Quantitative Electron Crystallographic Determinations of Higher Fullerenes in the Hexagonal Close Packed Polymorph

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The hexagonal closed packed crystal structures of the higher fullerenes, C76, C78, and C84, have been determined at room temperature in the [001] projection from single crystal electron diffraction intensity data. In all cases, the molecules in the crystal are rotating freely about their centers. As part of the structure analysis, independent determination of average molecular radii (a continuous variable in the structure factor calculation) yields values in reasonable agreement with predicted values for these molecules.

Introduction

In the 15 years since their discovery,[1] the buckminsterfullerenes have remained fascinating to crystallographers as a unique solid state form of carbon. The most abundant C60 and C70 species, with respective soccer and rugby ball shapes, have been extensively studied at various temperatures by a variety of diffraction techniques.[2−4] At room temperature they have been shown to crystallize as rotationally disordered molecules in either a face centered cubic (fcc) structure or a hexagonal closed packed (hcp) form. The fcc structure is preferred for C60, although the latter form can be crystallized when there is a small amount of impurity.[5] The latter hcp packing is preferred for C70 when grown at room temperature, but the former fcc structure can be crystallized when the nucleating substrate is maintained at an elevated temperature.[6] In any case, stacking faults[6,7] are commonly observed that retain the features of both polymorphs, i.e., the ABAB stacking or ABCBA twins. Quantitative crystal structures have been published for these molecules[2,3] with discussions of preferred orientations for C60. Although the crystallization of C60 is not much influenced by solvent effects,[8] that of the oblong C70 definitely is.[5]

Quantitative structural information has been less abundantly available for the higher fullerenes, e.g., C76, C78, and C84. Electron microscopy and diffraction of C76 and C84 again indicates the preference for face centered cubic packing,[9,10] substantiated by powder X-ray diffraction studies.[11,12] From such studies, a linear relationship has been demonstrated[9] for the increase of predicted average molecular radius with measured lattice constant in a series including C60, C70, C76, and C84.

The hexagonal close packed structure is less well characterized for these higher fullerenes than is the face centered cubic form. For this reason, electron crystallographic analyses of deposited films, the first quantitative single crystal determinations for the higher fullerenes, is described in this paper.

Materials and Methods

Fullerenes and their Crystallization. The fullerenes C76, C78, and C84 were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. C76,

described[13] as having D_2 (222) point group symmetry, is, therefore, chiral. While five structural isomers are possible for C78, two are commonly observed.[13,14] The major form has C_{2v} (*mm*2) symmetry and the minor, chiral, form has D_3 (32) symmetry. The latter C84 cluster can exist as 24 isomers. Two are often found in a 2:1 ratio.[13] These, respectively, have D_{2d} ($\bar{4}$2m) and D_2 (222) point group symmetry. Whereas the first two fullerenes have a significant aspect ratio to give them molecular shape characteristics reminiscent of C70, the latter C84 is nearly spherical in both isomeric forms, and is expected to resemble C60 in its crystallization behavior. Again, all of the samples have been examined as they have been received from the vendor and some, therefore, are expected to contain more than one structural isomer.

Crystals of the fullerene were grown by vapor deposition in vacuo onto heated substrates, either cleaved KCl crystal faces or mica, following earlier preparative descriptions.[4,6,9,10] The best results were obtained on the KCl substrates when they were maintained near 310 °C. After the substrates were cooled, a backing layer of amorphous carbon was deposited on top of the crystals. The combined film was then floated from the salt (or mica) face onto a distilled water surface. These films were then picked up with bare 300 mesh copper electron microscope grids and were allowed to dry before investigation in the electron microscope.

Electron Diffraction and Microscopy. Because the lateral crystallite size for the fullerenes is very small, in accord with previous observations,[1,15] conventional selected area diffraction techniques are not appropriate. Instead a microdiffraction mode, similar to the method described by Riecke,[16] was employed. Thus, the condenser lens system was utilized to isolate the crystalline area, ensuring an illumination diameter on the crystal of less than 1.0 μm. All electron diffraction experiments were carried out at room temperature and at 100 kV with a JEOL JEM-100CX II electron microscope. A 20 μm aperture was inserted into the second condenser lens and the illumination was minimized by full excitation of the first lens. Single-crystal patterns were recorded on Kodak DEF-5 screenless X-ray film, and the diffraction camera length was calibrated against a

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powder diffraction pattern from a gold film deposited onto one edge of the electron microscope grid.

