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Azafullerenes

Nitrogen Directs Multiple Radical Additions to the 9,9′-Bi-1-aza(C_{60}-I_h)[5,6]fullerene: X-ray Structure of 6,9,12,15,18-$C_{59}N(CF_3)_5$**

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Azafullerenes, in which a cage carbon atom is replaced by a nitrogen atom, are the only type of heterofullerenes that can be made in practical amounts,[1,2] and this makes it possible to probe the effects of cage-atom substitution on the physical and chemical properties.[3,4] Herein, we report a unique type of isomerism in azafullerenes bearing trifluoromethyl groups, which is attributed to the directing role of the nitrogen atom, and the first X-ray structure of the $C_{59}N$ derivative prepared directly from $(C_{59}N)_2$.

Figure 1 shows the negative-ion atmospheric-pressure chemical ionization (NI APCI) mass spectra of the products of the high-temperature trifluoromethylation of $(C_{59}N)_2$ with CF_3I obtained either in a sealed ampoule (top) or in a flow tube (bottom). The thermolysis of $(C_{59}N)_2$ yields a radical monomer $C_{59}N^{\bullet}$ which readily adds up to 15 (bottom spectrum) or even 19 CF_3 groups per cage (top spectrum) to form closed-shell species $C_{59}N(CF_3)_n$, where n is an odd number. In these reactions, a nonsoluble dark-brown solid dimer $(C_{59}N)_2$ is quantitatively converted into a volatile, thermally stable orange crystalline material, which is highly soluble in many organic and fluoroorganic solvents. When trifluoromethyl groups were added to C_{60} under similar conditions, the closed-shell species with even n values up to 22 were formed (see the Supporting Information). The product in the flow tube was separated by chromatography into four main fractions: I) $C_{59}N(CF_3)_{11\text{-}15}$, II) $C_{59}N(CF_3)_9$, III) $C_{59}N(CF_3)_7$, and IV) $C_{59}N(CF_3)_5$ (inset in Figure 1). This one-step HPLC process yielded a 98 % compositionally pure sample of $C_{59}N(CF_3)_5$ as proven by NI APCI mass spectrometry, which detects also a single isomer with C_s symmetry (see the ^{19}F NMR spectrum in Figure 2, top). The absence of terminal CF_3 groups (seen as quartets in the ^{19}F NMR spectra) implies that five CF_3 groups should be arranged in a *para*^{5} (or p^5) loop rather than as a ribbon of edge-sharing p-$C_6(CF_3)_2$ hexagons as most commonly observed in the $C_{60}(CF_3)_n$ compounds.[5] The absorption spectrum (see the Supporting Information) is similar to that of C_s-$C_{60}(CF_3)_6$.[6] The most probable addition pattern that agrees with the spectroscopic data and was previously observed for azafullerenes features an isolated pyrrole moiety on the fullerene core (Figure 1).[7]

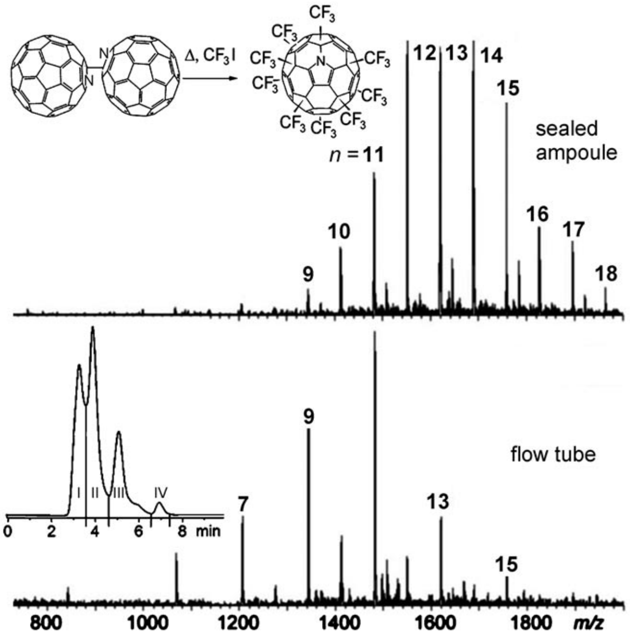

Figure 1. Negative-ion APCI mass spectra of the $C_{59}N(CF_3)_n$ products obtained in a sealed glass ampoule at 530 °C for 24 h (top) and a hot flow tube at 500 °C for 3 h (bottom). The HPLC trace (inset) of the crude product (100 % toluene eluent).

