Supporting information

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

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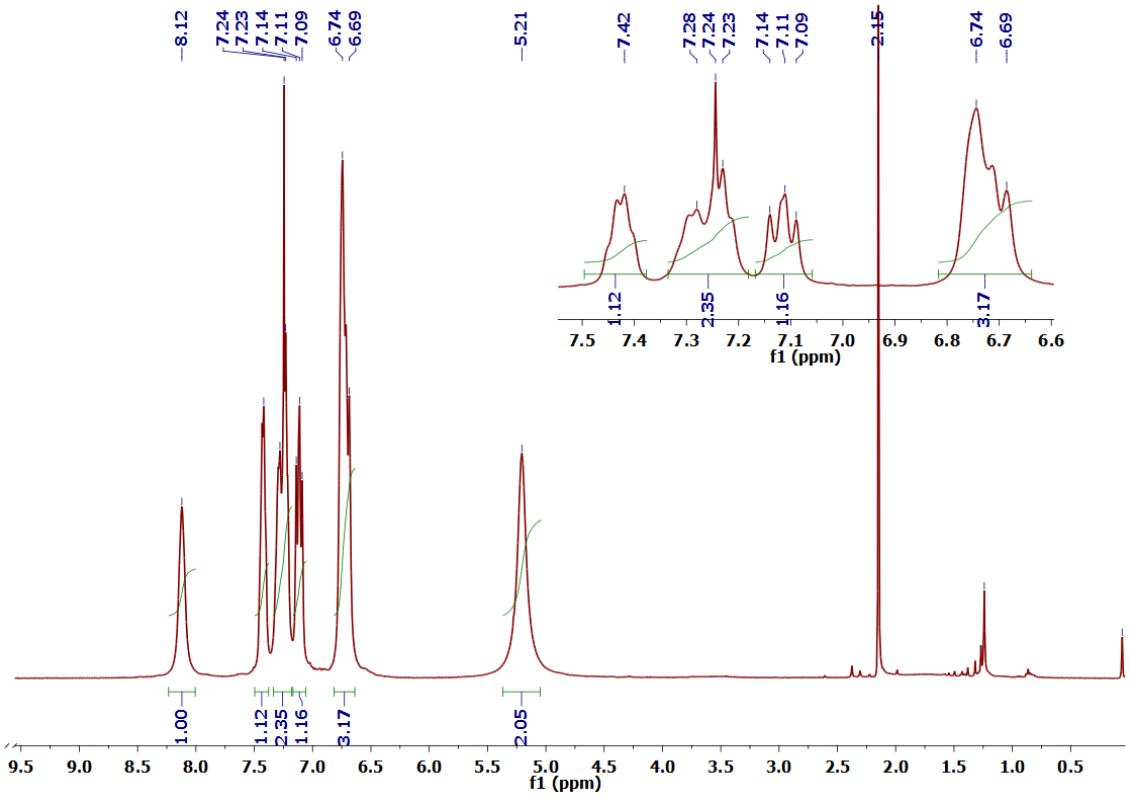

Figure S1: ^{1}H-NMR spectra of the synthesized compound in $CDCl_3$ (500 MHz).

FTIR (KBr pellet, cm^{-1}):- Bulk: 3323, 3175 (NH_2), 1667 (C=N), 1595 (C=C) in cm^{-1}, **E1:** 3434, 3287, 3138 (NH_2), 1643 (C=N), 1597 (C=C) in cm^{-1}, **E2:** 3320, 3165 (NH_2), 1666 (C=N), 1597 (C=C) in cm^{-1}, **Z:** 3305, 3169 (NH_2), 1665 (C=N), 1595 (C=C) in cm^{-1}. **^{1}H-NMR ($CDCl_3$, 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).

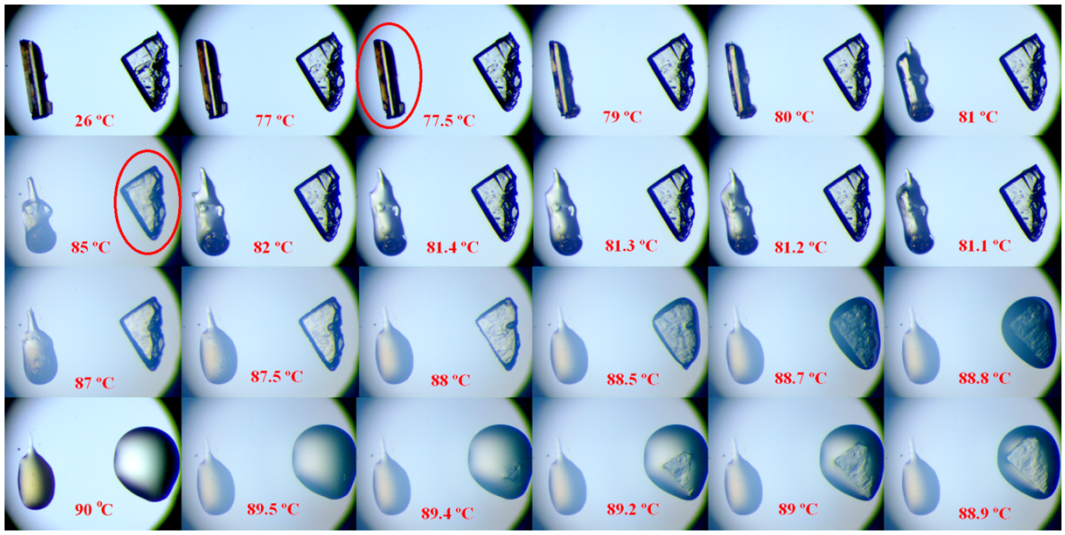

Figure S2: Hot-stage polarizing microscopic (HSM) pictures of the polymorphs (**E2** and **E1**) at different temperatures on heating from 25ºC to 90ºC @ 0.5ºC/min, distinguish both the forms.

