Synthesis and structure of cycloperfluoroalkylated derivatives of C_{70}, $C_{70}(C_2F_4)$ and $C_{70}(C_4F_8)_n$, $n = 1–6$†

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The addition reactions of biradicals thermally generated from 1,2-$C_2F_4I_2$ or 1,4-$C_4F_8I_2$ were applied to functionalize C_{70} fullerene. The mixtures of $C_{70}(C_2F_4)_m$ and $C_{70}(C_4F_8)_n$ products were separated by HPLC resulting in several individual compounds. Molecular structures of new cycloperfluoroalkylated C_{70}, $C_{70}(C_2F_4)$, $C_{70}(C_4F_8)$ (two isomers), $C_{70}(C_4F_8)_2$, $C_{70}(C_4F_8)_4$, $C_{70}(C_4F_8)_5$ (two isomers), and $C_{70}(C_4F_8)_6$ (two isomers) were determined by single crystal X-ray diffraction and discussed in terms of their addition patterns and relative energies of their formation.

Introduction

Fullerenes are unsaturated compounds and, therefore, can undergo different types of addition reactions. Cycloadditions of types [4+2], [2+2] *etc.* are well known in fullerene chemistry,[1] whereas cycloaddition of perfluoroalkyl alkenes or biradicals is poorly explored. About 15 years ago, the synthesis of cycloperfluoroalkyl adducts of fullerenes by thermal addition of different perfluoroalkyl alkenes was patented.[2] The resulting cycloperfluoroalkyl adducts were claimed to be useful as lubricants, in fluorocarbon-based cooling systems, in adhesives for fluorocarbon-based polymers, or in gas separation membranes. However, only complex mixtures of cycloperfluoroalkylated fullerenes have been obtained, and no attempts were made for isolation of individual compounds. The first individual cycloperfluoroalkyl adducts were prepared by high temperature reaction of $C_{60/70}$ with 1,2-$C_2F_4I_2$ followed by HPLC separation of the reaction products. Molecular structures were reported for $C_{70}(C_2F_4)_2$, two isomers of $C_{60}(C_4F_8)_2$, and $C_{60}(C_4F_8)_6$.[3] The formation of C_4F_8 instead of C_2F_4 derivatives in most cases was accounted for by telomerization of 1,2-$C_2F_4I_2$ at heating.[4] Further work in the system C_{60}–1,4-$C_4F_8I_2$ resulted in the isolation and X-ray investigation of five new $C_{60}(C_4F_8)_n$ compounds with $n = 2$, 3, 4, and 6 thus allowing a comparison for a wide range of molecular structures.[5]

Here we report the results of synthesis, isolation and structural characterization of several compounds in the systems C_{70}–1,2-$C_2F_4I_2$ and C_{70}–1,4-$C_4F_8I_2$. Molecular structures of cycloperfluoroalkyl adducts $C_{70}(R^F)_n$, $R^F = C_2F_4$ or C_4F_8 with $n = 1–6$ were determined by X-ray diffraction and discussed in terms of sequential addition of R^F groups to the C_{70} fullerene cage and relative energies of different isomers.

Experimental

Synthesis and analysis

Two series of experiments have been carried out. In the first series, C_{70} (99.98%, Term-USA) reacted with excess 1,2-$C_2F_4I_2$ (Aldrich, 98%) in a sealed glass ampoule at 380–420 °C for 6–24 h.[3] After ampoule opening the excess of reagent and I_2 were removed by heating in open air for some hours. In the second series of experiments C_{70} and 1,4-$C_4F_8I_2$ (Aldrich, 98%) were placed in a glass ampoule. After cooling with liquid nitrogen, the ampoule was evacuated, sealed off, and heated at 450–500 °C for 40–45 min. Reaction product was separated from the excess of the reagent and I_2 by heating at 100 °C for several hours. In both series, the reaction products were brown powders soluble in aliphatic (hexane *etc.*) and aromatic solvents (toluene, *o*-dichlorobenzene *etc.*).

The mass spectra of matrix-assisted laser desorption/ionization (MALDI, negative ion mode) were acquired with the use of a Bruker AutoFlex II time-of-flight reflectron device (N_2 laser, 337 nm, 1 ns pulse). Its electronic control system allowed us to record a post source decay (PSD) mass spectra. 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, ≥ 99%, Fluka) was used as a matrix, the matrix-to-analyte molar ratio being 1000–4000.

HPLC separation

The reaction products were subjected to HPLC separation using a Waters 1500 chromatographic system and a Cosmosil Buckyprep column (Nakalai Tesque Inc., 10 mm i. d. × 250 mm long); elution with toluene or toluene–hexane mixtures, flow rate 4.6 mL min^{-1}, monitored at 290 nm. Due to a large number of compounds in the reaction products and unsatisfactory separation due to close retention times, multi step HPLC

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† Electronic supplementary information (ESI) available: Calculated (DFT) relative energies of $C_{70}(C_2F_4)$ and $C_{70}(C_4F_8)$ isomers. CCDC reference numbers 746547–746555. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00444k

separation was required. After the first step separation using toluene or a toluene–hexane (3/2) mixture, the second separation was carried out using an eluent with lower toluene–hexane ratio (1/1 or 2/3). Sometimes, one more separation was needed.

