

Single C-C bond in $(C_{60})_2^{2-}$

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The structure of the dimer phases of RbC_{60} and KC_{60} were investigated by x-ray powder diffraction. We have established that the dimer molecule forms through a single C-C interfullerene bond in contrast to the four-membered rings of C_{60} polymers. Molecular orientation and space group symmetry were also determined. [S0163-1829(96)05643-3]

The monoanionic fullerides AC_{60} ($A=K,Rb,Cs$) have a rich phase diagram and show a number of interesting physical properties.¹⁻⁹ The most prominent feature is the existence of noncubic conducting and insulating phases observed when the high temperature (>400 K) rocksalt² phase is cooled slowly or quenched, respectively.³⁻⁵ The conducting phase is a linear polymer formed by the [2+2] cycloaddition reaction between double bonds,^{10,11} shrinking the interfullerene distance by ~ 1 Å from the usual van der Waals value.⁴ This particular form of interfullerene bond was first hypothesized for photopolymerized C_{60} (Ref. 12) and has subsequently been shown to occur in pressure-polymerized C_{60} (Refs. 13 and 14) and Na_2AC_{60} .¹⁵ An insulating phase is obtained by rapidly cooling from the rocksalt phase to below 273 K, thereby preventing polymerization. X-ray powder diffraction gave evidence for the formation of dimers in a monoclinic metastable phase.^{16,17} It was originally described as having either an orthorhombic unit cell of eight fullerenes (ortho-II) or a monoclinic unit cell of four,^{16,17} but the quality of the current data set excludes the orthorhombic lattice. Weak reflections, observed at low angles where the scattering factor of C_{60} can be approximated by a spherical charge distribution, revealed^{16,17} the ordering of dimer chains illustrated in Fig. 1. This allowed the determination of the interfullerene distance and the orientation of the whole dimer unit, but not the configuration of atoms within each fullerene.

Up to now, the atomic structure could not be determined for this low-symmetry, large unit cell structure. It was debated whether dimerization is the result of Peierls distortion¹⁶ or the formation of covalent interfullerene bonds.¹⁷ In this paper we report x-ray powder diffraction results, and demonstrate that dimers are covalently bonded, and the dimer molecule forms through a single C-C interfullerene bond. In agreement with our previous suggestions,¹⁷ this bonding configuration is different from that of the polymer. It is an intriguing question whether this dimer molecule occurs in other C_{60} compounds, and which are the conditions governing the different forms of interfullerene bond formation.

The polycrystalline samples were prepared by the usual solid state reaction of stoichiometric amounts of K or Rb and high purity (99.9%) C_{60} powder at 650 K. As in earlier studies, the powder samples were pure in the sense that only the fcc phase was observed at 473 K. However, this does not ensure that the sample will be structurally single phase after it is quenched. In previous data on the quenched dimer phase of RbC_{60} , a minority ($\sim 20\%$) fcc coexisted with the monoclinic dimer phase.¹⁷ It is not easy to correct the data for the influence of this phase, because the reflections severely overlap. It was noted in differential scanning calorimetry studies⁷ that if the temperature is cycled between 220 and 273 K, two weak endothermic peaks occur on the first heating, which are absent in the following cycles. We repeated this heat treatment and found that it eliminates the minority fcc phase. It is crucial to limit the time spent at 273 K, otherwise the metastable dimer phase will start to transform into the polymer.

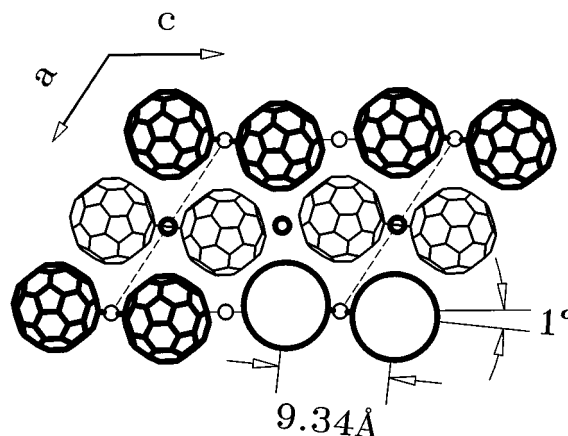


FIG. 1. Monoclinic lattice of the dimer phases of AC_{60} . The lower right corner shows the structureless dimer derived from previous works (Refs. 16 and 17), and the rest of the lattice shows the atomic configuration of RbC_{60} found in this work. Bold and normal fullerenes and alkali-metal atoms are at $y=0$ and $y=1/2$, respectively.

