09.3-29 THE CRYSTAL STRUCTURE OF DRIMENOL. By C. Escobar and D. Wittke. Opto. de Física, Fac. de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 5457, 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_{3}H_{6}O, is monoclinic with a = 12.384(1), b = 22.615(2), c = 7.462(1) Å, α = 93.23(1), β = 90°, 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 > σ(I) measured with an automatic diffractometer. The least-squares refinement included all non-hydrogen atoms with anisotropic thermal parameters and the H atoms of the radical CH_{4}H. All other H atoms were theoretically 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 cyclohexene ring (chair) and the cyclohexene ring (half chair) are fused trans. H bonds through the OH groups orivate chains of trimers running parallel to the c axis. Several hydrogen bonds there are only weak van der Waals forces.

09.2-28 CRYSTAL STRUCTURE OF (±)-3а-ETHYL-1,2,3а,6,7-HEXAHYDROFENTALENE. By A. Perkhin et al. (J.O.S., Perkhin I., in press) through a novel carbamid ion rearrangement arising from an acid-catalyzed intramolecular alkylation of a rigid 2,2'-unsaturated dioxymeth 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. IR, NMR, {^1}H NMR, {^13}C NMR, IR, UV, MS, mass spectrometry etc. failed to give unambiguously the structure and stereochemistry of this ketone.

The title compound has recently been synthesized at IACS, Calcutta by Prof. U.R. Ghatak et al. (J.O.S., Perkhin I., in press) through a novel carbamid ion rearrangement arising from an acid-catalyzed intramolecular alkylation of a rigid 2,2'-unsaturated dioxymeth 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. IR, NMR, {^1}H NMR, {^13}C NMR, IR, UV, MS, 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 Pnca 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 non-hydrogen atoms and hydrogen atoms placed geometrically and refined as a single isotropic group.

The title compound was obtained by cyclization 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 carbamidion 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. (J.O.S., Perkhin 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 = 16.30 Å, c = 10.31 Å. Photographic data were collected by Weissenberg camera using equi-inclination technique. Intensities were measured visually for 1392 reflexions of which 72.4% were above the threshold value of observation within the Cu Kα - 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.

09.2-30 CRYSTAL STRUCTURE OF A BRIDGED HYDROXY CYCLOPENTANONE, C_{5}H_{12}O. By S.C. Kundu 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 τ-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 title 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. (J.O.S., Perkhin 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 = 16.30 Å, c = 10.31 Å. Photographic data were collected by Weissenberg camera using equi-inclination technique. Intensities were measured visually for 1392 reflexions of which 72.4% were above the threshold value of observation within the Cu Kα - 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.
4α - hydroxy - 4β - methyl, 1,2,3,4,4a,9,10,10a - octahydro 4,10a - ethanophenanthrene - 12 - one.

At the present stage R has come down to 0.112 by the application of block-diagonal least-squares with anisotropic temperature 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 (C₁₈H₂₃O₅) crystallises in space group P2₁2₁2₁ with a=10.310(1), b=15.624(2), c=9.407(1) Å, Z=4. In the intensity data obtained by diffractometry, several reflections forbidden by space group appeared with I>3σ(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(I) stopped at R=0.065 with an unacceptable value of the standard deviation of an observation with unit weight S=0.64. Realistic weighting could be made by partitioning the data-set into approximately equal segments in increasing ranges of |F₀|, calculating R for each segment, and assuming σ(F)=RIF₀| for the 4th segment. Anomaly regarding forbidden reflections disappeared and refinement ended with R=0.05, R₁=0.09 and S=1.05.

09.2.32 THE STRUCTURE OF A KETO-LACTAM-ACID FROM LYCOCTONINE.

By M. Cygler and M. Przybylska

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Deamination of 4-amino-4-des-(oxymethylene)anhydro-lycoctonan gave an amorphous hydroxy-keto-lactam, I; 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 2.

The crystals are orthorhombic, P2₁2₁2₁, with a=13.910 (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 reflections with I>0(1 criterion). The enantiomorph depicted corresponds to the absolute configuration of lycoctonine. 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's of a chair form strongly distorted toward an envelope with C(17) at the flap. The presence of a strong intermolecular O-H...O bonding, indicated by IR (v_max 1604 cm⁻¹) was confirmed.