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# Synthesis and Structures of Fullerene Bromides and Chlorides

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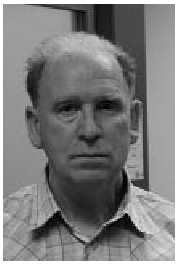
Halogenated fullerenes have been subjects of intensive investigations since the discovery of fullerene, because of their possible further derivatization. This paper reviews the synthesis and molecular structures of fullerene bromides and chlorides, covering earlier work in this field and progress in synthetic methods developed by the authors. The use of inorganic chlorides and oxychlorides for the chlorination of fullerenes allowed the preparation of new compounds that have been fully characterized by single-crystal X-ray diffraction and IR spectroscopy and confirmed by theoretical calculations. Comparison between fullerene bromides, chlorides, and fluorides has revealed that the maximum degrees of halogenation and compound stability increase from the bromides to the fluorides. The larger Cl and Br atoms and the lower C–Hal energies also engender significant differences in addition patterns of the $C_{60}Hal_n$ and $C_{70}Hal_m$ molecules in relation to those of the fluorides.

## 1. Introduction

Over the past decade, halogenated fullerenes have been intensely studied as versatile synthons in fullerene chemistry. Interest in the halogenation of fullerenes originates from their potential for subsequent derivatization. Iodination does not take place, whereas other halogens react with fullerenes under relatively mild conditions. Bromination in different organic solvents results in three fullerene bromides, the structures of which have been determined by diffraction methods. Chlorination with iodine monochloride in benzene allowed the isolation of two fullerene chlorides: $C_{60}Cl_6$[1] and $C_{70}Cl_{10}$.[2] Their addition patterns were derived from their NMR spectra and study of their substitution products. Recently, a chloride of a new fullerene, $C_{50}Cl_{10}$, was obtained from the products of soot condensation in the presence of $CCl_4$.[3] This illustrates an interesting



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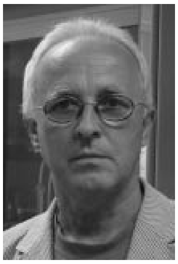

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**MICROREVIEWS:** This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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way to stabilize the fullerene cage with nonisolated pentagons by addition of halogen atoms.

Fluorination of fullerenes with metal fluorides or other fluorination agents (including elemental fluorine) produces a wide range of derivatives, from $C_{60}F_2$ to $C_{60}F_{48}$.[4] Because of their high thermal stabilities, fluorofullerenes – unlike chloro- and bromofullerenes – have been extensively investigated by electron impact (EI) mass spectrometry. In general, separation of the fluorofullerene mixtures usually carried out after the synthetic procedure can be achieved by HPLC (high-pressure liquid chromatography), due to the significantly different polarities of the molecules. Most of these fluorides have been characterized by their addition patterns, which are generally different from those in bromides and chlorides. The progress in the field of fullerene fluoride research is documented in recent review articles.[4–6]

In the few last years we have been focusing on the chemistry and structures of bromides and chlorides of $C_{60}$ and $C_{70}$. Significant refinement of the molecular structures of [60]fullerene bromides has been accomplished on new examples.[7] $C_{70}Br_{10}$ has been isolated and its molecular structure has been determined,[8] whilst a new synthetic method for the selective preparation of fullerene chlorides has been proposed.[9] Several new individual chlorides have been synthesized by this method, and their molecular structures have been determined.

Single-crystal X-ray crystallography has been used for structural studies. As a rule, structural analysis of fullerene bromides is easy, because they form well-shaped crystals. In contrast, growing of single crystals of fullerene chlorides is in most cases a separate and difficult task. These obstacles have been partially overcome by recrystallization of the compounds from different solvents; recrystallization from liquid bromine has been successful in many cases. The use of synchrotron radiation, however, has been necessary in numerous cases in which crystal sizes have been too small (by far) for carrying out of conventional X-ray diffraction experiments.

In addition to synthetic work and structural determinations, theoretical quantum chemical calculations and simulation of IR spectra have been performed for a wide range of compositions. This has allowed the following:

i. evaluation of the thermodynamic or kinetic stabilities of the compounds,

ii. predictions, in some cases, of the structures of the most stable isomers,

iii. conclusions on the purity of a compound by comparison of its experimentally measured and calculated IR spectra – IR spectra of individual compounds have served in subsequent work as important and reliable references for further investigation.

This review updates earlier reports and surveys the current progress of our research into fullerene bromides and chlorides. It focuses on the description of typical synthetic routes, the isolation and characterization of individual compounds, their molecular structures, the thermal, thermodynamic, and kinetic stabilities of different compounds, and their reactivities. Two types of structural representation are used in this review: Schlegel diagrams (flattened two-dimensional format centered on pentagon, hexagon, or C–C bond) and stick-and-ball views of the molecules. In the latter case, the figures have been produced with original data from crystallographic studies.

## 2. Synthesis

### Bromides

Bromides can be synthesized easily, either by bromination of fullerenes dissolved in organic solvent or by treatment with neat bromine.[10–13] Lower [60]fullerene bromides are insoluble in organic solvents, whilst low solubility in liquid bromine has been reported for $C_{60}Br_{24}$. The IR spectra of the [60]fullerene bromides have been published both in earlier[10] and in more recent papers.[12,13]

An early study of [70]fullerene bromination reported a bromofullerene with a possible composition of $C_{70}Br_{14}$ on the basis of elemental analysis and thermogravimetric measurements.[14] However, our recent study revealed that only one [70]fullerene bromide exists, and has the formula $C_{70}Br_{10}$. It is obtained by bromination of the [70]fullerene solution or by treatment of $C_{70}$ with liquid bromine, either in a pure form ($C_{70}Br_{10}$) or as a solvate with bromine ($C_{70}Br_{10}\cdot 3Br_2$); both are deep orange in color.[8] The IR spectra of "$C_{70}Br_{14}$" and $C_{70}Br_{10}$ are almost identical, except for three additional broader bands in that of "$C_{70}Br_{14}$."

Unexpectedly, the bromination of $C_{70}$ containing a very small amount (about 0.5%) of higher fullerenes produced $C_{78}Br_{18}$, isolated at the beginning of the bromination process as small, dark red crystals. The same compound was obtained in small quantities in the bromination of a mixture of higher fullerenes (ca. 22% $C_{78}$).[15]

### Chlorides

According to various sources, treatment of [60]fullerene with different chlorinating agents yields $C_{60}Cl_n$ products with bulk compositions ranging from $C_{60}Cl_6$ to $C_{60}Cl_{40}$.[16–19] The most reliable data have been obtained for $C_{60}Cl_6$, prepared by treatment of $C_{60}$ with ICl in benzene.[1] Its molecular structure was first suggested on the basis of $^{13}C$ NMR spectroscopy and was later confirmed by the structural study of the phenyl and methyl derivatives.[20] The results of a mass spectroscopic study (MALDI, matrix-assisted laser desorption ionization) showed that samples obtained by this method always contain small amounts of phenyl derivative by-products, due to a Friedel–Crafts side reaction with benzene.[20c] The products of a photochlorination of $C_{60}$ dissolved in $CCl_4$ were first claimed to contain $C_{60}Cl_{40}$,[18] but this statement was later retracted by the author.[21]

There have been some reports of the preparation of samples with the composition $C_{60}Cl_{24}$. Heating of $C_{60}$ in a chlorine flow was claimed to yield $C_{60}Cl_{24}$,[16,22] but the compositions of these samples were determined only by elemental analysis, thermogravimetry, or both. In another synthetic study, the product of UV irradiation of a solution of [60]-fullerene in chlorine-saturated carbon tetrachloride was suggested to be $C_{60}Cl_{24}$ on the basis of fast-atom bombardment (FAB) mass spectrometric data.[23] Chlorination of $C_{60}$ with ICl or $ICl_3$ carried out in 1,2-dichlorobenezene seems to yield chlorofullerenes with compositions varying between $C_{60}Cl_6$ and $C_{60}Cl_{26}$.[19] Treatment of $C_{60}$ with liquid chlorine under UV irradiation at room temperature gave a mixture of chlorofullerenes with compositions ranging from $C_{60}Cl_{12}$ to $C_{60}Cl_{32}$ according to MALDI-TOF mass spectrometry.[24] However, all of these samples presented in[19] and[22–24] were not sufficiently characterized.