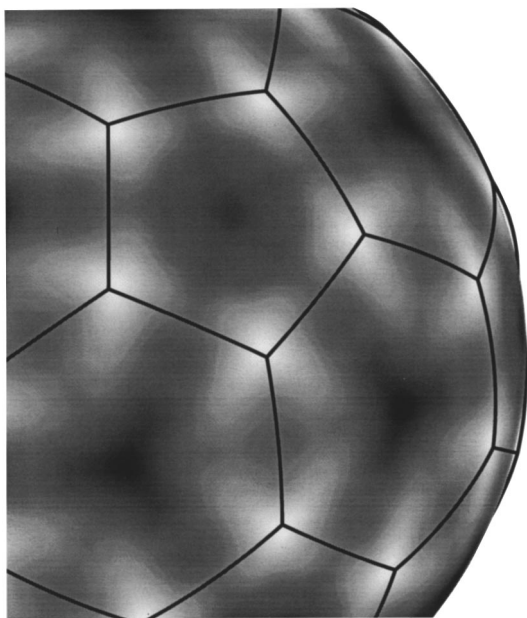


FIG. 2. Quality of fit parameter R_{wp} as a function of intradimer contact point on the surface of the fullerene molecule. On the linear grayscale white and black correspond to $R_{wp}=10\%$ and 14% , respectively.

Parallel beam x-ray diffraction experiments were performed at beamline X3B1 of the National Synchrotron Light Source with a wavelength of 1.1501 \AA . The polycrystalline sample was held in 1 mm glass capillary and the powder spectra were recorded at 220 K in the $2\theta=3^\circ-45^\circ$ range.

An unconstrained Rietveld refinement is not feasible for this complex structure. The powder diffraction technique cannot reliably locate each of the sixty carbon atoms in the irreducible volume of the unit cell. Instead, we rely on the fact that the fit is sensitive to the position of all of the carbon atoms; we approximate the structure with undistorted C_{60} molecules and search the space of fullerene orientations, spanned by three Euler angles, for the best agreement between the calculated and observed diffraction pattern. In this work we take an unbiased approach and do not presuppose covalent bonding within the dimer. As the space group is not known in advance, it has to be determined in parallel with

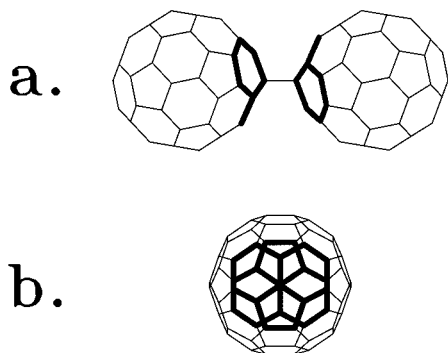


FIG. 3. *trans* conformation of the single-bonded $(C_{60})_2^{2-}$ dimer derived from this work. (a) View along **b** in the $\psi=270^\circ$ position. (b) View along the dimer axis showing the intrafullerene regions around the interdimer bond.

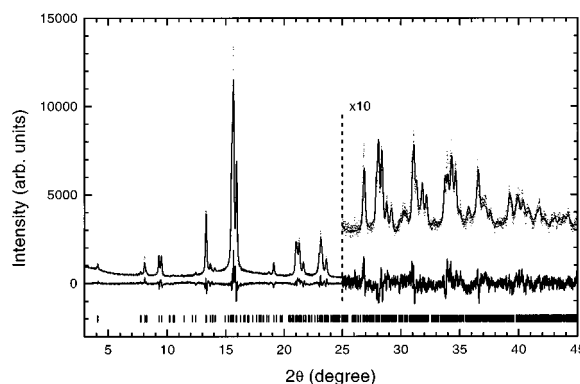


FIG. 4. Rietveld plot of RbC_{60} dimer phase for the model described in text.

