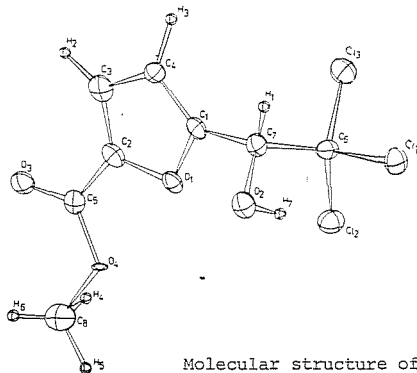


09.2-3 CRYSTAL STRUCTURE OF 1-(5-CARBOMETHOXY-2-FURYL)-2,2,2-TRICHLOROETHANOL. By F. Fajardo and R. Pomes, University of Oriente and Academy of Sciences of Cuba, Santiago de Cuba, CUBA.

$C_8H_7O_4Cl_3$, orthorhombic, space group $Pbcn$, $a = 22.00(1)$, $b = 13.72(1)$, $c = 7.13(1)\text{\AA}$, $Z = 8$, 406 $F(hkl)$'s.

A three-dimensional data set was collected at room temperature with $MoK\alpha$ radiation ($\lambda = 0.70926\text{\AA}$), using a perpendicular beams diffractometer with a graphite monochromator. Data were recorded by the θ - 2θ scan technique to a maximum 2θ value of 48° . The structure was solved by direct methods. The coordinates and the anisotropic temperature factors of the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms were refined by full-matrix least-squares methods to a final R value 0.046.



Molecular structure of $C_8H_7O_4Cl_3$

09.2-4 ON THE MOLECULAR STRUCTURES OF 4- AND 5-ARYLCYCLOPHOSPHAMIDES. By Ling-Kang Liu, Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 115, ROC.

As anticancer reagents, the cyclophosphamides have been studied metabolically as well as structurally. Monosubstitution of cyclophosphamide with an aryl group at C-4 or C-5 creates a second chiral center at C-4 or C-5 in addition to the original chiral P-2. Racemic 4- or 5-arylcyclophosphamides may simply be described as *cis* or *trans* by considering the P=O and the aryl group. Referring to their separation by silica-gel column, the faster eluting components, for both 4- and 5- aryl substitution, have the *cis* structure as confirmed by single crystal x-ray diffraction studies, while the slower diastereomers are *trans*, although IR and NMR data for 4- and 5- aryl substitution have shown reverse trends.

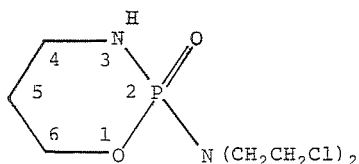


Figure. Cyclophosphamides.

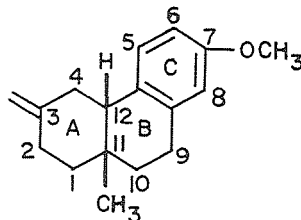
09.2-5 X-RAY STRUCTURE DETERMINATION OF O - β -D-MANNOPYRANOSYL(1 \rightarrow 4)- O - β -D-MANNOPYRANOSYL(1 \rightarrow 4)- O - α -D-MANNOPYRANOSE. $3H_2O$ (MANNOTRIOSE). By B. Sheldrick, W. Mackie and D. Akrigg, Astbury Department of Biophysics, University of Leeds, Leeds LS2 9JT, England.

The structure and conformation of the trisaccharide, mannatriose, are reported. The crystal structure space group is $P2_1$, $a = 11.834(2)$, $b = 12.224(1)$, $c = 9.223(2)\text{\AA}$, $\beta = 112.34(2)^\circ$, solved by using MULTAN and refined using SHELX, with anisotropic scale factors, from 1769 reflections with $I > 3(\sigma)I$. Final $R = 0.048$ with unit weights. The conformation of the molecule is stabilised by intra-molecular hydrogen bonds $O(13)-O(5)$ and $O(23)-O(15)$. Each molecule is extended, has its long axis at about 45° to the a and b axes, and is approximately perpendicular to the c axis, producing a pattern which resembles a herring-bone brick bond. Water molecules in the interstices take part in hydrogen bonds reinforcing the inter-layer connections.