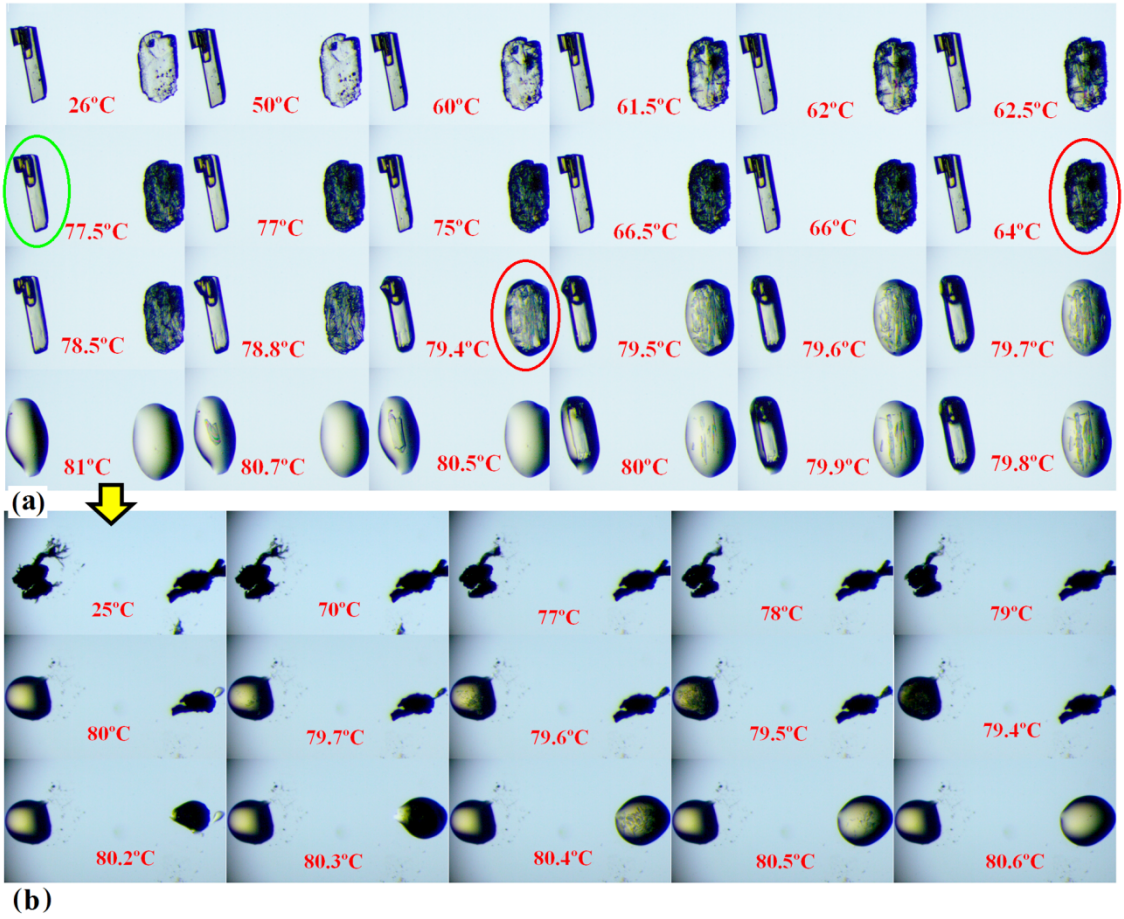

Figure S3: Hot-stage polarizing microscopic (HSM) pictures of the *E*/*Z*-isomers (**E2** and **Z**) at different temperatures on heating from 25ºC to 81ºC @ 0.5ºC/min, distinguish both the forms.

