Electron-Diffraction Investigation of the Fluorofullerene $C_{60}F_{48}$

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The structure of the fullerene $C_{60}F_{48}$ has been investigated in the gas phase by electron diffraction from a sample volatilized at 360 °C. The analysis was carried out under two assumptions: (1) the molecules have either D_3 or S_6 symmetry as suggested by NMR spectroscopy and verified by an X-ray study of the crystal, and only one of these is present in the gas; (2) all carbon−fluorine bonds have the same length. With the named symmetries, the structure of the carbon skeleton may be defined by the positions of 10 atoms forming two pentagons, one near the top of the molecule and one near the equator, and the locations of the fluorine atoms obtained as the resultant of three vectors originating from carbons not involving a double bond. Simultaneous refinement of the large number of geometrical parameters (30 for the carbon skeleton and 17 for the fluorines) either failed to converge or yielded implausible values, but successive refinements of small groups of four or five parameters were successful. Dozens of groups were tested and all of the resulting models gave satisfactory fits to the observed diffraction patterns. Although values of individual parameters in these models might differ appreciably, the values obtained as *averages* from the many refinements have good precision. Some of these averaged results (r_a/Å, ∠/deg) for the D_3/S_6 models, with estimated standard deviations, are the following: $r(\mathrm{C-F}) = 1.368(1)/1.368(1)$; $r(\mathrm{C{=}C}) = 1.327(3)/1.326(4)$; $r(\mathrm{C_{sp^2}-C_{sp^3}}) = 1.503(15)/1.500(11)$; $r(\mathrm{C_{sp^3}-C_{sp^3}}) = 1.585(44)/1.585(41)$; $\angle(\mathrm{C-C{=}C}) = 113.7(4)/113.6(4)$ and $\angle(\mathrm{C-C-C}) = 105.5(1)/105.5(2)$ within pentagons; and $\angle(\mathrm{C-C{=}C}) = 124.2(3)/124.0(4)$ and $\angle(\mathrm{C-C-C}) = 116.6(3)/116.5(3)$ within hexagons. The average distances from the center of the cage (spherical radii) are quite different for the three types of carbon atoms (those in a double bond, those adjacent to a double bond, and those not adjacent to a double bond) and quite different from the C_{60} value of 3.555Å for all atoms. For symmetries D_3/S_6 these radii (R/Å) are 3.937(23)/3.937(17) for sp^3 atoms not bonded to sp^2 ones and 3.781(18)/3.778(20) for sp^3 atoms bonded to sp^2 ones. The average radii to the sp^2 atoms are much shorter than those to the other atoms. These radii fall into two groups for each symmetry: for symmetry D_3 they are 3.018(14) and 3.190(15) Å, and for S_6, 3.017(11) and 3.180(15) Å. The surprising length of some of the carbon−carbon bonds and other features of the structures relative to the structure of C_{60} are discussed.

Introduction

In previous reports from the Oregon State Laboratory, we have described gas-phase electron-diffraction (GED) results for the structures of the fullerenes C_{60}[1] and C_{70},[2] the fullerene "fragment" corannulene, $C_{20}H_{10}$,[3] and the halogenated corannulene $C_{20}Cl_{10}$.[4] The bond-length values for C_{60} are very accurate (the uncertainties are about 0.002 Å[5]), but somewhat less so for C_{70} (0.008−0.025 Å), $C_{20}H_{10}$ (0.006−0.020 Å), and $C_{20}Cl_{10}$ (0.05−0.35 Å). The reason is that there are many more independent structural parameters in C_{70} (12), and in $C_{20}H_{10}$ and $C_{20}Cl_{10}$ (9), than in C_{60} (2).

The molecular structure of $C_{60}F_{48}$ is a problem of enormously greater complexity than any of those cited above. Despite the fact that the carbon skeleton is known to be similar to that of C_{60}, there are over 23×10^9 possible isomers of the molecular skeleton if no account is taken of molecular symmetry. Fortunately, there is NMR evidence[6] that the molecule has D_3 or S_6 symmetry, which reduces the number of possibilities to only nine. Of these, two have been predicted by Clare and Kepert's (hereafter CK) theoretical AM1 and DFT molecular orbital calculations[7] to be more stable than the others by 18 kcal/mol.[5] Figure 1 is a diagram of one of these forms, and a view of the skeletons of both forms is shown in Figure 2. Each of these forms has recently been identified by X-ray diffraction from a crystal comprising an adduct of the compound with mesitylene:[8] the crystal is disordered and both the D_3 and S_6 forms appear to be present in the adduct. With the evidence thus far cited, the likely components of $C_{60}F_{48}$ in the gas are either one or the other, or both, of the two forms present in the crystal.