In recent publications[9,25–30] we have reported selective syntheses of several fullerene chlorides of [60]- and [70]fullerenes through the use of inorganic chlorides and oxychlorides as chlorinating agents. Inorganic chlorides/oxychlorides such as $SbCl_5$, $VCl_4$, $PCl_5$, $MoCl_5$, ICl, $KICl_4$, $VOCl_3$, and $POCl_3$ contain elements with variable valencies. Their oxidizing powers are strongly dependent on the temperatures of the processes, at which they dissociate with formation of lower chlorides/oxychlorides and elemental chlorine. This is similar in principle to the fluorination of the fullerenes with metal fluorides at high temperatures.[4,5] The important difference between these processes is that the chlorinating agents are either liquids at room temperature or melt at the reaction temperature ($PCl_5$, $MoCl_5$, ICl). Additionally, they possess vapor pressures that reach values of about ten bars and even higher at the maximum temperatures used ($SbCl_5$ at 300 °C, for example). All the chlorinating agents are hygroscopic, so contact with air and moisture should be avoided, and for this reason, all the syntheses have been performed in sealed glass ampoules placed in ovens and protected for safety purposes by metallic tubes.

A large excess of chlorinating agent is usually used in the synthesis. After termination of the reaction, excess chlorinating agent and lower chloride (oxychloride) are removed by sublimation in a second section of the ampoule, cooled with liquid nitrogen. It is more convenient to remove the remaining inorganic components, however, by washing with 15% HCl and water, followed by drying of the product at 50 °C for some hours. Fullerene chlorides are yellow to orange powders, stable in air for many months.

Earlier, the lower [70]fullerene chloride, $C_{70}Cl_{10}$, was prepared by treatment of $C_{70}$ with ICl in benzene. It is not very stable on storage, possibly due to the presence of a small amount of organic component produced during synthesis. The use of inorganic chlorides for the chlorination of $C_{70}$ invariably resulted in the preparation of a higher chloride, $C_{70}Cl_{28}$, without the formation of intermediate products. The same compound was obtained when $C_{70}Br_{10}$ was the starting material.[9,29]

Examples of the preparation of individual fullerene chlorides with different chlorination agents and under different conditions (temperature, duration) are given in Table 1. The use of fullerene bromides instead of the parent fullerene allows the temperature of the synthesis or its duration (reaction time) or both to be decreased. It can be concluded that most "higher" inorganic chlorides/oxychlorides can serve as chlorinating agents for the synthesis of higher fullerene chlorides – $C_{60}Cl_{24}$, $C_{60}Cl_{28}$, and $C_{60}Cl_{30}$ (two isomers) – but combinations of physical and chemical properties make the chlorinating agents more or less suitable for the synthesis of individual chlorofullerenes. Optimal combination of the chlorinating agent and reaction conditions allows the selective preparation of individual fullerene chlorides. The presence of by-products in the final products can be explained by insufficient reaction times, low solubility of the fullerene (or the fullerene chloride) in the substrate, or high viscosity of the substrate ($MoCl_5$).

Recently, a new synthetic approach was serendipitously discovered in the attempted bromination of $C_{70}$ dissolved in $TiCl_4$.[31] When a large excess of bromine was used, a new [70]fullerene chloride, $C_{70}Cl_{16}$, with a composition between the lower chloride $C_{70}Cl_{10}$ and the higher one $C_{70}Cl_{28}$, could be reproducibly synthesized. Similar results were found for syntheses performed in liquid $SnCl_4$ and

Table 1. Chlorinating agents and reaction conditions for preparation of fullerene chlorides.

| Starting compound | Chlorinating agent | Temperature [°C] | Reaction time [d] | Isolated products | Refs. |
|---|---|---|---|---|---|
| $C_{60}$ | $POCl_3$ | 100 | 60 | $C_{60}Cl_6$[a] | [30] |
| $C_{60}$ | $VCl_4$ | 160 | 7 | $C_{60}Cl_{24}$ | [25] |
| $C_{60}$ | $MoCl_5$ | 210–225 | 1–11 | $C_{60}Cl_{24}$[b] | [25] |
| $C_{60}$ | $VOCl_3$ | 150 | 4 | $C_{60}Cl_{24}$[c] | [25] |
| $C_{60}Br_{24}$ | $SbCl_5$ | 140 | 14 | $C_{60}Cl_{24}$ | [9,28] |
| $C_{60}Br_{24}$ | $KICl_4$ | 210 | 6 | $C_{60}Cl_{24}$ | [25] |
| $C_{60}$ | ICl | 120 | 30 | $C_{60}Cl_{28}$ | [27] |
| $C_{60}$ | $VCl_4$ | 160 | 60 | $C_{60}Cl_{30}$ ($C_2$ isomer)[d] | [25,27] |
| $C_{60}$ | $SbCl_5$ | 250–280 | 1–3 | $C_{60}Cl_{30}$ ($D_{3d}$ isomer) | [26] |
| $C_{60}$ | ICl | 250–280 | 1–3 | $C_{60}Cl_{30}$ ($D_{3d}$ isomer) | [26] |
| $C_{60}$ | $MoCl_5$ | 300 | 3 | $D_{3d}$-$C_{60}Cl_{30}$[b] | [25] |
| $C_{70}$ | $VCl_4$ | 140–160 | 7 | $C_{70}Cl_{28}$ | [9,29] |
| $C_{70}$ | $SbCl_5$ | 200 | 1 | $C_{70}Cl_{28}$ | [9,29] |
| $C_{70}$ | $PCl_5$ | 180–200 | 2 | $C_{70}Cl_{28}$ | [29] |
| $C_{70}Br_{10}$ | $SbCl_5$ | 120–140 | 7 | $C_{70}Cl_{28}$ | [9,29] |

[a] Admixture of the $C_{60}$ solvate with $POCl_3$. [b] Unreacted $C_{60}$ was present. [c] Broad bands in the IR spectrum indicated the presence of some chlorofullerenes with similar addition patterns. [d] Admixture of a small amount of $C_{60}Cl_{28}$.

$AsCl_3$. If, however, the bromine concentration was low, then the lower chloride, $C_{70}Cl_{10}$ [more exactly, the mixed $C_{70}X_{10}$ compound with X = Cl, Br (5–10%)], was isolated. Similarly, treatment of [60]fullerene with $TiCl_4/Br_2$ mixtures with low bromine concentrations in the solution yielded $C_{60}X_6$ phases, whereas the $C_{60}X_{24}$ compound (with a Cl/Br ratio of about 1:1) was isolated if much higher concentration of bromine in the starting solution was used.[32] These results demonstrate a promising method for obtaining fullerene chlorides with intermediate chlorine contents.

The first chlorofullerenes to be isolated, $C_{60}Cl_6$ and $C_{70}Cl_{10}$, were characterized by $^{13}C$ NMR and IR spectroscopy.[1,2] $^{13}C$ NMR cannot be applied simply to other fullerene chlorides because of their rather low solubilities in most organic solvents. In contrast, IR spectroscopy is a convenient and fast method for the identification of fullerene chlorides and their mixtures. Theoretical calculation of optimized geometry was performed after the addition pattern of the individual compound had been established, either by comparison (with the corresponding fullerene bromide) or from X-ray crystallography. In a subsequent step, the IR spectrum was calculated and compared to the experimentally measured spectrum. The use of scaling factors has sometimes been necessary to achieve a good match. Thus, IR spectra data could be used in subsequent work to check the bulk purities of the compounds. Figure 1 shows IR spectra of some fullerene chlorides in the wavenumber region from 1750 to 400 $cm^{-1}$. The similarity of the IR spectra of $C_{60}Cl_{28}$ and $C_{60}Cl_{30}$ ($C_2$ isomer) is due to the related molecular structures of the two compounds and is discussed in detail in the next section.

