Ordered Structure of a Distorted C_{60}^{2-} Fulleride Ion

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The discovery of superconductivity[1] and ferromagnetism[2] in salts of C_{60} has focused attention on the electronic and structural properties of fulleride ions, C_{60}^{n-}. The lattice dimensions of many fullerides are known,[3,4] but little is known about the specific structural response of a discrete C_{60} molecule to the addition of electrons. Powder neutron diffraction data on Na_2CsC_{60} have very recently been interpreted in terms of a near equalization of carbon–carbon bond lengths.[5] Distortions from icosahedral symmetry are of particular interest because phenomena such as superconductivity and ferromagnetism are the cooperative result of small perturbations in the repeating molecular entity. Such intrinsic anisotropy could be an important component of mechanisms for explaining these phenomena.

Discrete C_{60}^{2-} and C_{60}^{3-} salts have recently been isolated and characterized.[6] Notably, their electronic ground states disobey Hund's rule and, as in the case of C_{60}^{-}, the Jahn–Teller theorem predicts a distortion from icosahedral symmetry to remove orbital degeneracy in the $(t_{1u})^n$ LUMO. We now report the experimental observation of a distortion in the crystal structure of the PPN^+ salt of C_{60}^{2-} (PPN^+ = bis(triphenylphosphine)iminium ion). This is the first single-crystal structure of a C_{60}^{2-} salt, and it is highly ordered. Two structures of C_{60}^{-} are known, but both are disordered,[7,8] as is Na_2CsC_{60}.[5]

Single crystals of $[PPN^+]_2[C_{60}^{2-}]$ were grown by allowing [PPN]Cl in acetonitrile to slowly diffuse via a syringe into an anaerobic acetonitrile solution of $[Na(crown)^+]_2[C_{60}^{2-}]$.[6] Crystal data: black, 0.3 × 0.4 × 0.15 mm, triclinic, $P\bar{1}$; $a = 12.7003(7)$ Å, $b = 13.1893(9)$ Å, $c = 13.8382(5)$ Å, $\alpha = 65.409(4)°$, $\beta = 85.052(3)°$, $\gamma = 76.853(4)°$; $Z = 1$, $\rho = 1.455$ g cm^{-3}. Data collection: Cu Kα, 10 kW, 108 K, $2\theta = 2.0$–$107.0°$, 3901 observed reflections $F > 2\sigma(F)$. Refinement: direct methods $R_{obs} = 4.24\%$, $R_w = 4.36\%$, data to parameter ratio 6.3.

The packing diagram (Figure 1) shows that the C_{60}^{2-} anion sits at a center of symmetry and is completely surrounded by PPN^+ cations. There are at least 22 phenyl groups (11 symmetry-related pairs) that closely approach the C_{60}^{2-} unit. They are derived from five distinct pairs of cations on a 4,3,2,1,1 basis.

The C_{60}^{2-} ion shows a small but significant distortion from icosahedral symmetry. This is indicated in Figure 2 by the bar graph of distances of the carbon atoms from the inversion center. The nature of the distortion is an axial elongation with an apparent rhombic squash. It can be visualized in Figure 2 by size and color coding of the carbon atoms whose distances from the inversion center are >0.007 Å longer (white) or shorter (red) than the mean (3.542(2) Å). There is a cluster of nine atoms with long radii which approximately defines a polar region. It includes a complete pentagon (atoms 8′, 9′, 25, 26, and 27). The 9–9′ diameter is the longest (7.126(5) Å). Secondary long poles are apparent on the 19–19′ diameter (7.106(5) Å). The "equatorial" region contains a predominance of atoms with short

