

09.2-22 CRYSTAL STRUCTURE OF (+)-8 α -HYDROXY-6 α -METHOXY 6 β , 8 β -PROPANO-5-BENZO SUBERONE-7 β -ACETIC ACID LACTONE, C₁₈H₂₀O₄. By Siddartha Ray and Alpna Seal, Dept. of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India.

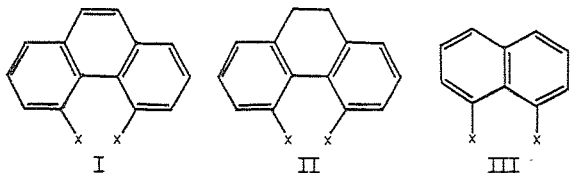
During an attempt of the synthesis of Icetone, isolated from *Salvia Balletaeflora*, an intermediate keton-lactone was obtained. But when attempts were made to transform this keto-lactone into the respective styrenoid compound through reduction of the aromatic conjugated ketone group, followed by dehydration, a mixture of complex products was obtained. Such a result was not compatible with the assigned structure of the ketolactone and the investigation was undertaken to find out the correct molecular structure.

The title compound crystallises in the space group P2₁/a. Structure was solved using MULTAN 78 programme package using 2653 diffractometric data. Reflections with $I \leq 2\sigma(I)$ were considered unobserved. Scale and Overall temperature factors were obtained from a Debye Plot using group scattering factors of the regular hexagonal benzene ring. Structure was refined to $R = 0.04$. There is nothing unusual in the bond distances and bond angles and the cyclic position of the molecule is reasonably planar. The correct molecular structure was established by X-ray study.

09.2-23 STRUCTURAL STUDIES OF STERICALLY CROWDED MOLECULES. By T.W. Hambley, R.C. Cosmo, and S. Sternhell, School of Chemistry, University of Sydney, NSW 2006, Australia.

The structures of sixteen aromatic compounds containing sterically crowded groups have been obtained with the aim of determining (i) the deformability of the aromatic rings and (ii) how close atoms can be forced together and whether this is dependent on the angle of approach of the atoms.

Three classes of compounds have been studied: (I) 4,5-disubstituted phenanthrenes; X = F, Cl, Br, OCH₃, CH₃, CF₃, (II) 4,5-disubstituted 9,10-dihydrophenanthrenes; X = H, F, Cl, Br, OCH₃, CH₃, CF₃, and (III) 1,8-disubstituted naphthalenes, X = Cl, Br, I. Large deviations (up to 0.1 Å) from planarity of the aromatic rings are observed in the structures of I and II. The total deformation of the aromatic rings is correlated with the overlap of the crowded groups. Crowded atoms are found closer together in type I compounds than in type III. This counter-intuitive result may (i) arise because of the different deformabilities of the aromatic frameworks in I and III, or (ii) indicate that it is easier to bring atoms close together side-on than it is head-on.

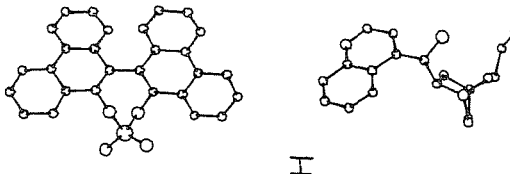


09.2-24 STUDIES OF NUCLEOBASES AND THEIR DERIVATIVES: CRYSTAL STRUCTURES OF 6-BENZYL-2-THIO URACIL (C₁₁H₁₀N₂OS), 5-iodo-1-METHYL URACIL (C₅H₅N₂O₂I) by Amit Halder, School of Agricultural Sciences, North Eastern Hill University, Medziphema -797106, Nagaland, India.

6-Benzyl-2-thio uracil crystallizes in the space group P2₁/a with $a=10.457(4)$, $b=20.131(6)$, $c=10.915(10)$ Å, $\beta=110.60(4)$. The structure was solved by MULTAN-78 and refined to $R=.045$. The structural analysis indicates that the two molecules of the asymmetric unit are in the diketo form. Two types of base pair occur-(i) through a pair of N(3)-H...O(4) and (ii) through a pair of N(1)-H...S(2) hydrogen bonds. Based on X-ray fibre diffraction data, two models (S.K. Mazumdar et al, J.Mol.Biol., 85, 213(1974) and S. Arnott et al. ibid, 149, 507(1981)) have been proposed for poly 2-thiouridylic acid - one model based on N(3)-H...O(4) and S(2)...H-N(3) pairing, and the other model with O(4)-H...O(4) and N(3)...H-N(3) tautomers. However the pairing scheme observed in the present study is different from the above two models.

5-iodo-1-methyl uracil crystallizes in the space group Pca2₁ with $a=24.910(14)$, $b=7.882(12)$, $c=7.429(2)$ Å. Solved by heavy atom method and refined to $R=.055$. The two molecules of the asymmetric unit forms a U:U pair through a pair of N(3)-H...O(4) hydrogen bond. This type of U:U pairing is the most common of the three types of U:U pairs possible in N(1) blocked uracil. It appears from the study that 5-iodo substitution does not prevent the molecule from forming the most common U:U pairing, although earlier studies (T.D. Sakore et al, J.Mol.Biol. 43, 385(1969)) suggest that the 5-iodo substitution changes the base pairing pattern between purine and pyrimidine.

09.2-25 THE STRUCTURE OF A RESOLVED AXIALLY DISSYMMETRIC BIARYL. By F.W.B. Einstein, R.H. Jones (Department of Chemistry, Simon Fraser University, Burnaby, Canada) and X. Songkai (Department of Chemistry, Zhongshan University, Guangzhou, Republic of China). Crystal data: triclinic; space group P1; $a=10.560(1)$ Å, $b=14.293(2)$ Å, $c=14.582(2)$ Å, $\alpha=71.86(1)$, $\beta=89.46(1)$, $\gamma=84.85(1)$, $V=2082.9$ Å³; Formula C₄₇H₃₉O₅N₂P; $z=2$, $(Mo-K)\alpha=1.13$ cm⁻¹, $D_c=1.255$ Mg m⁻³, scan range $0 < 2\theta < 45$ R=0.073 $R_w=0.087$ for 3846 observed ($I > 2.5\sigma(I)$) reflections, number of parameters = 500.



The absolute configuration of a novel axially dissymmetric diaryl hydrogen phosphate(I) has been determined as its cinchonine salt. X-ray diffraction data were collected on an ENRAF-NONIUS CAD4-F diffractometer using Mo-K radiation. The structure was solved by direct methods (location of the two "PO₄" moieties) and refined by full-matrix least-squares. The absolute configuration of I about its chiral axis is S-. Reduction of I with LiAlH₄ yields the free hydroxyl compound which has a laboratory rotation $[\alpha]_D^{18} = -56^\circ$. This is to be contrasted to the case in linear biaryl compounds where levoration was associated with an R configuration (Yamada and Akimoto, Tetrahedron Letters, 1968, 3967-3970). The crystal contains a non stoichiometric amount of methanol (approximately 2.75 molecules) on three sites, linked via a series of hydrogen bonds to give ribbons parallel to the b plane.