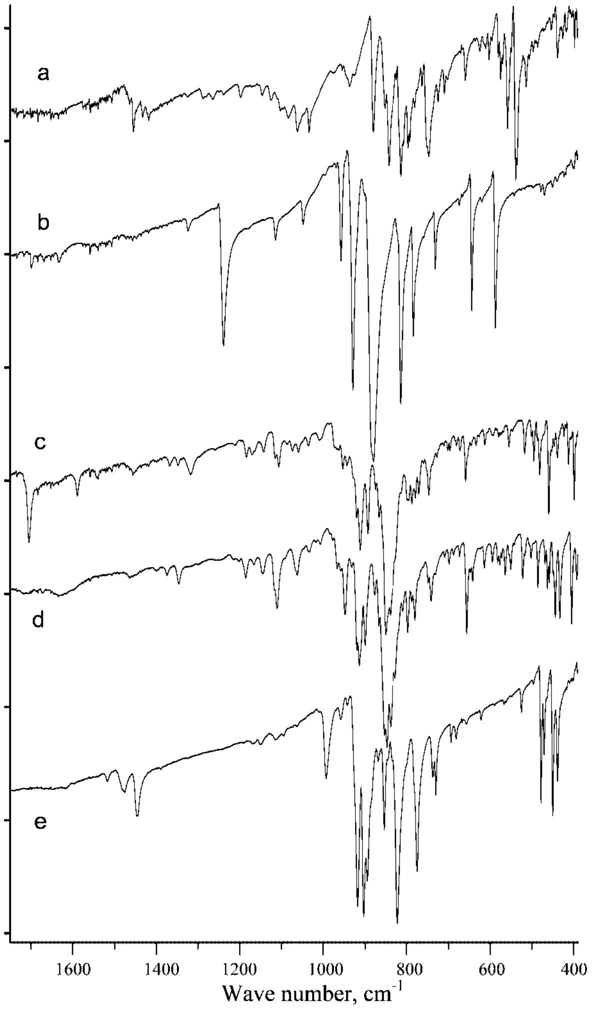

Figure 1. IR spectra of the [60]fullerene chlorides: $C_{60}Cl_6$ (a), $T_h$-$C_{60}Cl_{24}$ (b), $C_{60}Cl_{28}$ (c), $C_2$-$C_{60}Cl_{30}$ (d), and $D_{3d}$-$C_{60}Cl_{30}$ (e).

## 3. Molecular Structures

Two preliminary remarks are important for discussion of the molecular structures of fullerene halides. It is necessary to differentiate between the addition pattern derived from, for example, a $^{13}C$ NMR spectrum or, especially, a characteristic IR spectrum and the molecular structure determined by diffraction methods. The latter provides values for individual bond lengths and angles (both with estimated standard deviations: esds). The third possible type is the structure theoretically predicted on the basis of ab initio or semiempirical quantum chemical calculations. In this last case, the geometry parameters are given without esds. The results of experimental determination should be critically compared with theoretical predictions (calculated C–Hal bond lengths, for example, suffer from systematic errors). The symmetry of the molecule in the crystal state is very often lower than the high symmetry of the idealized (isolated) molecule. In such cases, averaging of some bond lengths (and angles) may be performed by taking account of esd values, which can vary significantly from structure to structure. Special analysis should be performed for structures suffering from disorder phenomena. Final conclusions about molecular symmetry should be drawn after consideration of all the factors described above and also of the fact that the molecule in the crystal is never in an isolated condition (possible small influence of crystal field). Figure 2 shows the addition patterns for the known structures of [60]fullerene bromides and chlorides.

The addition patterns for fullerene bromides and chlorides of equivalent stoichiometry appear to be the same, whereas those for fullerene fluorides vary, due to the lower steric requirements of the fluorine atom. $C_{60}Br_6$ and $C_{60}Cl_6$ molecules both have addition patterns of six halogen atoms in a skew pyramidal cap (Figure 2a and Figure 3). The molecular structure of $C_{60}Br_6$ was one of the first (together with $C_{60}Br_8$) to be determined by X-ray crystallography, for the solvate with bromine. In subsequent work with other solvates ($C_{60}Br_6 \cdot 0.5\,C_6H_5Cl \cdot 0.5\,Br_2$, $C_{60}Br_6 \cdot CS_2$) and with the nonsolvated compound, this molecular structure with $C_s$ symmetry has been determined with better precision.[7,13] In the structure of $C_{60}Br_6 \cdot CS_2$,[13] the crystallographic symmetry of the molecule ($m$) corresponds to that of the isolated molecule ($C_s$). The average C–Br bond length in this solvate, of 2.010 Å, is comparable with the values of 1.99–2.00 Å found earlier.[7,10] The changes in the carbon–carbon bond lengths in the $C_{60}Br_6$ molecule in relation to those in

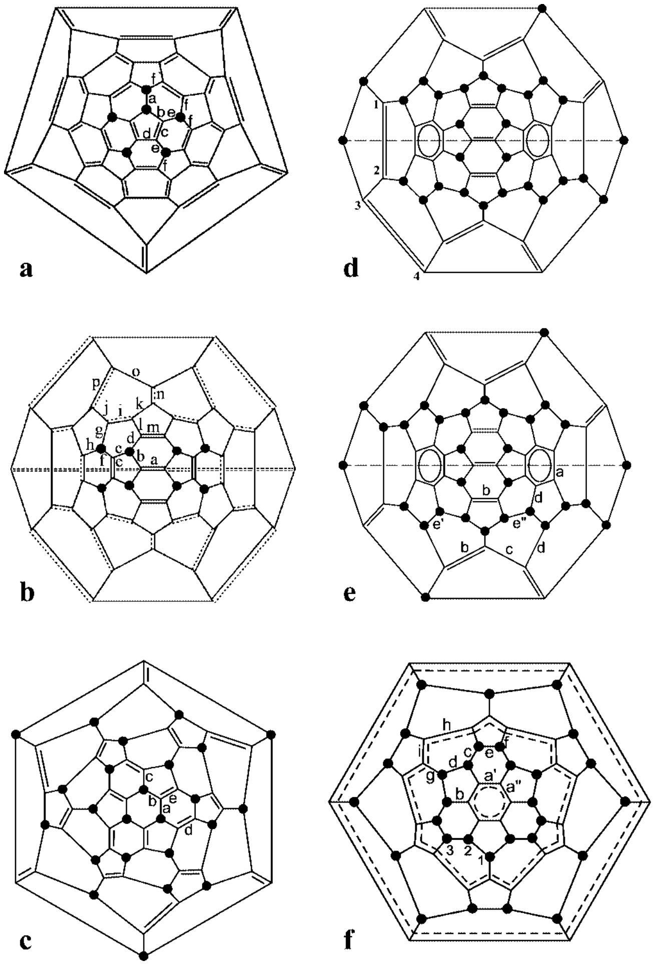

Figure 2. Schlegel diagrams of [60]fullerene bromides and chlorides: $C_{60}X_6$ (a), $C_{60}Br_8$ (b), $C_{60}X_{24}$ (c), $C_{60}Cl_{28}$ (d), $C_2$-$C_{60}Cl_{30}$ (e), and $D_{3d}$-$C_{60}Cl_{30}$ (f).

$C_{60}$ (1.453 and 1.383 Å for two types of predominantly single and double bonds)[33] are significant only for the brominated hemisphere. The largest elongation was observed for the bonds involving sp$^3$-hybridized C atoms (i.e., bearing Br atoms). The bond lengths of the types a (sp$^3$–sp$^3$), b, e, and f (sp$^3$–sp$^2$) are 1.559, 1.532, 1.486, and 1.524 Å, respectively. In the butadiene fragment, the c and d bonds have double (bond length: 1.352 Å) and intermediate (1.476 Å) character, respectively. The molecular structure of $C_{60}Cl_6$ in the crystalline state is similar to that of $C_{60}Br_6$, although the interatomic distances were less precise, due to the presence of two crystallographically independent $C_{60}Cl_6$ molecules, which are additionally slightly disordered in the crystal. The average C–Cl bond length is 1.82 Å.[30]

The molecular structure of $C_{60}Br_8$ has been crystallographically determined several times in different solvates, whereas $C_{60}Cl_8$ has not yet been isolated. In two crystalline solvates – $C_{60}Br_8 \cdot Br_2$[7] and $C_{60}Br_8 \cdot CHBr_3 \cdot 2Br_2$[13] – the crystallographically imposed symmetry (*mm*2) corresponds to the $C_{2v}$ symmetry of the isolated molecule (part b in Figure 2 and Figure 4). The structure of $C_{60}Br_8 \cdot Br_2$ has been determined with higher accuracy. The C–Br bond lengths are 1.992 and 2.008 Å. The arrangement of the Br atoms dictates the presence of isolated carbon–carbon double a, e, and m bonds with lengths of 1.33–1.35 Å and the presence of predominantly carbon–carbon double bonds (i and n) with lengths of 1.37–1.38 Å. The average length of the predominantly carbon–carbon single bonds (sp$^3$–sp$^2$) of the types b, c, d, f, g, and h is 1.510 Å. The carbon–carbon bond lengths in the unbrominated hemisphere differ only slightly from those in the $C_{60}$ molecule.