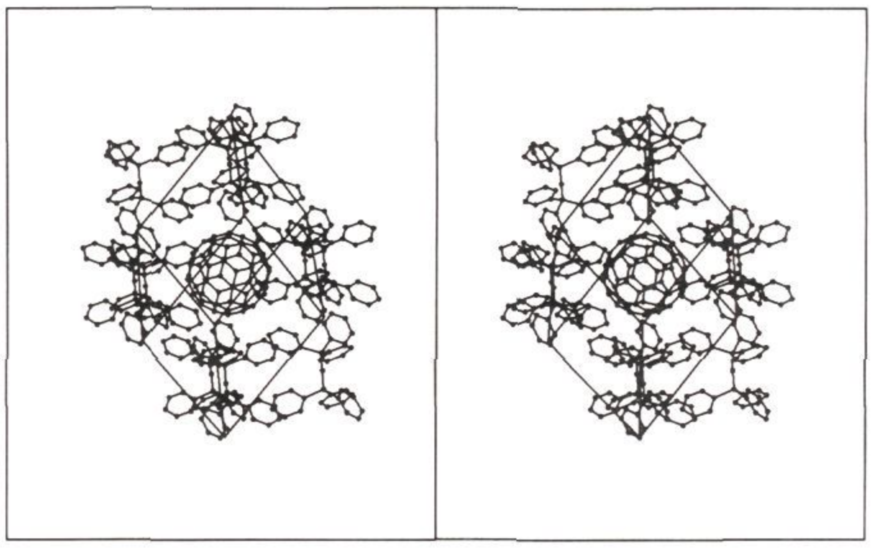

Figure 1. Stereoscopic packing diagram for $[PPN^+]_2[C_{60}^{2-}]$.

