Fullerenes

Preparation and Structural Characterization of Two Kinetically Stable Chlorofullerenes, $C_{60}Cl_{28}$ and $C_{60}Cl_{30}$**

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Dedicated to Professor Arndt Simon
on the occasion of his 65th birthday

Compared with bromo- and fluorofullerenes, fullerene chlorides have been studied to a lesser extent. However, they can find versatile application as synthons for valuable derivatives.[1] According to various sources, the reactions of [60]fullerene with different chlorinating agents yield $C_{60}Cl_n$ products with a bulk composition that varies from $C_{60}Cl_6$ to $C_{60}Cl_{40}$.[2] The most reliable data have been obtained for $C_{60}Cl_6$, which was prepared by treatment of C_{60} with ICl in solution in benzene. Its molecular structure was first suggested on the basis of ^{13}C NMR spectroscopy and was later confirmed in the structural study of related phenyl and methyl derivatives.[2b,3]

In our previous publication, higher chlorides of the variable-valency elements were suggested as effective chlorinating agents for fullerenes.[4] The use of $SbCl_5$ or VCl_4 resulted in the selective synthesis of T_h-$C_{60}Cl_{24}$ with high yields and isomeric purity. The structure was deduced by comparison of the experimental and theoretically calculated IR spectra. Very recently, a novel chlorofullerene, D_{3d}-$C_{60}Cl_{30}$, was synthesized and structurally characterized.[5] Here we report the preparation of two new chlorofullerenes, C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$, which have been characterized by means of X-ray single-crystal diffraction studies, IR spectroscopy, and quantum chemical calculations.

Pure T_h-$C_{60}Cl_{24}$ can be prepared by reacting C_{60} (30 mg) with VCl_4 (2 g) in sealed ampoules at 160 °C for 14 days.[4] An increase in the reaction time was accompanied by the appearance of new bands in the IR spectra and the disappearance of the bands characteristic of T_h-$C_{60}Cl_{24}$. After 2 months heating, a new compound was formed with a ratio of Cl:C of 29 ± 1 according to elemental analysis data.

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The IR spectrum of the new compound is presented in Figure 1 a.[6] Crystallization from bromine yielded a solvate whose composition $C_{60}Cl_{30}\cdot 1.5\,Br_2$ (**1**) was established by single-crystal X-ray crystallography.[7]

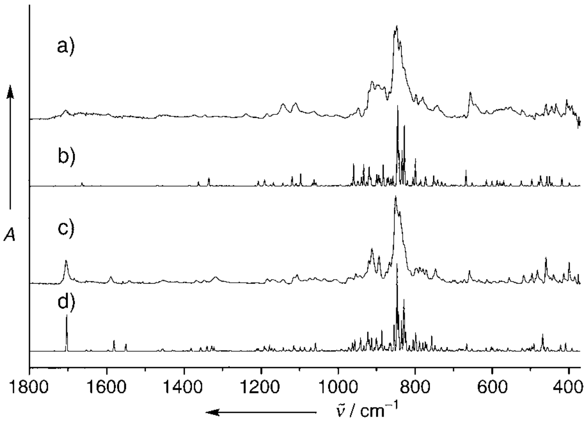

Figure 1. Experimental and calculated IR spectra of C_2-$C_{60}Cl_{30}$ (a and b) and C_1-$C_{60}Cl_{28}$ (c and d).

Chlorination of C_{60} with iodine monochloride at 120 °C for 30 days resulted in the formation of dark-brown crystals whose composition $C_{60}Cl_{28}\cdot ICl$ (**2**) was also determined by X-ray crystallography.[7] The IR spectrum of **2** is shown in Figure 1 c. Some other experiments carried out at the same temperature for a shorter time revealed the presence of T_h-$C_{60}Cl_{24}$ in the reaction mixture according to IR spectra. Notably, the reaction of T_h-$C_{60}Cl_{24}$ with $SbCl_5$ at 300 °C for two days afforded pure D_{3d}-$C_{60}Cl_{30}$.

