09.2-06 NEUTRON DIFFRACTION REFINEMENT OF THE STRUCTURE OF A PUSH-PULL ETHYLENE C₆H₄OSN₂. By Sandhya Bhakay-Tamhane, A. Seguela and R. Chidambaram, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

Push-pull substituted ethylenes D₂: C = C < A₁, A₂ 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, C₇H₁₁NO₂S, space group P2₁/c, a = 7.214, b = 8.935, c = 20.243 Å, β = 99.42°, Z = 4, has been studied using X-ray diffraction (D. Adhikesavalu and K. Venkatesan, 1983, 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(θ)/λ = 0.48(1)⁴ (λ = 0.109Å) 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) Å and the dihedral angle across the bond is 37.4(6)°. 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 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. Sandström, 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,α,β,γ (°)), space group, C=C bond length (Å) and rotation about C=C bond (°) 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); 7.965(1), 16.232(2), 7.343(1), 90.0, 99.42(2), 90.0, P2₁/c, 1.44(5); 90.0, P2₁/c, 1.44(5); 3; 1,3-Dimethyl-2(dicyanomethylene)-imidazolidine, 7.965(1), 16.232(2), 7.343(1), 90.0, 99.42(2), 90.0, P2₁/c, 1.44(5); 20; 1,3-Dimethyl-2(diacetamidemethylene)-imidazolidine, 7.965(1), 16.232(2), 7.343(1), 90.0, P2₁/c, 1.44(5); 7; 3; 1,3-Dimethyl-2(carbomethoxy-acetyl)-imidazolidine, 12.028(2), 7.168(2), 15.187(3), 90.0, 91.88(2), 90.0, P2₁/c, 1.44(5), 63; 2-Benzoyl-1-cyano-2-dimethylamino-2-methylthioethylene, 5.596(2), 6.938(3), 10.628(2), 75.64(2), 93.44(3), 95.47(3), P1, 1.44(3), 3; 1,3-Dimethyl-2(dicyanomethylene)-hexahydropyrimidine, 7.963(3), 8.073(2), 14.652(3), 90.0, 99.42(2), 90.0, P2₁/c, 1.44(5), 32. There is a linear relationship between the C=C bond length and rotation about the double bond. However, case (3) deviates from this linearity which appears to be due to crystal packing.

09.2-08 CRYSTAL STRUCTURE OF 4-METHYL PYRIDINE. By G. Heger, Kernforschungszentrum Karlsruhe, Institut für Angewandte Kernphysik I, Postfach 3640, D-7300 Karlsruhe, FRG.

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Crystals of 4-Methylpyridine were grown from the melt by the Bridgman method. As C₆H₄N₃H⁺ 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 CO₂ in a dry N₂ atmosphere for combined X-ray and neutron diffraction measurements.

Crystal data (120 K): tetragonal, a = 7.620 Å, c = 18.640 Å, space group P(1)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-CH₃ bonding lay on the two fold axis. The hydrogen atoms of the methyl group are disordered.

09.2-09 STRUCTURAL STUDIES OF O-PIVALOXY-2-GLUCOFURANURONOS-6,3-LACTONES. By R. Kollars-Točić, Z. Ružič-Točić, I. Jolić and G. Tolić, "Ruđer Bošković" Institute, Zagreb, Chemistry Department, University of Ljubljana, Kurnikova 6, 61000 Ljubljana, Yugoslavia.

Selective acylation of methyl-2-glucopyranosides and of 2-glucofuranuronos-6,3-lactones with pivaloyl (Me₂COC) 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.

R₁ = Piv; R₂ = 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 lactose 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.