ESRF	**Experiment title:** Structural studies of Fullerenes and Fullerides at High Pressures	**Experiment number:** HC242
Beamline: ID9-BL3	**Date of experiment:** from: 19 Oct. 95 to: 21 Oct. 95	**Date of report:** 27/2/96
Shifts: 9	**Local contact(s):** M. Hanfland, D. Häusermann	*Received at ESRF:* 01 MAR 1996

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Report:

The recent synthesis and isolation in bulk quantities of the nitrogen-substituted fullerene solid, $^1(C_{59}N)_2$, and its subsequent intercalation with alkali metals to afford azafulleride salts[2] with stoichiometry $A_6C_{59}N$ (A= K, Rb) opened the way to new opportunities in the quest for the synthesis of fullerene-based materials with novel structural, electronic and conducting properties. 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. As part of our present beam allocation on ID9, we performed angle-dispersive X-ray diffraction measurements on solid $(C_{59}N)_2$ up to 22 GPa at room temperature. Our results have now been submitted for publication to *J. Am. Chem. Soc.*[3] A less compressible solid than pristine C_{60} was revealed with a bulk modulus of K_0= 21.5(8) GPa and a pressure derivative $\frac{dK_0}{dP}$ = 4.2(1). We were able to probe the diverse character of the bonding interactions present in this solid, ranging from those in individual quasispherical $C_{59}N$ monomer units to the intradimer C–C bridging bonds and the weak interdimer van der Waals interactions. The ambient-pressure hexagonal structure (space group *P63/mmc*, lattice constants: a= 9.97 Å, c= 16.18 Å at ambient temperature and pressure) is stable to the highest pressure of the present experiment and the observed Pressure evolution of the intensities of selected reflections is

consistent with a very low molecular compressibility of **the** $C_{59}N$ monomers, compared to that of the bulk solid. The lack of strong anisotropy in the compressibility is rationalised in terms of the non-alignment of the C–C bridging bonds of the dimer with the hexagonal 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 characterised by almost isotropic bonding.

References

[1] Hummelen, **J.C. et *al.*, Science 1995,269, 1554.**

[2] Prassides, K. *et al., Science 1996,* in press.

[3] Brown, C.M. *et al., J. Am. Chem. Soc.* submitted for publication.

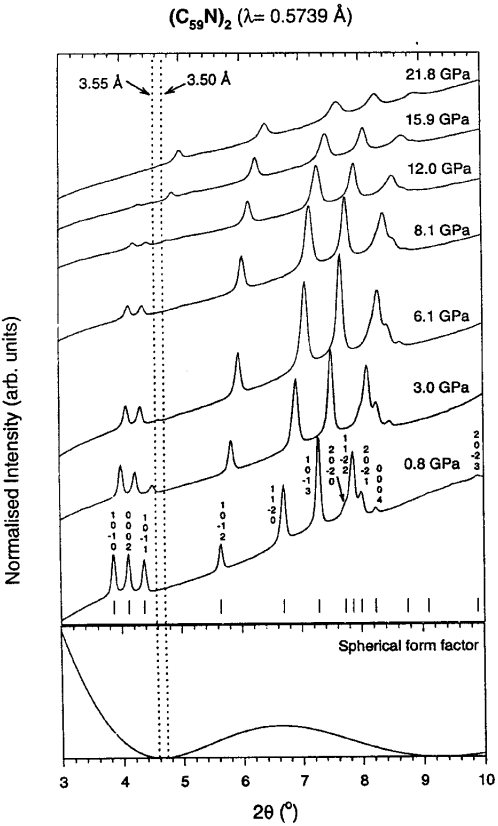
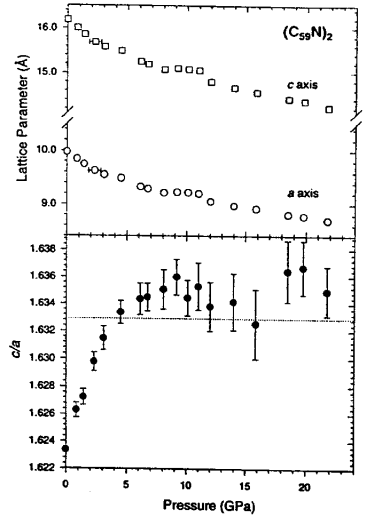


Figure 1. Pressure variation of the X-ray diffraction profiles of solid $(C_{59}N)_2$ at ambient temperature from 0.8 to 21.8 GPa (λ= 0.5739 Å). The observed reflections (space group $P6_3/mmc$) are labelled for the 0.8 GPa profile with the ticks below marking their positions. The bottom panel shows the calculated X-ray scattering form factor for quasi-spherical molecules of radius R= 3.55 Å.



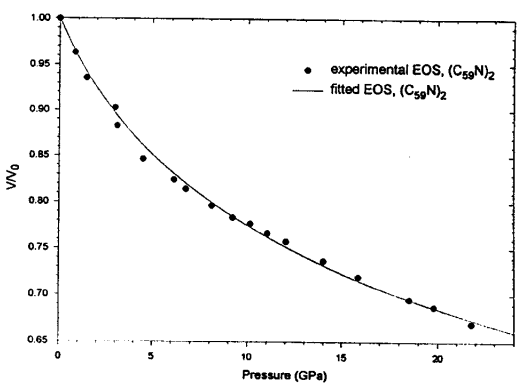


Fig. 2 Pressure dependence of (a) the hexagonal lattice constants *a* and *c* and (b) the (*c*/ *a*) ratio. The broken line marks the ideal value for a hcp structure.

Fig. 3 The ambient temperature equation-of-state (EOS) of solid $(C_{59}N)_2$.