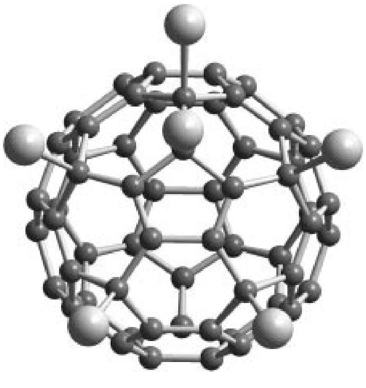

Figure 3. View of the $C_{60}Br_6$ molecule.

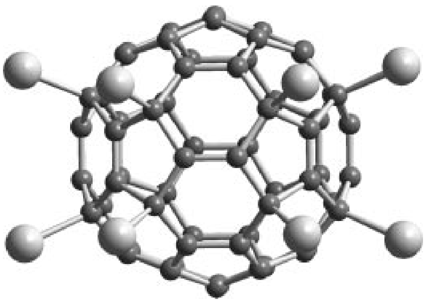

Figure 4. View of the $C_{60}Br_8$ molecule.

The molecular structures of $C_{60}X_{24}$ have been determined by several single-crystal X-ray measurements both for bromide and for chloride. Examples are $C_{60}Br_{24} \cdot Br_2$,[11] $C_{60}Br_{24} \cdot 2Br_2$,[7] and $C_{60}Br_{24} \cdot o\text{-}C_6H_4Cl_2 \cdot Br_2$[13] in the bromide case and $C_{60}Cl_{24} \cdot 2Br_2$[28] and $C_{60}Cl_{24} \cdot VOCl_3$[25] for chloride. For comparison, two isotypic structures – $C_{60}Br_{24} \cdot Br_2$ and $C_{60}Cl_{24} \cdot VOCl_3$ – in which both $C_{60}X_{24}$ molecules have relatively high crystallographically imposed $S_6$ symmetry were chosen. The $C_{60}X_{24}$ molecular structures with $T_h$ symmetry for the isolated molecules differ significantly only in the C–X bond lengths, whereas the carbon cages are essentially the same and contain 18 isolated double bonds and no 1,2-X···X contacts (part c of Figure 2 and Figure 5). The numbers of nonequivalent C and X atoms in the idealized molecule are lowered to three and one, respectively. This results in only one type of C–X bond, two types of double bond, and three types of single C–C bond. Average C–X bonds are 1.993 Å in the bromide and 1.822 Å in the chloride, whilst average bond lengths for single and double C–C bonds are 1.500 and 1.339 Å, respectively, in the bromide and 1.504 and 1.342 Å, respectively, in the chloride. In the chloride, the three types of single bond have distinguishable lengths of 1.508, 1.490, and 1.515 Å, whereas the two double bond types differ less from each other, 1.336 and 1.345 Å, in good agreement by and large with theoretically calculated values.[25]

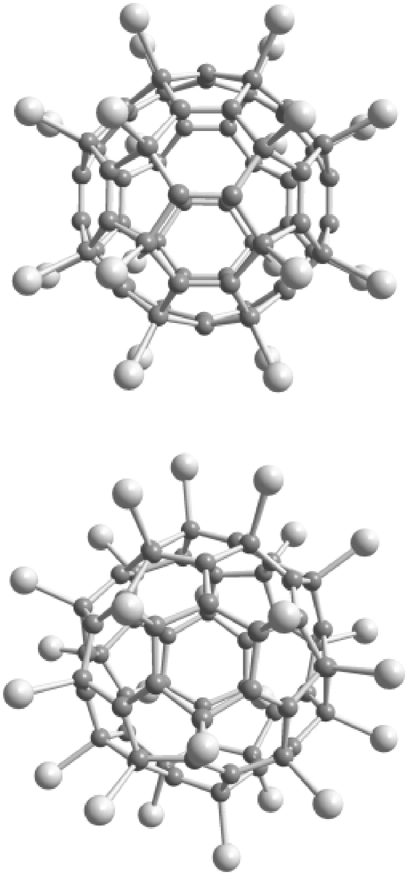

Figure 5. Views of the $T_h$-$C_{60}Cl_{24}$ molecule.

The distortions from the spherical shape are also similar in both molecules: the average distances of C atoms from the center of the cage are 3.765 Å for $sp^3$ C (3.768 Å in $C_{60}Br_{24}$) and 3.582 and 3.476 Å for the two $sp^2$ C atoms (3.586 and 3.481 Å in $C_{60}Br_{24}$).

The maximum number of bromine atoms on the [60]fullerene cage does not exceed 24, and this thus restricts the parallelism in molecular structures of [60]fullerene chlorides and bromides. The three following molecular structures have thus only been found for chlorides. Two higher fullerene chlorides – $C_1$-$C_{60}Cl_{28}$ (determined in the crystal of the solvate $C_{60}Cl_{28}$·ICl) and $C_2$-$C_{60}Cl_{30}$ (in the solvate $C_{60}Cl_{30}$·1.5 $Br_2$) – have similar addition patterns (Figure 2, parts d and e).[27] Their molecular structures are each characterized by the presence of two nonparallel aromatic rings and two long chains of $sp^3$ carbon atoms bearing Cl atoms. The destabilizing effect of many 1,2-Cl···Cl contacts is thus compensated for by the presence of stabilizing benzenoid cycles. The $C_{60}Cl_{28}$ molecule has no symmetry elements, though most of the atoms (except 1 and 4) have a counterpart following a 180° rotation around the pseudo twofold axis (parallel to the view direction on Figure 2, d). The addition of two Cl atoms to the $C_{60}Cl_{28}$ molecule in positions 1 and 4 produces the $C_{60}Cl_{30}$ molecule, which does possess a true twofold axis (part e in Figure 2 and Figure 6).

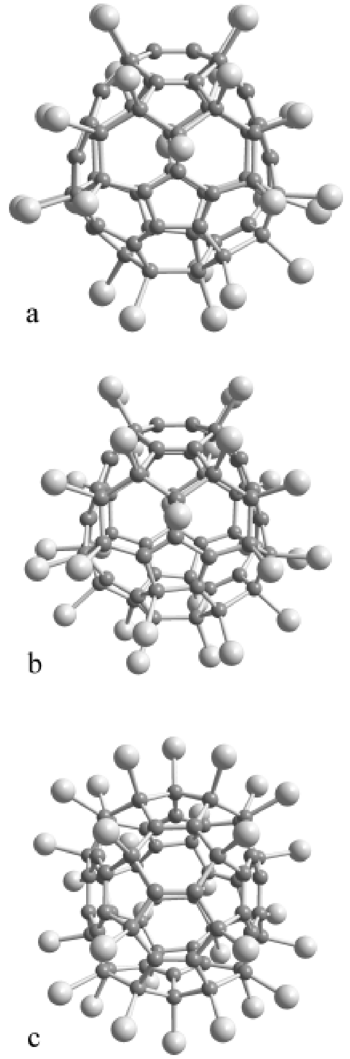

Figure 6. Views of the $C_{60}Cl_{28}$ (side, a) and $C_2$-$C_{60}Cl_{30}$ molecules (side, b, and top, c).

All the C–C bonds can be separated into five major groups according to their natures. These are isolated double bonds connecting nonaromatic $sp^2$ carbon atoms (average length 1.344 Å), aromatic bonds (1.385 Å), $sp^2$–$sp^2$ bonds between two double bonds (1.443 Å), $sp^2$–$sp^3$ bonds (1.500 Å), and, finally, considerably longer $sp^3$–$sp^3$ bonds (1.615 Å). Especially long C–C distances (up to 1.65–1.66 Å) are observed for the pair of the $sp^3$ carbons with neighboring $sp^3$ C atoms *cis* to one another. A similar effect has been found in 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, so bond lengths [Å] of 1.37, 1.44 and 1.36 Å in the 1–4 fragment in $C_1$-$C_{60}Cl_{28}$ become 1.53, 1.33, and 1.44 Å in $C_2$-$C_{60}Cl_{30}$.