High-resolution, low-dose electron micrographs were also obtained from some of the preparations, at magnifications of 140K and 270K. Two-dimensional lattices were very much in evidence, but in contrast to our previous studies of the C70 structure,[4] we have not utilized such images quantitatively for crystallographic phase determination. Excellent lattice images of C76 and C84 have been published previously.[9,10]

Electron diffraction patterns were scanned on a Joyce Loebl Mk IIIC flat-bed microdensitometer, and the traces of these scans were used to determine peak intensities as a triangular approximation of their areas. As is usual in the electron crystallography of microcrystals,[17] no Lorentz correction was applied to the raw intensities, so that the observed structure factor amplitudes were related simply to their square roots. Independent evaluations of $hk0$ diffraction patterns were made to establish the reproducibility of the intensity measurements[18] and, for extraction, of intensities. Symmetry equivalents were also averaged, after first ensuring that these values were self-consistent. Some difficulty was experienced for C84, for which a fully symmetric hexagonal closed pack structure was not commonly observed. The best patterns were obtained from slightly irregularly bent crystals so that the more stringent controls for accepting intensity data from the C76 and C78 preparations were relaxed somewhat. There was an accordant increase of the best crystallographic residual value in the analyses for this fullerene.

Crystal Structure Analysis. The hexagonal close packed structure assumes that the molecules are freely rotating in the unit cell. We have used the structure factor expression given by Andre et al.[19] for this analysis, i.e.

$$F_h = \sum_{i=1}^{n} f_i' \frac{\sin 2\pi r_i s}{2\pi r_i s} \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_c) \tag{1}$$

The electron scattering factor for carbon, adjusted for thermal motion, was multiplied by the Fourier transform of a disk (projection of a sphere) of radius r_i. In the latter exponential expression for the lattice transform (space group $P6_3/mmc$, plane group $p6m$), all unique lattice sites r_c were included. For the structure factor calculation, therefore, the quantity r_i, the effective average molecular diameter, was the continuous variable to be tested against the experimental structure factor magnitude, $|F_{obs}|$.

Results

Consistent with expectations for vapor deposition onto substrates held at high temperature,[6,9,10] the most commonly encountered crystalline form for the higher fullerenes was the face centered cubic (fcc) polymorph, space group $Fm3m$, in its [111] projection. An electron diffraction pattern is shown for C76 in Figure 1a, including weak reflections due to stacking faults.[9] Symmetrical diffraction patterns from hexagonally close packed (hcp) arrays were most commonly observed for C76 (Figure 1b) with about 26% occurrence. The measured hcp unit cell constant for C76 is $a = 11.00$ (5) Å. Corresponding measured values for C78 (15% occurrence) and C84 (25% occurrence) are $a = 11.12$ (6) and 11.34 (6) Å, respectively. The fcc lattice spacing is related to the hcp value by $a_{fcc} = \sqrt{2}a_{hcp}$. By independent measurement of such structures packing in the respective crystalline forms and by consultation of previous measurements from X-ray and electron diffraction experiments,[2-12] there appeared (Figure 2) to be an approximate
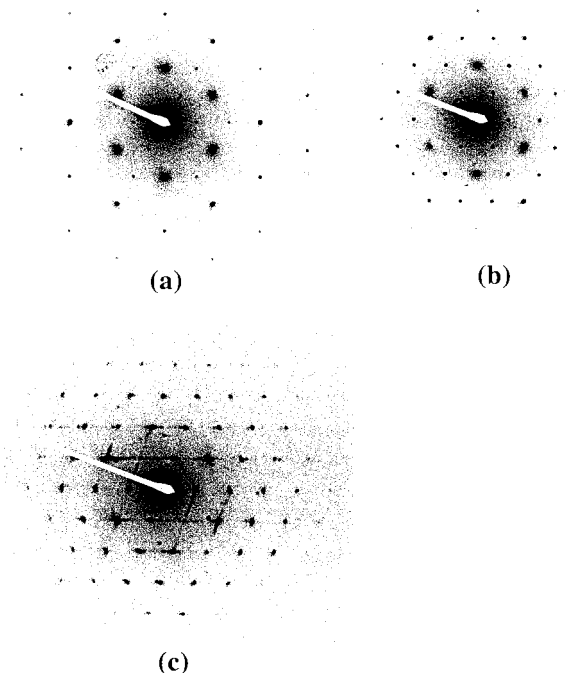