The central residue, with torsion angles of $\phi(1) = -94.5^\circ$, $\chi(1) = -149.0^\circ$, $\phi(2) = -73.8^\circ$ and $\chi(2) = -132.17^\circ$ provides a good model for a poly(1 \rightarrow 4)mannoside, c.f. β -cellotriase undecaacetate (Perez, S. & Brisse, F. Acta Cryst. (1977) B33, 2578-2584) for a poly(1 \rightarrow 4) glucoside.

09.2-6 CRYSTAL AND MOLECULAR STRUCTURE OF 1,2,3,4,9,10,11,12 - octahydro-7-methoxy-11- β -methyl-12- β -H-3-oxo-phenanthrene ($C_{16}O_2H_{20}$). S.G. Biswas, A. Kabraaj, Physics Department, Visva-Bharati University, Santiniketan-731235, West Bengal, India.

The presence of partially aromatised hydrocarbons related to steroids has been noticed in geological samples and the first identification of one type has been reported (J. Schaefer et al., Tetrahedron Lett., 1978, 4163). In connection with the total synthesis of this partially aromatised hydrocarbon and related compounds a stereospecific CIS-reduction of a hydrophenanthrene derivative yielded the title compound, an A/B CIS Ketone, as an intermediate (A. Chatterjee et al., J. Chem. Soc., Chem. Commun., 1982, 84).



It is suggested that compounds having this type of A/B CIS-configuration with a ring fusion methyl group and a ring fusion hydrogen, usually equilibrate between the two canonical conformers owing to their flexible nature. An X-ray diffraction study of this Ketone has been undertaken to confirm the stereospecificity of the CIS reduction.

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

The compound crystallizes in the space group $P2_1/c$ with $a = 9.922(2)$, $b = 8.462(2)$, $c = 16.068(2)$ Å, $\beta = 100.29(1)^\circ$, $D_m = 1.208$ gm/cm³, $D_c = 1.197$ gm/cm³, $\mu(\text{CuK}\alpha) = 6.175$ cm⁻¹ and $Z = 4$. The structure was solved by MULTAN with 1705 unique reflections collected on a diffractometer. 170 reflections with $E_{\text{max}} = 4.549$ and $E_{\text{min}} = 1.682$ were used to solve the phase problem and all the non-hydrogen atoms were shown by the search map of MULTAN. The positional and thermal parameters of non-hydrogen atoms were initially refined by full-matrix least square method. A difference map at $R = 0.12$ revealed some of the hydrogen atoms and the rest were generated. They were assigned isotropic temperature factors of non-hydrogen atoms to which they were attached. The positional parameters of hydrogen and non-hydrogen atoms and their isotropic and anisotropic thermal parameters respectively were refined by block diagonal least square method and the final R -value was 0.0432. The bond lengths and angles were well within the range of chemically accepted values and the non-bonded contacts were always greater than the sum of the Vander Waals radii.

The derived three-dimensional molecular architecture confirms the stereospecificity of the reduction process and the formation of a CIS Ketone. The ring fusion methyl group is axial to the B-ring and equatorial to the Ketone containing A-ring of the molecule, whereas the ring fusion hydrogen atom is equatorial to the B-ring and axial to the A-ring of the molecule. The estimated distance between the hydrogen atom attached to C_4 and the hydrogen atom attached to C_5 of the aromatic benzene ring reveals that the alternative conformer with the methyl group equatorial to B-ring and the hydrogen axial to it is not favoured in the crystalline state.

09.2-7 CRYSTAL AND MOLECULAR STRUCTURE OF 2-METHYL-1,2,3,9,10,10a-HEXAHYDRO-2 α ,10 α ,11-OXOETHANOPHENANTHRENE. By A.K. Pal*, S.C. Kundadas and B.S. Basak, X-ray Laboratory, Presidency College, Calcutta-73, India.