Even with this simplification−that only two forms need be considered−the structural problem for GED is formidable: not only does the structure of each conformer require the specification of a large number of geometrical parameters (30 for the carbon skeletons and 24 for the fluorines) but also the two

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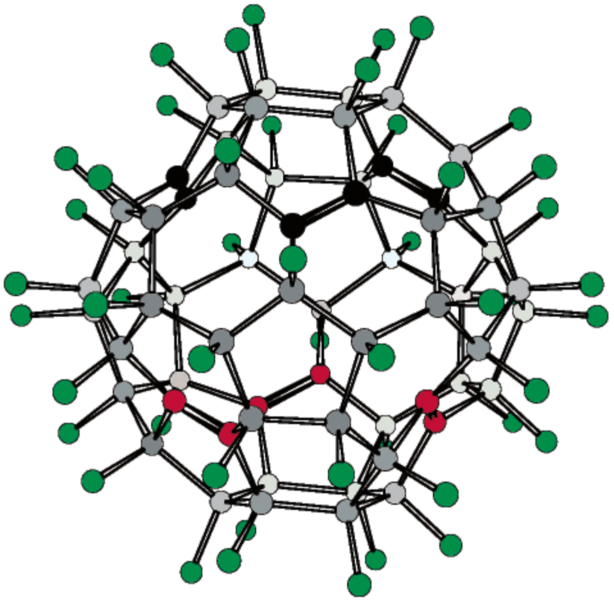

Figure 1. $C_{60}F_{48}$. Diagram of the S_6 symmetry isomer viewed approximately perpendicular to the C_3 axis. The darkest atoms are those nearest the viewer and the lightest furthest away.

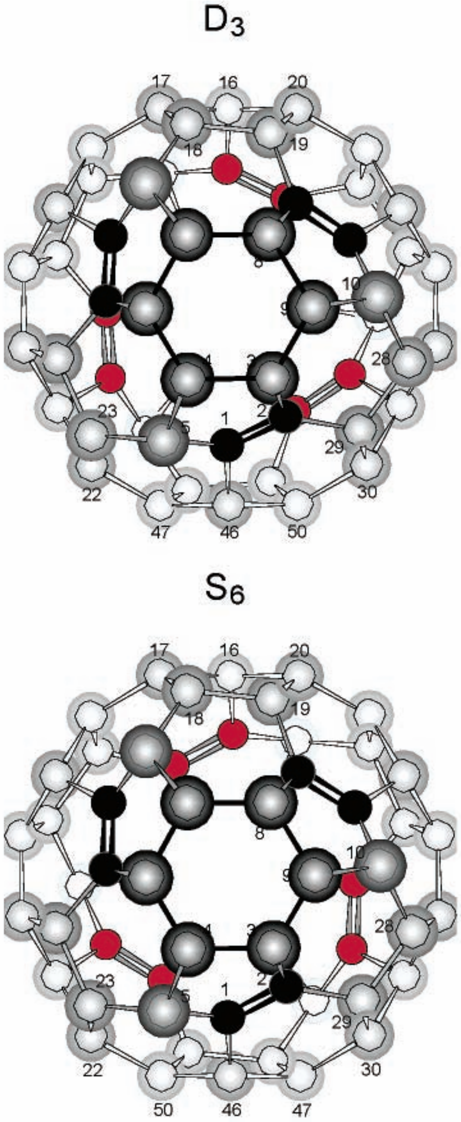

Figure 2. $C_{60}F_{48}$. Diagrams, with atom numbering, of the skeletons of the D_3 and S_6 isomers as seen along the 3-fold axes.

presumably coexistent conformers have similar interatomic distance distributions and are expected to coexist in the gas. A few years ago, we began a GED study of $C_{60}F_{48}$ which was later set aside because of the pressure of other work. However, the preliminary results included quite good fits to the diffraction data with a range of models of each of the two forms posited as the most stable from the theoretical work. This work verified what was intuitively obvious, namely that determinations of the finer details of the structures, such as accurate values of the lengths of the nonequivalent types of C−C bonds, were beyond the scope of a GED study. However, the results did suggest that it might be possible to measure accurately several items of interest, such as values for the *average* length of the different types of bonds and values for the *average* magnitudes of different types of bond angles. With this object in mind, we resumed and have now completed the study of $C_{60}F_{48}$. The results, reported here, do include reasonably precise values of the averages mentioned. They have interest by way of comparisons with the theoretical predictions, with the distances in the parent molecule C_{60}, and with the newly available structures found in the crystal.