Figure 1. Electron diffraction patterns from C76 deposited on KCl plates. (a) fcc pattern with weak forbidden reflections due to stacking faults. (b) hcp pattern. (c) pattern with disorder, perhaps due to translational shifts.
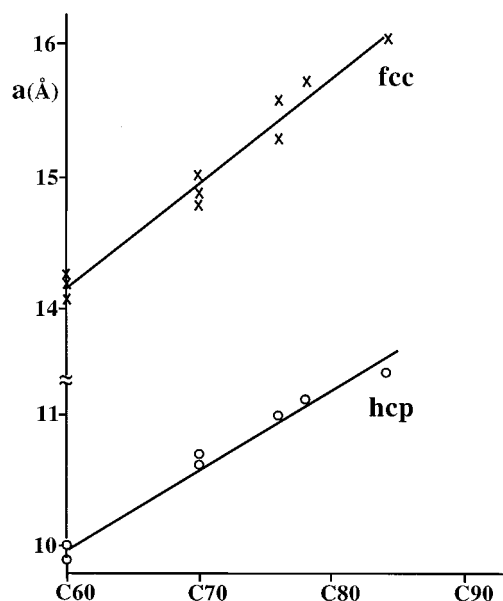

Figure 2. Plot of lattice constants for hcp and fcc structures of the fullerenes Cn vs carbon number n.

linear relationship of the lattice constants with increasing carbon number of the fullerenes. The diffraction symmetry of the hcp form of C84 often broke the strictly hexagonal distribution, for reasons that are not understood. For all molecules, some electron diffraction patterns are also obtained from an intermediate form somewhat between the hcp and fcc structures. (Such patterns from crystal forms with unspecified structure, undoubtedly the result of stacking disorder, occurred at about the same frequency as the readily identified hcp polymorph.) Occasionally, streaked patterns (Figure 1c) are also observed.

Using the molecular radius as a continuous variable in eq 1, the best fit of the calculated structure factors for C76 occurred
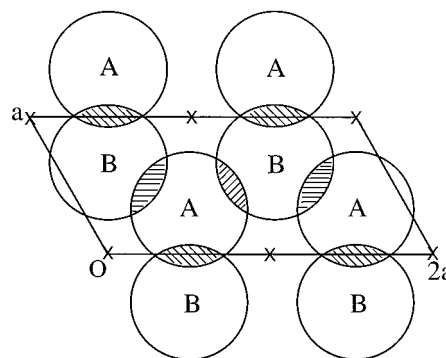
TABLE 1: Calculated and Observed Structure Factor Magnitudes for Higher Fullerenes in the Hexagonal Close Packed Form

$hk0$	$|F\text{obs}|$	$|F\text{calc}|$
	C76	
100	0.93	1.13
200	0.85	0.85
300	1.15	1.05
400	0.23	0.26
110	2.07	2.23
210	0.51	0.35
310	0.14	0.04
410	0.26	0.31
220	0.39	0.35
320	0.24	0.25
420	0.25	0.16
330	0.24	0.29
	C78	
100	0.94	0.94
200	0.89	0.75
300	1.19	1.02
110	1.99	2.24
210	0.46	0.45
220	0.07	0.14
	C84	
100	0.94	0.93
200	0.94	0.77
300	1.15	1.17
400	0.38	0.40
500	0.17	0.25
110	2.25	2.83
210	0.66	0.70
310	0.30	0.28
410	0.24	0.12
510	0.19	0.04
220	0.33	0.23
320	0.33	0.14
420	0.25	0.19
520	0.26	0.31
330	0.29	0.45
430	0.27	0.16

Figure 3. Arrangement of rotationally disordered fullerene spheres in the hexagonal close packed form. The separate A and B layers are superimposed.

TABLE 2: Comparison of Molecular Radii (Å) Determined from Crystallographic Analyses with Predicted Values[10]

molecule	r(obs)	r(calc)
C60	3.55	3.55
C70	3.88	3.83
C76	3.93	4.00
C78	4.10	4.05
C84	4.35	4.20

TABLE 3: Observed and Predicted Values for Hexagonal Cell Edge (a) of the hcp Fullerenes in (Å)

molecule	a(meas)	a(calc)
C60	10.02(3)	10.01
C70	10.70(8)	10.58
C76	11.00(5)	10.90
C78	11.12(6)	11.01
C84	11.34(6)	11.31

