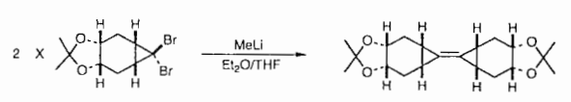
06-Crystallography of Organic Compounds

PS-06.06.07 CRYSTAL STRUCTURE AND CONFORMATION OF N- T-BUTOXYCARBONYL-ϵ-N'-BENZYLOXY CARBONYL - L-LYSYL- L-ISOLEUCINE METHYL ESTER By N. Sukumar* and M.N. Ponnuswamy, Department of Crystallography and Biophysics, University of Madras, Guindy campus, Madras - 600 025, India and R. Jayakumar, Chemical Lab, CLRI, Adyar, Madras - 600 020, India.

The dipeptide, a fragment of an inhibitor of angiotensin - converting enzyme and bradykinin-destroying plasma kinases, is crystallized by slow evaporation of ethanol at room temperature. The crystal data are as follows: monoclinic, space group $P2_1$, a = 5.003(1), b = 19.199(3), c = 15.270(2)A, β = 93.42(1)°, V = 1464.10A^3, μ=6.18mm^{-1}. The structure is solved by direct methods and refined by full matrix least-squares to R=0.10 for the 1379 observed reflections[$I \geq 1.5\sigma(I)$]. The t-boc group exists in *trans-trans* conformation. The peptide linkage is in *trans* conformation. The backbone torsion angles are as follows: θ_0= -177(2)°, ω_0= 175(2)°, ϕ_1= -108(2)°, ψ_1= 100(2)°, ω_1= -175(2)°, ϕ_2= 121(2)°, ψ_{21}= 144(2)°, ψ_{22}= 54(2)°. The side chain conformation of isoleucine has χ_{11}= -43(3), χ_{12} = 169(3) and χ_2 = 160(3) and the configuration can be described as [γ(III), δ(II)]. The sidechain conformation of lysine has χ_1= -74(2), χ_2= -169(2), χ_3= -180(2), χ_4= -172(2). The crystal structure is stabilized by N-H...O hydrogen bonds.

PS-06.06.08 THE MOLECULAR STRUCTURE OF A CYCLO-PROPYLIDENE DIMER. By R.J.Greenwood and M.F. Mackay,* Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia, and M.G. Banwell, J.N. Lambert and J.M. Walter, School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.

An X-ray crystallographic analysis has unequivocally established that the dimerization reaction given below yields the unexpected *syn*-bis{3aα,4aα,5aα,6aα-2,2-dimethyl-4*H*-cyclopropa[f]-1,3-benzodioxal-5-ylidene} with no *anti*-isomer detected. We believe the stereochemical outcome observed in the reaction could be quite generablisable and that the stereoselectivity associated with the initial halogen-metal exchange reaction determines whether the *syn*- or *anti*-dimer is obtained. The significance of the formation of the *syn*-dimer will be discussed.



Monoclinic crystals of $C_{20}H_{28}O_4$ belong to the space group *C2/c* with *a* = 35.245(5), *b* = 6.335(1), *c* = 29.090(4) Å, β = 143.49(1)° and *Z* = 8. Refinement with 1246 observed data converged at *R* = 0.055 and *S* = 2.46 (219 parameters varied). As the molecule adopts the *syn* conformation it has approximate C_{2v} point group symmetry so that the four oxygen atoms of the two *cis*-fused dioxalane rings lie on the same side of the molecule. The cyclohexane rings have regular boat forms as indicated by the asymmetry parameters ΔC_s 3.7 and 0.50°. One dioxalane ring has a conformation between an envelope and half chair (pseudo-rotational parameters Δ 15.6° and ψ_m -34.6° while the other is envelope (Δ -27.0° and Ψ_m -38.2°). The six atoms of the central dicyclopropylethene moiety are coplanar and the central C=C bond length is 1.31(1) Å.

