DOI: 10.1002/anie.200801922

Fullerenes

An Epilogue on the C_{78}-Fullerene Family: The Discovery and Characterization of an Elusive Isomer**

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

Among the higher fullerenes—closed carbon clusters with even numbers of atoms greater than 70—C_{78} has been a subject of many experimental, as well as theoretical investigations. According to the isolated pentagon rule (IPR), five isomers with different connectivities are possible for a cage constituted of 78 carbon atoms.[1] The first three representatives of this family—$C_{78}(1)$ (with D_3 point group symmetry), $C_{78}(2)$ and $C_{78}(3)$ (both with C_{2v} symmetry), have been found in soot extracts, isolated by means of HPLC techniques,[2] and characterized either crystallographically,[3] or by ^{13}C NMR analyses.[4] The next known stable, but insoluble isomer is $C_{78}(5)$ (D_{3h}), the connectivity pattern of which was recently confirmed through its derivative $C_{78}(CF_3)_{12}$.[5] Thus, the only unexplored member of this family, $C_{78}(4)$ (D_{3h}), is needed to complete the first multi membered group of fullerene isomers. Although $C_{78}(4)$ is predicted to be the least stable among all IPR C_{78} isomers across a wide temperature interval,[6] a fact justifying its absence in fullerene extracts,[6,7] its energy per carbon atom is comparable to that of C_{70}.[7] According to a calculation performed at the DFT (desity functional theory) level, [8] $C_{78}(4)$ possesses a large energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 2.47 eV, which is comparable to those of C_{70} (2.69 eV) and C_{60} (2.76 eV).[7] Since the insolubility of fullerenes has been attributed to polymerization due to low or zero HOMO–LUMO gaps,[9] $C_{78}(4)$ is presumably soluble. Kinetic factors were evoked to explain why this isomer has not been experimentally observed so far.[7]

Herein, we report the successful synthesis and isolation of the last member of the C_{78} IPR family, $C_{78}(4)$, as well as the confirmation of its connectivity pattern through single-crystal X-ray analysis of its chlorinated derivative $C_{78}(4)Cl_{18}$.[10] A detailed analysis of the X-ray data shows evidence of attractive intermolecular Cl···Cl interactions, the importance of which bears an essential insight into the nature of chemical bonding.

Fullerene soot containing pristine $C_{78}(4)$ was obtained by means of the RF (radio frequency)-furnace method, employing conditions different from those reported in the literature.[11] HPLC analysis of the resulting extract showed an uncommon peak at the tail of $C_{78}(3)$ fraction, as displayed in Figure 1. (A comparison between chromatograms corresponding to different extracts obtained from soots generated by the RF furnace, as well as a commercial soot extract is presented in the Supporting Information.)

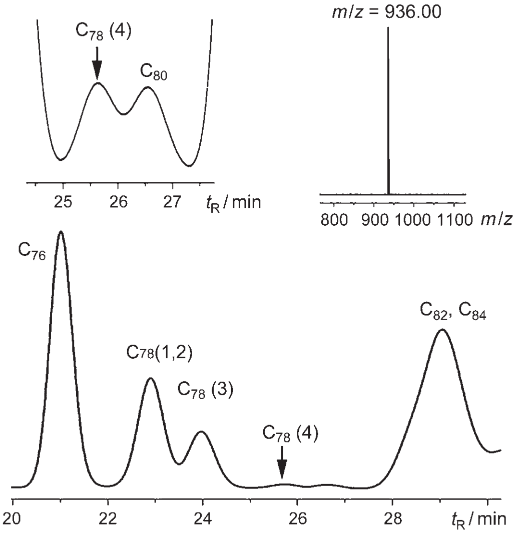

Figure 1. Bottom: HPLC profile of the fullerene extract containing $C_{78}(4)$. Top left: Magnification of the HPLC profile showing the presence of an uncommon peak at the tail of $C_{78}(3)$ fraction. Top right: Signal in the LDI mass spectrum implying that the newly isolated compound is a C_{78} isomer.

