The former “$C_{60}F_{16}$” is actually a double-caged adduct: $(C_{60}F_{16})(C_{60})$†

Alexey A. Goryunkov,[a] Ilya N. Ioffe,[a] Pavel A. Khavrel,[a] Stanislav M. Avdoshenko,[a] Vitaly Yu. Markov,[a] Z. Mazej,[b] Lev N. Sidorov[a] and Sergey I. Troyanov*[a]

Received (in Cambridge, UK) 25th October 2006, Accepted 23rd November 2006
First published as an Advance Article on the web 6th December 2006
DOI: 10.1039/b615457c

X-ray diffraction study of the substance originally believed to be $C_{60}F_{16}$ reveals a double-caged structure, $(C_{60}F_{16})(C_{60})$; MALDI mass spectra, ^{19}F NMR spectral data and reasons for stability are discussed.

The first isolation of “$C_{60}F_{16}$”, as was deduced on the basis of mass spectrometric and NMR data, from the mixture of products of [60]fullerene fluorination with K_2PtF_6 was reported as early as 2000.[1] The suggested structure of the product was derived from the structure of $C_{60}F_{18}$, the most abundant component of the mixture, *via* removal of two fluorine atoms; it retained the most important structural feature of $C_{60}F_{18}$, namely, its isolated benzenoid ring.[2,3] Additionally, “$C_{60}F_{16}$” was observed to form from $C_{60}F_{18}$ upon action of anisole in the presence of ferric chloride with a characteristic reaction time of several weeks[1] and *via* pyrolysis of $C_{60}F_{18}$.[4] However, in contrast to these indications of a close structural relationship between the isolated “$C_{60}F_{16}$” and $C_{60}F_{18}$, the retention time reported by Roger Taylor for the isolated “$C_{60}F_{16}$” fraction was surprisingly high, as compared to other C_{60} fluorides;[5] in particular, it was found to elute more than twice as slowly as $C_{60}F_{18}$. This observation led Roger Taylor to suggest that “$C_{60}F_{16}$” possibly has a much larger size, which could, taking into account the above mentioned relationship with $C_{60}F_{18}$, be due to formation of dimeric forms or complexes.[5] Further studies of the $C_{60}F_{18}$ chemistry by Taylor and coworkers resulted in synthesis of a large family of $C_{60}F_{16}$ derivatives obtained *via* substitution of two fluorine atoms in $C_{60}F_{18}$. Reaction of methoxyethoxymethyl azide with $C_{60}F_{18}$ in toluene solution leads to replacement of two fluorines by the $>NCH_2OCH_2CH_2OMe$ moiety giving a C_s symmetrical aziridinofluorofullerene, $C_{60}F_{16}NCH_2OCH_2CH_2OMe$.[6] Co-evaporation of toluene solutions of $C_{60}F_{18}$ and tetrathiafulvalene (TTF) in toluene produces an unsymmetrical $C_{60}F_{16}$:TTF adduct through a unique six-electron cycloaddition involving displacement of two fluorine atoms by a terminal C–C double bond of the fulvalene.[7] In the light of the above data, which suggest the $C_{60}F_{18}$-like shell of substituents to be strongly favorable, and the unusual chromatographic behavior, we felt it necessary to reinvestigate the compound previously believed to be $C_{60}F_{16}$.

The mixture of [60]fullerene (185 mg, 99.9% TermUSA) and $KMnF_4$ (1200 mg, 28-fold molar excess, prepared as described elsewhere[8]) was heated for 5 h at 470 °C and pressure *ca.* 1 Pa in a glass tube. This procedure yielded *ca.* 197 mg of crude fluorofullerene mixture. 130 mg of the said mixture were then dissolved in a minimum volume of dry toluene and filtered under conditions preventing moisture condensation. Quick evaporation to the final volume of 15 ml was followed by HPLC purification (10 mm × 25 cm Cosmosil Buckyprep column, toluene, 4.7 ml min^{-1}) to give recovered [60]fullerene (8.4 min, *ca.* 11 mg), $C_{60}F_{18}$ (34 min, *ca.* 54 mg) and a number of less abundant components. The fraction of interest (87 min in the present work or 84 min in ref. 1 due to slightly different HPLC conditions) was evaporated to yield plate-like brown crystals (*ca.* 4 mg).