PS-06.06.09 CRYSTAL STRUCTURE STUDIES ON N-PIPERIDIN-4-ONES by N.Sukumar and M.N.Ponnuswamy*, Department of Crystallography and Biophysics, University of Madras, Guindy campus, Madras-600025, India and R.Jeyaraman and J.C.Thenmozhiyal, Department of Chemistry, Btharathidasan University, Trichi-620024, INDIA.

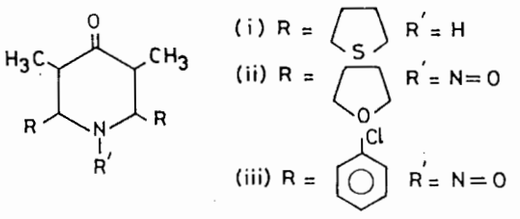
Many nitrosamines are known to be carcinogenic Some N-nitroso urea are used as antitumor agents or antibiotics. Their activity depends on the nature and position of the side group attached to it. The aim is to study the stereo dynamics of N-nitroso piperidines and correlate the stereochemistry with their cancer/anticancer properties. To determine the conformational features of the piperidines the X-ray study was undertaken. The piperidine ring without N-nitroso group was found to assume chair conformation.Depending upon the electronic and steric nature of substituents, there will be a deformation from the perfect chair conformation. The introduction of the N-nitroso group at the position of nitrogen atom is known to exert a large influence on the conformation of the substituents. The following compounds has been solved.

(i) 3,5-dimethyl-2,6-dithienylpiperidin-4-one (DTMP) : Mr=291.42, triclinic, $P2_1/n$, a=12.945(1), b=7.005(2), c=16.701(2)A, α=103.83(1)°, β=98.32(1)°, γ=93.65(1)°, V=694.28A^3, ρ=1.286gmcm^{-3}, R=0.059.

(ii) 2,6 - difuryl -3,5 - dimethyl - N - nitrosopiperdin - 4 - one (DFMPNO): Mr=288.30, orthorhombic $P2_12_12_1$, a=9.330(1), b=20.517(2), c=7.708(1)A, V=1475.58A^3, ρ=1.299gmcm^{-3}, R=0.069.

(iii)2,6-Di(o-chloro)phenyl-3,5-dimethyl-N-nitrosopiperidin-4-one(NOCDMPO): Mr=377.25 Monoclinic, $P2_1/n$, a=13.062(2), b=10.931(2), c=13.120(2)A, β=104.57(1), V=1816.92A^3, R=0.047.

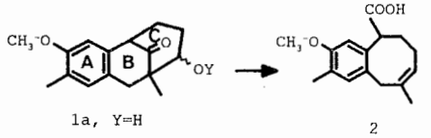
In DTMP, the piperidin ring is in the chair conformation, while DFMPNO and NOCDMPO adopt a conformation close to boat form. The angle between thienyl rings in DTMP is 139.8(2)° and furyl rings in DFMPNO is 116.0(1)° respectively. The angle between phenyl rings in NOCDMPO is 73.0(1)°. In all the three compounds, the packing of the molecule is stabilized by van der Waals interactions. Further, conformational analysis are in progress and details will be presented.



PS-06.06.10 SYNTHESIS AND CRYSTAL STRUCTURE OF 10-HYDROXY-4-METHOXY-5,9-DIMETHYL-TRICYCLO [3.3.1.0^{2,7}] TRIDECA-2,4,6-TRIENE-13-ONE. By M. Soriano-Garcia*, R. Villena Iribe, A. Covarrubias, J.S. Olguín and L.A. Maldonado. Instituto de Química and División de Estudios de Posgrado, Facultad de Química, Universidad Nacional Autónoma de México, Delegación Coyoacán, México D.F. 04510, México.

