanskikh, N. B. Tamm, L. N. Sidorov, S. I. Troyanov, *Inorg. Chem.* **2012**, *51*, 2719 – 2721.

[13] S.-F. Yang, T. Wei, E. Kemnitz, S. I. Troyanov, *Chem. Asian J.* **2012**, *7*, 290 – 293.