Selective Synthesis and Structure Determination of $C_{60}F_{48}$

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To date, $C_{60}F_{48}$ is the highest intact adduct derived from C_{60} to be obtained in significant quantities and verified by different spectral methods.[1a–c] However, neither structural features nor the synthesis of isomerically pure samples of this species have been reported. In view of the unusual reactivity[1c] and physicochemical properties[1d] of the higher fluorofullerenes, selective synthesis and structural analysis of $C_{60}F_{48}$ became a focus of our efforts. We now report the synthesis and structural determination of one major $C_{60}F_{48}$ isomer.

As we reported previously,[1a,c] the main product of direct fluorination of C_{60} at 275 °C[1a] or of C_{60} mixed with sodium fluoride at 250 °C[1c] is $C_{60}F_{46}$, with $C_{60}F_{48}$ comprising only 10–15% of the reaction product as determined by mass spectrometry. The fluorine NMR spectra of these mixtures are very complex and not amendable to definitive interpretation.

Further fluorination has now been achieved by increasing the temperature and time of fluorination of C_{60}–sodium fluoride mixtures to produce fluorofullerenes in 56% chemical yield, of which >60% proved to be a *single structure* (**1**) by ^{19}F NMR spectroscopy.[2] Mass spectrometry data indicated $C_{60}F_{48}$ to be the predominant component of the mixture.[3]

The ^{19}F NMR (Figure 1) provided the structure of **1**. The spectrum is characterized by eight salient peaks spanning 40ppm in a region (–131 to –170 ppm) typical of CF groups in fluorinated cage molecules (compare, e.g., –129.8 ppm for 1-fluoroadamantane or –147.6 ppm for 1-fluorobicyclo[2.2.2]octane).[4] All eight signals have the same integral intensities,[5] indicating a high symmetry to the molecule (eight sets of six equivalent fluorine atoms each). The eight lines comprise two distinct clusters of four signals each, one at high field (153 to –170 ppm) and one at low field (–131 to –139 ppm).[6]

Decisive structural information was obtained from homonuclear ^{19}F–^{19}F shift correlation (COSY) experiments.[5] The connectivities derived from these 2D spectra are summarized by the connecting bridges incorporated in Figure 1. Each bridge represents ^{19}F-coupling of two sets of CF groups. The structure (**1**, Figure 2) meets the requirements of these COSY derived connectivities.

To prove that this is the only valid structural assignment, a FORTRAN computer program was written[7] to identify all isomers of $C_{60}F_{48}$ having eight sets of six equivalent CF groups as required by the equal integrals of the eight peaks in Figure 1. Fourteen such structures were found.[5] Of these 14, *only two (an enantiomer pair) correspond to the connectivity pattern established by the COSY experiment.*

The enantiomer pair **1**, consisting of the *RR and SS isomers*,[8] is depicted in both Schlegel diagrams and conventional form in Figure 2, thus verifying the compliance of **1** with the observed connectivity. Attempts are underway to separate the enantiomers by chromatography on chiral stationary phases and to observe the different enantiomers in NMR by use of chiral solvents or additives.

Integration of the NMR spectrum[5] shows that the eight salient peaks of Figure 1 account for >60% of the total ^{19}F-signal intensity. It is truly remarkable that a generally nonregioselective reaction such as fluorination at elevated temperatures should give predominantly one enantiomer pair out of millions of possible isomers. Energetic and steric considerations[9] are probably the major factors governing the formation of predominantly this enantiomer pair. The possible mechanisms for the fluorination of C_{60} are now under investigation in order to more fully rationalize the specific generation of the observed enantiomer pair.

The development of other methods of selective fluorination and defluorination of buckminsterfullerenes and the determination of the exact structures of fluorofullerenes continue.

