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$C_{80}Cl_{12}$: A Chlorine Derivative of the Chiral D_2-C_{80} Isomer—Empirical Rationale of Halogen-Atom Addition Pattern

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Carbon cages composed of 80 atoms have recently been in focus mainly because of the large number of metallo- and cluster endohedral fullerenes that have became available, leaving behind the investigation of the hollow isomers of this fullerene. C_{80} has seven structural isomers obeying the isolated pentagon rule (IPR).[1] Two of them, D_{5d}-C_{80}(1) and D_2-C_{80}(2) (fullerene nomenclature according to reference [1]), have been found in fullerene extracts and isolated by means of HPLC techniques.[2,3] Recently, a third representative of the family, C_{2v}-C_{80}(5), was identified and its constitution pattern confirmed by ^{19}F NMR measurements of its exohedral derivative $C_{80}(5)(CF_3)_{12}$.[4] Although the relative abundance of C_{80}(2) to C_{80}(1) of about 30:1,[2] as well as the simple isolation procedure for C_{80}(2), provide ground for investigating the chemical reactivity of this species, no exohedral derivative of it has ever been synthesized. Probing the reactivity of this isomer appears particularly worthwhile when taking into consideration that it represents another chiral fullerene after D_2-C_{76}(1), the constitution pattern of which has recently been confirmed through its chlorine derivative $C_{76}Cl_{18}$.[5]

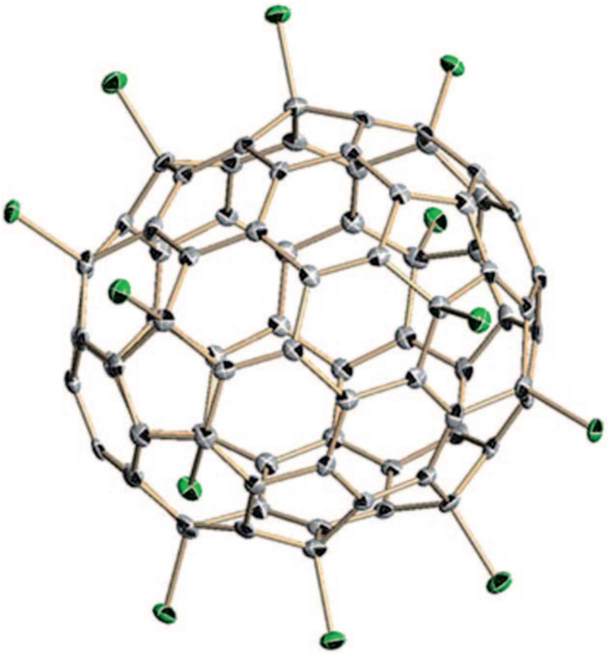

Figure 1. ORTEP plot of $C_{80}Cl_{12}$ molecule in the crystal. Displacement ellipsoids are drawn at 50% probability level.

Herein we report the synthesis and single-crystal structure analysis of $C_{80}Cl_{12}$, the first exohedral derivative of C_{80}(2). The synthetic method, employing a mixture of $TiCl_4$ and Br_2, is adopted from the procedure used for chlorinating C_{76}(1), which has proven highly selective resulting in well-crystallized enantiomorphs of C_{76}(1).[5] The quality of $C_{80}Cl_{12}$ crystals has allowed structure determination of high accuracy, presenting all atoms in ordered and fixed positions (Figure 1).[6] The solvent-free crystals of $C_{80}Cl_{12}$ consist of the two enantiomers of this fullerene species with the connectivity pattern of carbon atoms preserved as suggested for the pristine C_{80}(2) enantiomorphs.[1] The molecules exhibit D_2 point-group symmetry, unchanged from the parent species.

A notable feature in $C_{80}Cl_{12}$ is the addition pattern of the chlorine atoms. The most pyramidal carbon atoms, those having the largest θ_p angles ($\theta_p + 90°$ is the angle of π-orbital axis vector—POAV,[7]) and connecting two pentagons (through interpentagon carbon–carbon bonds—ICCB), are not attacked during chlorine addition to C_{80}(2), although in other cases they have been found to be the most reactive ones.[8] The “most inert” carbon atoms, the atoms that make up the junction of three hexagons (THJ; the yellow circles in Figure 2), are also not preferred for chlorine addition. Therefore, the reaction-favoured sites are at the carbon atoms that fuse a pentagon with two hexagons (pentagon–

