

## Effects of Pressure on the Azafullerene ( $C_{59}N$ )<sub>2</sub> Molecular Solid to 22 GPa

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The recent synthesis and isolation in bulk quantities of the nitrogen-substituted fullerene solid,<sup>1</sup> ( $C_{59}N$ )<sub>2</sub>, and its subsequent intercalation with alkali metals to afford azafulleride salts with stoichiometry  $A_6C_{59}N$  ( $A = K, Rb$ )<sup>2,3</sup> opened the way to new opportunities in the quest for the synthesis of fullerene-based materials with novel structural, electronic, and conducting properties. Solid ( $C_{59}N$ )<sub>2</sub> comprises dimeric molecular units linked by C–C bonds formed by C atoms neighboring the N atom on each monomer,<sup>1</sup> but, unlike solid  $C_{60}$ , whose properties have been exhaustively studied in recent years, little is known at present about the physical properties of such condensed heterofullerene phases. We recently reported the first experimental information on the structure and morphology of azafullerene in the solid state by electron microscopy and X-ray diffraction.<sup>4</sup> The as-prepared material showed a remarkable self-organization on the mesoscopic length scale, self-assembling into large ( $> 1 \mu\text{m}$ ), poorly crystalline, hollow spherical particles. In addition, a co-existing hexagonal crystalline phase was also present (space group  $P6_3/mcc$ , lattice constants:  $a = 9.97 \text{ \AA}$ ,  $c = 16.18 \text{ \AA}$  at ambient temperature and pressure). In this communication, we report the results of high-pressure powder synchrotron X-ray diffraction experiments on a crystalline solid azafullerene sample up to a pressure of 22 GPa in an attempt to probe the diversity of bonding interactions present in this material with pressure tuning of the intermolecular distances. We derive the pressure-volume equation-of-state (EOS) and find that the hexagonal phase observed at ambient pressure remains stable under hydrostatic compression to 22 GPa with a bulk modulus of  $K_0 = 21.5(8) \text{ GPa}$  and a pressure derivative  $dK_0/dP = 4.2(1)$ , signifying a somewhat less compressible solid than  $C_{60}$  in which<sup>5</sup>  $K_0 = 18.1(1.8) \text{ GPa}$  and  $dK_0/dP = 5.7(6)$ . The intensities of selected X-ray reflections evolve with pressure in a way consistent with a very low compressibility of the nitrogen-substituted azafullerene molecules themselves.<sup>6</sup>

Figure 1 illustrates the pressure evolution of the powder diffraction profiles of solid ( $C_{59}N$ )<sub>2</sub> between 0.8 and 21.8 GPa at room temperature. At low pressures, ten sharp reflections are clearly resolved and indexed on a hexagonal cell. The observed extinction conditions ( $hh2hl$ :  $l = 2n$  only) are consistent with space group  $P6_3/mmc$  or one of its subgroups. Accurate lattice parameters may be extracted from the diffraction data by employing the Le Bail<sup>11</sup> pattern decomposition technique

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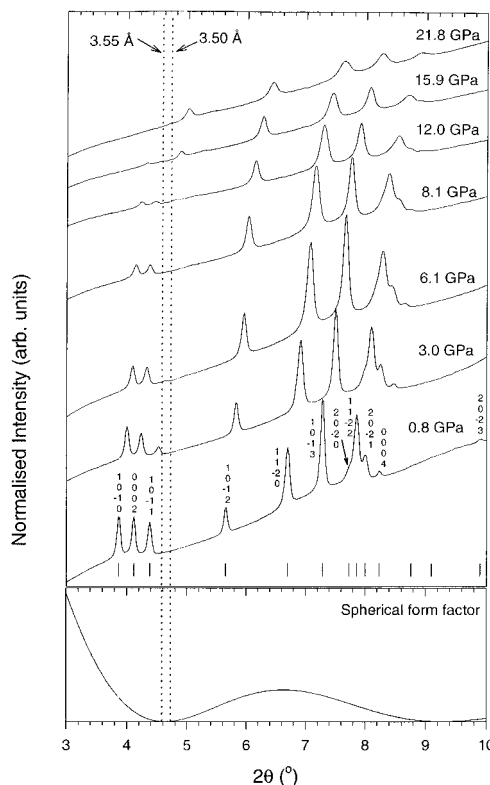
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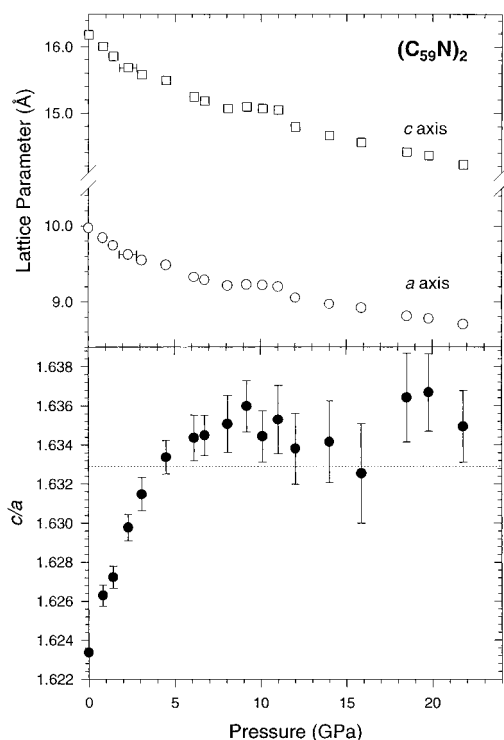