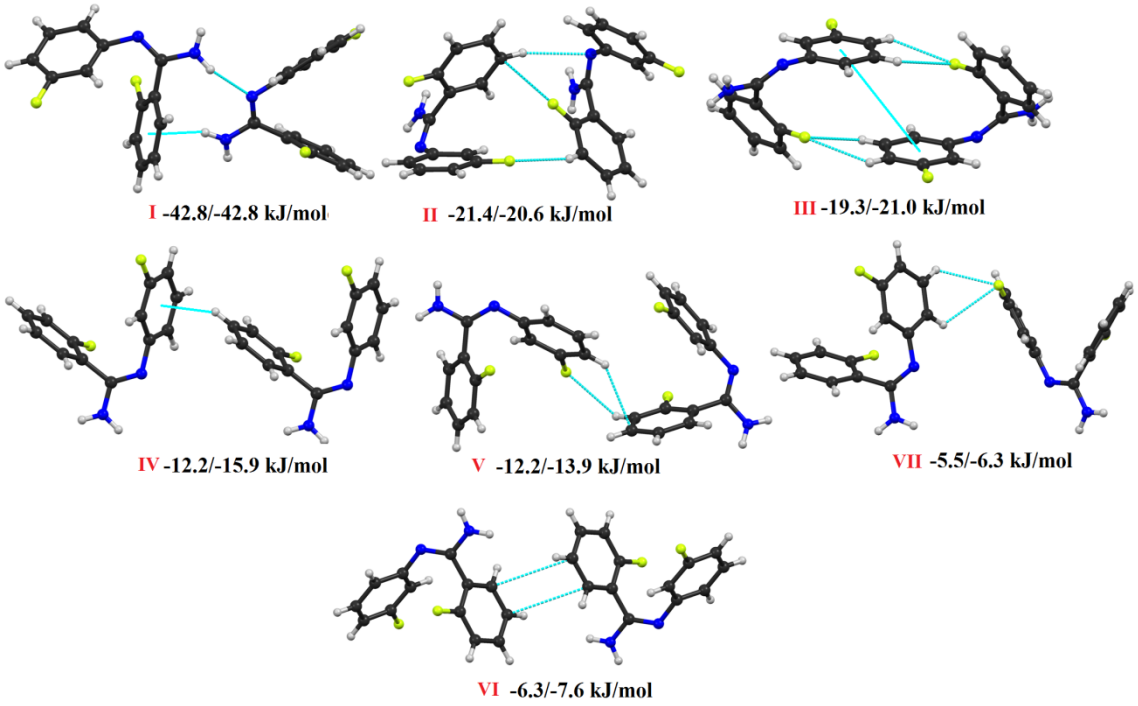

Figure S4: Molecular pairs of **E1** with decreasing interaction energies.

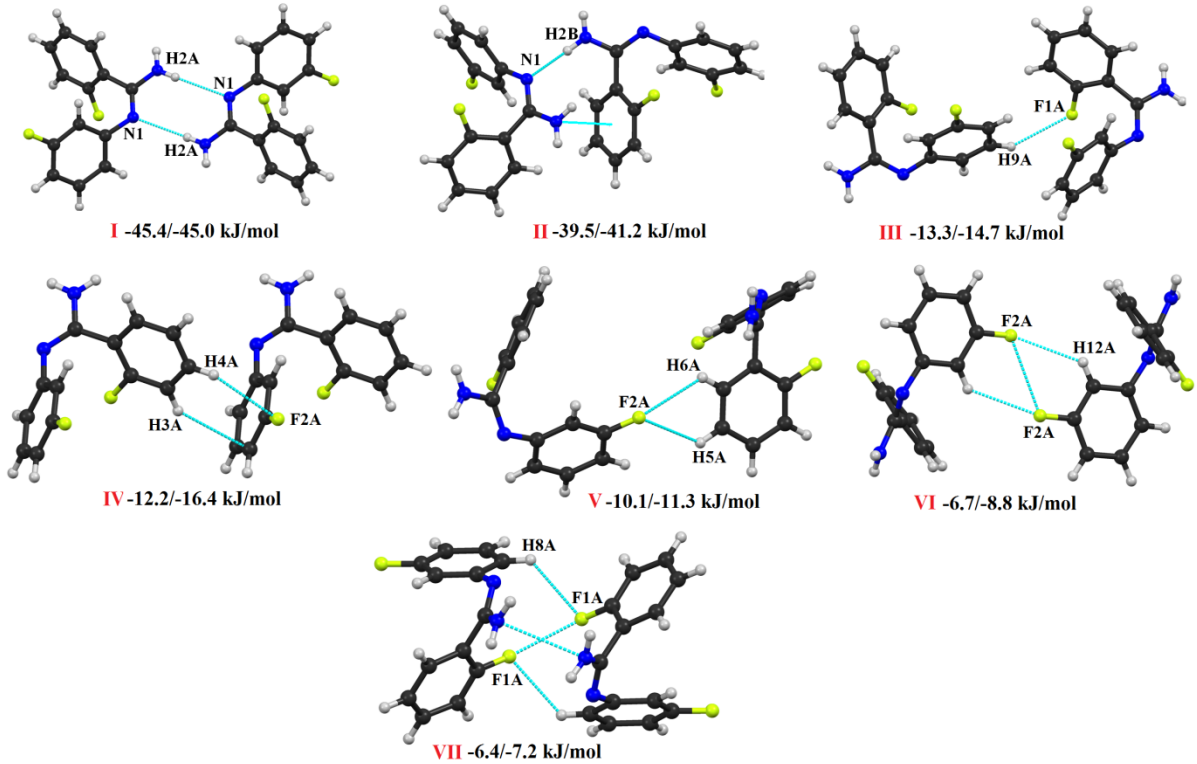

Figure S5: Molecular pairs of **E2** with decreasing interaction energies.