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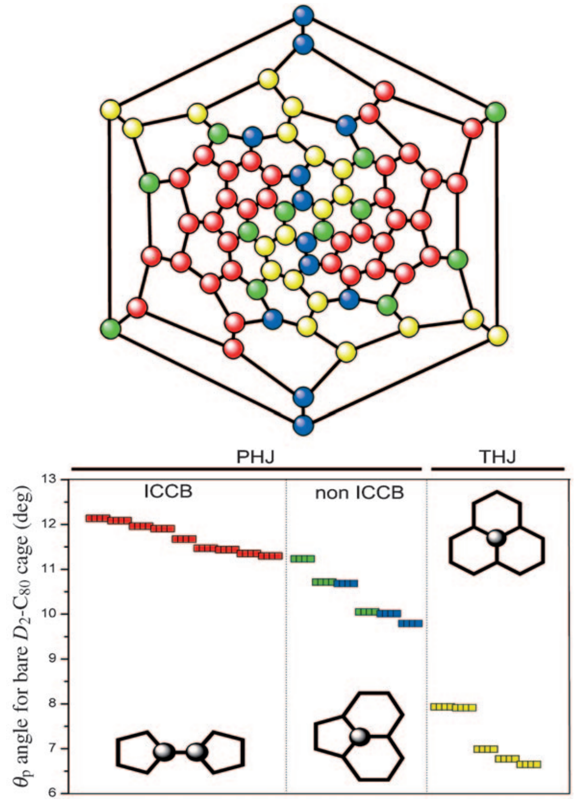

Figure 2. Bottom: A chart showing the θ_p angle distribution for bare-cage DFT-optimized D_2-C_{80}. ICCB (interpentagon C−C bond) carbon atoms are highlighted in red, PHJ (pentagon–hexagon junction) in blue (and green, where chlorine binds) and THJ (triple-hexagon junction) in yellow. Carbon atoms to which 12 Cl atoms are attached in $C_{80}Cl_{12}$ are highlighted in green. Top: Schlegel diagram of D_2-$C_{80}(2)$ presenting the same colour code for the carbon atoms as in the θ_p-chart.

hexagon junction—PHJ), but do not bridge two pentagons (to be distinguished from ICCB). Indeed, in most of the reported halogenated higher fullerenes,[9] the halogen atoms bind to carbon atoms at 1,4-positions in the hexagons (i.e., to PHJ carbon atoms) in such a way that contiguous ribbons of halogen atoms form. The tendency of generating ribbons of 1,4-addition exclusively was first reported by Strauss et al.,[10] proposing by this a principle of higher fullerene reactivity. However, the violation of this principle in the case of $C_{76}Cl_{18}$ in which ten out of eighteen chlorine atoms bind to ICCB carbon atoms, thus at 1,2-positions in hexagons,[5] needs to be discussed.

Based on Euler's theorems for systematically addressing topologies of convex polyhedra, the molecular structures of all IPR fullerenes higher than C_{60} contain THJ fragments. We have recently shown that in higher fullerenes the central C−C bonds in the pyrene fragments are the longest ones,[11] although the geometry of these fragments is suitable for effective conjugation. For comparison, in the isolated pyrene molecule the length of the corresponding bond is 1.422 Å,[12] while in $C_{84}(14)$ it varies from 1.464 to 1.484 Å.[11] Such elongation of these bonds is a direct consequence of the curvature introduced to the "inherently planar" pyrene fragments. Since a direct addition to THJ carbon atoms is unfavourable, the system endeavours to release strain in these extended areas by modifying them through introducing sp^3-hybridized carbon atom(s) at least in one of the member hexagons. On that account, the only possible sites for chlorine attack are the PHJs. As a parallel directing force, one has to consider the formation of quasi-aromatic systems (the two phenomena should not be regarded separately). Figure 3 provides an insight into the changes occurring to the π-system of the parent $C_{80}(2)$ fullerene cage upon chlorination. The