**Figure 1.** Pressure variation of the X-ray diffraction profiles of solid ( $C_{59}N$ )<sub>2</sub> at ambient temperature from 0.8 to 21.8 GPa ( $\lambda = 0.5739 \text{ \AA}$ ). The observed reflections consistent with the hexagonal space group  $P6_3/mmc$  are labeled for the 0.8 GPa profile with the ticks below marking their positions. The bottom panel shows the calculated X-ray scattering form factor for quasi-spherical molecules of radius  $R = 3.55 \text{ \AA}$ . The broken vertical lines mark the position of the zero in the form factor for radii between 3.50 and 3.55  $\text{\AA}$ .

(e.g.,  $a = 9.8396(8) \text{ \AA}$ ,  $c = 16.002(4) \text{ \AA}$  at 0.8 GPa;  $a = 8.7006(24) \text{ \AA}$ ,  $c = 14.225(12) \text{ \AA}$  at 21.8 GPa). As the applied pressure increases the reflections exhibit a monotonic shift toward high angles, accompanied by a gradual increase in peak line width.

One striking feature of the data in Figure 1 is the behavior of the low-angle peak triplet which indexes as  $(10\bar{1}0)$ ,  $(0002)$ , and  $(10\bar{1}1)$  in the hexagonal cell. At a first glance, it appears that a phase transition to another structure may be occurring in the vicinity of 3 GPa, as the intensity of the  $(10\bar{1}1)$  reflection gradually vanishes with increasing pressure. However, as the pressure increases further and the peaks continue to shift to

(6) The azafullerene sample used in the present study was prepared from a "holey bucky" as described previously<sup>1</sup> and was purified by HPLC on a Cosmosil "Buckyprep" column using toluene as eluent. Solid ( $C_{59}N$ )<sub>2</sub> was obtained from a solution in *o*-dichlorobenzene (ODCB), which was evaporated rapidly to dryness in a rotary evaporator. Recrystallization from a  $CS_2$  solution led to a highly crystalline material which was subsequently degassed under dynamic vacuum ( $\sim 10^{-6}$  Torr) at 140 °C for 12 h.<sup>8</sup> The sample was loaded in a diamond anvil cell (DAC), which was used for high pressure generation and was equipped with a stainless steel gasket. The diameter of the diamond culet was 600  $\mu\text{m}$ , and the sample was introduced in a hole made in the gasket 80  $\mu\text{m}$  deep and 200  $\mu\text{m}$  diameter. Cryogenic nitrogen loaded in the DAC at 77 K was used as pressure medium. A minimum pressure of  $\sim 0.5$  GPa was applied in order to seal the gasket hole. Pressure was increased at room temperature and was measured by the quasihydrostatic ruby scale.<sup>9</sup> High-quality X-ray diffraction powder patterns of ( $C_{59}N$ )<sub>2</sub> were collected by an angle-dispersive method using an image-plate detector up to a maximum pressure of 21.8 GPa (1 GPa  $\equiv$  10 kbar). High-brilliance synchrotron X-ray radiation from beamline ID9 of the European Synchrotron Radiation Facility (ESRF) was employed after monochromatization to a wavelength of 0.5739  $\text{\AA}$  using a single bounce Si (111) monochromator in Bragg geometry. The beam was focused vertically with a Pt coated Si mirror to a beamsize of 30  $\mu\text{m}$ . The horizontal beamsize was 70  $\mu\text{m}$ . Masking of the strong Bragg reflections coming from the ruby chip and integration of the two-dimensional diffraction images were performed with the local ESRF FIT2D software.<sup>10</sup>



**Figure 2.** Pressure dependence of (a) the hexagonal lattice constants  $a$  and  $c$  and (b) the  $(c/a)$  ratio. The broken line marks the ideal value of the  $(c/a)$  ratio for a hexagonal-close-packed structure.

