**Supporting information**

N-H···π induced configurational isomerism and the role of temperature in the Z to E isomerization of 2-fluoro-N-(3-fluorophenyl) benzimidamide

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Figure S1: **1H-NMR spectra of the synthesized compound in CDCl₃ (500 MHz).**

**FTIR (KBr pellet, cm⁻¹):**

- **Bulk:** 3323, 3175 (NH₂), 1667 (C=N), 1595 (C=C) in cm⁻¹, **E1:** 3434, 3287, 3138 (NH₂), 1643 (C=N), 1597 (C=C) in cm⁻¹, **E2:** 3320, 3165 (NH₂), 1666 (C=N), 1597 (C=C) in cm⁻¹, **Z:** 3305, 3169 (NH₂), 1665 (C=N), 1595 (C=C) in cm⁻¹. **1H-NMR (CDCl₃, 500 MHz):** δ 8.12 (s, 1H), 7.41 (s, 1H), 7.26 (m, 2H), 7.11 (t, J = 10.07 Hz, 1H), 6.62 (m, 3H), 5.21 (s, 2H).
Figure S2: Hot-stage polarizing microscopic (HSM) pictures of the polymorphs (E2 and E1) at different temperatures on heating from 25°C to 90°C @ 0.5°C/min, distinguish both the forms.

Figure S3: Hot-stage polarizing microscopic (HSM) pictures of the E/Z-isomers (E2 and Z) at different temperatures on heating from 25°C to 81°C @ 0.5°C/min, distinguish both the forms.
Figure S4: Molecular pairs of E1 with decreasing interaction energies.

Figure S5: Molecular pairs of E2 with decreasing interaction energies.
Figure S6: Molecular pairs of Z with decreasing interaction energies.

Figure S7: Hirshfeld surface fingerprint plots of the two polymorphs (E1 and E2) and Z-isomer, plotted with different atom···atom contacts.
**Figure S8 (a):** Modes of vibrations of the –NH$_2$ group calculated for the isolated molecule in the crystal geometry (E1).

**Figure S8 (b):** Vibrational frequencies plot for the isolated molecule in the crystal geometry (E1).
Figure S9 (a): Modes of vibrations of the –NH₂ group calculated for the molecular pair interacting via N-H···N and N-H···π in the crystal geometry (E1).

Figure S9 (b): Vibrational frequencies plot for the molecular pair in the crystal geometry (E1).
Figure S10 (a): Modes of vibrations of the –NH$_2$ group calculated for a model system where one N-H proton of the molecule is interacted with phenyl ring and the other N-H proton is interacted with the N atom of N-methylenemethanamine via N-H···π and N-H···N respectively (atomic coordinates were extracted from the E1).

Figure S10 (b): Vibrational frequencies plot for the model system.
**Figure S11**: Difference Fourier map through the N(1)=C(13)-N(2)H₂ plane for E₁, E₂ and Z. Positive counters are in solid blue and negative ones in broken red lines, at intervals of 0.05 eÅ⁻³.