Single crystal X-ray crystallographic study revealed formation of a double-caged [2 + 2]-cycloadduct consisting of the $C_{60}F_{16}$ and C_{60} fragments connected along [6,6]-double bonds, similarly to

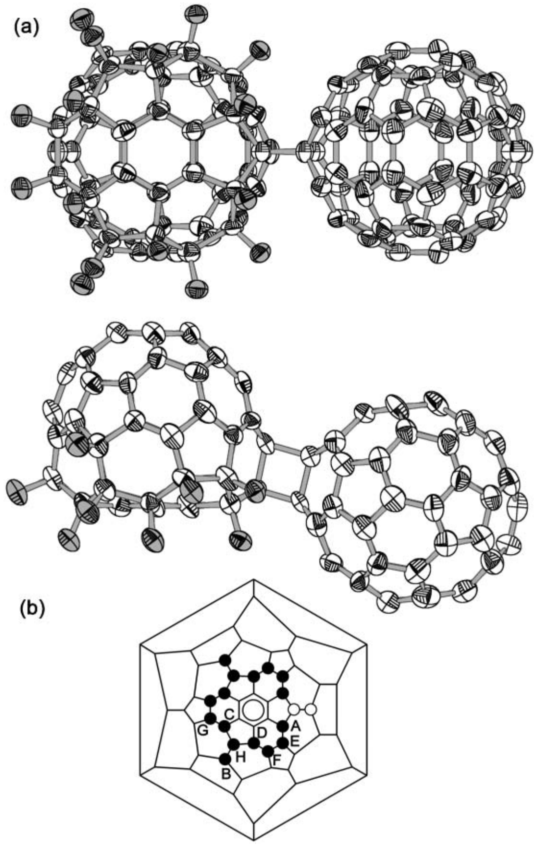

Fig. 1 (a) Two ORTEP projections of C_s–$(C_{60}F_{16})(C_{60})$ with thermal ellipsoids at the 40% probability level and (b) Schlegel diagram of the $C_{60}F_{16}$ subunit, showing ^{19}F NMR peak assignments from ref. 1; ● = F, ○ = site of [2 + 2]-cycloaddition of C_{60}.

---

[a] *Moscow State University, Chemistry Department, Leninskiye gory 1, Building 3, Moscow, 119992, Russia.*
E-mail: stroyano@thermo.chem.msu.ru; Fax: +7(495)9391240; Tel: +7(495)9391240
[b] *Jožef Stefan Institute, Department of Inorganic Chemistry and Technology, Jamova 39, SI-1000, Ljubljana, Slovenia*

† Dedicated to the memory of Roger Taylor.

$(C_{60})_2$ dimer,[9] by a bridging cyclobutane ring (Fig. 1a).‡ On the Schlegel diagram of the $C_{60}F_{16}$ subunit the connection sites are marked with empty circles (Fig. 1b). The whole $(C_{60}F_{16})(C_{60})$ molecule possesses mirror symmetry (C_s). Its fluorinated half is geometrically very similar to that of $C_{60}F_{18}$[2,3] and contains a virtually planar isolated aromatic (benzenoid) ring where all carbon atoms have a planar coordination with typical C–C distances in the ring of 1.39 ± 0.02 Å. The sp^2–sp^3 C–C bonds radiating from the benzenoid ring range within 1.44–1.49 Å (1.48 Å in $C_{60}F_{18}$[3]). Much longer are the sp^3–sp^3 C–C distances in the fluorinated sp^3 belt: from 1.55 to 1.67 Å, again showing only minor deviations from the geometry of the $C_{60}F_{18}$ molecule.[3] The bonds radiating from sp^3 carbon atoms of the bridging 4-membered cycle fall in the range of 1.53–1.60 Å on the $C_{60}F_{16}$ side (the longest being of the C–C(F) type) and 1.53–1.62 Å on the C_{60} side (the longest being the former [6,6]-bond). The bridging C–C bonds show moderate elongation to 1.56–1.58 Å. In the dimeric $(C_{60})_2$, all C–C distances at the cyclobutane ring have the same length of 1.58 Å.[9]

