10. When the sample is directly compressed between the anvils, the pressure in the central region of the sample becomes higher than that in the peripheral region and phase boundaries appear circular as a result of the pressure gradient.
11. L. Merrill and W. A. Bassett, *Rev. Sci. Instrum.* **45**, 290 (1974).
12. We determined sample temperatures to ±~2°C by monitoring the temperature of the DAC with a Chromel-Alumel thermocouple attached to the cell body. We established the relation between the sample temperature and the DAC temperature in a separate experiment by putting another thermocouple between the anvils. Once the relation between the temperature and the appearance of the sample (the number of the boundaries, uniformity of surface, and so on) was determined, the sample temperature could be roughly estimated (to ±~5°C) only by observing the appearance of the sample.
13. R. J. Hemley, L. C. Chen, H. K. Mao, *Nature* **338**, 638 (1989).
14. D. D. Klug, O. Mishima, E. Whalley, *Physica B* **139–140**, 475 (1986).
15. H. K. Mao, P. M. Bell, J. W. Shaner, D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
16. Y. P. Handa, O. Mishima, E. Whalley, *J. Chem. Phys.* **84**, 2766 (1986).
17. J. P. Poirier, *Nature* **314**, 12 (1985).
18. K. Takemura, O. Shimomura, K. Tsuji, S. Minomura, *High Temp. High Pressures* **11**, 311 (1979).

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The Structure of the C_{60} Molecule: X-Ray Crystal Structure Determination of a Twin at 110 K

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Single-crystal x-ray diffraction methods were used to determine the crystal and molecular structure of C_{60} buckminsterfullerene. At 110 kelvin C_{60} is cubic, apparent Laue symmetry *m3m*, but it exhibits noncrystallographic systematic extinctions indicative of a twin in which *I(hkl)* and *I(khl)* are superimposed. In fact, C_{60} crystallizes with four molecules in space group $T_h{}^6$–$Pa\bar{3}$ of the cubic system (Laue symmetry *m*3) with lattice constant *a* = 14.052(5) angstroms (Å) at 110 kelvin. The twin components are equal. A given component, which has crystallographically imposed symmetry $\bar{3}$ (C_{3i}), displays an ordered structure of a truncated icosahedron. The five independent C=C bonds that join C_6 rings average 1.355(9) Å; the ten independent C–C bonds that join C_6 and C_5 rings average 1.467(21) Å. The mean atom-to-atom diameter of the C_{60} molecule is 7.065(3) Å. The molecules are very tightly packed in the crystal structure, with intermolecular C···C distances as short as 3.131(7) Å.

THE RECENTLY DEVELOPED LARGE-scale production (*1, 2*) and separation (*3*) methods for the all-carbon molecules C_{60}, C_{70}, $C_{76/78}$, C_{84}, and C_{94} (fullerenes) have opened up new vistas in organic and organometallic chemistry. Applications of these new substances to various aspects of material science, including superconductivity (*4, 5*), ferromagnetism (*6*), and the production of diamond films (7), also appear to be promising. C_{60} (buckminsterfullerene), which is the most abundant fullerene to be generated, has been the object of much experimental and theoretical scrutiny over the past year. Structural characterization has included determination of the space group *Fm*3 (*8*) or *Fm*3*m* (*9*), *a* = 14.2 Å at room temperature, with a first-order phase transition at 249 K (*10*) to a primitive cubic cell, *a* = 14.04(1) Å at 11 K (*10*). The radial distribution function, obtained in neutron diffraction measurements on C_{60} powder at 300 K (*11*), contains 13 distinct features that have been assigned to all possible C–C separations across a truncated icosahedral molecule, as first proposed for this molecule by Kroto *et al.* (*12*).

