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Polymorphism in 4'-Hydroxyvalerophenone: A Structure/Energetics/Dynamics Perspective

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Compounds with the 4-HOC_6H_4 COR backbone, containing H-bond donor (**–**OH) and acceptor (**–**C(O)R) substituents separated by a phenyl ring, are suitable targets for studies on the impact of systematic changes in molecular structure on the packing of a crystalline solid, and its physical properties [1,2]. These studies are of significant technological interest, as different packing architectures can strongly influence the characteristics of a material (e.g., the color of dyes, the conductivity organic conductors, or the bioavailability of drugs) and thus affect the manufacture, processing, and performance of a product.

In this work, the complex polymorphic behavior of 4'-hydroxyvalerophenone (HVP, R = C_4H_9, Figure 1) was experimentally and theoretically explored from a holistic structural/energetics/dynamics perspective. Three different polymorphic structures were identified: form I, which was the most stable from room temperature up to fusion; form II, monotropically related to form I, which was prepared by crystallization from the melt; and form III, which is enantiotropically related to form II by a fast and reversible phase transition at 247.5 ± 0.4 K. Forms I and II are an example of conformational polymorphism, where the hydroxyl and carbonyl groups change from a *Z* conformation in form I to *E* in form II, while form III is only observed when cooling the structurally similar form II below the transition temperature.
Finally, MD simulations indicated that the preferential crystallization of the metastable form II from the melt, is likely to be related with the similarity between the liquid structure of HVP and the crystal arrangement of form II.

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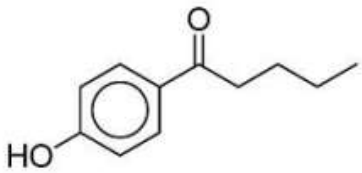

Figure 1. Molecular Structure of HVP

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