A First Experimental Electron Density Study on a C_{70} Fullerene: $(C_{70}C_2F_5)_{10}$

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The electron density of the C_{70} fullerene $C_{70}(C_2F_5)_{10}$ was determined from a high-resolution X-ray data set measured with synchrotron radiation (beamline F1 of Hasylab/DESY, Germany) at a temperature of 100 K. With 140 atoms in the asymmetric unit this fullerene belongs to the largest problems examined until now by electron density methods. Using the QTAIM formalism quantitative bond topological and atomic properties have been derived and compared with the results of theoretical calculations on the title compound and on free C_{70}.

Key words: Fullerenes, Electron Density, Topological Analysis, Synchrotron Radiation

Introduction

Although recent technical and methodical advances made experimental electron density (ED) determinations possible also on larger molecules, fullerenes with 60 or more atoms are still a major challenge. Their investigation is complicated by the generally poor crystal quality and by the high mobility of these molecules in the crystal structure. Since their discovery in the mid-eighties a considerable number of more than 800 X-ray structures of fullerenes and fullerene derivatives are listed in the Cambridge Data File [1]. Most of them (about 650) are of C_{60} fullerenes, about 100 are of C_{70} compounds, and the remaining ones are of various other types (C_{76}, C_{84}, *etc.*). Disorder is frequently found for the fullerene crystal structures. Of the C_{70} entries more than 50 % are reported to be more or less seriously disordered, among them the so far only available non-derivatized C_{70} X-ray structure [2]. Disorder is extremely unfavorable for experimental ED work. That is why only a few electron density studies have been reported on highly substituted C_{60} fullerenes [3 – 6], while no such investigations are known for any derivative of C_{70} until now.

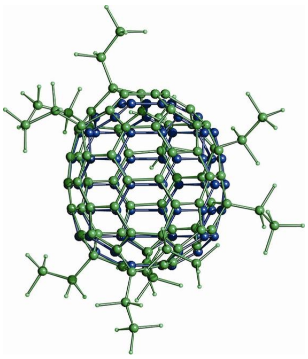

Fig. 1. (Color online). Graphical superposition of C_{70} (blue) and $C_{70}(C_2F_5)_{10}$ (green).

Here we report for the first time (to the best of our knowledge) on an experimental electron density investigation of a C_{70} fullerene derivative, $[C_{70}(C_2F_5)_{10}]$ [7]. Of the various isomers of this composition, isomer VI as specified in [8] was chosen (IUPAC notation 1,4,11,33,38,46,48,53,55,62-$C_{70}(C_2F_5)_{10}$, see also [8]). This isomer was studied based on a 100 K data set collected at the synchrotron beam line F1 of the Hasylab/ DESY (Hamburg, Germany), and on additional theoretical calculations. The electron densities were analyzed using the formalism of Bader's quantum theory of atoms in molecules (QTAIM) [9], to yield quantitatively atomic and bond topological properties. This is of special interest in the C_{70} case because even for free C_{70} the number of chemically independent atoms

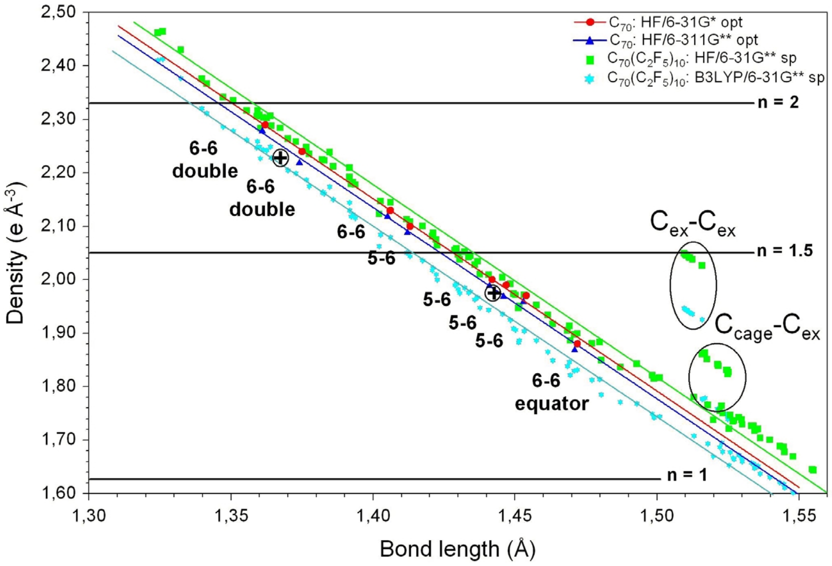

Fig. 2. Bond topological properties of C_{70} and $C_{70}(C_2F_5)_{10}$ obtained from HF and B3LYP calculations. The encircled crosses refer to the two bonds in free C_{60}. Bond orders after Bader are also plotted.

