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# Electronic Supplementary Information

# **'Quasi-isostructural polymorphism' in molecular crystals: Inputs from interaction hierarchy and energy frameworks**

D. Dey<sup>a</sup>, S. P. Thomas<sup>b</sup>, M. A. Spackman<sup>b</sup> and D. Chopra<sup>a</sup>\*

# **Experimental:**



Figure S1. Optical Images of the two polymorphic forms I and II.

# Synthesis

A round bottom flask (10 mL in volume) containing stirrer bar and 0.70 gm of powdered anhydrous aluminium chloride (1.2 eq<sup>v</sup>.) was charged with 0.55 ml of 2-fluorobenzonitrile (1 eq<sup>v</sup>.) at room temperature (25°C) on an oil bath. A guard tube (filled up with anhydrous calcium carbonate) was attached on top of the flask. Then the mixture was heated up to 100°C until a homogeneous melt (aluminium chloride.2-fluorobenzonitrile complex) was formed. To this 0.45 ml (1eqv.) of 3-fluoroaniline was added at a time. The whole mixture was stirred at 120°C for 6 hours. Then the mixture was kept at room temperature until it cooled down. The resultant black solid was crushed and extracted with 20 ml aqueous NaOH (12%) solution and 20 ml dichloromethane (2-3 times) into a separating funnel. Then the organic layer was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The final product (yield: 70%) was purified by silica gel chromatography (**Scheme S1**) and characterized by <sup>1</sup>H-NMR spectroscopy (**Figure S2**).



Figure S2: <sup>1</sup>H-NMR spectra of the synthesized compound in CDCl<sub>3</sub> (400 MHz).

(*Z*)-2-fluoro-*N*'-phenylbenzamide: Yield = 65%; FTIR (KBr pellet, cm<sup>-1</sup>): 3449, 3296, 3164 (NH<sub>2</sub>), 1633 (C=N), 1596 (C=C) in cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.92 (s, 2H) 7.48 (d, *J* = 7.53 Hz, 3H), 7.12 (d, *J* = 28.12 Hz, 4H), 4.90 (s, 2H).

Sample code	Form I	Form II
Formula	$C_{13}H_{11}N_2F$	C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> F
Formula weight	214.24	214.2
Temperature/K	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Solvent system	Hexane, RT	Benzene, RT
CCDC number	982074	1016402
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1

a (Å)	10.0641(3)	10.9351(8)
<b>b</b> (Å)	11.0425(3)	11.8469(9)
<i>c</i> (Å)	12.1824(3)	15.2049(12)
α (°)	114.9240(10)	96.758(2)
β (°)	95.0550(10)	109.718(2)
<b>γ</b> (°)	111.4760(10)	113.790(2)
V(Å <sup>3</sup> )	1094.39(5)	1621.4(2)
Z	4	6
Density(g cm <sup>-3</sup> )	1.300	1.316
μ (mm <sup>-1</sup> )	0.090	0.091
F (000)	448	672
θ (min, max)	1.92, 25.00	2.11, 30.63
Treatement of hydrogens	Fixed	Fixed
h <sub>min, max</sub> , k <sub>min, max</sub> , l <sub>min, max</sub>	(-11, 11), (-13, 13), (-14, 14)	(-15, 15), (-16, 16), (-21, 21)
No. of ref.	16663	59699
No. of unique ref./ obs. Ref.	3848, 3579	9959, 7724
No. parameters	294	437
R_all, R_obs	0.0361, 0.0338	0.0710, 0.0510
wR2_all, wR2_obs	0.0828, 0.0813	0.1386, 0.1264
$\Delta \rho_{\min, \max} (e Å^{-3})$	-0.251, 0.237	-0.380, 0.548
G. o. F.	1.020	1.021

## Crystal growth and single-crystal X-ray Diffraction

Suitable single crystals appropriate for X-ray diffraction measurements were obtained through a solvent evaporation method. Synthesized compound was dissolved in polar/non-polar solvent (HPLC grade) and then allowed to stand at different temperature until the solvent had completely evaporated. From I was obtained from the slow evaporation of hexane at room temperature and II was crystallized from the slow evaporation of benzene at room temperature. The morphologies of the crystal were shown in **Figure S1**. In benzene, two kinds of morphologies were obtained but internally the crystal structure is the same (Form II).

Single-crystal X-ray diffraction data were collected using a Bruker APEX II diffractometer equipped with a CCD detector using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) in phi( $\phi$ ) and omega( $\omega$ ) scan. The data collection for form I and II was carried out at 100(2) K. The unit cell measurement, data collection, integration, scaling and absorption corrections for these forms were done using Bruker Apex II software [1]. The data collection was carried out giving an exposure time of 6 seconds per frame and at the crystal-to-detector distance is 60 mm. The intensity data were processed by using the Bruker SAINT [2] suite of programs. The crystal structures were solved by direct methods using SIR 92 [3] and refined by the full matrix least squares method using SHELXL97 [4] present in the program suite WinGX (version 1.80) [5]. Empirical absorption correction was applied using SADABS [6]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms bonded to C and N atom, were positioned geometrically and refined using a riding model with  $U_{iso}(H) = 1.2U_{eq}$  (C, N). The molecular connectivity was drawn using ORTEP32 [7] and the crystal packing diagrams were generated using Mercury 3.5.1 (CCDC) program [8]. Geometrical calculations were done using PARST [9] and PLATON [10]. The detailed crystallographic data and the structure refinement parameters were summarized in **Table S1**.

