Examination of intermolecular electronic interactions in the crystal structure of $C_{60}(CF_3)_{12}$ by experimental electron density determination†

Lilianna Chęcińska,[a] Sergey I. Troyanov,[b] Stefan Mebs,[c] Christian B. Hübschle[c] and Peter Luger*[c]

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From a high resolution X-ray data set measured at 20 K the experimental electron density of the fullerene $C_{60}(CF_3)_{12}$ was derived and topologically analyzed to yield, in addition to bond topological and atomic properties, information about the density distribution in the region where hexagons of adjacent molecules approach closely at only 3.3 Å.

The synthesis and crystal structure of the title compound, $C_{60}(CF_3)_{12}$, have been reported recently.[1] It was shown that the compound possesses a unique molecular and crystal structure which is related to unusual physical properties such as low solubility and volatility.

The $C_{60}(CF_3)_{12}$ molecule exhibits the high point symmetry S_6 which is also adopted in the crystal, so that the asymmetric unit consists only of a $C_{10}(CF_3)_2$ fragment in space group $R\bar{3}$ and there are only 15 independent fullerene cage C–C bonds. There is an interesting close intermolecular approach in the crystal lattice in that the pole—non trifluoro-methylated—hexagons of adjacent molecules in the crystallographic *c*-direction are separated by a distance of only 3.311 Å (see Fig. 1), which is close to the usual interplanar distances of 3.1–3.4 Å for stacking of aromatic molecules in crystals.[3–5] It was found recently that a similar columnar arrangement of C_{60} molecules is present in an inclusion complex with two corannulene subunits.[6] However, in spite of a short intermolecular $C_{60}\cdots C_{60}$ contact of 3.1 Å, the fullerene molecule is disordered over two positions in this complex. It was considered that the particular intermolecular arrangement in $C_{60}(CF_3)_{12}$ could stabilize the structure with respect to dissolution or evaporation processes. Moreover, due to the close intermolecular approach of the hexagons, the question was open whether there were any electronic interactions in this region which we intended to examine by an experimental electron density study. This was made possible by the property of the title compound to provide well ordered and nicely diffracting crystals, which is rarely seen for fullerene derivatives.

From a high resolution X-ray data set‡ [$(\sin\theta/\lambda)_{max}$ = 1.33 Å^{-1}] of 235 064 reflections measured at 20 K, an experimental electron density distribution was obtained by application of the Hansen and Coppens multipole formalism.[7] A topological analysis using Bader's QTAIM theory[8] yielded bond topological and atomic properties quantitatively.

In contrast to the recently analyzed halogenated C_{60} fullerenes, $C_{60}F_{18}$ and $C_{60}Cl_{30}$,[9] the cage of the title compound is not strongly distorted by the twelve-fold CF_3 addition, so that the spread in fullerene C–C bond lengths (1.36–1.55 Å) is smaller than in the F and Cl derivatives. The distribution of electron density values $\rho(\mathbf{r}_{BCP})$ at the bond critical points (BCP's) *versus* C–C bond lengths shows a linear relation (see ESI†, Fig. S1) as was also reported earlier.[9]

For the evaluation of atomic volumes and charges using Bader's partition procedure, which makes use of the zero flux surfaces in the electron density gradient vector field $\nabla\rho(\mathbf{r})$, the algorithm available through the TOPXD program[10] was applied.

Averaged results are summarized in Table 1. The total atomic volumes (V_{tot}) are defined by the interatomic boundaries in the crystal. It is common practice to consider also the V_{001} volumes, defined by a cutoff at ρ = 0.001 au; these volumes are used to compare with charge densities of isolated molecules.

Since the outer regions of the atomic electron density do not contribute significantly to the charge integration, the Q_{tot} and Q_{001} values are practically equal, so that only one Q quantity is given in Table 1 (for the whole list of atomic properties, see ESI†).

In line with their chemical environments, the carbon atoms can be grouped into 3 types. Group A atoms are cage atoms with no

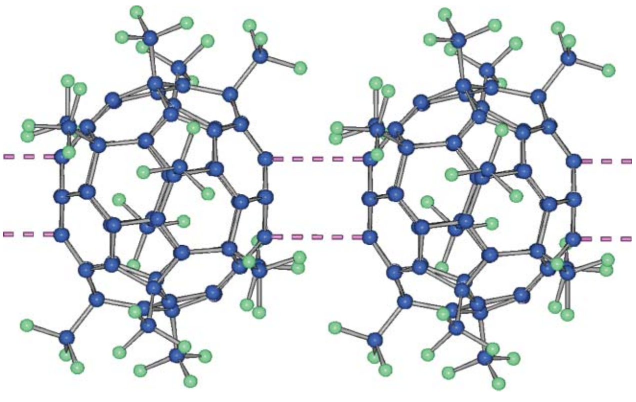

Fig. 1 Molecular structure of $C_{60}(CF_3)_{12}$ showing also the arrangement of adjacent molecules approaching at only 3.3 Å, indicated by dashed lines. SCHAKAL representation.[2]

