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LETTERS

The structure of $C_{60}F_{36}$

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Abstract—Detailed analyses of 1D and 2D ^{19}F NMR experiments confirm the theoretically predicted structure of the major most thermodynamically stable C_3 isomer of $C_{60}F_{36}$, which is distinctly tetrahedral in shape. © 2001 Elsevier Science Ltd. All rights reserved.

Contrary to the established structures of the D_3 isomer of $C_{60}F_{48}$,[1a,b] and the C_{3v} isomer of $C_{60}F_{18}$,[2,3] the structure of the major C_3 isomer of $C_{60}F_{36}$ (synthesized almost 5 years ago) remains a subject of controversy.[4–7] It was initially suggested that high temperature fluorination of C_{60} with MnF_3 yielded at least four main isomers of $C_{60}F_{36}$.[4] The crude samples gave 15 dominant signals in the ^{19}F spectra, which were tentatively divided into five sets of three signals each.[4] Subsequent HPLC purification and further 1D and 2D ^{19}F NMR analysis showed that 12 signals actually belong to a single isomer of C_3 symmetry, and the choice of several possible structures was presented.[5] In addition to the C_3 isomer, a more symmetrical T isomer was also identified, thus accounting for the remaining three NMR signals.[5] Later, one of the previously proposed structures of the C_3 isomer was selected,[6,7] based primarily on the results of ^{19}F 2D COSY experiments.[6] However, theoretical analysis (AM1 level) indicated a different structure for the most stable C_3 isomer.[8] Here we report the result of our independent study of $C_{60}F_{36}$.

Our ^{19}F NMR analyses of $C_{60}F_{36}$ samples[4,5,9] indicate mixtures of several fluorinated compounds, whereby the C_3 and T isomers (ratio $\sim$12:1)[10] of $C_{60}F_{36}$ comprise about a half of the total sample. The observed chemical shifts of the C_3 isomer (in $CDCl_3$ and benzene-d_6) are presented in Table 1. The 12 signals are labeled **A** through **L**, according to the order of their chemical shifts in $CDCl_3$.

Direct structural analysis on the basis of these chemical shifts and of ^{19}F–^{19}F scalar couplings is complicated by the large number of potential solutions. A computer model[11] identified 2695 isomers of $C_{60}F_{36}$ having C_3 (or higher) symmetry (2572 enantiomer pairs and 123 achiral solutions). A further complication arises from the propensity of the fluorine atoms to give large long-range scalar couplings, especially through a system of filled π-orbitals.[12] In some cases these long-range ^{19}F–^{19}F coupling constants can be larger than vicinal (^3J) constants.[12]

Table 1. ^{19}F Chemical shifts of $C_{60}F_{36}$ (C_3 isomer) in $CDCl_3$ and benzene-d_6

Signal	Chemical shift in $CDCl_3$[a]	Chemical shift in benzene-d_6 (Δ)[a]	Signal	Chemical shift in $CDCl_3$[a]	Chemical shift in benzene-d_6 (Δ)[a]
A	−130.3	−131.1 (−0.8)	**G**	−144.2	−144.6 (−0.4)
B	−138.8	−137.9 (+0.9)	**H**	−144.7	−145.1 (−0.4)
C	−139.6	−140.3 (−0.7)	**I**	−148.8	−147.9 (+0.9)
D	−141.2	−140.3 (+0.9)	**J**	−153.6	−153.0 (+0.6)
E	−142.0	−142.7 (−0.7)	**K**	−154.5	−153.9 (+0.6)
F	−144.0	−144.8 (−0.8)	**L**	−166.2	−165.6 (+0.6)

[a] All chemical shifts and Δ values are in ppm versus internal reference ($CFCl_3$).

Keywords: $C_{60}F_{36}$; structure; ^{19}F NMR.

