Electronic Supplementary Information

Isostructural Polymorphs: Qualitative Insights from Energy Frameworks

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• Synthesis

m-MeO-CMONS [(*Z*)-3-(3,4-dimethoxyphenyl)-2-(4-nitrophenyl)acrylonitrile] was synthesized by following the procedure as reported earlier [1]. All the reagents were obtained from Sigma-Aldrich and used without further purification. The reaction mixture was cooled to room temperature and then 10% hydrochloric acid was added slowly to the reaction mixture to bring the pH to neutral and thereby removed the excess piperidine. The reaction mixture was then washed with ethyl-acetate and water. The organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure (scheme S1). The crude product was purified by column chromatography and characterized by FT-IR (Fig. S1), UV-Vis (Fig. S2) and ¹H NMR spectroscopy (Fig. S3).



Scheme S1

Yield = 90%, FT-IR (diamond crystal), 2956, 2916 (Ar-C-H), 2934 (=C-H), 2846 (C-H), 2207 (CN), 1510, 1338 (NO), 1597 (C=C), 1567 (Ar-C=C), 1035 (C-O).



Fig. S1: Solid state FT-IR Spectra of polymorphs P1, P2 and P3 including the Bulk sample.



Fig. S2: (top) showing full ¹H-NMR spectra (bottom) showing the multiplets of *m*-MeO-CMONS in CDCl₃ (400 MHz).

¹H-NMR (CDCl₃, 400 MHz) : δ 8.27 (d, *j*=12, 2H), 7.81 (d, *j*=8, 2H), 7.76 (s, 1H), 7.59 (s,1H), 7.41 (d, *j*=8, 1H), 6.95 (d, *j*=8, 1H), 3.96 (d, *j*=4, 6H)



Fig. S3: UV-Vis spectra of P1, P2 and P3 crystal forms in ethyl acetate solvent.

• Crystal Growth

m-MeO-CMONS was crystallized *via* slow solvent evaporation method. The solvents, crystallization conditions and the outcome of the crystallization experiments are listed in **Table S1**. Some of conditions resulted no crystals (marked as "-" in **Table S1**). X-ray diffraction experiments were carried out on the best quality crystals grown from the conditions highlighted in **Table S1**. Interestingly, crystal of from **P2** was achieved only from the crystallization using toluene at RT. The crystal morphologies as captured using Olympus SZX10 Polarized Microscope equipped with digital camera are shown in **Fig. S4**.

Solvent(s)	Temperature	Crystal habit; quality	Form
Methanol/chloroform (10:1)	LT	Prism; good	P1
	RT	Prism; fair	P1
Acetone/Hexane (10:1)	LT	Block; poor	P1
	RT	-	-
Dichloromethane	LT	Block; good	P3
	RT	Block; fair	P1
1,4-dioxane	LT	Block; good	P1
	RT	Block; poor	P1
Toluene	LT	Prism; good	P3
	RT	Prism; good	P2
Acetic Acid	LT	-	-
	RT	Block; good	P3
Ethanol/Hexane (10:1)	LT	-	-
	RT	Block; good	P1
THF/Hexane (10:1)	LT	Block; good	P1
	RT	Block; fair	P1
Chloroform/Hexane (10:1)	LT	-	-
	RT	-	-
Acetonitrile/Hexane (10:1)	LT	-	-
	RT	-	-

Table S1. Detail of crystallization experiments (RT = Room temperature, LT = Low temperature).



Fig. S4: Optical Images of the three polymorphic crystals.

Molecular Conformational Analysis

The atomic numbering scheme for **P1** is shown in **Fig. S5**, the same numbering scheme was followed for forms **P2** and **P3**. The symmetry independent molecules in the asymmetric units are highlighted in orange (molecule A) and green (molecule B) colors. The distinct molecular arrangement in their respective unit cells are shown in **Fig. S6**. For **P1**, both the molecule A and molecule B are forming a single layer whereas those of in the forms **P2** and **P3** are in different layers.