the molecular orientations. All observed reflections have $h+k$ even, implying either a C-centered or pseudocentered cell. There are five plausible monoclinic space group symmetries: $P2_1/a$ and $C2$ generate all four fullerenes in the unit cell from a specification of one, either with or without an inversion center. $C2/m$ also requires a single generating C_{60} molecule but the extra $a-c$ mirror plane introduces binary orientational disorder of dimers. Lower space group symmetries, $P2_1$ or Pa , are required to describe more general conformations of a dimer unit for which all 120 atomic positions must be given. Furthermore, the diffraction lines index equally well to two slightly different sets of the lattice parameters which differ only because of the deviation from orthorhombic metrics.¹⁸ In this analysis, we have considered each combination of the above,¹⁹ and run approximately 10^6 Rietveld fits.²⁰

The initial steps of data analysis are the following. First the peak shape and monoclinic lattice parameters are determined by the LeBail technique,²¹ which optimizes the profile fit without the use of any structural information. Then starting ball position and alkali-metal occupancy are optimized from the low angle data. While the tilt around the monoclinic **b** axis is essential for describing superreflection intensities, we did not find any evidence for a tilt out of the $a-c$ plane, probably because it would lead to worse packing of molecules. Next, we generate atomic coordinates by rotating a fullerene from a standard orientation so that the Eulerian angles (defined in Ref. 22) θ and ϕ define the intradimer contact point on the fullerene surface, and ψ rotates the dimer about its axis. Finally, we run a Rietveld refinement of the ball position and carbon and alkali-metal thermal parameters. This yields a measure of the quality of the fit, the weighted profile R factor R_{wp} as a function of the fullerene orientations. (Results are identical for other figures of merit, such as Bragg R factor R_I .) The contrast between the best and worst fits can be increased by using only the high- q region of the diffraction data.

In the space groups $P2_1/a$, $C2$, and $C2/m$ we can find the minimum R_{wp} at each (θ, ϕ) and represent it on a spherical surface (see Fig. 2). There is a convincing global minimum for both data sets and all space groups at $(\theta, \phi) = (90^\circ, 12^\circ)$. In this orientation two vertices of C_{60} face each other, i.e., the contact point coincides with a carbon atom. This is very near to the bonding configuration hypothesized in Refs. 17 and 23. Other high-symmetry configurations cor-

TABLE I. Structural parameters of the dimer phases of RbC₆₀ and KC₆₀.

RbC ₆₀	
Lattice parameters:	17.141(5)×9.929(5)×19.277(5) Å ³ β=124.40°
Space group:	P2 ₁ /a (cell choice 3 of No. 14)
LeBail fit	R _{wp} =6.7%, χ ² =2.8
Rietveld fit	R _{wp} =8.3%, χ ² =4.3
center of the rigid C ₆₀ :	0.006 0.000 0.246
Eulerian angles:	θ=90° φ=12° ψ=318°
Atomic coordinates:	Rb(1) 0.000 0.500 0.016 Rb(2) 0.000 0.500 0.516
Rb occupancy:	0.95
Rb thermal parameter:	B = 5 Å ²
C thermal parameter:	B = 3 Å ²
closest Rb(1)-C distance:	3.20 Å
closest Rb(2)-C distance:	3.35 Å
KC ₆₀	
Lattice parameters:	17.153(5)×9.793(5)×19.224(5) Å ³ β=124.10°
Space group:	P2 ₁ /a (cell choice 3 of No. 14)
LeBail fit	R _{wp} =7.1%, χ ² =3.1
Rietveld fit	R _{wp} =8.9%, χ ² =4.8
center of the rigid C ₆₀ :	0.007 0.000 0.246
Eulerian angles:	θ=90° φ=12° ψ=281°
Atomic coordinates:	K(1) 0.000 0.500 0.013 K(2) 0.000 0.500 0.513
K occupancy:	0.93
K thermal parameter:	B = 4 Å ²
C thermal parameter:	B = 2 Å ²
closest K(1)-C distance:	3.15 Å
closest K(2)-C distance:	3.26 Å

