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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.

high-energy electron beam passes through the center of an evacuated chamber and intersects a jet of gas emitted from a nozzle positioned with its tip about 1 mm from the beam and connected to a sample container outside the chamber. Because of the low volatility of C_{60}, conveyance of the vapor from outside the apparatus was unsuitable. We used instead an electrically heated nozzle-oven, fitted with a needle valve, located inside the diffraction chamber close to the electron beam. Since the temperature at which sufficient vapor pressure would be obtained for the experiment was unknown, tests for scattering were necessary. The oven was first held for about 2 hours at 200°C (a temperature known to be insufficient to volatilize the sample) with the valve open to remove any solvent remaining from the extraction process. The valve was then closed and the sample gradually heated. During the heating the valve was opened at suitable intervals to check for possible scattering that would be evident on a fluorescent screen appropriately positioned for that purpose. At about 300°C substantial scattering was seen, but it disappeared after a short interval. It is not known whether the scattering was from firmly adsorbed solvent that was not removed at 200°C, or whether it was from C_{60}; if the latter, its disappearance could be accounted for by a reduction of surface area (and consequently a much reduced rate of evaporation) caused by formation of larger crystallites (*10*). At about 700°C sufficient sample was being evaporated to give excellent diffraction patterns with 4- to 6-min exposures (*11*). Diffraction patterns were recorded at nozzle-to-plate distances of 700 and 300 mm to obtain lower- and higher-angle scattering. About 300 mg of sample was required for the production of two plates at the longer and three at the shorter camera distance.

Reduction of the data and their treatment by our usual procedures (*12*) led to the experimental intensity curves of Fig. 1 and the corresponding radial distribution curve of Fig. 2. If the structure has icosahedral symmetry, the geometry of the molecule is defined by only two parameters, which for convenience we chose as the radius vector from the center of the icosahedral sphere to the center of the five-member ring and the radius of the circle comprising the five-member rings. The 1770 distances between

Fig. 1. Intensity curves for C_{60}. The experimental intensity, $s^4I_t(s)$, from each plate, amplified by a factor of 10, is shown superimposed on the backgrounds. The molecular structure-sensitive part of the experimental intensity to be compared with the theoretical curve is given by $sI_m(s) = s[s^4I_t(s) - \text{background}]$ (*12*). The theoretical curve corresponds to the model of Table 1. The differences are experimental minus theoretical. The ordinate is intensity on an arbitrary scale, the abscissa is defined by $s = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle.

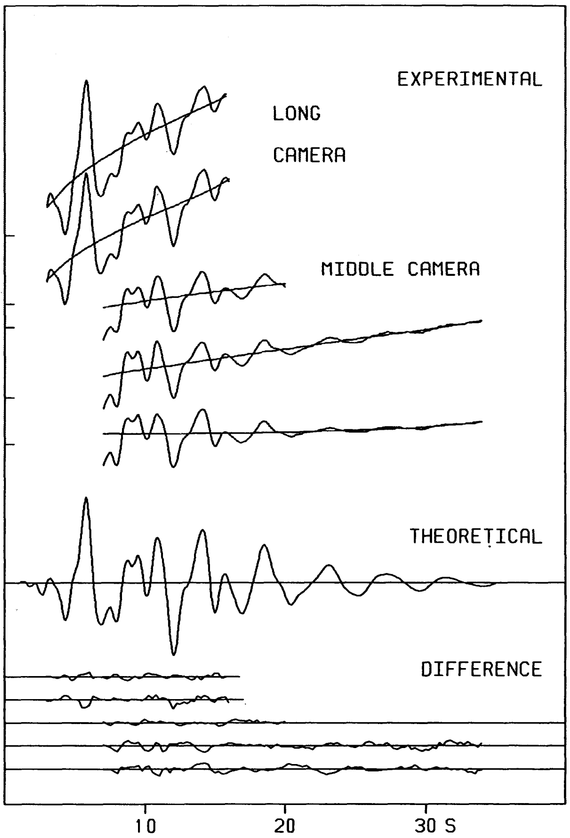


Fig. 2. Radial distribution of distances in C_{60}. The experimental curve was calculated from a composite of the experimental intensity curves shown in Fig. 1, multiplied by $\exp(-0.0020s^2)$ to minimize series termination errors. The vertical bars indicate the distances given in Table 1; their lengths are proportional to the weights of the terms. The difference curve is experimental minus theoretical (not shown).

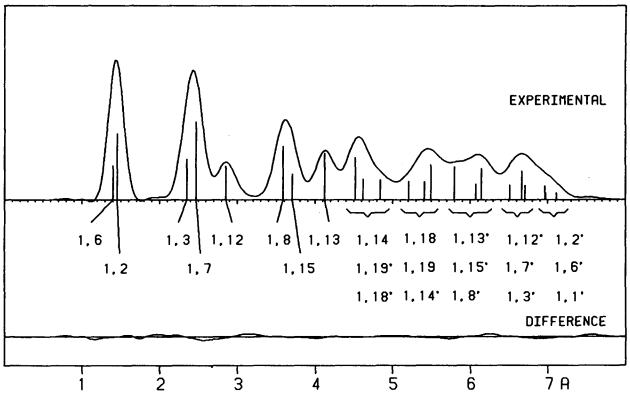
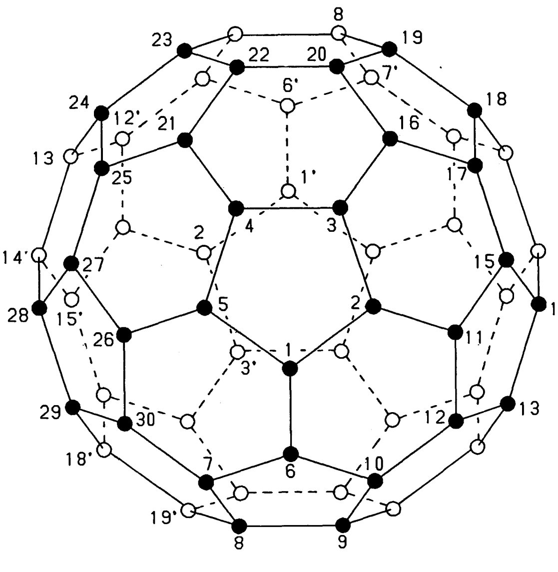


