Mendeleev Communications

Mendeleev Commun., 2025, **35**, 45–46

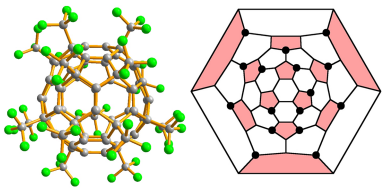
Eight new trifluoromethyl derivatives of [60]fullerene, $C_{60}(CF_3)_{16}$

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: NBTamm@phys.chem.msu.ru

DOI: 10.71267/mencom.7552

Eight new $C_{60}(CF_3)_{16}$ isomers have been synthesized by high-temperature trifluoromethylation of [60]fullerene with gaseous CF_3I, isolated by HPLC, and structurally characterized by single crystal X-ray diffraction using synchrotron radiation.



$C_{60}(CF_3)_{16}$ isomer V

Keywords: fullerene C_{60}, trifluoromethylation, HPLC separation, structure elucidation, synchrotron radiation.

Trifluoromethylated fullerenes C_{60} and C_{70} belong to the large group of compounds which are obtained, separated and structurally characterized experimentally and considered theoretically.[1,2] The structural characterization of $C_{60}(CF_3)_n$ compounds with $n = 2$–10 was achieved by either ^{19}F NMR spectroscopy[2–4] or, more directly, with single crystal X-ray diffraction,[5–9] whereas the latter method is more useful for the derivatives with $n \geqslant 12$.[10–12] In the last few years, based on the development of the methods of chromatographic separation and X-ray structure determination, several new isomers, three of $C_{60}(CF_3)_{12}$[11] and 12 of $C_{60}(CF_3)_{14}$,[12] have been reported so that the number of isomers with known molecular structure reached 9 for $C_{60}(CF_3)_{12}$ and 15 for $C_{60}(CF_3)_{14}$. In this communication, we present the data on the synthesis, separation, and structural studies of eight new $C_{60}(CF_3)_{16}$ isomers, thus increasing the number of structurally characterized isomers to 11.

The synthesis of $C_{60}(CF_3)_n$ derivatives was carried out in ampoules by the reaction of C_{60} fullerene with gaseous CF_3I at 420 °C for 36–48 h. The reaction product was dissolved in *n*-hexane and subjected to HPLC separation in *n*-hexane using a semipreparative Cosmosyl Buckyprep column. The composition of the HPLC fractions was controlled by MALDI–TOF mass spectrometry. Each of the so obtained HPLC fractions was additionally separated using a semipreparative Cosmosyl Buckyprep-D column thus producing isomerically pure or nearly pure subfractions of $C_{60}(CF_3)_n$ compounds with *n* ranging from 12 to 18.[†] The crystals were grown from hexane solution or by recrystallization from toluene or *p*-xylene. Because of typically very small size of the crystals their X-ray diffraction study was performed using synchrotron radiation.[‡]

The data on the synthesis and characterization of $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$ are reported earlier[11,12] whereas those on three $C_{60}(CF_3)_{16}$ isomers denoted as 16-I, 16-II, and 16-III are available in ref. 10. Eight new isomers of $C_{60}(CF_3)_{16}$ are denoted according to the increasing retention times in the HPLC separation process as 16-IV–16-XI. Three selected molecular structures of 16-IV, 16-V, and 16-VII are shown in Figure 1.

The addition patterns of all 11 structurally characterized $C_{60}(CF_3)_{16}$ isomers are presented in Figure 2 as Schlegel diagrams. Theoretically calculated relative formation energies in kJ mol^{-1} are given for each isomer.[13,14] In the most isomers, all 12 cage pentagons are occupied with one or two CF_3 groups. Two isomers, 16-III and 16-VI, have one unoccupied pentagon whereas isomer 16-VII has two such pentagons in the carbon cage (see Figure 1). This feature is believed to decrease the isomer stability but in fact, there are some stabilizing structural fragments on the carbon cage such as isolated (*i.e.*, localized)

† *Experimental details.* HPLC separation was performed by means of a Waters LC system equipped with a Cosmosyl Buckyprep column (10 I.D×250 mm) with pyrenylpropyl bonded phase, and Cosmosyl Buckyprep-D column (10 I.D.× 250 mm) with nitrocarbazoyl bonded phase. The negative-ion MALDI mass spectra were acquired using a Bruker AutoFlex II reflector time-of-flight mass spectrometer (N_2 laser, 337 nm, 2.5 ns pulse). DCTB in a molar ratio of >1000 : 1 relative to the analyte was employed as a MALDI matrix.