Though many fractions isolated by one or multi step separation have been obtained, only some gave crystalline materials after slow evaporation of the solvent or by recrystallization from another solvent (*n*-hexane, *o*-$C_6H_4Cl_2$) thus allowing their structural investigation by means of X-ray diffraction.

X-ray crystallography

Data collection for single crystal X-ray study of compounds $C_{70}(C_2F_4)$ and $C_{70}(C_4F_8)_n$ was performed with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring (λ = 0.9050 Å, BL14.2, PSF of the Free University of Berlin, Germany). Absorption correction was not applied in all cases. Structure solution and refinement were carried out with SHELXS97 (or SHELXD) and SHELXL97, respectively.[7] Crystallographic data and some details of data collection and structure refinement for nine cycloperfluoroalkylated C_{70} compounds are presented in Table 1. $C_{70}(C_4F_8)_n$ molecules are designated by 70-*n*-*N* where *n* is the number of C_4F_8 groups and *N* (Roman numbers) is a consecutive number of the isomer. Only three crystal structures, 70-1-I, 70-4-I, and 70-5-II, do not show any disorder phenomena, whereas disorder of cycloperfluoroalkyl groups or solvent molecules is characteristic for all the other structures. In the structure of $C_{70}(C_2F_4)\cdot 2C_6H_4Cl_2$ both solvent molecules are strongly disordered between several positions. C_4F_8 groups are disordered in structures 70-1-II (in both independent molecules), 70-5-I (two of five groups), 70-6-I (three groups), and 70-6-II (one group). The structure of 70-2-I possesses pseudo mirror symmetry of the fullerene molecule and contains a hexane solvate molecule with partial occupancy. Due to different crystal sizes, degrees of crystallinity, and disorder phenomena in some cases, structural determinations have been performed with different accuracy characterized by esd's of C–C bond lengths varied between 0.004 and 0.020 Å. However, the addition patterns of all compounds investigated here were determined unambiguously which allowed their comparison and discussion.

Quantum chemical calculations

Optimization of geometric parameters and energy calculations were performed at the DFT level with the use of the PRIRODA package.[8] PBE exchange–correlation functional[9] and the built-in TZ2P-quality basis set were used. The quantum chemical code employs RI expansion of the electron density for both coulomb and exchange–correlation terms. Calculation results for relative energies of $C_{70}(C_2F_4)$ and $C_{70}(C_4F_8)$ isomers are presented in the ESI.†

Results and discussion

Synthesis and separation

It is known that 1,2-$C_2F_4I_2$ undergoes telomerization above 180 °C, which results in the formation of dimeric, oligomeric, and even polymeric $I(C_2F_4)_nI$ molecules.[10] Our former high temperature syntheses in the systems $C_{60/70}$–1,2-$C_2F_4I_2$ reported in ref. 3 and 5 revealed that, especially at longer reaction times, $C_{70}(C_4F_8)_n$ prevailed over $C_{70}(C_2F_4)_m$ compounds in the reaction products. Typical examples for the systems C_{70}–1,2-$C_2F_4I_2$ and C_{70}–1,4-$C_4F_8I_2$ are presented in Fig. 1 as MALDI mass spectra of the reaction products.

According to MALDI MS analyses, the reaction products obtained by the reaction of C_{70} with $C_2F_4I_2$ typically contained compounds with $C_{70}(C_2F_4)_m$ (formal) compositions with *m* ranging from 1 to 16 (Fig. 1a). Molecular $C_{70}(C_2F_4)_m^-$ or $C_{70}(C_4F_8)_{m/2}^-$ ions with even *m* in the spectrum clearly dominate the mixture that could correspond to either $C_{70}(C_2F_4)_m$ or $C_{70}(C_4F_8)_{m/2}$ molecules. In fact, the structurally characterized compounds $C_{70}(C_4F_8)$ (two isomers) and $C_{70}(C_4F_8)_2$ were isolated from this reaction product. The

Table 1 Crystallographic data and some details of data collection and refinement for the structures of $C_{70}(C_2F_4)$ and $C_{70}(C_4F_8)_n$