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[a] *Department of Crystallography and Crystal Chemistry, University of Lodz, Pomorska 149/153, 90-236 Lodz, Poland.*
E-mail: lilach@uni.lodz.pl; Fax: +48 42 6790447; Tel: +48 42 6355741
[b] *Chemistry Departments, Moscow State University, Leninskie Gory, 119992, Moscow, Russia. E-mail: stroyanov@thermo.chem.msu.ru; Fax: +007 495 9391240; Tel: +007 495 9395396*
[c] *Freie Universität Berlin, Institut für Chemie und Biochemie-Kristallographie, 14195 Berlin, Fabeckstr. 36a, Germany.*
E-mail: luger@chemie.fu-berlin.de; Fax: +49 030 83853464;
Tel: +49 030 83853411

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Table 1 Averaged atomic volumes and charges (in Å^3 and e) for the different atom groups in $C_{60}(CF_3)_{12}$

Group	Type	*N*	V_{tot}	V_{001}	*Q*
A	C(cage)	8	10.39(50)	9.79(22)	0.00(3)
B	C(cage-CF_3)	2	6.41(6)	6.40(5)	0.12(7)
C	C(*exo*-F_3)	2	3.24(4)	3.24(4)	1.69(1)
D	F	6	16.4(11)	14.7(4)	−0.60(3)
Free C_{60}	C(cage)	1	11.6	11.0	0.0

addend, while group B atoms are also cage atoms, but carrying a CF_3 group. Group C atoms are the *exo*-cage carbon atoms of the CF_3 groups. Group D represents the fluorine atoms. It can easily be seen that the group A atoms have similar volumes and charges as in free C_{60} with a slight volume reduction of 1.2 Å^3. A strong volume shrinkage is already seen for the group B atoms, but a further strong volume decrease happens for the *exo*-cage carbons of the CF_3 groups, leading to an exceptionally small volume of 3.24 Å^3, accompanied by a strong positive charge of 1.69 e to compensate most of the negative charges of the three fluorine atoms.

It has already been stated earlier[11] that with increasing substitution carbon loses volume which is taken by the electronegative fluorines. While for a monofluoro substituted sp^2-carbon atom in pentafluorobenzoic acid[11] a volume of 8.5 Å^3 was reported, a volume of 4.1 Å^3 was found for a difluoro substituted sp^3-carbon in a perfluorinated cyclobutane derivative.[11] To extrapolate to a tetrafluoro carbon atom, we have derived atomic volumes/charges from a DFT calculation (B3LYP/6-311++G(3df,3pd)[12] on CF_4 and, to allow a reasonable comparison with the chemical environment of the CF_3 groups in the title compound, also CF_3–CH_3 was calculated. For the latter model compound, the atomic volume and charge for the carbon atom bonded to the fluorines (3.32 Å/1.76 e) were found to be very close to the experimental results for the title compound (3.24(4) Å/1.69(1) e). For CF_4, a further decrease in the carbon atom volume to 1.89 Å^3 was obtained. Depending on the number of fluorine substituents their strong negative charge is almost entirely compensated for by the parent carbon, so that for CF_4 the theory gives a positive charge of 2.52 e for the carbon. As shown in Table 1, the *exo*-cage carbon of the CF_3 group compensates about 94% of the overall negative charges of the three fluorine atoms.

Fig. 2 depicts a representation of the electrostatic potential of the title molecule mapped on the iso-surface of the electron density at a value of 0.002 au (0.0134 e Å^{-3}). The electronegativity difference between carbon and fluorine leads to a moderate potential gradient from the CF_3 addends to the C_{60} cage on this surface. The procedure of Politzer *et al.*[15] was used to analyze this potential surface quantitatively. Average positive/negative surface values are 0.04/–0.02 e Å^{-1}. These quantities are low compared to the highly polarized $C_{60}F_{18}$ molecule, where the corresponding positive/negative surface values were found as 0.21/–0.12 e Å^{-1}.[9,16]

Fig. 3 shows a static deformation density map in a plane perpendicular to the pole hexagons defined by two opposite C–C bonds, so that the density between the closely approaching hexagons is visible. A certain asymmetry with charge accumulation in the region towards the neighboring molecule is seen; however, this finding should be considered with care, since it was found earlier[17,18] that generally deformation density maxima are outwardly shifted from the surface of the C_{60} cage.