Another isomer of $C_{60}Cl_{30}$ has an idealized $D_{3d}$ symmetry for the isolated molecule (Figure 2, f). The molecular structure of this isomer of $C_{60}Cl_{30}$ has been determined by three sets of single-crystal X-ray measurements: for $C_{60}Cl_{30}\cdot 0.09\,Cl_2$,[26] $C_{60}Cl_{30}\cdot 2\,ICl$,[26] and $C_{60}Cl_{30}\cdot 2\,CS_2$.[25] The measurement accuracy for $C_{60}Cl_{30}\cdot 2\,CS_2$ seems to be a little better than that of the two others, so the results for the adduct with carbon disulfide are presented here. Whereas the isolated molecule of $C_{60}Cl_{30}$ should possess $D_{3d}$ symmetry, the crystallographically imposed symmetry is reduced to $C_{2h}$. There are two planar aromatic six-membered benzenoid rings on the opposite sides of the cage and an equatorial 18π all-*trans* annulene (18π trannulene) belt in the chlorofullerene molecule (part f in Figure 2 and Figure 7). Similar 18π trannulene cycles, though less separated from other parts of the fullerene cage, were reported for a series of derivatives: $C_{60}F_{15}[CBr(COOR)_2]_3$[34] and $C_{60}[CMe(COOR)_2]_6$.[35]

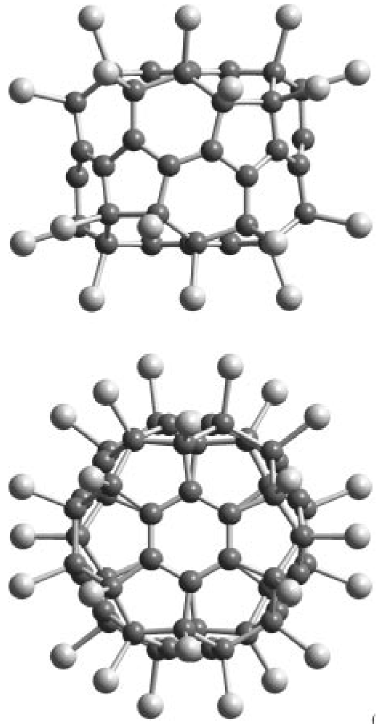

Figure 7. Views of the $D_{3d}$-$C_{60}Cl_{30}$ molecule.

$D_{3d}$-$C_{60}Cl_{30}$ represents the molecule with the most isolated trannulene belt, separated from the benzenoid rings by the two 15-membered belts of $sp^3$ carbons bearing chlorine atoms. Such a structural arrangement results in a unique cylindrical, drum-shaped carbon cage. The aromatic six-membered rings are almost perfectly planar; the sum of valence angles involving aromatic carbons exceeds 359.9°. The 6/6 (a′) and 5/6 (a′′) C–C bonds in these rings are virtually equivalent in length (1.370 and 1.375 Å, respectively). A similar equalization of the 6/6 (h, 1.382 Å) and 5/6 (i, 1.391 Å) bonds occurs in the equatorial trannulene ring, serving as additional evidence of its aromatic character. As would be expected, the $sp^2$–$sp^3$ C–C bonds are longer than the $sp^2$–$sp^2$ ones: 1.474 Å (b), 1.509 Å (f), and 1.499 Å (g). Further elongation is characteristic of the $sp^3$–$sp^3$ C–C bonds, with lengths of 1.578 (c), 1.621 (d), and 1.696 Å (e); the longest bond is again found for the pair with a *cis* position of the neighboring $sp^3$ atoms (see above). For comparison, similar bonds in $C_{60}F_{18}$[36] and $C_{60}F_{36}$[37] have lengths of "only" 1.67 Å.

Three addition patterns are known for low-, moderately, and highly chlorinated $C_{70}$, but only the $C_{70}$ pattern with a low chlorine content is observed for a brominated [70]fullerene (Figure 8a–c). The arrangement of ten chlorine atoms as a belt around the molecular equator in $C_{70}Cl_{10}$ had been deduced earlier from $^{13}C$ NMR spectroscopy,[2] substitution reactions,[38a] and theoretical modeling.[38b] The same arrangement was established for [70]fullerene decabromide by a crystallographic investigation of two compounds: $C_{70}Br_{10}$ and $C_{70}Br_{10}\cdot 3\,Br_2$.[8] The halogenated $sp^3$ carbon atoms are situated in a closed belt around the $C_{70}$ cage equator (part a in Figure 8 and Figure 9). Nine pairs of neighboring halogen atoms are attached in the 1,4-positions of the hexagons and only one pair is in the 1,2-position.

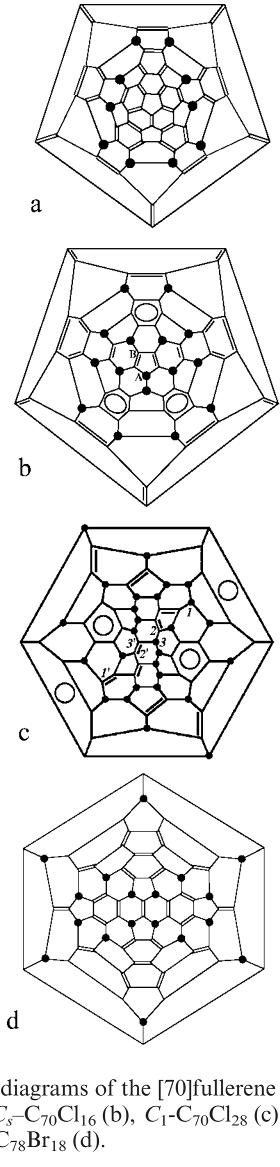

Figure 8. Schlegel diagrams of the [70]fullerene bromides and chlorides $C_{70}X_{10}$ (a), $C_s$–$C_{70}Cl_{16}$ (b), $C_1$-$C_{70}Cl_{28}$ (c), and the [78]fullerene bromide $C_{2v}$–$C_{78}Br_{18}$ (d).

The molecular structures of $C_{70}Cl_{16}$ (determined for bromine solvates $C_{70}Cl_{16}\cdot 0.5\,Br_2$ and $C_{70}Cl_{16}\cdot 3\,Br_2$[31]) demonstrate a remarkable combination of a chlorine belt around

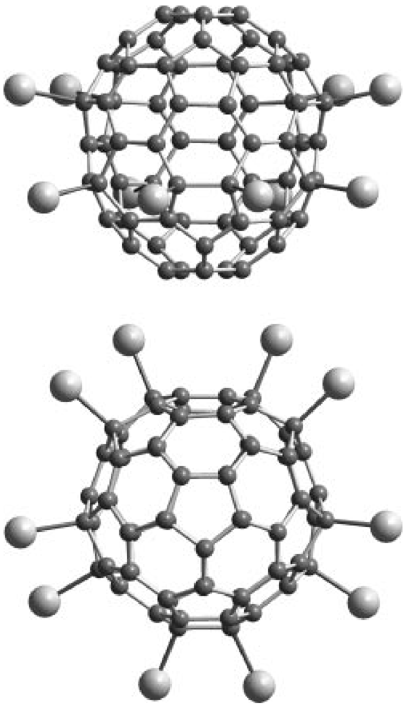

Figure 9. Views of the $C_{70}Br_{10}$ molecule.

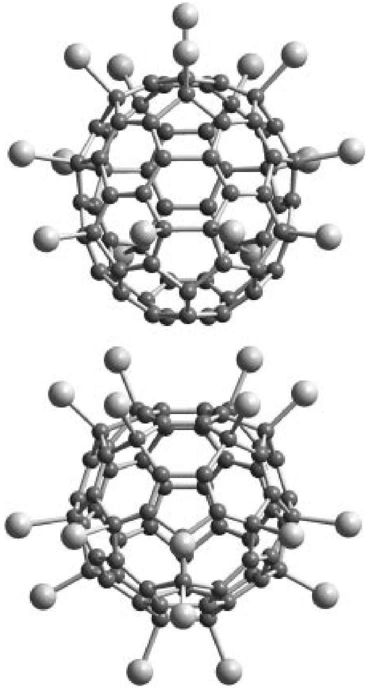

Figure 10. Views of the $C_{70}Cl_{16}$ molecule ($C_s$ isomer).

the equator and a skew pyramidal chlorine cap on a pole (part b in Figure 8 and Figure 10). The six-halogen skew pyramidal cap, combined with a cyclopentadiene fragment in the pentagon, is characteristic of $C_{60}X_6$ structures (see above). A crystallographic study revealed the presence of two isomers of $C_{70}Cl_{16}$, differing only in the position of the Cl atom (A or B) in the cap pentagon.

The longest bond between $sp^3$ carbon atoms in the equatorial belt has a length of 1.65 Å. The $sp^2$–$sp^3$ C–C bonds are shorter, with averaged values of 1.51 Å. The one isolated and two nearly isolated six-membered aromatic rings are characterized by average C–C distances of 1.39 Å. There are two isolated double C–C bonds with an average bond length of 1.34 Å. The average C–Cl bond has a length of 1.85 Å.