Isomer[a]	$C_{70}(C_2F_4)$	70-1-I	70-1-II	70-2-I	70-4-I	70-5-I	70-5-II	70-6-I	70-6-II
Solvent molecule/s	2*o*-$C_6H_4Cl_2$	C_6H_{14}	—	0.75 C_6H_{14}	—	C_6H_{14}	—	—	—
M	1234.70	1126.91	1040.74	1305.41	1640.86	1927.07	1840.90	2040.94	2040.94
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	*Pc*	*Aba*2	*Pnma*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pbca*
a/Å	13.189(1)	21.4945(3)	17.139(1)	34.703(2)	22.599(2)	12.348(1)	23.734(2)	12.065(1)	21.400(1)
b/Å	17.205(1)	10.1855(4)	11.117(1)	28.282(2)	16.530(1)	16.089(1)	11.947(1)	16.414(1)	19.730(1)
c/Å	20.177(2)	20.2452(7)	20.154(1)	9.977(1)	11.926(1)	16.660(1)	20.846(2)	16.440(1)	30.490(1)
α (°)	90	90	90	90	90	88.074(3)	90	92.965(3)	90
β (°)	93.820(4)	107.742(3)	107.078(4)	90	90	89.552(3)	103.370(3)	95.770(3)	90
γ (°)	90	90	90	90	90	79.563(3)	90	101.288(3)	90
Volume/$Å^3$	4568.3(6)	4221.5(2)	3670.7(4)	9792(1)	4455.1(6)	3253.2(4)	5750.7(9)	3168.0(4)	12874(1)
Z	4	4	4	8	4	2	4	2	8
D_c/g cm^{-3}; μ/mm^{-1}	1.795; 0.341	1.773; 0.127	1.883; 0.138	1.771; 0.145	2.446; 0.237	1.967; 0.195	2.126; 0.215	2.140;0.224	2.106; 0.221
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Refls collected/R_{int}	62591/0.064	36731/0.052	34665/0.094	57432/0.148	58578/0.157	44640/0.033	77080/0.050	41930/0.048	141713/0.187
Data/parameters	9751/962	7441/795	12846/1496	10078/883	6226/538	11850/1362	10783/1180	12407/1380	14027/1306
R_1 [$I \geq 2\sigma(I)$]/wR_2 all)	0.108/0.262	0.087/0.232	0.134/0.322	0.104/0.288	0.067/0.179	0.078/0.192	0.144/0.391	0.070/0.186	0.079/0.198
$\Delta\rho$ (max/min)/eÅ^{-3}	0.74/−0.54	0.60/−0.39	0.68/−0.54	0.41/−0.40	0.75/−0.52	0.72/−0.67	0.76/−0.58	0.71/−0.63	0.75/−0.58

[a] $C_{70}(C_4F_8)_n$ isomers are denoted as 70-*n*-*N* where *n* is the number of C_4F_8 groups and *N* (Roman number)—a successive number of the isomer.

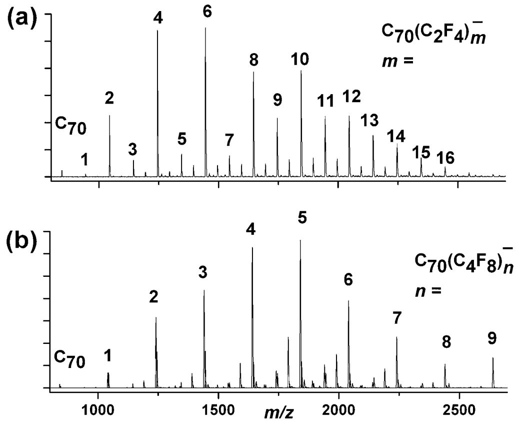

Fig. 1 MALDI mass spectra of the reaction products in the systems C_{70}–1,2-$C_2F_4I_2$ (a) and C_{70}–1,4-$C_4F_8I_2$ (b).

presence of compounds with odd *m*, though in small amounts, was proved by the PSD spectra. They pointed out that odd-numbered $C_{70}(C_2F_4)_m^-$ ions originate predominantly from the corresponding molecules rather than from $C_{70}(C_2F_4)_{m+1}$ compounds. At shorter reaction times, telomerization of $C_2F_4I_2$ takes place to a lesser extent, more C_{70} remains unreacted and the differences in abundance of compounds with even and odd *m* become less pronounced (for details see Fig. 1b in ref. 3). From the product obtained by the 6 h reaction of C_{70} with $C_2F_4I_2$, $C_{70}(C_2F_4)$ was successfully isolated and structurally characterized in this work (Table 1).

To simplify the system, we used 1,4-$C_4F_8I_2$ in the subsequent work. Due to the fact that 1,4-$C_4F_8I_2$ is less susceptible to telomerization at higher temperatures, the compositions of possible products are more restricted to $C_{70}(C_4F_8)_n$. Higher thermal stability of 1,4-$C_4F_8I_2$ allowed us to decrease the reaction time by increasing the temperature to 500 °C. In fact, the spectrum in Fig. 1b demonstrates the presence of $C_{70}(C_4F_8)_n$ compounds with *n* ranging from 1 to 9. However, this spectrum also showed two series of minor peaks being 99.99 (C_2F_4) and 149.99 Da (C_3F_6) distant from major ones. PSD spectra unambiguously indicated their molecular origination.

