

**06.2-09** AN X-N DEFORMATION DENSITY STUDY OF POTASSIUM HYDROGEN DIFORMATE AT 120K. By K. Hermansson and R. Tellgren, Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden.

The X-N deformation density of potassium hydrogen diformate,  $\text{KH}(\text{CHO})_2$ , has been studied at 120K. The crystal structure is orthorhombic; centrosymmetric space group  $\text{Pbca}$ . Neutron diffraction data were collected at a wavelength of 0.7228 Å in the range  $\sin\theta/\lambda < 0.69 \text{ \AA}^{-1}$ . The X-ray data were collected using  $\text{MoK}\alpha$  radiation. A total of ~14000 reflections were measured out to  $\sin\theta/\lambda = 1.2 \text{ \AA}^{-1}$ .

In the crystal structure of potassium hydrogen diformate (Larsson & Nahringsbauer, Acta Cryst. (1968) B24, 666) a very short hydrogen bond of 2.437 Å connects the two formate groups. In most structures where such a short hydrogen bond is found, there is some symmetry restriction on the bond. This is not the case in potassium hydrogen diformate where the two formate groups are crystallographically non-equivalent. The O-H and H...O distances are 1.166 and 1.272 Å, respectively. X-N maps have been calculated in order to show the deformation density in the hydrogen bond as well as in the bonding and lone-pair regions of the two formate groups.

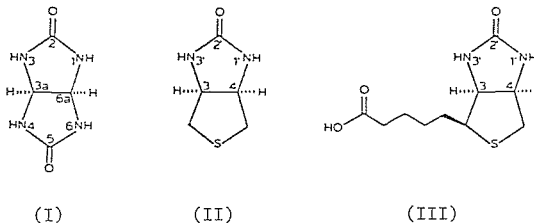
**06.2-10** THE DEFORMATION ELECTRON DENSITY IN PHOSPHINETRIYLTRIAACETONITRILE,  $\text{P}(\text{CH}_2\text{CN})_3$  STUDIED BY X-RAY DIFFRACTION AND AB INITIO CALCULATIONS. By Sine Larsen<sup>a</sup>, Sten Rettrup<sup>a</sup> and Otto Dahl<sup>b</sup>, Department of Physical Chemistry<sup>a</sup> and Department of General and Organic Chemistry<sup>b</sup>, University of Copenhagen, DK-2100 Copenhagen, Denmark.

$\text{P}(\text{CH}_2\text{CN})_3$  is remarkable in being a low molecular weight phosphine, which is crystalline, airstable and has a low nucleophilic reactivity. The crystal structure at room temperature (Dahl & Larsen, J. Chem. Research. (S) (1979) 396) shows that in  $\text{P}(\text{CH}_2\text{CN})_3$  the P-C bond length is slightly longer and the C-P-C bond angle slightly smaller than in  $\text{P}(\text{CH}_3)_3$ . These changes might indicate that the phosphorous lone pair has an increased "s-character" in  $\text{P}(\text{CH}_2\text{CN})_3$ , consistent with the high lone pair ionization potential (10.6 eV cf. 8.6 eV for  $\text{P}(\text{CH}_3)_3$ ).

To elucidate the electron distribution in  $\text{P}(\text{CH}_2\text{CN})_3$  low temperature (90K) X-ray diffraction data was collected, maximum  $\sin\theta/\lambda = 1.35$ . Using these data deformation density maps  $\Delta\rho = \rho(\text{obs}) - \rho(\text{cal})$  were calculated. The calculated density was derived from the high angle X-ray data. With the purpose of investigating the differences in the electron distribution between  $\text{P}(\text{CH}_3)_3$  and  $\text{P}(\text{CH}_2\text{CN})_3$  ab initio calculations of deformation densities have been undertaken for a series of model compounds. A comparison will be made between the experimental and theoretical deformation densities.

**06.2-11** HIGH RESOLUTION DIFFRACTION STUDIES OF BIOTIN (VITAMIN H) AND ITS VITAMERS. By George T. DeTitta, Robert H. Blessing and Grant Moss, Medical Fndn. of Buffalo, Inc., Buffalo, NY 14203, U.S.A.

Two polymorphs of glycoluril (I) and one form of *cis*-tetrahydro-2-oxo-thieno[3,4]imidazole (II) have been studied by X-ray diffraction to high resolution ( $\sin\theta/\lambda \leq 1.2 \text{ \AA}^{-1}$ ) at room temperature and refined using multipole deformation models (F. Hirshfeld (1977) Israel J. Chem., 16, 226-229). In addition, two independent medium resolution ( $\sin\theta/\lambda \leq 1.0 \text{ \AA}^{-1}$ ), low temperature (115K) data sets of the parent vitamin biotin (III) have been measured\* and are under refinement. From the high resolution studies, the electronic structure of the ureido ring, and the effect of the heteroatomic sulfur therein, will be discussed. Research supported in part by US-HHD-AM19856.



\* One set measured at Dept. Chemistry, NRC-Ottawa with E. Gabe and Y. LePage.

**06.2-12** ELECTRON DENSITY DISTRIBUTIONS IN THE BONDS OF THE CYCLOBUTADIENE SYSTEM.

By H. Irngartinger and M. Nixdorf, Institute for Organic Chemistry, University of Heidelberg Im Neuenheimer Feld 270, D-6900 Heidelberg, West-Germany.

The electron density distributions in the bonds of the cyclobutadiene derivative **1** have been determined from X-X data measured at  $110 \pm 1 \text{ K}$ . Unlike the difference densities from room temperature measurements of **2** (H. Irngartinger, H.-L. Hase, K.-W. Schulte and A. Schweig, Angew. Chem. 89, 194 (1977)) now we obtained quantitative results. Compound **1** crystallizes



in a centric conformation as **2** and in a chiral conformation. For this investigation we have chosen the latter one (P1, Z=2; a=11.464(1), b=9.148(1), c=10.527(2) Å,  $\alpha=115.62^\circ(1)$ ,  $\beta=69.26^\circ(1)$ ,  $\gamma=88.32^\circ(2)$ ), which shows a twist conformation for the seven membered rings. The bonds of the four membered ring are bent. The deviations of the electron density maximum of the C=C double bond (1.352 Å) from the bond axis is  $7^\circ$ , the corresponding value for the C-C single bond (1.590 Å) is  $18^\circ$ . The density maxima of these bonds have heights of 0.5 and  $0.3e/\text{Å}^3$  respectively. The density distribution of the double bond shows a large elongation perpendicular to the four membered ring. The deformation densities of the other bonds in **1** are localized on the bond axes.