The molecular structure of the highly chlorinated $C_{70}$ species, $C_{70}Cl_{28}$, contains four benzenoid rings and chains of the $sp^3$ carbon atoms bearing Cl atoms (Figure 8, c). Apparently the crystals of $C_{70}Cl_{28}\cdot 1.76\,Br_2$ contain at least three different isomeric $C_{70}Cl_{28}$ molecules, superposition of which results in $C_2$ crystallographic symmetry. However, all three isomers contain four benzenoid rings in the same position. The minor differences between the isomers involve the positions of one or two chlorine atoms attached to the [70]fullerene cage. Figure 11 shows the arrangement of 28 Cl atoms in the thermodynamically most stable $C_1$ isomer. C–C bonds can be separated into four major groups according to their natures: these are isolated double or conjugated bonds connecting nonaromatic $sp^2$ carbons (average length: 1.38 Å), aromatic bonds (1.39 Å), $sp^2$–$sp^3$ bonds (1.50 Å), and, finally, considerably longer $sp^3$–$sp^3$ bonds (1.61 Å). The C–Cl bonds (1.82 Å) are also longer than the typical value for conventional chlorocarbons (1.77 Å); this suggests that these bonds are relatively weak.

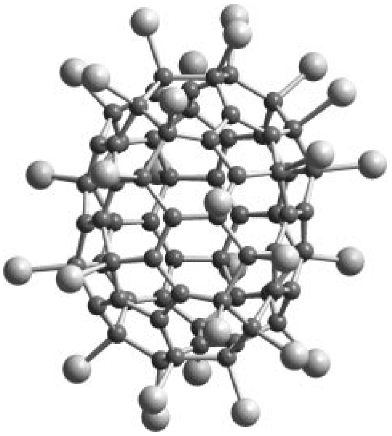

Figure 11. View of the $C_{70}Cl_{28}$ molecule ($C_1$ isomer).

The first single-crystal X-ray structure of a halogenated higher fullerene – $C_{78}Br_{18}$ – revealed that the addition pattern of 18 bromine atoms on the $C_{78}$ cage corresponds to a partial retention of conjugated double bond systems and the formation of isolated double C–C bonds. Two $C_{78}Br_{18}$ isomers are present in the crystal, both showing $C_{2v}$ symmetry (part d in Figure 8 and Figure 12). These isomers originate from two isomers of $C_{78}$, the most stable among the five isomers obeying the isolated pentagon rule. The isomeric $C_{78}Br_{18}$ molecules differ only in the positions of some C–C bonds parallel or perpendicular to the equatorial mirror plane. The three benzenoid rings contribute to the stability of these molecules. There is a distinct gradation in the C–C bond lengths dependent on the bond character:

predominantly single (av. 1.433 Å) or double (av. 1.387 Å). Isolated double bonds are much shorter (1.33 Å on average), whereas the independent $sp^2$–$sp^3$ C–C bonds are substantially longer (avg. 1.525 Å). Two C–Br bonds have virtually the same length (avg. length 2.000 Å).

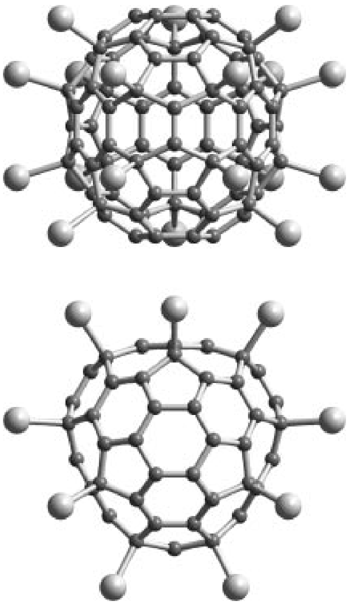

Figure 12. Views of the $C_{78}Br_{18}$ molecule ($C'_{2v}$ isomer).

For the halogenated fullerenes presented here, knowledge of the structure can in some cases help to explain the chemical behavior. In the 15-membered $sp^3$ belts in the $D_{3d}$-$C_{60}Cl_{30}$ molecule, some C–C bonds are significantly longer than others. The syntheses of $D_{3d}$-$C_{60}Cl_{30}$ carried out in the presence of oxygen yielded products containing appreciable amounts of $C_{60}Cl_{30}O_2$ according to IR spectroscopy and X-ray diffraction data. It was found that the crystals of such products contained up to 60% dioxide.[25,26] The structure determination showed the O atoms to be inserted into the most elongated (weak) C–C bonds of type e (Figure 2, f). Similar positions for oxygen insertion are known for $C_{60}F_{18}$, resulting in the individual compound $C_{60}F_{18}O$[39] or its mixture with the non-oxygenated product.[36b]

Other reported chemical reactions have mostly been substitutions in $C_{60}Cl_6$ and $C_{70}Cl_{10}$ with methyl, phenyl, alkoxy, and hydroxy groups.[20,38a,40] A high degree of chlorination seems to hinder the substitution reaction sterically. The $D_{3d}$-$C_{60}Cl_{30}$ molecule, containing only unsaturated fragments exclusively as aromatic rings, appears to be especially stable towards nucleophilic substitution.

Because of the differences in energy of C–X bonds, the thermal stabilities of fullerene bromides and chlorides differ drastically, between 110 and 220 °C for bromides and between 350 and 500 °C for chlorides. In each group, the compound with the most symmetrical molecular structure decomposes at a higher temperature than the others. $C_{60}Br_{24}$ is most stable among [60]fullerene bromides, due to a highly symmetrical molecular structure. A very high thermal stability of up to 450–500 °C was observed for $C_{60}Cl_{30}$, with $D_{3d}$ symmetry of the molecule, because the removal of any chlorine perturbs the stable aromatic fragments.

## 4. Thermodynamic and Kinetic Stability

Experimental results on the formation and molecular structures of fullerene bromides and chlorides allow analysis of their relative stabilities. In addition, some theoretical publications have covered the thermodynamic or kinetic stabilities of fullerene derivatives with bulky addends, such as chlorine and bromine atoms.

The formation of the $C_{60}X_6$ isomer with the skew-pyramidal addition pattern has been justified by quantum chemical calculations for different isomers.[41] On the other hand, the same isomer has also been shown to be favored on the basis of a kinetic model including the formation of radicals and their quenching.[42] Apparently, high stability of the $C_s$ isomer is connected with the formation of a cyclopentadiene fragment with two conjugated double bonds. For $C_{60}X_8$ compounds with X = Cl or Br, a higher stability of the $C_{2v}$ isomer (Figure 2, b) has also been confirmed theoretically by calculations of the relative energies of several isomers.[41]

The structure of $C_{60}X_{24}$ (X = Cl or Br) contains the maximum number of halogen atoms under the condition that no 1,2 X···X contacts are present in the addition pattern. It is believed that this isomer has the lowest energy.[28] This composition represents the highest degree of bromination, but not chlorination. Quantum chemical calculations based on the DFT level of theory were performed to examine the relative stabilities of various higher chlorides of $C_{60}$.[26,27] They revealed that the stabilities of chlorofullerenes possessing degrees of chlorination higher than that in $C_{60}Cl_{24}$ are influenced by two main factors: destabilizing van der Waals repulsions between the adjacent chlorine atoms and the stabilizing effect of the aromatic fragments, such as benzenoid rings. Particularly high steric strain was found in the structures containing chlorine atoms surrounded by three others (“triple contacts”). If the “triple contacts” are ruled out, there can be a maximum of two isolated benzenoid rings in the closed-shell chlorofullerene molecules. The two benzenoid rinds can be parallel or inclined to one another. For the $C_{60}Cl_{30}$ composition, the isomers of lowest energy for parallel and nonparallel arrangements of two aromatic hexagons correspond to the $D_{3d}$ and the $C_2$ isomers of $C_{60}Cl_{30}$, respectively. DFT B3LYP computations of the relative energies show that the $C_2$-$C_{60}Cl_{30}$ isomer is 78 kJ·mol$^{-1}$ less stable than the $D_{3d}$ isomer [its high stability was predicted by I. N. Ioffe in a private communication to one of the authors (S. I. T.) some months before the compound was prepared]. 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 would be obtained from $D_{3d}$-$C_{60}Cl_{30}$ by removal of two chlorine atoms. Hence, $C_1$-$C_{60}Cl_{28}$ and $C_2$-$C_{60}Cl_{30}$, which were both isolated as individual compounds, are the only kinetically stable chlorofullerenes. This has been experimentally confirmed by heating the sample of $C_2$-$C_{60}Cl_{30}$ at 300 °C in the presence of $SbCl_5$, which resulted in its complete transformation into $D_{3d}$-$C_{60}Cl_{30}$. In general, potential barriers of structural rearrangement for chlorofullerenes are overcome over 250 °C: chlorination of $C_{60}$ and $C_{60}Cl_{24}$ with $SbCl_5$ at 280–300 °C, for example, results in the same product, $D_{3d}$-$C_{60}Cl_{30}$.[25]

Among the investigated chlorofullerenes, there is only one pair of molecules that can be easily converted into one another. Because of the similarity in their addition patterns, $C_2$-$C_{60}Cl_{30}$ can be easily obtained from $C_1$-$C_{60}Cl_{28}$ by the addition of two Cl atoms. A reverse process, the formation of $C_1$-$C_{60}Cl_{28}$ from $C_2$-$C_{60}Cl_{30}$, has been observed experimentally, when a sample of $C_2$-$C_{60}Cl_{30}$ was heated at 240 °C in an ampoule.