It should be noted that, due to the suppression effect,[6] negative ion MALDI mass spectra may show underestimated contents of unreacted fullerenes (C_{60} or C_{70}) up to their complete absence, especially in samples of fullerene derivatives with electron-withdrawing addends such as C_2F_4 and C_4F_8 groups. In most experiments, small amounts of white films, most probably, of polymeric nature, were observed on the ampoule's walls. However, this did not influence the subsequent HPLC separation process because of insolubility of the films. Several $C_{70}(C_4F_8)_n$ isomers with higher numbers of attached C_4F_8 groups (n = 4–6) have finally been isolated from this system and characterized by X-ray crystallography.

As has been established by MALDI MS analyses, the reaction products in both systems contained wide ranges of compositions. In fact, chromatographic investigation showed that all compositions are represented by several constitutional isomers. Therefore, the isolation of individual, isomerically pure compounds turned out to be a challenging task. One step chromatographic separation in toluene was only possible for the two mono adducts, $C_{70}(C_2F_4)$ and $C_{70}(C_4F_8)$-I, due to their lower solubility and larger retention times. In all other cases, two or more separation steps in eluents with successively decreasing toluene–hexane ratios were required. All these cases are presented in Table 2 showing initial, intermediate, and final steps of isolation of nine compounds structurally studied in this work.

Table 2 HPLC isolated compounds, which gave crystalline materials, and their retention times (min)

		Eluent; toluene–hexane volume ratio[a]			
Reagent	Compound	1/0	1/1	2/3	1/2
$C_2F_4I_2$	$C_{70}(C_2F_4)$-I	**13.25**			
$C_2F_4I_2$	$C_{70}(C_4F_8)$-I	**11.30**			
$C_2F_4I_2$	$C_{70}(C_4F_8)$-II	10.71	**46.7**		
$C_2F_4I_2$	$C_{70}(C_4F_8)_2$-I	7.42	—	42.16	**55.01**
$C_4F_8I_2$	$C_{70}(C_4F_8)_4$-I	—	—	**23.83**	
$C_4F_8I_2$	$C_{70}(C_4F_8)_5$-I	4.25	6.04	**7.78**	
$C_4F_8I_2$	$C_{70}(C_4F_8)_5$-II	4.26	6.04	**7.48**	
$C_4F_8I_2$	$C_{70}(C_4F_8)_6$-I	3.42	**3.56**		
$C_4F_8I_2$	$C_{70}(C_4F_8)_6$-II	3.97	**5.37**		

[a] Retention times in final separations of fractions containing individual isomers are given in bold.

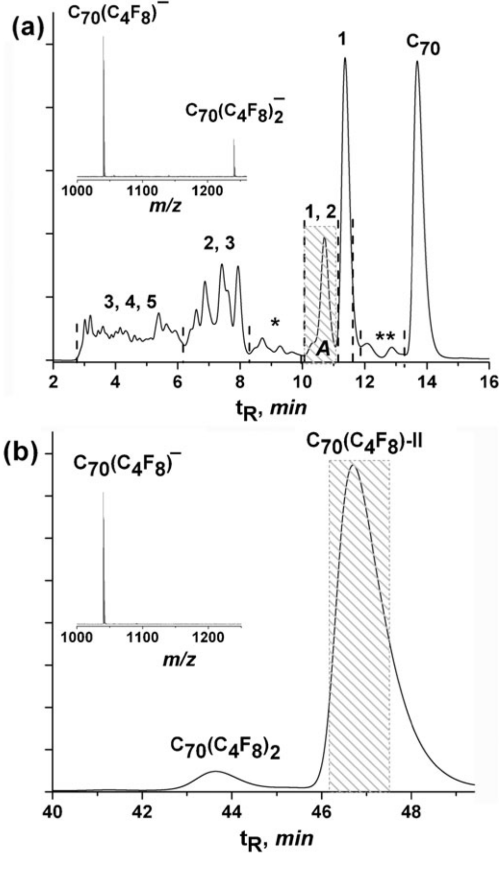

Fig. 2 Two step separation of $C_{70}(C_4F_8)$-II. HPLC trace of the reaction product from the system C_{70}–$C_2F_4I_2$ recorded in toluene with fraction *A* collected for the second step; fractions indicated by * and ** contained isomers with n = 1.5, 3 and n = 1, 2, respectively (a). HLPC trace of fraction *A* in a toluene–hexane mixture (1/1). Insets show the MALDI spectra of the fraction in shaded regions (b).

An example of two step isolation of $C_{70}(C_4F_8)$-II is given in Fig. 2. Fraction *A* chromatographically isolated from the crude reaction product in the system C_{70}–1,2-$C_2F_4I_2$ by elution in pure toluene was subjected to further separation using a toluene–hexane mixture (1/1) thus resulting in the isolation of the individual compound. The isolation of $C_{70}(C_4F_8)_2$ was achieved by a three step HPLC separation. Isomerically pure $C_{70}(C_4F_8)_4$ was obtained by using a toluene–hexane (2/3) mixture as the eluent.