respond to local maxima or saddle points of $R_{wp}(\theta, \phi)$. Choosing the correct space group is a delicate problem. $R_{wp}(\psi)$ has two equal minima at positions related by the a - c mirror plane and their disordered mixture is also possible. The situation is very similar to the $Pmnn$ - $Immm$ ambiguity found in the polymer phase.¹¹ Rietveld fits in all three space groups have their minima at the same value of ψ but this angle is different for KC₆₀ and RbC₆₀. $P2_1/a$ gives the best R_{wp} (by 1.3% for KC₆₀ and 0.3% for RbC₆₀) implying that there is no orientational disorder. We conclude that the dimer conformation is *trans* and the same dimer has different orientation in the two materials. We note that $P2_1/a$ is the only space group that allows the same molecule (i.e., *trans*) without disorder in the different orientations we find for KC₆₀ and RbC₆₀. The dimer molecule is shown in Fig. 3 and its orientation in the RbC₆₀ lattice in Fig. 1.

Next we relaxed the condition that the two halves of the dimer be related by an inversion or twofold rotation about the monoclinic \mathbf{b} axis. In that case, the orientations of the two fullerenes in a dimer are specified by independent Euler angles, $(\theta_1, \phi_1, \psi_1)$ and $(\theta_2, \phi_2, \psi_2)$. The second dimer, at $(1/2, 1/2, 0)$, is generated by the symmetry operation in either space group $P2_1$ or Pa . With various choices of (θ_1, ϕ_1) and

(θ_2, ϕ_2) , we made two-dimensional maps of $R_{wp}(\psi_1, \psi_2)$ around high symmetry configurations (e.g., atoms, middle of bonds, or faces chosen as contact points), by rotating the two halves of the dimer independently. Again, the single-bonded *trans* dimer with inversion symmetry gave the best fit in the same $P2_1/a$ configuration described above.

The best Rietveld fit for RbC₆₀ is shown in Fig. 4 and the structural parameters for both samples are summarized in Table. I. In this fit, the model is improved (R_{wp} from 9.4% to 8.2%) from the undistorted fullerene approximation by pulling out the bonding carbon atom and its three neighbors. The intermolecular C-C distance is set to 1.54 Å in tetrahedral coordination, without introducing additional refinable parameters. Unfortunately, it is not possible to get a stable refinement of the positions of individual carbon atoms, as it was for the higher symmetry polymer phase.¹¹ The likely explanation is that we are already so close to the best possible (LeBail) fit that the “driving force” on each atom is random noise. The next largest improvement in the fit comes from anisotropic thermal motion of the cations, similar to that seen in the AC₆₀ and Na₂AC₆₀ polymers.^{11,15}

In conclusion, we have established that in metastable phases of KC₆₀ and RbC₆₀, covalently bonded (C₆₀)₂²⁻ dimer anions form through a single C-C interfullerene bond.

This type of interfullerene bond is different from the four-membered rings of C_{60} polymers, which was first suggested by the fact that the dimer→polymer phase transition is not direct.^{17,24} The sequence of AC_{60} phases has been successfully modeled with a single C-C bonded dimer.²³ Such an interfullerene bond was already found in solution for dimerized C_{60} radicals²⁵ and for $(C_{59}N)_2$,²⁶ which is isoelectronic to $(C_{60})_2^{2-}$. There have been many calculations of the stability for various $(C_{60})_2$ dimers,²⁷ but only one has considered²⁸ the single-bonded, doubly charged anion structure found here. We have recently learned that Prassides and co-workers²⁹ have found a monoclinic lattice for $(C_{59}N)_2$, which is similar to the dimer fulleride considered here.

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¹J. Winter and H. Kuzmany, *Solid State Commun.* **84**, 935 (1992).

²Q. Zhu *et al.*, *Phys. Rev. B* **47**, 13 948 (1993).

³A. Janossy *et al.*, *Phys. Rev. Lett.* **71**, 1091 (1993).

