

Effect of Charge State on Polymeric Bonding Geometry: The Ground State of $\text{Na}_2\text{RbC}_{60}$

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Theoretical calculations have predicted all fullerene polymers to have interfullerene connections via $[2 + 2]$ cycloaddition. We find that the ground state of $\text{Na}_2\text{RbC}_{60}$ is a one-dimensional polymer of fullerene molecules connected by *single* carbon-carbon bonds. We discuss and exclude possible steric and kinetic reasons for this discrepancy. Our results imply that it is the charge state of the fullerene molecule that drives the bonding mechanism, causing $(\text{C}_{60}^{\ominus})_n$ and neutral $(\text{C}_{60})_n$ to favor cycloaddition and $(\text{C}_{60}^{3-})_n$ to favor single carbon-carbon bonds. [S0031-9007(97)05104-1]

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The story of polymerization of C_{60} and its derivatives is still full of surprises, as shown by the recent discovery of a two-dimensional cross-linked polymeric fulleride, Na_4C_{60} [1]. While direct bonding of C_{60} molecules has now been reported in a variety of cases [1–9], a systematic study of steric, kinetic, and electronic influences on the formation of fulleride polymers has not been possible to date because the systems in which interfullerene bonds have been found are very dissimilar. Theoretical calculations have consistently found one-dimensional C_{60} chains linked via $[2 + 2]$ cycloaddition (as found in the RbC_{60} ground state [2]) to be the most stable configuration for C_{60} polymers [10–14]. In this Letter, we present the ground state of $\text{Na}_2\text{RbC}_{60}$ as a one-dimensional polymer of C_{60} molecules connected by a *single* carbon-carbon bond (Fig. 1), in contrast to the ground state of the otherwise similar RbC_{60} system (Fig. 2). Answering the question of why the former links fullerene molecules with a single bond, whereas the latter does so with two carbon-carbon bonds is the first step to a complete explanation of the phenomenon of interfullerene bonding. We argue here that the charge state of the fullerene molecule is decisive in determining the bonding mechanism.

Theoretical findings that C_{60} chains bonded by $[2 + 2]$ cycloaddition are generally the most stable polymer configuration were extrapolated from calculations on neutral $(\text{C}_{60})_2$ dimers [10–13]. More recently, a number of studies have *assumed* that bonding mechanism [14–17], even when calculating properties of charged $(\text{C}_{60}^{\ominus})_n$ polymers, e.g., for $j = 1, 3$ [15] or $j = 1, 2$ [16]. The discovery of a single-bonded dimer phase in RbC_{60} and KC_{60} [3] (in addition to the $[2 + 2]$ -bonded one-dimensional polymeric ground state [2]) has shown that this simple picture is insufficient. Subsequently, it was found that the single-bonded structure found experimentally [3] is favored in calculations over a hypothetical $[2 + 2]$ -bonded isomer only if doubly charged dimers $(\text{C}_{60}^{2-})_2$ are considered in-

stead of neutral ones [18,19], casting serious doubts on the validity of any such extrapolations (whether from neutral to charged systems or from dimers to polymers). This leaves the field open to guidance from significant experimental results.

Single carbon-carbon bonds as interfullerene connections have been observed in two-dimensional cross-linked polymeric Na_4C_{60} [1] and in metastable $(\text{C}_{60}^{\ominus})_2$ dimers [3], but neither of these allows a direct comparison to a related $[2 + 2]$ cycloadduct structure. It is known that $\text{Na}_2\text{AC}_{60}$ ($A = \text{Rb}, \text{Cs}$), both cubic fulleride superconductors at ambient pressure, lose their cubic symmetry at pressures ≤ 3 kbar [4]. However, it was claimed that this system, like RbC_{60} , polymerizes via $[2 + 2]$ cycloaddition, in spite of the fact that the interfullerene distance found along the bonding direction was significantly longer (9.35 Å) than in the latter system (9.12 Å) [4]. Recently, we have found that $\text{Na}_2\text{RbC}_{60}$ also loses its cubic symmetry when cooled slowly to temperatures below $T = 230$ K and suggested the formation of interfullerene bonds in this new phase [5]. ^{13}C and ^{23}Na NMR experiments also show a signature of this phase transition [20].

Magnetization measurements at several different cooling rates have shown that it is the cubic phase that is a superconductor with $T_c = 3.5$ K, and that the polymer shows no superconductivity. We note that this contrasts an earlier claim of a superconducting polymeric phase of $\text{Na}_2\text{CsC}_{60}$ at elevated pressure [21]. In view of our observation of slow and incomplete transformation from the cubic to the polymeric phase, we suspect that a small minority cubic fraction provided the superconducting signal.