Interestingly, $C_{60}X_6$ compounds with a similar addition pattern of skew-pentagonal pyramid (SPP) are formed abundantly, if not regioselectively, in various room-temperature reactions (see references in the Supporting Information). However, SPP-C_s-$C_{60}(CF_3)_6$ was found only as a minor isomer in the high-temperature synthesis, whereas C_1-$C_{60}(CF_3)_6$ with a ribbon addition pattern (*para*^{3}-*meta*-*para*; p^3mp) was at least ten times more abundant.[5,6] The C_s isomer is also 14.4 kJ mol^{-1} less stable than p^3mp-C_1-$C_{60}(CF_3)_6$ at the DFT

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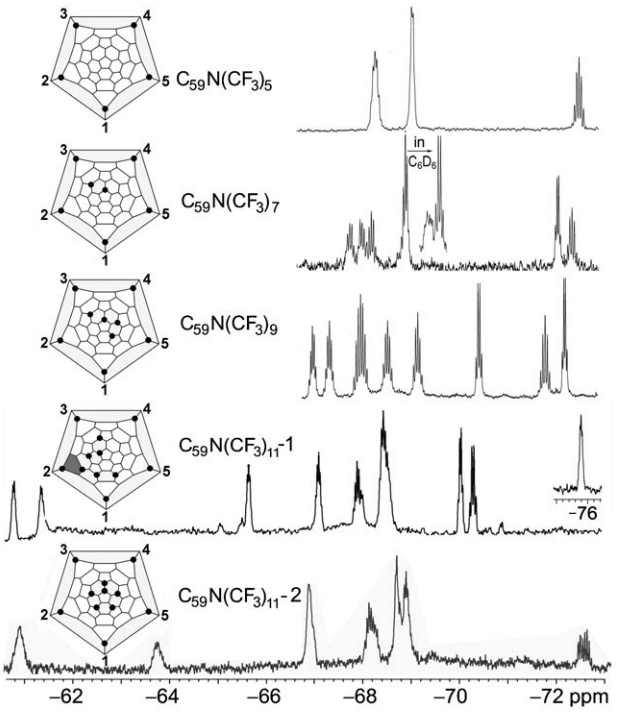

Figure 2. Fluorine-19 NMR spectra (367.48 MHz, $CDCl_3$) and the Schlegel diagrams of the most probable addition patterns (from top to bottom) of C_s-$C_{59}N(CF_3)_5$, $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$, and two isomers of $C_{59}N(CF_3)_{11}$ (C_6F_6 internal standard, $\delta = -164.9$). The numbered positions on the outer pentagon of the Schlegel diagrams designate the N atoms in the five possible isomers in each Schlegel diagram. The inset in the NMR spectrum of $C_{59}N(CF_3)_7$ shows the resolution of overlapped multiplets in C_6D_6.

