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

Suitably substituted butadienes (diacety-
lenes) 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 con-
jugated polymer chains which are oriented
along well defined crystallographic direc-
tions. 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, morpholo-
gical 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 $Li_4GeO_4$ has re-
cently 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: $a=b=\sqrt{\frac{1}{2}}+\sqrt{2}\sqrt{5}/12$,
$c=\sqrt{4/3}$, 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 par-
ticipate 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 octa-
hedra. A complete genealogy of close packed structures
can now be established. Applications of these relation-
ships are useful among other things for systematizing
certain classes of ionic conductors, for classifying po-
tential conduction pathways in solid electrolytes and
for the interpretation of some high pressure transforma-
tions.

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 para-
meter 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-diformyl-
hydrazine, 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 m
symmetry, whereas in the crystal, the molecule is
asymmetric with one C-H bond nearly normal (92.4°)
to the plane of the non-hydrogen atoms. Pyrimidization
of 1.5° is observed at the $sp^2$ carbon in acetamide, but
not in fluoroacetamide where both the observed and
calculated conformations have m symmetry. The cal-
culated energy for the observed conformer (90°) is 1.7
kJ/mol$^{-1}$ higher than the minimum. In s-diformylhyd-
razine, the calculated minimum energy conformer has
2 symmetry with a C-N-N-C torsion angle of 142°. The
conformer observed in the crystal has 2/m symmetry,
and is calculated to be 13 kJ/mol$^{-1}$ higher in energy.

The theory correctly reproduces the small differ-
ences observed in the same bond lengths in different
molecules. Absolute differences between the calc-
ulated and observed bond lengths arise from approx-
imations 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 correl-
ation 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 hyd-
rogen bonded dimer. With these corrections, the re-
sidual 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 ≈0.025
Å. When corrected for thermal motion, the experimen-
tal C-H bond lengths are ≈0.03 Å longer than the
theoretical values.