

**09.2-06** NEUTRON DIFFRACTION REFINEMENT OF THE STRUCTURE OF A PUSH-PULL ETHYLENE  $C_{13}H_{14}OSN_2$ . By Sandhya Bhakay-Tamhane, A. Sequeira and R. Chidambaram, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

Push-pull substituted ethylenes  $\begin{matrix} D_1 \\ \diagdown \\ C \\ \diagup \\ D_2 \end{matrix} > C = C < \begin{matrix} A_1 \\ \diagup \\ C \\ \diagdown \\ A_2 \end{matrix}$  are known to have a strong conjugative interaction between the donor and acceptor parts of the molecule. One such substituted ethylene, 1-benzoyl-1-cyano-2-dimethylamino-2-methylthioethylene,  $C_{13}H_{14}OSN_2$ , space group  $P2_1/c$ ,  $a = 7.214$ ,  $b = 8.935$ ,  $c = 20.243 \text{ \AA}$ ,  $\beta = 99.42^\circ$ ,  $Z = 4$ ; has been studied using X-ray diffraction (D. Adhikesavalu and K. Venkatesan, 1980, Private Communication). We have studied this structure using a TDC-312 computer-controlled 4-circle neutron diffractometer. A least-squares refinement in the structure based on 1078 independent data up to  $\sin\theta/\lambda = 0.44 \text{ \AA}^{-1}$  ( $\lambda = 1.036 \text{ \AA}$ ) yielded a final R-value on F of 0.064. The thermal parameters of practically all the atoms are very high and seem related to the lack of strong intermolecular interaction in the structure. A detailed analysis of the thermal motion has been carried out. The C=C bond is  $1.44(1) \text{ \AA}$  and the dihedral angle across the bond is  $37.4(6)^\circ$ . There is good general agreement between the neutron and X-ray results. The structural and thermal parameters obtained from the two investigations are compared using half-normal probability plots. The structural details, with specific emphasis on the distortions occurring due to the push-pull substituents, and the thermal motion analysis will be presented.

**09.2-07** CRYSTAL AND MOLECULAR STRUCTURES OF POLARISED ETHYLENES. By D. Adhikesavalu and K. Venkatesan, Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India.

Low barrier to rotation around carbon-carbon double bond in ethylenes which on one hand carry electron attracting and on the other electron withdrawing substituents has been detected and measured by NMR (e.g. G. Isaksson & J. Sandstrom, Acta Chem. Scand. (1973) 27, 1183). As there has been no systematic X-ray crystallographic investigation of polarised ethylenes, we have carried out a detailed analysis with different electron donating and electron withdrawing groups. All the structures were solved by the direct methods program MULTAN 80. The name of the compound, cell dimensions ( $a, b, c$  ( $\text{Å}$ ),  $\alpha, \beta, \gamma$  ( $^\circ$ )), space group, C=C bond length ( $\text{Å}$ ) and rotation about C=C bond ( $^\circ$ ) of the compounds investigated are, in that order: 1-Benzoyl-1-cyano-2-dimethylamino-2-methylthioethylene, 7.214(4), 8.935(5), 20.243(6), 90.0, 99.42(2), 90.0,  $P2_1/c$ , 1.414(5), 38; 1,3-Dimethyl-2(dicyanomethylene)-imidazolidine, 7.965(1), 16.232(2), 7.343(1), 90.0, 113.54(1), 90.0,  $P2_1/a$ , 1.407(3), 20; 1,3-Dimethyl-2(diacetylmethylene)-imidazolidine, 7.731(2), 8.580(2), 11.033(3), 97.66(2), 98.86(2), 101.78(2),  $P1$ , 1.466(4), 73; 1,3-Dimethyl-2(carbomethoxy-acetyl)-imidazolidine, 12.028(2), 7.168(2), 15.187(5), 90.0, 91.88(2), 90.0,  $P2_1/n$ , 1.462(5), 63; 2(diacetylmethylene)-imidazolidine, 5.596(2), 6.938(3), 10.852(4), 75.64(3), 93.44(3), 95.47(3),  $P1$ , 1.442(3), 5; 1,3-Dimethyl-2(dicyanomethylene)-hexahydropyrimidine, 7.983(3), 8.075(2), 14.652(3), 90.0, 90.0, 90.0,  $P2_1/cn$ , 1.429(6), 32. There is a linear relationship between the C=C bond length and rotation about the double bond. However, case (5) deviates from this linearity which appears to be due to crystal packing.

**09.2-08** CRYSTAL STRUCTURE OF 4-METHYLPYRIDINE.

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Crystals of 4-Methylpyridine were grown from the melt by the Bridgman method. As  $C_6H_7N$  has a melting point of 276 K, all manipulations had to be carried out below about 250 K. Single crystals were prepared in a glove box on solid  $CO_2$  in a dry  $N_2$  atmosphere for combined x-ray and neutron diffraction measurements.

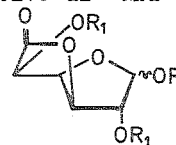
Crystal data (120 K): tetragonal,  $a = 7.620 \text{ \AA}$ ,  $c = 18.640 \text{ \AA}$ , space group  $I4_1/a$ ,  $Z = 8$ . The structure was solved by direct methods. The current agreement factor based on 440 observed reflections (x-ray) yielded 0.11, the refinement of the neutron data is still in progress.

The asymmetric unit contains half a molecule. The N-atom and the C- $CH_3$  bonding lay on the two fold axis. The hydrogen atoms of the methyl group are disordered.

**09.2-09** STRUCTURAL STUDIES OF  $\alpha$ -PIVALOYL-D-GLUCOPURANURONO-6,3-LACTONES. By B. Kojić-Prodić, Ž. Ružić-Toroš, I. Golič and S. Tomić, "Ruđer Bošković" Institute, P. O. Box 1016, 41001 Zagreb, Chemistry Department, University of Ljubljana, Murnikova 6, 61000 Ljubljana, Yugoslavia.

Selective acylation of methyl- $\alpha$ -D-glucopyranosides and of D-glucofuranurono-6,3-lactones with pivaloyl ( $Me_3CO$ )chloride, led to a series of partially protected compounds. Products of this type are potentially useful in the synthesis of biologically active di- and trisaccharides.

R = Piv; Me; H  
R<sub>1</sub> = Piv; Ac; H



An X-ray structure determination of this series is being carried out to provide information on molecular configuration and conformation. Mainly, the glucofuranose ring appears in a twisted conformation whereas the lactone ring exhibits an envelope form. An influence of the orientation and the size of the substituents and packing forces on the ring conformation was studied.