Fig. 3 illustrates the isolation of one isomer of $C_{70}(C_4F_8)_6$-II and two isomers of $C_{70}(C_4F_8)_5$, respectively, by two and three step HPLC procedures. Toluene fraction *B* that contained $C_{70}(C_4F_8)_n$ with $n = 5$ and 6 showed no evidence of separation of $C_{70}(C_4F_8)_5$ (fraction *C*) by elution in a toluene–hexane (1/1) mixture. Fraction *C* could, however, be separated into two components by elution in the toluene–hexane (2/3) mixture thus allowing the isolation of two isomers of $C_{70}(C_4F_8)_5$. An independent two step HPLC separation with the use of a toluene–hexane (1/1) mixture resulted in a successful isolation of isomer $C_{70}(C_4F_8)_6$-I.

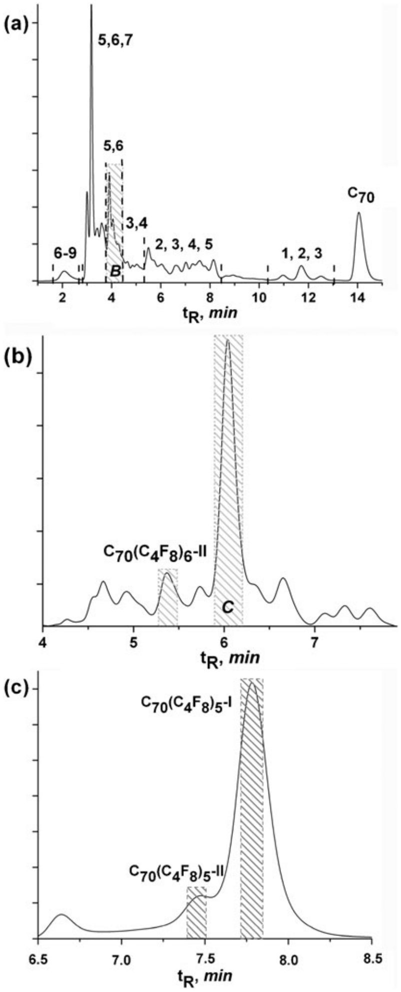

Fig. 3 HPLC isolation of $C_{70}(C_4F_8)_6$-II and two isomers of $C_{70}(C_4F_8)_5$. HPLC trace of the reaction product from the system C_{70}–$C_4F_8I_2$ recorded in toluene with fraction *B* collected for the second step (a). HPLC separation of fraction *B* in a toluene–hexane mixture (1/1) resulted in the isolation of 70-6-II and fraction *C* (b). Chromatogram of fraction *C* recorded in a toluene–hexane mixture (2/3) showing the isolation of 70-5-I and –II (c).

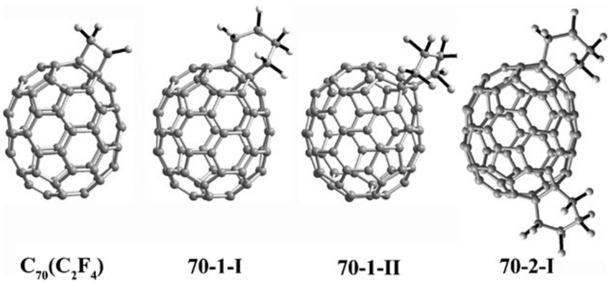

Fig. 4 Perspective views of $C_{70}(C_2F_4)$, $C_{70}(C_4F_8)$-I (70-1-I), $C_{70}(C_4F_8)$-II (70-1-II), and $C_{70}(C_4F_8)_2$-I (70-2-I).

Nine new cycloperfluoroalkyl derivatives of C_{70} together with $C_{70}(C_2F_4)_2$ studied in a previous work[3] provide a good initial basis for discussion of reaction pathways and comparison of molecular structures. However, the reaction systems are in fact much more complex due to the presence of a large number of individual compounds. For example, according to the combined HPLC (using eluents with different toluene–hexane ratios) and MALDI MS analyses, the reaction products, $C_{70}(C_4F_8)_n$, in the C_{70}–1,4-$C_4F_8I_2$ system contain several (*k*) isomers for each *n* as given below in the form *n* (*k*): 1 (3), 2 (6), 3 (11), 4 (13), 5 (10), 6 (4), and 7 (2). Although compounds with $n = 8$ and 9 were present in the reaction product according to the MALDI mass spectra (Fig. 1b), they could not be detected in the separated fractions, probably because of their loss due to the lack of retention.

Molecular structures

Perspective views of all molecules investigated by X-ray crystallography are presented in Fig. 4 and 6. For molecules with disorder of R^F cyclo fragments, only the main components of disordered groups are shown. Comparison and discussion of molecular structures are clearer using Schlegel diagrams provided with the marked positions of attachments and connecting polygonal lines for cyclopefluoroalkyl groups (Fig. 5 and 7). Lowest locant IUPAC abbreviations[11] for all molecules are given in the footnote‡.

