Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 312–313
Mendeleev Communications

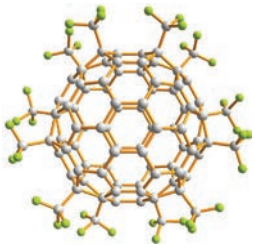
A minor isomer of C_{84} fullerene, D_{6h}-$C_{84}(24)$, captured as a trifluoromethylated derivative, $C_{84}(CF_3)_{12}$

Nadezhda B. Tamm and Sergey I. Troyanov*

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.2016.07.015

An isomer of C_{84} fullerene, D_{3d}-$C_{84}(24)(CF_3)_{12}$, has been isolated by the HPLC method from the products of trifluoromethylation of C_{84} fullerene mixture. Its molecular structure has been determined by a single crystal X-ray diffraction using synchrotron radiation. In the addition pattern, 12 CF_3 groups are arranged as a loop of edge-sharing *para*-$C_6(CF_3)_2$ hexagons. Isomer D_{6h}-$C_{84}(24)$ has been identified in the form of a derivative for the first time.



Among higher fullerenes present in the fullerene soot, C_{84} is the most abundant though its content relative to the sum of C_{60} and C_{70} does not exceed several percents. Fullerene C_{84} has 24 topologically possible isomers obeying the Isolated-Pentagon-Rule (IPR).[1] Earlier study of ^{3}He@C_{84} (isomer mixture) by ^{3}He NMR spectroscopy suggested the existence of at least nine isomers of C_{84} in the fullerene soot.[2] The fullerene soot obtained by the arc-discharge method with the use of undoped graphite rods contains several isomers of C_{84}, which have been extracted, isolated by HPLC, and identified by ^{13}C NMR spectroscopy.[3–5] Among them D_2-$C_{84}(22)$ and D_{2d}-$C_{84}(23)$ belong to the most abundant isomers,[3,4] whereas D_{2d}-$C_{84}(4)$, D_2-$C_{84}(5)$, C_2-$C_{84}(11)$, C_s-$C_{84}(14)$, and C_s-$C_{84}(16)$ are the minor ones.[5] In addition, two isomers of C_{84} with high cage symmetry, D_{3d}-$C_{84}(19)$ and D_{6h}-$C_{84}(24)$, were detected in the fullerene soot produced using Gd-doped graphite rods.[6]

A majority of pristine isomers of C_{84}, identified by ^{13}C NMR spectroscopy, have been confirmed by crystallography in co-crystals with metal porphyrins[7] or as exohedral derivatives.[8–13] The isomer $C_{84}(14)$ was identified in co-crystals with silver tetraphenylporphyrin.[7] High-temperature chlorination and X-ray crystallographic investigation of chlorides resulted in the confirmation of isomers 5 (in $C_{84}Cl_{20/32}$)[8] as well as 11, 14, and 16 (in the same crystal of $C_{84}Cl_{22}$).[9] The synthesis, isolation, and X-ray crystallography of perfluoroalkylated fullerenes, $C_{84}(CF_3)_n$ or $C_{84}(C_2F_5)_n$, allowed C_{84} isomers 4,[10] 5,[8] 11,[10,11] 16,[9,10,12] 22,[13,14] and 23[15] to be confirmed. In addition, a new isomer, C_{2v}-$C_{84}(18)$, has been identified crystallographically in several $C_{84}(CF_3)_n$ compounds.[10,12] However, both isomers $C_{84}(19)$ and $C_{84}(24)$, detected previously by ^{13}C NMR spectroscopy, have not been isolated as any derivative till now.

Herein, we report the synthesis, isolation, and crystal structure of $C_{84}(24)(CF_3)_{12}$, which represents the first evidence of the presence of isomer D_{6h}-$C_{84}(24)$ in the fullerene soot obtained using undoped graphite rods.

The extract from the arc-discharge fullerene soot was separated by the HPLC using a preparative Buckyprep column (20 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as an eluent. According to MALDI-TOF MS analysis the isolated fraction of C_{84} fullerene was slightly contaminated by C_{82}. The trifluoromethylation of this fraction with the gaseous CF_3I was carried out in quartz tubes at 450 °C for 1.5 h followed by a procedure described previously.[12,13,15] The product containing mainly $C_{84}(CF_3)_n$ (n = 6–16) was dissolved in toluene and subjected to HPLC separation using a semi-preparative Buckyprep column (10 mm i.d. × 250 mm, Nacalai Tesque Inc.) and toluene as an eluent at a flow rate of 3.5 ml min^{-1}. The toluene fraction eluted between 7.5 and 7.8 min was further separated using the same column and hexane–toluene mixture (4:6, v/v) as an eluent at a flow rate of 4.6 ml min^{-1}. According to MALDI-TOF MS analysis the fraction collected between 9.8 and 10.5 min contained predominantly $C_{84}(CF_3)_{12}$ with the small amount of $C_{84}(CF_3)_{14/16}$. Small crystals were obtained by recrystallization from *o*-dichlorobenzene. X-ray diffraction study with the use of synchrotron radiation revealed the structure of $C_{84}(24)(CF_3)_{12}$.[†]

