

**MS10.11.07 STRUCTURAL STUDIES OF HETERO-FULLERENES AND THEIR INTERCALATED DERIVATIVES.** Kosmas Prassides\* and Fred Wudl\*\* \* School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK \*\* Institute Polymers and Organic Solids, Departments of Chemistry and Materials, University of California, Santa Barbara, CA 93106, USA

The structure of the recently synthesised azafullerene solid has been studied by synchrotron X-ray diffraction both as a function of temperature and pressure. At ambient pressure, the as-prepared solid adopts a hexagonal crystal structure (space group  $P6(3)/mmc$ ) that persists in the temperature range between 80 and 500 K. Angle-dispersive X-ray diffraction data to pressures in excess of 20 GPa reveal a smooth evolution of the  $(c/a)$  ratio which reaches a plateau of 1.633 in the vicinity of 5 GPa. Sublimation of the azafullerene solid leads to a different low-symmetry structural form which shows clear evidence of superlattice formation consistent with the presence of dimeric  $(C_{59}N)_2$  units. Reaction of the azafullerene solid with potassium and rubidium leads to the isolation of crystalline derivatives with stoichiometry  $K_6C_{59}N$  and  $Rb_6C_{59}N$ . Temperature-dependent synchrotron X-ray diffraction data reveal body-centred-cubic structures, essentially isostructural with the analogous derivatives of  $C_{60}$  and comprising of monomeric  $(C_{59}N)_6$  units.

**PS10.11.08 QUANTITATIVE NANODIFFRACTION FROM CARBON NANOTUBES.** J. M. Cowley, Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504, USA.

Electron diffraction patterns obtained with coherent electron beams less than 1 nm in diameter may now be recorded digitally by use of a CCD detector and quantitative structural analyses may be made of small regions such as portions of the walls of carbon nanotubes. It has been known theoretically for a long time that, for coherent diffraction with a small beam, the diffraction pattern for even very thin specimens should have no center of symmetry unless both the incident beam and the illuminated area of the specimen are symmetric about the same point. However no tests on specimens of known structure have appeared feasible. Carbon nanotubes having an ideal structure with circular cylindrical symmetry are of interest in this connection because their curved walls provide non-symmetric objects of known structure. Measurements of the intensities of diffraction patterns from such walls show asymmetries in good agreement with the calculations made for ideal structures [J. M. Cowley and S. D. Packard, *Ultramicroscopy*, In Press]. Patterns from the planar regions of walls of those nanotubes having polygonal cross-sections are characteristically different. Observations on diffraction pattern asymmetries may thus be used to deduce information on the curvature of nanotube, or nano-particle, walls in regions where the structure is less obvious such as at the ends of nanotubes and at bends in the walls. Diffraction patterns from single-walled nanotubes and clusters of single-walled tubes are more difficult to record because the scattering is very weak, but can give valuable information on the helicity of the tubes, the regularity of the packing of the clusters and the deformations associated with tube bending.

**PS10.11.09 FULLERENE CRYSTALS: DIFFRACTION EFFECTS AND THE ORIENTATION ORDERING PROBLEMS.** Ruben A. Dilanian, Oksana G. Rybchenko, Eugene V. Shulakov, Veniamin Sh. Shekhtman, Institute of Solid State Physics, RAS, Chernogolovka, Moscow distr., 142432, Russia.

The crystallographic analysis of the  $C_{60}$  molecules orientational ordering in a crystal structure and their influence on the features of diffraction pattern was carried out. The different leaves of correlation's between symmetry axes of icosahedral molecule and cubic lattice are considered. It established the magnitudes of rotation angles ( $44.47^\circ$  and  $75.53^\circ$ ) by transition from face-centered (Fm3) to primitive (Pm3, Pa3, Pn3) cubic structure. The result used for analysis of possible orientational ordering models, including modulation structure and discrete orientational glass.

The next interesting problems is the peculiarities of diffraction picture and its variations near the order-disorder phase transition. We have analyzed the Fourier image of the  $C_{60}$  molecules and its superposition with Laue interference function. For disordered state the Fourier image defined the good visibility of diffraction pattern only by small range of angle and also the special extinction by condition  $h^2+k^2+l^2=4n^2$ . For the "freezing" structure, including all variations of orientational ordering by lower temperature and possible other structure transformations, the image is quite differ. The spherical symmetry of Fourier image is lost and as following the local maxima are arised by large diffraction angle. The comparison of calculated diffraction distributions and the experimental data are discussed.

**PS10.11.10 STRUCTURE OF THE  $C_{60}$ •TMPD NEW COMPLEX.** V. V. Gritsenko, O. A. Dyachenko, V. A. Nadochenko, Institute of Chemical Physics in Chernogolovka, RAS, Chernogolovka, Moscow region, 142432 Russia,

The crystal structure of a  $C_{60}$ •TMPD (1) (TMPD — N,N,N',N'-tetramethylparaphenylenediamine) new complex with charge transfer was studied by X-ray analysis. The charge transfer is confirmed by IR-spectrum data. The red shift for the number of vibrational modes, especially for the  $1428\text{ cm}^{-1}$  mode, is observed in IR-spectra, which corresponds to a partial charge transfer from the amine molecule to  $C_{60}$ . The X-ray structural data also testify to the charge transfer in 1: the TMPD molecules is flat, that pointing to the molecule charging.

It is shown that there are fullerene layers between which the TMPD molecules are arranged in the crystal structure. The shortened contacts of the C...C type ( $3.21(2)$ — $3.32(1)\text{Å}$ ) are discovered between TMPD and fullerenes (Fig. 1). Such contact shortening is obviously based upon the donor-acceptor interaction of TMPD with  $C_{60}$ . The presence of the shortened C...C contacts accounts for the relative ordering of the fullerenes in the structure 1.

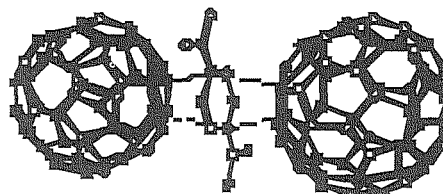


Fig. 1