Structures of $C_{70}(R^F)$ and $C_{70}(R^F)_2$. Molecular structures of 8,25-$C_{70}(C_2F_4)$ and 70-1-I (Fig. 4) have the same addition pattern with C_s symmetry shown in Fig. 5. The positions near to the pole are believed to be more reactive due to higher

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‡ Lowest locant IUPAC abbreviations[10] are given with positions of cycles connected by brackets.

8,25-$C_{70}(C_2F_4)$; 70-1-I: 8,25-$C_{70}(C_4F_8)$; 70-1-II: 7,22-$C_{70}(C_4F_8)$

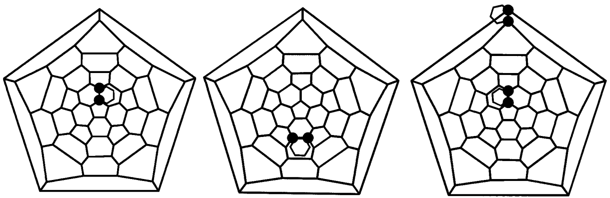
70-2-I: 8,16,25,35-$C_{70}(C_4F_8)_2$; 70-4-I: 1,4,11,19,31,41,51,64-$C_{70}(C_4F_8)_4$

70-5-I: 1,4,11,19,29,41,49,60,66,69-$C_{70}(C_4F_8)_5$

70-5-II: 1,4,11,19,23,24,31,39,67,68-$C_{70}(C_4F_8)_5$

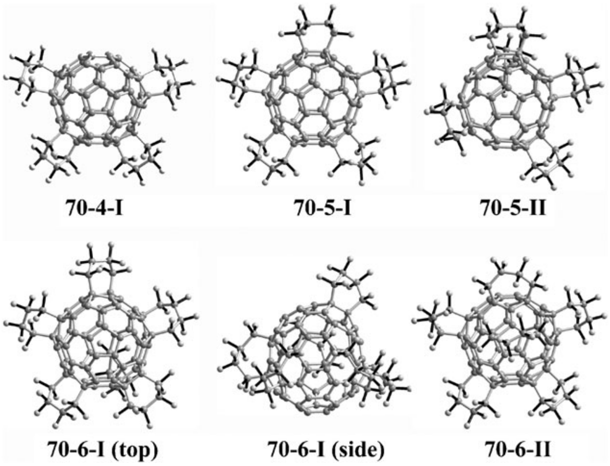
70-6-I: 1,4,11,19,23,24,31,39,51,58,61,64-$C_{70}(C_4F_8)_6$

70-6-II: 1,4,10,19,25,28,41,46,49,60,66,69-$C_{70}(C_4F_8)_6$



70-1-I (0) 70-1-II (13.7) 70-2-I

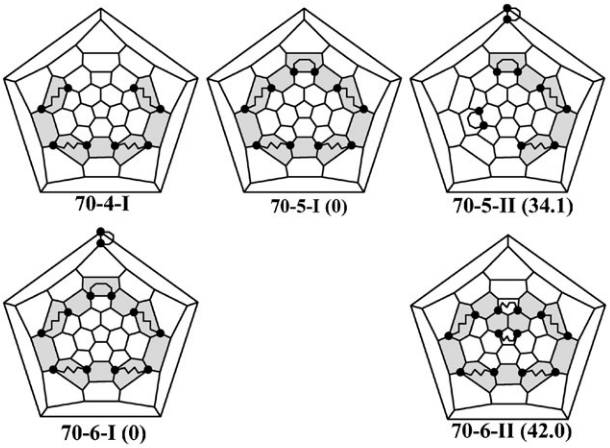
Fig. 5 Schlegel diagrams of $C_{70}(C_4F_8)$-I (70-1-I), $C_{70}(C_4F_8)$-II (70-1-II), and $C_{70}(C_4F_8)_2$-I (70-2-I). Relative energies (kJ mol^{-1}) for a pair of isomers are given in the parentheses.



70-4-I 70-5-I 70-5-II

70-6-I (top) 70-6-I (side) 70-6-II

Fig. 6 Perspective views of $C_{70}(C_4F_8)_4$ (70-4-I), $C_{70}(C_4F_8)_5$-I (70-5-I), $C_{70}(C_4F_8)_5$-II (70-5-II), $C_{70}(C_4F_8)_6$-I (70-6-I, two projections), and $C_{70}(C_4F_8)_6$-II (70-6-II).