Further, the structures of the three forms were compared by overlaying the asymmetric unit of one form over the other. The overlay diagrams were drawn by selecting a same set of atoms (N2, C7 and C9) in molecule A of the respective forms (**Fig. S7**). The overlay diagrams clearly bring out the orientational differences of the molecules among the polymorphs.



(a) P1 vs P2 overlay, P1 in green, P2 in brown



(b) P1 vs P3 overlay, P1 in green, P3 in pink



(c) P2 vs P3 overlay, P2 in brown, P3 in pink

Fig. S6 : Molecular overlay diagrams (a) molecule **P1A** is superimposed over molecule **P2A**, (b) molecule **P1A** is superimposed over molecule **P3A** and (c) molecule **P2A** is superimposed over molecule **P3A**. Conformational difference between the two symmetry independent molecules in each form is also examined *via* overlay diagram as shown in **Fig. S8**. Once again same set of atoms (N2, C7 and C9), as considered above, were selected for this comparison. The marginal variations in torsion angles about the C7=C9 bond between molecule A and molecule B are listed in **Table S2**. The angle between the overlay plane of molecules A and B in all the three forms is also small, indicating that the two symmetry independent molecules are having similar conformation.



Fig. S7: Overlay diagram of the symmetry independent two molecules in the asymmetric unit.

Table S2: List of torsion angles and the angles between the overlaying planes of the symmetry independent molecules.

Form	Molecule	Torsion	Angle (°)	Angle (°) between the overlaying planes
D1	A-orange	C4-C7-C9-C10	176.24	2 80
PI	B-green	C4A-C7A-C9A-C10A	-175.77	2.80
	A-orange	C4-C7-C9-C10	176.49	2.72
PZ	B-green	C4A-C7A-C9A-C10A	176.99	3.72
	A-orange	C4-C7-C9-C10	176.67	
P3	B-green	C4A-C7A-C9A-C10A	177.28	4.44

• Crystal Packing









Fig S8: The π ··· π interactions between the molecular layers in the crystal lattice of **P1**, **P2** and **P3** showing the different interacting nature among the polymorphs.



• Fingerprint Plots

Fig. S9: Hirshfeld surface associated 2D fingerprint plots generated on the symmetry independent molecules.

XPac Analysis

For P1 vs P2





For P1 vs P3

XPac results (filter settings a / p / d : 7 / 10 / 0.00) SC A: 2D supramolecular construct Dissimilarity index: x = 3.8Stretch parameter: D = 0.04 Å For n = 18 neighbour(s) and p = 23 points - delta[a] (angles) = 0.8° - delta[p] (planes) = 3.7°



For P2 vs P3



delta(p) [°] vs. delta(a) [°]



• Interaction Energy Calculation (CrystalExplorer)

Computational Procedure

The interaction energies for all the three polymorphs, P1, P2 and P3 have been estimated in following steps. Since all the three forms have two symmetry independent molecules in the asymmetric unit the energy calculations were done for one molecule at a time to reflect the energy contributions from each of the molecules in the structure. We split the structure into two residues; while viewing down the baxis the top molecule was considered as residue 1 and the below one as residue 2. A cluster of radius 3.8 Å was then generated around the residue 1 and the energy calculation was performed. In the following step 'reset crystal' option was used to generate the cluster of radius 3.8 Å around the residue 2 and the energy calculation was repeated. In the final step, both the residues were selected after resetting the crystal once again and the cluster of radius 3.8 Å was generated for the overall energy calculation. Actually, the final step does not do any calculations but put the information together from the previous sets of calculations. The color coded cluster of molecules for residue 1 and residue 2 along with their individual energy profiles and also the final energy profile are given below for clarity (Fig. S11 - S13). The energies estimated from the final profile were then verified against the calculations performed on individual residues. This was done by considering all the energies from residue 1 and residue 2 but energies with same value of distance between molecular center of mass, R, are counted only once (Table S4 – S6). The energy values are summarized in Table S7.





Fig. S10: Color coding for the neighboring molecules around residue1 (top) and residue 2 (bottom) of P1. The residues are shown with atom type color.





