

**04.X-05** SOLID-STATE POLYMERIZATION OF DIACETYLENES. By V. Enkelmann, Institut für Makromolekulare Chemie, Hermann Staudinger Haus, Stefan-Meier-Str. 31, D7800 Freiburg, W. Germany.

Suitably substituted butadienes (diacetylenes) polymerize in the solid-state. The polymerization is initiated thermally or by irradiation and leads to 1,4 addition of neighbouring monomers to linear, fully conjugated polymer chains which are oriented along well defined crystallographic directions. In many cases the reaction proceeds homogeneously so that macroscopic, defect free, polymer single crystals can be obtained. The dependence of reactivity on the monomer packing, the mechanism of polymer growth in the monomer lattice in comparison with other solid-state reactions and phase transitions connected with the polymerization process will be described using crystal structure analyses of monomers and polymers, morphological and spectroscopic studies and Brillouin scattering.

**04.1-01** HOW TO PACK SPHERES DENSELY AND HOW TO STUFF THEIR OCTAHEDRAL AND TETRAHEDRAL INTERSTICES. By W. H. Baur, Department of Geological Sciences, University of Illinois, Chicago, Illinois 60680, U.S.A.

It is useful to classify close packings (sphere packing density  $D > 0.68$ ) of equal size spheres on the basis of the coordination numbers (CN) of the spheres. Up to now four main types of dense sphere packing were known: hexagonal closest packing (hcp), with CN=12 and  $D=0.74$ ; tetragonal body centered, CN=10,  $D=0.70$ ; body centered cubic, CN=8,  $D=0.68$  and face centered cubic (fcc) CN=12,  $D=0.74$ . An additional tetragonal close packing with CN=11,  $D=0.72$ , which is realized, among many others, by the anions in the rutile type and in  $\text{Li}_4\text{GeO}_4$  has recently been described (W. H. Baur, Mat. Res. Bull. 16, No. 3, 1981). A further tetragonal, less dense packing CN=9,  $D=0.69$  is being introduced here:  $a=b=\sqrt{2}+\sqrt{2\sqrt{5}/12}$ ,  $c=\sqrt{4/3}$ , spheres of unit diameter in 4-fold position f (Wyckoff notation) of space group  $P4_2/mnm$ , with  $x=\sqrt{5/12}/(1+2\sqrt{5/12})$ . In each of these packings the spheres are symmetry equivalent. They can easily be transformed into each other by changing the symmetry and the dimensions of the unit cells. Fourteen different, but topologically equivalent coordinating spheres participate around each central sphere in the six packings. Per sphere there are 3/2 octahedral interstices in each packing. Two of these correspond to the ideal octahedral holes of fcc and hcp. Distorted octahedral voids are used to generate tetrahedral interstices. Depending on the type of packing different rules apply to the sharing of corners, edges and faces of the tetrahedra and octahedra. A complete genealogy of close packed structures can now be established. Applications of these relationships are useful among other things for systematizing certain classes of ionic conductors, for classifying potential conduction pathways in solid electrolytes and for the interpretation of some high pressure transformations.

**04.1-02** AB-INITIO MOLECULAR ORBITAL VERSUS LOW TEMPERATURE NEUTRON DIFFRACTION MOLECULAR STRUCTURES FOR SOME ORGANIC MOLECULES. G. A. Jeffrey and J. R. Ruble, Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260; R. K. McMullan, Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973; D. J. DeFrees, J. S. Binkley and J. A. Pople, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213.

The ab-initio calculations were carried out with full geometry optimization at the Hartree-Fock level with a 3-21G basis set using GAUSSIAN 78 and 80 (J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seegar, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn & J. A. Pople, QCPE 13, 406, 1981). The single crystal neutron diffraction data were measured at the Brookhaven HFBR using a DISPLEX closed-cycle refrigerator. Anisotropic parameter refinement was by full-matrix least squares using ORFLS. Thermal motion analysis was by the segmented-body method using ORSBA. Bond lengths and valence angles were corrected for thermal motion. The molecules studied were acetamide (rhombohedral phase) at 23 K, fluoroacetamide at 20 K, formamidoxime at 16 K, s-diformylhydrazine at 15 K, glyoxime at 9 K. The thermal motion corrections were between 0.001 and 0.006 Å for the non-hydrogen bond lengths, 0.008 and 0.013 Å for the bonds to hydrogens.

For two of the molecules, acetamide and s-diformylhydrazine, the calculated theoretical minimum energy conformation for the isolated molecule is different from that observed in the crystal. In acetamide, the theoretical minimum energy conformer has  $\bar{m}$  symmetry, whereas in the crystal, the molecule is asymmetric with one C-H bond nearly normal ( $92.4^\circ$ ) to the plane of the non-hydrogen atoms. Pyrimidization of  $1.5^\circ$  is observed at the  $sp^2$  carbon in acetamide, but not in fluoroacetamide where both the observed and calculated conformations have  $\bar{m}$  symmetry. The calculated energy for the observed conformer ( $90^\circ$ ) is 1.7 kJ/mol<sup>-1</sup> higher than the minimum. In s-diformylhydrazine, the calculated minimum energy conformer has 2 symmetry with a C-N-N-C torsion angle of  $142^\circ$ . The conformer observed in the crystal has 2/m symmetry, and is calculated to be 13 kJ/mol<sup>-1</sup> higher in energy.

The theory correctly reproduces the small differences observed in the same bond lengths in different molecules. Absolute differences between the calculated and observed bond lengths arise from approximations in the theory, crystal field effects, and thermal motion effects. The first is estimated from higher order calculations on simpler molecules, up to the MP3/6-31G\* level, allowing for electron correlation and polarization. The effect of hydrogen bonding on C-N and C=O bond lengths is estimated from HF/3-21G calculations on the formamide monomer and hydrogen bonded dimer. With these corrections, the residual discrepancies in bond lengths were reduced to less than 0.015 Å, with two exceptions. The N=C and N-O bonds in the oximes are observed longer and shorter, respectively, than those calculated, by  $\approx 0.025$  Å. When corrected for thermal motion, the experimental C-H bond lengths are  $\approx 0.03$  Å longer than the theoretical values.

This work was supported, in part, by the Dept. of Energy at Brookhaven National Lab., and by NSF Grant CHE-79-01061 at Carnegie-Mellon University.