C60. Therefore, the apparent linear relationship in Figure 2 cannot be rigorously correct since the change in lattice constant a with fullerene carbon number n should be a quadratic equation, as indicated. A comparison of calculated values, $a = d(Cn) + 2.91$ Å, with observed values also revealed a reasonable fit (Table 3) within the ca. 1% error of the measured lattice constant.

at $r_i = 3.93$ Å, where $R = 0.14$ (Table 1). For C78, the resolution of the hexagonal diffraction pattern is somewhat lower. An optimal R-value minimum (0.12) was identified at the radius 4.10 Å (Table 1). The minima are somewhat shallow so that there is an approximate 3% uncertainty in the radius determination for these two fullerenes. For the C84, the minimum ($R = 0.21$) occurred at $r_i = 4.35$ Å, somewhat larger than the predicted value. Note that the resolution of this data set is comparable to that of C76 but the violation of strict hexagonal symmetry of the diffraction patterns may affect the intensity measurements for this fullerene, as evidenced by the rather large residual value.

In the calculation of structure factor magnitudes for all materials, a very small isotropic temperature factor, near $B = 0.0$ Å^2, was used. That a more typical value for organic molecules (e.g., $B = 6.0$ Å^2) did not lower the crystallographic residual indicates that the data were compromised slightly by multiple scattering effects.[4] Potential maps calculated from phased structure factor amplitudes resembled the hcp structural maps published earlier for fullerite.[20] The nature of the spherical packing in the [001] projection is shown in Figure 3.

Combining these independent determinations of molecular radii with those obtained earlier[2,4] for C60 ($r_i = 3.55$ Å) and C70 ($r_i = 3.88$ Å), one can calculate the average distance between molecular spheres, from ($a_{hcp} - 2r_i$). This value is 2.91 (18) Å, in accord with previous observation.[11] Experimentally determined radii are compared in Table 2 to those calculated[10] from $d(Cn) = 7.1(n/60)^{1/2}$ (Å), where 7.1 Å is the diameter of

Discussion

The foregoing crystal structure analyses for three higher fullerenes in the hcp form complements the previous powder X-ray determinations for two of them in the fcc structure.[11,12] These results also can be correlated to observations for pure C60 and C70. While the nearly spherical C84 in a single molecular form may prefer the fcc structure, the presence of two isomers may also promote the hcp packing in a way found when just 2% of C70 is cocrystallized in a solid solution[5] with C60. The rugby-ball-like C76, which has one isomeric form, also resembles the latter C70 in its hcp packing, but the fcc can be nucleated at higher temperature.[9] Obviously, all evidence of chirality is obliterated by the spherical averaging of the freely rotating molecule in the crystal.

Diffraction from the newly examined C78 is somewhat puzzling. There are two predominant isomeric forms, but one is greatly preferred.[13,14] The significant loss of diffraction resolution (Table 1), compared to C76 or C84, however, may denote a co-packing of two species to form a solid solution, which induces significant substitutional disorder. The chemical frameworks[14] for the two molecular species seem to have somewhat different shapes, one with an end that is bowl shaped and the other with a flattened molecular tip. Lower resolution

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is also commonly observed in the recorded fcc electron diffraction patterns from this molecule. The loss of diffraction resolution is much more significant than that found for the hcp forms of fullerites[20] or the 2% solid solution[5] of C70 with C60.

It is also gratifying to find that quantitative electron crystallographic analyses can independently determine the average molecular radius (Table 2) and therefore the effective intermolecular packing distance. Due to the shallowness of the *R*-factor minimum vs change in r_i, mentioned above, the radii are not well specified, however. The measurement is also compromised somewhat by multiple scattering perturbations. However, the values for C76 and C78 seem to be just as accurate as those found in independent Rietveld refinements of, e.g., C76. In this cited X-ray determination,[11] r_i = 3.9 Å was given with a ±0.1 Å standard deviation. On the other hand, because it was nearly impossible to identify a truly hexagonally symmetric hcp pattern from C84, the radius listed in Table 2 may be incorrect due to errors in the measured diffraction intensities.

Different molecular architectures and symmetries (even formally chiral ones) for the higher fullerenes, therefore, lead to a rotationally averaged centrosymmetric packing of spheres, identical with the previously studied case of the more abundant C60 and C70 fullerenes.[2−4] The favored crystal structure depends mostly on the molecular aspect ratio, although preparative conditions can influence the final crystal form. When it is near unity, the face centered cubic structure is favored. When the aspect ratio is larger than unity, the hexagonally close packed form is encountered. Coexisting isomers promote solid solutions similar to the fullerites and will also promote the hcp crystal form.

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