Identification of "$C_{60}F_{16}$" as a $(C_{60}F_{16})(C_{60})$ cycloadduct provides helpful insights into its chromatographic, mass spectrometric and spectroscopic behavior. The double-caged structure of $(C_{60}F_{16})(C_{60})$ provides a natural explanation for the high HPLC retention time of "$C_{60}F_{16}$", the observed values being in line with, for example, *ca.* twofold increase of retention time for dimeric $(C_{60})_2$ and cycloadduct $(C_{60})_2O$ relative to C_{60} and $C_{60}O$.[10,11] The negative ion MALDI mass spectrum of the $(C_{60}F_{16})(C_{60})$ chromatographic fraction is dominated by the C_{60}^-, $C_{60}F_n^-$ (n = 14–16), and $C_{120}F_{15}^-$ signals (Fig. 2).§ The latter is likely to be formed from double-caged $C_{120}F_{16}$ adduct *via* loss of a fluorine atom, which is typical for negative MALDI spectra of fluorofullerenes.[12] The experimental distributions of isotopomers for $C_{60}F_{16}^-$ and $C_{120}F_{15}^-$ are also in good agreement with theoretical data as shown in insets of Fig. 2. The formation of $C_{60}F_{16}^-$ ion and its fragments as well as C_{60}^- is obviously due to the weakness of the bonds between the two carbon cages, discussed below in more detail. In earlier work, the electron ionization (EI) mass spectrum of the fraction eluted at the same retention time (*ca.* 84 min) was dominated by $C_{60}F_n^+$ ions with n = 4–16.[1] No double-caged species were observed and the isolation of single-caged $C_{60}F_{16}$ was thus suggested. However, taking into account the much higher sublimation enthalpy one would expect for $(C_{60}F_{16})(C_{60})$ cycloadduct and the relatively weak bonding between $C_{60}F_{16}$ and C_{60} cages, it seems most probable that $(C_{60}F_{16})(C_{60})$ undergoes dissociative thermal desorption, leaving no chance to detect a parent molecule under the conventional EI mass spectrometry conditions.

The ^{19}F chemical shifts of $(C_{60}F_{16})(C_{60})$ calculated at the DFT level of theory with the use of GIAO methodology also demonstrate much better agreement with the experimental NMR data from ref. 1 than the spectrum calculated for the single-caged $C_{60}F_{16}$ structure.¶ On Fig. 3 we plot the calculated data scaled according to the procedure described in ref. 8 *versus* the experimental chemical shift values. It is clearly seen that for single-caged $C_{60}F_{16}$ the correlation gets significantly worse for the fluorine atoms most close to the missing bridging cycle (marked "A" and "E" following the notations of ref. 1, see Fig. 1b). The correlation for the $(C_{60}F_{16})(C_{60})$ should be even better when taking into account the systematic 1–3 ppm upfield shift of the reference experimental values used for scaling in ref. 8 relative to those published by Taylor *et al.* for the same reference molecules, such as $C_{60}F_{18}$[13] and $C_{60}F_{36}$,[14] as well as for "$C_{60}F_{16}$".[1]