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To reduce the number of possible structures that need to be considered, an NMR search for specific fragments was undertaken. The targeted moiety was $CF(CF)_3$. That fragment was expected to have a distinct NMR 'signature'. Thus, the signal of the central fluorine atom should be shifted upfield relative to the signals of the surrounding fluorine atoms.[1a,2] In addition, the central fluorine should have well-defined couplings with three surrounding fluorine atoms (ddd, dt or q).[1a,2] Using both the previously reported[5,6] and our own NMR data (see below) three, and only three, $CF(CF)_3$ moieties were identified, namely **L**(**BDE**); **K**(**AAH**) and **J**(**CFG**).

Further structural evidence was gathered using solvent-induced chemical shift effects ($CDCl_3$/benzene-d_6). It was anticipated that signals of fluorine atoms adjacent to benzene rings in $C_{60}F_{36}$ could be identified because of the specific π–π interactions of these rings with an aromatic solvent. The result of these studies is presented in the Table 1. Six signals (**A**, **C**, **E**, **F**, **G**, **H**) exhibit an upfield shift of −0.4 to −0.8 ppm, and the remaining six signals are shifted downfield by +0.6 to +0.9 ppm. In order to ascertain the significance of this observation, the same experiment was conducted on two fluorofullerenes of known structure: the T isomer of $C_{60}F_{36}$ and the D_3 isomer of $C_{60}F_{48}$. The former, which has four aromatic fragments and no isolated double bonds,[5–7] displayed upfield shifts of −0.2 and −0.7 ppm for the two signals representing the 24 fluorine atoms adjacent to the aromatic rings in benzene-d_6 compared to $CDCl_3$. The signal of the remaining 12 fluorine atoms shifted downfield by +0.7 ppm. In contrast, the D_3 isomer of $C_{60}F_{48}$, which has six isolated double bonds and no benzene rings,[1a,b] shows only downfield shifts of +0.8 to +1.0 ppm. Thus, the upfield shifts of signals **A**, **C**, **E**, **F**, **G**, and **H** (see Table 1) indicate that these 18 fluorines are adjacent to three aromatic rings. The occurrence of three benzene rings in the C_3 isomer of $C_{60}F_{36}$ was postulated previously,[5–7] and is now substantiated by these experiments.

The preceding observations narrow the set of possible solutions sufficiently to resolve the structure of the C_3 isomer, even without invoking full analysis of 2D COSY experiments. To ensure that no viable candidates were overlooked, a FORTRAN program[11] was written which generated all possible isomers of $C_{60}F_{36}$ having C_3 symmetry or higher, and highlighted those which fit the criteria mentioned above, i.e. the presence of three benzene rings and three $CF(CF)_3$ moieties. Only two enantiomer pairs displayed both criteria. One of these pairs (corresponding to isomer # 65 in Ref. 8) was discarded because it possesses two 'degenerate' $CF(CF)_3$ fragments of type **X**(**YYZ**) instead of only one observed experimentally. Fig. 1 depicts the double bond placement of the remaining possibility. This enantiomer pair corresponds to the structure previously predicted to be the most thermodynamically stable C_3 isomer of $C_{60}F_{36}$.[8]

Using the established double bond placement, the knowledge of which signals represent fluorines adjacent to aromatic rings and which belong to $CF(CF)_3$ moieties, and a minimal set of observed ^{19}F–^{19}F couplings,[5,6] the unambiguous assignment of all signals can be made. That assignment, also depicted in Fig. 1, is consistent with the previously published 2D ^{19}F COSY data,[6] *with the notable exception of signal **I***. This signal is reported[6] to have couplings with signals **B** and **D**, whereas the proposed assignment requires that it should also couple with **E** and **F** (^3J). To resolve this apparent discrepancy, we performed 2D COSY DQF ^{19}F NMR experiments which allow detection of small scalar couplings.[13] These experiments showed (Table 2) that the signal **I** indeed couples with all four signals (**B**, **D**, **F**, and **E**), as expected for the structure in Fig. 1. In this particular case ^4J (**I**–**B**), and ^5J (**I**–**D**) through a double bond π system are larger than ^3J (**I**–**E**, **I**–**F**).