(n_a = 5) and bonds (n_b = 8) is substantially higher than for free C_{60} (n_a = 1, n_b = 2). With 140 atoms in the asymmetric unit this fullerene derivative belongs to the largest problems examined by ED methods.

Results and Discussion

In contrast to some halogenated C_{60} fullerenes, where the halogen addition changes the shape of the C_{60} cage drastically [5], the addition of ten perfluoroethyl groups has only limited influence on the C_{70} body as the graphical superposition with the free C_{70} molecule (Fig. 1) shows. Also the cage C–C bond lengths are only moderately influenced by the C_2F_5 groups. While the 8 different bonds in free C_{70} cover a bond length range from 1.36 Å for a 6-6 double bond to 1.47 Å for the equatorial 6-6 bond (obtained from Hartree Fock geometry optimization), the corresponding range for the title compound, obtained from the X-ray analysis, is somewhat larger, 1.33 – 1.56 Å. *Exo* cage C–C bonds are between 1.54 and 1.56 Å with the C–C bonds to the terminal carbons the slightly shorter ones (average C_{cage}–C_{ex} = 1.551(5) Å, average C_{ex}–C_{ex} = 1.545(5) Å). For the C–F bonds a small bond length difference is seen, whether they are in a CF_2 group (average C–F = 1.348(5) Å) or in a CF_3 group (average C–F = 1.326(4) Å).

Although the optimum conditions for an experimental ED study, *viz.* nicely diffracting crystals and absence of disorder, were not properly satisfied (see Experimental Section), a full quantitative interpretation of the experimental ED distribution with respect to bond topological and atomic properties could be made. All experimental findings were considered in relation to the corresponding results from Hartree Fock and density functional calculations [10].

Bond topological analysis

According to Bader's definition, bond critical points $\mathbf{r}_{BCP}$ (which satisfy the condition that the gradient vector field $\nabla\rho(\mathbf{r})$ vanishes at $\mathbf{r}_{BCP}$) were located for all covalent bonds. A first summary of the data obtained from theory is illustrated in Fig. 2 for the title compound and, for comparison, for free C_{70}. For both molecules the electron densities $\rho(\mathbf{r}_{BCP})$ are plotted *versus* the corresponding bond lengths. These distributions can satisfactorily be fitted by straight lines. As already mentioned, eight chemically different C–C bonds exist in the free C_{70} fullerene. The strongest one, the (6,6) double bond, and the weakest bond, a (6-6) bond in the molecular equator, are characterized by the highest and smallest $\rho(\mathbf{r}_{BCP})$ value, respectively. If the electron density at a bond critical point is known, a topological bond order n_B can calculated from an exponential relation given by Bader [9] after

$$n_B = \exp[C_1(\rho(\mathbf{r}_{BCP}) - C_2)]$$

where the parameters C_1 = 1.02289 and C_2 = 1.64585 were derived from an earlier theoretical calculation