We suppose that formation of $(C_{60}F_{16})(C_{60})$ in the course of C_{60} fluorination involves the true single-caged $C_{60}F_{16}$ as a direct precursor. The latter can either be further fluorinated to $C_{60}F_{18}$ or trapped by a [2 + 2]-cycloaddition reaction with unreacted C_{60} molecule activated by considerable reaction temperatures. However, as discussed above, sublimation of intact $(C_{60}F_{16})(C_{60})$ from the synthetic mixture seems very unlikely; therefore, formation of the cycloadducts should take place in the somewhat cooler zone of the reactor where condensation of sublimed $C_{60}F_{18}$, $C_{60}F_{16}$ and other fluorinated molecules together with unreacted C_{60} occurs. Low yields of $C_{60}F_{16}$ compared to the main product, $C_{60}F_{18}$, and the considerable sublimation rate of C_{60} under the reaction conditions (470 °C), should, apparently, provide enough C_{60} in the sublimed fraction to trap virtually all $C_{60}F_{16}$. A similar reaction between $C_{60}F_{16}$ and $C_{60}F_{18}$ seems much less likely since fluorination of fullerene balls tends to increase the energy of the

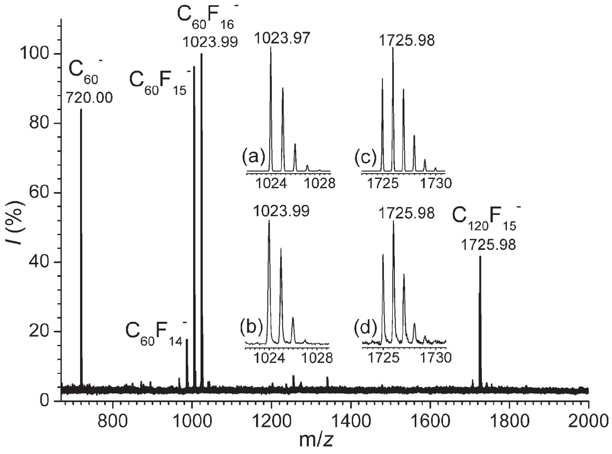

Fig. 2 MALDI mass spectrum of $(C_{60}F_{16})(C_{60})$. The theoretical (top) and experimental (below) distributions of isotopomers for $C_{60}F_{16}^-$ (a, b) and $(C_{60}F_{15})(C_{60})^-$ (c, d) are shown in insets.

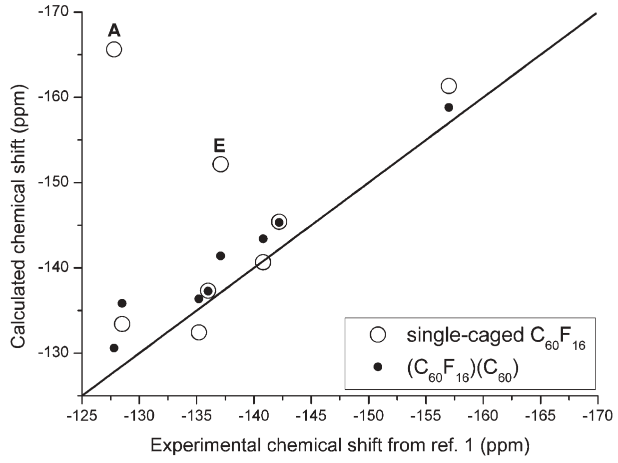

Fig. 3 Correlation between the experimental ^{19}F chemical shift values and the calculated data for single-caged $C_{60}F_{16}$ and $(C_{60}F_{16})(C_{60})$. The line of exact correspondence is given for reference.

HOMO–LUMO transition required for [2 + 2]-cycloaddition; therefore reaction between two fluorinated molecules should be more hindered than reaction involving the more easily excitable C_{60}. In this respect, it would be interesting to compare the recently characterized $(C_{60}F_{16})(C_{60})$, the only isolated product of solid phase fluorination of C_{60} to contain 16 fluorine atoms, with the products coming from thermal or chemical defluorination of $C_{60}F_{18}$. The absence of C_{60} in these processes as well as different reaction conditions might result in other molecular structures such as single-caged $C_{60}F_{16}$ and $(C_{60}F_{18})(C_{60}F_{16})$ or, possibly, $(C_{60}F_{16})_2$ dimers.

