

Schematic view of the overall 10[5x2]-fold interpenetration of class IIIa

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Keywords: Halogen Bonding, Molecular Assemblies, Interpenetrated Networks

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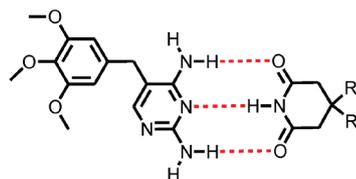
The co-crystallization of trimethoprim with glutarimide derivatives by means of molecular recognition. C. Q. Ton and E. Egert, *Institute of Organic Chemistry and Chemical Biology,*

Goethe-University, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany

E-mail: egert@chemie.uni-frankfurt.de

Trimethoprim is an API which is used against bacterial infections and inhibits dihydrofolate reductase [1]. It shows the necessary donor/acceptor groups for the complexation with glutarimide derivatives which have been selected for co-crystallization experiments because of their structural similarity with barbiturates [2].

1:1 co-crystals between trimethoprim and three glutarimide derivatives (glutarimide [I], 3,3-dimethyl glutarimide [II] and 3,3-tetramethylene glutarimide [III]) have been successfully synthesized. All these complexes show the expected hydrogen-bond pattern (ADA/DAD with A = acceptor and D = donor). Additional N-H...N hydrogen bonds between trimethoprim molecules lead to a diverse arrangement in the crystal packing. Complex I crystallized in $P2_1/n$ with one complex in the asymmetric unit while complexes II and III crystallized in $P-1$ with one and two complexes in the asymmetric unit, respectively. The structure of complex I is characterized by the formation of rings between two complexes (generated by inversion) through N-H...O (methoxy) interactions [$R_2^2(20)$ ring in graph-set notation]. The ring units are further interlinked with each other by N-H...N hydrogen bonds. The complexes II and III show similar hydrogen-bond interactions and crystal-packing arrangements. In both cases three classical hydrogen bonds connect the glutarimide with the pyrimidine-2,4-diamine fragment of trimethoprim. These complexes are centrosymmetrically bridged through a pair of N-H...N hydrogen bonds, involving the two amino groups and the pyrimidine ring nitrogen. A thorough analysis of the hydrogen bonds in each crystal as well as the differences and similarities in the crystal packing within these three complexes will give insight into the design of co-crystals. Furthermore, a comparison of the conformations of trimethoprim in different structural environments demonstrates its conformational flexibility [3].



complex I $\Rightarrow R_1 = R_2 = H$

complex II $\Rightarrow R_1 = R_2 = CH_3$

complex III $\Rightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}$

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FA4-MS26-P24

Molecular interactions in complexes of 4,4'-Dinitrobiphenyl. Peet van Rooyen, David Liles, Eric Modau. *Department of Chemistry, University of Pretoria, Pretoria, South Africa.*

E-mail: phvr@up.ac.za

The focus of this study was to investigate the nature of molecular donor-acceptor interactions in the solid state, using spectroscopic techniques such as IR, Raman, NMR and X-ray crystallography. Complexes of para disubstituted and 4-monosubstituted biphenyl formed with 4,4'-dinitrobiphenyl (DNBP), demonstrate intense colours, from pale yellow to dark red, upon formation. These colours are dissimilar to the colour combination of the parent compounds. Typical interactions observed in such molecular complexes include π - π interactions, hydrogen bonding, charge transfer and van der Waals interactions. Complexes of DNBP, as the host molecule, included a variety of mono- and disubstituted biphenyl donors or guests, such as dihalo, diamino, di- and monohydroxy groups[1], as well as urea with a 1:1 host:guest ratio [2] and thiourea with a 7:6 ratio. Molecular complexes formed between DNBP with difluorobiphenyl with a 3:1 ratio and DNBP with dibromobiphenyl and diiodobiphenyl, both with 4:1 ratios, showed similar packing styles. The crystal structures of these complexes showed retention of the non-planar conformation of DNBP with a dihedral angle between the phenyl rings of around 35° [3]. However, the dihedral angle between the phenyl rings of the difluoro-, diiodo- and dibromobiphenyl in these complexes indicate that these guests are essentially planar. The conformation for DNBP has also been confirmed using density functional theory (Gaussian03) calculations that showed good agreement between the theoretically calculated and experimentally observed IR and Raman spectra in the solid state. It appears as if the packing of the complexes in the solid state is directed mainly by the similar packing of DNBP units in these complexes. Some of the molecular ratios for these complexes that vary, depending on the electronic properties of the donor molecules, were determined using NMR spectroscopy.