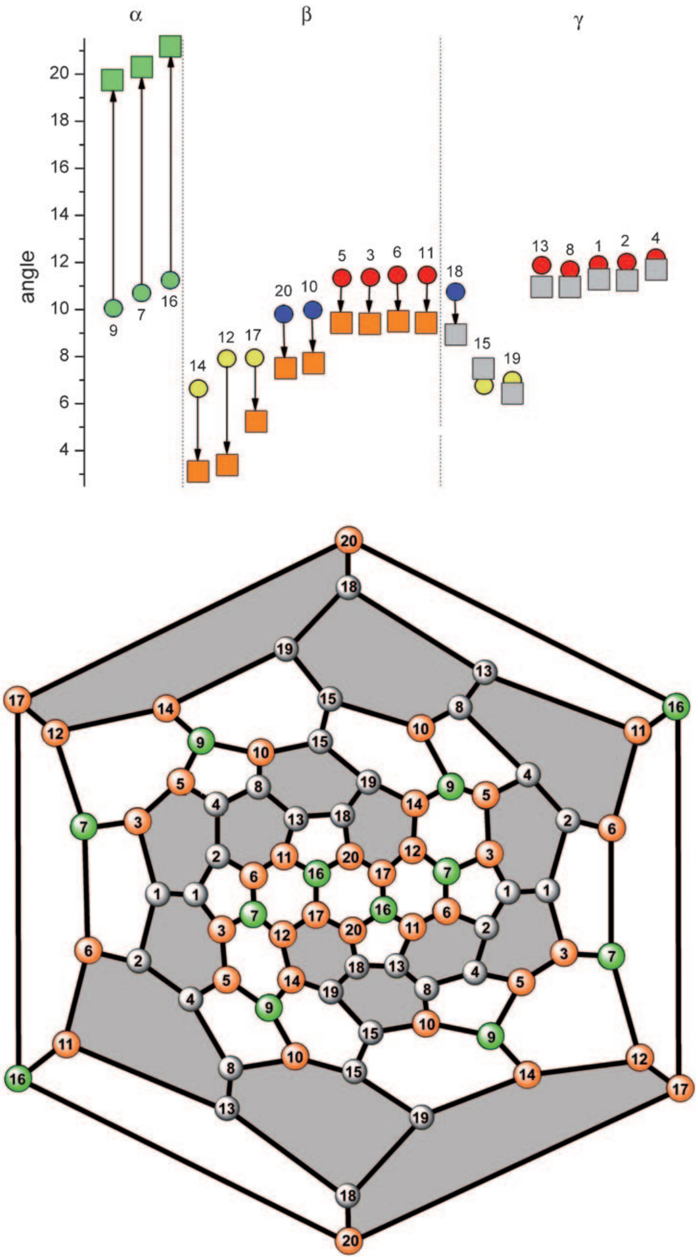

Figure 3. Top: Schematic representation of θ_p angle change after chlorine addition to bare-cage $C_{80}(2)$—circles depict the carbon atoms in the pristine fullerene (the colour codes bear the same meaning as in Figure 2), whereas squares correspond to those in $C_{80}Cl_{12}$. Bottom: Schlegel diagram of $C_{80}Cl_{12}$ showing two extended "aromatic" systems (in gray).

carbon atoms to which chlorine atoms connect in $C_{80}Cl_{12}$ have changed their hybridization to sp^3 (class α), destroying all THJ in the sense described above. The sp^2-hybridized carbon atoms connected to C_{sp^3} neighbours (class β) have significantly decreased θ_p angles, while the rest remained more or less the same (class γ—C_{sp2} connected to C_{sp2} only). The trend of decreasing pyramidalization after chlorine addition observed for the sp^2-hybridized carbon atoms evidently stabilizes the molecule by creating rather extended quasi-aromatic systems (two belts comprising eight hexagons each are depicted in gray in Figure 3).

Now, if we go back to the proposed principle of higher fullerene reactivity, the formation and orientation of 1,4-addition ribbons are conditioned by the contiguous arrangement of THJ carbon atoms (see Figure 2, top), as well as by the generation of stable conjugated systems. Further reaction of the fullerene molecule is possible if energy is gained by introducing another π-system. A good example here is provided by the structures of $C_{70}X_{10}$ (X = Cl, Br),[9c,13] and $C_{70}Cl_{16}$.[14] In $C_{70}X_{10}$ the halogen atoms build up a loop of 1,4-addition around the equatorial mirror plane of C_{70}, releasing by this the strain in THJ fragments and leaving behind essentially the same alternant bond pattern characteristic for C_{60}. Halogenating $C_{70}X_{10}$ further results in the product $C_{70}Cl_{16}$, in which the additional six chlorine atoms replicate the addition pattern in $C_{60}X_6$ (X = Cl, Br).[15e,f] Since in I_h-C_{60} there are no THJ fragments and only two types of bonding exist (one of them ICCB), the existence of a whole homologous series of halogen derivatives[15] demonstrates the "availability" of the ICCB carbon atoms for chlorine addition. Therefore, the presence of a string of contiguous 1,2-addition in $C_{76}Cl_{18}$, in which ten chlorine atoms are attached to ICCB carbon atoms, is not unusual (for further reference consult the Supporting Information), as far as all "obstructive" THJ are eliminated and an extended "aromatic" system is created.