Experimental Section

The sample of $C_{60}F_{48}$ (300 mg, ca. 0.2 mmol) was prepared by reacting C_{60} with F_2[9] and characterized by ^{19}F NMR, EI (electron impact) mass spectrometry, chemical analysis, and XPS (X-ray photoelectron spectroscopy). These data showed that the sample was 95+ percent compositionally pure (EI−MS), and consisted of at least 80−90% a single isomer (NMR). $C_{60}F_{48}$ was found to be a thermally stable compound which sublimes without degradation.[8b] This observation indicated it would be possible to volatilize the sample in our high-temperature oven.[1] This proved to be true: heating it to 350−360 °C provided a sample vapor pressure sufficient for the experiments. Three films (Kodak Electron Image 8 × 10 in) at the long (75 cm) and four at the intermediate (30 cm) camera distance were prepared, developed 10 min in Kodak D-19 developer diluted 1:1, and scanned by microphotometry several times. The electron-accelerating voltage was 60 kV and the electron wavelength was calibrated against CO_2 ($r_a(C{=}O) = 1.1646$ Å, $r_a(O \cdot\cdot O) = 2.3244$ Å). Other data pertinent to the experiments were an r^3 sector, electron-beam currents of 0.5−0.6 μA, exposure times of 1−3 min, and ambient apparatus pressure during sample run-in of 1.5×10^{-6} Torr. The procedures for obtaining the scattering data from the microphotometric measurements have been described.[10] The results are seen in Figure 3 and the molecular intensity data in the form $sI_m(s)$ are available as Supplementary Information.

Structure Investigation

Models. Figure 4 shows the experimental radial distribution (RD) curve calculated from a composite of the scattered molecular intensities after multiplication by $Z_C Z_F/(A_C A_F)^{-1}\exp(-0.002s^2)$, where $A = s^2F$ with F being the electron-scattering factor.[11] The RD curve is striking because of the obviously large number of very long, unresolved, distances that the expert will immediately recognize as a structural problem whose solution is well beyond the capability of GED without the help of data from other sources. We conducted preliminary tests on six types of model only two of which are consistent with the NMR spectrum of the sample. These were the ones of symmetries D_3 and S_6 mentioned in the Introduction. Their skeletons are shown in Figure 2; the fluorine atoms are on all carbons not connected

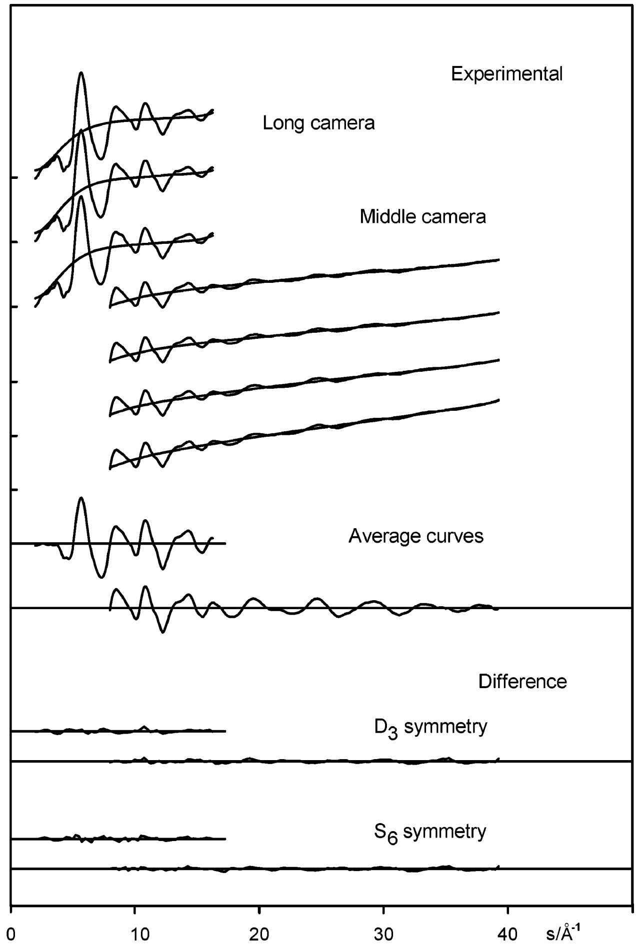

Figure 3. Scattered intensity curves for $C_{60}F_{48}$. The experimental data from individual plates are shown magnified 10 times with respect to the backgrounds on which they are superimposed. The average curves are from the long and middle distances with backgrounds removed. The difference curves are experimental minus theoretical for the models of Tables 1−3.