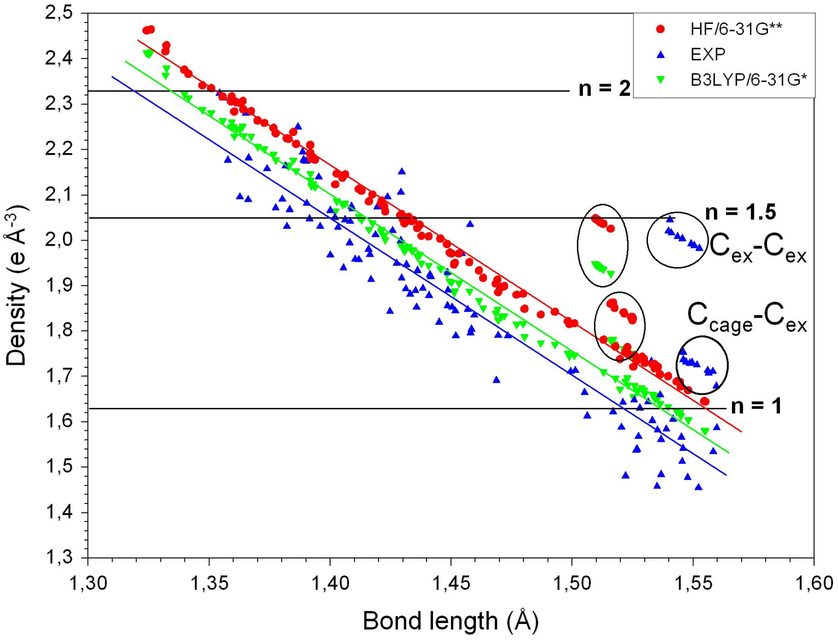

Fig. 3. Bond topological properties of $C_{70}(C_2F_5)_{10}$ from theory and experiment.

[11]. The two formal (6,6) double bonds in free C_{70} have bond orders somewhat less than $n_B = 2$. Interestingly, their strength is close to the (6-6) bond in free C_{60} (also shown in Fig. 2). The (5-6) bonds cluster around $n_B = 1.5$ while the weakest of all cage C–C bonds, the equator (6-6) bond, is of a bond order well below $n_B = 1.5$.

For $C_{70}(C_2F_5)_{10}$ a discrete C–C bond length pattern is no more discernible, the values are continuously distributed in the range between 1.33 and 1.56 Å. Two parallel least-squares lines are shown in Fig. 2 for the two theoretical calculations on the title compound. On an average the HF $\rho(\mathbf{r}_{BCP})$ values are 0.07 e Å^{-3} higher than the corresponding DFT results. This is in line with a corresponding finding for the two halogenated C_{60} fullerenes, $C_{60}Cl_{30}$ and $C_{60}F_{18}$ [5], where the difference between HF and DFT was 0.05 e Å^{-3} for the chlorinated and 0.1 e Å^{-3} for the fluorinated fullerene.

The experimental $\rho(\mathbf{r}_{BCP})$ *vs.* bond length distribution is shown in Fig. 3. The spread of contributing entries is larger than for the corresponding theoretical values, however, most of the data points are in an interval of ±0.1 e Å^{-3} with respect to the least-squares line. We have recently derived reproducibility and transferability indices for the electron density at the bond critical point from various experimental ED studies [12]. Since these quantities are 0.07 – 0.09 e Å^{-3}, the experimental spread for this C_{70} fullerene derivative illustrated in Fig. 3 is quite acceptable.

The experimental least-squares line is only 0.05 e Å^{-3} below the corresponding B3LYP line, so that the agreement between experiment and theory appears to be very good and confirms similar findings of the earlier study on the halogenated C_{60} fullerenes [5].

The *exo*-cage C–C bonds do not fit into the linear relation of the cage C–C bonds. Their lengths are all close to 1.55 Å, but the ED's at the bond critical points are increased by 0.2 e Å^{-3} for C_{cage}–C_{ex}-type bonds and more than 0.4 e Å^{-3} for C_{ex}–C_{ex} bonds. This effect is less pronounced in the theoretical calculations, but clearly visible, and was also observed in the ED of the recently examined $C_{60}(CF_3)_{12}$ fullerene [6]. It is known that the C–C bonds between fluorinated carbon atoms have increased *s* character, which increases their bonding density but should be accompanied by a bond length shortening. Due to steric reasons (close F···F contacts in the C_2F_5 group of 2.6 – 2.7 Å) the shortening of the C–C bond is not significant, so that only increased ED on the bonds is seen.

The ED values on C–F bonds are summarized in Table 1. There is a small difference whether the bond is at a CF_2 or a CF_3 group and a considerable difference between experiment and theory. Nevertheless the results of C–F bonds at the CF_3 group compare fairly well with the findings in $C_{60}(CF_3)_{12}$ reported earlier [6].