## **Crystallographic Modelling of Disorder**

The occupancies of the disordered fluorine atom (connected with the carbon atom in the *ortho* position of the phenyl ring on the aniline side) at two positions were refined by using the PART command in SHELXL97, namely F1A & F1B and F2A & F2B ('A' contains the higher occupancy for that atom). The anisotropic displacement parameter for these two sites was fixed using the EADP instruction.

#### **Molecular conformation**

*ORTEP* diagrams of the two polymorphs have been shown in **Figure 1**. Both the forms crystallized in the centrosymmetric space group *P*-1 with different number of symmetry-independent molecules in the asymmetric unit. The molecule consists of two phenyl ring: the 1<sup>st</sup> ring (no fluorine substitution) is connected with the  $sp^2$  hybridized carbon atom (attached with  $-NH_2$  group) of the C=N double bond and the 2<sup>nd</sup> ring (containing one fluorine atom in *ortho* position) is connected with the nitrogen atom N1 in opposite side (*anti*) of the C=N double bond. The molecule contains two strong N-H donors, a strong acceptor 'N' including a weak acceptor F connected with the  $sp^2$  hybridized carbon atom and weak aromatic C( $sp^2$ )-H donors. It can form strong as well as weak intermolecular interaction in the crystal packing using these donors and acceptors. In case of form I, the C-C-N-C torsion angles are -179.5(1) and 174.7(1) for the molecules (labelled as A and B respectively). But in II, the values are different: 177.2(1), 179.4(1) and 176.5(1) (for the molecules labelled as A, B and C respectively).

Form	Molecule	Torsion	Angle (°)
I	A	C1-C13-N1-C7A	-179.5(1)
	B	C14-C26-N3-C20	-174.7(1)
П	A	C1-C13-N1-C7	177.2(1)
	B	C14-C26-N3-C20A	-179.4(1)
	C	C27-C39-N5-C33	-176.5 (1)

**Table S2**. List of torsions of individual symmetry independent molecules present in the two polymorphic forms



Figure S3. Overlay diagrams between the symmetry independent molecules in (a) Form I and (b) Form II respectively.

### Thermal characterization

The melting points of the two forms I and II, including that of the bulk powder were measured with a Perkin-Elmer DSC (Differential Scanning Calorimeter) 6000 instrument under nitrogen gas atmosphere. Accurately weighted samples (2-3 mg) were prepared in a covered aluminium pan and the experiment was performed with respect to a vacuum covered aluminium pan. The sample was heated from 25°C to 96°C with a heating rate of 1°C/min and again cooled up to 25°C. Such two heating cooling cycles were performed for both the forms including bulk compound. For hot stage microscopy (HSM) analysis, a stereomicroscope equipped with a hot stage apparatus (Linkam LTS420) was used. Photographs were taken with a Leica EC3 camera connected with the microscope. Single crystals of I and II were placed on a glass slide and focussed under the microscope and then heated at 0.5°C/min.



**Figure S4**. Hot-stage microscopy (HSM) images of the polymorphs (**I** and **II**) at different temperatures on heating from 25°C to 93°C @ 0.5°C/min.

The thermal stabilities of the polymorphs were analyzed using differential scanning calorimetry (DSC) method for the bulk powder as well as the crystals of the two different forms (Figure 4). The bulk powder melted at 92.2°C ( $\Delta H = -97.31 \text{ J/g}$ ). During the cooling process, at the same cooling rate (1°C/min) it solidified at 47.12°C. In the 2<sup>nd</sup> heating cycle, the compound melted at the same temperature (92.2°C,  $\Delta H = -96.28 \text{ J/g}$ ) and solidified at 59.53°C. Both the forms (I and II) were observed to melt at similar temperatures, namely 91.45°C and 91.48°C respectively. Form I melts completely at 92.7°C (the enthalpy change is 103.18 J/g), while form II melts (the enthalpy change is 110.77 J/g) completely at 92.5°C in the 1<sup>st</sup> heating cycle. Although both the polymorphic forms melted at the same temperature, there is a significant difference in the solidification region between the Form I and Form II. From the DSC curves of the bulk compound and Form I, it is clear that the bulk compound corresponds to the Form I. The nature of the DSC curve of Form I in the solidification region (for both the cycles) is similar with the solidification of the first cooling cycle for the bulk compound, but not with the second cooling cycle for the bulk. The solidification nature of the second cooling cycle for the bulk is similar with the solidification for Form II (for both the cycles). For the solidification nature of the second cooling cycle of Form I, it is clear that Form I (lower Z' structure) has a tendency to solidify in Form II (higher Z' structure). To get more insights into the nature of these polymorphs, hot stage microscopy experiments were performed. Both the forms were taken on a glass slide under the microscope. The physical

location of crystals of Form I and Form II are shown by red arrow and green arrow (Figure S4). At a temperature of 92°C, both the forms started melting together. Form I completely melted at 92.8°C but the form II melted completely at 93.1°C.



