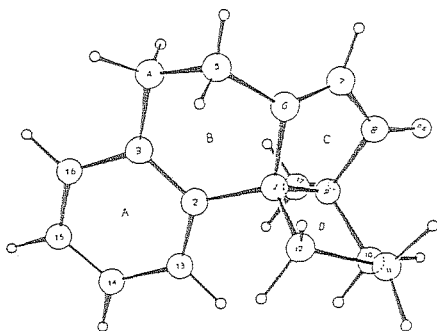


09.2-28 CRYSTAL STRUCTURE OF (\pm)-3a-METHYL-1,2,3,3a,6,7-HEXAHYDRO-PENTALENO 1,6a-a NAPHTHALEN-4-ONE, $C_{17}H_{18}O$. B.N.Lahiri, Dept of Physics, University of Burdwan, Golapbag, Burdwan 713104, India, Birendra Nath Das, Dept of Physics, Vivekananda College, Calcutta 700063, and S.Chaudhuri, RSIC, Bose Institute, Calcutta 700009.

The title compound has recently been synthesized at IACS, Calcutta by Prof U.R.Ghatak et al. (J.C.S., Perkin I, in press) through a novel carbenium ion rearrangement arising from an acid-catalyzed intramolecular alkylation of a rigid β, γ -unsaturated diazomethyl ketone. The complete stereostructure of this highly strained tetracyclic unsaturated ketone having an angular methyl group has been established by the present x-ray crystal structure analysis. It may be mentioned that the usual spectroscopic methods, viz., 1H NMR, ^{13}C NMR, IR, UV, mass spectrometry etc. failed to give unambiguously the structure and stereochemistry of this ketone.

The compound crystallizes, from a solution in petroleum ether, in the orthorhombic space group Pbc₂a with 8 molecules in the unit cell of dimensions $a=11.312(1)$, $b=12.834(3)$, $c=18.158(4)$ Å. The structure has been solved by direct methods and refined by full matrix least squares with anisotropic thermal parameters for nonhydrogen atoms to a final conventional R index of 0.054 for 657 independent reflexions observed above $2.5\sigma(F_o^2)$ level out of 2235 reflexions in the range of $2\theta=4-130^\circ$ measured on a four-circle diffractometer with graphite monochromatized $CuK\alpha$ radiation. All the hydrogen atoms have been located as dominant peaks on a difference electron density map and refined isotropically. A perspective view of the molecule is shown.



Benzenoid ring A, $C_{sp^2}-C_{sp^2}$ bond lengths 1.360-1.439, mean 1.386(9) Å; endocyclic angles 117.8-123.0, mean 120.0(8) $^\circ$. Cyclopentane ring D, $C_{sp^3}-C_{sp^3}$ bond lengths 1.526-1.561, mean 1.543(10) Å; endocyclic angles 101.3-106.3, mean 103.7(7) $^\circ$. Cyclohexene ring B, $C_{sp^2}-C_{sp^2}$ bond lengths 1.463-1.514, mean 1.497(9) Å, $C_{sp^2}-C_{sp^3}$ 1.501(12) Å; endocyclic angles at the sp^2 carbons 117.0-123.0, mean 120.8(7) $^\circ$ and at the sp^3 carbons 108.7-111.5, mean 110.3(7) $^\circ$. Cyclopentenone ring C, $C_{sp^2}-C_{sp^2}$ single bond 1.445(10) Å, double bond 1.325(10) Å, $C_{sp^2}-C_{sp^3}$ 1.542(8) Å, $C_{sp^2}-CH_3$ 1.523(9) Å and $C=O$ 1.197(8) Å; endocyclic angles at the sp^2 carbons 106.8-112.2, mean 110.3(7) $^\circ$ and at the sp^3 carbons 103.5(6) $^\circ$ and 103.6(6) $^\circ$.

The molecule contains planar A ring. The B ring has unexpected nearly planar conformation. This is probably due to the influence of A ring leading to partial π electron delocalisation in B ring. It is confirmed by the shortage of $C_{sp^2}-C_{sp^3}$ 1.463(10) Å in the ring. The shortest intermolecular contact of 3.494(9) Å indicates that in the solid state the molecules are held together only by van der Waals forces.

