

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

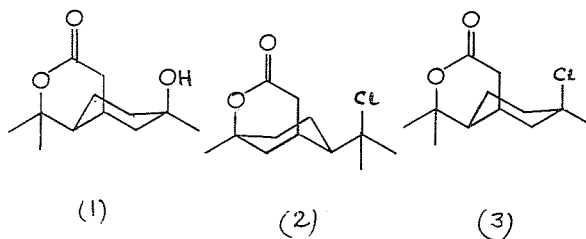
09.2-19 THE CRYSTAL STRUCTURE OF THE 2:1 INCLUSION COMPOUND BETWEEN DEOXYCHOLIC ACID AND PINACOLONE by V.M. Coiro, F. Mazza, G. Pochetti, Istituto di Strutturistica Chimica "G. Giacomello" C.P. 10, 00016 Monterotondo Stazione, Roma and by E. Giglio, Dipartimento di Chimica, Università di Roma, P.le A. Moro, 5, 00185 Roma (Italy).

3 α ,12 α -dihydroxy-5 β -cholan-24-oic acid (deoxycholic acid, DCA) forms several inclusion compounds of the "channel" type with a large variety of organic molecules. The reversible valence isomerization of norbornadiene (NBD) to quadricyclane (QDC) is an attractive process for the chemical storage of solar energy (R.R. Hautala, J. Little, and E.M. Sweet (1977) *Solar Energy*, 19, 503). Carrying out the reaction NBD \rightarrow QDC inside the channels avoids side reactions during the photochemical process. The crystal lattices of the inclusion compounds with NBD (DCANBD, A. D'Andrea, W. Fedeli, E. Giglio, F. Mazza and N.V. Pavel (1981) *Acta Cryst.* B37, 368) and with QDC (DCAQDC, V.M. Coiro, E. Giglio, F. Mazza and N.V. Pavel (1984) *J. Incl. Phenom.* in press) have been investigated in order to understand the lattice-controlled photoinduced reaction NBD \rightarrow QDC. Because of the total lack of overlap between the electronic absorption spectrum of NBD and the solar radiance spectrum, the direct conversion NBD \rightarrow QDC by sunlight is precluded. However, sensitizers capable to favour the reaction do exist: among these we have chosen pinacolone (PNC) and have investigated the crystal structure of the 2:1 complex between DCA and PNC (DCAPNC) in order to verify whether the shape and size of the channel are sterically compatible with those observed for DCANBD and DCAQDC.

DCAPNC: 2 C₂₄H₄₀O₄ · C₆H₁₂O, s.g. P2₁2₁2₁, a = 27.132(7), b = 13.543(2), c = 14.228(2) Å. The structure has been refined to a final R and R_w of 0.089 and 0.091 respectively for 3067 reflections with I > 1.5 σ (I). The crystal packing of DCAPNC is very similar to those of DCANBD and DCAQDC and is characterized by an assembly of antiparallel pleated bilayers formed by molecules of DCA held together through hydrogen bonds. PNC occupies approximately the same position as NBD and QDC. In the light of the present data it should be possible to cocrystallize in the channels of DCA both NBD and PNC molecules.

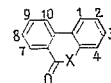
09.2-20 TWO STRUCTURAL ISOMERS IN THE SAME SINGLE CRYSTAL. By M.J. Begley, S.J. Bodicoat and L. Crombie, Department of Chemistry, University of Nottingham, Nottingham, England.

When the hydroxylactone (1) reacted with HCl dissolved in acetic acid a crystalline product was obtained. The X-ray structure determination revealed that the crystal consisted of a mixture of the two structurally isomeric chlorolactones (2) and (3) that had co-crystallised in the ratio 60:40. Although structurally very different these isomers can apparently pack in the solid state with the positions of Cl, O and 6 of the carbons overlapping. The remaining 6 carbons appeared in two different positions with partial occupancies corresponding to structures (2) and (3). The 2 compounds were subsequently separated by HPLC and the structure of each pure compound determined. The major component (2) crystallised in the same space group (Pbc₂) with similar cell dimensions to the mixture. Compound (3) crystallised in P2₁/c with non related dimensions.



09.2-21 CRYSTAL AND MOLECULAR STRUCTURES OF NITROSUBSTITUTED PHENANTHRIDONES AND DIBENZOPYRANONES. By L.A. Chetkina, E.S. Popova, V.K. Belsky. L.Ya. Karpov Physico-Chemical Institute, Moscow, U S S R.

The X-ray structure determination of some polynitrosubstituted phenanthridones (I) and dibenzopyranones (II) interesting because of their photophysical properties was undertaken.



I X = NH

II X = O

- Ia. 2,4,8,10-Tetranitrophenanthridone: Space group P2₁2₁2₁, Z=4, 826 reflections, R=0.031.
- Ib. 2,4,8-Trinitro-10-acetoxypheanthridone: Space group P2₁2₁2₁, Z=4, 1129 reflections, R=0.028.
- IIa,b. 2,3,8-Trinitro-6H-dibenzo/b,d/pyran-6-one (two polymorphs): a) Monoclinic, space group P2₁/n, Z=4, 1279 reflections, R=0.032. b) Orthorhombic, space group P2₁2₁2₁, Z=4, 719 reflections, R=0.029.
- IIc. 2,3,4,8-Tetranitro-6H-dibenzo/b,d/pyran-6-one: Space group P2₁/b, Z=4, 1355 reflections, R=0.033.

The tricyclic system is close to planar, especially for the compounds II. In Ia,b the iminogroup of the heterocycle is intramolecularly H-bonded to nitro-oxygen of the adjacent nitrogroup: NH...O 2.615 Å (Ia) and 2.640 Å (Ib). The biggest angles of rotation are for 10-nitrogroup in Ia (65.7°) and acetoxypgroup in Ib (73.8°). The modifications IIa and IIb have the different rotation angles of nitrogroups in the positions 2 and 3: 52.2° and 36.0° in IIa, 17.0° and 66.7° in IIb. In IIc the corresponding angles in the positions 2,3,4 are equal to 22.6°, 65.8° and 57.1° respectively.