‡ *Crystal data.* Synchrotron X-ray diffraction data were collected at 100 K at the BESSY storage ring (BL14.2/3, Berlin, Germany) using a MAR225 CCD detector. $C_{60}(CF_3)_{16}$ (16-IV), $C_{76}F_{48}$, monoclinic, $P2_1/n$, $a = 14.371(1)$, $b = 20.787(3)$ and $c = 19.175(2)$ Å, $\beta = 91.42(3)°$, $V = 5726.4(11)$ Å^3, $Z = 4$. $C_{60}(CF_3)_{16}\cdot 0.5$ toluene (16-V), $C_{79.5}H_4F_{48}$, triclinic, $P\bar{1}$, $a = 13.116(1)$, $b = 13.332(1)$ and $c = 19.6391(7)$ Å, $\alpha = 81.501(5)°$, $\beta = 85.013(8)°$, $\gamma = 64.995(10)°$, $V = 3076.9(4)$ Å^3, $Z = 2$. $C_{60}(CF_3)_{16}$ (16-VI), $C_{76}F_{48}$, monoclinic, $P2_1/n$, $a = 11.645(1)$, $b = 22.960(1)$ and $c = 21.644(1)$ Å, $\beta = 90.168(10)°$, $V = 5786.9(6)$ Å^3, $Z = 4$. $C_{60}(CF_3)_{16}\cdot 0.25$ toluene (16-VII), $C_{77.75}H_2F_{48}$, monoclinic, $P2_1/n$, $a = 12.427(1)$, $b = 39.341(2)$ and $c = 24.149(3)$ Å, $\beta = 92.10(2)°$, $V = 11806.2(18)$ Å^3, $Z = 8$. $C_{60}(CF_3)_{16}$ (16-VIII), $C_{76}F_{48}$, monoclinic, $P2_1/n$, $a = 13.671(1)$, $b = 16.6761(6)$ and $c = 24.661(2)$ Å, $\beta = 90.130(8)°$, $V = 5622.2(6)$ Å^3, $Z = 4$. $C_{60}(CF_3)_{16}$ (16-IX), $C_{76}F_{48}$, triclinic, $P\bar{1}$, $a = 12.171(1)$, $b = 12.196(1)$ and $c = 20.911(2)$ Å, $\alpha = 87.66(2)°$, $\beta = 87.07(3)°$, $\gamma = 71.51(2)°$, $V = 2938.9(6)$ Å^3, $Z = 2$. $C_{60}(CF_3)_{16}\cdot 0.5$ *p*-xylene (16-X), $C_{80}H_5F_{48}$, triclinic, $P\bar{1}$, $a = 12.351(1)$, $b = 12.890(1)$ and $c = 20.750(2)$ Å, $\alpha = 80.12(2)°$, $\beta = 86.65(1)°$, $\gamma = 66.62(2)°$, $V = 2987.1(6)$ Å^3, $Z = 2$. $C_{60}(CF_3)_{16}$ (16-XI), $C_{76}F_{48}$, triclinic, $P\bar{1}$, $a = 12.035(1)$, $b = 12.350(1)$ and $c = 21.504(1)$ Å, $\alpha = 98.906(6)°$, $\beta = 97.782(10)°$, $\gamma = 112.895(10)°$, $V = 2840.9(4)$ Å^3, $Z = 2$.

CCDC 2361868–2361875 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

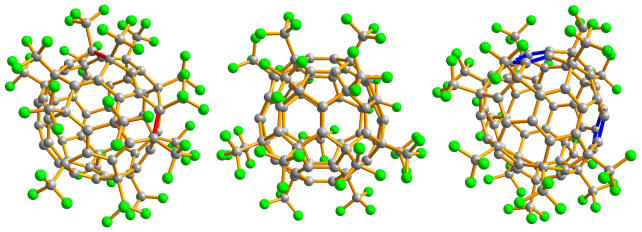


Figure 1 Views of three isomeric $C_{60}(CF_3)_{16}$ molecules. C–C bonds of *ortho* attachments in isomer 16-IV are indicated with red color. In the molecule of 16-VII, two unoccupied pentagons are shown in blue. Isomer 16-V is selected for presentation as the most stable one among all known $C_{60}(CF_3)_{16}$ compounds.

