Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2023, **33**, 503–504

Mendeleev Communications

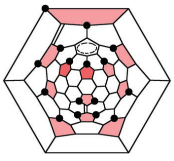
Chlorofullerenes with isomeric C_{86} carbon cages: $C_{86}(16)Cl_{16}$ and $C_{86}(17)Cl_{18,20}$

Shangfeng Yang[a] **and Sergey I. Troyanov***[b]

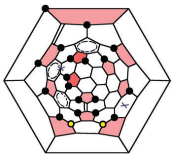
[a] *Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, 230026 Hefei, China*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 1240; e-mail: stroyano@thermo.chem.msu.ru*

DOI: 10.1016/j.mencom.2023.06.020

Chlorofullerenes $C_{86}(16)Cl_{16}$ and $C_{86}(17)Cl_{18,20}$ were prepared by chlorination of C_s-$C_{86}(16)$ and C_2-$C_{86}(17)$, respectively, with VCl_4 at 320–340 °C. An X-ray crystallographic study with the use of synchrotron radiation revealed the chlorination patterns which show certain similarity due to only small differences between isomeric C_{86} cages.



C_1-$C_{86}(16)Cl_{16}$



C_1-$C_{86}(17)Cl_{18/20}$

Keywords: higher fullerenes, C_{86}, chlorination, IPR isomers, structure elucidation.

The chemistry of higher fullerenes is studied very scarcely because of small contents in fullerene soot and the existence of many cage isomers.[1] In the last 15 years, some progress was achieved in the preparation and structural identification of higher hollow fullerene isomers in the range of C_{76}–C_{108} as chloro- and trifluoromethyl derivatives.[2–5] It turned out that high-temperature chlorination can not only produce exohedral chlorides of the starting pristine isolated pentagon rule (IPR) fullerenes but also promote skeletal transformations under the formation of chlorinated non-IPR fullerenes.[6]

Herein we report the synthesis and structure elucidation of chlorinated IPR fullerene C_{86} that contributes to the structural chemistry of higher fullerenes.

Fullerene C_{86} has 19 topologically possible IPR isomers.[1] ^{13}C NMR spectrometry and UV/Vis spectroscopy studies of C_{86} fractions chromatographically isolated from fullerene soot proved the presence of two isomers, C_s-$C_{86}(16)$ and C_2-$C_{86}(17)$, in an approximately 1 : 4 ratio.[7,8] The isomer numbers in parentheses are given according to the spiral algorithm for IPR isomers.[1] The higher stability of isomers $C_{86}(16)$ and $C_{86}(17)$ in comparison with other isomers of C_{86} fullerene was also confirmed by theoretical calculations.[8–10] Importantly, the carbon cages of these isomers differ by the position of only one C–C bond, *i.e.*, they are formally interconvertible by one Stone–Wales rearrangement (SWR).[11] Crystallographic study of co-crystals of C_{86} with Ni(OEP) (OEP, octaethylporphyrin) established the presence of isomers $C_{86}(16)$ and $C_{86}(17)$ statistically disordered in the crystal in equal amounts.[12]

Because of the difficulties in isomer separation, the chemistry of fullerene C_{86} was studied mainly using non-separated mixtures of both isomers. High-temperature trifluoromethylation of a higher fullerene mixture (C_{76}–C_{96}) followed by HPLC separation of CF_3 derivatives resulted in the isolation and structure elucidation of two isomeric $C_{86}(17)(CF_3)_{16}$ and one $C_{86}(17)(CF_3)_{18}$ compounds, thus confirming the cage connectivity of isomer C_2-$C_{86}(17)$.[13] More structural results were obtained for the products of high-temperature chlorination with a ($TiCl_4$ + Br_2) mixture or VCl_4. Two crystal structures of $C_{86}(17)Cl_{18}$ as $TiCl_4$ solvates, one structure of $C_{86}(17)Cl_{19.61}$, and a three-component structure containing $C_{86}(16)Cl_{16}$, $C_{86}(17)Cl_{18.55}$, and $C_{86}(17)Cl_{20.7}$ have been reported, though with poor precision in the latter case.[14] Fractional numbers for Cl in formulas correspond to the mixtures of two compounds with integer numbers of Cl atoms.

