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Polymorphism, isomorphism and variability in the inclusion chemistry of a diol host compound

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The process of molecular recognition in inclusion compounds is governed by the intermolecular interactions which occur between the various host and guest molecules making up the resultant crystalline assembly. We have studied the diol host, 2,2'-bis (hydroxydiphenylmethyl-1,1'-binaphthyl(H), which crystallised in three different polymorphic structures and formed a series of inclusion compounds with pyridine(P), morpholine(M) and benzene(B). Different stoichiometries were obtained by manipulating the proportions of the guests and the crystallisation temperatures. Four of these inclusion compounds, H.3P, H.2P.M, H.2P.B and H.P.M.B, are isomorphous and the guests are located at fixed sites in the crystal structure. Their thermal analysis results were explained in terms of the host···guest interactions. The three polymorphs of the host compound show strong structural similarities as depicted by their Hirshfeld surface fingerprint plots, which exhibit dominant H···H interactions. The conformation of the host molecule remains essentially constant, and is governed by an intramolecular O-H···O hydrogen bond in the polymorphs of the apohost and in all the nine inclusion compounds analysed.

Keywords: polymorphism, isomorphism, inclusion compound

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New crystal forms of gabapentin

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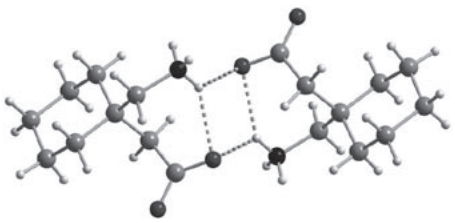
The neuroleptic drug gabapentin exists in different crystal forms: metal salts, cocrystals or different polymorphs. Three monoclinic polymorphs which are stable at room temperature[1] are described here. There is a considerable difference in the densities of the three polymorphs (1.257, 1.247 and 1.216 Mg m^{-3} for the α-, β- and γ - forms respectively) which can be attributed to small differences in the molecular conformations, packing and intermolecular N-H ···O=C hydrogen bonds. Although centrosymmetric hydrogen-bonded pairs can be identified in all of them, only the β-form exhibits intramolecular hydrogen bonding (Figure 1). Furthermore, small exo- or endo-therms have been observed by DSC at around 85 ℃ when heating the β or γ forms, a phenomenon that appears to be associated with minute changes in the hydrogen bonded networks of these polymorphs.



Here, the similarities and differences in molecular conformation and packing of the gabapentin polymorphs, and new metal salts and cocrystals are compared.

[1] H.A. Reece and D.C. Levendis, *Acta Cryst. (2008)* ***C64****, o105-o108*.

Figure 1. The centrosymmetric dimer of the β-polymorph of gabapentin.

Keywords: gabapentin, polymorph, cocrystal

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The effect of substituents on the occurrence of polymorphism in diaminodicyanopyrazine dyes

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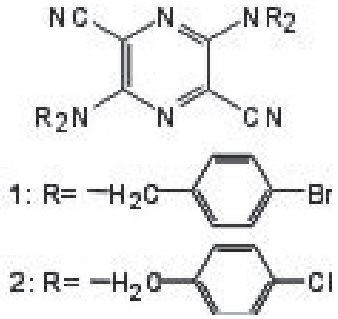
2,5-Diamino-3,6-dicyanopyrazine dyes, characterized by intense fluorescence in solution and in the solid state, have been developed as functional dyes since 1990's. A series of derivatives with benzyl substituents on the amino groups have been found to have some conformational polymorphs with different colours. In *para*-halogenated derivatives (Figure), **1** was found to crystallize in three differently coloured polymorphs. On the other hand, **2** was found to crystallize in a yellow form in most cases. In this study, the effect of substituents on the occurrence of polymorphism was investigated by conformational searches and crystal structure predictions. The conformational searches showed that the terminal halogen substituents have no significant influence on the stability of the isolated conformers. Crystal structure predictions for the calculated conformers were then performed. The result revealed that the halogen substituents have strong influence on the relative crystal energies in the stable forms. The difference in a polymorph occurrence between **1** and **2** will be discussed on the basis of the calculated results.