double C=C bonds or benzenoid rings. The isolation of C=C bonds (typical bond length 1.33–1.35 Å) occurs when a two carbon of a C–C bond are surrounded by four sp^3-hybridizized C atoms. The partially isolated C=C bonds are surrounded by three sp^3 C atoms. The number of fully or partially isolated C=C bonds on the carbon cage in the molecules of $C_{60}(CF_3)_{16}$ ranges from seven (16-III, 16-IV, 16-VII, and 16-X) to ten (16-VIII and 16-XI). The partially isolated benzenoid rings (by five sp^3 C atoms) with typical *av*. C–C bond length 1.39–1.40 Å are found in isomers 16-VI, 16-VII, 16-X, and 16-XI. A characteristic structural fragment in multi-addend fullerene derivatives is a so-called skewed pentagonal pyramid (SPP).[5] Five addends are arranged around a pentagon one site of which is occupied by the sixth addend thus resulting in an *ortho* attachment with typically elongated C–C (6:6) bond (1.58–1.61 Å). The stabilizing effect in an SPP is due to the formation of a butadiene-like C=C–C=C fragment in the pentagon. The SPP fragments in the $C_{60}(CF_3)_{16}$ molecules are present in isomers 16-II and 16-IV. Another case of *ortho* attachment concerns a 5:6 C–C bond in a pentagon, also resulting in C–C bond elongation as found in the molecular structures of isomers 16-IV, 16-X, and 16-XI. Both types of *ortho* attachment are present in isomer 16-IV as shown in Figure 1.

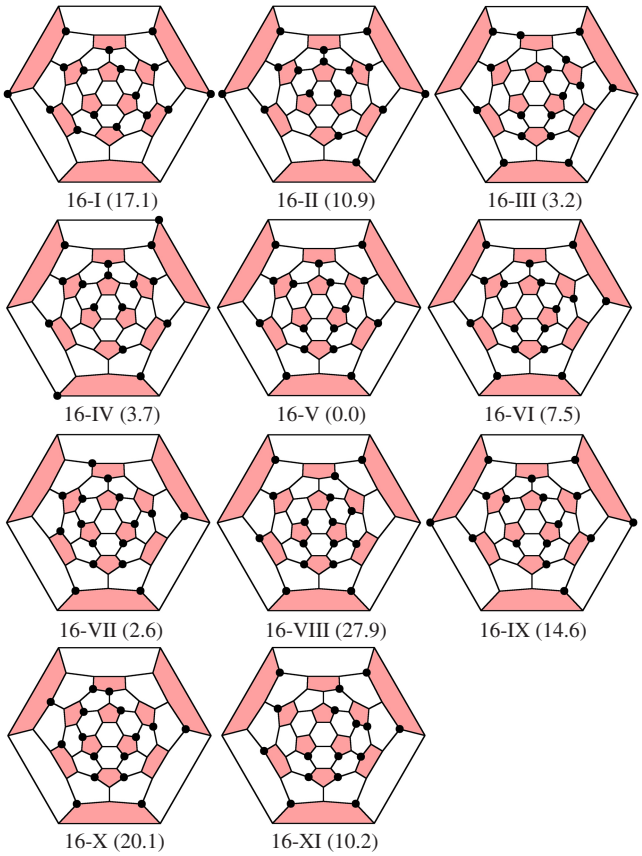


Figure 2 Schlegel diagrams of 11 $C_{60}(CF_3)_{16}$ isomers, eight of which, 16-IV–16-XI, were structurally characterized in this work. Cage pentagons are shown in red. Black circles indicate the positions of CF_3 attachments. Theoretically calculated relative formation energies are given in parentheses in kJ mol^{-1}.

Several $C_{60}(CF_3)_{16}$ isomers possess very similar trifluoromethylation patterns. The closest similarity, 14 common attachment positions, is observed in isomer pairs 16-II/16-IV, 16-III/16-VI, 16-V/16-VI, 16-V/16-IX, 16-VII/16-X, and 16-VIII/16-XI.

