A tale of two polymorphs: experimental and theoretical studies of temperature-induced polymorphism of \( N^2,6\)-diaryl-1,3,5-triazine-2,4-diamine

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The crystallisation of \( N^2,6\)-diaryl-1,3,5-triazine-2,4-diamine in ethanol resulted in two polymorphs (hereafter denoted as \( \alpha \) and \( \beta \)). The \( \alpha \) polymorph crystallised in monoclinic \( P\overline{2}_1/c \) with \( Z' = 4 \) (i.e. \( \alpha_1, \alpha_2, \alpha_3, \) and \( \alpha_4 \)) while the \( \beta \) appeared as \( P\overline{2}_1/n \) with \( Z' = 1 \). Main structural differences are observed in the orientation of the methoxyphenylamino and trimethoxyphenyl residues appended to the central triazine ring with the dihedral angle between the respective planes varied between 50.11° to 67.70° and 2.76° to 15.71° in both polymorphs. As a result, \( \alpha \) and \( \beta \) exhibit some distinctive features in their molecular packing, in which an optimum \( \pi \cdots \pi \) stacking between all three aromatic rings is observed in the former, while the latter is restricted to the \( \pi \cdots \pi \) stacking between triazine rings. Conformational analysis showed that the \( \beta \) polymorphs is the closest representation to the global minimum structure out of 28 calculated local conformers across the potential energy surface, and the stability is in the order of \( \beta > \alpha_3 > \alpha_1 > \alpha_4 > \alpha_2 \) with the relative energy difference being in the range of 0.02 to 9.15 kcal/mol. However, it is the \( \alpha \)-form that possesses a greater lattice energy of \(-53.3 \) kcal/mol as compared to that of \(-34.2 \) kcal/mol for the \( \beta \)-form mainly owing to the difference in \( Z' \) value. PXRD measurement revealed that the crystal structure remains in the \( \alpha \) form at \(-20^\circ C\), and it starts to transform to the \( \beta \) form by 0.7% under the ambient conditions at day 1 and completely converts to the \( \beta \) form at day 12.

**Figure 1** (a). Molecular superimposition of \( \alpha_1 \) (red), \( \alpha_2 \) (green), \( \alpha_3 \) (blue), \( \alpha_4 \) (ink), \( \beta \) (yellow) and the optimised structure (black); (b) the relative Gibbs free energy and Boltmann distribution for all possible conformers of \( N^2,6\)-diaryl-1,3,5-triazine-2,4-diamine.