06-Crystallography of Organic Compounds

A series of 1,4-dihydropyridinones (1), 1,4,5,6-tetrahydropyridines (2), 1,4-dihydro-1,6-naphthyridines (3), 1,4,5,6-tetrahydronaphthyridines (4) have been synthesized as potential calcium antagonists and analyzed by X-ray diffraction. 
In the solid state the unsymmetrically substituted 4-aryl group is always in axial position oriented either toward the C-4 hydrogen (symperiplanar) or away from the C-4 hydrogen (anti-periplanar).


The compound (I) was formed as a reaction product in the preparation of an isothiazolopyrimidine analog (2) based on antibiotic with sulfur atom replacing thienyl moieties of some pyridopyrimidinethione derivatives (3) reported to possess significant antimicrobial and antihistaminic activities (Dave, Shah, Desai, Srinivasan, 1983). * Ind. J. Pharm. Sci. 44(4), 83. The compound is possibly a rearrangement product of the isothiazolopyrimidine analog (2), and may be similar to the rearrangements reported in several other ring systems (Brown, 1961). Nature 189, 828.

The intramolecular hydrogen bond may be formed by the amino-hydrogen atom and imino-nitrogen atom between N(3)H-N(4). The molecules in the crystal form dimers by two intermolecular N(7)H-N(1) hydrogen bond bridging the pyrimidine rings.

The crystal structure of 2,10-dioxo-6-ethoxy-benzene- [3.4.d] 1,3.6.2 dioxa dihydrophosphin 6-oxide 5(6.S) 8-(pyranyloxy)-15H- benzo[b] [2.1.d] 1,2-s(3.6.2) diokathia dihydrophosphin 3-oxide: conformation of 8-membered heterocyclic ring.

Biologically the cyclic forms of organophosphorus compounds containing phosphoryl units react rapidly with proteins and nucleic acids in the cell to alkylate carboxyl, sulfhydroxyl and amino groups. Suitably substituted phosphoryl units in the molecule exhibit significant physiological activity (Schrader, 1963). These molecules play an important role as insecticides, pesticides, nerve gases, etc. Diokathiphosphin derivatives have applications as bactericides, fungicides, lubricants, insecticides, etc. The structures of the title compounds have been investigated to know the effect of the substituents on the conformation of the heterocyclic ring.

(1) Crystals of the first compound are colourless transparent from methanol and tolue. CuKα: R (factor) = 3.55. Orthorhombic Pna. Z = 8, 8 = 0.055(2) and 8 = 0.09(4) for 1293 (1293) significant reflections.


[Diagram of molecular structures and crystal packing]
06-Crystallography of Organic Compounds

06.05 New Structure Reports

PS-06.05.13 STRUCTURE OF 2-(4-CHLOROPHENYL)-4- HYDROXY-5, 5- DIMETHYL-4-(1, 2, 4- TRIAZOL-1- ILMETHYL)-1- OXASPIRO-12, 5 OCTADECanes. By Kowlagheb S.T., Kermor M.Z., Toshki V.P., Durrouva Ya.A., Komarev O.T., Putslyuk Yu.G., Zaoudnik V.K.


We have developed a stereospecific method for obtaining oxiran I and II, to determine why compound I possesses more fungicidal activity than compound II. The x-ray investigation of isomers was undertaken.

C<sub>25</sub>H<sub>24</sub>O<sub>2</sub>N<sub>3</sub>Cl<sub>2</sub>, molecular weight = 562, Triclinic, P<sub>1</sub>, a = 9.376(3), b = 10.326(2), c = 13.870(3), α = 85.86(2), β = 87.51(2), γ = 103.59(2), V = 373.6(4) Å<sup>3</sup>, Z = 2, D<sub>calc</sub> = 1.42 g/cm<sup>3</sup>, CuKαλ = 1.5418 Å, λ = 0.80 Å.

49 single reflections measured for two enantiomers, 3 = 20° < 90°, with a Gulet-R3M diffractometer with a graphite monochromator in the incident beam. The data were collected at 35°C, 80% with 2 (θ) = 0°. The data were stored for a 20° range, 10° < 2θ < 140°, with a 0.02, 0.01 scan mode, variable scan speed, scan width 1.0°. Intensities of two standard reflections (021, 111), measured at 50 main intervals showed no significant deviations for mean. Only Lorentz-Polarization corrections were applied. Data adjusted to an approximately absolute scale, U = 0.01 Å<sup>2</sup>.

The structure was solved by direct methods, using the program OMITRXL (Grosse D.D., Journal of Appl. Cryst., 1984, 17, 42-46), least-squares refinement of all non-H atoms with anisotropic thermal parameters and all of the H atoms were located by difference Fourier synthesis and refined with isotropic temperature factors (U(H) = 0.15 to 0.3 Å<sup>2</sup>). The final R and wR values were 0.04 and 0.067 respectively.

The molecules are held in the crystal by discrete molecules linked by Vanc der Waals forces.

PS-06.05.03 STRUCTURE OF N-ISOPROPYL, 2-CYANO- FURFURALACRYLAMIDE. By J. Dupea R., T. Pomea X-Ray Laboratory, National Center for Scientific Research, P.O.Box 690, Havana, Cuba, R. Villena and M. Soriano Institute of Chemistry, UNAM, 04510, Mexico, D.F.

C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O, molecular weight = 184, Monoclinic, space group C<sub>2</sub>h, a = 5.083(2), b = 15.551(6), c = 13.647(5), β = 98.8(3), V = 1665.5(7) Å<sup>3</sup>, Z = 4, Dcal = 1.24 g/cm<sup>3</sup>, λ = 0.70 Å. 1420 independent reflections were measured for two enantiomers, h < 20 < 20, with a NIGLET R3M diffractometer Four-Circle using CuKα radiation (λ = 0.15417 Å) with a graphite monochromator in the incident beam.