Although nuclear magnetic resonance (NMR) measurements (*13, 14*), whose time scale differs from that of diffraction studies, suggest the possibility of rapid, nearly isotropic rotation of C_{60} even below 249 K, synchrotron x-ray powder diffraction results (*10*) establish beyond doubt that orientational ordering in C_{60} sets in at the transition temperature. These data can be successfully fit with the use of an idealized (*15*) icosahedral geometry for the C_{60} molecule in space group $Pa\bar{3}$ (*16*). Although a satisfactory refinement is obtained with a constrained rigid model that involves as a variable an angle of rotation of a given molecule about its local $\bar{3}$ axis, refinement of an unconstrained model that would reveal the details of the molecular geometry did not prove possible (*17*). This constrained rigid model is consistent with neutron diffraction measurements on C_{60} powder at 14 K (*18*). Low-temperature solid-state ^{13}C-NMR measurements with use of Carr-Purcell sequencing (*19*) have also established icosahedral molecular symmetry while providing limits on the two unique (in this symmetry) C–C bond distances [1.40(2) and 1.45(2) Å], in good agreement with the Hartree-Fock calculations of Scuseria (*15*) (1.370 and 1.448 Å). Similarly, a number of vibrational spectroscopic probes (*20, 21*) of C_{60} thin films are consistent with the presumed molecular structure. While single-crystal x-ray structures, determined without geometrical constraints, for chemically derivatized C_{60} [$C_{60}(OsO_4)(4\text{-}t\text{-butylpyridine})_2$ (*22*) and $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})\cdot C_4H_8O$ (*23*)] in fact show perturbed icosahedral frameworks, the x-ray crystal structure of pure, underivatized C_{60} has remained elusive. Here we present such a structure.

C_{60}-containing soot was prepared by contact-arc evaporation of graphite under He (*1, 24*). Fullerenes were extracted in toluene, and C_{60} was separated from C_{70} and higher carbon clusters by column chromatography (*3*). The C_{60} sample was washed in cold cyclohexane to remove possible hydrocarbon contaminants. It was further purified by partially redissolving it in benzene and filtering the residual solid. Crystals obtained after allowing the benzene to evaporate were dissolved in hot cyclohexane. The solution was slowly cooled to room temperature and then to 195 K. C_{60} crystals were harvested upon subsequent warming of the frozen solution to room temperature. Their purity was ascertained by infrared (IR), Raman, and fast atom bombardment (FAB) mass spectroscopy.

Several crystals were examined by x-ray methods in the temperature range 150 to 110 K with similar results. Ultimately, x-ray diffraction data were collected from a crystal of approximate dimensions 0.2 mm by 0.2 mm by 0.3 mm that had been placed in the cold stream (110 K) of a Nonius CAD4 diffractometer. Of the 4914 observations [$h,k,l \geq 0$, $\theta(CuK\alpha) \leq 75°$; $h,k,l \leq 0$, $\theta(CuK\alpha) \leq 50°$], 3168 have $I \geq 3\sigma(I)$, a clear indication of the lack of disorder. The observations conform to Laue symmetry *m*3*m*, with an *R*-index for averaging of 5.2%. However, the data display systematic extinctions of the zonal reflections when both indices are odd. The presence of these noncrystallographic extinctions is a reasonably certain manifestation of twinning (*25*). These extinctions can be understood if the material is a twin with equal or nearly equal components, each of which is in space group $T_h^6 - Pa\bar{3}$; this is a particularly attractive explanation, since the synchrotron x-ray powder data have been very well fit with an idealized molecule in this space group (*16*). Consequently, such a model was used for the present refinement of the x-ray data. The initial data were averaged in Laue symmetry *m*3 to afford 1068 F^2_{obs} values. The F^2_{calc}

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values from the model are given by αF^2_{hkl} + $(1 - \alpha)F^2_{khl}$, where α would be 0.5 if the two twin components were to contribute equally. (Subsequent calculations established that $\alpha = 0.50$.) The usual function $\Sigma w(F^2_{\mathrm{obs}} - F^2_{\mathrm{calc}})^2$ was minimized. Rotation of the molecule about its $\bar{3}$ axis in 2° intervals between 0° and 120° followed by refinement of scale factor established that the coordinates from the constrained refinement (*17*) are indeed a good starting point for the unconstrained refinement. The final calculation involved 91 variables and converged to $R(F^2)$ of 0.142 and to the usual R index, $R(F)$, of 0.10 for the 783 observations having $I \geq 3\sigma(I)$. While this agreement between observation and model is not as good as the self-consistency of the data would predict, it is probably the best that can be accomplished without more elaborate and possibly unjustified models for thermal vibration or for twinning.