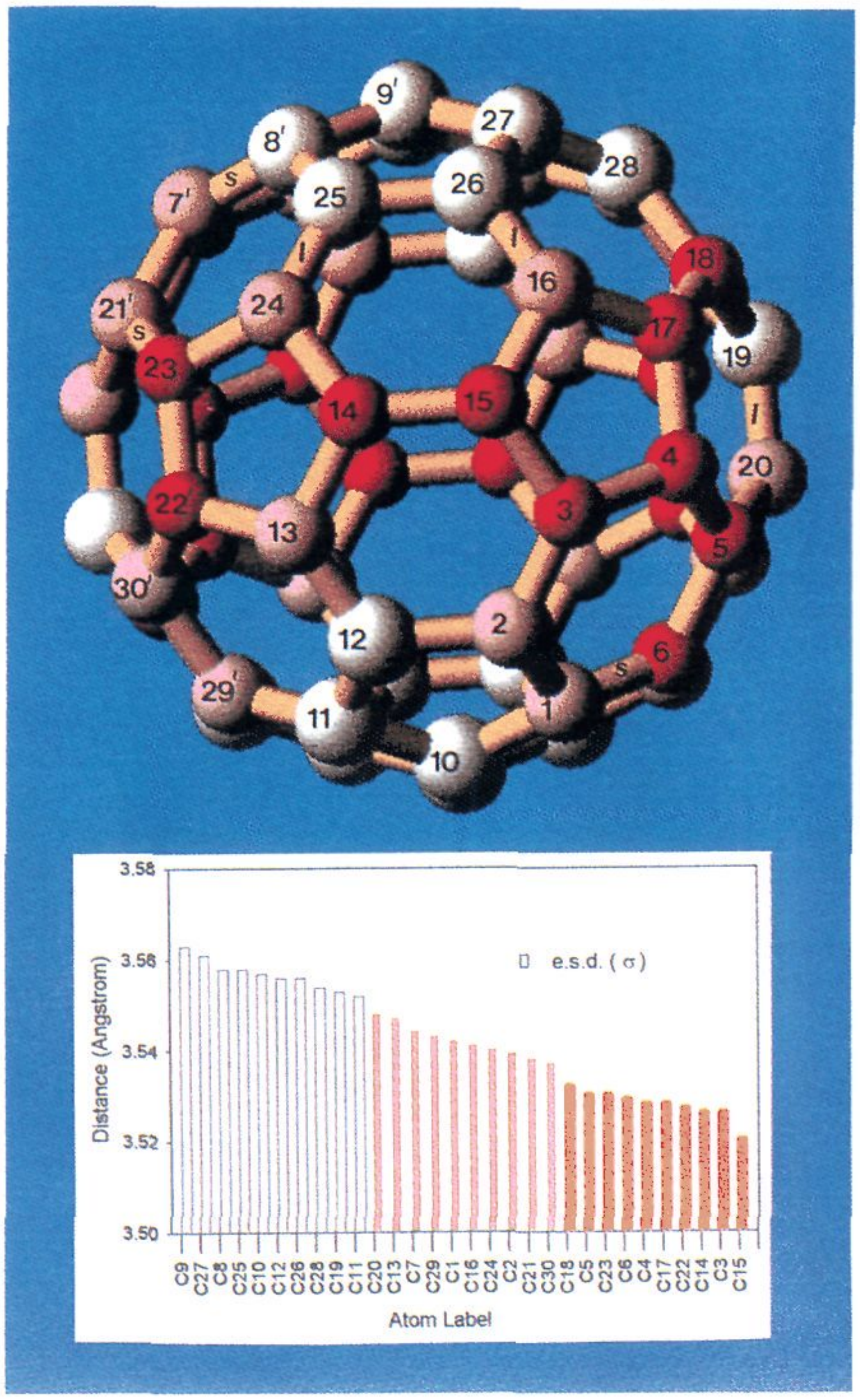

Figure 2. Size and color visualization of the distortion in C_{60}^{2-}. Carbon atoms >0.007 Å from the mean center-to-C-atom distance are white and enlarged, and those <0.007 Å are red and reduced, relative to those near the mean (pink). The three longest 6:6 ring juncture bonds are labeled *l*; the three shortest, s.

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Table 1. Bond Distances (Å) in C_{60}^{2-}

6:6 Ring Juncture Bonds							
C(19)–C(20)	1.412(5)	C(14)–C(15)	1.404(4)	C(27)–C(28)	1.398(4)	C(17)–C(18)	1.394(4)
C(12)–C(13)	1.407(4)	C(4)–C(5)	1.403(5)	C(22)–C(30′)	1.398(6)	C(7)–C(8)	1.391(5)
C(24)–C(25)	1.407(5)	C(2)–C(3)	1.402(5)	C(11)–C(29′)	1.396(4)	C(21)–C(23′)	1.390(5)
C(16)–C(26)	1.404(4)			C(9)–C(10)	1.395(5)	C(1)–C(6)	1.388(4)
5:6 Ring Juncture Bonds							
C(18)–C(28)	1.457(4)	C(22)–C(23)	1.447(5)	C(23)–C(24)	1.452(5)	C(3)–C(15)	1.440(4)
C(29)–C(30)	1.457(4)	C(15)–C(16)	1.445(4)	C(10)–C(11)	1.451(4)	C(3)–C(4)	1.439(4)
C(27)–C(9′)	1.456(4)	C(20)–C(21)	1.444(6)	C(18)–C(19)	1.451(5)	C(16)–C(17)	1.439(4)
C(7)–C(21)	1.455(4)	C(25)–C(26)	1.444(4)	C(1)–C(2)	1.449(5)	C(6)–C(7)	1.436(5)
C(5)–C(6)	1.454(5)	C(8)–C(25′)	1.444(5)	C(11)–C(12)	1.449(6)	C(19)–C(30)	1.434(5)
C(13)–C(14)	1.454(5)	C(2)–C(12)	1.442(4)	C(1)–C(10)	1.448(5)	C(26)–C(27)	1.434(4)
C(8)–C(9)	1.454(4)	C(13)–C(22)	1.441(4)	C(4)–C(17)	1.447(5)	C(5)–C(20)	1.433(4)
C(28)–C(29)	1.453(5)	C(14)–C(24)	1.441(4)				