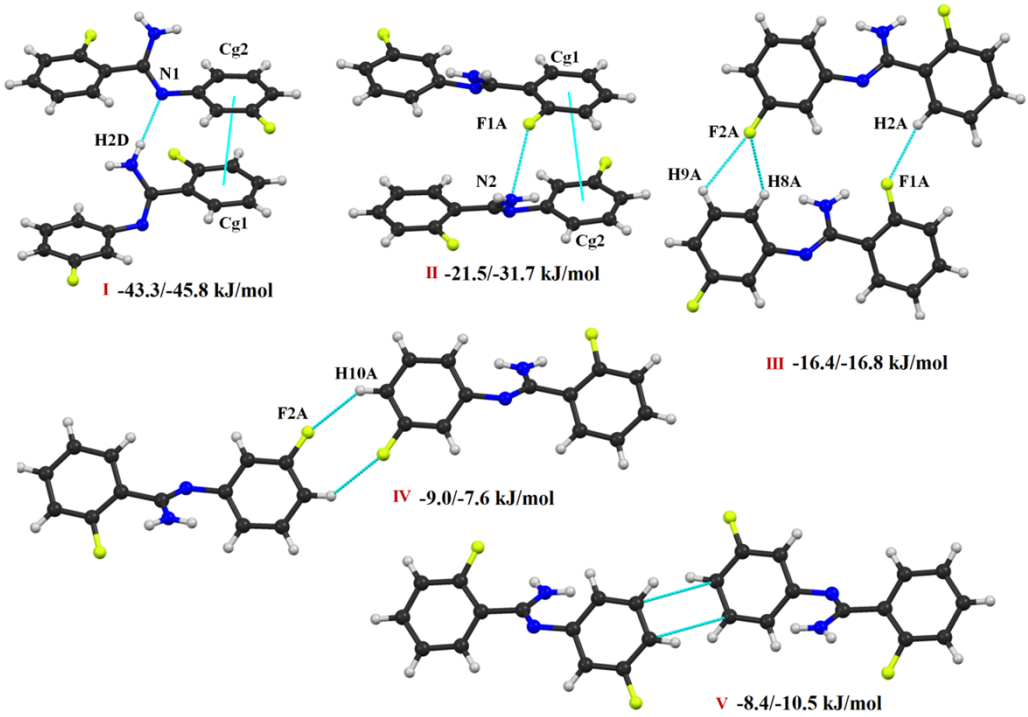

Figure S6: Molecular pairs of **Z** with decreasing interaction energies.

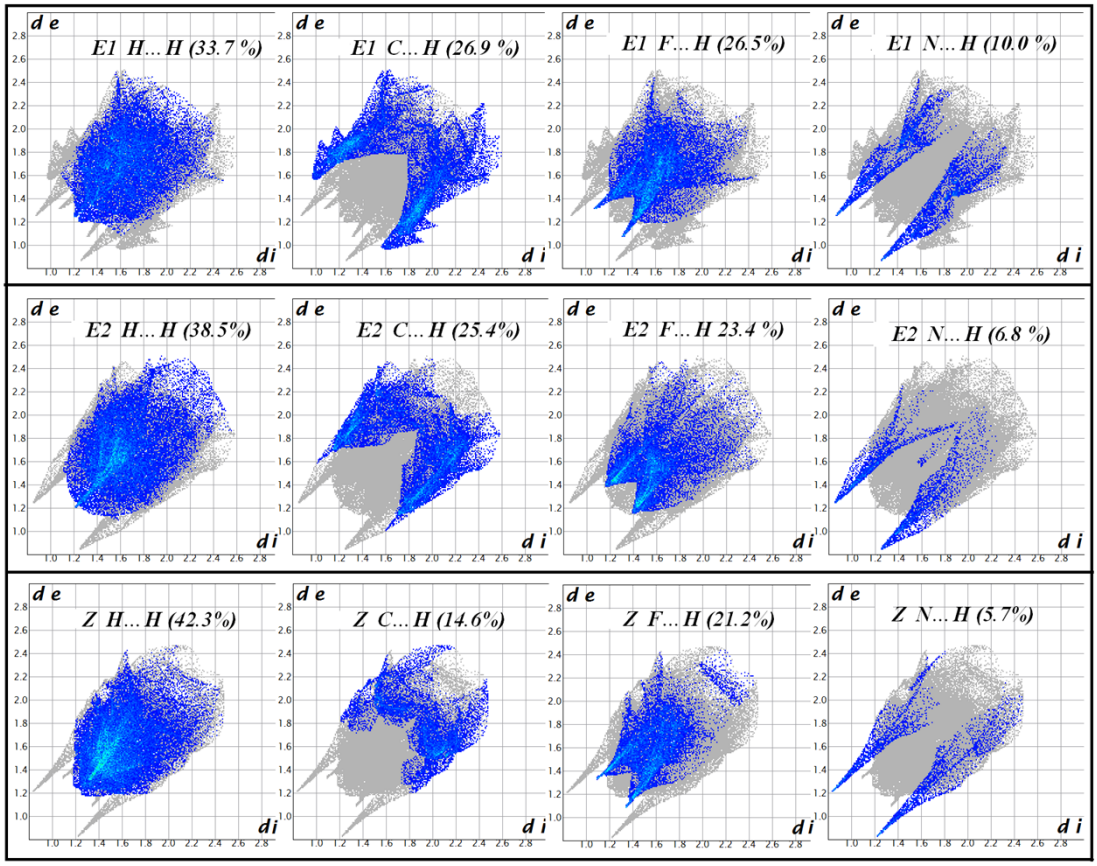

Figure S7: Hirshfeld surface fingerprint plots of the two polymorphs (**E1** and **E2**) and **Z**-isomer, plotted with different atom···atom contacts.