Figure 1 is a stereo view of the C_{60} molecule. Although the molecule has crystallographically imposed $\bar{3}$ (C_{3i}) symmetry, it appears to be more symmetrical than that. For example, the ten independent atoms are separated from their inversion-related counterparts by the narrow range of 7.048(11) to 7.074(11) Å, with the mean atom-to-atom diameter of the C_{60} molecule being 7.065(3) Å. The two independent five-membered rings and the four independent six-membered rings are planar to within experimental error. The five independent C=C bonds that join the C_6 rings range from 1.340(7) to 1.391(6) Å and average 1.355(9) Å; the ten independent C–C bonds that join the C_6 and C_5 rings range from 1.378(9) to 1.561(10) Å and average 1.467(21) Å. These may be compared with the corresponding distances of 1.388(9) and 1.432(5) Å in the Os derivative (*22*), 1.388(30) and 1.445(30) Å in the Pt derivative (*23*), 1.370 and 1.448 Å predicted from an earlier ab initio calculation (*15*), and 1.406 and 1.446 Å from a more recent one (*26*).

The observation of high-temperature superconductivity in A_3C_{60} (A = alkali metal) (*4, 5*) makes a comparison of the present crystal structure with that proposed (*27*) for K_3C_{60} of interest. Synchrotron-radiation measurements on K_3C_{60} powders at room temperature have been interpreted in terms of four formula units crystallizing in space group $Fm3m$ of the cubic system with a lattice constant of 14.24 Å, only slightly larger than that found for C_{60}. The K^+ cations are proposed to occupy the eight tetrahedral holes (at ¼,¼,¼) and the four octahedral holes (at ½,½,½). Space for these cations could be ensured only if all C_{60} units "lock in" to one of two possible orientations, which are proposed to be equally probable. In both orientations eight of the twenty hexagonal faces are oriented along the [111] direction, but they differ in the positions for the pentagonal faces. Figure 2 shows a stereo view of part of the present crystal structure about the hole centered at ½,½,½; the shortest center-C distance is 3.64 Å. Figure 3 shows a stereo view of part of the structure about the hole centered at ¼,¼,¼; the shortest center-C distance being 2.67 Å. The related K···C distances are 3.67 and 3.27 Å in the proposed K_3C_{60} structure (*27*). It is clear that in the C_{60} structure the molecules have "locked-in" to an orientation that differs from that proposed for K_3C_{60}. This is probably not surprising in view of the steric and electronic constraints imposed by the K^+ cations. The molecules in the C_{60} crystal structure are tightly packed; while most of the intermolecular distances are in the graphitic range of about 3.3 Å, intermolecular distances as short as 3.131(7) Å occur.

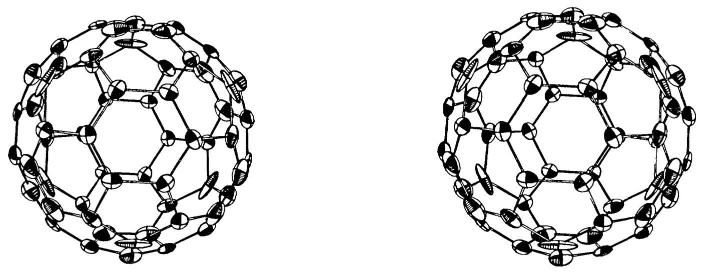

Fig. 1. A stereo drawing of the C_{60} molecule. The 50% probability ellipsoids of thermal vibration are shown. Here and in succeeding figures only one twin component is shown.

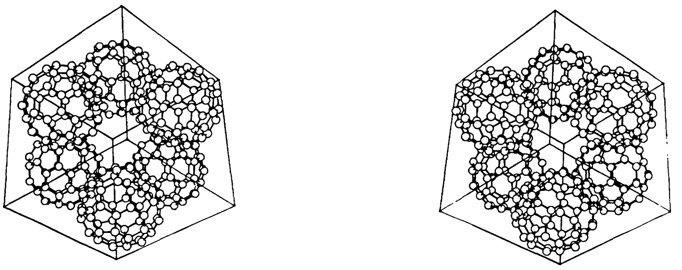

Fig. 2. A stereo drawing of the C_{60} crystal structure about the pseudo-octahedral hole at ½,½,½. Here and in Fig. 3 the C atoms are drawn as spheres.

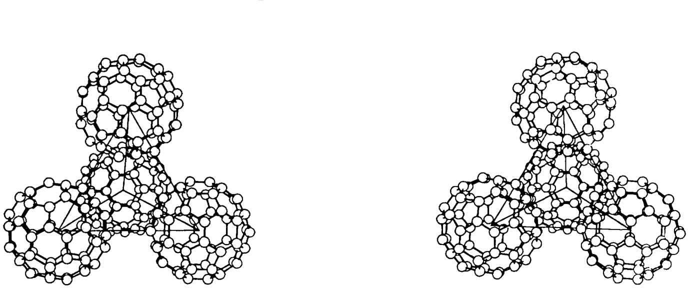

Fig. 3. A stereo drawing of the C_{60} crystal structure about the pseudo-tetrahedral hole at ¼,¼,¼.