Fig. S11: Color coding for the neighboring molecules around residue1 (top) and residue 2 (bottom) ofP2. The residues are shown with atom type color.





- Fig. S12: Color coding for the neighboring molecules around residue1 (top) and residue 2 (bottom) of P3. The residues are shown with atom type color.
- **Table S3.** Molecular pairs and the interaction energies (kJ/mole) obtained from energy framework calculation for **P1**.

Energy Profile for Residue 1

Energy Profile for Residue 2

Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-x, -y, -z	13.28	B3LYP/6-31G(d,p)	-9.1	-2.6	-24.2	13.5	-24.0
-	5.88	B3LYP/6-31G(d,p)	-0.8	-2.8	-39.0	22.8	-22.3
x, y, z	17.06	B3LYP/6-31G(d,p)	-10.6	-1.8	-4.6	9.6	-10.8
-	12.43	B3LYP/6-31G(d,p)	4.9	-2.0	-15.5	10.3	-3.2
-	8.94	B3LYP/6-31G(d,p)	-24.8	-5.5	-28.8	30.0	-36.9
-x, -y, -z	6.65	B3LYP/6-31G(d,p)	-16.0	-3.4	-67.8	41.8	-51.8
-x, -y, -z	5.43	B3LYP/6-31G(d,p)	-19.1	-3.3	-74.1	48.1	-56.6
-	7.94	B3LYP/6-31G(d,p)	-23.4	-4.5	-21.7	23.7	-32.5
-	9.11	B3LYP/6-31G(d,p)	-2.8	-2.4	-10.2	5.8	-9.9
-	8.63	B3LYP/6-31G(d,p)	1.8	-0.4	-3.8	0.0	-1.6
-	9.21	B3LYP/6-31G(d,p)	0.2	-1.7	-19.2	8.9	-12.0
-	13.20	B3LYP/6-31G(d,p)	-10.3	-3.2	-16.2	12.8	-19.4
-	13.92	B3LYP/6-31G(d,p)	-0.3	-0.7	-5.1	2.0	-4.0
-x, -y, -z	12.24	B3LYP/6-31G(d,p)	-4.2	-2.2	-16.3	13.5	-11.8

Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-	5.88	B3LYP/6-31G(d,p)	-0.8	-2.8	-39.0	22.8	-22.3
-x, -y, -z	10.53	B3LYP/6-31G(d,p)	-10.5	-2.2	-38.2	28.7	-28.0
-x, -y, -z	8.49	B3LYP/6-31G(d,p)	-11.9	-3.3	-51.2	34.0	-38.1
-	7.94	B3LYP/6-31G(d,p)	-23.4	-4.5	-21.7	23.7	-32.5
-x, -y, -z	3.21	B3LYP/6-31G(d,p)	-30.7	-3.6	-125.5	93.0	-85.8
-	13.20	B3LYP/6-31G(d,p)	-10.3	-3.2	-16.2	12.8	-19.4
-	8.94	B3LYP/6-31G(d,p)	-24.8	-5.5	-28.8	30.0	-36.9
-	12.43	B3LYP/6-31G(d,p)	4.9	-2.0	-15.5	10.3	-3.2
-	8.63	B3LYP/6-31G(d,p)	1.8	-0.4	-3.8	0.0	-1.6
-	13.92	B3LYP/6-31G(d,p)	-0.3	-0.7	-5.1	2.0	-4.0
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	9.21	B3LYP/6-31G(d,p)	0.2	-1.7	-19.2	8.9	-12.0
-х, -у, -z	17.37	B3LYP/6-31G(d,p)	-1.0	-0.2	-1.4	0.1	-2.3

Scale factors for benchmarked energy models See Table 1 of Turner et al., J. Phys. Chem. Lett. 5, 4249 (2014)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF HF/3-21G electron densities	0.882	0.593	0.852	0.681
CE-MP2 MP2/6-31G(d,p) electron densities	1.027	0.722	0.842	0.605
CE-B3LYP B3LYP/6-31G(d,p) electron densities	1.063	0.756	0.843	0.595