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Keywords: molecular complexes, guest-host structures, dinitrophenyl.

FA4-MS26-P25

Low-melting molecular complexes of chloroform and dichloromethane. Dmitry S.Yufit, Judith A.K.Howard, *Department of Chemistry, Durham University, South Rd., Durham, DH1 3LE, UK*
E-mail: d.s.yufit@dur.ac.uk

In continuation of our studies of low-melting co-crystals [1], both components of which are liquid under ambient conditions, the crystals of new molecular complexes of chloroform (I) and dichloromethane(II) have been grown *in situ* and structurally characterized. The structures of new co-crystals of II with cyclohexanone, 1,4-dioxane and butanone-2 are compared with corresponding complexes of I and with the structures of pure components of these co-crystals. In spite of seeming simplicity of the components, the structures display a variety of types and motifs of intermolecular interactions. Indeed, if the (Cl)C-H...O contacts are present in all studied structures, different spatial arrangements of these contacts combined with a delicate balance of weaker interactions of C-H...Cl, C-H...O and even of O...Cl types make the structures of each of these compounds unique, curious and challenging for prediction. Examples of unforeseen products of co-crystallization experiments will also be discussed.

[1] Yufit D.S., Howard J.A.K., *CrystEngComm*, 2010, 12, 737-741

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FA4-MS26-P26

Absolute Structure of Two Derivatives of a Longipinene from *Stevia lucida*. Graciela Díaz de Delgado^a, Pablo A. Chacón^b, Juan M. Amaro-Luis^b, Hyunsoo Park^c, José Miguel Delgado^a, ^aLaboratorio de Cristalografía and ^bLaboratorio de Productos Naturales, Universidad de Los Andes, Mérida, Venezuela, ^cIUMSC, Indiana University, USA.
E-mail: migueld@ula.ve

7 β ,9 α -Dihydroxy-longipin-2-en-1-one (**1**), obtained by basic hydrolysis of a mixture of diesters of longipin-2-ene-1-one, afforded a 7 β -hydroxy-9-one (compound **2**) via Collins oxidation and a 7,9-dione (compound **3**) via Jones oxidation. Compound **2** is orthorhombic, $P2_12_12_1$, with $a=6.7905(2)$, $b=11.4566(3)$, $c=17.4319(5)$ Å, $V=1356.13(7)$ Å³, $Z=4$. The refinement converged to $R=0.0301$, $wR=0.0790$, $S=1.043$. Compound **3** is also orthorhombic, $P2_12_12_1$, with $a=6.4241(1)$, $b=10.5101(2)$, $c=19.1813(4)$ Å, $V=1295.08(4)$ Å³, $Z=4$. The refinement converged to $R=0.0290$, $wR=0.0743$, $S=1.057$. In compound **2**, the hydroxyl group participates in a R(9) hydrogen bond with the ketone O at C1 of a molecule with symmetry operation $2-x, -1/2+y, 1/2-z$. They produce zig-zag chains along b which interact with similar chains through hydrogen bonds between an H from the methyl group at C10

and the ketone O2 at C9. Additionally, there is one intramolecular hydrogen bond between the methyl group at C10 and the ketone O2 at C9 with graph set symbol S(5). In the absence of the hydroxyl at C7, the hydrogen bond patterns and packing of compound **3** is different. Pairs of molecules related by $-1+x, y, z$ are connected by a hydrogen bond between an O atom and the H's of two methyl groups, resulting in a R₂¹(8) graph set. They form chains along the a -axis which interact via van der Waals forces.

Keywords: Natural Products, Hydrogen Bonding, Absolute Structure