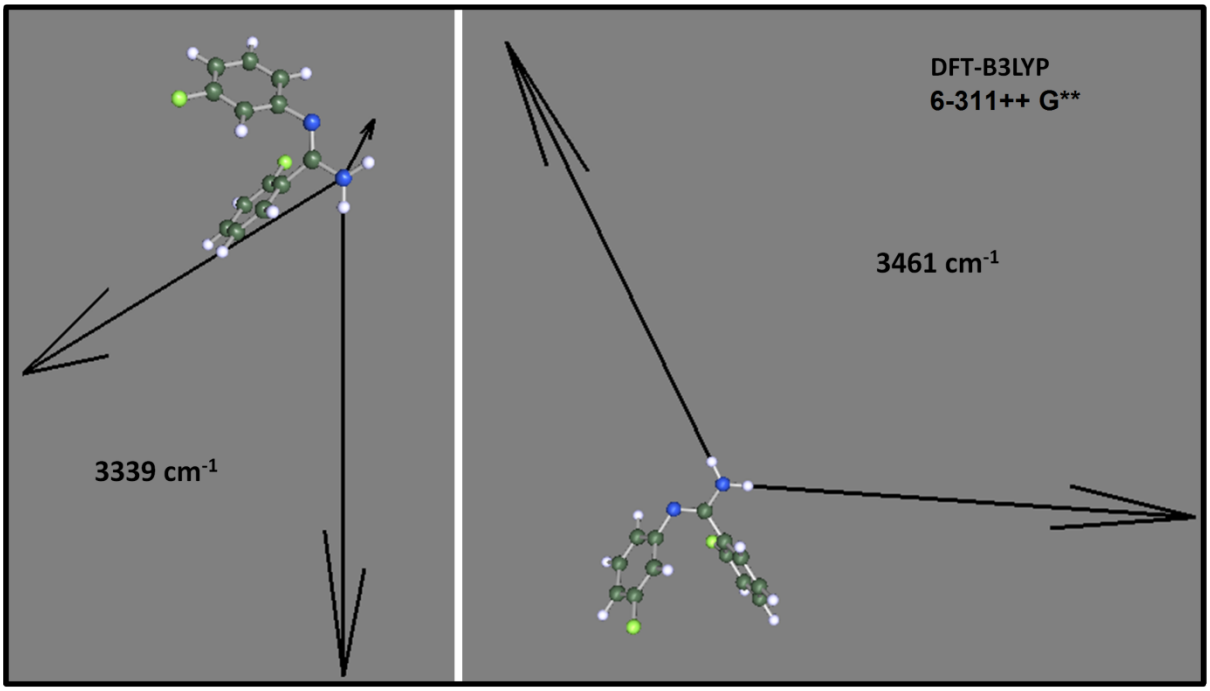

Figure S8 (a): Modes of vibrations of the $-NH_2$ group calculated for the isolated molecule in the crystal geometry (**E1**).

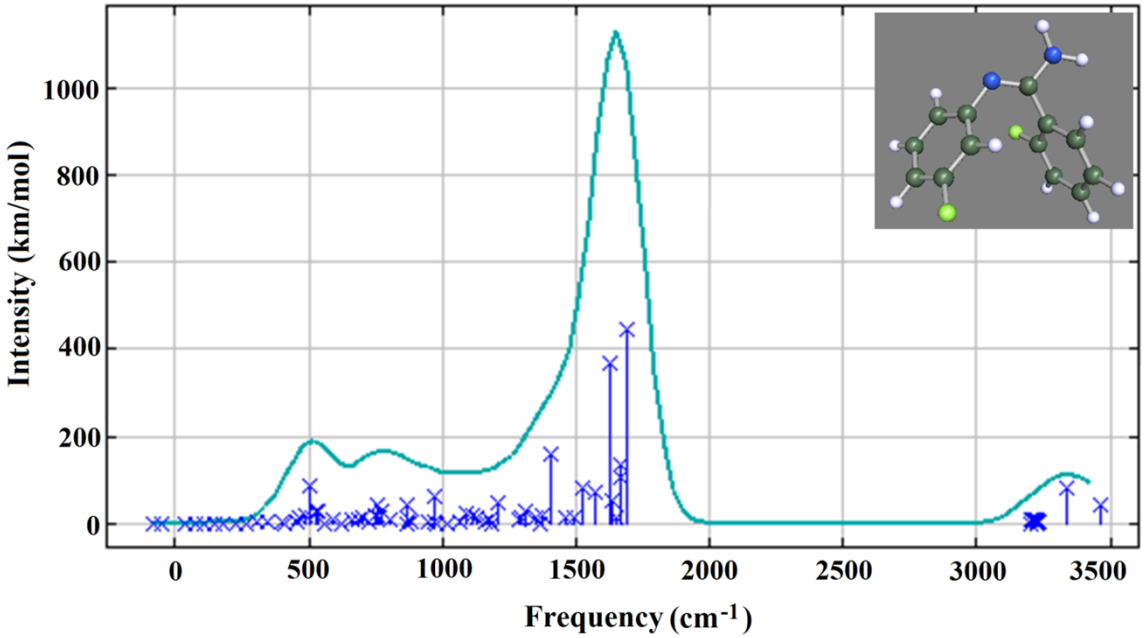

Figure S8 (b): Vibrational frequencies plot for the isolated molecule in the crystal geometry (**E1**).