The formation of the chlorofullerenes $C_{60}Cl_{28}$ (**2**) and $C_{60}Cl_{30}$ (**1**) is quite remarkable. Their molecular structures are characterized by the presence of two planar aromatic rings (which are inclined to one another) and two long chains of sp^3-hybridized carbon atoms that bear chlorine atoms (Figure 2 and Figure 3). The $C_{60}Cl_{28}$ molecule has no symmetry elements (C_1), although the counterparts of most atoms (except C35 and C42) are located following 180° rotation around the pseudo-C_2 axis (parallel to the view directions on Figure 2 (left) and Figure 3 (left)). The addition of two Cl atoms to the $C_{60}Cl_{28}$ molecule at positions C35 and C42 produces the $C_{60}Cl_{30}$ molecule, which then possesses a (non-crystallographic) twofold axis (Figure 2 b).

Quantum chemical DFT (density functional theory) calculations of the molecular structures of the chlorofullerenes[8a] revealed a comparatively good agreement between experimental and calculated C–C bond lengths. C–C bonds can be separated into five major groups according to their nature: isolated double bonds that connect nonaromatic sp^2-hybridized carbon atoms (average length, calcd for $C_{60}Cl_{28}$: 1.355; observed: 1.344 Å), aromatic bonds (calcd: 1.392; observed: 1.385 Å), $C(sp^2)$–$C(sp^2)$ bonds between two double

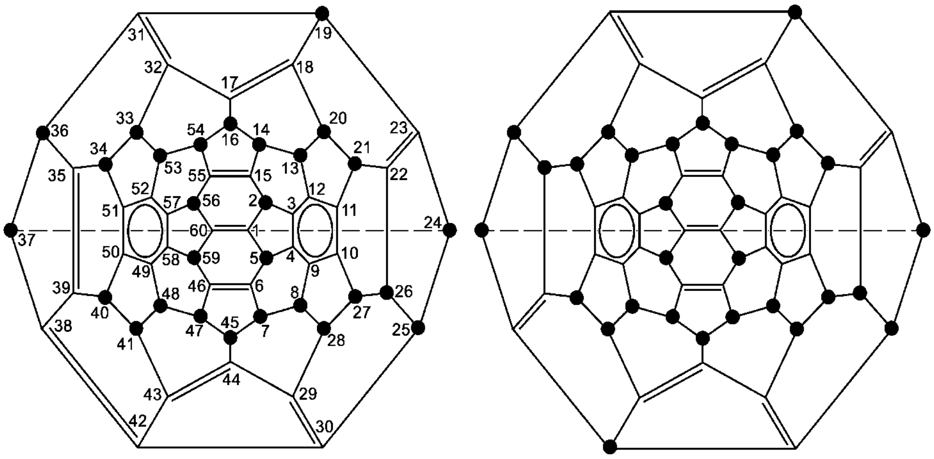

Figure 2. Schlegel diagrams of C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ with a numbering scheme for carbons that is identical for both molecules. For convenience, a nonstandard numbering scheme was used that fixed the sum of the numbers for equivalent positions in C_2-$C_{60}Cl_{30}$ to 61.

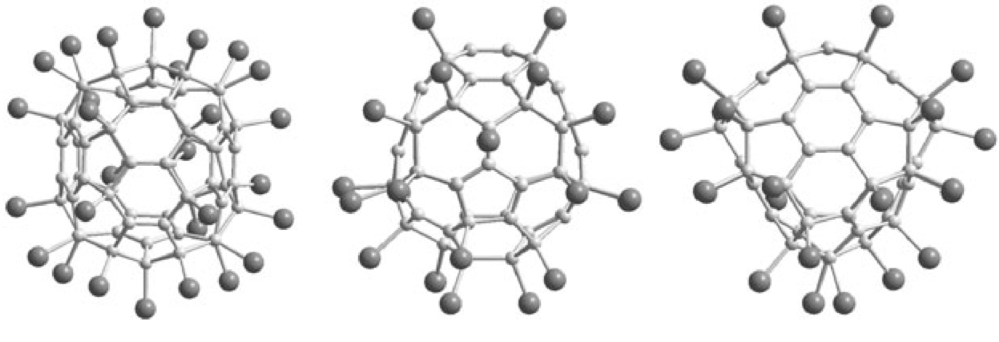

Figure 3. Top and side views of the C_1-$C_{60}Cl_{28}$ molecule.