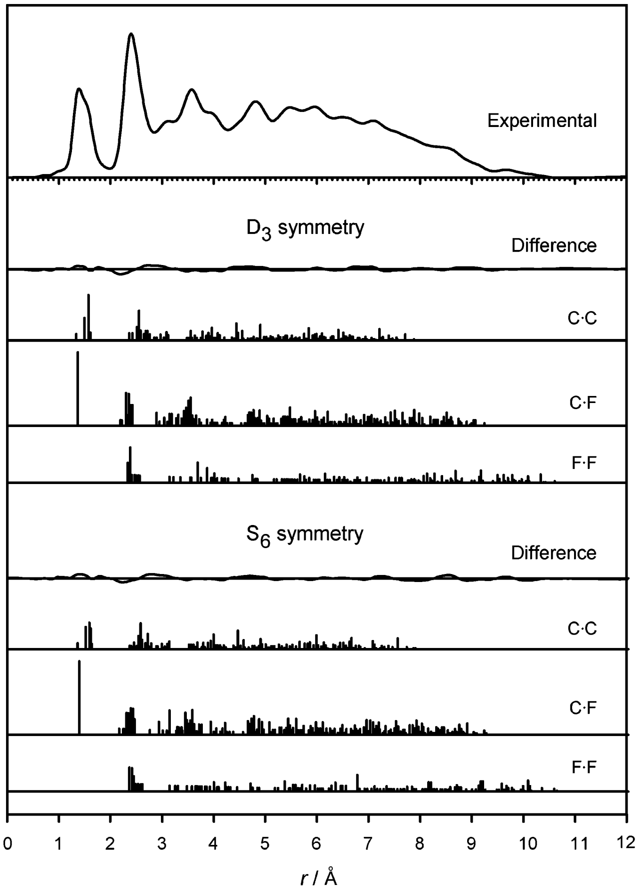

Figure 4. Radial distribution curves for $C_{60}F_{48}$. Vertical bars show positions of interatomic distances for the models of Tables 1−3 and have lengths proportional to the weights of the terms. The damping factor B was equal to $\exp(-0.0025s^2)$. The difference curves are experimental minus theoretical.

by double bonds. Of the remaining models, one was of D_{3d} symmetry and had two opposing six-member rings devoid of fluorine atoms. Two more were those designated by CK as E_1O_1 (T_d symmetry) and E_1O_2 (D_3). A final model was stimulated by, and based on, an extrapolation of the $C_{60}F_{18}$ structure which has all the fluorine atoms in one hemisphere and a flattened cage with a fluorine-atom-free hexagonal ring at the center of the fluorinated crown.[12] The tests consisted of a comparison of the radial distribution of distances from CK's theoretical structures with the experimental curve. The first two models, which have by far the lowest energies of those studied by CK, gave much more satisfactory fits than the others, and our follow-up work was concentrated on them.

The skeletal structure of these low-energy forms of a $C_{60}F_{48}$ molecule with either D_3 or S_6 symmetry can be described in terms of the coordinates of 10 carbon atoms that make up two five-membered rings; for example, the groups $C_1...C_5$ and $C_{16}...C_{20}$ seen in Figure 2. For D_3 the positions of the remaining atoms are obtained by the operation of the C_3 axis and a C_2 axis of rotation and for S_6 by operation of the C_3 axis and the symmetry center. The carbon atoms as a whole form two sets of three pentagons, one set sharing a bond with the topmost six-member ring and one close to the equator. The topmost pentagons contain one double bond each and those close to the equator only single bonds. The skeletons of the D_3 and S_6 models differ only in the positioning of the lower hemisphere of atoms, as may be seen by comparing the corresponding views of each shown in Figure 2. With the indicated symmetry assumptions one need specify only the parameters of the atoms in one of the topmost five-member rings and in one of the equatorial ones to generate the skeleton of the molecule. This was done with use of a convenient set of parameters for each carbon atom that consisted of its cylindrical coordinates R_i, α_i, and Z_i. R is the radius vector from the z axis in the center of the carbon cage, α is the azimuthal angle between the projection of R on the xy plane and a y-axis vector, and Z coincides with the 3-fold axis of the molecule. The y axis was chosen to coincide with one of the 2-fold axes in D_3 symmetry, and the x axis was placed to intersect C_{16} in S_6 symmetry.

There are five fluorine atoms bonded to the equatorial pentagons, but only three to the topmost ones because of the double bonds. The positions of all fluorine atoms can be generated from the positions of the eight fluorine atoms on the skeleton-defining pentagons. To position each fluorine atom three vectors, initially unit vectors, were constructed perpendicular to the three C−C(F)−C planes adjacent to the C−F bond. The sum of these vectors determines the direction of this bond, and by changing their relative weights (lengths), the C−F bond direction is changed. In practice, one of the vectors always had weight 1.0, and each of the others was multiplied by a separate factor to achieve the directional change. The sum of the three vectors was then scaled to the C−F bond length. There are thus 30 carbon atom parameters and 24 fluorine atom parameters, which are reduced to 17 parameters by the assumption of equal C−F bond lengths. A total of 983 interatomic distances for the model of D_3 symmetry and 965 for that of S_6 symmetry are generated by these structure-defining parameters.

The models also required inclusion of vibrational amplitude parameters. One has no way of estimating these directly for a molecule as complicated as $C_{60}F_{48}$, so we made some assumptions based on our C_{60} results.[1] For example, a curve of amplitude vs interatomic distance taken from this study provided a plausible set of starting values for carbon−carbon distances that could be collected into several groups and then independently "group refined". Starting values for the carbon−fluorine and fluorine−fluorine terms were obtained from similar curves based on our experience about how these terms might be expected to differ from the carbon−carbon ones.

