Fullerenes

A [70]Fullerene Chloride, $C_{70}Cl_{16}$, Obtained by the Attempted Bromination of C_{70} in $TiCl_4$**

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The use of liquid inorganic chlorides as chlorinating agents for fullerenes resulted recently in the synthesis of several new chlorofullerenes. In addition to $C_{60}Cl_6$, which was obtained many years ago and investigated by ^{13}C NMR and IR spectroscopy,[1] four highly chlorinated [60]fullerenes, $C_{60}Cl_{24}$,[2] $C_{60}Cl_{28}$,[3] and two isomers of $C_{60}Cl_{30}$,[3,4] have been prepared and characterized by means of single-crystal X-ray crystallography and IR spectroscopy. The application of this method to the chlorination of C_{70} produced a highly chlorinated fullerene, $C_{70}Cl_{28}$, which, according to the single-crystal X-ray crystallographic study, comprised three isomers with similar structures.[5] Earlier, $C_{70}Cl_{10}$ was prepared by treating C_{70} with ICl in benzene; its addition pattern has been deduced from ^{13}C NMR spectroscopic analysis,[6a] substitution reactions,[6b] and theoretical modeling studies.[6c] Thus, the chlorination of the fullerenes under mild conditions results in "lower" chlorides, whereas the use of strong chlorinating agents at elevated temperatures produces "higher" chlorides of both [60]- and [70]fullerenes. These results raise the question as to whether "missing" intermediate chlorides could be obtained by variation of the reactants and/or reaction conditions.

Herein, we report the synthesis of such an intermediate chloride of [70]fullerene, $C_{70}Cl_{16}$, and its characterization by single-crystal X-ray crystallography, IR spectroscopy, and DFT calculations. Notably, the new fullerene chloride was obtained during an attempt to brominate C_{70} in $TiCl_4$. Typically, neat bromine (0.5 mL) was added to a solution of C_{70} (30 mg) in $TiCl_4$ (2.0 mL) in a glass ampoule. The ampoule was evacuated on cooling and sealed. A yellow crystalline precipitate formed after heating the mixture at 60–80 °C for 1–2 days. Work-up consisted of distilling off the bromine and excess $TiCl_4$ into a second section of the sealed ampoule by cooling it with liquid nitrogen. Alternatively, the ampoule was opened and the mixture was poured into 15 % HCl. The yellow precipitate so formed was washed with dilute HCl and then water before removal by filtration and drying at 50 °C for

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several hours. The product was stable in air for many months. Thermal decomposition occurs between 240 and 360 °C (a typical temperature range for fullerene chlorides[7]) with the evolution of chlorine and small amounts of bromine, as monitored by mass spectrometric analysis of the evolved gases.