Keywords: polymorphism, crystal structure prediction, conformational analysis

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Isomorphous pharmaceutical salts of lamotrigine with counterion dependence on water solubility

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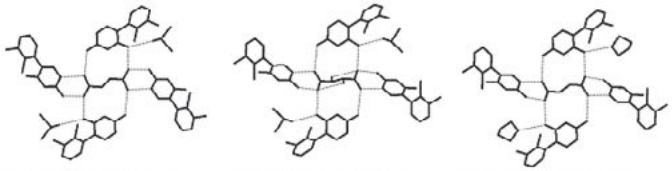
Lamotrigine is an anticonvulsant drug with low water solubility. In order to enhance it, lamotrigine salts of four different counterions were prepared. Six structures have been solved from single crystal X-ray diffraction data. Four of these salts crystallized in $P2_1/c$

and $P2_1/n$ space groups, being isomorphous dicarboxylic acid salts of lamotrigine. The corresponding powder samples have been characterized by thermal methods (DSC-TGA), PXRD, FT-IR spectroscopy and their water solubility have been determined. In all cases water solubility of the presented lamotrigine salts are higher respect to lamotrigine free base. The water solubility value appears directly related with the solubility of the acid involved in the salt, thus the higher is the water solubility of the free acid, the higher is the solubility of the salt formed. The isomorphous nature of the salts obtained allows relating their solid state properties with those of the counterion involved in each salt. The importance of the counterion solubility on the final solubility of the salts is rationalized considering their crystal structures.



Keywords: isomorphism, pharmaceutical, structure-property realtionships

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Polymorphs and humidity-induced transition of a serotonin receptor antagonist, $C_{29}H_{33}N_3O_2.HCl.xH_2O$

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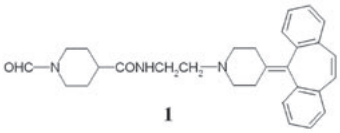
The serotonin (5-HT_{2A}) receptor antagonist, *N*-[2-[4-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene)-piperidino]ethyl]-1-formyl-4-piperidinecarboxamide ($C_{29}H_{33}N_3O_2$; **1**) monohydrochloride crystallizes as a monohydrate (Form α1) from an acetone solution and as a trihydrate (Form β3) from an aqueous solution. Humidity-induced phase transitions proceed in both hydrates. Form α1 changes to an anhydride (Form α0) below 5 % relative humidity. While β3 transforms to an anhydride (Form β0) through a dihydrate (Form β2) and a monohydrate (Form β1) in 0-30 % relative humidity range. Both transitions are reversible, and hysteresis is observed in only the case of Form β. The crystal structures of Forms α1, α0, β3, and β2 were determined. **1** consists of a non-polar dibenzocycloheptene ring and a polar tail. Hydrophilic and hydrophobic layers are constructed in both crystal forms, and crystal water molecules and Cl^- ions are located in hydrophilic region surrounded by polar groups. Characteristics of crystal structures, transformation of hydrogen-bonding schemes, and conformational changes of **1** coupled with the phase transitions are discussed.



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Keywords: polymorphs, phase transitions, hydrates

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Order-disorder transitions in sodium vanadylphosphate $Na_4VO(PO_4)_2$

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The new vanadyl phosphate $Na_4VO(PO_4)_2$ was synthesized and investigated by X-ray powder and single-crystal diffraction, high-temperature X-ray diffraction, electron diffraction and high-resolution electron microscopy. Its crystal structure contains isolated infinite chains of the corner-sharing VO_6 octahedra. The octahedra within the chains are additionally linked to each other by the tetrahedral PO_4 groups. Sodium atoms are situated in the positions between the chains. Depending on the conditions of synthesis, the number of sodium atoms in the unit cell of the $Na_{4+x}VO(PO_4)_2$ compounds may vary resulting in a change of the oxidation state of vanadium atoms and a change of their coordination environment. Electron diffraction study revealed an existence of various structural transformations occurring in situ in the transmission electron microscope. The charge redistribution was supposed in the gamma-modification of $Na_{4+x}VO(PO_4)_2$ where the V^{4+d} and V^{4-d} cations orderly occupy octahedral positions in different chains. The origin of this phenomena is discussed.

Keywords: order-disorder transitions, low-dimensional materials, vanadium compounds

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Polymorphs of picryl bromide

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Polymorphism is a phenomenon that has been observed often during the rich history of energetic materials development. Different polymorphs of the same compound can have different properties, which, in turn, can lead to substantial alterations in their stability and performance. Two polymorphs of the common energetic precursor, 2,4,6-trinitrobromobenzene (picryl bromide), were discovered in 1933, however no x-ray crystal structures were reported then, or have since been reported. Structural details of the two known polymorphs, the alpha and beta forms are detailed here. In addition, three new polymorphs are also presented, the gamma, delta, and epsilon forms. Two different triad motifs, consisting of C-H···O hydrogen bonds and N-O···Br dipole induced interactions, universal to all five forms of picryl bromide will be discussed, as well as apparent nitro-pi associations between adjacent layers of molecules.

Keywords: polymorph, energetic, intermolecular interaction