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Overall Energy Profile

Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-x, -y, -z	13.28	B3LYP/6-31G(d,p)	-9.1	-2.6	-24.2	13.5	-24.0
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-	8.94	B3LYP/6-31G(d,p)	-24.8	-5.5	-28.8	30.0	-36.9
-x, -y, -z	6.65	B3LYP/6-31G(d,p)	-16.0	-3.4	-67.8	41.8	-51.8
-x, -y, -z	5.43	B3LYP/6-31G(d,p)	-19.1	-3.3	-74.1	48.1	-56.6
-	7.94	B3LYP/6-31G(d,p)	-23.4	-4.5	-21.7	23.7	-32.5
-	9.11	B3LYP/6-31G(d,p)	-2.8	-2.4	-10.2	5.8	-9.9
-	8.63	B3LYP/6-31G(d,p)	1.8	-0.4	-3.8	0.0	-1.6
-	9.21	B3LYP/6-31G(d,p)	0.2	-1.7	-19.2	8.9	-12.0
-	13.20	B3LYP/6-31G(d,p)	-10.3	-3.2	-16.2	12.8	-19.4
-	13.92	B3LYP/6-31G(d,p)	-0.3	-0.7	-5.1	2.0	-4.0
-x, -y, -z	12.24	B3LYP/6-31G(d,p)	-4.2	-2.2	-16.3	13.5	-11.8
-x, -y, -z	10.53	B3LYP/6-31G(d,p)	-10.5	-2.2	-38.2	28.7	-28.0
-x, -y, -z	8.49	B3LYP/6-31G(d,p)	-11.9	-3.3	-51.2	34.0	-38.1
-x, -y, -z	3.21	B3LYP/6-31G(d,p)	-30.7	-3.6	-125.5	93.0	-85.8
x, y, z	17.06	B3LYP/6-31G(d,p)	-8.3	-1.5	-4.3	5.8	-10.2
-x, -y, -z	17.37	B3LYP/6-31G(d,p)	-1.0	-0.2	-1.4	0.1	-2.3

Table S4. Molecular pairs and the interaction energies (kJ/mole) obtained from energy framework calculation for **P2**.

Energy Profile for Residue 1

Energy Profile for Residue 2

Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-	8.89	B3LYP/6-31G(d,p)	-21.4	-5.1	-27.8	25.9	-34.6
-	8.09	B3LYP/6-31G(d,p)	-5.6	-2.5	-32.6	21.3	-22.6
-x, -y, -z	3.66	B3LYP/6-31G(d,p)	-17.5	-2.9	-99.6	60.3	-68.9
-	12.14	B3LYP/6-31G(d,p)	-3.3	-2.3	-14.6	7.3	-13.2
-	7.74	B3LYP/6-31G(d,p)	-21.9	-4.1	-23.5	23.0	-32.5
-x, -y, -z	12.18	B3LYP/6-31G(d,p)	-2.2	-2.0	-15.8	11.9	-10.1
x, y, z	16.86	B3LYP/6-31G(d,p)	-8.3	-1.6	-5.0	7.8	-9.7
-	13.04	B3LYP/6-31G(d,p)	-10.0	-3.1	-16.3	13.0	-19.0
-	13.96	B3LYP/6-31G(d,p)	-1.3	-0.7	-4.6	2.4	-4.3
-х, -у, -z	6.78	B3LYP/6-31G(d,p)	-12.1	-2.5	-59.7	35.0	-44.2
-	12.12	B3LYP/6-31G(d,p)	3.3	-1.8	-15.0	8.9	-5.2
-x, -y, -z	18.05	B3LYP/6-31G(d,p)	-0.1	-0.2	-1.1	0.1	-1.1
-	9.06	B3LYP/6-31G(d,p)	-1.6	-1.8	-20.3	10.3	-14.1
-	8.98	B3LYP/6-31G(d,p)	-2.9	-2.7	-12.6	7.8	-11.1