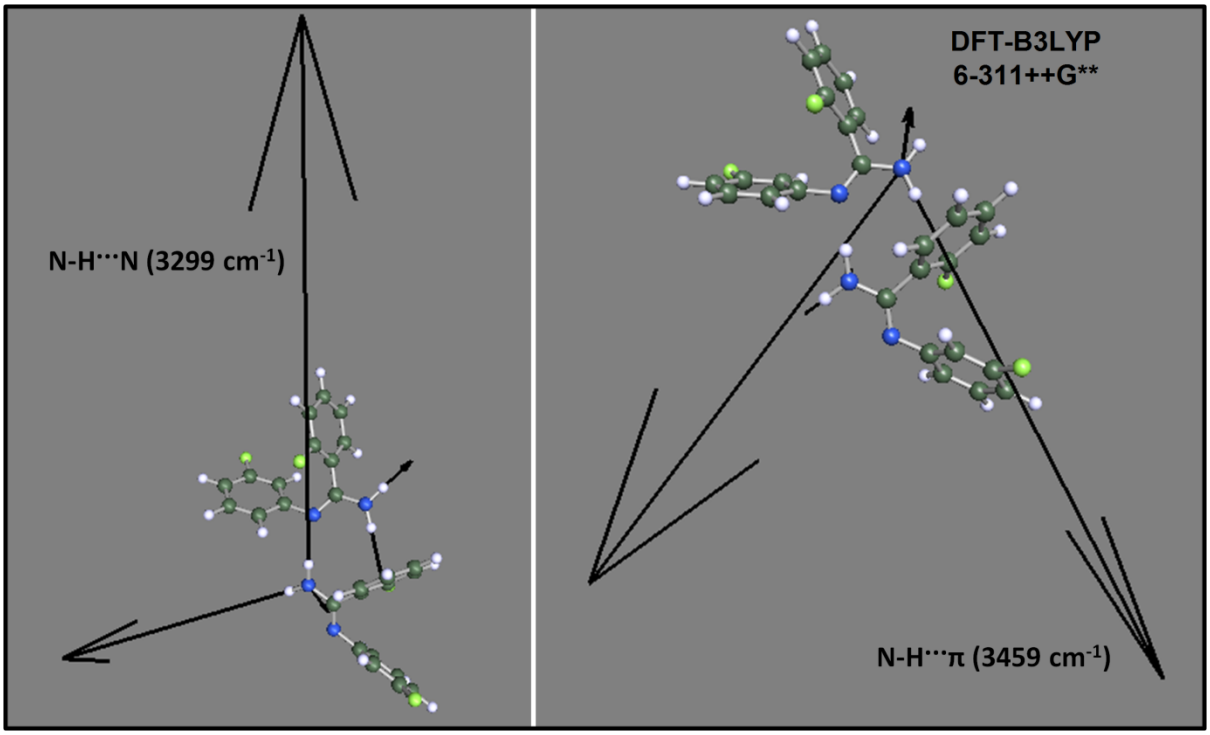

Figure S9 (a): Modes of vibrations of the $-NH_2$ group calculated for the molecular pair interacting *via* N-H···N and N-H···π in the crystal geometry (**E1**).