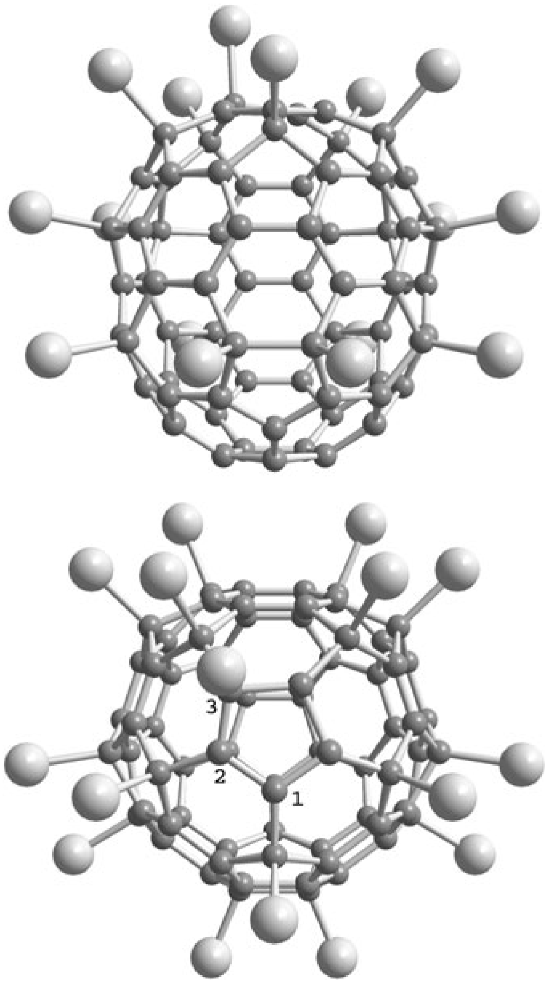

Figure 1. Side and top views of the C_1 isomer of $C_{70}Cl_{16}$.

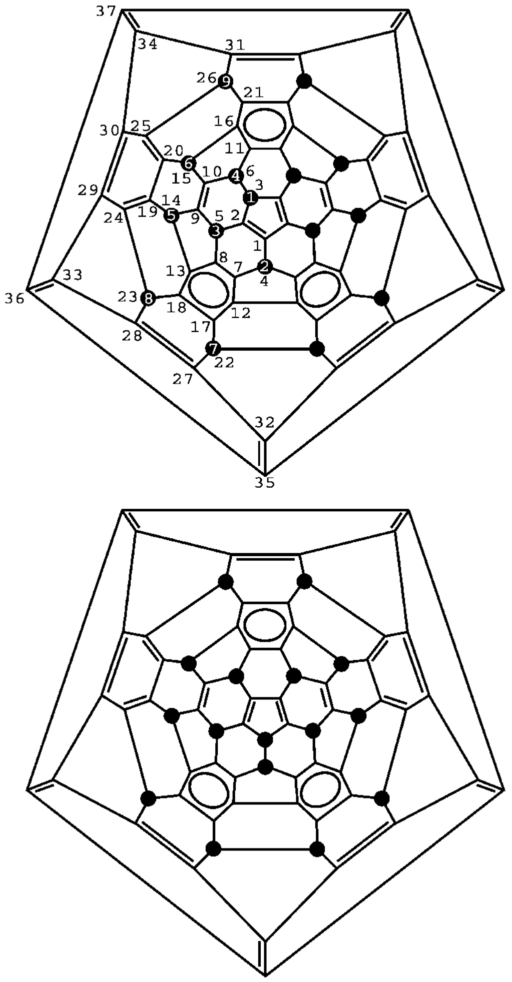

Figure 2. Schlegel diagrams for the experimentally observed C_1 (top) and C_s (bottom) isomers of $C_{70}Cl_{16}$ showing the labeling scheme for the independent C and Cl atoms. An alternative labeling with contiguous numbering for the whole molecules is given in the Supporting Information.

The crystal-structure determination revealed the product had a composition of $C_{70}Cl_{16}{\cdot}0.5\,Br_2$ (**1**).[8] The molecular structure of $C_{70}Cl_{16}$ shows a remarkable combination of a chlorine belt around the equator and a skew pyramidal chlorine cap at one of the poles (Figures 1 and 2). The same belt of ten halogen atoms (Cl5–Cl9 in **1**) with nine 1,4 and one 1,2 X⋯X contacts is also present in $C_{70}Cl_{10}$[6] and $C_{70}Br_{10}$,[9] whereas a X_{10} belt without a 1,2 contact was reported recently for the $C_{70}(OO\textit{t}Bu)_{10}$ derivative.[10] The combination of a skew pyramidal cap of six halogen atoms (Cl1–Cl4) with a cyclopentadiene fragment in the pentagon is characteristic of $C_{60}X_6$ structures with X being Cl[1] or Br.[11] A similar fragment was found in the $C_{70}(OO\textit{t}Bu)_6$ derivative, but not on the top pentagon.[10] Both enantiomeric $C_{70}Cl_{16}$ molecules with C_1 symmetry are present in the crystal of **1**; their overlapping results in overall C_s symmetry with statistically disordered C3 and Cl1 atoms. A comparison of the experimental and calculated[12] IR spectra demonstrates their close similarity (Figure 3), thus suggesting the high purity of $C_{70}Cl_{16}$ in compound **1**.