Finally, we performed MM calculations (SYBYL) of this enantiomer pair. The results showed that C_3 isomer of $C_{60}F_{36}$ has very distinct pyramidal ('tetrahedral') structure (Fig. 2).

The deformation of the nearly spherical C_{60} during fluorination is due to severe crowding in fluorinated parts of the molecule. As a result, less fluorinated regions of the molecule assume almost planar conformations, while more highly fluorinated regions assume vertices-like conformations. This particular tetrahedral shape makes the C_3 isomer an attractive building block for crystal engineering and other nanotechnology applications.[15a–d]

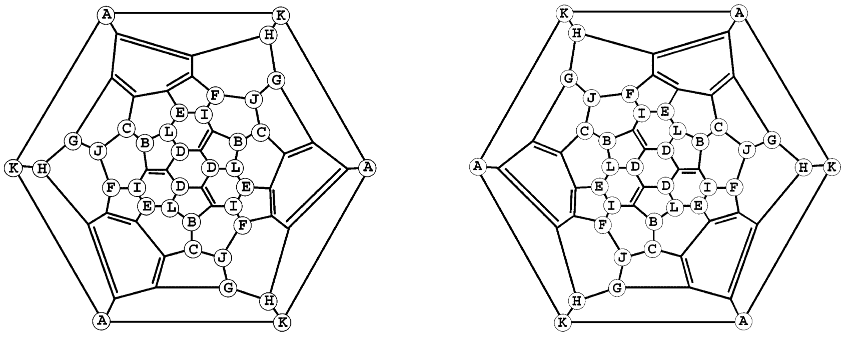

Figure 1. Shlegel diagrams of the enantiomer pair (C_3 isomer).

Table 2. ^{19}F–^{19}F scalar coupling correlation table of the C_3 isomer of $C_{60}F_{36}$[a]

Signal	Observed correlations[b]	Expected correlations[c]	Signal	Observed correlations[b]	Expected correlations[c]
A	K, H, G, E	***K***, *H*, *G*, E, C, F	G	H, J, A, C	***H***, ***J***, *A*, *C*, E, F
B	C, L, D, I	***C***, ***L***, *D*, *I*	H	G, K, A, C	***G***, ***K***, *A*, *F*, C, E
C	B, J, E, G, F, H	***B***, ***J***, *E*, *G*, F, H, A	I	E, F, B, D	***E***, ***F***, *B*, *D*
D	L, B, I	***L***, *B*, *I*	J	C, F, G	***C***, ***F***, ***G***
E	I, L, C, F, A	***I***, ***L***, *C*, *F*, A, G, H	K	A, H	***A***, ***H***
F	I, J, E, C	***I***, ***J***, *E*, *H*, C, G, A	L	B, D, E	***B***, ***D***, ***E***

[a] Tables 1 and 2 establish that the material examined in this study is identical to that previously reported (Refs. 4–6).

[b] Previously reported[6] correlations are underlined; those additionally observed during this study are not.

[c] Expected correlations for the structure in Fig. 1: ^3J are ***bold italic***; $^{4,5}J$ (through a system of π-orbitals) are *italic*; $^{6,7}J$ are not italicized. Please note that the table includes all possible long-range couplings through benzene rings (up to ^7J), some of which may be too small to be detected even with 2D DQF COSY experiments.

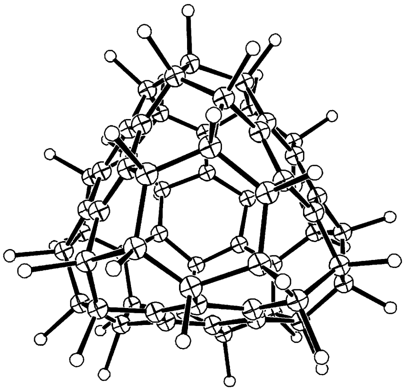

Figure 2. ORTEP[14] drawings of 'tetrahedral' C_3 isomer of $C_{60}F_{36}$.

