High-*Z*' phases of n-butanol

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The amphiphilic molecule *n*-butanol (C_4H_9OH), despite its industrial relevance and long-standing chemical importance, has long posed experimental challenges due to its pronounced tendency to form amorphous states under cooling or compression. In this study, we present the single-crystal investigations of *n*-butanol conducted under both low-temperature and high-pressure conditions, enabled by *in situ* crystallization within a glass capillary and in a diamond anvil cell, respectively.

At ambient pressure and low temperature, *n*-butanol crystallizes in the triclinic space group *P*1 (phase α).[1,2] The asymmetric unit contains two symmetry-independent molecules, A and B (Z' = 2). These molecules form O–H···O chains closely approximating 2_1 screw axis symmetry linking the alternating molecules A and B along the [100] direction. The compression above 1.2 GPa yield another form of butanol (phase β) of the monoclinic space group $P2_1/n$, with three independent molecules (Z' = 3). In the structure, two distinct hydrogen-bonding chains are apparent: one composed of molecules A and C related by glide symmetry, and another formed solely by molecules B around a 2_1 screw axis.

Although differing in the conditions where they were obtained, both phases retain a similar aggregation motif, with H-bond chains in both forms formed by two independent molecules. This indicates a common mechanism for the formation of the pre-associated molecular clusters.[3] The emergence of $Z' > 1$ in both structures underscores the influence of conformational frustration and directional intermolecular forces in shaping molecular packing under varying thermodynamic constraints.[4]

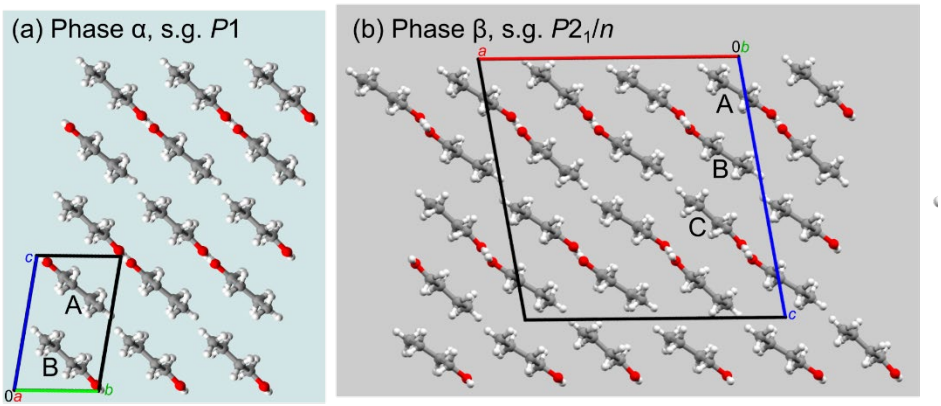

Figure 1. Structure of two polymorphs of n-butanol: (a) low-temperature phase α, and (b) high-pressure phase β.

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