The new compound was separated from the crude extract by multi step recycling HPLC using a Buckyprep column, and identified as an isomer of C_{78} on the basis of its M^+ signal in the mass spectrum (Figure 1). Employing a mixture of toluene/dichloromethane (4:1) as a mobile phase was found to be crucial in the separation of pure $C_{78}(4)$, since it coelutes with the fraction of $C_{78}(3)$ under conventional conditions (toluene as eluent). Considering the chromatographic behavior of all known soluble IPR isomers of C_{78} (isomers 1 to 3) under the given conditions as well as the insolubility of $C_{78}(5)$, we ascribed the newly isolated compound to $C_{78}(4)$. To prove our hypothesis, crystals of the chlorinated derivative $C_{78}(4)Cl_{18}$ were prepared using a mixture of $TiCl_4$ and Br_2, which has proved to be a powerful and selective chlorinating agent.[12] $C_{78}(4)Cl_{18}$ forms solvent-free crystals in the hexag-

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

[**] We gratefully acknowledge generous support from 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://dx.doi.org/10.1002/anie.200801922.

onal space group $P6_3/m$. The hcp (hexagonal close-packed) analogue arrangement of the fullerene molecules exhibits large tunnels with a diameter of approximately 2.4 Å extending along [001], which are big enough for small molecules such as hydrogen to penetrate (Figure 2). The quality of the crystals obtained has allowed an accurate structure determination presenting all atoms in ordered and fixed positions. The experimentally derived and DFT-calculated C–C bond lengths in $C_{78}(4)Cl_{18}$ are in good agreement (Figure 3). The stabilizing factor in $C_{78}(4)Cl_{18}$ is the formation of nine "aromatic" rings—a trend typical for halogenated fullerenes. (The addition pattern of chlorine atoms can be found in the Supporting Information.) Three of these rings are characterized by a high degree of equivalence in the bond lengths that range from 1.39 to 1.41 Å, very close to those in benzene (1.395 A). According to the structural criterion of aromaticity,[13] these fragments possess high π-electron delocalization and are fully aromatic. To the best of our knowledge, such a high level of equivalence of C–C bonds in fullerene cages has not been observed previously. Interestingly, all 18 chlorine atoms can virtually be divided into three groups, each consisting of six chlorine atoms lying in one plane. This arrangement leads to the formation of three, almost equilateral, "chlorine hexagons" which are parallel to the planes of the "benzene rings" (see the Supporting Information).

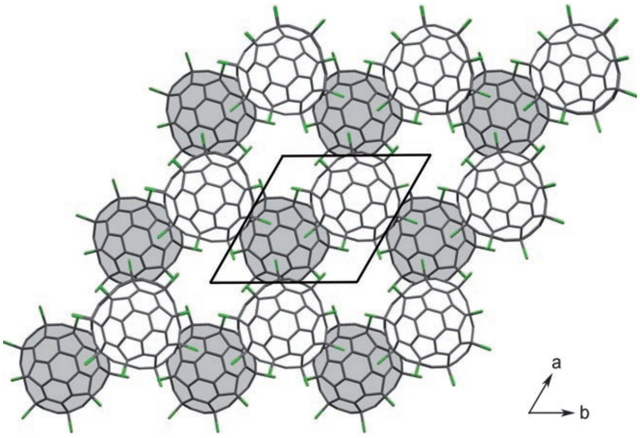

Figure 2. Projection of the structure of $C_{78}(4)Cl_{18}$ onto the [001] plane. Shaded: lower layer, unshaded: upper layer. The large tunnels whose inner "surface" consists only of chlorine atoms, are clearly visible.

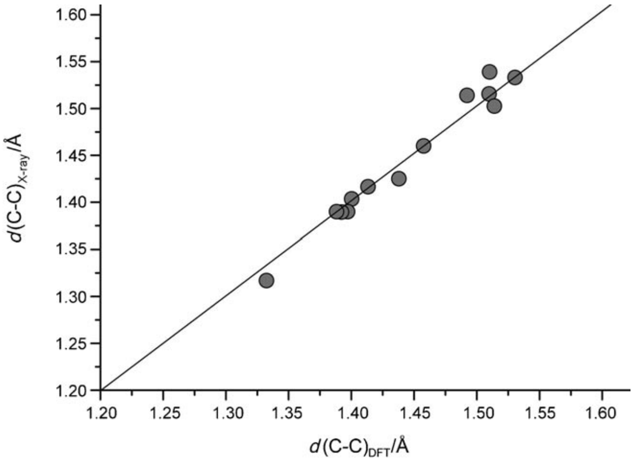

Figure 3. Correlation between the experimentally obtained and DFT calculated C–C distances. Three different groups are easily observed: "pure" double (around 1.35 Å), aromatic (1.40–1.45 Å), and single C–C bonds (1.50–1.55 Å).