Acknowledgements

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References

1. (a) Gakh, A. A.; Tuinman, A. A.; Adcock, J. L.; Sachleben, R. A.; Compton, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 819–820; (b) Troyanov, S. I.; Troshin, P. A.; Boltalina, O. V.; Ioffe, I. N.; Sidorov, L. N.; Kemnitz, E. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2285–2287.
2. Boltalina, O. V.; Markov, V. Yu.; Taylor, R.; Waugh, M. P. *J. Chem. Soc., Chem. Commun.* **1996**, 2549–2550.
3. Neretin, I. S.; Lyssenko, K. A.; Antipin, M. Yu.; Slovokhotov, Yu. L.; Boltalina, O. V.; Troshin, P. A.; Lukonin, A. Yu.; Sidorov, L. N.; Taylor, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3273–3276.
4. Boltalina, O. V.; Borschevskii, A. Y.; Sidorov, L. N.; Street, J. M.; Taylor, R. *J. Chem. Soc., Chem. Commun.* **1996**, 529–530.
5. Boltalina, O. V.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 649–653.
6. Boltalina, O. V.; Bühl, M.; Khong, A.; Saunders, M.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1475–1479.
7. Jenkins, S.; Heggie, M. I.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2415–2419.
8. Clare, B. W.; Kepert, D. L. *J. Mol. Struct. (THEOCHEM)* **1999**, *466*, 177–186.
9. Chilingarov, N. S.; Nikitin, A. V.; Rau, D. V.; Golyshevskii, I. V.; Kepman, A. V.; Sidorov, L. N. *Dokl. Akad. Nauk* **1999**, *365*, 774–776.
10. The ~12:1 molar ratio of C_3:T results from the integration of ^{19}F NMR spectra, whereby each signal of the C_3 isomer represents three fluorines, and each one of the T isomer represents twelve fluorine atoms. The ratio varied between ~14:1 and ~10:1 for freshly prepared samples. Essentially the same C_3:T ratio can be calculated from the previously reported ^{19}F spectra of crude $C_{60}F_{36}$ samples.[4]
11. FORTRAN source code (10 pages), input and output files are available from the authors upon request.
12. Gakh, Y. G.; Gakh, A. A.; Gronenborn, A. M. *Magn. Reson. Chem.* **2000**, *38*, 551–558 and references cited therein.
13. Derome, A. E. *Modern NMR techniques for chemistry research*; Pergamon Press: Oxford, 1990; pp. 183–258 and references cited therein. A more detailed discussion of the COSY-DQF method can be found at http://www.chem.wisc.edu/areas/organic/courses/NMR-Gemmecker/chem843-4.PDF (Gemmecker, G. *Advanced NMR Spectroscopy*, 1999).
14. ORTEP drawings were performed using ORTEP-3 for Windows: Farrugia, L. J. *J. Appl. Cryst.* **1997**, 565; Burnett, M. N.; Johnson, C. K. Oak Ridge National Laboratory, Report ORNL-6895, 1996.
15. (a,b) *Crystal Engineering*; (NATO ASI Study Series C, Mathematical and Physical Sciences, Vols. 538 and 539), Kluwer Academic, 1999 [(a) Vol. 538: *From Molecules and Crystals to Materials*; Braga, D.; Grepioni, F.; Orpen, A.G., Eds. (b) Vol. 539: *The Design and Application of Functional Solids*; Seddon, K. R.; Zaworotko, M., Eds.]; (c) *Solid-State Supramolecular Chemistry*: *Crystal Engineering*; MacNicol, D. D.; Toda, F.; Bishop, R., Eds.; *Comprehensive Supramolecular Chemistry*; Lehn, J.-M.; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vogtle, F., Eds.; Pergamon Press: Oxford, 1996; Vol. 6; (d) Dagerrassu, A. D. *Crystal Engineering*; Elsevier Science, 1989.