**Figure S5.** FTIR spectra of the two polymorphs including the bulk compound in the solid state.

## Hirsfeld surface analysis

The Hirshfeld surface associated fingerprint plots were performed using CrystalExplorer 3.1 [11] suggests a facile way to obtain the information on trends in crystal packing. The derivation of the Hirshfeld surface and a representation of the corresponding 2D fingerprint-plots provides a convenient means of quantifying the interactions in crystal structures and polymorphs.

#### **Energy framework analysis**

Further, the values of the relevant interaction energies estimated from PIXEL calculations may be compared with the interaction energies obtained from a molecular wavefunction based method in *CrystalExplorer* [12]. This method has been shown to yield accurate values of interaction energies at relatively cheap computational cost. These energies are calculated based on B3LYP/6-31G (d,p) molecular wave functions with the single point geometries

from the crystal structure data. The method includes electrostatic, polarization, dispersion and exchange-repulsion terms. These terms are scaled to obtain accurate estimates of interaction energies benchmarked against B3LYP-D2/6-31G (d,p) counterpoise-corrected energies resulting in a mean absolute deviation (MAD) of around 1 kJ mol<sup>-1</sup> (and a MAD of 2.5 kJ mol<sup>-1</sup>against CCSD(T)/CBS model energies).

#### **Computational Procedures**

The dimer interaction energies associated with the presence of various non-covalent interactions present in the crystal packing were estimated using PIXEL (version 12.5.2014) [13-19] program. Gaussian 09 program [20] was used to generate the requird PIXEL input. The total lattice energy of the molecule is classified into the corresponding Coulombic, polarization, dispersion and repulsion energies. In addition to that, we have performed DFT + Disp/B97D (basis set: aug-cc-pVTZ) calculations using TURBOMOLE [21] to compare the interaction energies obtained from the PIXEL. Furthermore, the *ab initio* calculations for some selected dimers at the crystal geometry (with the hydrogen atoms moved to their neutral value) were performed at the MP2/6-311++G\*\* level using Gaussian 09. The formatted checkpoint file (fchk) was used as input file for AIMALL (version 13.05.06) [22] calculation. The electron density features at the bond critical points, which are computed, is as follows: (i) electron density ( $\rho_b$ ), (ii) Laplacian ( $\nabla^2 \rho_b$ ) and (iii) kinetic energy density ( $G_b$ ). E<sub>int</sub>= 0.429 G<sub>b</sub> (in au) [23].

### **Powder X-ray Diffraction**



Figure S6: Profile fitting of powder pattern of Bulk and Form I (calculated).



Figure S7: Profile fitting of powder pattern of Bulk, Form I (calculated) and Form II (calculated).



Figure S8: Profile fitting of powder patterns of Form I (experimental) and Form I (calculated).



Figure S9: Profile fitting of powder pattern of Form II (experimental) and Form II (calculated).

#### **XPac analysis**

XPac method [24-25] is a suitable method for the investigation of the extent of similarity between two crystal structures. In this program, the components of the two crystal structures to be compared are termed as supramolecular constructs (SC). Supramolecular construct implies geometrical similarity, meaning similarity of two configurations of points rather than similarity in terms of connectivity. Each  $\delta_a / \delta_p$  diagram contains a region with randomly distribute data points at high angles, which is associated with the non-matching structure fragments. X /  $\delta_d$  diagram reveals the extent of stretching in one structure compared to the other.





Figure S10. 2D Supramolecular constructs between two polymorphic forms (I and II) by XPac analysis.

**Table S3.** Interaction energies (in kcal/mol) of the molecular pairs and related intermolecular interactions in Form I ( $\mathbf{E}_{a} = \text{DFT} + \text{Disp/B97D}$  using aug-cc-pVTZ basis set;  $\mathbf{E}_{\text{CE}} = \text{energy}$  obtained from *Crystalexplorer*).

