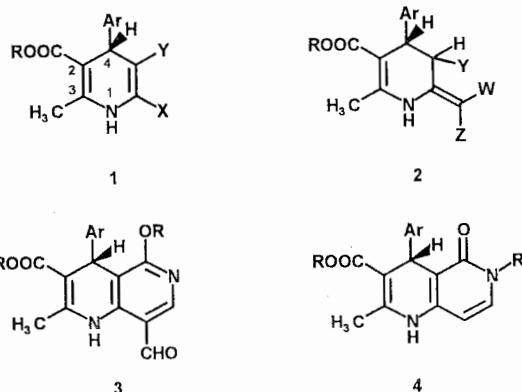


## 06-Crystallography of Organic Compounds

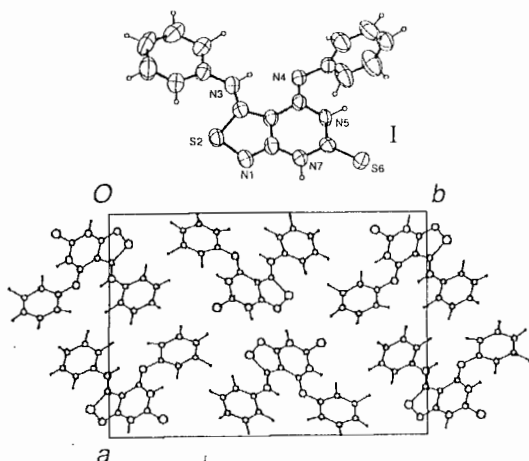
A series of 1,4-dihydropyridines (1), 1,4,5,6-tetrahydropyridines (2), 1,4-dihydro-1,6-naphthyridines (3), 1,4,5,6-tetrahydro-1,6-naphthyridines (4) have been synthesized as potential calcium antagonists and analyzed by X-ray diffraction.

In the solid state the unsymmetrically substituted 4-aryl group is always in axial position oriented either toward the C-4 hydrogen (synperiplanar) or away from the C-4 hydrogen (antiperiplanar). The orientation of the aryl group might influence receptor binding (G. Rovnyak et al., *J. Med. Chem.*, 1988, 31, 936).



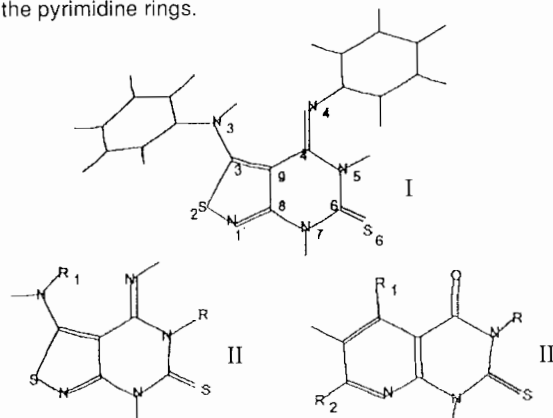
PS-06.05.11 CRYSTAL STRUCTURE OF 3-PHENYL-AMINO-4-PHENYLIMINOISOTHIAZALO-[3,4-d]PYRIDINE-6(5H-7H)-THIONE. P. Phavanantha\*, C. Patarapanich<sup>o</sup>, S. Akarapanichkorn<sup>o</sup> and T. Taga\*. \* Chulalongkorn Univ., Crystallography Lab., Bangkok 10330, Thailand. \* Kyoto Univ., Faculty of Pharmaceutical Sciences, Kyoto, Japan.

3-phenylamino-4-phenyliminoisothiazalo-[3,4-d]pyrimidine-6(5H-7H)-thione,  $C_{17}H_{13}N_5S_2$ ,  $M_r = 351.45$ , monoclinic,  $P2_1/a$ ,  $a = 15.590(4)$ ,  $b = 22.176(4)$ ,  $c = 4.724(2)$  Å,  $\beta = 92.68(2)$ ,  $V = 1631.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m(297K) = 1.400$ ,  $D_x = 1.431$  g cm<sup>-3</sup>,  $CuK\alpha$ ,  $\lambda = 1.54178$  Å,  $\mu = 29.72$  cm<sup>-1</sup>,  $F(000) = 728$ ,  $T = 298$  K,  $R = 0.061$  for 1474 reflections.



The compound (I) was formed as a reaction product in the preparation of an isothiazalopyrimidine analog (II) based on isosterism with sulfur atom replacing ethylenic moieties of some pyridopyrimidinethione derivatives (III) reported to possess significant antimicrobial and antihistaminic activities [Dave, Shah, Desai, Srinivasan (1982). *Ind. J. Pharm. Sci.* 44(4), 83]. The compound is possibly a rearrangement product of the isothiazalopyrimidine analog (II), 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 bonds bridging the pyrimidine rings.