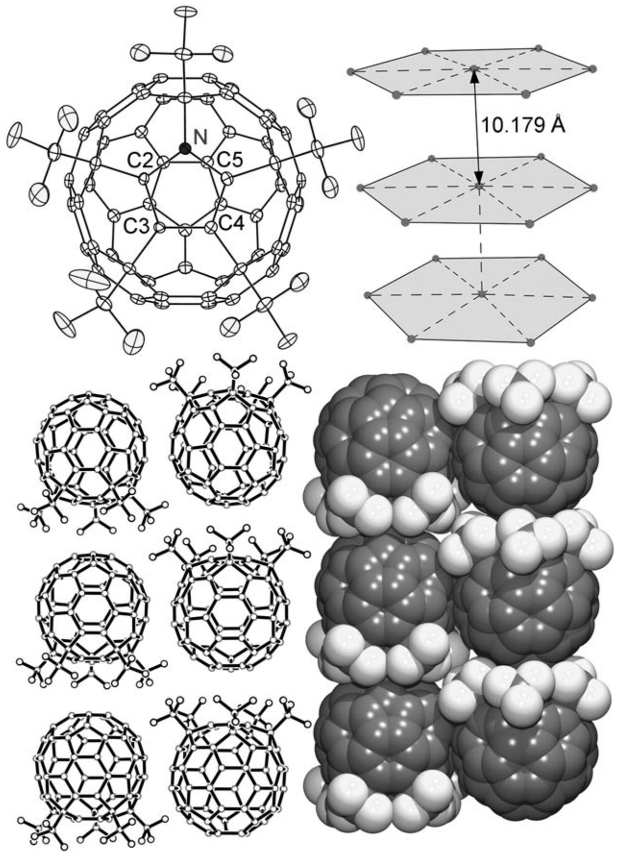

Figure 3. X-ray structure of $C_{59}N(CF_3)_5$ (50% probability ellipsoids). The $C_{59}N(CF_3)_5$ molecules form columns with head-to-tail orientation. The layers of the $C_{59}N(CF_3)_5$ molecules are stacked in an AAA sequence and form primitive hexagonal arrays with an interlayer distance of 10.179 Å. The dots are centroids of the azafullerene molecules.

level of theory. The opposing effects of the steric strain, caused by the unfavorable adjacent positions of two bulky CF_3 groups, and formation of the stabilizing fully isolated *cis*-butadiene moiety may explain both the presence of SPP-C_s-$C_{60}(CF_3)_6$ and its lower abundance relative to p^3mp-C_1-$C_{60}(CF_3)_6$.[6] It is therefore not surprising that the C_s-$C_{59}N(CF_3)_5$ isomer with the pyrrole moiety, which lacks a sixth CF_3 group in the unfavorable *ortho* position, is more than 50 kJ mol^{-1} more stable than the structures with other addition patterns including ribbon structures similar to C_1-$C_{60}(CF_3)_6$ (see the Supporting Information). Consequently, the C_s-$C_{59}N(CF_3)_5$ isomer is formed highly regioselectively in the high-temperature trifluoromethylation of $(C_{59}N)_2$; not even trace amounts of other isomers of $C_{59}N(CF_3)_5$ were found in the crude product.

The X-ray structure of C_s-$C_{59}N(CF_3)_5$ confirmed the proposed addition pattern (see Figure 3).[8] The C_s-$C_{59}N(CF_3)_5$ molecule is disordered by the overlap of five molecules rotated by 72° relative to each other, and as a result, the nitrogen atom is disordered among five positions in the N1···C4 pentagon. The molecules are arranged in nearly close-packed layers and stacked in register, 10.179 Å apart (centroid–centroid distance of the cage), giving rise to a very unusual non-close-packed stacking arrangement AAA… (Figure 3). No structure composed of only one type of atoms exhibits such packing, and it is rarely found for binary interstitial compounds (e.g., WC[9]). In contrast, in the SPP structures of $C_{60}Br_6$[10] and $C_{60}Cl_6$,[11] close-packed layers of molecules are stacked in ABAB… and ABAC… sequences, respectively. (For comparison, C_{60} crystallizes with a cubic-close-packed (ccp) structure.[12]) It is likely that the unique shape of the $C_{59}N(CF_3)_5$ molecules with the concave region formed by the loop of five CF_3 groups (and in the absence of the sixth addend, which is present in all $C_{60}X_6$ structures) allows the molecules to pack very closely and directly above one another. In the $C_{60}X_5H$ (X = CH_3,[13] *p*-*t*BuC_6H_4,[14] $C_{12}H_9$[15]) structures, molecules are also packed in columns. However, the packing in $C_{60}(p\text{-}t\text{Bu}C_6H_4)_5H\cdot 3\,C_5H_{12}$ is a distorted ccp structure (ABC…) with interlayer distances of 13.593 and 13.753 Å. In the $C_{60}(C_{12}H_9)_5H$ structure, the large size of the added $C_{12}H_9$ groups and the presence of a hydrogen atom in the SPP fragment as well as solvent molecules in the lattice, result in a large distortion of the hexagonal layers and a longer stacking period (11.093 A). The packing in the $C_{60}(CH_3)_5H$ structure is a distorted hexagonal-close-packed (hcp) array (ABAB…, see the Supporting Information) with a stacking period within the zigzag columns of 10.153 Å. It has been hypothesized (and in some cases experimentally tested[14,16]) that fullerene acceptors packed in the active layer of an organic photovoltaic cell may play an important role in providing a more controlled morphology and better mobility. The formation of the unusual columnar stacking of the $C_{59}N(CF_3)_5$ molecules with one of the closest cage-to-cage distances observed for this class of fullerene derivatives may be of interest for the design of organic electronic devices.