⁴O. Chauvet *et al.*, *Phys. Rev. Lett.* **72**, 2721 (1994).

⁵M.C. Martin *et al.*, *Phys. Rev. B* **49**, 10 818 (1994); **51**, 3210 (1995).

⁶M. Kosaka *et al.*, *Phys. Rev. B* **51**, 12 018 (1995).

⁷L. Granasy *et al.*, *Solid State Commun.* **97**, 573 (1996).

⁸F. Bommeli *et al.*, *Phys. Rev. B* **51**, 14 794 (1995).

⁹Y.J. Uemura *et al.*, *Phys. Rev. B* **52**, R6991 (1995); W.A. MacFarlane *et al.*, *ibid.* **52**, R6995 (1995).

¹⁰S. Pekker *et al.*, *Solid State Commun.* **90**, 349 (1994).

¹¹P.W. Stephens *et al.*, *Nature* **370**, 636 (1994).

¹²A.M. Rao *et al.*, *Science* **259**, 955 (1993).

¹³Y. Iwasa *et al.*, *Science* **264**, 1570 (1994); G. Oszlanyi and L. Forro, *Solid State Commun.* **93**, 265 (1995).

¹⁴M. Nunez-Regueiro *et al.*, *Phys. Rev. Lett.* **74**, 278 (1995); C.H. Xu and G.E. Scuseira, *ibid.* **74**, 274 (1995).

¹⁵Q. Zhu, *Phys. Rev. B* **52**, R723 (1995).

¹⁶Q. Zhu *et al.*, *Phys. Rev. B* **51**, 3966 (1995).

¹⁷G. Oszlanyi *et al.*, *Phys. Rev. B* **51**, 12 228 (1995).

¹⁸The two sets of lattice parameters are denoted by a, b, c, β and a', b', c', β' , where $a \approx a'$ and $\beta \approx \beta'$. Their relation is expressed as $a'^2 = a^2 + c^2 + 2accos\beta$ and $a^2 = a'^2 + c^2 + 2a'ccos\beta'$.

¹⁹Details of the analysis inappropriate for inclusion in this paper are contained in a paper by G. Bendele *et al.* (unpublished).

²⁰For Rietveld refinements we used the programs FULLPROF written by J. Rodriguez-Carvajal, ILL, Grenoble, France and PROFPV

written by D.E. Cox, NSLS, Brookhaven, USA.

²¹A. LeBail *et al.*, *Mater. Res. Bull.* **23**, 447 (1988).

²²We use Cartesian coordinates expressed in angstroms. The y axis of the coordinate system is along the monoclinic **b**, the z axis along the dimer axis, i.e., rotated 1.2° toward **a** from **c**, and **x** = **y** × **z**. The origin of this Cartesian system is also translated by 4.67 Å along **z**. The sixty carbon atoms are generated from the positions (column vectors) C1(0.700,0.000,3.479), C2(3.031,1.425,1.173), and C3(2.598,0.725,2.306) by the point group *m*3, and subjected to the rotations

$$\begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \\ \times \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

²³T. Pusztai *et al.*, *Europhys. Lett.* **32**, 721 (1995).

²⁴K. Kamaras *et al.*, *Phys. Rev. B* **52**, 11 488 (1995).

²⁵J.R. Morton *et al.*, *J. Am. Chem. Soc.* **114**, 5454 (1992).

²⁶J.C. Hummelen *et al.*, *Science* **269**, 1554 (1995).

²⁷D.L. Strout *et al.*, *Chem. Phys. Lett.* **214**, 576 (1993); N. Matsuzawa *et al.*, *J. Phys. Chem.* **98**, 2555 (1994); M. Menon *et al.*, *Phys. Rev. B* **49**, 13 966 (1994); G.B. Adams *et al.*, *ibid.* **50**, 17 471 (1994); S. Osawa *et al.*, *Fullerene Sci. Technol.* (to be published).

²⁸J. Kurti and K. Nemeth, *Chem. Phys. Lett.* **256**, 119 (1996).

²⁹K. Prassides (private communication).