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n-Alkanes and most of their α- and α,ω-substituted derivatives show a remarkable alternation in their melting points with increasing chain length [1,2]. The same phenomenon also occurs within series of substances with a constant number of C-atoms. One of these isomeric series are the octenes where the melting points of the 2- and 4-octenes are relatively higher than those of 1- and 3-octenes. This holds for the series of *cis*- as well as for the series of *trans*-isomers.

Single crystals of all *trans*-octenes have been grown *in situ* using a miniature zone melting procedure [3], and their X-ray analyses have been carried out. Crystal structures of *cis*-octenes have been determined by X-ray powder diffraction using lattice energies minimisations [4]. The structural similarities and differences between the *trans*- and *cis*-isomers of each serie could be analyzed based on the packing arrangements of hydrocarbon chains and the end groups. The melting point alternation in both isomeric series can be explained based on the calculations of lattice energies.

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Keywords: molecular packing, lattice energy calculations, melting point alternation

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Influence of the p-substituent for the Diastereomeric Resolution of Carboxylic Acids

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The salts of (S)- and (R)-1,4-benzodioxane-2-carboxylic acid with three (S)-1-arylethylamines have been investigated [1]. Their melting points and their solubilities in alcoholic solvents revealed large differences between the benzodioxanecarboxylates of (S)-1-(p-nitrophenyl)ethylamine and (S)-1-(p-methylphenyl)ethylamine. Therefore this latter amines were selected to resolve (±)-1,4-benzodioxane-2-carboxylic acid by diastereoselective crystallisation finding that both of them display a high resolution ability for such substrate, which contrasts with the null efficiency of unsubstituited 1-phenylethylamine. The crystal structures of the salts showed that there is correlation between the efficiencies of the optical resolutions of the amines with the resolving reagents and the crystal structures of the salts. A hydrogen bond layer was found to be common to the less soluble salt crystals, consisting of stable columnar structures with planar boundary surface [2]. In contrast, in the corresponding more soluble salts no particularly stabilized crystal structure is formed, only columnar structures are present. There results strongly suggest, that for successful resolution it is necessary realize hydrogen bond layers, consisting of stable columns with planar boundary surfaces, in the crystal of one of the pairs of diastereomeric salts

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Keywords: diasteromeric method, chiral discrimination, crystal engineering

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Structure by 2D NMR and X-ray Crystallography of a Triterpene from *M. imbricate*

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Many specimens of *Maytenus* (Celastraceae) are used in medicine folk in different Brazilian regions and shown a diversity of secondary metabolites, like as flavonoids, glycosides, maitansinoids, alkaloidic and non alkaloidic sesquiterpenes, friedelanes, oleananes, lupanes, quinonoids triterpenes and pentacyclic triterpenes (PCTTs) of the other series. To PCTTs are attributed pharmacological properties like as antiseptic, ant-asthmatic and antimicrobial action, antispermatogenic, antispasmodic, analgesic and ant-ulcer effect, insecticide, antitumoral, moluscicide, allelopatic and anti-inflammatory effect.

The compound was isolated from the powder extract of *Maytenus imbricata*. From the Mass Spectrometry (MS), ^{1}H and ^{13}C NMR and X-ray data it was possible to determine the molecular formula $C_{30}H_{50}O_2$. The structure of the compound were established by two-dimensional NMR spectroscopic techniques and later confirmed by single crystal X-ray diffraction as 3β,30-dihydroxy-lup-20(29)-ene.

The crystal structure shows one molecule in the asymmetric unit. The symmetry was examined carefully and it was concluded that $P4_1$ is the correct space group. The crystal packing is stabilized by two intermolecular hydrogen bonds, which give rise to the formation of five infinite helical chain along *c* per unit cell. Analysis with Mogul program showed all bound length and bound angle between corresponding atom in the molecule are in good agreement with expected.

Keywords: triterpenes, NMR, X-ray crystallography

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The Structure Characterization of Molecules with ESR Spin Labels of Pyroline and Piperidine Type

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A series of molecular structures bearing ESR spin labels of pyroline and piperidine types has been determined. The review of all structures shows common features of hydrogen bonds formed by nitroxyl oxygen atoms and neighboring hydrogen donors. In addition to molecules bearing a single spin label (SSL) [1] , the list contains a number of double spin labels (DSL) and three spin labels (TSL). Intentionally rigid spacers bearing the spin labels fix the inter-radical distance in interval 6-30 Å in case of DSLs . The spin label moiety itself remains virtually untouched by any external influences as the chemical composition of spacer, crystal packing, hydrogen bonds, etc.

The double spin label [3,3'-oxybis(ethyleneoxycarbonyl)bis(2,5-dihydro-2,2,5,5-tetramethyl pyrrol-1-yloxyl)], i.e. DSL with a poly(ethyleneoxide) spacer was prepared as a paramagnetic tracer for ESRI studies of diffusion processes in polymer gels and concentrated polymer solutions [2]. It is of special interest also for its phase transition at 248 K where the molecules lose their two fold symmetry and the space group transfers with lowering the temperature from Iba2 to $Pbc2_1$ keeping the molecular stacking virtually unchanged.

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Keywords: spin label, organics, X-ray structure

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Crystallization of the Azithromycin 11,12-hydrogenborate. Can We Have the Control?

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Azithromycin is the most important macrolide of *azalide* class (derived from erythromycin A by insertion of an N-methyl group in the lactone ring), and shows higher antibiotic effect than the parent compound, particularly against Gram-negative bacteria. Its synthesis is based on the Beckmann rearrangement of eryrhromycin A oxime to yield the imino ether, and several ways have been reported to reduce the imino ether and finally achieve the azithromycin. One of these routes involve the synthesis of a precursor of the azithromycin, the azithromycin 11,12-hydrogen borate [1], whose acid hidrolysis affords azithromycin.