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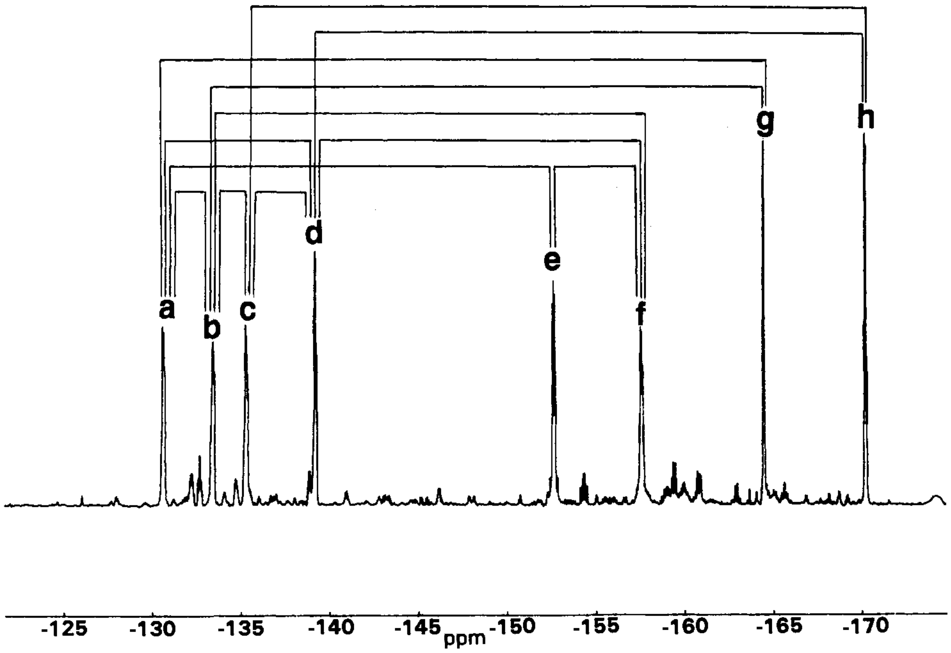

Figure 1. ^{19}F NMR spectrum of $C_{60}F_{48}$ (**1**). Lines between peaks indicate connectivities established by COSY.

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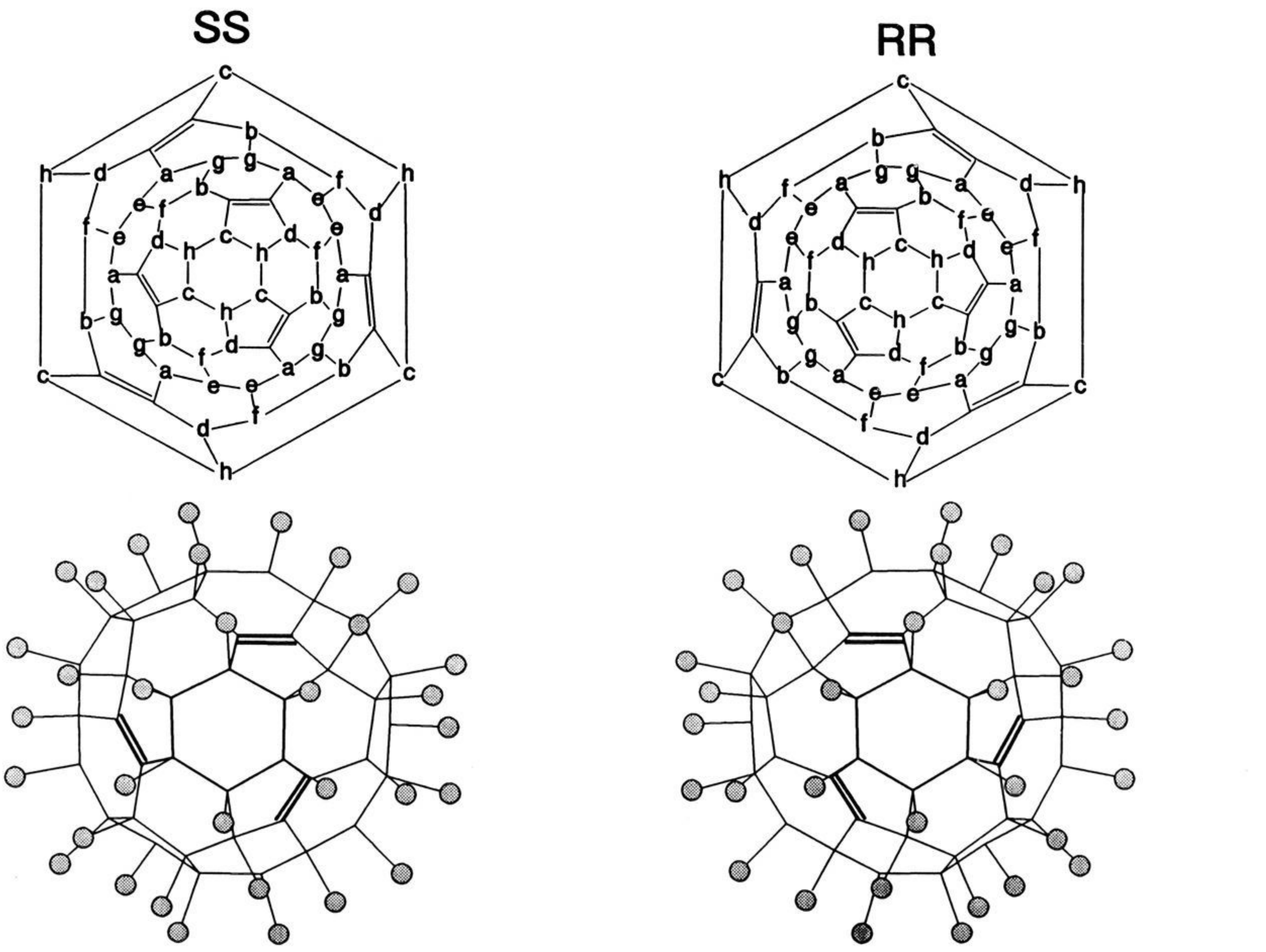

Figure 2. Structure of the enantiomer pair **1**. In the Schlegel diagrams, the letters correspond to the letters in Figure 1 and the fluorine atoms are omitted.