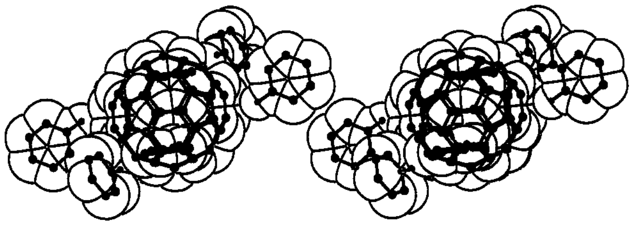

Figure 3. Stereoview of the three closest approaching pairs of PPN$^+$ phenyl groups. For clarity, only C_6H units are shown. The orientation of C_{60}^{2-} is the same as in Figure 2.

radial distances (red), and 15–15′ is the shortest diameter (7.040(5) Å). Inspection of Figure 2 reveals an approximate mirror plane in the plane of the paper. If idealized, the distortion would be described by C_{2h} symmetry, but the actual symmetry is only C_i.

The quasi-ellipsoidal elongation arises from a predominance of long bonds in the equatorial region having more or less longitudinal orientation. This naturally pushes the poles apart and is illustrated in Figure 2 for some of the 6:6 ring juncture bonds ("double" bonds). Of the 15 symmetry-related pairs (Table 1), the three longest (labeled *l*) tend to be longitudinally oriented. The three shortest (labeled s) are more latitudinal. The statistical significance of the distortions can be judged from the bond distances and standard deviations listed in Table 1. The maximum difference in length among bonds of the same type is 0.024 Å, well in excess of three standard deviations (0.005 Å). The results of isotropic versus anisotropic refinement gave the same result to within 0.002 Å for all bonds.

Relative to neutral C_{60}, the mean 6:6 ring juncture bond length in the dianion has increased from 1.391(8)[9] to 1.399(2) Å. The mean 5:6 bond has decreased from 1.455(8) to 1.446(2) Å. Although these changes are at the margins of statistical significance, their direction is in accord with the nature of the t_{1u} orbital, which, generally speaking, is antibonding with respect to the 6:6 bonds and bonding with respect to the 5:6 bonds. Ab initio calculations on the *mono*anion, C_{60}^-, produce average bond length changes of similar magnitude.[10] Theory also predicts an ellipsoidal elongation in response to the $(t_{1u})^1$ Jahn–Teller degeneracy.

Why is C_{60}^{2-} so ordered?[11] The answer seems to lie in the close approach of three symmetry-related pairs of phenyl H atoms to the centers of hexagonal faces near the "equator" of the quasi-ellipsoid (mean H···C distances = 2.85(5), 2.88(5), 2.92(3) Å). Their equatorial location probably reflects an electrostatic attraction of $C^{\delta-}$–$H^{\delta+}$ dipoles to a concentration of $(t_{1u})^2$ electron density near the equator. Their attraction to hexagons probably reflects a local electron richness relative to pentagons. In a space-filling view (Figure 3), the H atoms appear to nestle in hexagonal wells of electron density locking the C_{60}^{2-} in place like three pairs of calipers. The next closest H atoms are 0.3 Å more distant. Donor–acceptor interactions are the probable source of order in other well-defined C_{60} structures,[9,12] and we note a potential parallel with Na$^+$ ions in Na_2CsC_{60}, which are preferentially located over hexagon rings.[5]

In summary, we have provided the first structural proof of distortion in C_{60}^{n-} ions. All C_{60}^{n-} ions up to $n = 5$ have Jahn–Teller degenerate electronic states and may show related distortions.

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Supplementary Material Available: Full crystallographic details, atomic coordinates, table of center to C atom distances, bond lengths and angles, anisotropic displacement coefficients, H-atom coordinates and, cation numbering scheme (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) Although the structure was determined at 108 K to optimize precision, data collected at room temperature show that it is also ordered at room temperature.

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