A Crystallographic Analysis of C_{60} (Buckminsterfullerene)

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Crystallographic analysis of C_{60} grown from a hexane solution revealed a structure which is neither hexagonal nor cubic closest packed [space group $P6_3/m$, a = 33.54(1), c = 10.113(8) Å]; packing models which are consistent with the Patterson map are described.

As a newly isolated form of elemental carbon,[1] the solid state structure of C_{60} (Buckminsterfullerene)[2] is of considerable current interest. Kratschmer *et al.* have reported electron and X-ray diffraction studies of C_{60} powder and crystals obtained from benzene.[1a] They interpreted their data by 'assuming that the C_{60} molecules are behaving approximately as spheres stacked in a hexagonal close-packed (hcp) lattice with a c/a ratio of 1.633,' and calculated lattice constants a = 10.02 Å and c = 16.36 Å. This conforms with the expected size of C_{60} (nearest-neighbour distance 10.02 Å) and the measured density of their crystals (calculated density 1.678 g cm^{-3}, flotation density 1.65 ± 0.05 g cm^{-3}). However, 'the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions' suggested significant disorder. Fleming has determined a face-centred cubic (fcc) lattice for crystals of C_{60} grown by sublimation.[3] This structure contains C_{60} molecules in a cubic-close-packed (ccp) arrangement. The lattice constant a = 14.198(1) Å at 25 °C corresponds to a van der Waals diameter of 10.04 Å, consistent with Kratschmer's data. We have grown a crystal of C_{60} from solution which is not as efficiently packed as the hcp and ccp forms reported previously, and describe here the crystallographic analysis of this new crystalline form of pure carbon.

A shiny black 1.5 × 1.5 × 0.6 mm polyhedral crystal of C_{60} was obtained by the slow evaporation of a hexanes solution. A 0.15 × 0.30 × 0.30 mm fragment was carved from this material† and found to be a single crystal based on Laue photographs. Precession photographs indicated hexagonal Laue symmetry and yielded preliminary cell dimensions which agreed with those obtained by the detailed X-ray analysis.‡ The crystal was found to have a different unit cell than that of crystals obtained from benzene[1a] or *via* sublimation.[3] The average value of F^2 in the data set fell off very rapidly with $\sin(\theta)/\lambda$, implying that there is either extensive thermal motion in the crystal or that there is significant disorder. Consequently, the structure could not be solved completely.

A Patterson synthesis revealed several very strong vectors which were in the length range of 9.8–11.2 Å. These and the other strong Patterson vectors were interpreted as overlapping intermolecular C–C vectors and analysed to give the predicted centroids for two independent half-molecules of C_{60} in the asymmetric crystallographic unit. Analysis of the Patterson peaks gives strong restraints on the locations of the centroids of the molecules, as does the fact that the length of the c-axis (10.11 Å) is close to the van der Waals diameters obtained by Kratschmer[1a] and Fleming[3] (10.02 and 10.04 Å).

Two models were found to be consistent with the Patterson map. In the 'triangle' model, the molecules form triangular units of six molecules in the ab plane with one independent molecule on the inside and the other at the points. These then alternate in the z-direction at z = 1/4 and z = 3/4 (Fig. 1). The 'triskele' model can be derived from the 'triangle' model by moving one of the two independent molecules from z = 1/4 to z = 3/4 (Fig. 2). Attempted refinement of these models using artificial 'atoms' with a scattering factor based on the overall disordered scattering factor from an idealised model of C_{60} led to R values of 49% for the 'triangle' model and 56% for the 'triskele' model. Inclusion of an idealised molecule of C_{60} at each centroid position did not significantly change the R