Our present experimental work was performed with the isolated, isomerically pure samples of $C_{86}(16)$ and $C_{86}(17)$. A chromatographic separation was carried out *via* a two-stage recycling HPLC procedure in toluene. The identity and isomeric purity of the obtained subfractions were controlled by mass spectrometry and UV/Vis spectroscopy.[15] Chlorination of the $C_{86}(16)$ and $C_{86}(17)$ samples (*ca*. 0.1 and 0.3 mg, respectively) was performed in thick-walled glass ampoules using an excess of VCl_4 as a chlorination agent by heating at 320–340 °C for 7–10 days. The chlorination products were washed with dilute HCl and water to remove the excess of VCl_4 and VCl_3 and then dried in open air at 40 °C affording tiny, orange-colored crystals of chlorofullerenes. The crystals were studied by X-ray diffraction with the use of synchrotron radiation, revealing the formation of $C_{86}(16)Cl_{16}$ and $C_{86}(17)Cl_{18.73}$ in accordance with the cage connectivities of the starting fullerene isomers (Figure 1).[†]

[†] *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.3, PSF, Germany) using a MAR225 CCD detector (λ = 0.8950 Å). The crystal structures were solved by SHELXD and refined with SHELXL. $C_{86}(16)Cl_{16}$, monoclinic, $P2_1/c$, a = 12.4330(8), b = 21.639(1) and c = 21.104(1) Å, β = 92.574(3)°, V = 5672.0(5) Å^3, Z = 4. Anisotropic refinement with 10018 reflections and 919 parameters converged to wR_2 = 0.087 and R_1 = 0.034 for 9832 reflections with $I > 2\sigma(I)$. $C_{86}(17)Cl_{18.73}$, monoclinic, $P2_1/c$, a = 12.1190(8), b = 20.572(2) and c = 23.847(1) Å, β = 90.31(2)°, V = 5945.3(7) Å^3, Z = 4. Anisotropic refinement with 13123 reflections and 1033 parameters converged to wR_2 = 0.133 and R_1 = 0.055 for 11097 reflections with $I > 2\sigma(I)$.

CCDC 2235183 and 2235184 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

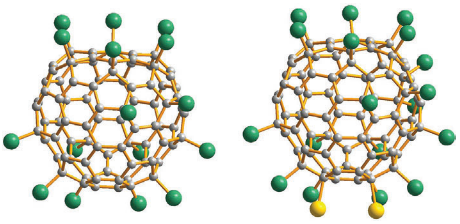

C_1-$C_{86}(16)Cl_{16}$ C_1-$C_{86}(17)Cl_{18/20}$

Figure 1 Molecular structures of $C_{86}(16)Cl_{16}$ and $C_{86}(17)Cl_{18,20}$. In $C_{86}(16)Cl_{16}$, the carbon cage and the arrangement of 14 Cl atoms are mirror-symmetric. In $C_{86}(17)Cl_{18,20}$, the carbon cage has apparent deviations from mirror symmetry, whereas most Cl atoms are attached in mirror-symmetric positions. Two Cl atoms with partial occupancies (highlighted by the yellow color) belong to the $C_{86}(17)Cl_{20}$ molecule which is present in co-crystal together with $C_{86}(17)Cl_{18}$.

Isolation and structural characterization of $C_{86}(16)Cl_{16}$ are performed using an isomerically pure C_s-$C_{86}(16)$ sample. In the previous report,[14] the structure of $C_{86}(16)Cl_{16}$ with the same addition pattern was included as one of the three different components containing derivatives of both isomers C_s-$C_{86}(16)$ and C_2-$C_{86}(17)$. As a result, the precision of a new structural determination is better approximately by a factor of 10, which allowed a discussion of fine structural features of this chlorofullerene. The compositionally mixed $C_{86}(17)Cl_{18}$/$C_{86}(17)Cl_{20}$ (overlapped) molecules are shown in Figure 1 with two highlighted Cl atoms, belonging to $C_{86}(17)Cl_{20}$ only. It can be seen that an overall, nearly mirror-symmetric arrangement of Cl atoms is very similar to the chlorine arrangement in $C_{86}(16)Cl_{16}$.