This structure was studied in solution state through NMR spectroscopy [2], but no study was done so far in solid state, to know the accurate structure and the molecular conformation

In the present communication, we show the results of the analysis by x-ray diffraction of the crystals obtained in different conditions of crystallization: solving the borate in hot acetone and slowly cooling, or solving the borate in acetone and changing the polarity by adding water.

Both solids are crystalline, as is shown on their powder patterns, with different structural parameters, and including the second sample a percentage of amorphous material.

Controling the conditions of crystallization, we can decide what crystal obtain. The knowledge of its crystal structure and composition can give us information about the role of the solvent in controling the final crystal form.

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Keywords: crystallization, azithromycin, hydrogenborate

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Modelling Disorder in 3,3'-dimethoxybenzil, $C_{16}H_{14}O_4$

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This work is part of an extended study of benzil ($C_{14}H_{10}O_2$) and derivatives which aims to understand the role that molecular flexibility plays in determining crystal packing and polymorphism [1,2]. In this study diffuse X-ray scattering is used to probe both the inter- and intra-molecular correlated motions of a series of similar compounds in order to gain insight into how molecular motion influences crystal packing. In future studies it is hoped to apply the methodology to compounds of pharmaceutical interest which display polymorphism. In the present paper we present results for the compound 3,3'-dimethoxybenzil, $C_{16}H_{14}O_4$, 33'DMOB. For this molecule the molecular flexibility is afforded by rotations about three C–C and two C–O single bonds, defined by the dihedral angles, ϕ_1–ϕ_5. Other molecular groups are considered rigid. Diffuse scattering arises from differences between the local structure of a crystal and the underlying *average* structure. Such differences (termed disorder) may be either static or dynamic in origin. The disorder in 33'DMOB is purely thermal, and conventional crystal structure determination using Bragg scattering yields a perfectly normal average structure with no anomalous atomic displacement patterns. Nevertheless all studies have observed strong and highly structured thermal diffuse scattering.

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Keywords: diffuse scattering, molecular flexibility, monte carlo simulation

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Serendipitous Rediscovery of Three Polymorphs of Benzidine

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The search for a co-crystal of benzidine (4, 4'-biphenyldiamine) as a donor with potential acceptors has revealed three polymorphs of the source material benzidine for which, somewhat surprisingly, no structure has been reported according to a CSD search Nov. 2003.

For about 130 years, benzidine and its derivatives had very wide industrial use, mainly as dyes and pigments in a variety of applications. By the middle 1970's the use of benzidine totaled 0.5-1 million kg. At that time the compound itself was found to be carcinogenic, and its commercial use has essentially been abandoned, apparently along with interest in its structure and properties.

The biphenyls attracted the attention of many crystallographers [1 and references therein]. One of the principle reasons for interest in this compound was the fact that in the gas phase the molecule had been shown to be non-planar, while in the crystal the molecule's presence on a crystallographic inversion center requires it to be planar.

The three reported structures are characterized by the molecules packing of Z'>1 (1.5, 3 and 4.5), which according to the CSD are found in only 0.25%, 0.4% and 0.002% of the total structures.

The three forms were grown from two component solutions (one is benzidine) as well as from solutions of benzidine only. In some crystallization experiments the polymorphs grew concomitantly [2].

[1] a) Brock C. P., Minton R. P., *J. Am. Chem. Soc.*, 1989, **111**, 4586-4593; b) Brock C. P., *J. Res. Natl. Inst. Stand. Technol*., 1996, **101**, 321-325. [2] Bernstein J., Davey R. J., Henck J. -O., *Angew. Chem. Int. Ed.*, 1999, **38**, 3440-61.

Keywords: polymorph, co-crystal, concomitant crystallization

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Structures of Some Hydroxynaphthaldehyde Schiff Bases

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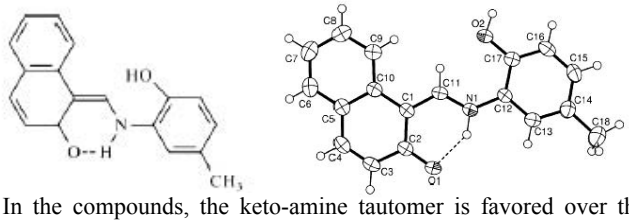
The molecules of compound, $C_{18}H_{15}N_1O_2$ (I) and $C_{17}H_{12}N_1O_2Cl_1$ (II) are not exactly planar, and adopts the keto-amine tautomeric form with an N---H…O and intermolecular O---H…O hydrogen bonds.



In the compounds, the keto-amine tautomer is favored over the phenol-imine form. The rather short C2-O1 and C1-C11 bonds can be considered as C=O and C=C double bonds, respectively. This fact, together with the very short C3-C4 bond, suggests the presence of a significant quinoidal effect. A similar quinoidal effect was observed in our previous work [1].

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Keywords: tautomerism, hydrogen bonds, diffraction structure analysis

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Two Polymorphs – Which One is Stable at Ambient Conditions?

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NN414 (6-chloro-3-(1-methylcyclopropyl)-amino-4*H*-thieno[3,2-*e*]-1,2,4-thiadiazine 1,1-dioxide) is an opener of ATP sensitive potassium channels, which attenuates hyperinsulinemia. The compound prevents diabetes and improves glucose tolerance without affecting body weight or body composition in preclinical studies. Apart from its therapeutic effects it is also interesting because of its