Owing to the relatively low imposed symmetry ($\bar{3}$) there is no requirement that the C_{60} truncated icosahedron achieve its full symmetry in the crystal structure. Indeed, it can be seen in Figs. 2 and 3 that the atoms that would be equivalent in the idealized polyhedron have different nonbonding environments. These differences, in principle, could lead to variations in metrical parameters. Although in the present structure these variations appear to be statistically significant, we would prefer to ignore them in view of the complexities of deriving a structure from a twinned crystal. However, it is unlikely that a more reliable structure of the C_{60} molecule can be obtained by x-ray diffraction techniques, unless untwinned crystals can be prepared, perhaps by growing the material well below the phase transition (249 K) or by co-crystallizing the material with a solvent molecule to change the symmetry of the cell. Thus far, this latter approach has proved unsuccessful (*28*).

REFERENCES AND NOTES

1. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **347**, 354 (1990).
2. J. B. Howard, J. T. McKinnon, Y. Makarovsky, A. L. Lafleur, M. E. Johnson, *ibid.* **352**, 139 (1991).
3. F. Diederich *et al.*, *Science* **252**, 548 (1991).
4. A. F. Hebard *et al.*, *Nature* **350**, 600 (1991).
5. K. Tanigaki *et al.*, *ibid.* **352**, 222 (1991).
6. P.-M. Allemand *et al.*, *Science* **253**, 301 (1991).

7. R. Meilunas, R. Chang, S. Liu, M. Kappes, *Appl. Phys. Lett.*, in press.
8. R. M. Fleming *et al.*, in *Clusters and Cluster-Assembled Materials*, R. S. Averback, D. L. Nelson, J. Bernholc, Eds. (MRS Symposia Proceedings No. 206, Materials Research Society, Pittsburgh, PA, 1991), pp. 691–695.
9. V. P. Dravid, S. Liu, M. M. Kappes, *Chem. Phys. Lett.*, in press.
10. P. A. Heiney *et al.*, *Phys. Rev. Lett.* **66**, 2911 (1991).
11. F. Li, D. Ramage, J. S. Lannin, J. Conceicao, *ibid.*, in press.
12. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1985).
13. C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, J. R. Salem, *J. Phys. Chem.* **95**, 9 (1991).
14. R. Tycko *et al.*, *ibid.*, p. 518.
15. G. E. Scuseria, *Chem. Phys. Lett.* **176**, 423 (1991).
16. R. Sachidanandam and A. B. Harris, *Phys. Rev. Lett.*, in press.
17. D. E. Cox, private communication.
18. J. R. D. Copley *et al.*, *Physica B*, in press.
19. C. S. Yannoni *et al.*, *J. Am. Chem. Soc.* **113**, 3190 (1991).
20. D. S. Bethune *et al.*, *Chem. Phys. Lett.* **179**, 181 (1991).
21. R. Meilunas *et al.*, *J. Appl. Phys.*, in press.
22. J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren, F. J. Hollander, *Science* **252**, 312 (1991).
23. P. J. Fagan, J. C. Calabrese, B. Malone, *ibid.*, p. 1160.
24. R. E. Haufler *et al.*, *J. Phys. Chem.* **94**, 8634 (1990).
25. M. J. Buerger, *Crystal Structure Analysis* (Wiley, New York, 1960), pp. 53–74.
26. M. Häser *et al.*, *Chem. Phys. Lett.* **181**, 497 (1991).
27. P. W. Stephens *et al.*, *Nature* **351**, 632 (1991).
28. R. M. Fleming *et al.*, *Phys. Rev. B* **44**, 888 (1991).

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Bond Lengths in Free Molecules of Buckminsterfullerene, C_{60}, from Gas-Phase Electron Diffraction

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Electron diffraction patterns of the fullerene C_{60} in the gaseous state have been obtained by volatilizing it from a newly designed oven-nozzle at 730°C. The many peaks of the experimental radial distribution curve calculated from the scattered intensity are completely consistent with icosahedral symmetry for the free molecule. On the basis of this symmetry assumption, least-squares refinement of a model incorporating all possible interatomic distances led to the values $r_g(C_1–C_2) = 1.458$ (6) angstroms (Å) for the thermal average bond length within the five-member ring (that is, for the bond fusing five- and six-member rings) and $r_g(C_1–C_6) = 1.401(10)$ Å for that connecting five-member rings (the bond fusing six-member rings). The weighted average of the two bond lengths and the difference between them are the values 1.439(2) Å and 0.057(6) Å, respectively. The diameter of the icosahedral sphere is 7.113(10) Å. The uncertainties in parentheses are estimated 2σ values.