An important method for medium size ring formation involves fragmentation of appropriately functionalized bicyclic systems. In our laboratory the NaOH-induced fragmentation of the benzobicyclic ketomesylates 1b were studied. Although both isomers gace the expected benzocyclooctene product 2, the yields were strikingly different depending of the isomer used as starting material. The title compound (1a) $C_{16}H_{20}O_3$, is crystallized in orthorhombic spce group, $Pca2_1$, a=8.594(2), b=14.045(6), c=11.509(6) Å, Z=4, R=0.034 and Rw=0.046. This X-ray diffraction study establishes the molecular structure of the title compound (1a). The carbon skeleton of three six-membered rings (A, B and C). The A and B rings are *cis*-fused. The A, B and C rings adopt a twist-chair, envelope and chair conformations, respectively. The stereochemistry of the OH group is axial. Therefore, the 1b is the isomer with equatorial OH, a result consistent with a favorable antiperiplanar bonding arrangement for optimal fragmentation (Clayton, R.B., Henbest, H.B. & Smith, M., J. Chem. Soc., 1957, 1982-1993) in this isomer.

The crystal structure is stabilized by an intramolecular hydrogen bond and two C-H···O hydrogen bond interactions.



1a, Y=H
1b, Y=Ms

2

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PS-06.06.11 CRYSTAL STRUCTURE OF 2,2 -(BENZENE SULPHONYL)-1-PARA CHLOROBENZOYL CYCLOPROPANE by S.Shanmugs Sundara Raj*, M.N.Ponnuswamy and G.Shanmugam, Department of Crystallography and Biophysics, University of Madras, Guindy Campus Madras-600 025, INDIA.

The cyclopropane ring undergoes drastic geometrical changes under influence of electron donar substituents. The interaction between a cyclopropane ring and an approximately oriented t-acceptor substituent, (for eg. carbonyl group) shortens the vicinal bonds. The title compound $C_{22}H_{17}O_5S_2Cl$ crystallizes in the monoclinic system. $P2_1/c$ with cell constants a=10.511(2), b=15.452(1), c=13.025(2)A, β=103.70(1)°, V=2055.3(1)A^3, Z=4, Dcal=1.489Mgm^{-3}, T=292k and CuKα radiation(λ=1.5418A).The structure was solved by direct methods and refined by full-matrix least-squares procedures using 3385 observed reflections to a final R=0.056 and wR=0.066. The cyclopropane ring is in equilateral triangle form and the benzenesulphonyl and the phenyl groups are trans to each other. The packing is stabilized by van der Waals forces.

PS-06.06.12 CRYSTAL STRUCTURE OF D- AND L- AMINO ACID SALTS OF OPTICAL RESOLVING REAGENT (-)-PHENYLETHANE SULFONIC ACID. By Tadamasa Date*, Kimio Okamura, and Ryuzou Yoshioka, Tanabe Seiyaku Co. Ltd., Research Laboratory of organic chemistry, Kawagisi, Toda, Saitama, Japan.

The Optical active (-)-Phenylethane Sulfonic acid is an excellent reagent for the optical resolution of amino acids. Generally, L-amino acid salts are observed to precipitate preferrentially, but D-isomer precipitates in the case of Leu when dissolved in water. We have analyzed the crystal structures of D- and L- amino acid salts of (-)-PES, listed in Table 1. From the comparison of each diastereomeric crystals, we found the next characteristic features; 1) In crystals, the infinite hydrogen bonded molecular chain listed in fig. 1 are observed. In less soluble crystals, the shorter hydrogen bond between -COOH and O_3S- observed. In more soluble crystals, the hydrogen bond of this type are longer or cannot be observed. In the case of L-Val salt, hydrogen bond distance of -COOH and O_3S- is shorter than D-isomer. But this hydrogen bonds don't form infinite hydrogen bond. 2) In amino acids containing hydroxyl group or the salts having crystal water, Hydrogen bond between OH and O_3S are considered to affect on solubility of the salts.

Table 1

D-, L-Ala.(-)-PES
D-, L-Val.(-)-PES
D-, L-Leu.(-)-PES
D-, L-Ser.(-)-PES
D-, L-HPG.(-)-PES

HPG : Hydroxyphenylglycin

Fig. 1