Motifs	Symmetry code	Distance	East	En	En	En	E <sub>T</sub>	E	Ecr	Possible	Geometry
litetiis	Symmetry coue	/(Å)	-LCoul	Pol	Disp	ыкер	-100	La	LCE	Interactions	(Å/ °)
I (AB)	-x+1, -y+1, -z	5.399	-9.4	-3.9	-9.0	11.5	-11.7	-10.8	-11.4	N2-H2B…N3	2.15, 159
										С2-Н2…N3	2.78, 134
II (AB)	-x+2, -y+1, -z	4.954	-9.2	-4.1	-10.0	11.7	-11.5	-11.3	-12.0	C15-H15…F1A	2.71, 164
										N4-H4B···N1	2.08, 150
										C5-H5…F2	2.68, 119
III (AB)	x, y, z	4.833	-4.0	-1.6	-9.3	6.1	-8.9	-9.6	-9.0	N4-H4A…F1A	2.19, 144
IV (BB)	-x+1, -y+1, -z	5.253	-3.8	-2.0	-10.3	9.2	-6.9	-7.7	-7.2	C25-H25…N3	2.79, 163
										C24-H24…Cg1′	2.83, 136
V (AA)	-x+2, -y+2, -z	6.061	-1.1	-0.3	-4.8	1.3	-4.9	-5.6	-4.5	C11-	2.83, 136
										Η11Α····C6(π)	
VI (BB)	-x+1, -y, -z	7.187	-1.7	-1.1	-8.5	6.7	-4.6	-6.8	-6.0	Cg1'···Cg1'	3.707(3)
										C17-H17····F2	2.54, 143
VII (AB)	x-1, y-1, z	7.374	-1.4	-0.9	-4.7	3.4	-3.6	-3.8	-3.8	C18-H18…N1	2.60, 164
VIII (AA)	-x+2, -y+1, -z	5.068	-1.0	-0.7	-5.1	2.0	-2.8	-3.9	-3.3	F1A…Cg1′	3.134(3)
IX (BB)	-x+1, -y, -z-1	8.453	-1.4	-0.4	-1.9	1.5	-2.3	-2.2	-2.2	C22-H22…F2	2.46, 148
X (AA)	-x+2, -y+1, -z-1	11.415	-0.8	-0.2	-2.2	1.1	-2.1	-2.1	-1.9	С9А-С10А(π)	3.806(3)
										····C9A-C10A(π)	
XI (AB)	x-1, y-1, z-1	9.637	-0.8	-0.4	-2.5	1.9	-1.9	-2.2	-2.0	C5-H5…F2	2.73, 150
XII (AA)	-x+2, -y+2, -z+1	10.750	-0.2	-0.2	-2.5	1.1	-1.8	-2.4	-2.0	С4-С3(π) …С4-	3.670(3)
										C3(π)	



Figure S11: Molecular pairs of form I in order of decreasing interaction energy.

**Table S4.** Interaction energies (in kcal/mol) of the molecular pairs and related intermolecular interactions in Form II ( $\mathbf{E}_{\mathbf{a}} = \text{DFT} + \text{Disp/B97D}$  using aug-cc-pVTZ basis set;  $\mathbf{E}_{\text{CE}} = \text{energy}$  obtained from *Crystalexplorer*).

Motifs	Symmetry	Distance	E <sub>Coul</sub>	E <sub>Pol</sub>	E <sub>Disp</sub>	E <sub>Rep</sub>	E <sub>Tot</sub>	Ea	E <sub>CE</sub>	Possible	Geometry
	code	(Å)								Interactions	(Å/ °)
I (AB)	x, y, z	5.112	-9.2	-4.0	-8.9	11.1	-10.9	-11.2	-11.5	N2-H2B…N3	2.07, 153
II (BC)	-x+1, -y+1, - z+1	5.220	-8.3	-3.6	-8.9	10.9	-9.9	-9.6	-10.3	N4-H4B…N5	2.11, 146
III (AC)	-x+1, -y+1, -	5.152	-6.3	-3.0	-8.5	9.5	-8.5	-9.0	-9.3	N6-H6B…N1	2.26, 122
	z+2									N6-H6A…π(C12)	2.50, 127
										$\pi(C37) \cdots \pi(C10)$	3.724(2)
IV (CC)	-x+2, -y+1, -	5.134	-3.2	-1.5	-8.9	5.7	-7.9	-8.9	-7.8	С28-Н28…π(С34-	2.67, 155
	z+2									C35)	
V (AB)	-x, -y+1, -z+1	5.102	-3.1	-1.4	-8.2	5.0	-7.7/	-8.0	-7.5	N2-H2A…F2A	2.22, 134
										$\pi(C22A)\cdots\pi(C10)$	3.630(2)
VI (AC)	x+1, y, z	5.321	-3.2	-1.5	-9.5	7.3	-6.9/	-7.8	-7.0	C34-H34…N1	2.80, 147
										C12-H12…N5	2.81, 174
										C35-H35…Cg1	3.07, 141
										С11-Н11…π(С28-	2.81, 141
										C29)	