Compound	No. of F atoms at C	C–F bond length (Å)	ρ ($\mathbf{r}_{BCP}$) (e Å^{-3})	Method
$C_{60}(CF_3)_{12}$ [6]	3	1.337(5)	2.13(2)	exp
		1.337	1.90(2)	B3LYP/6-311++G(3df,3pd) sp
$C_{70}(C_2F_5)_{10}$	3	1.326(4)	2.21(1)	exp
		1.341	1.84	HF/6-31G** sp
		1.341	1.89	B3LYP/6-31G* sp
$C_{70}(C_2F_5)_{10}$	2	1.348(5)	2.14(1)	exp
		1.364	1.71	HF/6-31G** sp
		1.364	1.76	B3LYP/6-31G* sp

Table 1. Average C–F bond lengths and ED values on the bond critical points [$\rho(\mathbf{r}_{BCP})$].

Atomic properties

Following Bader's AIM theory a molecule can be partitioned into atomic fragments. According to Bader, an atom is the union of a nuclear critical point [(3; −3) critical point] and its associated basin of attracted trajectories of the electron density gradient vector field $\nabla\rho(\mathbf{r})$ with zero flux surfaces (ZFS) as boundaries. The integration procedure available through the XDPROP subprogram of XD was applied to evaluate atomic volumes and charges. The results are summarized for the atoms of the title compound and also for free C_{70} for comparison in Table 2. The total atomic volumes V_{tot} are defined by the interatomic boundaries in the crystal. It is common practise to consider also the V_{001} volume, defined by a cut-off at $\rho = 0.001$ au, as it results from theoretical calculations on isolated molecules. So this quantity is given for the HF calculation of free C_{70} in Table 2.

Although for free C_{70} five chemically distinguishable carbon atoms exist, their atomic volumes and charges (from a HF/6-311G** optimization) are very close together in a range 10.6 – 10.8 Å^3 for the volumes and practically at 0.0 e for the charges.

With respect to experimental atomic properties of the title compound, different atom types can be identified. The cage carbon atoms which do not carry a C_2F_5 group have the largest volumes of 8.5 – 12.9 Å^3 and charges close to zero or slightly positive. Cage carbon atoms bonded to a C_2F_5 group are considerably smaller with a small positive charge. The volume decreases further with increasing positive charge for *exo* cage carbon atoms *via* CF_2 carbons to CF_3 carbons, caused by the strong electronegativity of fluorine. The same effect was observed for the carbon atoms involved in CF_3 bonding in $C_{60}(CF_3)_{12}$. We have calculated also volumes and charges for tetrafluoromethane from a B3LYP/6-311++G(3df,3pd) geometry optimization, showing a carbon atom saturated with 4 fluorine atoms. For this molecule the carbon volume was even further reduced to 1.9 Å^3 with a charge of 2.52 e.

Table 2. Experimental Bader volumes and charges.

Type	V_{tot} (Å^3)	q (e)	N
C(cage)	8.5 – 12.9	0.0 – 0.3	60
C(cage-C_2F_5)	6.2(1)	0.2(1)	10
C(F_2)	4.2(1)	1.14(6)	10
C(F_3)	2.4(1)	2.17(3)	10
F(CF_2)	17.1(13)	−0.73(3)	20
F(CF_3)	18.3(15)	−0.83(1)	30
C_2F_5	96(4)	−0.62(3)	10
C(free C_{70})[a]	10.6 – 10.8	0.0–0.05	

[a] V_{001} from HF/6-311G** optimization.

The fluorine atoms have volumes of, roughly, 17 – 18 Å^3, and they all have high strong negative charges close to −0.76 e. No significant differences are seen whether they belong to a CF_2 or a CF_3 group. Fluorine is known to have very constant atomic volumes and charges independent of the hybridization status of the carbon atom it is bound to [13]. For $C_{60}F_{18}$and for compounds considered in previous studies on other fluoro-substituted hydrocarbons [14, 15] fluorine volumes and charges in the same range as found in this study have been reported.

If the entire volume of the C_{70} cage in the title compound is calculated from the sum of the contributing atomic volumes we get $V_{tot}(C_{70}) \approx 676$ Å^3 which is by 10 % smaller than the V_{001} volume of free C_{70} (≈ 750 Å^3). Hence the total volume of the C_{70} cage is reduced upon addition of the ten perfluoroethyl groups. An even stronger volume reduction (by 20 – 30 %) was found for the halogenated C_{60} fullerenes described in ref. [5].