bonds (calcd: 1.439; observed: 1.443 Å), C(sp^2)–C(sp^3)bonds (calcd: 1.500; observed: 1.500 Å), and, finally, considerably elongated C(sp^3)–C(sp^3) bonds (calcd: 1.621; observed: 1.615 Å). Especially long C–C bond lengths (up to 1.65–1.66 Å) are observed for the 6/6 bonds of this latter type. A similar correspondence has been found for the $C_{60}Cl_{30}$ molecule. However, the addition of two Cl atoms to the $C_{60}Cl_{28}$ molecule results in local repositioning of the double bonds. Thus, bond lengths (Å) of 1.37–1.44–1.36 in the C35–C39–C38–C42 fragment in **2** become 1.53–1.33–1.44 in **1**.

IR spectra for C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ revealed their close similarity, especially in the range of the strongest absorptions between 700 and 1000 cm^{-1}. The most prominent differences in the spectra of **1** and **2** can be found for two bands at 1705 and 1589 cm^{-1} that are characteristic of $C_{60}Cl_{28}$ (Figure 1 d). According to DFT vibrational simulations, which give a very good match with the experimental spectrum (Figure 1 c) of $C_{60}Cl_{28}$ (**2**), these characteristic modes correspond, respectively, to the stretching vibration of the double bond between two pentagons (C38–C42) and the symmetric vibration of two double bonds in the "bare" pentagon (C29–C30 and C43–C44). In other words, these vibrations are located on the fragment which is subjected to further chlorination to yield C_2-$C_{60}Cl_{30}$ (**1**) and therefore these bands are absent in the calculated IR spectrum of the latter (Figure 1 b). At the same time, the experimental IR spectrum of **1** (Figure 1 a) showed weak absorptions near 1705 and 1589 cm^{-1} which indicates the presence of a small amount of $C_{60}Cl_{28}$ in the sample.

Chlorination of C_{60} with $SbCl_5$ or ICl carried out at higher temperature (above 250 °C) finally resulted in another chlorofullerene, namely, D_{3d}-$C_{60}Cl_{30}$.[5] DFT B3LYP computations of the relative energies[8b] show that C_2-$C_{60}Cl_{30}$ synthesized in this work is 78 kJ mol^{-1} less stable than the D_{3d} isomer. Moreover, the C_1-$C_{60}Cl_{28}$ isomer is 6 kJ mol^{-1} less stable than the hypothetical C_2-$C_{60}Cl_{28}$, which could be obtained by the removal of two chlorine atoms from D_{3d}-$C_{60}Cl_{30}$.[9] Hence, DFT computations favor the alternative addition patterns, especially for $C_{60}Cl_{30}$. Indeed, a sample of **1** heated with $SbCl_5$ at 300 °C for 2 days has been completely transformed into D_{3d}-$C_{60}Cl_{30}$ according to the IR spectra.

Experimental observations as well as theoretical calculations, therefore, unambiguously demonstrate that C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$, which have been synthesized and investigated in this work, are kinetically stable chlorofullerenes. Owing to similarity in the addition patterns, C_2-$C_{60}Cl_{30}$ can be easily obtained from C_1-$C_{60}Cl_{28}$ by the addition of two chlorine atoms. Substantial differences in the addition patterns for T_h-$C_{60}Cl_{24}$ (no aromatic rings, only isolated double bonds), C_1-$C_{60}Cl_{28}$ or C_2-$C_{60}Cl_{30}$ (two nonparallel aromatic rings), and D_{3d}-$C_{60}Cl_{30}$ (two parallel aromatic rings along with equatorial 18-π trannulene belt) prevent transformation of less-chlorinated fullerenes into more-chlorinated ones by the simple addition of chlorine atoms (with an exception pointed out above). Therefore, such transformations should include the rearrangement of many chlorine atoms on the fullerene cage and can be regarded as a "chlorine dance".[10] Similar phenomena, "fluorine dance", were found to proceed in the course of fluorination of C_{60}.[11] If the chlorination of C_{60} occurs at temperatures lower than 200 °C, some intermediates of "chlorine dance" can be isolated in their pure form as shown in this work. At higher chlorination temperatures, only the thermodynamically stable D_{3d}-$C_{60}Cl_{30}$ should be obtainable.