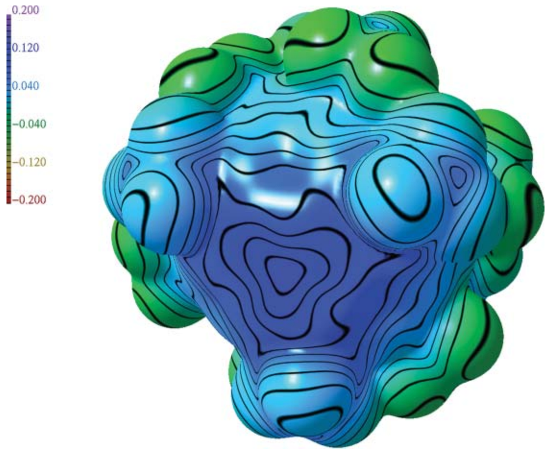

Fig. 2 Electrostatic potential of $C_{60}(CF_3)_{12}$ calculated from the experimental charge density using the method of Su and Coppens[13] and mapped onto the iso-electron-density surface ρ = 0.002 au. The colour code is shown by the colour bar; contour interval 0.01 e Å^{-1}. Drawing generated with MOLISO[14] (c) 2007 Christian B. Hübschle.

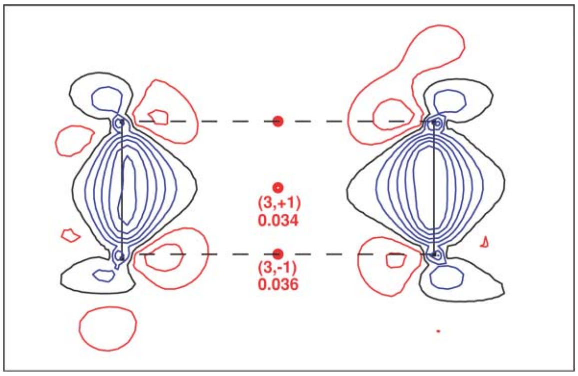

Fig. 3 Static deformation density between the closely approaching hexagons in a plane through C–C bonds of both sides. Bond (3,−1) and ring (3,+1) critical points are also shown with their corresponding electron densities in e Å^{-3}.

Topological analysis of the intermolecular region yielded bond, ring and cage critical points (see also Fig. 3) with very low electron density values of roughly 0.02–0.04 e Å^{-3} compared, for example, to the five/six-membered ring critical points of free C_{60} (0.3/0.15 e Å^{-3}).[17] We note that similar topological properties were reported earlier from theoretical DFT studies of π–π-interactions.[19]

More pronounced is the charge density concentration visible on the Hirshfeld surface[20,21] in Fig. 4. The strongest local density can be seen above the pole hexagon; the color-gradient legend shows that the crystal electron density mapped on the surface in this region is around 0.04 e Å^{-3}. This is a small value compared to other intermolecular interactions like hydrogen bonds, for which this quantity can reach values around 0.25 e Å^{-3}. However, in the case of hydrogen bonds, the density concentration is closely restricted to the region around the bonding direction, while Fig. 4 shows an extended area of significant interaction through the large torus of higher electron density on the Hirshfeld surface which is

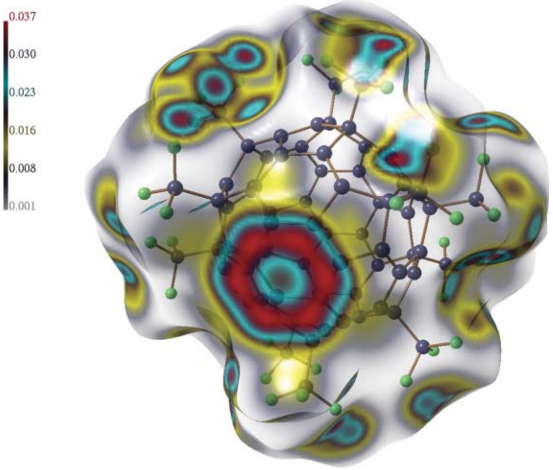

Fig. 4 Hirshfeld surface of $C_{60}(CF_3)_{12}$. The color (see color bar) gives the value of the crystal electron density on the surface. The deeply colored section represents the region above the pole hexagon. Drawing generated with MOLISO[14] (c) 2007 Christian B. Hübschle.

1.66 Å apart from the hexagon plane, so that this representation indicates some charge concentration and hence some weak intermolecular hexagon–hexagon interactions in this region.

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Notes and references

‡ Crystallographic data: $C_{60}(CF_3)_{12}$, M = 1548.72, rhombohedral, R$\bar{3}$, a = 20.720(3), c = 9.729(2) Å, V = 3617.3 Å^3, Z = 3, T = 20 K. Data collection on a large four-circle Eulerian cradle (Huber, type 512) equipped with a double-stage closed cycle He cryostat (Displex, Air Products, USA) and a Bruker-APEX area detector (MoKα radiation, graphite monochromator, λ = 0.71068 Å). Total no. of reflections 235 064, unique 14 587 (12 688 with $I > 3\sigma$), R_{int} = 0.06, multipole refinement with XD[22] up to hexadecapoles. $R(F)/R_{\text{all}}(F)/R_{\text{w}}(F)$ = 0.024/0.031/0.022, Gof = 2.05, $N_{\text{ref}}/N_{\text{v}}$ = 465, max/min res. dens. $\leqslant$ |0.30| e Å^{-3} (see also ESI†: Fig. S2). CCDC 657409. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b712694h

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