More detailed discussion of the addition patterns is possible with the use of Schlegel diagrams (Figure 2). Mirror symmetry of the C_s-$C_{86}(16)$ carbon cage is obvious but the attachmemt of only 14 Cl atoms in the C_1-$C_{86}(16)Cl_{16}$ molecule is symmetrical whereas the two other Cl atoms distort mirror symmetry. Two isolated C=C bonds and one isolated benzenoid ring contribute to the stabilization of the addition pattern of $C_{86}(16)Cl_{16}$.

The orientation of the Schlegel diagram of $C_{86}(17)Cl_{18,20}$ is chosen to demonstrate a similarity in the connectivities of both carbon cages. Indeed, only one Stone–Wales C–C bond rotation (SWR) is required to interconvert these two C_{86} isomers as shown in Figure 2 by marking two differently located cage pentagons. It is remarkable that the positions of the attached Cl atoms in $C_{86}(17)Cl_{18}$ remain nearly mirror-symmetric (14 of 18 Cl atoms) and, thus, are very similar to those in the $C_{86}(16)Cl_{16}$ molecule. The stabilizing substructures on the carbon cage are two isolated C=C bonds and three benzenoid rings. Note that the addition of two Cl atoms to $C_{86}(17)Cl_{18}$, under the formation of $C_{86}(17)Cl_{20}$, proceeds also in mirror-symmetric positions marked on the Schlegel diagram with yellow color. The averaged composition of the co-crystal is $C_{86}(17)Cl_{18.73}$. Co-crystallization of $C_{86}(17)Cl_{18}$ and $C_{86}(17)Cl_{20}$ was reported previously in ref. 14. In the reported structures with three crystallographically independent molecules, chlorofullerene with the averaged composition $C_{86}(17)Cl_{18.55}$ was present but the C–C bond precision was very low. In the crystal structure with the average composition $C_{86}(17)Cl_{19.61}$,[14] the C–C bond precision is much better, but the unit cell parameters and structure symmetry are different from those of $C_{86}(17)Cl_{18.73}$ reported in this communication. The existence of different crystalline phases for compositions between $C_{86}(17)Cl_{18}$ and $C_{86}(17)Cl_{20}$ can be attributed to the difference in the shape and volume of the molecules in the crystal packing. It should be noted that the chlorination pattern of $C_{86}(17)Cl_{18}$ is very similar to the trifluoromethylation pattern of $C_{86}(17)(CF_3)_{18}$ reported previously (17 common attachment positions).[13] The difference concerns the absence of an attachment in adjacent positions in the CF_3 derivative whereas the ClC–CCl fragment is present in $C_{86}(17)Cl_{18}$ (see Figure 2), which can be attributed to a larger size of the CF_3 group in comparison with the size of the Cl atom.[16]

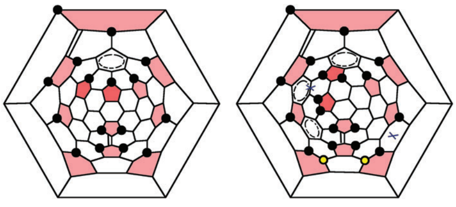

C_1-$C_{86}(16)Cl_{16}$ C_1-$C_{86}(17)Cl_{18/20}$

Figure 2 Schlegel diagrams of $C_{86}(16)Cl_{16}$ and $C_{86}(17)Cl_{18,20}$. Cage pentagons are shown with the red color. The difference of the carbon cage connectivities concerns the position of two pentagons which are highlighted with a deeper color. Black circles denote the positions of chlorine attachments. The positions of two added Cl atoms in the structure of $C_{86}(17)Cl_{20}$ are highlighted with yellow spots. Isolated C=C bonds and isolated or nearly isolated benzenoid rings are shown with double lines and dashed ovals, respectively. Two small crosses on the Schlegel diagram of $C_{86}(17)Cl_{18,20}$ indicate the position of a two-fold axis of the C_2-$C_{86}(17)$ carbon cage.