Structure Refinements and Results. Parameter values for trial models were chosen to yield structures similar to those obtained from theory for the lowest energy forms of D_3 and S_6 symmetry[3] and kindly communicated to us by CK. Our usual least-squares method,[13] which adjusts the parameters of a structure to improve the fit of the theoretical intensity distribution to the experimental one, was applied to these trial structures. As expected, only a few of the many parameters could be varied simultaneously without experiencing either divergence of the process or convergence of some parameters to unreasonable values. Accordingly, we devised several sets of refinements in each of which only small groups of parameters, both structural and vibrational, were refined while all others were frozen. These sets were characterized by various schemes for refinement within the set. In some cases, the same starting structure was used for each of the groups being refined. In others the succeeding refinements were "successive"; that is, the parameters of the previous refinement, both structural and vibrational, were frozen at their new values while the next group was tested. The composition of these groups of selected parameters was varied over wide ranges in a large number of refinements for models of both symmetries. The fluorine atom angle parameters were tested extensively in some of the preliminary work, but about the same quality of agreement was obtained for models having a reasonable range of values for these parameters. For most of the succeeding work, the C−C−F angle parameters were frozen.

Special procedures were devised to obtain single, overall representations of the structure of each of the two forms of $C_{60}F_{48}$ that were consistent with the many refinements carried out on each. We first determined the average values of the parameters used to describe the structures, i.e., the cylindrical coordinates of the carbon atoms in each structure. (The fluorine atom parameters were frozen as in the main body of refinements.) In the final refinement for each structure the cylindrical coordinates were frozen at these average values and only the average C−C and C−F bond lengths and the amplitude groups were allowed to vary. The results of the pair of final refinements constitute our best estimate of the structures of the D_3 and S_6 versions of the molecule. Estimates of the uncertainties associated with the interesting internal coordinates such as bond lengths, bond angles, and spherical radii (the distances from the center of the cage to carbon atoms not equivalent by symmetry) were obtained by calculating the standard deviation of the values of each coordinate from the average over the many individual refinements carried out for each symmetry. The final results for the structures obtained from about 50 of the refinements are given in Tables 1−3. The vast number of different distances in the molecule precludes a listing of their associated vibrational amplitudes. In the models of each symmetry these range from 0.046 to 0.13 Å for carbon−carbon distances, 0.054 to 0.19 Å for carbon−fluorine distances, and from 0.07 to 0.19 Å for fluorine−fluorine distances. The value of the quality-of-fit factor *R* for the two final models was about 0.10. The fit to experiment given by these models is good, as is seen from the small deviations from the zero line in the scattered intensity and radial distribution difference curves found in Figures 3 and 4. Similarly good fits were also obtained from many of the individual refinements.

TABLE 1: Average Values for Bond Distances (r_a/Å) in the Most Probable Isomers of $C_{60}F_{48}$

	D_3[a]		S_6[a]	
parameter[b]	exptl[c]	theor[d]	exptl[c]	theor[d]
$r(C-F)_{av}$	1.368(1)	1.394	1.368(1)	1.394
topmost pentagon				
$r(C_1{=}C_2)$	1.327(3)	1.339	1.326(4)	1.338
$r(C_2-C_3)$	1.490(6)	1.518	1.491(3)	1.518
$r(C_3-C_4)$	1.666(36)	1.594	1.644(73)	1.594
$r(C_4-C_5)$	1.600(47)	1.621	1.603(51)	1.621
$r(C_5-C_1)$	1.518(15)	1.514	1.506(10)	1.515
between pentagons				
$r(C_3-C_9)$	1.507(15)	1.549	1.526(42)	1.549
$r(C_2-C_{29})$	1.499(11)	1.486	1.497(13)	1.485
$r(C_1-C_{46})$	1.504(12)	1.484	1.508(6)	1.484
$r(C_5-C_{23})$	1.553(17)	1.567	1.569(18)	1.568
$r(C_{30}-C_{50,47})$[e]	1.603(15)	1.600	1.598(4)	1.601
$r(C_{47,50}-C_{22})$[e]	1.591(12)	1.600		
pentagon near equator				
$r(C_{16}-C_{17})$	1.570(15)	1.581	1.590(22)	1.591
$r(C_{17}-C_{18})$	1.598(30)	1.597	1.589(8)	1.593
$r(C_{18}-C_{19})$	1.577(11)	1.575	1.574(11)	1.575
$r(C_{19}-C_{20})$	1.573(15)	1.575	1.576(4)	1.578
$r(C_{20}-C_{16})$	1.595(22)	1.581	1.572(15)	1.572
av values by bond type				
$r(C_{sp^2}\text{-}C_{sp^3})_{av}$	1.503(15)	1.501	1.500(11)	1.501
$r(C_{sp^3}\text{-}C_{sp^3})_{av}$	1.585(44)	1.584	1.585(41)	1.584

[a] Quality of fit factor *R* (equal to $[\sum_i w_i)_i^2/3_i(I_i(\text{obsd}))^2]^{1/2}$; $\Delta_i = \Delta_i(\text{obsd}) - I_i(\text{calcd})$ with $I_i = s_i I_m(s_i)$, is 0.097 for D_3 and 0.093 for S_6. [b] See Figure 2 for atom numbering. [c] Quantities in parentheses are standard deviations. [d] From ref 6. [e] Second subscript refers to S_6 model for which the two distances are equal.