09.2-29 THE CRYSTAL STRUCTURE OF DRIMENOL. By C. Escobar and O. Wittke, Dpto. de Física, Fac. de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 5487, Santiago, Chile.

This natural product was isolated more than twenty years ago. Its constitution and stereochemistry was determined by chemical and spectroscopical methods (H.H. Appel, C.J.W. Brooks and K.H. Overton, J. Chem. Soc. (1959) 3322), but no X-Ray Structure investigation has been published yet.

Drimenol, $C_{15}H_{26}O$, is monoclinic with $a = 12.384(1)$, $b = 22.615(2)$, $c = 7.462(1)$ Å, $\beta = 93.23(1)^\circ$, $Z=6$, space group $P2_1$.

The structure was solved by direct methods (MULTAN76 program) and refined to an $R=0.058$ for 3177 reflexions with $I > \sigma(I)$ measured with an automatic diffractometer. The least squared refinement included all non-hydrogen atoms with anisotropic thermal parameters and the H atoms of the radical CH_2OH . All other H atoms were theoretically 2 positioned.

The three molecules of the asymmetric unit have the same configuration and, making due allowance for the estimated errors, the same dimensions and angles. The cyclohexane ring (chair) and the cyclohexene ring (half chair) are fused trans. H bonds through the OH groups originate chains of trimers running parallel to the c axis. Between these chains there are only weak van der Waals forces.

09.2-30 CRYSTAL STRUCTURE OF A BRIDGED-HYDROXY CYCLOPENTANONE, $C_{17}H_{24}O_2$. By S.C. Kunda Das and B.S. Basak, X-ray Laboratory, Presidency College, Calcutta-700073, India.

A facet of diazocarboxyl chemistry that generates a great deal of interest is the acid-catalysed cyclisation of diazomethyl ketones through π -participation of suitably situated olefinic bonds. In this study the title compound was obtained by cyclisation of a rigid polycyclic unsaturated diazomethyl ketone under certain reaction conditions. The fact that a highly rearranged compound was obtained by interesting rearrangement of an initially formed carbo-cation was established and confirmed by X-ray crystal structure determination of the compound. The compound (Fig. 1) has been synthesized by Prof. U.R. Ghatak et al. (U.R. Ghatak et al., J. Chem. Soc., Perkin Trans. 1, 1981, in press). The crystals belong to the tetragonal system having space group $I4$ with 8 molecules in the unit-cell of dimensions $a=b=16.30$ Å, $c=10.31$ Å. Photographic data were collected by Weissenberg camera using equi-inclination technique. Intensities were measured visually for 1392 reflections of which 72.4% were above the threshold value of observation within the $CuK\alpha$ -sphere. The structure has been solved by direct methods.

Full-matrix least-squares refinement with isotropic thermal parameters brought the R value to 0.149.

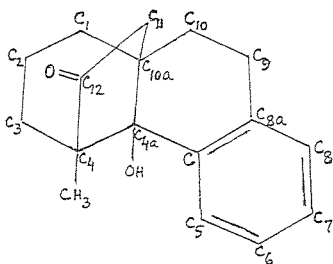


Fig. 1

4a - hydroxy - 4b - Methyl, 1,2,3,4,4a,9,10,10a - octahydro 4, 10a - ethanophenanthren-12 - one.

At the present stage R has come down to 0.112 by the application of block-diagonal least-squares with anisotropic temp. factors for all non-hydrogen atoms and isotropic temperature factor for 16 hydrogen atoms. The positions of the remaining 4 hydrogen atoms are yet to be found. The final stage of refinement is awaited. The bond lengths and bond angles are quite satisfactory.

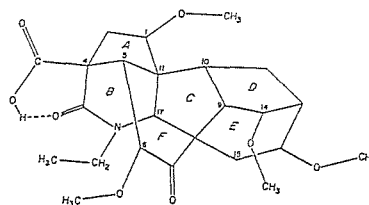
09.2-31 A SIMPLE WEIGHTING SCHEME USED IN THE STRUCTURE DETERMINATION OF α -HYDROXY- γ -LACTONIC ACID. By Alpana Seal and Siddhartha Ray, X-ray Crystallography Laboratory, Department of Magnetism, Indian Association for the Cultivation of Science, Calcutta 700 032, India.