In the more accurately determined molecular structure of $C_{86}(16)Cl_{16}$, C–C bond lengths range from the short, isolated sp^2–sp^2 C=C (*av*. 1.317 Å) over aromatic C–C in a benzenoid ring (1.410 Å) to the longest sp^2–sp^3 C–C(Cl) (*av*. 1.510 and 1.530 Å for 6 : 6 and 5 : 6 C–C bonds, respectively). The lengths of C–Cl bonds are 1.801(2)–1.833(2) Å (*av*. 1.817 Å), *i.e.*, in a typical range for most IPR chlorofullerenes.

In summary, high-temperature chlorination of the C_s-$C_{86}(16)$ and C_2-$C_{86}(17)$ samples with VCl_4 resulted in the isolation and structure elucidation of $C_{86}(16)Cl_{16}$ and $C_{86}(17)Cl_{18,20}$, respectively. While $C_{86}(16)Cl_{16}$ is obtained as an individual compound, $C_{86}(17)Cl_{18,20}$ contains both $C_{86}(17)Cl_{18}$ and $C_{86}(17)Cl_{20}$ molecules which overlap in the same crystallographic site, resulting in an overall composition $C_{86}(17)Cl_{18.73}$. An X-ray diffraction study revealed the molecular structures with similar chlorination patterns, featuring the presence of stabilizing substructures on the carbon cages such as benzenoid rings and isolated C=C bonds.

References

1 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.
2 N. B. Tamm, D. V. Ignat'eva, L. A. Aslanov and S. I. Troyanov, *Chem. – Asian J.*, 2018, **13**, 2027.
3 S. Yang and S. I. Troyanov, *Mendeleev Commun*., 2022, **32**, 640.
4 N. B. Tamm, R. Guan, S. Yang and S. I. Troyanov, *Eur. J. Inorg. Chem.*, 2020, 2092.
5 S. Wang, S. Yang, E. Kemnitz and S. I. Troyanov, *Inorg. Chem*., 2016, **55**, 5741.
6 S. Yang, I. N. Ioffe and S. I. Troyanov, *Acc. Chem. Res.*, 2019, **52**, 1783.
7 Y. Miyake, T. Minami, K. Kikuchi, M. Kainosho and Y. Achiba, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 2000, **340**, 553.
8 G. Sun and M. Kertesz, *Chem. Phys*., 2002, **276**, 107.
9 Z. Slanina, S.-L. Lee and L. Adamowicz, *Int. J. Quantum Chem*., 1997, **63**, 529.
10 M. Kiuchi and J. Aihara, *THEOCHEM*, 2004, **685**, 97.
11 A. J. Stone and D. J. Wales, *Chem. Phys. Lett.*, 1986, **128**, 501.
12 Z. Wang, H. Yang, A. Jiang, Z. Liu, M. M. Olmstead and A. L. Balch, *Chem. Commun*., 2010, **46**, 5262.
13 S. I. Troyanov and N. B. Tamm, *Crystallogr. Rep*., 2009, **54**, 598.
14 S. Yang, T. Wei and S. I. Troyabov, *Chem. – Eur. J*., 2014, **20**, 14198.
15 K. Jinno, H. Matsui, H. Ohta, Y. Saito, K. Nakagawa, H. Nagashima and K. Itoh, *Chromatographia*, 1995, **41**, 353.
16 O. V. Boltalina, A. A. Popov, I. V. Kuvychko, N. B. Shustova and S. H. Strauss, *Chem. Rev*., 2015, **115**, 1051.

Received: 23rd January 2023; Com. 23/7090