Discussion

Our analysis of the $C_{60}F_{48}$ structure presumes that the gas consists of molecules having only D_3 or only S_6 symmetry. This assumption is a good one if the energy difference of the two forms is greater than about 2 kcal/mol; in such a circumstance 85% of the gas will be the form of lower energy, and our system models are appropriate. However, the applicability of the "either/or" models may be questioned if the system components have the same energy, in which case the gas would be a 50−50 mixture of both. It was clear that a model for such a system would be too complicated to handle. Not only would the very large number (>960) of distances in a single form be doubled but also many of them have very similar values in the two forms. A sense of the problem may be obtained by imagining the sorting-out of a combination of the two distance distributions shown in Figure 4. How reliable, then, are our parameter values derived from models of only one form if both forms are actually present in the gas? The answer is seen in the data of Tables 1−3 where the values for a given parameter are seen to be nearly the same for the two forms. In other words, a model made up of a combination of the two forms would doubtless lead to an average of these values that would differ very little from its components.

In a molecule of the fullerene C_{60}, every atom is bonded to only three others, and hence all bonds are of essentially sp^2 character. These carbon−carbon bonds are of two types, those

TABLE 2: Average Interior Bond Angles/deg in Pentagons and Hexagons of the Most Probable Isomers of $C_{60}F_{48}$

parameter[a]	D_3		S_6	
	exptl[b]	theor[c]	exptl[b]	theor[c]
pentagon I[d]				
$\angle(C_5-C_1=C_2)$	111.2(8)	113.0	111.3(10)	113.0
$\angle(C_1=C_2-C_3)$	116.2(7)	112.8	115.8(14)	112.9
$\angle(C_2-C_3-C_4)$	101.1(14)	103.8	101.6(27)	103.8
$\angle(C_3-C_4-C_5)$	103.0(16)	103.2	102.9(5)	103.3
$\angle(C_4-C_5-C_1)$	102.9(8)	103.1	103.0(12)	103.1
pentagon II[d]				
$\angle(C_{19}-C_{20}-C_{16})$	105.6(3)	105.9	106.2(10)	105.9
$\angle(C_{20}-C_{16}-C_{17})$	108.8(10)	108.8	108.5(5)	108.8
$\angle(C_{16}-C_{17}-C_{18})$	106.6(7)	106.3	106.4(3)	106.3
$\angle(C_{17}-C_{18}-C_{19})$	107.5(4)	107.6	107.7(2)	107.6
$\angle(C_{18}-C_{19}-C_{20})$	108.6(4)	108.5	108.4(7)	108.5
av values within pentagons				
$\angle(C-C=C)$	113.7(3)	112.9	113.5(5)	113.0
$\angle(C-C-C)$	105.5(1)	105.9	105.6(2)	105.9
hexagon III[d]				
$\angle(C_4-C_3-C_9)$	120.0(26)	119.9	120.7(22)	120.0
$\angle(C_3-C_9-C_8)$	118.6(21)	118.2	117.7(18)	118.2
hexagon IV[d]				
$\angle(C_2-C_3-C_9)$	116.4(21)	112.9	115.7(20)	112.9
$\angle(C_3-C_9-C_{10})$	115.1(29)	113.8	115.2(35)	113.8
$\angle(C_9-C_{10}-C_{28})$	120.2(10)	121.4	119.8(19)	121.3
hexagon IV (contd)				
$\angle(C_{10}-C_{28}-C_{29})$	115.7(9)	115.2	115.8(7)	115.4
$\angle(C_{28}-C_{29}-C_2)$	114.0(16)	112.4	114.0(9)	112.1
$\angle(C_{29}-C_2-C_3)$	118.0(7)	118.8	118.6(23)	119.0
hexagon V[d]				
$\angle(C_1=C_2-C_{29})$	125.6(9)	124.9	125.4(22)	124.7
$\angle(C_2-C_{29}-C_{30})$	114.6(7)	113.7	114.9(10)	113.9
$\angle(C_{29}-C_{30}-C_{50,47})$	117.2(18)	116.7	117.2(4)	117.3
$\angle(C_{30}-C_{50,47}-C_{46})$	116.7(16)	117.4	116.1(4)	116.3
$\angle(C_{50,47}-C_{46}-C_1)$	112.5(8)	113.4	113.7(14)	114.3
$\angle(C_{46}-C_1=C_2)$	122.9(12)	124.8	122.2(22)	124.8
hexagon VI[d]				
$\angle(C_{23}-C_5-C_1)$	111.8(11)	112.7	111.8(14)	113.1
$\angle(C_5-C_1-C_{46})$	115.9(10)	118.6	116.5(20)	118.6
$\angle(C_1-C_{46}-C_{47,50})$	111.4(5)	113.3	110.3(10)	112.3
$\angle(C_{46}-C_{47,50}-C_{22})$	116.8(24)	115.9	117.0(6)	117.0
$\angle(C_{47,50}-C_{22}-C_{23})$	119.8(29)	120.4	120.0(4)	120.0
$\angle(C_{22}-C_{23}-C_5)$	116.2(14)	116.2	115.6(8)	116.0
av values within hexagons				
$\angle(C-C=C)$	124.2(3)	124.9	123.8(4)	124.8
$\angle(C-C-C)$	116.6(3)	117.2	116.4(3)	116.7