The title compound ($C_{18}H_{20}O_5$) crystallises in space group $P2_12_12_1$ with $a=10.210(1)$, $b=15.674(2)$, $c=9.407(1)$ Å, $Z=4$. In the intensity data obtained by diffractometry, several reflections forbidden by space group appeared with $I > 3\sigma_c(I)$ based on counting statistics only. The structure was solved by direct methods assuming correctness of space group but refinement with weight based on σ_c stopped at $R=.065$ with an unacceptable value of the standard deviation of an observation with unit weight $S=.64$. Realistic weighting could be made by partitioning the data-set into approximately equal segments in increasing ranges of $|F_o|$, calculating R for each segment, and assuming $\sigma(F)=R_1|F_o|$ for the i th segment. Anomaly regarding forbidden reflections disappeared and refinement ended with $R=.05$, $R_1=.05$ and $S=1.03$.

09.2-32 THE STRUCTURE OF A KETO-LACTAM-ACID FROM LYCOCTONINE. By M. Cygler and M. Przybylska Division of Biological Sciences, and O.E. Edwards, Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6.

Deamination of 4-amino-4-des-(oxymethylene)anhydro-lycotonam gave an amorphous hydroxy-keto-lactam, 1. Mild oxidation of this gave a keto-lactam-carboxylic acid, 2. X-ray analysis of 2 demonstrates that an unexpected molecular rearrangement occurs in the formation of 1.

The crystals are orthorhombic, $P2_12_12_1$ with $a=13.810(1)$, $b=15.527(2)$, $c=10.644(1)$ Å, $Z=4$. The structure was solved by direct methods and refined to $R=0.036$ for 2474 reflexions with $I > \sigma(I_{net})$. The enantiomorph depicted corresponds to the absolute configuration of lycotonine. All rings in the molecule are *cis* fused. Five-membered rings A, C and D adopt envelope conformations with C(5), C(11) and C(14) at the flaps, respectively. Six-membered ring B is close to an envelope form with C(5) at the flap. Ring E exists in a conformation intermediate between boat (C(14) and C(15) are above the plane of the other atoms) and twist. Ring F is of a chair form strongly distorted toward an envelope with C(17) at the flap. The presence of a strong intramolecular OH...O bond, indicated by IR (ν_{max} 1604 cm^{-1}) was confirmed.



2

09.2-33 X-RAY CRYSTAL STRUCTURE OF A NOVEL ALKALOID FROM THE MEDICINAL PLANT PIPER GUINEENSE. By K.A. Woode, F.L. Phillips and I. Addae-Mensah, Chemistry Department, University of Ghana, Legon, Ghana, and J.C.J. Bart, Istituto di Ricerche "G. Donegani" S.p.A., Via G. Fauser 4, 28100 Novara, Italy, and S. Chaudhuri, RCSI, Bose Institute, 93/1 Acharya Prafulla Chandra Road, Calcutta 70009, India. As part of structural studies on the constituents of the medicinal plant *Piper guineense* (Ashanti or West African Black Pepper), the crystal structure of the novel alkaloid, N-piperidyl-5-(2-methoxy-4,5-methylenedioxyphenyl)-*trans*-2-*cis*-4-pentadieneamide has been determined from X-ray diffractometer data.

$C_{18}H_{21}O_4N$; M^+ m/e 315.1469; Orthorhombic $Pca2_1$ (No. 29), $a=16.907(1)$, $b=6.325(1)$, $c=15.007(1)$ Å, $V=1604.80$ Å³, $Z=4$, $D_c=1.30$ g cm^{-3} , $F(000)=672$, $\lambda(CuK\alpha)=1.5418$ Å, $\mu(CuK\alpha)=7.61$ cm^{-1} .

The structure was solved by direct methods and refined by full-matrix least squares to $R=0.095$ for 1399 independent reflections. Results of the X-ray analysis confirm that the compound is a *trans*-2-*cis*-4-isomer of the pharmacologically active amide alkaloid, Wisanine (Herbststein, Schowtzer, Addae-Mensah, Torto and Woode, Acta Cryst., (B), in press; Addae-Mensah, Torto, Dimonyeka, Baxter and Sanders, Phytochemistry, (1977), 16, 757-759). The present compound is the first naturally occurring mixed-isomer piperidine-type alkaloid to be reported (Addae-Mensah, Torto, Torto and Achenbach, Planta Medica, in press).