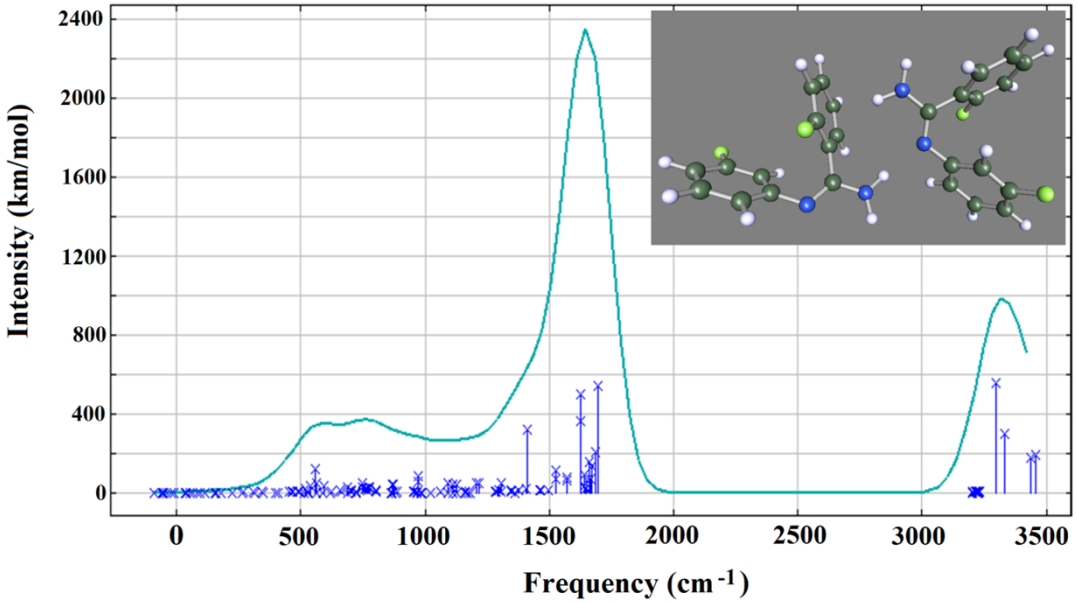

Figure S9 (b): Vibrational frequencies plot for the molecular pair in the crystal geometry (**E1**).

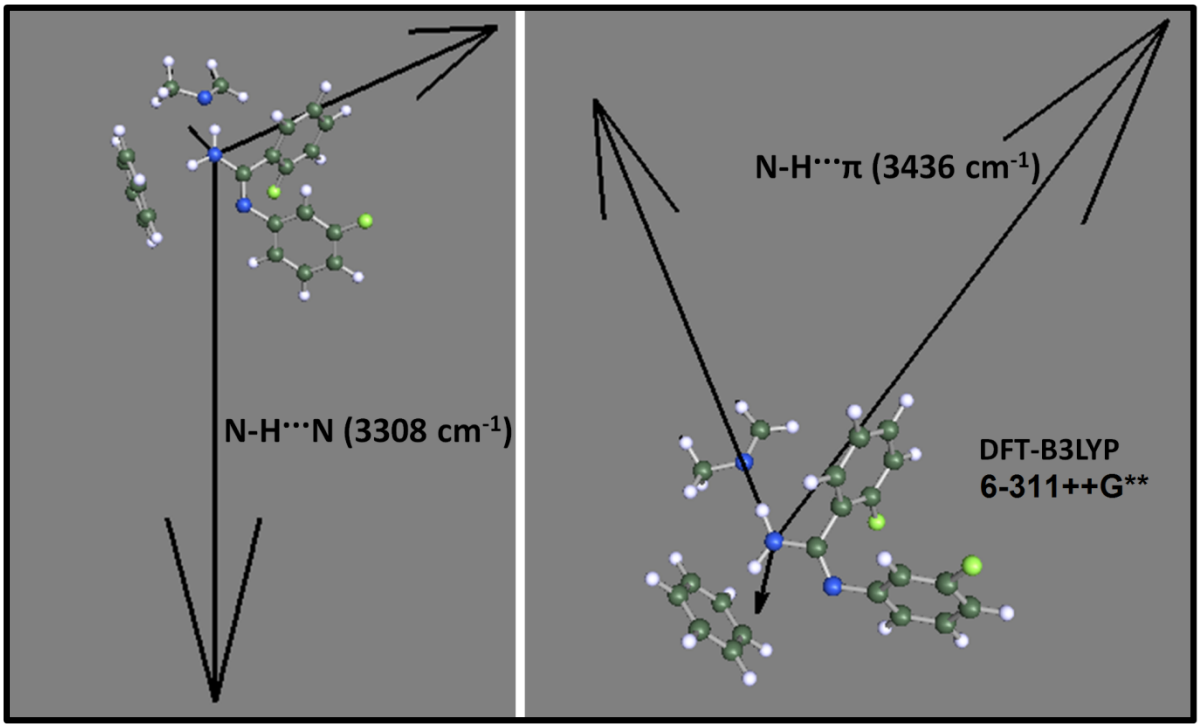

Figure S10 (a): Modes of vibrations of the $-NH_2$ group calculated for a model system where one N-H proton of the molecule is interacted with phenyl ring and the other N-H proton is interacted with the N atom of N-methylenemethanamine *via* N-H···π and N-H···N respectively (atomic coordinates were extracted from the **E1**).