Theoretical calculations of relative stability of C_{84} isomers revealed higher stability of two major isomers 22 and 23 and moderate to low stability of several other isomers (in the decreasing stability order): 24 ~ 16 ~ 11 > 19 ~ 15 > 12 > 4 ~ 14 > 18 ~ 5 ~ 21.[16] Therefore, the isolation of a derivative of $C_{84}(24)$ is not unexpected. It was more surprising that numerous derivatives of other, equally or less stable, isomers of C_{84} were previously isolated easier and in higher quantities. Thus, the fullerene soot produced from undoped graphite rods also contains isomer $C_{84}(24)$ though in very small amounts.

Two projections of the $C_{84}(24)(CF_3)_{12}$ molecule are presented in Figure 1. Pristine D_{6h}-$C_{84}(24)$ possesses the high point sym-

† *Crystal data.* Synchrotron X-ray data were collected at 100 K at the BESSY storage ring (BL14.2, PSF, Berlin, Germany) using a MAR225 CCD detector, λ = 0.88561 Å. The crystal structure was solved by SHELXD software and refined with SHELXL software. $C_{84}(CF_3)_{12}$ crystals are monoclinic, $C2/m$ with a = 11.274(1), b = 23.991(2), and c = 10.905(1) Å, β = 100.37(1)°, V = 2901.3(5) Å^3, and Z = 2. Anisotropic refinement with 3119 reflections and 382 parameters converged to wR_2 = 0.143 and R_1 = 0.072 for 1151 reflections with $I > 2\sigma(I)$. Three independent CF_3 groups are disordered around C–CF_3 axes with occupation ratios of 0.79/0.21(1), 0.69/0.31(2), and 0.65/0.35(2).

CCDC 1448772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

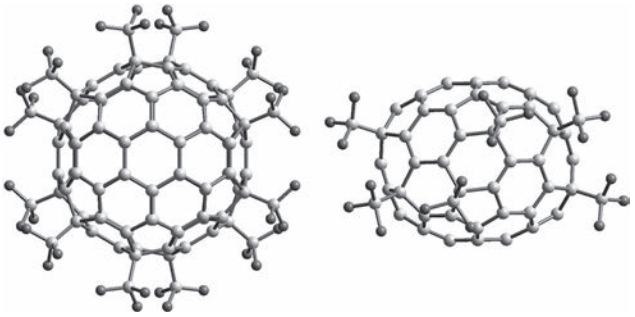


Figure 1 Two views of the D_{3d}-$C_{84}(24)(CF_3)_{12}$ molecule. The projections on the left and right sides are presented along the C_3 (non-crystallographic) and C_2 axes, respectively.

metry with two coronene substructures on the opposite poles of the carbon cage, which results in the flattened shape of the trifluoromethylated molecule. For the same reason, the addition occurs in the positions near the equatorial region of the cage. The idealized molecular symmetry of the $C_{84}(24)(CF_3)_{12}$ molecule, *i.e.*, symmetry of the addition pattern, is D_{3d}, whereas the crystallographic symmetry is reduced to C_{2h}.

Schlegel diagram of $C_{84}(24)(CF_3)_{12}$ is shown in Figure 2. It is clear that all CF_3 groups are attached on both sides of the equatorial plane in a loop of twelve edge-sharing *para* $C_6(CF_3)_2$ hexagons. This contiguous addition pattern of 12 CF_3 groups is unique, if only the additions in *para* positions in hexagons are considered and additions to the much less preferable positions of triple hexagon junctions (THJs) are excluded.

According to our DFT calculations, the experimental molecule of $C_{84}(24)(CF_3)_{12}$ possesses the lowest relative formation energy (0.0 kJ mol^{-1}) in comparison with any molecule with non-contiguous addition pattern by at least 56 kJ mol^{-1}. It was also found that the conformation of CF_3 groups, which corresponds to the main component of the disordered X-ray structure, is not optimal energetically due to some repulsion of neighboring CF_3 groups. Therefore, in the molecule of C_i symmetry with the optimized conformation of CF_3 groups, all F···F contacts are longer than 2.78 Å, whereas the optimized molecule started from the X-ray conformation of C_{2h} symmetry exhibits several shorter F···F contacts in the range of 2.56–2.73 Å. Accordingly, the latter is 14 kJ mol^{-1} less stable than the conformationally optimized molecule.