Electrostatic potential

Fig. 4 depicts a representation of the electrostatic potential (EP) [16] of the title molecule mapped on the *iso*-surface of the ED at a value of 0.067 e Å^{-3} (0.001 au). The visualization was generated with MOLISO [17]. The electronegativity difference between carbon and fluorine leads to a strong potential gradient between the C_2F_5 regions and the cage

Table 3. Politzer analysis [18] of the EP on the ED iso-surface at 0.067 $Å^{-3}$ (0.001 au) for the title compound and for $C_{60}F_{18}$ [5].

	$C_{60}F_{18}$	$C_{70}(C_2F_5)_{10}$
$V_s{}^+$ (e $Å^{-1}$)	0.214	0.190
$V_s{}^{-+}$ (e $Å^{-1}$)	−0.115	−0.065
Π (e $Å^{-1}$)	0.164	0.140
$\sigma_+{}^2$ (e $Å^{-1})^2$	0.061	0.024
$\sigma_-{}^2$ (e $Å^{-1})^2$	0.044	0.020

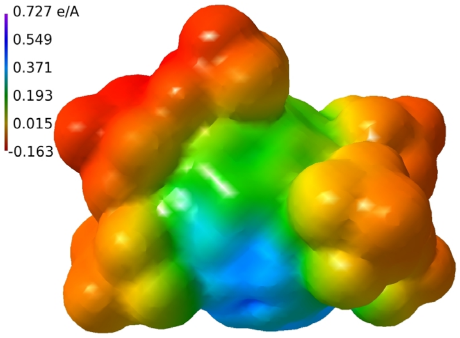

Fig. 4. Electrostatic potential of $C_{70}(C_2F_5)_{10}$ mapped on the ED iso-surface at 0.067 e $Å^{-3}$ (0.001 au), displayed with MOLISO.

Table 4. Crystal structure data for the title compound.

Formula	$C_{70}(C_2F_5)_{10}$
M_r	2030.89
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
T, K	100
a, Å	13.028(3)
b, Å	13.172(4)
c, Å	21.183(7)
α, deg	82.979(3)
β, deg	73.435(6)
γ, deg	70.517(7)
V, $Å^3$	3283.25
ρ, g cm^{-3}	2.05
μ, mm^{-1}	0.1
Crystal shape	block
Crystal dimensions, mm^3	0.2 × 0.2 × 0.1
Synchrotron radiation λ, Å	0.5600(2)
$(\sin\theta/\lambda)_{max}$, $Å^{-1}$	1.0
Collected reflections	357196
Completeness, %	90.9
Unique reflections	49991
Redundancy	7.1
R_{int}	0.0616
Observed reflections $[F_o \geq 4\,\sigma(F_o)]$	35575
R_1 $[F_o \geq 4\,\sigma(F_o)]$	0.0485
R_1 (all data)	0.0706
wR_2	0.1371
Gof	0.973
Multipole refinement:	
$R(F)$	0.0403
$R_{all}(F)$	0.0627
$R_w(F)$	0.0520
$R(F^2)$	0.0535
$R_{all}(F^2)$	0.0572
$R_w(F^2)$	0.0947
Gof	1.04
N_{ref}/N_v	23.0

surface. An extended positive potential exists in a region of the cage where no C_2F_5 addends are present. A similar polarization between fluorinated and non-fluorinated parts of the molecule was also seen in $C_{60}F_{18}$ [5]. Table 3 shows the results of a quantitative analysis of the EP on the given ED iso-surface according to Politzer *et al.* [18] for the title compound, and for comparison also for $C_{60}F_{18}$. The positive and negative average potential values $V_s{}^+$ and $V_s{}^-$, the average deviation Π from the overall average potential and the corresponding variances were calculated as given in ref. [19]. $V_s{}^+$ and $|V_s{}^-|$ are larger for $C_{60}F_{18}$ than for the title compound, indicating a stronger polarization for this C_{60} fullerene, which is also supported by the larger Π value.

Conclusion

As already mentioned, experimental ED work on fullerenes is a challenging task since in most cases crystal size and quality do not allow the collection of a sufficient number of high order reflections above the background. The problems increase with increasing molecular size and if disorder is present. Nevertheless, thanks to the use of the bright synchrotron primary radiation an X-ray data set of the fullerene $C_{70}(C_2F_5)_{10}$ could be measured that allowed to derive a reliable ED distribution. Fortunately, disorder was restricted to only one of the ten C_2F_5 groups. The QTAIM formalism [9] was applied to characterize quantitatively atomic and bond topological properties. The corresponding experimental results are in most cases in line with those derived by theoretical methods at HF and density functional level within the generally accepted uncertainties.