[a] For meaning of double subscripts see footnotes to Table 1. [b] Uncertainties in parentheses are estimated standard deviations. [c] Reference 6. [d] See Figure 2 for identity of pentagons and hexagons via atom numbers.

TABLE 3: Average Spherical Radii (r_a/Å) of Carbon Atoms in the Most Probable Isomers of $C_{60}F_{48}$

parameter[a]	D_3		S_6	
	exptl[b]	theor[c]	exptl[b]	theor[c]
$R(1)$	3.018(14)	3.096	3.017(11)	3.098
$R(2)$	3.190(15)	3.102	3.180(15)	3.106
$R(3)$	3.791(18)	3.792	3.791(30)	3.792
$R(4)$	3.915(21)	3.937	3.925(22)	3.935
$R(5)$	3.773(11)	3.788	3.777(12)	3.784
$R(16)$	3.771(11)	3.771	3.767(8)	3.773
$R(17)$	3.955(16)	3.972	3.951(9)	3.959
$R(18)$	3.941(21)	3.954	3.943(9)	3.951
$R(19)$	3.787(23)	3.777	3.779(14)	3.783
$R(20)$	3.938(14)	3.923	3.929(11)	3.938
averages				
$\langle R(C_{sp^2})_{atom1}\rangle$[d]	3.018(14)	3.096	3.017(11)	3.098
$\langle R(C_{sp^2})_{atom2}\rangle$[d]	3.190(15)	3.102	3.180(15)	3.106
$\langle R(C_{sp^3-sp^2})\rangle$[e]	3.781(18)	3.782	3.778(20)	3.783
$\langle R(C_{sp^3})\rangle$[f]	3.937(23)	3.947	3.937(17)	3.946

[a] The first 10 items are radial distances from center of the carbon sphere to the indicated atom. [b] Values in parentheses are standard deviations. [c] Reference 6. [d] Average distance from center of the sphere to atoms in C═C groups; see text. [e] Average distance from center of the sphere to atoms adjacent to C═C groups. [f] Average distance from center of the sphere to atoms not adjacent to C═C groups.

between two five-member rings and those within five-member rings, which have respective lengths (r_a) equal to 1.398(10) and 1.455(6) Å.[1] When 48 fluorine atoms become attached to the carbons in C_{60} to form $C_{60}F_{48}$, the bonds formed by these carbons are now essentially sp^3, which is a type that is normally longer than sp^2 by several hundredths of an ångström. In $C_{60}F_{48}$ these sp^3 bonds are themselves of two types depending on whether both ends of the carbon−carbon link are also attached to fluorine atoms (sp^3−sp^3 bonds) or whether only one end has an attached fluorine atom (sp^2−sp^3 bonds). The resulting differences between the skeletons of C_{60} and $C_{60}F_{48}$ are found in the data of Table 3. In C_{60}, all atoms are equidistant (3.555 Å) from the center of the sphere. It is clear that the transformation of 48 nominally trigonal carbon atoms in C_{60} to tetrahedral ones in $C_{60}F_{48}$ will lead to different spherical radii for the carbon atoms with different types of bonding. As was found in the crystallographic work,[8] the distances from the center of the $C_{60}F_{48}$ sphere to the carbon atoms fall into three groups: distances to the doubly bonded carbon atoms, those to the atoms adjacent to doubly bonded atoms, and those to the sp^3 atoms linked only to other sp^3 atoms. As Table 3 shows, the average spherical radius (i.e., the average of the two tabulated items) to the doubly bonded atoms is about 0.4 Å less than the C_{60} value of 3.555 Å, but the radii to the carbon atoms adjacent to the double bonds, and to those not adjacent, are respectively greater than the C_{60} value by 0.2 and 0.4 Å.