PS-06.05.12 CRYSTAL STRUCTURES OF (I) 2,10-DICHLORO 6-ETHOXY-DIBENZO [d,g][1,3,6,2] DIOXATHIAPHOSPHOCIN 6-OXIDE and (II) 8-(PHENOXY)-16H-DINAPHTHO [2,1-d:1,2'-g][1,3,6,2] DIOXATHIAPHOSPHOCIN 8-OXIDE: CONFORMATION OF 8-MEMBERED HETEROCYCLIC RING: M. KRISHNAIAH, S. MANI NAIDU, N. JAGADEESH KUMAR, Department of Physics, College of Engineering, Sri Venkateswara University, TIRUPATI-517 502, INDIA.

Biologically the cyclic forms of organo-phosphorus 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. Dioxaphosphocin 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 hetero ring.

(I) Crystals of the first compound are colourless transparent from methanol and toluene,  $C_{14}H_{10}Cl_2O_2FSCl_2$ ,  $M_r = 377.18$ ; Orthorhombic  $Pnma$ ,  $a = 15.331(3)$ ,  $b = 11.253(2)$  and  $c = 8.973(4)$  Å,  $V = 1548.0(8)$  Å<sup>3</sup>;  $Z = 4$ ;  $\rho = 1.615$  and  $\rho = 1.618$  g cm<sup>-3</sup>;  $\mu(CuK\alpha) = 62.32$  cm<sup>-1</sup>;  $F(000) = 768$ ; Final  $R = 0.051$  &  $R_w = 0.059$  for 1293 ( $I \geq 3\sigma(I)$ ) significant reflections.

## 06-Crystallography of Organic Compounds

191

(II) Crystals of the second compound are colourless from methanol and toluene,  $C_{20}H_{27}O_4PS$ ; monoclinic, Space group  $P2_1/n$ ,  $a=12.842(1)$ ,  $b=20.902(2)$  and  $c=16.548(2)$  Å;  $\beta=103.92(2)^\circ$ ;  $V=4311.45(10)$  Å<sup>3</sup>;  $Z=8$ ,  $\rho=1.406$  and  $\rho=1.415$  g/cm<sup>3</sup>;  $\mu(MoK\alpha)=2.5$  cm<sup>-1</sup>;  $F(000)=1888$  Final  $R=0.039$  &  $R_w=0.046$  for 5452 ( $I \geq 3\sigma(I)$ ) significant reflections.

Structures I & II were solved by direct methods (Shelxs-86) using 1736 and 7562 reflections measured on CAD-4 diffractometer with  $CuK\alpha$  and  $MoK\alpha$  radiations respectively. Both structures were refined by Full-matrix least-squares method using Shelx-76.

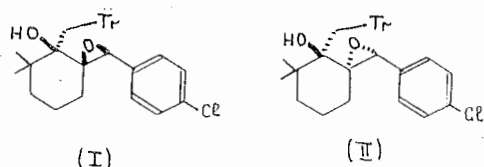
The dioxathiaphosphocin ring shows a boat-chair like conformation in the former where as a boat like conformation in the later and this may be due to different substituents fused to the heterocyclic ring. Details of the geometrical parameters will be discussed.

## PS-06.05.13 STRUCTURE OF STEREOISOMERIC

2-(4-CHLOROPHENYL)-4-HYDROXY-5,5-DIMETHYL-4-(1,2,4-TRIAZOL-1-ILMETHYL)-1-OXASPIRO-[2.5]OCTANES. By Maltnovsky S.T., Krimer M.Z., Tashchik V.P., Dubrovina Ya.A., Komarova O.V., Putsykin Yu.G., Zavodnik V.E.

Institute of Chemistry, Academy of Sciences of Moldova, Kishinev, 277028, Moldova. The Research Institute for Plant Protection Chemicals, Moscow, 109088, Russia.

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



Crystals of I and II ( $C_{18}H_{22}ClN_3O_2$ ) are monoclinic,  $P2_1/c$ ,  $Z=4$ . Crystal data: (I)  $a=9.706(3)$ ,  $b=21.254(5)$ ,  $c=9.368(3)$  Å,  $\beta=116.79(2)^\circ$  and (II)  $a=7.477(2)$ ,  $b=15.055(3)$ ,  $c=16.097(4)$  Å,  $\beta=100.42(2)^\circ$ . Final R-factors for I and II are 0.035 and 0.034, respectively. The main conformational difference between the molecules concerns the arrangement of oxiran fragments. The triazol cycle in II is oriented towards the oxiran fragment. In (I) these rings are oriented in opposite directions. The activity of the compounds is thought to depend on the stabilization of the triazol cycle through intermolecular contacts such as those present in isomer I.