The driving force of dimerization, unprecedented in other fullerene fluoride systems, can be elucidated by quantum chemical calculations. As we mentioned above, the benzenoid cycle both in $C_{60}F_{18}$ and $(C_{60}F_{16})(C_{60})$ is almost perfectly planar, whereas in single-caged $C_{60}F_{16}$ coordination of some atoms in the cycle is slightly less so, according to DFT calculations. As was shown for $C_{60}Cl_{30}$,[15] the planarity of isolated benzenoid cycles, governed by the local surroundings of such a cycle on the fullerene cage, is an important factor in their energetic favorability. In particular, perfect planarity can be achieved when a benzenoid cycle is completely encircled by a belt of 15 sp^3 carbons bearing addends, which is not the case for $C_{60}F_{16}$, where one such carbon atom remains in the sp^2 state. Thus, addition to this carbon atom (and, additionally, to the neighboring one to form a closed shell structure) should have a favorable planarity-improving effect and should thus be more exothermic than analogous addition to bare C_{60}. Indeed, our DFT results demonstrate that the heat of fluorination of C_{60} to $C_{60}F_2$ is 56 kJ mol^{-1} lower than the corresponding heat of fluorination of $C_{60}F_{16}$ to $C_{60}F_{18}$. Similarly, the computed energy of the intercage bond in $(C_{60}F_{16})(C_{60})$ exceeds that in $(C_{60})_2$ dimer by 62–65 kJ mol^{-1} both at the DFT (33.6 kJ mol^{-1} *vs.* -28.8 kJ mol^{-1}) and HF (76.4 kJ mol^{-1} *vs.* 11.0 kJ mol^{-1}) level of theory, MP2 calculations providing an even higher gap (214.0 kJ mol^{-1} *vs.* 128.4 kJ mol^{-1}). The more reliable absolute value probably comes from Hartree-Fock calculations since they demonstrate reasonable agreement with the experimental values of dimerization energy for C_{60}, namely 10 ± 14 kJ mol^{-1} [16] and 18 kJ mol^{-1}.[17]

In conclusion, we provide a novel example of double-caged fluorofullerene, $(C_{60}F_{16})(C_{60})$, with a bridging 4-membered carbon cycle. Unlike dimeric $(C_{60})_2$, it can form even at reduced pressure and is expected to be much more stable towards dissociation. This recent discovery corrects an earlier characterization of the same compound as single-caged $C_{60}F_{16}$.

This work was supported by the Russian Foundation for Basic Research (06-03-32942a, 05-03-04006), INTAS (YS-04-83-3316), and the Russian Federal Agency of Science and Innovation (02.120.11.80.2). We thank Dr A. A. Granovsky and Dr A. A. Popov for computational support.

Notes and references

‡ *Crystal data*: Synchrotron X-ray data for the crystal of $(C_{60}F_{16})(C_{60})\cdot 2PhMe$ were collected at 100 K at the BL14.2 Beam Line at the BESSY (PSF, Free University Berlin, Germany) using a MAR345 image plate detector, $\lambda = 0.9100$ Å. Crystals are monoclinic, $P2_1/m$, $a = 11.1816(5)$ Å, $b = 21.107(1)$ Å, $c = 18.277(1)$ Å, $\beta = 106.687(3)°$, $V = 4131.9(4)$ Å^3, $Z = 2$. Reflections collected 12501, independent 4094. Anisotropic refinement with 706 parameters yielded a conventional R_1 (F) = 0.076 for 2753 reflections with $I > 2\sigma(I)$ and wR_2 (F^2) = 0.194 for all reflections. The $(C_{60}F_{16})(C_{60})$ molecule is situated on a mirror plane. The esd's are 0.006 Å for C–F and 0.008 Å for C–C bond distances. Some additional atoms with very large thermal displacement parameters were also located and probably belong to a strongly disordered molecule which, however, could not be identified reliably (only toluene was used in the separation and crystal growing procedures). CCDC 625333. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615457c

§ *Mass spectrometry*. The molecular composition for crude reaction product as well as HPLC fractions was established on the basis of the matrix-assisted laser desorption/ionization (MALDI) mass spectra (negative mode). A Bruker AutoFlex time-of-flight reflectron mass spectrometer equipped with a N_2 laser (337 nm wavelength and 1 ns pulse) was applied. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) {⩾99%, Fluka} was taken as a matrix, the matrix-to-analyte molar ratio being 1000–4000.