In order to determine the molecular structure, and in particular the nature of the interfullerene bonding of the $\text{Na}_2\text{RbC}_{60}$ ground state, it is necessary to distinguish relatively subtle structural differences. We have collected high resolution x-ray powder diffraction patterns at

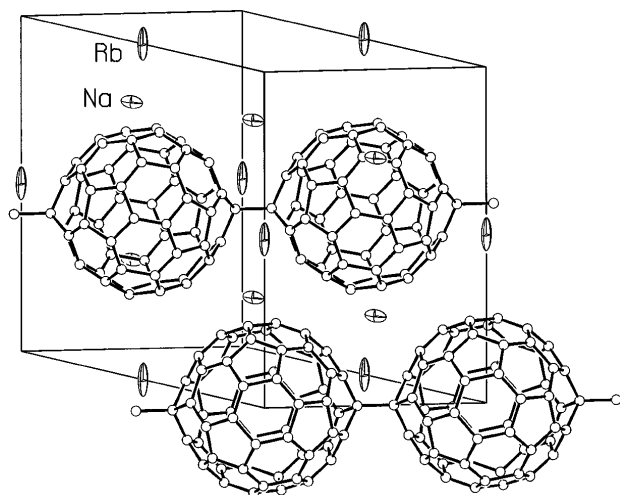


FIG. 1. Crystal structure of the $\text{Na}_2\text{RbC}_{60}$ polymer derived in this work.

$T = 180$ K and $T = 20$ K on beamline X3B1 of the National Synchrotron Light Source at Brookhaven National Laboratory, with $\lambda = 1.15006(1)$ Å and for $2\theta = 6^\circ$ – 50° . We first verified that the sample consists of the known (space group $Pa\bar{3}$) cubic phase [22] at $T = 280$ K. This is frozen when the sample is cooled quickly to low temperatures. It is also present in slowly cooled samples (20% when cooled 1 K/h here), but could be included in the analysis as a secondary phase. A small (<3%) impurity unaffected by cooling has been subtracted along with a smooth background.

The unit cell of the low-temperature structure is derived from the primitive-cubic room-temperature structure by a 0.6 Å contraction along one of the cubic face diagonals and a 0.4° tilt of one of the axes, resulting in monoclinic ($P2_1/a$) lattice parameters of $a = 13.711$ Å, $b = 14.554$ Å, $c = 9.373$ Å, $\beta = 133.53^\circ$ (at $T = 180$ K). Since this unit cell is fairly large and contains 126 atoms, the positions and bond lengths cannot all be determined *independently* from x-ray powder diffraction. However, the fact that the fullerenes remain intact (as polymerization is completely reversible upon heating) provides a favorable circumstance. We can specify the orientation of the fullerene molecules in the lattice using just three parameters, which are defined analogous to Euler angles: ϕ and θ specify a point of contact along the shortened c axis and ψ specifies a rotation about c . Hence, the reliability of information gained about the orientation of the fullerene is much larger than the reliability of information about any single carbon atom. Without making any *a priori* assumptions, we have performed a three-dimensional search over all possible C_{60} orientations. We find only one convincing minimum in the weighted-profile R -factor R_{wp} : A single carbon atom located on the c axis, with a rotation angle about c of $\psi = 82^\circ$ (where $\psi = 90^\circ$ would describe the on-ball double bond associated with the contact atom pointing along b). To illustrate this, Fig. 3 shows a plot of R_{wp} vs ψ for several fullerene points-of-contact.

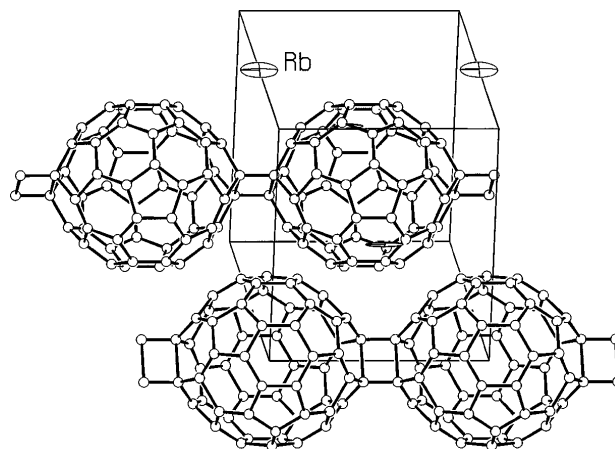


FIG. 2. Crystal structure of the RbC_{60} polymer from Stephens *et al.* [2].