70-4-I 70-5-I (0) 70-5-II (34.1)

70-6-I (0) 70-6-II (42.0)

Fig. 7 Schlegel diagrams of $C_{70}(C_4F_8)_4$-I (70-4-I), $C_{70}(C_4F_8)_5$-I and -II (70-5-I and 70-5-II), and $C_{70}(C_4F_8)_6$-I and -II (70-6-I and 70-6-II). Relative energies (kJ mol^{-1}) for pairs of isomers are given in the parentheses.

curvature as compared with three other positions near or on the equator of the C_{70} cage. For comparison, dimerization of C_{70} to C_{140} with the formation of a cyclobutane ring occur at these sites.[12] The structure of 70-1-II (Fig. 4 and 5) also possesses C_s symmetry of the addition pattern (not of the whole molecule), but the C_4F_8 group is attached in positions 7 and 22, *i.e.* to the 6 : 6 C–C bond more distant from the cage pole. Six-membered rings in both molecules have boat conformations in accordance with the DFT optimized structures (see ESI†). Calculations of relative energies showed isomer 70-1-II to be 13.7 kJ mol^{-1} less stable than isomer 70-1-I. Approximately the same energy gap, 14.3 kJ mol^{-1}, was calculated to exist between 8,25-$C_{70}(C_2F_4)$ and 7,22-$C_{70}(C_2F_4)$ in favour of the former.

It is known that the addition to one fullerene site results in an activation of the second sites in *ortho* and *para* positions in hexagons. Whereas addition of a C_2F_4 group in the *ortho* position should be accompanied by a steric strain in the four-membered cyclobutane ring, the same addition mode of a much longer C_4F_8 group results in a less strained six-membered cycle with a chair conformation. In contrast, *para* addition of a C_2F_4 group should be accompanied by a large strain due its closeness to the cage, whereas such addition of a C_4F_8 group is stereochemically more favourable. Thus, a *para* attachment of a C_2F_4 group is less favourable than any of the *ortho* attachments by 73–168 kJ mol^{-1}, whereas the difference between the best *para* and *ortho* additions of a C_4F_8 group is just 25 kJ mol^{-1} (see ESI†). Chromatographic analysis of the reaction product in system C_{70}–1,4-C_4F_8 revealed the presence of one more isomer of $C_{70}(C_4F_8)$ (Fig. 2a). Although its structure is unknown, addition in *para* positions in the hexagon could be suggested because such *para* additions of C_4F_8 groups were found in some other $C_{70}(C_4F_8)_n$ derivatives (see below). Our DFT calculations revealed that 1,4-$C_{70}(C_4F_8)$ characterized by *para* addition in the equatorial region ranks third in stability after 8,25 and 7,22 isomers (24.9 kJ mol^{-1}, Table S2, ESI). For comparison, the preferable addition mode of two separate addends to fullerene cages strongly depends on their size. Thus, the experimental data and theoretical calculations revealed preferable formation of *ortho* 1,2-$C_{60}F_2$[13] and *para* 1,4-$C_{60}(CF_3)_2$.[14] The formation of the theoretically most stable *para* 7,24-$C_{70}(CF_3)_2$ has been proposed on the basis of ^{19}F NMR spectra.[15] Recently its molecular structure has been confirmed by single crystal X-ray crystallography.[16]

It is not surprising that diadduct 70-2-I with approximate overall C_{2v} symmetry exhibits two cycloadditions in *ortho* positions to 6 : 6 bonds near the cage poles (Fig. 4 and 6). The same addition pattern was found in the $C_{70}(C_2F_4)_2$ molecule reported earlier.[3] Some other diadducts found in the reaction product might comprise combinations of different 1,2 and 1,4 additions. By comparison, all low energy addition patterns of $C_{70}(CF_3)_4$ isomers exhibit a combination of only *para* or *para* and *meta* positions in $C_6(CF_3)_2$ hexagons.[15]

Structures of $C_{70}(C_4F_8)_{4–6}$. Though many $C_{70}(C_4F_8)_3$ compounds were detected by MALDI MS in the reaction product, their molecular structures could not be determined.§ The molecular structure of 70-4-I possesses crystallographically imposed C_s symmetry and contains all four C_4F_8 groups

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§ However, during the final stages of preparation of this manuscript, the crystal structure of $C_{70}(C_4F_8)_3$ was determined. It contains three *ortho*-additions in positions 7,22, 33,34 and 46,47, *i.e.* a combination of additions in 70-1-I and 70-1-II.

attached in the *para* positions in hexagons situated in the equatorial region (Fig. 6 and 7) so that the attachment sites correspond to those in C_s-$C_{70}(CF_3)_8$[17] or C_s-$C_{70}(CH_3)_8$.[18]

The C_s molecular structure of 7-5-I (Fig. 6 and 7) can be derived from 7-4-I by addition of one C_4F_8 group attached in the *ortho* position in the hexagon (to a 5 : 6 C–C bond) thus closing the equatorial belt. In this way, the system of conjugated C–C bonds of C_{70} is divided into two parts. Theoretically, this addition pattern was found to be most stable for $C_{70}X_{10}$ structures with X = H, F, or Br.[19] Experimental findings confirm this addition pattern for X = H,[20] Cl,[21] Br,[22] and mixed Cl/Br addends.[23] However, the most stable isomer of $C_{70}(CF_3)_{10}$ differs by the position of two CF_3 groups thus avoiding the *ortho* contact.[24] The addition pattern of 70-5-II (Fig. 5 and 7) is characterized by a combination of three C_4F_8 groups in the equatorial region (one *ortho* and two *para* additions) and two C_4F_8 groups attached in *ortho* positions near to the opposite poles of the C_{70} cage as in the molecules of 70-1-I and 70-1-II, respectively. DFT calculations of relative energies of 70-5-I and 70-5-II gave a large difference of 34.1 kJ mol^{-1} in favour of the former isomer.