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 an equatorial 18-π trannulene belt) prevents transformation of less chlorinated fullerenes into more chlorinated ones by simple addition of Cl atoms (with an exception pointed out above). Such transformations should therefore involve the rearrangement of many Cl atoms on the fullerene cage and can be regarded as "chlorine dances". Similar phenomena, "fluorine dances", were found to proceed during $C_{60}$ fluorination.[43] If the chlorination of $C_{60}$ occurs at a temperature lower than 220–240 °C, some "chlorine dance" intermediates can be isolated in pure form as discussed above. At higher chlorination temperatures, only the thermodynamically stable $D_{3d}$-$C_{60}Cl_{30}$ can be obtained.

Chlorination of $C_{70}$ provides only a few comparable examples. Theoretical calculations have shown that both $C_{70}Br_{10}$ and $C_{70}Cl_{10}$ with equatorial addition patterns are thermodynamically stable halogenation products.[44] Although the mechanism of the formation of $C_{70}Cl_{16}$ on chlorination of $C_{70}$ with the $Br_2/TiCl_4$ mixture remains unclear, it can be assumed that the formation of a chloride with a higher chlorine content than $C_{70}Cl_{10}$ is due to the high Lewis acidity of $TiCl_4$ promoting the formation of $Br^+$ or BrCl species in the system. Alternatively, the reaction may proceed through a radical mechanism involving the addition of $Br^{\cdot}$ with subsequent Br/Cl exchange. It was assumed that addition to $C_{70}X_{10}$ occurs at sites of maximum free valence in closed-shell molecules and of maximum spin density in the radicals (as also assumed earlier [42] to account for the formation of $C_{60}X_6$ and $C_{70}X_{10}$ isomers in the radical addition of bulky groups to $C_{60}$ and $C_{70}$). It was found that the location of the most reactive site in $C_{70}X_{10}$ (X = Br or Cl) near the one pole of the molecule should finally result in the structures of the $C_{70}Cl_{16}$ shown in Figure 8, b.[31] Thus, both energetic and kinetic considerations favor the experimentally observed isomers of $C_{70}Cl_{16}$.

Our DFT calculations for the relative stabilities of possible $C_{70}Cl_m$ isomers ($m \geq 24$) demonstrated that the principles governing the addition patterns for highly chlorinated molecules are quite different from those for lower [70]fullerene chlorides[29] but that they are similar to the main principles for higher chlorides of [60]fullerene (see above). It seemed the main factor affecting stability was the number of isolated benzenoid cycles in the molecule. Stabilizing effects for the formation of such aromatic fragments surpassed the negative steric effects of 1,2-contacts of chlorine atom, except in cases in which some chlorine atoms had three such contacts. The maximum number of benzenoid rings of a closed-shell derivative of $C_{70}$, provided that all the addends have no more than two 1,2-contacts with the others, is four, and their location pattern is unique. As a result, among the numerous isomers of $C_{70}Cl_{28}$ considered in the calculations, those containing four benzenoid rings were 80 to 100 $kJ\cdot mol^{-1}$ more stable than the structures with only three rings and around 200 $kJ\cdot mol^{-1}$ more stable than the isomers with a minimal number of 1,2-contacts and no aromatic fragments. Here we see an obvious analogy with the addition patterns observed in some highly chlorinated and highly fluorinated $C_{60}$ fullerene molecules such as $C_{60}F_{36}$ (*T* isomer),[37] $C_{70}Cl_{38}$,[45] and $C_{74}F_{38}$.[46] The calculations predict the benzenoid cycles in $C_{70}Cl_{28}$ to be less planar, and hence less aromatic. DFT calculations demonstrate that among three isomers found in the crystal of $C_{70}Cl_{28}\cdot 1.76\,Br_2$, one isomer is approximately 9 $kJ\cdot mol^{-1}$ more stable than the second and about 40 $kJ\cdot mol^{-1}$ more stable than the third. At the same time, of over 30 isomers of $C_{70}Cl_{28}$ containing four benzenoid rings, many possess comparable stabilities, their energy values lying between those of the first and third isomers. This implies that the observed isomers are partially kinetic products and that, therefore, formation of other isomers is, in principle, possible. According to the DFT calculations, the enthalpy of consecutive chlorination with $Cl_2$ remains negative only up to $C_{70}Cl_{28}$. However, the formation of $C_{70}Cl_{30}$ still seems to be possible with the use of strong chlorinating agents. The single isomer of $C_{70}Cl_{30}$ satisfies the condition of "four rings and no triple Cl···Cl contacts".[29] Further chlorination of $C_{70}Cl_{30}$, which would result in the destruction of the benzenoid rings or an increase in the Cl···Cl adjacency, will probably not take place due to high endothermicity.

## 5. Conclusion

New fullerene chlorides can be selectively synthesized by use of metal chlorides (oxychlorides) or a mixture of $Br_2$ with a strong Lewis acid. Because of the increase in the energies of C–Hal bonds, the highest degree of halogenation increases from bromo- through chloro- to fluorofullerenes: 24, 30, and 48 for [60]- and 10, 28, and 44 for [70]-fullerene, respectively. For the same reason, the thermal stability increases significantly in same order.

Molecular structures of the bromo- and chlorofullerenes are similar for compounds of the same compositions. The fluorofullerenes have different compositions and addition patterns, due to the lower steric demand of F atoms relative to Cl or Br atoms. Addition patterns of fullerene bromides and chlorides have a tendency to avoid 1,2-contacts (if possible), whereas such 1,2-contacts and even "triple" contacts are common in the molecular structures of fullerene fluorides, which generally possess contiguous addition patterns.

In most cases the presence of aromatic rings contributes to the stabilities of halofullerene molecules. For fullerene chlorides, such contributions compensate for the destabilizing effect of the 1,2-Cl···Cl contacts. A special feature of fullerene chlorides is their ability to form kinetically stable products with energies much higher than those of thermodynamically stable compounds. This offers additional possibilities in the preparation of new fullerene chlorides, when synthetic procedures are carried out at a not too high temperature.

## Acknowledgments

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[1] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1993**, 1230–1232.

[2] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1995**, 683–684.

[3] S.-Y. Xie, F. Gao, X. Lu, R.-B. Huang, C.-R. Wang, X. Zhang, M.-L. Liu, S.-L. Deng, L.-S. Zheng, *Science* **2004**, *304*, 699.

[4] a) R. Taylor, *J. Fluorine Chem.* **2004**, *125*, 359–368; b) R. Taylor, *Chem. Eur. J.* **2001**, *7*, 4075–4083.

[5] L. N. Sidorov, O. V. Boltalina, *Russ. Chem. Rev.* **2002**, *71*, 535–562.

[6] O. V. Boltalina, N. A. Galeva, *Russ. Chem. Rev.* **2000**, *69*, 609–622; O. V. Boltalina, *J. Fluorine Chem.* **2001**, *101*, 273–278.

[7] S. I. Troyanov, P. A. Troshin, O. V. Boltalina, E. Kemnitz, *Fullerenes Nanotubes Carbon Nanostruct.* **2003**, *11*, 61–77.

[8] S. I. Troyanov, A. A. Popov, N. I. Denisenko, O. V. Boltalina, L. N. Sidorov, E. Kemnitz, *Angew. Chem.* **2003**, *115*, 2497–2500; *Angew. Chem. Int. Ed.* **2003**, *42*, 2395–2398.