The title compound ($C_{17}H_{18}O$) is one of a number of important organic compounds studied in our laboratory. The compound crystallized in space group $P2_1/c$, $a = 10.109(4)$, $b = 11.725(5)$, $c = 11.159(1)$ Å, $\beta = 94.24(5)^\circ$, $V = 1319$ Å³, $D_c = 1.20$ g cm⁻³ for $Z = 4$, $D_m = 1.18$ g cm⁻³, $F(000) = 512$, $\mu(\text{MoK}\alpha) = 0.78$ cm⁻¹, $\lambda(\text{MoK}\alpha) = 0.7107$ Å.

Three-dimensional diffraction data were recorded on a four-circle diffractometer by ω -2 θ scans. A total of 2314 reflections were collected, including 1058 with $|F_o| \leq 4\sigma(F_o)$. The structure was solved by direct methods using the 1978 version of MULTAN. The structure was refined isotropically and also anisotropically using the program MAMIE for full-matrix least-squares and the program BLOK for block-diagonal least-squares calculations, respectively. Prior to anisotropic refinement, the positions of the hydrogen atoms were determined by difference synthesis. The refinement ended with $R = 0.048$.

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09.2-8 CRYSTAL AND MOLECULAR STRUCTURE OF cis-METHYL-3,4,4a,9,10,10a-HEXAHYDROPHENANTHRENE-2(1H)-ONE-4a-ACETATE.

By A.K. Pal*, S.C. Kundadas and B.S. Basak, X-ray Laboratory, Presidency College, Calcutta-73, India.

The crystal structure analysis of the title compound is part of a structural study of biologically important organic compounds. The compound ($C_{17}H_{20}O_3$) crystallised in space group $P\bar{1}$, $a = 6.413(1)$, $b = 10.501(3)$, $c = 10.862(4)$ Å, $\alpha = 82.71(2)$, $\beta = 87.73(2)$, $\gamma = 85.29(2)^\circ$, $V = 724$ Å³, $D_c = 1.24$ g cm⁻³ for $Z = 2$, $D_m = 1.23$ g cm⁻³, $F(000) = 584$, $\mu(\text{MoK}\alpha) = 0.91$ cm⁻¹, $\lambda(\text{MoK}\alpha) = 0.7107$ Å. Three-dimensional counter data were recorded using ω -2 θ scans. A total of 1880 reflections were measured, including 944 with $|F_o| \leq 4\sigma(F_o)$. The structure was solved by direct method using the 1978 version of MULTAN. It was refined first isotropically and then anisotropically using the programs MAMIE and BLOK for full-matrix least-squares and block-diagonal least-squares calculations, respectively. The hydrogen atoms were located prior to the anisotropic refinement. The refinement converged with $R = 0.055$.

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09.2-9 CRYSTAL AND MOLECULAR STRUCTURE OF 6-(3-HYDROXY-3-METHYL-1-BUTINYL)-7-METHOXY-2H-1-BENZO-PYRAN-2-ONE (SUBERINOL).

By R.R. Bandyopadhyay* and B.S. Basak, X-ray Laboratory, Presidency College, Calcutta-700073, India.

The crystal structure of suberinol ($C_{15}H_{16}O_4$) has been determined as part of a study of the structures of biologically important organic compounds. Suberinol crystallized in space group $P2_1/c$, $a = 7.94$, $b = 15.64$, $c = 10.99$ Å, $\beta = 103.97^\circ$, $V = 1324$ Å³, $D_c = 1.30$ g cm⁻³ for $Z = 4$, $D_m = 1.29$ g cm⁻³, $F(000) = 552$, $\mu(\text{CuK}\alpha) = 7.87$ cm⁻¹, $\lambda(\text{CuK}\alpha) = 1.5418$ Å. Three-dimensional X-ray diffraction data (OKl to 6kl, h0l, hl \bar{l}) were recorded photographically using a Unicam Weissenberg goniometer. The structure was solved by direct methods. Isotropic followed by anisotropic refinement calculations were made by means of the full-matrix least-squares program MAMIE and the block-diagonal least-squares program BLOK, respectively. The final $R = 0.09$. Bond lengths and bond angles agree with the values in similar compounds.

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