The crystal structure of $C_{80}Cl_{12}$ displays another remarkable feature: ten out of twelve chlorine atoms from each fullerene molecule are involved in short intermolecular Cl···Cl contacts (3.3–3.5 Å) with their neighbouring molecules. The other two chlorine atoms also form short intermolecular contacts, but with carbon atoms (3.230 Å). While six of the Cl···Cl separations can be explained by the available theories for short halogen contact formation,[16,17] four display energetically unfavourable geometry with respect to the angles between the two C−Cl covalent bond axes and that separating the chlorine atoms (Figure 4).[16] To our knowledge, such type of contacts has not been previously observed and can be explained neither by close packing of anisotropic van der Waals bodies (Figure 4, the top representation to the right),[16] nor by the so called halogen bonding (Figure 4, the central representation to the right).[17]

In summary, the connectivity pattern of the carbon atoms in the chiral D_2-$C_{80}(2)$ fullerene has been confirmed through single-crystal X-ray analysis of its chlorine derivative $C_{80}Cl_{12}$. Careful analysis of the addition patterns of chlorine atoms in the presented structure, together with the structures of other halogenated fullerenes, has suggested a stepwise character of fullerene reactivity. The system's endeavour to release tension in the extensive fragments of triple hexagon junctions by changing the hybridization of some carbon atoms to sp^3 might well be defined as the initial step in exohedral derivatization of fullerene species. Depending on the nature of the additive, the process might terminate at that stage (e.g., when spacious groups are considered) or continue further. A prerequisite for the direction and extent of addition is the formation of a stable conjugated system(s).

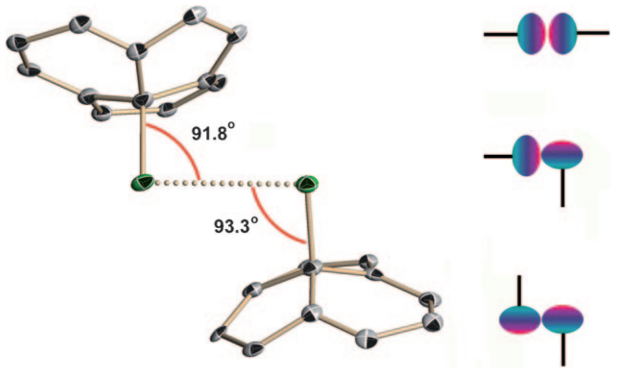

Figure 4. Left: A close contact formation between two chlorine atoms from neighbouring fullerene molecules in the crystal structure of $C_{80}Cl_{12}$ (for clarity, only fragments of the two molecules are shown). Right: Possible mutual orientations of chlorine atoms in close contact formation—the top representation shows an example of close packing of anisotropic atoms, the central visualizes the so-called halogen bonding, whereas the bottom presents the case in $C_{80}Cl_{12}$ crystal.

Experimental Section

The pristine fullerene was produced by evaporation of graphite along the RF-furnace route, details of which have been published elsewhere.[18] Collected soot was soxhlet extracted and separated by multistep HPLC. The new fullerene halide was obtained through chlorination of $C_{80}(2)$ (0.05 mg) in mixture of $Br_2/TiCl_4$ (1.0 mL, 1:200 v/v) in a closed glass ampoule. Orange crystals formed directly on the glass wall after heating the mixture at 150 °C for five days. Subsequently, the ampoule was opened and the excess solvent decanted. The product was found to be stable in air for at least one month. X-ray diffraction data were collected using a Bruker APEX II CCD difractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator). The crystal structure was solved and all atoms refined in the anisotropic approximation by using SHELXTL.[19] Quantum chemical calculations were performed using the DFT method of B3LYP/6-31G* with Gaussian 03.[20]

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Keywords: chirality · chlorination · fullerenes · structure elucidation

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[6] Crystals of D_2-$C_{80}Cl_{12}$: 0.04×0.02×0.02 mm; monoclinic; space group $C2/c$; $a=21.043(3)$, $b=11.1665(14)$, $c=21.510(3)$ Å; $\alpha=\gamma=90°$, $\beta=106.235(2)°$; $V=4852.8(11)$ Å^3; $Z=4$; 2θmax$=55.56°$; $-27\leq h\leq 27$, $-14\leq k\leq 14$, $-28\leq l\leq 28$; $\lambda=0.71073$ Å.; $T=100(2)$ K.; reflections/parameters = 13.7325; full-matrix least-squares refinement on F^2; $\mu=0.746$ mm^{-1} (exp. absorpt. min/max = 0.9708/0.9852); final R indices $[F_o>4\sigma(F_o)]$ are $R1=0.0422$ and $wR2=0.0769$. CCDC 706381 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

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