RESEARCH ON THE PROPERTIES OF the molecule "buckminsterfullerene," C_{60}, has been increasing rapidly. Among the many results now available, however, there is little information about the lengths of the bonds. To date the most accurate values appear to be those from nuclear magnetic resonance (NMR) work (*1*) (1.45 ± 0.015 Å for the bonds within the five-member ring and 1.40 ± 0.015 Å for the bonds connecting five-member rings). There are also measurements from neutron diffraction [1.44 Å (*2*) and 1.42 Å (*3*) for the weighted average distance]. All of these measurements were done on material in condensed phases. There are also results from semiempirical and ab initio quantum mechanical calculations; the most recent of these includes the effect of electron correlation at the MP2 level and predicts the bond lengths at 1.445 Å and 1.405 Å (*4*). We carried out the electron-diffraction study described here for two reasons. First, it seemed quite likely the results for the bond lengths would be more precise than any presently available, and second, these results for the gas-phase molecule would be free from the effects of intermolecular interaction that could conceivably play a role in condensed phase measurements.

Our sample of C_{60} was produced at IBM with an arc fullerene generator (*5, 6*) and removed from the soot utilizing toluene in a soxhlet extractor. The extract was purified by liquid chromatography (basic alumina) with a gradient elution system of hexane and chlorinated solvents, and characterized by NMR (*7, 8*) and mass spectroscopy; separation has also been obtained using a 95/5 hexane/toluene system (*9*).

The electron diffraction work was done at Oregon State University. In a usual type of diffraction experiment, a well-columnated,

Table 1. Interatomic distances and root-mean-square amplitudes of vibration in C_{60}. The symbol r_g denotes the thermal average distance, r_a the distance consistent with the scattering equations, and l the root-mean-square amplitude of vibration. Quantities in parentheses are estimated 2σ uncertainties; those for r_g are estimated to be the same as for r_a. Amplitudes in curly brackets were refined as a group. The term numbering corresponds to that in Fig. 3.

Term	r_a(Å)	r_g(Å)	l(Å)	Term	r_a(Å)	r_g(Å)	l(Å)
R*	3.332_7 (4_8)			r_5†	1.237_9 (5_3)		
$\langle r_{bond}\rangle$‡	1.436 (2)	1.439		Δr_{bond}§	0.057 (6)	0.057	
1–6	1.398 (10)	1.401	0.062 (8)	1·19	5.408 (10)	5.411	0.136 (34)
1–2	1.455 (6)	1.458	0.065 (5)	1·14′	5.491 (8)	5.494	0.133 (23)
1 · 3	2.355 (10)	2.357	0.080 (10)	1·13′	5.795 (8)	5.798	0.129 (18)
1 · 7	2.471 (5)	2.474	0.083 (7)	1·15′	6.072 (8)	6.075	0.136 (13)
1 · 12	2.853 (6)	2.857	0.097 (9)	1·8′	6.143 (8)	6.146	0.136
1 · 8	3.581 (5)	3.584	0.100 (7)	1·12′	6.513 (9)	6.516	0.144 (18)
1 · 15	3.699 (6)	3.702	0.099 (12)	1·7′	6.667 (9)	6.670	0.144
1 · 13	4.120 (6)	4.123	0.109 (8)	1·3′	6.709 (10)	6.712	0.144
1 · 14	4.517 (7)	4.520	0.115 (10)	1·2′	6.960 (10)	6.963	0.145 (31)
1 · 19′	4.617 (9)	4.619	0.106 (23)	1·6′	6.972 (10)	6.975	0.145
1 · 18′	4.841 (8)	4.844	0.117 (26)	1·1′	7.110 (10)	7.113	0.145
1 · 18	5.208 (9)	5.212	0.145 (40)				

*Structure-defining parameter: distance from center of the icosahedral sphere to center of five-member ring. †Structure-defining parameter: radius of circle comprising the five-member rings. ‡Weighted average of bond lengths. §Bond length difference.