The cyclic voltammogram of C_s-$C_{59}N(CF_3)_5$ shows two reversible reduction steps at −0.05 and −0.54 V versus the $C_{60}^{0/-}$ redox pair (at a scan rate of $20\,mV\,s^{-1}$), which is very similar to the redox behavior of C_s-$C_{60}(CF_3)_6$ (−0.07 and −0.53 V, Figure 4); this finding is in harmony with our prior observations of a predominant role of the fullerene addition pattern on the redox properties in fullerene $(R_F)_n$.[5] A solution of C_s-$C_{59}N(CF_3)_5$ is ESR-silent, but a broad featureless ESR signal (width of ca. 40 G, $g = 2.0006$) superimposed by a narrow peak (width 2.1 G, $g = 2.0019$) was observed after reduction with roughly one equivalent of cobaltocene. The narrow ESR line corresponds to less than 2% of the spin concentration and is assigned to an unidentified impurity having a different electronic structure, while the broad signal is safely attributed to the radical anion C_s-$C_{59}N(CF_3)_5^{\bullet-}$. The spectrum resembles the ESR spectrum of the C_{60} monoanion, which also exhibits a broad ESR signal and is often accompanied by a narrow line (spike) as a result of fullerene derivative impurities.[17] The signal of the C_{60} anion is broad because the lowest unoccupied molecular orbital (LUMO) of C_{60} is threefold degenerate and split in the anion as a result of Jahn–Teller distortion. The gap between the split components is very small, and hopping of the electron between these orbitals results in the broadening of the ESR signal. The same holds for the broad ESR signal of the $C_{59}N(CF_3)_5^{\bullet-}$ anion radical. The $C_{60}(CF_3)_5^-$ monoanion, which is isoelectronic to $C_{59}N(CF_3)_5$, has C_{5v} symmetry and its twofold degenerate LUMO has E_1 symmetry. Therefore, Jahn–Teller distortion and broadening of the ESR signal is also expected for the $C_{60}(CF_3)_5^{2-}$ dianion (which is isoelectronic to $C_{59}N(CF_3)_5^-$). Although $C_{59}N(CF_3)_5$ has only approximately C_s symmetry (DFT optimization gives rigorous C_1 symmetry because of the twisted CF_3 groups), its LUMO and LUMO + 1 states are quasidegenerate (the PBE/TZ2P-predicted gap is only 0.002 eV) and resemble closely the components of the twofold degenerate LUMO of $C_{60}(CF_3)_5^-$ (see Figure 4 and the Supporting Information). The lack of π-electronic communication between the fullerene core and the π system of the pyrrole fragment results in effective C_{5v} symmetry for the former, and hence all arguments about the degenerate LUMO and Jahn–Teller distortion also apply to $C_{59}N(CF_3)_5^-$. DFT calculations show that the bond lengths of the fullerene part in $C_{59}N(CF_3)_5$ are indeed almost equal to those of the C_{5v}-$C_{60}(CF_3)_5^-$ anion with deviations of only 0.001–0.002 Å (see the Supporting Information). In the Jahn–Teller-distorted $C_{60}(CF_3)_5^{2-}$ dianion the symmetry is reduced to C_s and very similar changes are found in the DFT-optimized structure of $C_{59}N(CF_3)_5^-$.