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Note Added in Proof: The ^{13}C NMR spectra of the solutions of **1** in $CFCl_3$–$CDCl_3$ (acquired subsequent to submission of this manuscript) are in agreement with the proposed structure. Also, careful examination of less intense peaks in the ^{19}F spectra allows identification of a minor (~10–15%) component, the (*RS*) mesoform. Full analysis of the ^{19}F and ^{13}C NMR spectra will appear in a full paper currently in preparation.

Supplementary Material Available: Detailed ^{19}F NMR spectra and the relaxation times experimental data for $C_{60}F_{48}$, 2D COSY, source version, output, and bond-numbering map of the FORTRAN program "C60F48", Schlegel diagrams of the 14 structures found by "C60F48", mass spectra of the $C_{60}F_{48}$ sample (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(1) (a) Tuinman, A. A.; Mukherjee, P.; Adcock, J. L.; Hettich, R. L.; Compton, R. N. *J. Phys. Chem.* **1992**, *96*, 7584. (b) Tuinman, A. A.; Gakh, A. A.; Adcock, J. L.; Compton, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 5885. (c) Gakh, A. A.; Tuinman, A. A.; Adcock, J. L.; Compton, R. N. *Tetrahedron Lett.* **1993**, *34*, 7167. (d) Kniaz, K.; Fischer, J. E.; Selig, H.; Vaughan, G. B. M.; Romanow, W. J.; Cox, D. M.; Chowdhury, S. K.; McCauley, J. P.; Strongin, R. M.; Smith, A. B., III. *J. Am. Chem. Soc.* **1993**, *115*, 6060.

(2) A finely ground mixture of C_{60} (75 mg) and 2.0 g of NaF was placed in a 4-mm quartz tube and dried at 150 °C for 2 h in a flow of N_2. The N_2 flow was replaced with one of pure F_2 (1.3 mL/min), and the tube was heated at 250 °C for 20 h. The sample was cooled in a flow of N_2 and extracted three times with 4–5-mL portions of $CFCl_3$. The extract was filtered and the solvent removed in a flow of dry N_2. The residue (130 mg) was dried in high vacuum (0.01 Torr) at 65–70 °C overnight and then mixed with 2.4 g of NaF and fluorinated additionally for 30 h at 275 °C as described above. Extraction with $CFCl_3$ gave 95 mg (56%) of predominantly $C_{60}F_{48}$ (**1**, >60% isomeric purity based on NMR assay). ^{19}F NMR experiments were run on Bruker MSL-400 in CCl_4 or $CDCl_3$. Chemical shifts are referenced to $CFCl_3$ internal standard. EI–MS, FD–MS, and EC–MS of the samples were performed as previously described.[1a]

(3) Different mass spectrometric ionization techniques show somewhat different results for this compound. $C_{60}F_{48}$ as a fraction of the total $C_{60}F_{2n}$ signal increases when going from electron ionization (EI) to electron capture (EC) to field desorption (FD) (the best results were 69% using FD).[5] A report describing the effect of various parameters on the observed mass spectra of highly fluorinated fullerenes is in preparation and will be presented elsewhere.

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(5) Details of this and other pertinent information too voluminous to include in this communication have been deposited as supplementary material.

(6) The low-field peaks are close to the region where CF_2 groups are usually found, *i.e.*, 115–125 ppm,[4] and we have previously demonstrated[1b] that the fullerene skeleton can be cracked, leading to the formation of CF_2 groups. To eliminate the possibility of such groups contributing to this spectrum, the relaxation times of all ^{19}F observed in the spectra were measured.[5] All these ^{19}F were found to relax within a narrow time window, (average $t_{1/2}$ for low-field cluster = 1.03 s; average $t_{1/2}$ for high field cluster = 1.00 s); all are therefore deemed to belong to CF groups.

(7) The program "C60F48"[5] generates all possible arrangements (>20 000 000) of six double bonds on the buckminsterfullerene skeleton. Those arrangements having eight sets of six equivalent sp^3 carbon atoms are identified by checking the distances of each of these atoms to each of the double bond midpoints.

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