## 06.06 - New Structure Reports

PS-06.06.01 CRYSTAL AND MOLECULAR STRUCTURE OF 1 $\alpha$ -METHYL-1,2,3,9,10,10a-HEXAHYDRO-1 $\beta$ ,10 $\alpha\beta$ -11-OXOPROPENO-PHENANTHERENE ( $C_{18}H_{20}O$ ). S.G. Biswas Dept. of Physics, Visva-Bharati University, Santiniketan, W. Bengal, India.

The X-ray investigation of the title compound, a synthesised stereospecific intramolecular rearrangement aiming at synthesising complex diterpenoids, was undertaken to establish its precise molecular architecture.

The intensities of X-ray reflections were measured on a CAD-4 diffractometer using monochromated  $Mo-K\alpha$  radiation with  $\lambda=2.2817$  Å. The intensity data was corrected for Lorentz and polarisation factors but no absorption corrections were made. Crystal data. Monoclinic,  $a=9.934(8)$ ,  $b=17.725(11)$ ,  $c=7.607(6)$  Å,  $\beta=97.86(4)^\circ$ ; space group  $P2_1/C$ ,  $Z=4$ ,  $D_c=1.249$  gm cm<sup>-3</sup>,  $D_m=1.22$  gm cm<sup>-3</sup>,  $F(000)=542$ ,  $\rho(Mo-K\alpha)=0.8$  mm<sup>-1</sup>,  $R=0.071$  with 1134 observed reflections. The structure was solved by MULTAN-84 and refined by full-matrix least square method (SHELX-76). The computed bond length and angles are fairly within the range of chemically expected values and the non-bonded contacts were always greater than sum of the Vander Waals radii.

## PS-06.06.02 STRUCTURE OF 2-CYANO-FURFURYLACRYLAMIDE. By R. Pomés\*, J. Duque X-

Ray Laboratory, National Center for Scientific Research, P.O.Box 6990, Havana, Cuba. R. Villena and M. Soriano Institute of Chemistry, UNAM, 04510, Mexico, D.F.

$C_8H_6N_2O_2$ , molecular weight = 162, Triclinic,  $P\bar{1}$ ,  $a=9.876(3)$ ,  $b=10.325(4)$ ,  $c=3.870(8)$  Å,  $\alpha=93.86(2)^\circ$ ,  $\beta=97.61(2)^\circ$ ,  $\gamma=103.52(3)^\circ$ ,  $V=378.3(4)$  Å<sup>3</sup>,  $Z=2$ ,  $D_{calc}=1.42$  g/cm<sup>3</sup>,  $CuK\alpha$  ( $\lambda=1.54178$  Å),  $\mu R=3.08$  cm<sup>-1</sup>.

949 unique reflections measured for two octants,  $3 < 2\theta < 90^\circ$ , with a NICOLET R3M diffractometer four-circle with a graphite monochromator in the incident beam. The data were collected at 25°C, 804 with  $I > 3\sigma(I)$  were used for refinement. range of  $hkl: -1 < h < 10$ ,  $-10 < k < 10$ ,  $-4 < l < 4$ ,  $R_{int}=0.03$ ,  $\sigma/2\sigma$  scan mode, variable scan speed, scan width 1.0°. Intensities of two standard reflections (021, 111), measured at 50 min intervals showed no significant deviations for mean. Only Lorentz-Polarization corrections were applied. Data adjusted to an approximately absolute scale,  $U=0.03$  Å<sup>2</sup>.

The structure was solved by direct methods, using the program MITRIL (Gilmore C.J., 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 a difference Fourier syntheses and refined with isotropic temperature factors. ( $\Delta\rho$ ) from 1.5 to 3 eÅ<sup>-3</sup>. The final R and wR values were 0.064 and 0.067 respectively.

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

## PS-06.06.03 STRUCTURE OF N-ISOPROPYL, 2-CYANO-FULFURYLACRYLAMIDE. By J. Duque\*, R. Pomés X-

Ray Laboratory, National Center for Scientific Research, P.O.Box 6990, Havana, Cuba. R. Villena and M. Soriano Institute of Chemistry, UNAM, 04510, Mexico, D.F.

$C_{11}H_{12}N_2O_5$ , molecular weight = 204, Monoclinic, space group  $P2_1/n$ ,  $a=5.083(2)$ ,  $b=15.551(6)$ ,  $c=13.647(5)$  Å,  $\beta=98.94(3)^\circ$ ,  $V=1065.5(7)$  Å<sup>3</sup>,  $Z=4$ ,  $D_{calc}=1.27$  g/cm<sup>3</sup>,  $\mu R=2.26$  cm<sup>-1</sup>. 1421 independent reflections were measured for two octants,  $3 < 2\theta < 90^\circ$ , with a NICOLET R3M diffractometer Four-Circle using  $CuK\alpha$  radiation ( $\lambda=1.54178$  Å) with a graphite monochromator in the incident beam.