

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 (\AA), α, β, γ ($^\circ$)), space group, C=C bond length (\AA) 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.

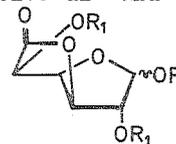
Crystal data (120 K): tetragonal, $a = 7.620 \text{ \AA}$, $c = 18.640 \text{ \AA}$, space group $I4_1/a$, $Z = 8$. The structure was solved by direct methods. The current agreement factor based on 440 observed reflections (x-ray) yielded 0.11, the refinement of the neutron data is still in progress.

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 α -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- α -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
R₁ = 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.