VII	x, y, z	6.774	-1.5	-1.0	-8.9	6.2	-5.3	-7.2	-6.7	C4-H4…F3	2.63, 129
(AC)										C30-H30…F1	2.53, 117
										Cg1···Cg1″	3.797(2)
VIII	-x+1, -y+1, -	6.253	-0.9	-0.2	-4.3	1.4	-4.2	-4.8	-3.7	C24A-	3.01, 146
(BB)	z+1									H24A…π(C15)	
IX (AA)	-x+1, -y+1, -	7.212	-1.1	-0.6	-3.9	1.8	-3.7	-4.2	-3.5	Н6…Н6	2.23
	z+2										
X (BB)	-x, -y+1, -z+1	4.912	0.2	-0.6	-5.4	2.1	-3.7	-5.2	-4.4	C21A-F2A…Cg1′	3.211
XI (BC)	x, y, z	7.779	-1.5	-1.1	-5.1	4.3	-3.4	-3.4	-3.1	C31-H31…N3	2.62, 160
										Н15…Н30	1.98
XII	x, y-1, z	8.448	-1.4	-0.4	-1.9	1.4	-2.3	-2.3	-2.2	С9-Н9…F3	2.43, 145
(AC)										C37-H37…F1	2.53, 150
XIII	x, y+1, z	9.178	-1.1	-0.6	-3.1	2.8	-2.0	-2.7	-2.3	C16-H16…F3	2.70, 144
(BC)	-										



Figure S12: Molecular pairs of form II in order of decreasing interaction energy





Figure S13. Colour coding based on the distance from a central molecule (which is coloured using elemental colour code) in form I.

Symop	Dist.	Wavefunc.	Coul.	Polariz.	Disp.	Repul.	Total
-	4.83	B3LYP/6-31G(d,p)	-15.5	- <mark>3.</mark> 6	-42.5	29.2	-37.8
-	7.37	B3LYP/6-31G(d,p)	-5.4	-1.8	-18.1	13.7	-14.2
-	5.40	B3LYP/6-31G(d,p)	-37.1	- <mark>8.</mark> 7	-35.1	46.8	-47.8
-x, -y, -z	8.45	B3LYP/6-31G(d,p)	-5.1	-0.9	-9.2	7.6	-9.3
-x, -y, -z	7.19	B3LYP/6-31G(d,p)	-6.6	-1.9	-40.9	29.8	-25.2
x, y, z	12.18	B3LYP/6-31G(d,p)	-0.7	-0.3	-7.9	5.1	-4.5
-	10.57	B3LYP/6-31G(d,p)	0.3	-0.1	-0.8	0.0	-0.4
-	9.64	B3LYP/6-31G(d,p)	-3.2	-0.5	-10.8	8.1	-8.2
-x, -y, -z	5.25	B3LYP/6-31G(d,p)	-14.2	-2.5	-42.8	38.4	-30.2
-x, -y, -z	12.68	B3LYP/6-31G(d,p)	-0.5	-0.2	-6.5	3.3	-4.2
2	11.72	B3LYP/6-31G(d,p)	-0.0	-0.1	-2.6	0.1	-2.2
-	14.03	B3LYP/6-31G(d,p)	0.1	-0.0	-0.5	0.0	-0.4
-	4.95	B3LYP/6-31G(d,p)	-36.4	- <mark>9.3</mark>	-40.0	48.8	- <mark>50.4</mark>
-	12.11	B3LYP/6-31G(d,p)	0.1	-0.1	-3.8	0.8	-2.7
-	13.84	B3LYP/6-31G(d,p)	0.2	-0.1	-1.1	0.0	-0.7
-	9.96	B3LYP/6-31G(d,p)	0.3	-0.0	-1.0	0.0	-0.5
-x, -y, -z	8.37	B3LYP/6-31G(d,p)	2.6	-0.3	-2.0	0.0	0.8
-x, -y, -z	8.80	B3LYP/6-31G(d,p)	0.7	-0.2	-1.5	0.0	-0.6
x, y, z	12.18	B3LYP/6-31G(d,p)	-2.1	-0.3	-10.9	9.2	-6.2
-x, -y, -z	5.07	B3LYP/6-31G(d,p)	4.0	-2.3	-27.1	10.7	-14.1
-x, -y, -z	6.06	B3LYP/6-31G(d,p)	-4.4	-0.4	-21.0	6.6	-18.7
-x, -y, -z	10.75	B3LYP/6-31G(d,p)	-0.5	-0.4	-12.6	5.8	-8.0
-x, -y, -z	11.41	B3LYP/6-31G(d,p)	-3.0	-0.3	-8.8	5.0	-7.8
-x, -y, -z	12.78	B3LYP/6-31G(d,p)	-0.5	-0.0	-0.6	0.0	-1.1

Table S5. Molecular pairs and the stabilization energies (kJ/mole) obtained from energy framework calculation for Form I.

> Scale Factors for Benchmarked Energy Models See Spackman(2014)

Scale Factor Key:

Ke = electrostatic energy Kp = polarization energy Kd = dispersion energy Kr = repulsion energy

Energy Model	Ke	Кр	Kd	Kr
HF/3-21G	0.882	0.593	0.852	0.681
MP2/6-31G(d,p)	1.027	0.722	0.842	0.605
B3LYP/6-31G(d,p)	1.063	0.756	0.843	0.595





**Figure S14.** Colour coding based on the distance from a central molecule (which is coloured using elemental colour code) in form II.