The fully ordered crystals of $C_{78}(4)Cl_{18}$ provide the possibility to precisely determine not only all the bond lengths but also the intermolecular distances. A closer look at the crystal structure reveals some unexpected phenomena. Firstly, all the chlorine atoms (18 per molecule) are involved in short intermolecular Cl···Cl contacts (Figure 4), which are all shorter than the sum of the van der Waals radii of two chlorine atoms. At the same time, all the C–Cl bonds are extremely elongated, reaching values of 1.87 Å. According to the classical concept of the covalent C–Cl bond, an increased interatomic distance must lead to localization of a strong negative charge on the chlorine atom. However, the short intermolecular distances between chlorine atoms do not fit with this general postulate. Since there are no other intermolecular contacts besides Cl···Cl, which we regard to be significant in influencing the molecular packing, the short Cl···Cl separations are presumably a result of attractive interactions between chlorine atoms. Stronger evidence of the nature of the attraction can be obtained by considering two- and three-centered Cl···Cl contacts (Figure 4) in which

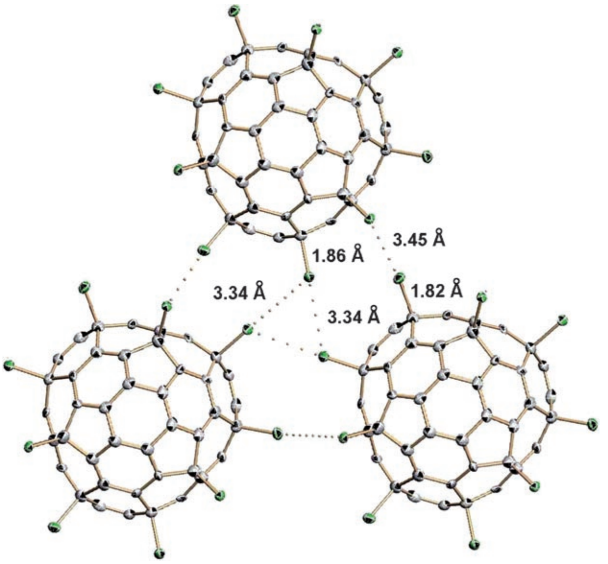

Figure 4. ORTEP plot of $C_{78}(4)Cl_{18}$ molecules in the crystal showing short two- and three-centered Cl···Cl contacts (represented by dotted lines). Symmetrically identical C–Cl bonds have different lengths as the intermolecular interactions in which they are involved (constituting two- or three-centered contacts) are of different magnitudes. Thermal ellipsoids are drawn at the 50% probability level.

structurally equivalent C–Cl bonds are involved (according to the D_{3h} point group symmetry of $C_{78}(4)Cl_{18}$). The respective C–Cl bonds (1.87 Å) in the three-centered Cl···Cl contacts, are longer than those in the two-centered contacts (1.82 Å, Figure 4). In the case of the three-centered contacts the accumulation of a "heavy" negative charge would be expected to create a strong repulsive force. However, exactly the opposite tendency is observed—the intermolecular Cl···Cl distances are shorter in the three-centered contacts than in the two-centered contacts (3.34 Å and 3.45 Å respectively, Figure 4). The unique structure of $C_{78}(4)Cl_{18}$ provides the possibility to analyze the influence of intermolecular interactions on the C–Cl bond lengths and to conclude that the elongation of C–Cl bonds involved in the shorter Cl···Cl contacts is a result of attractive interactions between chlorine atoms.

In summary, the last member of the C_{78}-fullerene family, $C_{78}(4)$, was synthesized and its connectivity pattern confirmed through single-crystal X-ray analysis of the chlorinated derivative $C_{78}(4)Cl_{18}$. Hence all IPR isomers of C_{78} are formed during graphite vaporization and their relative abundance correlates with the individual isomer stability. Thus it can be concluded that kinetic factors do not play any significant role in the process of fullerene formation. The presence of "unusual" Cl···Cl attractive interactions was found, initiating further theoretical investigations, which are already in progress.

Experimental Section

The pristine fullerene was produced by evaporation of graphite by means of the RF-furnace method, details of which have been published elsewhere.[11] $C_{78}(4)$ was synthesized by heating the carbon cylinder up to 2600 °C and increasing the pressure to 380 mbar. The collected soot was extracted (Soxhlet) and separated by multistep HPLC. The new fullerene halide was obtained through chlorination of $C_{78}(4)$ (0.1 mg) in a mixture of $Br_2/TiCl_4$ (1:150 v/v, 1.5 mL) in a closed glass ampoule. Slightly yellowish crystals formed directly on the glass wall after the mixture had been heated at 130 °C for one week. Subsequently, the ampoule was opened and the excess solvent decanted. The product was found to be stable in air for at least one month.

Received: April 24, 2008

Keywords: C_{78} · fullerenes · halogenation · structure elucidation

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