

STRUCTURE AND THERMAL BEHAVIOR OF TWO FULLERENE DERIVATIVES

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Introduction

As the solid-state structure and dynamics of pristine C_{60} are dominated by the molecule's nearly spherical architecture, one expects that small perturbations of this architecture would lead to compounds with qualitatively similar solid-state characteristics. Indeed, studies of $C_{60}O$ epoxide and 6,5-annulene $C_{61}H_2$ have shown that their crystal structures and thermal behavior are almost identical to those of pristine C_{60} , with only minor modifications arising from packing constraints [1,2]. Presumably, however, as the perturbations of the molecular architecture become increasingly large, deviations from pristine C_{60} behavior should become much more dramatic, and, beyond a certain point, the derivative compounds should become orientationally ordered at all temperatures, as is indeed seen in osmylated C_{60} , or $C_{60}(OsO_4)(4\text{-tert-butylpyridine})_2$ [3]. To address these issues, we have examined the solid-state structures and thermal behavior of both the 6,6-cyclopropane isomer of $C_{61}H_2$ and the 6,6-cyclopropane isomer of $C_{63}H_6$ using x-ray powder diffraction (XRPD) and differential scanning calorimetry (DSC).

Experimental

Two cyclopropane derivatives, 6,6- $C_{61}H_2$ and 6,6- $C_{63}H_6$, were studied [4,5]. The thermal behavior of the two derivatives was examined via DSC using a TA Instruments 2920 DSC. XRPD measurements were performed on Beamlines X3B1 and X7A at Brookhaven National Laboratory's National Synchrotron Light Source.

Results and Discussion

The room-temperature XRPD profile for $C_{61}H_2$ cyclopropane is shown in Figure 1(a). With the exception of two small impurity reflections, the room-temperature

pattern indicates that the $C_{61}H_2$ molecules are orientationally disordered in a face-centered cubic lattice of symmetry Fm-3m with a lattice parameter of 14.19 Å as is also observed in the 6,5-annulene isomer [2]. The refinement of the room-temperature data was performed by fitting integrated intensities using an fcc structural model in which the orientationally disordered carbon cages were approximated by charged spherical shells and in which the methylene carbon was allowed to occupy both octahedral and tetrahedral voids. The radius of the carbon cage was determined to be 3.550 ± 0.007 Å, and the radius of the methylene carbon refined to a value of 5.0 ± 0.2 Å. As the octahedral occupancy converged to 1.0 ± 0.2 , it is clear that each molecule, as in the case of annulene isomer, is cylindrically disordered about its methylene axis, and the orientation of the methylene axis itself is statistically disordered among the 6 octahedral voids.

Unlike the annulene isomer, however, the low-temperature orientationally ordered phase of $C_{61}H_2$ cyclopropane does not appear to be a simple cubic Pa-3 structure. Rather, the 40 K pattern, shown in Figure 1(b), suggests that the orientationally ordered phase is a low-symmetry orthorhombic structure with lattice parameters of 13.97, 14.00, and 14.25 Å. Ongoing analysis indicates that, although the molecules are at or close to face-centered positions, the symmetry is lower than or equal to primitive orthorhombic.

Perhaps more surprisingly, however, DSC performed on $C_{61}H_2$ cyclopropane revealed two endotherms upon heating, thus indicating the existence of two first-order phase transitions with onset temperatures of 199 and 208 K, both of which are considerably lower than the onset temperature of 290 K associated with the annulene isomer [2]. The presence of two first-order phase transitions suggests that there must be an intermediate phase; as a result, we have carefully measured the XRPD as a function of temperature in the vicinity of these transitions in an attempt to identify this intermediate phase. Although an

intermediate tetragonal phase in which the $C_{61}H_2$ molecules are uniaxially disordered along a single crystallographic axis is favorable on theoretical grounds, we are still in the process of determining the structure of this phase due to complications arising from phase coexistence.

XRPD studies of 6,6-cyclopropane $C_{63}H_6$, a "larger" cyclopropane in which the two hydrogens in $C_{61}H_2$ cyclopropane have been replaced by methyl groups, indicate that this C_{60} derivative is orientationally ordered at all temperatures that fall within the stability regime of the solid itself. XRPD patterns were collected at temperatures ranging from 20 to 413 K, and a high-resolution room-temperature pattern is shown in Figure 2. No evidence of a high-symmetry orientationally disordered phase was observed prior to the actual decomposition of the $C_{63}H_6$ material, which occurred around 413 K as indicated by a sudden irreversible decrease in intensity. Preliminary analysis of the room-temperature pattern suggests that the ordered structure possesses tetragonal symmetry with $a = 16.19 \text{ \AA}$ and $c = 11.39 \text{ \AA}$, although it should be noted that this indexing scheme leaves three weak peaks of anomalous widths unindexed.

Conclusions

While the 6,6-cyclopropane $C_{61}H_2$ molecule differs from the 6,5-annulene isomer only in the point of attachment of the methylene group, the dramatic difference in the low-temperature orientationally ordered structures and in the orientational ordering behavior of the two isomers possibly indicates that the attachment of the methylene group in the cyclopropane isomer leads to a greater net perturbation of the molecular architecture and thus renders a low-temperature orientationally ordered simple cubic phase sterically and energetically unfavorable. $C_{63}H_6$ cyclopropane, however, no longer exhibits plastic crystalline behavior, and therefore allows for a rough estimate of the maximum side-group size compatible with a high-temperature orientationally disordered phase.

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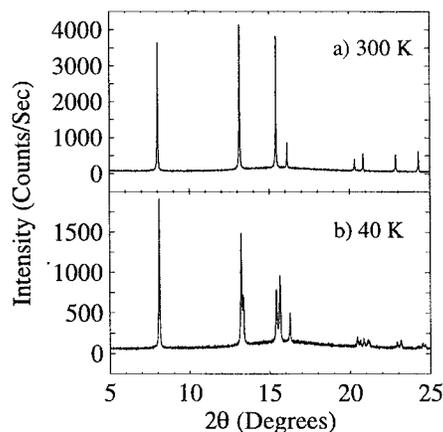


Figure 1. XRPD patterns for $C_{61}H_2$ cyclopropane collected (a) at 300 K and (b) at 40 K.

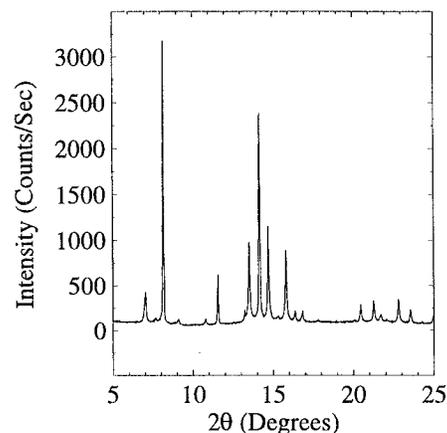


Figure 2. Room-temperature XRPD pattern for $C_{63}H_6$ cyclopropane.

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