**Table S6**. Molecular pairs and the stabilization energies (kJ/mole) obtained from energy framework calculation for Form **II**.

 					2.2		
Symop	Dist.	Wavefunc.	Coul.	Polariz.	Disp.	Repul.	Total
-x, -y, -z	11.52	B3LYP/6-31G(d,p)	-0.6	-0.2	-2.5	0.0	-2.8
-x, -y, -z	4.91	B3LYP/6-31G(d,p)	0.7	-1.9	-28.8	11.2	-18.3
-	10.41	B3LYP/6-31G(d,p)	0.1	-0.1	-0.9	0.0	-0.6
-	11.12	B3LYP/6-31G(d,p)	-0.9	-0.3	-7.5	3.9	-5.1
-	5.10	B3LYP/6-31G(d,p)	-12.1	-3.0	-36.4	23.8	-31.6
4	11.52	B3LYP/6-31G(d,p)	-2.1	-0.3	-9.6	5.9	-7.1
-	8.59	B3LYP/6-31G(d,p)	2.2	-0.2	-1.5	0.0	0.9
-	5.22	B3LYP/6-31G(d,p)	-32.9	-8.5	-34.3	45.6	-43.2
x, y, z	11.85	B3LYP/6-31G(d,p)	-2.2	-0.4	-9.4	9.0	-5.2
-x, -y, -z	6.25	B3LYP/6-31G(d,p)	-3.4	-0.3	-18.7	6.9	-15.5
-x, -y, -z	10.33	B3LYP/6-31G(d,p)	0.6	-0.3	-11.1	2.7	-7.4
-	9.18	B3LYP/6-31G(d,p)	-4.5	-0.7	-13.5	11.5	-9.8
-	7.78	B3LYP/6-31G(d,p)	-5.6	-1.8	-18.4	16.6	-13.0
-	5.11	B3LYP/6-31G(d,p)	-36.6	-9.3	-35.1	46.0	-48.1
-	12.83	B3LYP/6-31G(d,p)	0.0	-0.2	-4.4	0.9	-3.3
x, y, z	11.85	B3LYP/6-31G(d,p)	-1.1	-0.3	-9.3	5.6	-5.9
-	8.45	B3LYP/6-31G(d,p)	-5.2	-0.8	-9.1	7.3	-9.4
-	12.58	B3LYP/6-31G(d,p)	-0.6	-0.2	-7.2	4.3	-4.3
-	5.15	B3LYP/6-31G(d,p)	-24.6	-7.1	-36.4	38.7	-39.2
-	12.79	B3LYP/6-31G(d,p)	0.0	-0.0	-0.6	0.0	-0.4
-x, -y, -z	11.68	B3LYP/6-31G(d,p)	-0.6	-0.0	-0.6	0.0	-1.2
2	6.77	B3LYP/6-31G(d,p)	-6.0	-2.3	-43.3	27.8	-28.1
-	5.32	B3LYP/6-31G(d,p)	-12.0	-2.2	-39.5	30.4	-29.6
-x, -y, -z	5.13	B3LYP/6-31G(d,p)	-13.0	-3.0	-37.7	25.5	-32.7
-	13.05	B3LYP/6-31G(d,p)	0.1	-0.1	-2.3	0.5	-1.7
-x, -y, -z	12.37	B3LYP/6-31G(d.p)	-0.4	-0.0	-2.1	0.1	-2.2
-x, -y, -z	13.61	B3LYP/6-31G(d.p)	0.4	-0.0	-0.6	0.0	-0.1
-x, -y, -z	8,95	B3LYP/6-31G(d.p)	1.6	-0,2	-1.3	0.0	0.4
x. v. z	11.85	B3LYP/6-31G(d,p)	-0.7	-0.2	-7.6	3.8	-5.1
-XV7	7.21	B3LYP/6-31G(d p)	-4.8	-1.2	-15.5	7.2	-14.8
-XV7	8.99	B3LYP/6-31G(d,p)	-1.8	-0.7	-12.2	5.2	-9.6
A, -y, -2	0.39	05c11/0-510(u,p)	-1.0	-0.7	-12.2	5.2	-5.0



Figure S15. Packing network of Form I (olive colour: IB) below the *bc* plane showing the two types of supramolecular motifs:  $R_2^2(8)$  associated with C-H<sup>...</sup>N weak interaction (highlighted in yellow) and C-H<sup>...</sup>F weak intermolecular interaction (highlighted in skyblue), alongwith C-H<sup>...</sup> $\pi$  and  $\pi$ <sup>... $\pi$ </sup> intermolecular interactions.



**Figure S16.** Formation of  $\mathbf{R}_2^2(\mathbf{8})$  motifs utilizing C-H…N and C-H…F intermolecular interaction respectively associated with C-H… $\pi$ ,  $\pi$ … $\pi$  and C-H…F interactions down the *ab* plane between the symmetry-independent molecules **A** (olive colour) and **C** (red colour).