This study has shown that even for this molecule with 140 atoms, where optimum conditions for experimental ED work did not exist, this task can successfully be carried out, if disorder affects only minor parts of the molecule, and if a high intensity primary X-ray source can be used. This allowed to the best of our knowledge the first experimental ED determination of a C_{70} fullerene derivative. We note that in the course of this study high-resolution data sets of four further C_{70} fullerenes were collected, which were all inappropriate for an ED determination. Further ED studies on similar and higher fullerenes are desirable to get further insight into quantitative atomic and bonding properties of this exciting class of compounds.

Experimental Section

X-Ray experiments and multipole refinements

Sample preparation and crystal growth were made as described earlier [7].

A high-resolution X-ray data set was measured with synchrotron radiation (beamline F1 at Hasylab/DESY, Hamburg, Germany) at 100 K with nitrogen gas stream cooling. A MAR CCD area detector of type 165 was used at F1. The MAR control and data processing software allowed frame-to-frame increments of 2° enabling short beam time periods, so that combined with the high synchrotron primary intensity the exposure time for more than 350000 reflections was 41 h at F1. The XDS software [20] was used for the integration of the MAR detector data. For a summary of crystallographic and experimental data, see Table 4. We note that the given crystal size and quality would have resulted in only weak intensities in the high-order region of reciprocal space, so that the high primary intensity of a synchrotron source was essential to obtain a sufficiently resolved data set for ED work. Even with these conditions a resolution beyond $(\sin\theta/\lambda)$ = 1.0 $Å^{-1}$ could not be reached, and an amount of 30 % unobserved reflections had to be accepted (see Table 4).

The known atomic parameters from the conventional spherical model [7] were taken to establish the starting parameters for the subsequent aspherical atom analysis. This was based on the Hansen-Coppens multipole formalism [21] implemented in the XD program package [22]. The atomic electron density $\rho_a(\boldsymbol{r})$ in this model is

$$\begin{aligned}\rho_a(r) &= \rho_{\text{core}}(r) + P_v\kappa^3\rho_{\text{val}}(\kappa r)\\ &+ \sum_{l=0}^{l\,\max}\kappa'^3 R_l(\kappa' r)\sum_{m=-1}^{1}P_{lm}Y_{lm}(\theta,\phi),\end{aligned}\qquad(1)$$

where the first two terms represent the spherical core and valence density and the last term accounts for aspherical contributions. In all refinements the quantity $\sum_H w_H(|F_o(H)| - k|F_c(H)|)^2$ was minimized by using the statistical weights $w_H = \sigma(F_o(H))^{-2}$ and only those structure factors which met the criterion $F_o(H) \geq 4\sigma(F_o(H))$ were included.

The multipole model was expanded up to the hexadecapole level (l = 4) for all atoms except for the atoms of the disordered C_2F_5 group, for which only the monopole level was used. According to the different atom types, altogether four contraction/expansion parameters (κ) were introduced and refined, three for carbon atoms (C(cage), $C(F_2)$, $C(F_3)$) and one for F. As atomic site symmetry, a cylindrical symmetry was applied for the fluorine atoms, *mm*2 to the carbons of the CF_2 and *3* for the carbons of the CF_3 groups. No symmetry was applied for the cage carbon atoms. The chemically equivalent C_2F_5 groups and the cage carbon atoms bonded to the perfluoroethyl groups were constrained. The refinement of 35575 observed reflections ($F_o \geq 4\ \sigma(F_o)$) after convergence yielded agreement factors of $R(F)$ = 0.040 and $R_w(F)$ = 0.052, see also Table 4.

Theoretical calculations

Since no experimental ED data for free C_{70} did exist and to allow a comparison with the experimental results of $C_{70}(C_2F_5)_{10}$, ED's were also derived theoretically from *ab initio* calculations at the Hartree-Fock (HF) and density functional (B3LYP) levels of theory by using the GAUSSIAN 98 [10] program package. For free C_{70} geometry optimizations were calculated by using HF/6-31G* and HF/6-311G** standard basis sets. For $C_{70}(C_2F_5)_{10}$ single-point *ab initio* calculations were carried out with HF/6-31G** and B3LYP/6-31G*. The topology of the electron densities was analyzed with AIMPAC [23].

CCDC 740939 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.

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