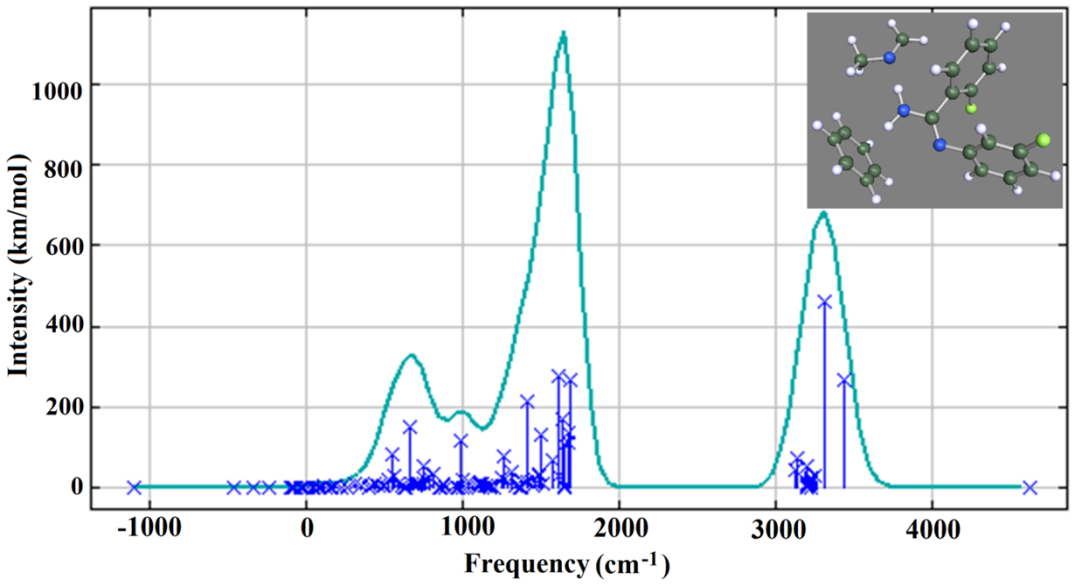

Figure S10 (b): Vibrational frequencies plot for the model system.

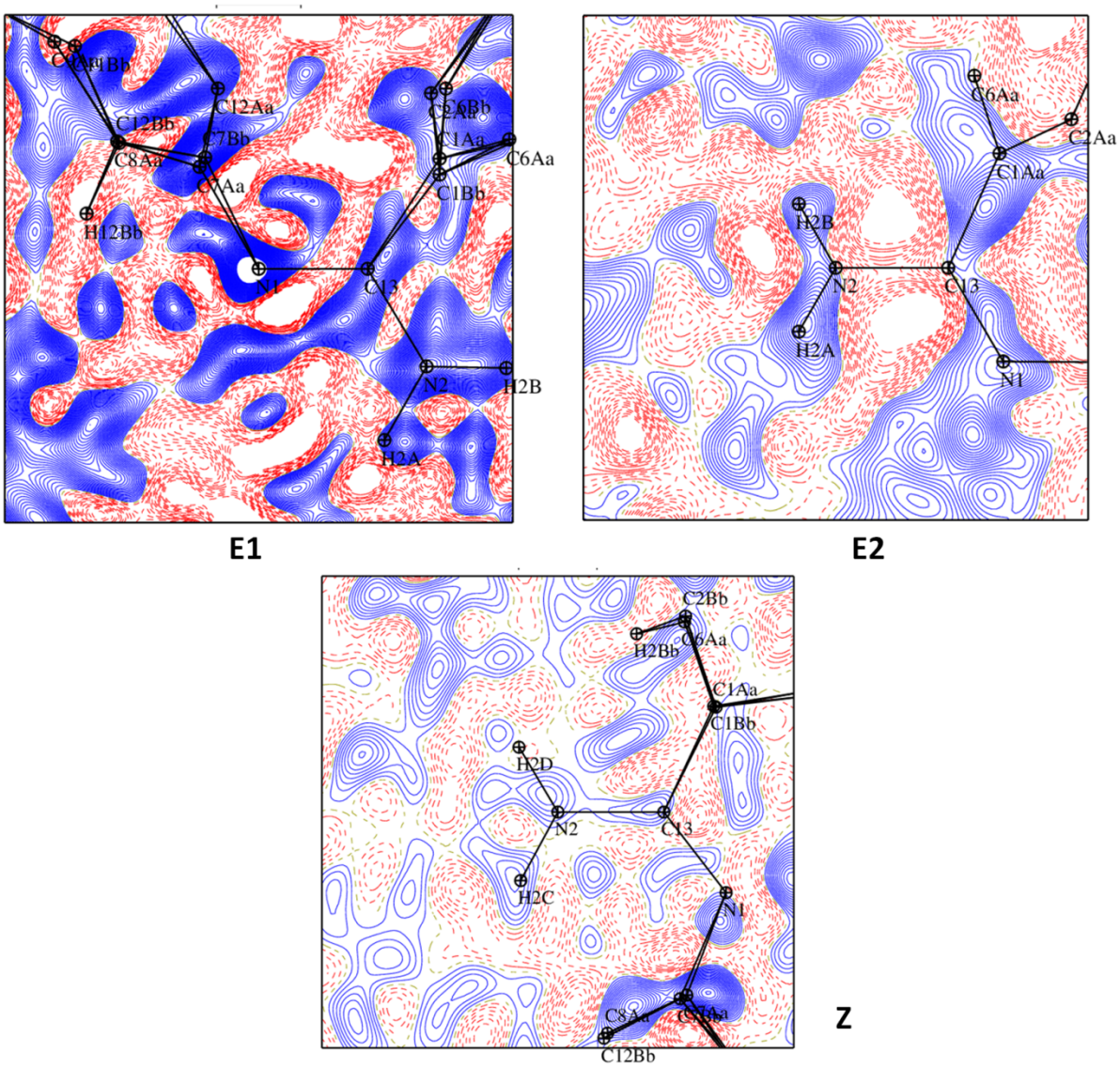

Figure S11: Difference Fourier map through the N(1)=C(13)-N(2)H_2 plane for **E1**, **E2** and **Z**. Positive counters are in solid blue and negative ones in broken red lines, at intervals of 0.05 eÅ^{-3}.