Predicting molecular isomerism of symmetrical and unsymmetrical *N,N'*-diphenyl formamidines in the solid-state: crystal structure, Hirshfeld surface analysis, pairwise interaction energy, ΔH_{fusion} and ΔS_{fusion} determination

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N,N'-diphenyl formamidines have *E* and *Z* isomers with either synperiplanar or antiperiplanar conformational combinations around the formamidine –N=C(H)–N(H)– backbone. The molecular isomerism of *N,N'*-diphenyl formamidines have been extensively studied in solution state [1]. However, no reports have been found regarding their preferred isomerism in the solid state. In this work, the steric and electronic effects on the molecular isomerism of eight *N,N'*-diphenyl formamidine derivatives in solid-state were evaluated using X-ray crystallography [2]. The eight compounds constitute of four symmetrical and four unsymmetrical *N,N'*-diphenyl formamidine derivatives having a general formula of [N-(Ar),N′-(Ar′)] where (Ar = Ar′) and (Ar ≠ Ar′), respectively. Five of the compounds were characterized using single crystal X-ray diffraction. Solid-state structure analysis showed two molecular isomers, E_{syn} and E_{anti}, and they form distinct classical hydrogen bonding patterns (Fig. 1). Correlations between molecular isomerism, pairwise interaction energies, infrared spectroscopy and thermal properties were established in this work. This provides a unique crystal engineering approach to predicting the isomerism of *N,N'*-diphenyl formamidines without crystal structure determination.

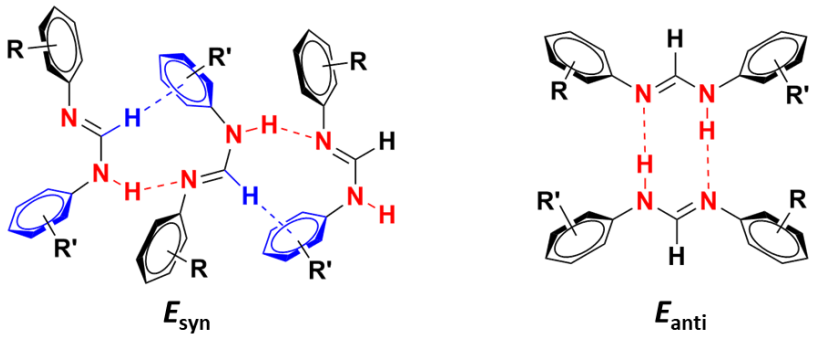

Figure 1. Molecular isomerism and intermolecular interactions of *N,N'*-diphenyl formamidines in this work (symmetrical formamidines: R = R' and unsymmetrical formamidines: R ≠ R').

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[2] Zamisa, S. J., Bongoza, U. & Omondi, B. (2021). *CrystEngComm* **23**, 4459-4474.

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