The span of relative formation energy, 27.9 kJ mol^{-1}, can be regarded as not large because the higher values, 90.2 and 32.1 kJ mol^{-1}, were calculated for experimentally isolated $C_{60}(CF_3)_{12}$ and $C_{60}(CF_3)_{14}$ isomers, respectively.

In summary, eight new $C_{60}(CF_3)_{16}$ isomers have been synthesized, chromatographically isolated, and structurally characterized. The addition patterns of all 11 experimental isomers are discussed in terms of the formation of isolated C–C bonds, benzenoid rings, SPP substructures and other *ortho* additions on the C_{60} carbon cage, thus contributing to the chemistry of trifluoromethylated fullerenes.

The research was carried out under partial support of the program ‘Chemical Thermodynamics and Theoretical Material Science’ (121031300039-1).

References

1 O. V. Boltalina, A. A. Popov, I. V. Kuvychko, N. B. Shustova and S. H. Strauss, *Chem. Rev.*, 2015, **115**, 1051; https://doi.org/10.1021/cr5002595.
2 A. A. Popov, I. E. Kareev, N. B. Shustova, E. B. Stukalin, S. F. Lebedkin, K. Seppelt, S. H. Strauss, O. V. Boltalina and L. Dunsch, *J. Am. Chem. Soc.*, 2007, **129**, 11551; https://doi.org/10.1021/ja073181e.
3 A. A. Goryunkov, I. V. Kuvychko, I. N. Ioffe, D. L. Dick, L. N. Sidorov, S. H. Strauss and O. V. Boltalina, *J. Fluorine Chem.*, 2003, **124**, 61; https://doi.org/10.1016/S0022-1139(03)00173-8.
4 I. E. Kareev, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Chem. Commun.*, 2006, 308; https://doi.org/10.1039/b513477c.
5 I. E. Kareev, N. B. Shustova, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, A. A. Popov, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc*., 2006, **128**, 12268; https://doi.org/10.1021/ja063907r.
6 E. I. Dorozhkin, A. A. Goryunkov, I. N. Ioffe, S. M. Avdoshenko, V. Yu. Markov, N. B. Tamm, D. V. Ignat’eva, L. N. Sidorov and S. I. Troyanov, *Eur. J. Org. Chem.*, 2007, 5082; https://doi.org/10.1002/ejoc.200700487.
7 I. E. Kareev, N. B. Shustova, B. S. Newell, S. M. Miller, O. P. Anderson, S. H. Strauss and O. V. Boltalina, *Acta Crystallogr.*, 2006, **E62**, o3154; https://doi.org/10.1107/S1600536806024561.
8 I. E. Kareev, I. V. Kuvychko, S. F. Lebedkin, S. M. Miller, O. P. Anderson, K. Seppelt, S. H. Strauss and O. V. Boltalina, *J. Am. Chem. Soc.*, 2005, **127**, 8362; https://doi.org/10.1021/ja050305j.
9 E. V. Bukovsky, B. W. Larson, T. T. Clikeman, Y.-S. Chen, A. A. Popov, O. V. Boltalina and S. H. Strauss, *J. Fluorine Chem.*, 2016, **185**, 103; https://doi.org/10.1016/j.jfluchem.2016.02.007.
10 S. I. Troyanov, A. A. Goryunkov, E. I. Dorozhkin, D. V. Ignat’eva, N. B. Tamm, S. M. Avdoshenko, I. N. Ioffe, V. Yu. Markov, L. N. Sidorov, K. Scheurel and E. Kemnitz, *J. Fluorine Chem*., 2007, **128**, 545; https://doi.org/10.1016/j.jfluchem.2007.01.008.
11 N. B. Tamm, V. A. Brotsman and S. I. Troyanov, *Mendeleev Commun.*, 2023, **33**, 821; https://doi.org/10.1016/j.mencom.2023.10.027.
12 N. B. Tamm, V. A. Brotsman and S. I. Troyanov, *Izv. Akad. Nauk, Ser. Khim.*, 2024, **73**, 3324 (in Russian).
13 D. N. Laikov, *Chem. Phys. Lett*., 1997, **281**, 151; https://doi.org/10.1016/S0009-2614(97)01206-2.
14 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; https://doi.org/10.1103/PhysRevLett.77.3865.

Received: 24th June 2024; Com. 24/7552