Knowing the orientation of the fullerene in the lattice determines that they are connected by single carbon-carbon bonds along the c axis. Furthermore, the fit improved significantly in this configuration (by 0.5% in R_{wp} ; a difference $>0.08\%$ is considered statistically significant [23]) when we let the position (along c) of the bonding carbon atom refine. The range of the resulting C-C distance between fullerenes allowed by the data (at the 3σ level) is between 1.5 and 1.9 Å. Figure 4 shows our final Rietveld refinement. To determine a more precise value of the interfullerene bond length other, local probes will be necessary and of interest. We note here that if the interfullerene bond length is fixed to 1.61 Å (equal to the intermolecular C-C bond length calculated for the azafullerene $(\text{C}_{59}\text{N})_2$ dimer [24]), the quality-of-fit does

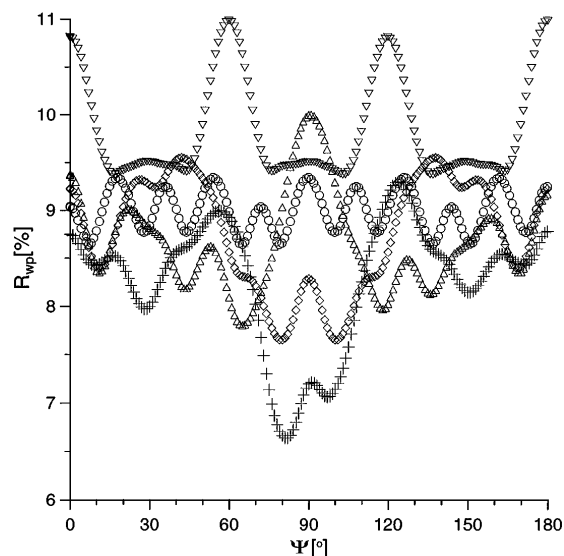


FIG. 3. Plots of weighted-profile R factors R_{wp} vs rotation angle ψ for the following features of the fullerene molecule pointing along c : +, single C atom; \diamond , center of double bond; \triangle , center of single bond; \circ , center of pentagon; ∇ , center of hexagon.

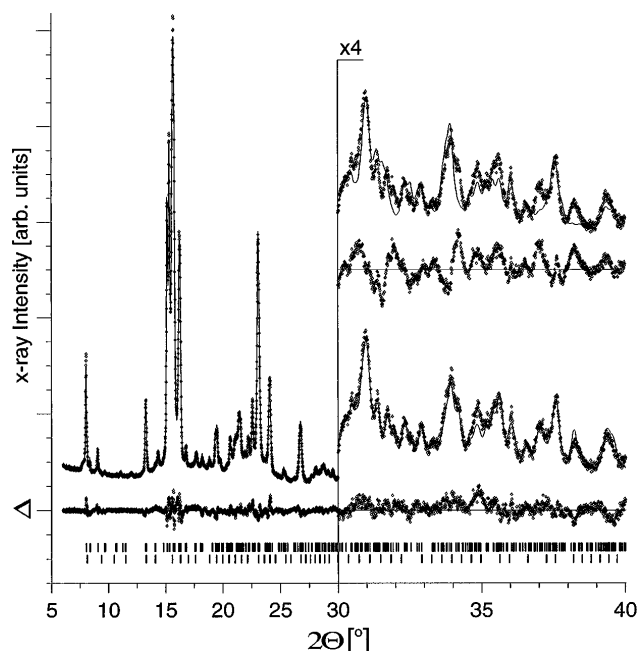


FIG. 4. Left and lower right: Best Rietveld refinement of $\text{Na}_2\text{RbC}_{60}$ at $T = 180$ K ($R_{\text{wp}} = 4.08\%$, $\chi^2 = 5.4$) corresponds to single-bonded polymer structure in Fig. 1. Note change of scale for region of the fit sensitive to fullerene orientation. Upper right: "Second-best" fullerene orientation, corresponding to hypothetical $[2 + 2]$ cycloadduct structure (see text, $R_{\text{wp}} = 5.42\%$, $\chi^2 = 9.5$).

not become worse and none of the other, on-ball, bond lengths increase above 1.55 \AA . On a similar note, the x-ray refinements are not able to distinguish whether the remaining C-C bond lengths in this system show the alternation between single and double bonds characteristic of neutral C_{60} .

In order to see how this orientation compares to the next best (a hypothetical structure with bonding via $[2 + 2]$ cycloaddition), we have performed equivalent Rietveld refinements for both cases. The result favors the single-bonded structure by 1.3% in R_{wp} . To emphasize how drastic such a difference really is, the right side of Fig. 4 shows the regions sensitive to fullerene orientations for both cases. While the lower fit, corresponding to the structure illustrated in Fig. 1, gives an excellent fit to the data, the upper fit shows significant deviations across the entire range between calculated model and experimental data. The latter corresponds to a structure with bonding geometry analogous to the RbC_{60} polymer [2], as illustrated by Fig. 2.

