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Conformational Polymorphism in Molecular Organic Crystals: 4'-Hydroxyvalerophenone, as a Case Study

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Abstract: Polymorphism, the ability of a molecule to crystallize in more than one solid structure, is a phenomenon commonly observed in many organic compounds. Different packing arrangements are often accompanied by changes in the physical and chemical properties of the solid (e.g. color, melting point, solubility, etc.), so that different polymorphs should, in fact, be regarded as different materials. This represents a major challenge for the industrial production of organic materials with highly reproducible properties.

The systematic analysis of polymorphism in families of compounds consisting of structurally related molecules can offer insights into how variations in molecular size, shape and different interactions result in alterations of the packing architecture and of the relative stability of different crystals. Recently, our group has studied the 4-hydroxybenzoyl family of compounds. This family has the general formula $HOC_6H_4C(O)R$ (R = H, n-alkyl), and the molecular structures differ solely on the length of the alkyl group attached to the carbonyl. The compounds have displayed a propensity to form polymorphs both due to changes in their molecular conformation (such as in the case of 4'-hydroxyacetophenone) [1] or through adjustments in their packing architecture (such as in 4-hydroxybenzaldehyde) [2] and are, thus, an attractive target for these studies.

In this work, the polymorphic behavior of 4'-hydroxyvalerophenone (HVP, $C_{11}H_{14}O_2$, **Figure 1**), is analyzed from a structural and energetic perspective, by several techniques such as X-ray diffraction, differential scanning calorimetry, and hot-stage microscopy. From the obtained results, the occurrence of conformational polymorphism in HVP, when recrystallizing the compound from the melt (Form II), was confirmed and the thermodynamic relationship between the two forms was analyzed.

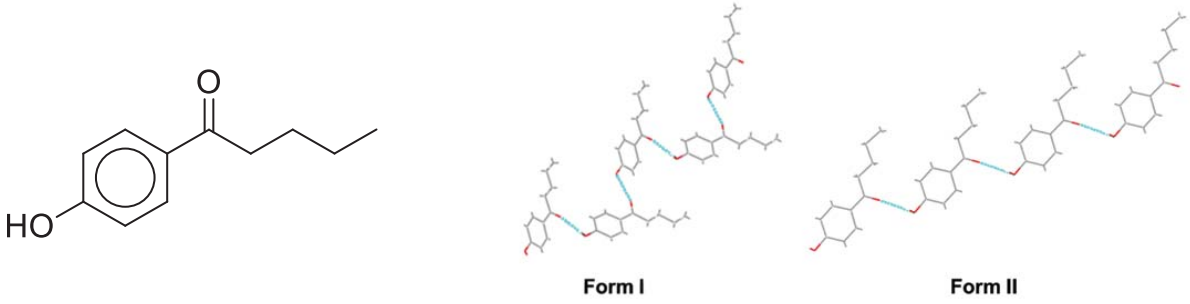

Figure 1: Molecular structure of 4-hydroxyvalerophenone (HVP) and crystal structure of both polymorphs.

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