Since both the D_3 and S_6 forms of the molecule have the same number of bonds of each type, one might expect similar average values for each bond type in molecules of each symmetry. As Table 1 shows, this expectation is borne out: there is no difference between the average values for the C═C bond in the D_3 and S_6 models, nor in the $C_{sp^3}-C_{sp^3}$ type, and the $C_{sp^2}-C_{sp^3}$ type differs by only 0.002 Å, each well within the listed uncertainties. These average values are the most precise measurements of the many parameters because, unlike the values for the individual distance types, they change only slightly as the refinement conditions are changed.

Typical r_g values for a $C_{sp^2}-C_{sp^3}$(F) bond are about 1.49 Å: examples are 1.493(9) Å in 3,3,3-trifluoropropene-1[14] and 1.493(14) Å in 1-chloro-3-fluoropropene-1.[15] These are very close to our r_a distances for the same type of bond in $C_{60}F_{48}$. (r_g values are typically about 0.003−0.005 Å longer than r_a, but the uncertainties associated with the cited values and with our experimental one suggest the difference is not detectable.) On the other hand, the average C_{sp^3}(F)−C_{sp^3}(F) bond in $C_{60}F_{48}$ is about 0.05 Å longer than the "normal" value for such bonds in aliphatic hydrocarbons (it is 1.537(3) Å in neopentane[16]), and 0.07 Å greater than those in molecules with fluorine atom ligands, such as monofluoroethane (r_a = 1.512(3) Å)[17] or 1,2-difluoroethane (r_g = 1.503(3) Å).[18] Why is it that the $C_{sp^3}-C_{sp^3}$ bonds are much longer than normal? A plausible answer lies in the effect of strain that arises when a set of 48 sp^3 carbon atoms are created from sp^2 ones on the surface of a C_{60} sphere. These atoms must lie at a greater distance from the center of the sphere than the remaining 12 sp^2 atoms in order to move the bond angle from the average nominal planar value of 120° toward the nominal tetrahedral value of 109.5°. Such a repositioning of the 48 converted atoms, constrained by the requirement of near planarity for the bonds to the 12 sp^2 carbons, inevitably leads to both bond-angle and bond-distance strain which is distributed in a way to lengthen the single bonds and increase the bond angles at sp^3 carbon atoms from their preferred value of 109.5°. The bond-distance changes can be seen in a comparison of the values in Table 1 with the C_{60} values of 1.455(6) Å and 1.398(10) Å, and the bond-angle changes in a comparison of the values in Table 2 with those expected for the interior of approximately planar pentagons (108°) and hexagons (120°).

The positions of the fluorine atoms on the C_{60} skeleton, particularly with respect to the carbon−carbon double bonds, is of interest because the positions should reflect the nature of any mutual interaction. Unfortunately, these positions are very difficult to determine. However, it appears that the fluorines are bent slightly toward the double bonds rather than away as was suggested by the theoretical work.[7] The evidence is seen in a comparison of the three F−C−C bond angles where the carbon atom holding the fluorine is bonded to one sp^2 carbon and two sp^3 carbons. In this case the average value of the $F-C-C_{sp^2}$ angle is about 4° smaller than $F-C-C_{sp^3}$ in both D_3 and S_6 symmetries − 108.0° vs 104.3° with standard deviations of about 2.0°. The overall average F−C−C average is 106.0(24)°.

The amplitudes of vibration associated with the 900+ interatomic distances, which were refined in several groups, are reasonable. For the C−C/C−F bonds their average is 0.057/0.055 Å, but the amplitude for C═C could not be refined and was set to 0.046 Å. The average nonbond C···C values range from 0.06 to 0.13 Å, the C···F from 0.09 to 0.18 Å, and the F···F from 0.11 to 0.20 Å.

Our parameter values for $C_{60}F_{48}$ are seen from Tables 1−3 to be in good agreement with the theoretical ones of CK. A comparison of the gas-phase structure of $C_{60}F_{48}$ obtained here and that in the crystal[8] also has interest. The C═C double-bond length in the crystal for molecules of D_3 symmetry was found to be 1.301(4) Å, somewhat shorter than our average of 1.331(6) Å, but the crystallographic average for the C−F bond length at 1.374(11) Å is about the same as ours, 1.367(3) Å, when allowance is made for the uncertainties. The $C_{sp^2}-C_{sp^3}$ and $C_{sp^3}-C_{sp^3}$ bond lengths in the crystal respectively average to 1.518(19) and 1.578(29) Å, in good agreement with our values for the D_3/S_6 molecules of 1.502(8)/1.500(11) and 1.582(22)/1.584(20) Å. (The crystallographic averages are our calculations based on the published values.) The uncertainties associated with these averages are estimates of one standard deviation for both the X-ray work and the present study.

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Supporting Information Available: Table S1 containing the Cartesian coordinates for both models presented in the text and Table S2 containing the scattered intensity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) For those unfamiliar with the units used in this article, 1 kcal = 4.184 kJ and 1 Å = 0.1 nm.

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