In summary, the family of chlorofullerenes is growing. Besides $C_{60}Cl_6$, T_h-$C_{60}Cl_{24}$, and D_{3d}-$C_{60}Cl_{30}$, two new compounds have been isolated, C_1-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$, with the latter being the less stable isomer of $C_{60}Cl_{30}$. Their molecular structures contain two inclined aromatic rings and chains of "chlorinated" carbon atoms. C_1-$C_{60}Cl_{28}$ can be easily transformed into C_2-$C_{60}Cl_{30}$ by the addition of two chlorine atoms, a situation that is unique for known halogenated C_{60} structures. Finally, these molecules are kinetically stable intermediates in the process of "chlorine dance" on the way from $C_{60}Cl_{24}$ to the thermodynamically stable D_{3d}-$C_{60}Cl_{30}$.

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[6] IR spectra were recorded on a NICOLET-200 FT spectrometer (KBr pellets, average of 128 scans, 0.5-cm^{-1} resolution).

[7] Data collection for a crystal of $C_{60}Cl_{30}\cdot 1.5\,Br_2$ (**1**) was performed on a MAR345 image plate at 100 K by using synchrotron radiation at the BESSY storage ring ($\lambda = 0.9184$ Å, PSF BL14.2 of the Free University of Berlin, Germany). **1**: triclinic, $P\bar{1}$, $a = 13.023(1)$, $b = 13.226(1)$, $c = 20.523(2)$ Å, $\alpha = 87.692(5)$, $\beta = 73.942(5)$, $\gamma = 62.424(5)°$, $V = 2995.1(4)$ Å^3, $Z = 2$; 16913 reflections collected, 7888 independent. Structure solution with SHELXS-97. The final anisotropic LS refinement (SHELXL-97) with 839 parameters converged to $wR_2 = 0.162$ and $R_1 = 0.061$. The data for $C_{60}Cl_{28}\cdot ICl$ (**2**) were collected on an IPDS diffractometer (Stoe, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 150 K. **2**: monoclinic, $P2_1/c$, $a = 13.125(2)$, $b = 24.042(4)$, $c = 18.110(3)$ Å, $\beta = 100.58(1)°$, $V = 5618(1)$ Å^3, $Z = 4$; 41306 reflections collected, 11857 independent. The ICl molecule is disordered over three positions. Anisotropic LS refinement with 821 parameters gave the final values of $wR_2 = 0.102$ and $R_1 = 0.040$.

CCDC 247259 and CCDC 247260 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.

[8] a) DFT calculations of molecular structures and IR spectra were performed with the PRIRODA package (see: D. N. Laikov, *Chem. Phys. Lett.* **1997**, *281*, 151) by using PBE functional (see: J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865) and TZ2P-quality basis set; b) Point-energy calculations at PBE/TZ2P geometry were also performed at B3LYP/cc-pVTZ (-f) level (see: A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648) within PC GAMESS package, see: A. A. Granovsky, http://classic.chem.msu.su/gran/gamess/index.html.

[9] Relative energies for $C_{60}Cl_{30}$ and $C_{60}Cl_{28}$ computed at the PBE/TZ2P level of theory were 111 and 40 $kJ\,mol^{-1}$, respectively. Significant differences between PBE and B3LYP relative energies may be attributed partially to the approximate character of PBE/TZ2P values as computations with PRIRODA employed approximate expansion of the electron density in an auxiliary basis set to accelerate the evaluation of Coulomb- and exchange-correlation terms.

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