¶ *Quantum chemical calculations*. The geometry optimization and energy value were evaluated at the DFT level of theory with the use of the PRIRODA code,[18] which employs an efficient implementation of the resolution-of-the-identity (RI) approach. A PBE exchange-correlation GGA-type functional[19] and a built-in TZ2P basis set were used. The calculations at the HF/6-31G* and MP2/6-31G levels of theory were carried out with the use of the PC-GAMESS package.[20]

1 A. G. Avent, O. V. Boltalina, A. Y. Lukonin, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1359.
2 I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Yu. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Y. Lukonin, L. N. Sidorov and R. Taylor, *Angew. Chem., Int. Ed.*, 2000, **39**, 3273.
3 I. V. Gol'dt, O. V. Boltalina, L. N. Sidorov, E. Kemnitz and S. I. Troyanov, *Solid State Sci.*, 2002, **4**, 1395.
4 A. D. Darwish, A. K. Abdul-Sada and R. Taylor, *The Electrochemical Society Proceedings Volume PV 2004-12: Fullerenes and Nanotubes – Materials for the New Chemical Frontier*, ESC, Pennington, NJ, USA, 2004, pp. 139—144.
5 R. Taylor, *C. R. Chim.*, 2006, **9**, 982.
6 G. Burley, A. Darwish, J. Street and R. Taylor, *Tetrahedron Lett.*, 2004, **45**, 3617.
7 A. D. Darwish, A. G. Avent, O. V. Boltalina, I. Gol'dt, I. Kuvytchko, T. Da Ros, J. M. Street and R. Taylor, *Chem.–Eur. J.*, 2003, **9**, 2008.
8 A. A. Goryunkov, I. E. Kareev, I. N. Ioffe, A. A. Popov, I. V. Kuvychko, V. Yu. Markov, I. V. Goldt, A. S. Pimenova, M. G. Serov, S. M. Avdoshenko, P. A. Khavrel, L. N. Sidorov, S. F. Lebedkin, Z. Mazej, B. Zemva, S. H. Strauss and O. V. Boltalina, *J. Fluorine Chem.*, 2006, **127**, 1423.
9 G.-W. Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, 1997, **387**, 583.
10 R. Taylor, M. Barrow and T. Drewello, *Chem. Commun.*, 1998, 2497.
11 K. Komatsu, K. Fujiwara, T. Tanaka and Y. Murata, *Carbon*, 2000, **38**, 1529.
12 A. V. Streletskii, I. N. Ioffe, S. G. Kotsiris, M. P. Barrow, T. Drewello, S. H. Strauss and O. V. Boltalina, *J. Phys. Chem. A*, 2005, **109**, 714.
13 O. V. Boltalina, V. Yu. Markov, R. Taylor and M. P. Waugh, *Chem. Commun.*, 1996, 2549.
14 O. V. Boltalina, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 649.
15 P. A. Troshin, R. N. Lyubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz and S. I. Troyanov, *Angew. Chem., Int. Ed.*, 2005, **44**, 234.
16 M. V. Korobov, V. M. Senyavin, A. G. Bogachev, E. B. Stukalin, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, V. Agafonov and A. Szwarc, *Chem. Phys. Lett.*, 2003, **381**, 410.
17 A. V. Markin, B. V. Lebedev, N. N. Smirnova, V. A. Davydov and A. V. Rakhmanina, *Thermochim. Acta*, 2004, **421**, 954.
18 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
19 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
20 A. A. Granovsky, http://classic.chem.msu.su/gran/gamess/index.html; M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.