[9] S. I. Troyanov, N. B. Shustova, A. A. Popov, M. Feist, E. Kemnitz, *Russ. J. Inorg. Chem.* **2004**, *49*, 1303–1308.

[10] P. R. Birkett, P. B. Hitchcock, H. W. Kroto, R. Taylor, D. R. M. Walton, *Nature* **1992**, *357*, 479–481.

[11] F. N. Tebbe, R. L. Harlow, D. B. Chase, D. L. Thorn, G. C. Campbell, J. C. Calabrese, N. Herron, R. J. Young, E. Wasserman, *Science* **1992**, *256*, 822–825.

[12] P. A. Troshin, D. Kolesnikov, A. V. Burtsev, R. N. Lubovskaya, N. I. Denisenko, A. A. Popov, S. I. Troyanov, O. V. Boltalina, *Fullerenes Nanotubes Carbon Nanostruct.* **2003**, *11*, 47–60.

[13] P. A. Troshin, E. Kemnitz, S. I. Troyanov, *Russ. Chem. Bull.* **2004**, *53*, 2787–2792.

[14] G. Waidmann, M. Jansen, *Z. Anorg. Allg. Chem.* **1997**, *623*, 623–626.

[15] a) S. I. Troyanov, E. Kemnitz, *Eur. J. Org. Chem.* **2003**, 3916–3919; b) S. Troyanov, A. Turnbull, L. Sidorov, E. Kemnitz, 205th Meeting of the Electrochemical Society, San-Antonio TX, May 9–14, **2004**, M13: *Fullerenes, Nanotubes, and Carbon Nanostructures*, Abstr. 444.

[16] G. A. Olah, I. Bucsi, C. Lambert, R. Aniszfeld, N. J. Trivedy, D. K. Sensharma, G. K. S. Prakash, *J. Am. Chem. Soc.* **1991**, *113*, 9385–9387.

[17] F. N. Tebbe, J. Y. Becker, D. B. Chase, L. E. Firment, E. R. Holler, B. S. Malone, P. J. Krusic, E. Wasserman, *J. Am. Chem. Soc.* **1991**, *113*, 9900–9901.

[18] F. Cataldo, *Full. Sci. Techn.* **1996**, *4*, 1041–1059.

[19] P. A. Troshin, O. Popkov, R. N. Lyubovskaya, *Fullerenes Nanotubes Carbon Nanostruct.* **2003**, *11*, 165–185.

[20] a) P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin. Trans. 2* **1997**, 457–461; b) H. Al-Matar, Ala'a K. Abdul-Sada, A. G. Avent, P. W. Fowler, P. B. Hitchcock, K. M. Rogers, R. Taylor, *J. Chem. Soc. Perkin. Trans. 2* **2002**, 53–58; c) Yu. V. Vasil'ev, A. V. Streletskiy, I. V. Kouvitchko, O. V. Boltalina, P. R. Birkett, E. E. B. Campbell, M. V. Korobov, T. Drewello, *Int. J. Mass Spectrom.* **2003**, *228*, 979–984.

[21] a) D. Heymann, F. Cataldo, R. Fokkens, N. M. M. Nibbering, R. D. Vis, *Full. Sci. Techn.* **1999**, *7*, 159–180; b) F. Cataldo, *Full. Sci. Techn.* **1999**, *7*, 311–316.

[22] B. S. Rasbirin, A. N. Starukhin, A. V. Chugreev, V. P. Smirnov, Yu. S. Grushko, S. G. Kolesnik, P.-F. Coheur, J. Lievin, R. Colin, *Phys. Solid State* **2002**, *44*, 2204–2209.

[23] A. J. Adamson, J. H. Holloway, E. G. Hope, R. Taylor, *Full. Sci. Techn.* **1997**, *5*, 629–642.

[24] A. V. Streletskiy, I. V. Kouvitchko, S. E. Esipov, O. V. Boltalina, *Rapid Commun. Mass Spectrom.* **2002**, *16*, 99–102.

[25] S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov, *Russ. Chem. Bull.* **2005**, *54*, issue 7 (in press).

[26] P. A. Troshin, R. N. Lyubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz, S. I. Troyanov, *Angew. Chem.* **2005**, *117*, 238–241; *Angew. Chem. Int. Ed.* **2005**, *44*, 234–237.

[27] S. I. Troyanov, N. B. Shustova, A. A. Popov, L. N. Sidorov, E. Kemnitz, *Angew. Chem.* **2005**, *117*, 436–439; *Angew. Chem. Int. Ed.* **2005**, *44*, 432–435.

[28] N. B. Shustova, A. A. Popov, L. N. Sidorov, A. P. Turnbull, E. Kemnitz, S. I. Troyanov, *Chem. Commun.* **2005**, 1411–1413.

[29] S. I. Troyanov, N. B. Shustova, I. N. Ioffe, A. P. Turnbull, E. Kemnitz, *Chem. Commun.* **2005**, 72–74.

[30] N. B. Shustova, D. Yu. Chernyshov, P. Pattison, S. I. Troyanov (manuscript in preparation).

[31] S. I. Troyanov, A. A. Popov, *Angew. Chem.* **2005**, *117*, 4287–4290; *Angew. Chem. Int. Ed.* **2005**, *44*, 4215–4218.

[32] S. I. Troyanov, A. A. Popov (manuscript to be published).

[33] M. Fedurco, M. M. Olmstead, W. R. Fawcett, *Inorg. Chem.* **1995**, *34*, 390–392.

[34] X.-W. Wei, A. D. Darwish, O. V. Boltalina, P. B. Hitchcock, J. V. Street, R. Taylor, *Angew. Chem.* **2001**, *113*, 3077–3080; *Angew. Chem. Int. Ed.* **2001**, *40*, 2989–2992.

[35] T. Canteenwala, P. A. Padmawar, L. Y. Chiang, *J. Am. Chem. Soc.* **2005**, *127*, 26–27.

[36] a) I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Yu. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Yu. Lukonin, L. N. Sidorov, R. Taylor, *Angew. Chem.* **2005**, *112*, 3411–3415; *Angew. Chem. Int. Ed.* **2000**, *39*, 3273–3276; b) S. I. Troyanov, O. V. Boltalina, I. V. Kuvytchko, P. A. Troshin, E. Kemnitz, P. B. Hitchcock, R. Taylor, *Full. Sci. Techn.* **2002**, *10*, 243–260; c) I. V. Goldt, O. V. Boltalina, L. N. Sidorov, E. Kemnitz, S. I. Troyanov, *Solid State Sci.* **2002**, *4*, 1395–1401.

[37] P. B. Hitchcock, R. Taylor, *Chem. Commun.* **2002**, 2078–2079.

[38] a) A. G. Avent, P. R. Birkett, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *Tetrahedron* **1996**, *52*, 5235–5246; b) S. J. Austin, P. W. Fowler, J. P. B. Sandall, P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1027–1028.

[39] O. V. Boltalina, B. de La Vaissiere, P. W. Fowler, P. B. Hitchcock, J. P. B. Sandall, P. A. Troshin, R. Taylor, *Chem. Commun.* **2000**, 1325–1326.

[40] a) P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **2001**, 68–72; b) A. G. Avent, P. R. Birkett, A. D. Darwish, S. Houlton, K. S. T. Thomson, X.-W. Wei, *J. Chem. Soc. Perkin Trans. 2* **2001**, 782–786.

[41] B. W. Clare, D. L. Kepert, *J. Mol. Struct. (Theochem)* **2003**, *621*, 211–231.

[42] K. M. Rogers, P. W. Fowler, *Chem. Commun.* **1999**, 2357–2358.

[43] a) A. A. Gakh, A. A. Tuinman, *Tetrahedron Lett.* **2001**, *42*, 7137–7139; b) A. G. Avent, R. Taylor, *Chem. Commun.* **2002**, 2726–2727.

[44] B. W. Clare, D. L. Kepert, *J. Mol. Struct. (Theochem)* **1999**, *491*, 249–264.

[45] a) P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin, R. Taylor, *Chem. Commun.* **2005**, 75–77; b) P. B. Hitchcock, A. G. Avent, N. Martsinovich, P. A. Troshin, R. Taylor, *Org. Lett.* **2005**, *7*, 1975–1978.
[46] A. A. Goryunkov, V. Yu. Markov, I. N. Ioffe, R. D. Bolskar, M. D. Diener, I. V. Kuvychko, S. H. Strauss, O. V. Boltalina, *Angew. Chem.* **2004**, *116*, 1015–1018; *Angew. Chem. Int. Ed.* **2004**, *43*, 997–1000.

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