Any proposed model of fullerene bonding geometries must necessarily be in agreement with every observed case of interfullerene bonding, whether in thermodynamically stable phases [1,2,5], phases reached by rapid cooling [3], by exposure to photons [6], under pressure [4,7,8], or by chemical means [9]. Having established the single-bonded nature of the ground state of $\text{Na}_2\text{RbC}_{60}$ and its strong similarity to $[2 + 2]$ -bonded RbC_{60} allow us for the first time to approach this question in a system-

atic manner. Both systems are face-centered cubic above room temperature with full orientational disorder of the fullerenes, and both will form their respective polymeric ground states only if cooled slowly.

However, since $\text{Na}_2\text{RbC}_{60}$ contains two extra Na^+ cations over RbC_{60} per fullerene we have to consider possible steric influences. In cubic trivalent alkali fullerenes, one alkali cation per fullerene occupies the large octahedral site at $(\frac{1}{2}, 0, 0)$ and two occupy the smaller tetrahedral site at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, with site selectivity according to ion size in ternary systems. The hole in the RbC_{60} polymer corresponding to the tetrahedral site of the cubic parent structure is $t = (0, 0.521, 0.220)$ in fractional coordinates of the orthorhombic lattice from Stephens *et al.* [2]. The minimum t -C distance is 2.59 \AA , slightly larger than the minimum Na-C distance of 2.51 \AA in $\text{Na}_2\text{RbC}_{60}$. While this is not the only measure of the t site's ability to hold the Na^+ cation in the $[2 + 2]$ structure, there would clearly be enough room for it (possibly with some small distortion of the lattice), if $[2 + 2]$ bonding were indeed the preferred interfullerene connection.

The polymeric phase described here is formed from the $Pa\bar{3}$ primitive cubic phase [20], in which the fullerenes hop among orientations [25], none of which allow either the single or the $[2 + 2]$ interfullerene bond without rotation. Therefore polymerization must occur during orientational jumps, and so it is unlikely that the cubic phase influences the choice of bonding connections. We note here that in the case of the $[2 + 2]$ cycloadduct polymer RbC_{60} , the polymeric phase forms from an fcc ($Fm\bar{3}m$) precursor phase of fully orientationally disordered fullerene molecules. Hence, that choice of polymer structure is not dictated by kinetics either.

This leads us to consider the fullerene charge state as primary cause for the difference between these two systems. Calculations on $(\text{C}_{60})_2$ dimers [18,19] have already shown that the preferred interfullerene connection is different when doubly charged $(\text{C}_{60}^-)_2$ dimers are considered instead of neutral ones. This suggests that the fullerene charge state is an important factor governing the stability of various interfullerene bonding configurations.

We argue here that the fullerene bonding mechanism is indeed driven by the charge state of the fullerene. Unlike the $[2 + 2]$ cycloaddition reaction (which requires no extra electrons), covalent interfullerene bonding via a single bond requires two extra electrons per bond. The $(\text{C}_{60}^{\cdot-})_n$ species is unique in that it possesses a single unpaired electron, so after one interfullerene C-C bond is formed, the reaction stops, and polymerization via this route is not possible. However, if there are further electrons available (in C_{60}^{j-} with $j > 1$), polymerization becomes feasible.

This model is consistent with all observed cases of interfullerene bonding. It explains why single interfullerene bonds can occur in the dimer phase of RbC_{60} but not in the polymer phase. Polymerization of RbC_{60} occurs through the $[2 + 2]$ cycloaddition reaction, while $\text{Na}_2\text{RbC}_{60}$ forms single-bonded chains. It also explains

the fact that neutral C_{60} is photopolymerized [6], pressure polymerized [7,8], or chemically dimerized [9] only in the $[2 + 2]$ cycloadduct structure, regardless of how many of its neighbors it is bound to, and it is consistent with the other single-bonded structure found to date, cross-linked Na_4C_{60} [1], in which each C_{60}^{4-} anion participates in four single interfullerene bonds.

It will be interesting to see this model tested by high level theoretical treatments such as LDA. We have recently learned of a first quantum-chemical calculation comparing the energetics of various possible fullerene dimer and polymer structures as a function of charge state n for C_{60}^{n-} [26]. In general agreement with our experimental results, it was found that there is a crossover between $n \leq 1$, where a one-dimensional polymer connected via $[2 + 2]$ cycloaddition is favored, and $n \geq 4$, where a two-dimensional single-bonded polymer is favored.

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