Another compound (**2**) obtained when the reaction was carried out with a larger amount of bromine had a composition of $C_{70}Cl_{16}{\cdot}3\,Br_2$ according to the single-crystal X-ray analysis.[8] In spite of the poor crystal quality, the X-ray crystallographic study of **2** has unambiguously revealed the presence of two isomers of $C_{70}Cl_{16}$, namely, those with chlorinated positions at C1 (C_s) and C3 (C_1), in a ratio of approximately 3:4 (Figure 2). The IR spectrum of **2** was virtually identical to that of **1**.

Averaged experimental C−C bond lengths in **1** correspond satisfactorily to those calculated at the PBE/TZ2P level of theory.[12] The longest bond (C22−C22a) between sp^3 carbon atoms is 1.65 Å (calcd: 1.64 Å), while sp^2–sp^3 C−C bonds are shorter with an averaged value of 1.51 Å (calcd: 1.51 Å). Two independent six-membered isolated (C11-C16-C21-C21a-C16a-C11a) and nearly isolated (C7-C8-C13-C18-C17-C12)

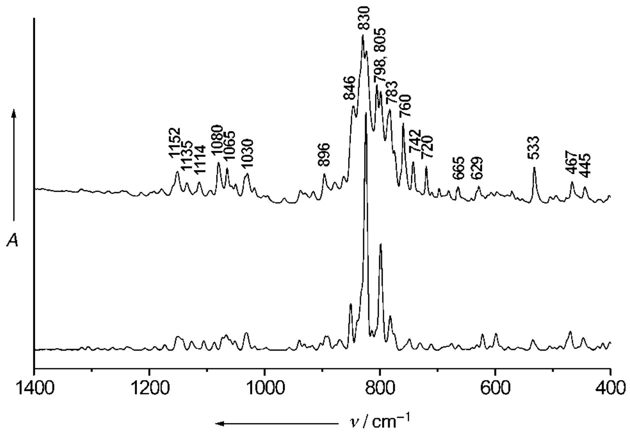

Figure 3. Experimental IR spectrum (above) of (**1**) and calculated one for C_1-$C_{70}Cl_{16}$ (below) using force-field scaling factors found for the $C_{60}Cl_{24}$ molecule.[2]

aromatic rings are characterized by averaged C–C bond lengths of 1.39 Å (calcd: 1.40 Å). Finally, there are two isolated double C–C bonds with an average bond length of 1.34 Å (calcd: 1.34 Å). Bond lengths in the chlorinated cap region are distorted as a result of disorder in the crystal. The average C–Cl (Cl2–Cl9) bond has a length of 1.85 Å, whereas the apparent effective position of C3 (between two actual positions in each enantiomer) results in a strongly elongated C3···Cl1 distance (2.04 Å).

DFT calculations performed at the PBE/TZ2P level revealed that three isomers of $C_{70}Cl_{16}$ with different positions of the chlorinated carbon atoms in the cyclopentadiene ring on the cap are essentially isoenergetic with the relative energies of 0 (for C1), 2.8 (C3), and 7.6 kJ mol^{-1} (C2).[13] Alternative $C_{70}Cl_{16}$ structures with a cap of six chlorine atoms on the opposite pole of the cage were found to be 33–40 kJ mol^{-1} less favorable; this result may be attributed to the presence of only two benzenoid rings in their addition patterns compared to three such rings in the synthesized isomers.