The C_s symmetrical addition pattern of 70-6-I contains those of 70-5-I and 70-1-I, *i.e.* a combination of the equatorial belt of five C_4F_8 groups and one C_4F_8 group on the pole (Fig. 5 and 7). The molecular structure of 70-6-II, also possessing (non-crystallographic) C_s symmetry, differs from 70-6-I in the positions of four addition sites (two C_4F_8 groups attached in 1,3 positions in pentagons) which isolate a double C–C bond on the C_{70} cage (Fig. 7). The molecule with the same addition pattern of twelve CF_3 groups on the C_{70} cage ranks 11th in energy (+19.9 kJ mol^{-1}) relative to the most stable isomer of $C_{70}(CF_3)_{12}$.[25] According to theoretical DFT calculations, isomer 70-6-I is 42.0 kJ mol^{-1} more stable than 70-6-II.

Each addition to fullerene changes the hybridization of the atoms involved in cage C–C bonds. In the cycloperfluoroalkylated $C_{70}(R^F)_n$ the largest bond length changes occur due to *ortho* additions to 6 : 6 or 5 : 6 C–C bonds. Whereas the corresponding 6 : 6 and 5 : 6 bonds in the C_{70} molecule both have average values within 1.37–1.39 Å,[26] they are strongly elongated after cycloaddition to averaged values of 1.58–1.62 Å for 6 : 6 C–C bonds in mono-, di-, penta- (70-5-I), and hexaadducts (70-6-I) and to 1.64–1.65 Å for 5 : 6 C–C bonds in structures 70-5-I, 70-5-II, and 70-6-I. In contrast, some 6 : 6 C–C bonds in the structure 70-6-II are shortened due to their full or nearly full isolation from the conjugated system by sp^3 carbon atoms (attachment positions). Such bonds have bond lengths 1.33–1.34 Å, typical for C–C double bonds in alkenes.

A comparison of cycloperfluoroalkylated $C_{70}(R^F)_n$ structures with n = 1–6 reveals interesting variations in addition modes dependent on the number of attached cyclo R^F groups. One or two groups are always attached in *ortho* positions to 6 : 6 C–C bonds in polar regions. When four or more groups are added, preferable attachments occur in *para* positions in the equatorial region, probably due to the favourable conjugation in the remaining π-system(s).[20] The fifth and sixth cyclo R^F group can be attached again in the *ortho* position near to the pole.

Conclusions

The synthesis of cycloperfluoroalkylated C_{70} in the systems C_{70}–1,2-$C_2F_4I_2$ and C_{70}–1,4-$C_4F_8I_2$ followed by HPLC separation of reaction products and X-ray crystallographic investigation resulted in the determination of molecular structures of nine individual $C_{70}(R^F)_n$ compounds with n = 1–6. Comparison of the addition patterns revealed the exclusive *ortho* addition mode for n = 1 and 2, whereas the *para* addition mode was predominantly found for n = 4–6 together with several *ortho* additions for n = 5 and 6. In contrast, molecular structures of cycloperfluoroalkylated $C_{60}(R^F)_n$ obtained in the system C_{60}–1,4-$C_4F_8I_2$[5] show cycloadditions preferably in *ortho* and *meta* positions on the C_{60} fullerene cage. Thus an attachment in the *ortho* position is typical for cycloadditions, whereas *para* positions are characteristic for additions of separate perfluoroalkyl groups.

Although only a small part of all $C_{70}(C_4F_8)_n$ compounds present in the C_{70}–1,4-$C_4F_8I_2$ system has been structurally investigated, some relationships between isomers with different n can be proposed based on similarities in their addition patterns. Therefore, isomers 70-1-I, 70-4-I, and 70-5-I might be the precursors for 70-2-I, 70-5-I, and 70-6-I, respectively, in the course of cycloperfluoroalkylation. A comparison of relative stabilities of the isolated and structurally characterized $C_{70}(C_2F_4)_n$ and $C_{70}(C_4F_8)_n$ compounds (n = 1, 2) suggests their formation to be preferably controlled by thermodynamic rather than by kinetic factors. However, this is obviously not the case for higher derivatives, because large energy differences were found for pairs of the experimentally characterized $C_{70}(C_4F_8)_5$ and $C_{70}(C_4F_8)_6$ isomers. Further study of cycloperfluoroalkylated fullerenes should provide more information in this respect and about some specific properties of these compounds as well.

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