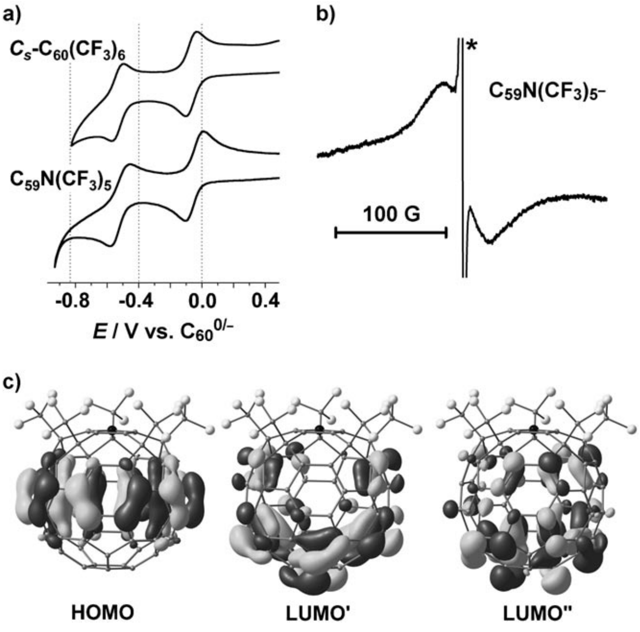

Figure 4. a) Cyclic voltammograms of C_s-$C_{60}(CF_3)_6$ and $C_{59}N(CF_3)_5$ in $TBABF_4/CH_2Cl_2$; b) ESR spectrum of $C_{59}N(CF_3)_5^-$ (an asterisk marks the impurity line); c) The highest occupied molecular orbital (HOMO) and two components of the quasitwofold degenerate LUMO of $C_{59}N(CF_3)_5$.

The isolation of the products with more CF_3 groups, $C_{59}N(CF_3)_{n>5}$, turned out to be more difficult than that of the $C_{60}(CF_3)_{n>6}$ products. Even after separating fractions I–III by multistage HPLC (Figure 1, inset) we were able to isolate only four pure isomers of the many that were present: $C_{59}N(CF_3)_7$, $C_{59}N(CF_3)_9$, and two isomers of $C_{59}N(CF_3)_{11}$ (see Figure 2 and the Supporting Information). Other fractions contained two or more practically inseparable isomers with supposedly very similar structures as evidenced by the similarity of their ^{19}F NMR spectra and HPLC retention times (see the Supporting Information). DFT calculations revealed that all stable isomers of $C_{59}N(CF_3)_{n>5}$ are based on the addition motif of C_s-$C_{59}N(CF_3)_5$ with the additional CF_3 groups forming either isolated p-$C_6(CF_3)_2$ hexagon(s) or ribbons of edge-sharing p-$C_6(CF_3)_2$ hexagons on the opposite pole. This is a new type of isomerism of heterofullerene derivatives with a much higher number of isomers compared to $C_{60}(CF_3)_n$, since each CF_3 addition pattern yields up to five isomers because of the different positions of N in the pyrrole fragment. Such isomers are often almost isoenergetic but in some cases the energy difference can be up to $10\,kJ\,mol^{-1}$ (see the Supporting Information). For example, the most stable addition patterns of C_1-$C_{59}N(CF_3)_7$ and C_1-$C_{59}N(CF_3)_9$, consistent with the ^{19}F NMR spectra, have five different locations of the N atom within the pyrrole moiety, and the relative energies of such isomers are within $2\,kJ\,mol^{-1}$ (Figure 2). In C_1-$C_{59}N(CF_3)_7$, two CF_3 groups form an isolated p-$C_6(CF_3)_2$ hexagon, while in C_1-$C_{59}N(CF_3)_9$ four CF_3 groups are arranged in a *pmp* ribbon as in the most abundant isomer of C_1-$C_{60}(CF_3)_4$.[5] From the combined analysis of the spectroscopic data and the DFT-calculated relative stabilities, we proposed that both isolated isomers of $C_{59}N(CF_3)_{11}$ have a pyrrole moiety as part of their addition patterns, while the remaining six CF_3 groups are arranged either in *pmpmp*- (isomer 1) or SPP- (isomer 2) addition pattern (Figure 2). It

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should be noted that an analogous isomer of $C_{60}(CF_3)_{12}$ with two SPP motifs was isolated as a minor product, and it is 32 $kJ\,mol^{-1}$ less stable than the most stable $C_{60}(CF_3)_{12}$ isomer.[18] The close resemblance of the UV/Vis spectrum of $C_{59}N(CF_3)_{11}$-2 (isomer 2) and the double-SPP isomer $C_{60}(CF_3)_{12}$ supports the proposed addition pattern (see the Supporting Information).

In conclusion, the synthesis and characterization of five members of azafullerenes bearing trifluoromethyl groups show a profound effect of the cage nitrogen atom on the addition patterns.

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