It is known from our recent investigation of the bromination of [70]fullerene that even the use of liquid bromine does not result in the addition of more than ten Br atoms to the [70]fullerene cage.[9] Therefore, the formation of $C_{70}Cl_{16}$ can not be explained by two successive steps, such as bromination to give $C_{70}Br_{16}$ and halogen exchange. $TiCl_4$ itself can not chlorinate C_{70}; the solvate $C_{70}\cdot 2\,TiCl_4$ has been isolated from a solution of C_{70} in $TiCl_4$ and characterized by single-crystal X-ray crystallography.[14] Although the mechanism of the [70]fullerene chlorination by the mixture of Br_2 and $TiCl_4$ remains unclear, it can be assumed that the formation of the chloride higher than $C_{70}Cl_{10}$ results from the high Lewis acidity of $TiCl_4$. The formation of Br^+ or BrCl species in Br_2/Lewis acid systems is known to promote the electrophilic bromochlorination of olefins.[15] Clearly, $TiCl_4$ also participates in a Br/Cl exchange that results in the thermodynamically more stable chloride. The exclusive formation of chlorides as the reaction products is documented, for example, for the system Br_2/$SbCl_5$/norbornene.[16] However, bromination of C_{70} with Br_2 in molten $TiBr_4$ produced only $C_{70}Br_{10}$, possibly because of the absence of BrCl molecules in this system.

Alternatively, the reaction may proceed through a radical mechanism involving the addition of $Br^{\bullet}$ with subsequent Br/Cl exchange. In this case, the formation of $C_{70}Cl_{16}$ can be rationalized with a simple kinetic model,[17] when it is assumed that addition occurs in turn to the sites of maximum free valence in closed-shell molecules and of maximum spin density in the radicals; furthermore, 1,2-addition of a bulky addend (Br or Cl) is avoided unless it is necessary to quench the radical. This model successfully explains the formation of $C_{60}X_6$ and $C_{70}X_{10}$ isomers by the radical addition of bulky groups to C_{60} and C_{70}.[17] We have found by using bond orders from extended Hückel calculations that the most reactive site in $C_{70}X_{10}$ (X = Br or Cl) is C4. Further addition occurs in the sequence C5-C6-C5a-C6a until the radical $C_{70}X_{15}^{\bullet}$ is formed. The maximum spin density in $C_{70}X_{15}^{\bullet}$ is located on C1 (0.38), C3 (0.20), and C3a (0.20), whereas the spin density on the C2 and C2a sites is only 0.03. Thus, both energetic and kinetic considerations favor the experimentally observed isomers of $C_{70}Cl_{16}$.

In summary, the reaction between C_{70} and a Br_2/$TiCl_4$ mixture resulted in the isolation of the new chlorofullerene $C_{70}Cl_{16}$. X-ray crystallography elucidated the structure of two $C_{70}Cl_{16}$ isomers, which are the most stable according to theoretical calculations. Formation of these isomers was also rationalized from kinetic considerations based on the Hückel theory. This new reaction represents a promising synthetic approach for the preparation of chlorofullerenes with a level of addition that lies between that of the "lower" and "higher" fullerene chlorides.

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[8] Data collection for crystals of $C_{70}Cl_{16}\cdot 0.5\,Br_2$ (**1**) and $C_{70}Cl_{16}\cdot 3\,Br_2$ (**2**) was performed on a MAR345 image plate at 100 K using synchrotron radiation on the BESSY storage ring (PSF BL14.2 of the Free University of Berlin, Germany). **1**: hexagonal, space group $P6_3/m$, $a = 21.631(2)$, $c = 19.019(2)$ Å, $V = 7707(1)$ Å^3, $Z = 6$; reflections collected 17141, independent 2701. Structure solution with SHELXS-97. The final anisotropic LS refinement (SHELXL-97) with 423 parameters converged to $wR_2 = 0.128$ and $R_1 = 0.052$. **2**: orthorhombic, space group $Ama2$, $a = 18.743(1)$, $b = 24.595(2)$, $c = 13.117(1)$ Å, $V = 6046.7(7)$ Å^3, $Z = 4$; reflections collected 9015, independent 2885. Anisotropic LS refinement with 476 parameters gave the final values of $wR_2 = 0.213$ and $R_1 = 0.088$. CCDC-261277 and -261278 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.

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