Fig. 3. Diagram of the C_{60} molecule. Numbers for all atoms (solid circles) in the upper hemisphere are shown unprimed. Atoms with corresponding primed and unprimed numbers are related by the center of symmetry.



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different pairs of atoms comprise 23 different distance types (which may be identified by reference to the numbering scheme shown in Fig. 3 and to the list in Table 1). The structure was refined by least-squares fitting of a theoretical intensity curve to those observed (*13*); the parameters adjusted were the two structure-defining radii and 18 vibrational amplitudes (including three groups indicated by the bracketed quantities of Table 1). To be able to refine such a large number of amplitudes is unusual; it owes to the high number ratio of interatomic distance to structure-specifying parameters.

The type of distance consistent with the electron-scattering equations is r_a. Owing to the effects of vibration, neither r_a nor the physically more meaningful thermal average distance r_g (*14*) is consistent with equilibrium molecular symmetry. Imposition of symmetry on an r_a distance set will thus lead to compromises in the fit. The distance values obtained for stiff molecules under these circumstances usually do not differ more than a few thousands of an angstrom from those that would be obtained without symmetry restriction. For C_{60}, imposition of icosahedral symmetry on the r_a distances seems to have been an excellent assumption, judged by the nearly level character of the difference (residual) curves (Figs. 1 and 2).

The thermal average (r_g) bond lengths are expected to be about 0.003 to 0.005 Å longer than the equilibrium values, but their difference should be nearly the same as the r_e (equilibrium) difference. The thermal average bond length should also be longer than the distances in the crystal when the latter are not corrected for thermal motion, both because of the temperature difference between the two experiments, and because distances in the crystal are calculated from determinations of atomic positions. Although there are no values for C_{60} itself, there are x-ray measurements for an osmylated C_{60}: Average values are $r(C_1–C_2) = 1.423(5)$ Å and $r(C_1–C_6) = 1.388(9)$ Å (*15*). Our bond lengths are in good agreement with the NMR values (*1*). In principle, the results from these two experiments should differ, both because of the great experimental temperature difference and because the r values retrieved from them have different definitions (electron diffraction: $\langle r \rangle$; NMR: $\langle 1/r^3 \rangle^{-1/3}$). The uncertainties on the values, however, are larger than the expected difference.

The measured root-mean-square amplitudes of vibration (l) reveal C_{60} to be a very stiff molecule relative to usual standards. For example, the longest distances in the molecule, that is, those between atoms on opposite sides of the sphere, have associated amplitudes only slightly greater than are found for some of the distances in much smaller molecules at room temperature. As expected, the bond amplitudes are somewhat larger than would be expected for this type of structure at room temperature, but whether the increase is consistent with the temperature of our experiment cannot be judged without appropriate normal-coordinate analysis.

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The First Step in Vision: Femtosecond Isomerization of Rhodopsin

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The kinetics of the primary event in vision have been resolved with the use of femtosecond optical measurement techniques. The 11-*cis* retinal prosthetic group of rhodopsin is excited with a 35-femtosecond pump pulse at 500 nanometers, and the transient changes in absorption are measured between 450 and 580 nanometers with a 10-femtosecond probe pulse. Within 200 femtoseconds, an increased absorption is observed between 540 and 580 nanometers, indicating the formation of photoproduct on this time scale. These measurements demonstrate that the first step in vision, the 11-*cis*→11-*trans* torsional isomerization of the rhodopsin chromophore, is essentially complete in only 200 femtoseconds.

LIGHT DETECTION BY THE VISUAL system is one of nature's most important information transduction processes. It consists of a series of chemical reactions that are initiated by the absorption of a photon and culminate in the stimulation of the optic nerve. It has long been known that the primary step in vision is the photoisomerization of the retinal chromophore in rhodopsin (*1*). However, understanding the dynamics of this isomerization remains a fundamental problem in photochemistry and biology. The time course of many photochemical reactions can be studied with compressed femtosecond optical pulses (*2*). Such pulses were previously used to observe the isomerization of the retinal chromophore in bacteriorhodopsin, a related pigment which functions as a light-driven proton pump (*3*). Recent advances in the generation of femtosecond pulses in the blue-green spectral region now make it possible to study a much wider range of ultrafast processes with a time resolution of 10 fs (*4*). We report here the room temperature investigation of the *cis-trans* isomerization in rhodopsin which reveals that the first step in vision occurs on a 200-fs time scale and is one of the fastest photochemical reactions ever studied.

Rhodopsin (λ_{max} ~500 nm) consists of the 11-*cis* retinal prosthetic group (Fig. 1) bound within the protein opsin. Yoshizawa and Wald (*5*) determined that the absorption of light results in the *cis*-to-*trans* isomerization of 11-*cis* retinal to form a red-absorbing photoproduct, bathorhodopsin. Early measurements of the isomerization kinetics

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