Figure S17: Packing overlay between form I (only IB is involved) and form II (IIA and IIC are involved).



Scheme S2: Some common motifs present in both the forms I and II.



**Figure S18**. Comparison between the crystal packing of the two polymorphic forms (I and II). Red, olive and purple colour codes indicate the different symmetry independent molecules maintained in the crystal packing.



**Figure S19**: Relative contribution of atom atom contacts in the crystal packing for the two polymorphic forms.

### Quantum Theory of Atoms in Molecules (QTAIM)

In order to get quantitative insights into the nature of strong as well as weak intermolecular interactions for some selected molecular pairs, we have performed the topological analysis using QTAIM [26-28] approaches using the program AIMALL. It is of interest to evaluate whether the presence of weak intermolecular contacts involving the N-H bond with weak acceptors, namely –F and the aromatic rings can be deemed to be a "hydrogen bond" in accordance with the rules of IUPAC [26]. In **Figure S20**, we have shown the molecular graphs indicating the bond critical points along the bond path between two interacting

molecules in the crystal. Table S7 lists all the topological parameters obtained for the strong N-H···N hydrogen bond and weak N-H··· $\pi$  intermolecular interactions.



**Figure S20.** Molecular graphs for some selected molecular pairs (Form I and Form II) associated with N-H<sup>...</sup>N and N-H<sup>...</sup>F intermolecular interactions indicating the intra- and intermolecular bond critical points (BCPs) as brown closed circles.

Table S7: Topological parameters at the BCP's of some selected intermolecular	· interactions.
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Motifs	Interactions	d(Å)	Rii(Å)	$\rho_{\rm BCP}(e/Å^3)$	$\nabla^2 \rho_{PCP}$ (e/Å <sup>5</sup> )	$V_{\rm b}$ (a.u.)	$G_{\rm b}$ (a.u.)	D.E <sup>G</sup>
			3( )	F Der (			- 6 (	(kcal/mol)
II	N2-H2B…N3	2.15	2.17	0.133	1.481	-0.012243	0.013766	3.70
III	N4-H4B…N1	2.08	2.11	0.152	1.718	-0.015067	0.016448	4.42
_	H2····H2B (intra)	1.97	2.37	0.097	1.441	-0.059783	0.012366	3.32
I III	N4-H4A…F1A	2.18	2.22	0.080	1.173	-0.009114	0.010638	2.86
ΠI	N2-H2B····N3	2.07	2.09	0.155	1.761	-0.015466	0.016816	4.52
ПП	N4-H4B····N5	2.11	2.14	0.145	1.636	-0.014036	0.015501	4.17
пп	N4-H6B…N1	2.26	2.31	0.144	1.370	-0.010818	0.012513	3.36
_	N6-H6A…π(C12)	2.50	2.57	0.066	0.793	-0.005625	0.006925	1.86

II_IX	H6····H6 (inter)	2.23	2.29	0.045	0.524	-0.003780	0.004612	1.24
	H2…H2B (intra)	1.99	2.42	0.092	1.389	-0.009293	0.011852	3.19

#### **Cambridge Structural Database analysis**

We have searched the Cambridge Structural Database (CSD; version 5.36, Nov 2014) for the compounds known to be polymorphs with  $Z' \ge 2$ . The CSD searched results is given in the in **Search S1-S4**. We have performed this analysis taking different constraints (R factor  $\le 0.1$ , not disordered, not polymeric, no errors, no ions, no powder structures and only organics) along with limited number of elements (mainly C, H, N, O and F). In **Search S1**, there was no restriction of other elements with C, H, N and O atoms and total number of hits is 652. But in **Search S2**, the other elements are not allowed along with C, H, N and O atoms. Subsequently, the number of hits was decreased to 387. On further addition of one more element (fluorine) in the element as constraints, a total of 50 hits in **Search S3** are obtained. The sets of polymorphs were selected in a way so that at least one structure has  $Z' \ge 2$ ; 35 such sets were obtained from 50 hits. **Table S7** lists all these unique 35 sets of polymorphs with space group, Z' and Z along with their refcodes.

Search:	Search S1				
Date/Time done:	Tue Jun 16 09:30:14 20	15	No. of molecules in the asymmetric unit $(7) > -2$		
Database(s):	CSD version 5.36 upda CSD version 5.36 (Nove CSD version 5.36 (Nove	No. of chemical unit in entry $-1$			
Restriction Info:	No refcode restrictions	applied	-1		
Filters:	R factor <= 0.1 Not dis No errors Not po		Text: polymorph		
	No ions Only Organics	No powder structures	Elements: C H N O		
Percentage Completed:	100%	Al	llow other elements : Yes		
Number of Hits:	652				
Search:	Search S2				
Date/Time done:	Tue Jun 16 09:30:14 20	15	No. of molecules in the asymmetric unit $(7) > -2$		
Database(s):	CSD version 5.36 upda	tes (Nov 2014)	asymmetric unit $(2) > 2$		
	CSD version 5.36 (Nove CSD version 5.36 (Nove	ember 2014) ember 2014)	No. of chemical unit in entry		
Restriction Info:	No refcode restrictions	applied			
Filters:	R factor <= 0.1 No errors	Not disordered Not polymeric	Text: polymorph		
	No ions Only Organics	No powder structures	Elements: C H N O		
Percentage Completed:	100%	Al	low other elements : <b>No</b>		
Number of Hits:	387				