higher angles, the intensities of the (0002) and (10 $\bar{1}$ 0) reflections also successively diminish, while the (10 $\bar{1}$ 1) reflection re-emerges with a nonzero intensity. This is reminiscent of the behavior of face-centered-cubic solid C<sub>60</sub> under pressure<sup>5</sup> whence the (200) reflection has zero intensity at low pressures as a result of an accidental coincidence at the same  $d$ -spacing between its position and the existence of a node in the X-ray scattering form factor of the hollow spherical molecules. The intensity changes in the low-angle region in solid (C<sub>59</sub>N)<sub>2</sub> can be interpreted along the same lines. Assuming the C<sub>59</sub>N units can be modeled to a first approximation as hollow spherical shells of uniform charge density  $\rho$  and radius  $R$ , the molecular form factor,  $f(\theta)$  is given by  $f(\theta) = \rho \sin(2\pi R/d)/(2\pi R/d)$ , where  $d$  is the lattice spacing. The lower panel in Figure 1 shows the Bragg angle dependence of the X-ray scattering form factor,  $[f(\theta)/\rho]^2$  which exhibits zeros in the range 4.7–4.6° for C<sub>59</sub>N radii  $R \approx 3.50$ –3.55 Å. Even though the C<sub>59</sub>N units should exhibit a nonuniform charge density distribution on their shell,<sup>1,12,13</sup> orientational disorder (static and/or dynamic) effects are expected to smooth out such deviations. The observed behavior of the low angle peak triplet can then be understood as its members successively pass through the zero in the form factor and re-emerge on its high angle side. Such an interpretation is consistent with a compressibility of the molecule significantly lower than that of the bulk solid.

Figure 2a shows the pressure evolution of the hexagonal lattice constants  $a$  and  $c$ . They both exhibit very similar monotonic pressure dependence, indicating the absence of substantial

anisotropy in the compressibility along  $a$  and  $c$ . A sensitive way of following the anisotropy is to focus on the  $(c/a)$  ratio, as it changes with increasing pressure (Figure 2b). This reveals that the structure of (C<sub>59</sub>N)<sub>2</sub> is somewhat less compressible along the  $c$  direction, as  $(c/a)$  smoothly increases from an initial value of 1.623 at ambient pressure toward 1.634 at ~6.5 GPa and then remains essentially unchanged to the highest pressure. These observations can be rationalized if the bridging C–C bonds of the (C<sub>59</sub>N)<sub>2</sub> dimers (of length 1.61 Å)<sup>13</sup> are exactly aligned with neither the basal plane nor the unique axis of the hexagonal cell. Indeed the experimentally observed smaller compressibility along the  $c$  axis is consistent with the C–C bonds inclined to it at a smaller angle than that formed with the basal plane; for instance, this is realized when the bonds are aligned roughly parallel to the (1/3, 2/3, 1/2) direction, as implied by preliminary Rietveld refinements of ambient pressure diffraction data. Finally, the limiting  $(c/a)$  value reached at ~6.5 GPa is close to the ideal ratio of 1.633 expected for a hexagonal close packed structure that would imply little difference between intradimer and interdimer distances. We note that it is exactly in this pressure range that the interdimer center-to-center distances are compressed to values of ~9.3–9.4 Å, essentially identical with those found for the bonded pairs of C<sub>59</sub>N units both in Rietveld analysis of ambient pressure synchrotron X-ray powder diffraction data<sup>12</sup> and density-functional-based calculations.<sup>13</sup>

Figure 3 (supporting information) presents the ambient-temperature equation-of-state of solid (C<sub>59</sub>N)<sub>2</sub> together with a least-squares fit to the semiempirical second order Murnaghan EOS.<sup>14</sup> The latter results in an atmospheric-pressure isothermal bulk modulus of  $K_0 = 21.5(8)$  GPa (compressibility,  $\kappa = 4.6(2) \times 10^{-2}$  GPa<sup>-1</sup>) and a pressure derivative of  $dK_0/dP = 4.2(1)$ . The bulk modulus of azafullerene is only marginally larger than that measured for solid C<sub>60</sub><sup>5</sup> and implies a somewhat tighter crystal packing; the volume of the azafullerene unit cell is ~98% that of C<sub>60</sub> at ambient pressure, increasing to ~99% at 20 GPa and implying stiffer nearest-neighbor bonds. It is noteworthy that the azafullerene molecular units survive intact and their intermolecular bonding character is retained to pressures as high as 22 GPa.

In conclusion, angle-dispersive X-ray diffraction measurements were performed on solid (C<sub>59</sub>N)<sub>2</sub> up to 22 GPa at room temperature, revealing a somewhat less compressible solid than pristine C<sub>60</sub>. We were able to probe the diverse character of the bonding interactions present in this solid, ranging from those in individual quasispherical C<sub>59</sub>N monomer units to the intradimer C–C bridging bonds and the weak interdimer van der Waals interactions. The lack of strong anisotropy in the compressibility is rationalized in terms of the nonalignment of the C–C bridging bonds of the dimer with the unit cell axes. As the pressure increases, however, the interdimer distances compress faster than the intradimer ones, and, at ~6.5 GPa, they are both of comparable magnitude, leading to a novel high-pressure solid structure which appears to be characterized by almost isotropic bonding.

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**Supporting Information Available:** Figure 3 (1 page). See any current masthead page for ordering and Internet access instructions.

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