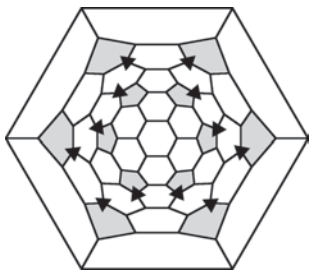


Figure 2 The Schlegel diagram of D_{3d}-$C_{84}(24)(CF_3)_{12}$. Cage pentagons are highlighted in gray. Black triangles indicate the positions of attached CF_3 groups.

In summary, high-temperature trifluoromethylation of the mixture of C_{84} isomers followed by the HPLC separation, recrystallization, and X-ray diffraction study has revealed the crystal and molecular structure of D_{3d}-$C_{84}(24)(CF_3)_{12}$. The addition pattern of 12 CF_3 groups to C_{84} carbon cage is characterized by a near-equatorial loop of edge-sharing *p*-$C_6(CF_3)_2$ hexagons. The presence of isomer D_{6h}-$C_{84}(24)$ in the fullerene soot produced using undoped graphite rods has been confirmed for the first time.

This work was supported by the Russian Foundation for Basic Research (project no. 15-03-04464).

References

1 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.
2 M. Saunders, H. A. Jimenez-Vazquez, R. J. Cross, W. E. Billups, C. Gesenberg, A. Gonzalez, W. Luo, R. C. Haddon, F. Diederich and A. Herrmann, *J. Am. Chem. Soc*., 1995, **117**, 9305.
3 D. E. Manolopoulos, P. W. Fowler, R. Taylor, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 3117.
4 T. J. S. Dennis, T. Kai, T. Tomiyama and H. Shinohara, *Chem. Commun.*, 1998, 619.
5 T. J. S. Dennis, T. Kai, K. Asato, T. Tomiyama, H. Shinohara, T. Yoshida, Y. Kobayashi, H. Ishiwatari, Y. Miyake, K. Kikuchi and Y. Achiba, *J. Phys. Chem. A*, 1999, **103**, 8747.
6 N. Tagmatarchis, A. G. Avent, K. Prassides, T. J. S. Dennis and H. Shinohara, *Chem. Commun*., 1999, 1023.
7 L. Epple, K. Amsharov, K. Simeonov, I. Dix and M. Jansen, *Chem. Commun*., 2008, 5610.
8 S. Yang, C. Chen, T. Wei, N. B. Tamm, E. Kemnitz and S. I. Troyanov, *Chem. Eur. J*., 2012, **18**, 2217.
9 M. A. Lanskikh, N. B. Tamm, L. N. Sidorov and S. I. Troyanov, *Inorg. Chem*., 2012, **51**, 2719.
10 N. B. Tamm, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Chem. Eur. J.*, 2009, **15**, 10486.
11 I. E. Kareev, I. V. Kuvychko, N. B. Shustova, S. F. Lebedkin, V. P. Bubnov, O. P. Anderson, A. A. Popov, O. V. Boltalina and S. H. Strauss, *Angew. Chem. Int. Ed*., 2008, **47**, 6204.
12 N. A. Romanova, M. A. Fritz, K. Chang, N. B. Tamm, A. A. Goryunkov, L. N. Sidorov, K. Scheurell, E. Kemnitz and S. I. Troyanov, *Russ. Chem. Bull., Int. Ed*., 2014, **63**, 2657 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 2657).
13 K. Chang, M. A. Fritz, N. B. Tamm, A. A. Goryunkov, L. N. Sidorov, C. Chen, S. Yang, E. Kemnitz and S. I. Troyanov, *Chem. Eur. J.*, 2013, **19**, 578.
14 N. A. Romanova, M. A. Fritz, N. B. Tamm and S. I. Troyanov, *Mendeleev Commun.*, 2014, **24**, 78.
15 N. A. Romanova, M. A. Fritz, K. Chang, N. B. Tamm, A. A. Goryunkov, L. N. Sidorov, C. Chen, S. Yang, E. Kemnitz and S. I. Troyanov, *Chem. Eur. J*., 2013, **19**, 11707.
16 G. Sun and M. Kertesz, *J. Phys. Chem. A*, 2001, **105**, 5212.

Received: 11th January 2016; Com. 16/4813