Search:	Search S3					
Date/Time done:	Tue Jun 16 09:30:14 20	)15	No. of molecules in the			
Database(s):	CSD version 5.36 upda CSD version 5.36 (Nove CSD version 5.36 (Nove	No. of chemical unit in entr				
Restriction Info:	No refcode restrictions	applied	-1			
Filters:	R factor <= 0.1 No errors	Not disordered Not polymeric	Text: polymorph			
	No ions Only Organics	No powder structures	Elements: CHNOF			
Percentage Completed:	100%	Al	llow other elements : Yes			
Number of Hits:	50 (out of 50 hits, 35 hits are unique)					
Search:	Search S4					
Date/Time done:	Tue Jun 16 09:30:14 20	)15	No. of molecules in the asymmetric unit $(7) > -2$			
Database(s):	CSD version 5.36 updates (Nov 2014)		asymmetric unit $(Z) \ge 2$			
	CSD version 5.36 (November 2014) CSD version 5.36 (November 2014)		No. of chemical unit in entry $= 1$			
Restriction Info:	No refcode restrictions	applied	-			
Filters:	R factor <= 0.1 No errors	Not disordered Not polymeric	Text: polymorph			
	No ions Only Organics	No powder structures	Elements: CHNOF			
Percentage Completed:	100%	Al	low other elements : <b>No</b>			
Number of Hits:	31 (out of 31 hits, 16 hits are unique)					

**Table S7.** Polymorphs with  $Z' \ge 2$  obtained from Cambridge Structural Database (Search S3).

Serial	Refcode	Z'	Ζ	Space	Serial	Refcode	<i>Z</i> ′	Z	Space
No.				group	No.				group
1	DOKNOI	2	8	Pca2 <sub>1</sub>	18	IWOCON	2	8	$P2_1/n$
	DOKNOI01	2	4	<i>P</i> -1	19	LEHWAX01	2	8	$P2_1/n$
2	DOMZIQ	5	5	<i>P</i> 1	20	LEXVEP01	6	12	<i>P</i> -1
3	VISQOF02	4	16	P43	21	MIRDEX	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>
4	VOLJIR	2	8	Сс	22	NAVCIX	2	4	<i>P</i> -1
5	YEBQED02	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>	23	NAVZIU02	2	2	<i>P</i> 1
6	AJEYAQ03	6	12	<i>P</i> 2 <sub>1</sub>	24	NIZVAU01	2	4	<i>P</i> -1
7	ASETOI02	2	4	<i>P</i> -1		NIZVAU02	2	8	$P2_1/a$
8	BIPDEJ	2	4	<i>P</i> -1	25	OYEWUL01	2	2	<i>P</i> 1
	BIPDEJ01	2	4	<i>P</i> -1	26	PEDWOM	3	12	$P2_1/n$
	BIPDEJ03	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>	27	QUKVUN01	2	4	<i>P</i> -1
9	BUNKOK01	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>	26	REPWUG01	2	4	<i>P</i> -1
	BUNKOK11	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>	27	RUYZOA	2	4	<i>P</i> -1
10	DATZAA	2	16	Pbca		RUYZOA01	2	4	<i>P</i> -1
11	FPAMCA16	4	16	<i>P</i> 2 <sub>1</sub> / <i>c</i>	28	TEHMEY01	2	8	$P2_1/n$
12	FURACL	4	8	<i>P</i> -1	29	TITVAU01	4	8	Рс
	FURACL01	4	8	<i>P</i> -1	1	TITVAU02	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>

	FURACL14	4	8	<i>P</i> -1		TITVAU03	2	8	<i>P</i> 2 <sub>1</sub> / <i>c</i>
13	GOGQOJ	4	16	Сс	30	TIYQAU	2	2	<i>P</i> 1
14	GORBOE	2	8	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	31	VETVOG01	2	8	$P2_{1}/c$
15	HOKMAW	2	8	<i>Pca</i> 2 <sub>1</sub>	32	VISQOF01	4	8	<i>P</i> -1
16	IRUQOB	2	2	<i>P</i> 1	33	WASTEP01	2	4	<i>P</i> -1
17	IVUQOF01	2	8	$P2_1/n$	34	WEWWA	2	8	$P2_1/c$
	IVUQOF03	2	16	<i>C</i> 2/ <i>c</i>	35	ZEBVEJ	4	4	<i>P</i> 1
	IVUQOF04	2	16	Pbca		ZEBVEJ01	2	4	<i>P</i> 2 <sub>1</sub>

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