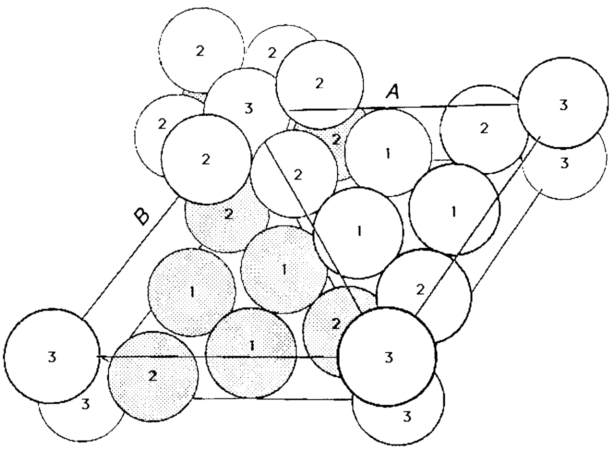

Fig. 1 'Triangle' model for packing of C_{60} molecules (represented by spheres of radius 3.0 Å for clarity). Molecules in the z = 3/4 plane are shaded. The two symmetry independent molecules are labelled 1 and 2. The 13th molecule in the unit cell (disordered, see text) is labelled 3.

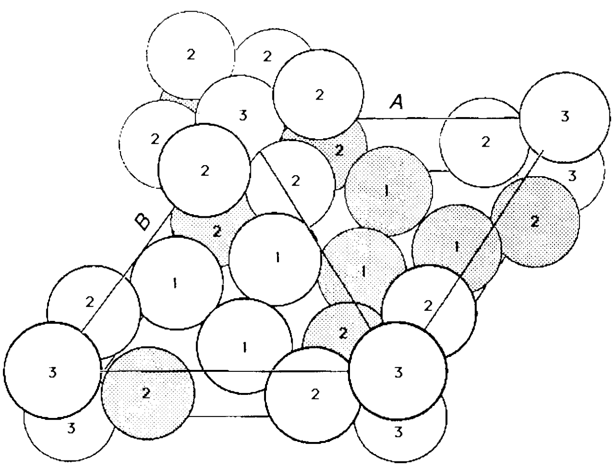

Fig. 2 'Triskele' model for packing of C_{60} molecules (represented by spheres of radius 3.0 Å for clarity). Molecules in the z = 3/4 plane are shaded. The two symmetry independent molecules are labelled 1 and 2. The 13th molecule in the unit cell (disordered, see text) is labelled 3.

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† The remaining material showed C_{60} in the electron impact mass spectrum and was determined to be a >99 : 1 mixture of C_{60} and C_{70} according to HPLC.[4]

‡ *Crystal data* for C_{60}: T = −63 °C, M = 720.7, space group $P6_3/m$, a = 33.54(1), c = 10.113(8) Å, U = 9853(14) $Å^3$, Z = 13, D_c = 1.57 g cm^{-3}, D_m = 1.56(1) g cm^{-3}. Of 4868 reflections collected, Mo-Kα, $2 \leq 2\theta \leq 45°$, 4587 were unique. The final residuals for 325 variables refined against the 1031 data for which $F^2 > 1.5\sigma(F^2)$ were R = 28.3%, R_w = 19.8% and GOF = 4.52. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

values until each molecule was slightly rotated around the *c*-axis, giving a small reduction in the *R* value. Refinement of the individual carbon atoms of the model then reduced the *R* values to 28% for the 'triangle' model and 35% for the 'triskele' model. Both of these models have 12 molecules per unit cell and feature a hole running along the *z*-axis at the origin. The observed density of these C_{60} crystals, 1.56(1) g cm^{-3} measured by flotation in CsCl (aq.), combined with the cell volume, indicates that there are 13 molecules in the unit cell. Given the constraints of the space group, the 13th molecule in the unit cell must be almost completely disordered. It may reside in the hole along the *z*-axis, as represented in the figures.

This X-ray analysis of C_{60}, combined with those reported by others,[1a,3] establishes that the solid state structure of this form of elemental carbon is variable and dependent on the conditions of crystallisation.

J. M. H. is grateful to the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (New Faculty Grant), the Shell Oil Company Foundation (Shell Faculty Fellowship), Xerox Corporation, Monsanto Company and the Merck Sharp & Dohme Research Laboratories for financial support. J. R. H. thanks the NASA SETI Foundation and R. J. S. thanks the National Science Foundation for support.

Received, 18th December 1990; Com. 0/05706A

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