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Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-х, -у, -z	3.28	B3LYP/6-31G(d,p)	-30.3	-3.3	-120.9	92.9	-81.4
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-х, -у, -z	13.23	B3LYP/6-31G(d,p)	-9.3	-2.6	-18.2	12.2	-19.8
-	8.98	B3LYP/6-31G(d,p)	-2.9	-2.7	-12.6	7.8	-11.1
-х, -y, -z	6.36	B3LYP/6-31G(d,p)	-11.7	-2.8	-56.2	39.6	-38.3
-	12.12	B3LYP/6-31G(d,p)	3.3	-1.8	-15.0	8.9	-5.2
-х, -у, -z	17.06	B3LYP/6-31G(d,p)	-1.7	-0.2	-1.6	0.0	-3.3
-	13.04	B3LYP/6-31G(d,p)	-10.0	-3.1	-16.3	13.0	-19.0
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-	12.14	B3LYP/6-31G(d,p)	-3.3	-2.3	-14.6	7.3	-13.2
-	7.74	B3LYP/6-31G(d,p)	-21.9	-4.1	-23.5	23.0	-32.5
-x, -y, -z	12.18	B3LYP/6-31G(d,p)	-2.2	-2.0	-15.8	11.9	-10.1
x, y, z	16.86	B3LYP/6-31G(d,p)	-8.3	-1.6	-5.0	7.8	-9.7
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-	13.96	B3LYP/6-31G(d,p)	-1.3	-0.7	-4.6	2.4	-4.3
-x, -y, -z	6.78	B3LYP/6-31G(d,p)	-12.1	-2.5	-59.7	35.0	-44.2
-	12.12	B3LYP/6-31G(d,p)	3.3	-1.8	-15.0	8.9	-5.2
-x, -y, -z	18.05	B3LYP/6-31G(d,p)	-0.1	-0.2	-1.1	0.1	-1.1
-	9.06	B3LYP/6-31G(d,p)	-1.6	-1.8	-20.3	10.3	-14.1
-	8.98	B3LYP/6-31G(d,p)	-2.9	-2.7	-12.6	7.8	-11.1
-x, -y, -z	3.28	B3LYP/6-31G(d,p)	-30.3	-3.3	-120.9	92.9	-81.4
x, y, z	16.86	B3LYP/6-31G(d,p)	-7.1	-1.6	-5.4	6.0	-9.7
-x, -y, -z	13.23	B3LYP/6-31G(d,p)	-9.2	-2.6	-18.2	12.2	-19.8
-x, -y, -z	6.36	B3LYP/6-31G(d,p)	-11.7	-2.8	-56.2	39.6	-38.3
-x, -y, -z	17.06	B3LYP/6-31G(d,p)	-1.7	-0.2	-1.6	0.0	-3.3

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-x, -y, -z	5.20	B3LYP/6-31G(d,p)	-14.0	-3.0	-72.6	46.6	-50.7
-x, -y, -z	14.49	B3LYP/6-31G(d,p)	-3.5	-1.8	-11.0	6.7	-10.4
-	8.92	B3LYP/6-31G(d,p)	-23.8	-5.5	-28.5	29.0	-36.2
-x, -y, -z	3.24	B3LYP/6-31G(d,p)	-27.9	-3.4	-119.7	83.0	-83.7
-	9.14	B3LYP/6-31G(d,p)	-3.6	-2.8	-11.6	8.1	-10.9
-	12.48	B3LYP/6-31G(d,p)	4.7	-1.8	-13.7	8.4	-2.9
-	12.01	B3LYP/6-31G(d,p)	0.8	-0.3	-2.8	0.0	-1.7
x, y, z	17.01	B3LYP/6-31G(d,p)	-8.5	-1.6	-4.5	6.8	-10.0
-	13.18	B3LYP/6-31G(d,p)	-10.6	-3.2	-15.9	12.4	-19.7
-	11.10	B3LYP/6-31G(d,p)	-6.4	-2.6	-19.9	15.6	-16.3
-	7.93	B3LYP/6-31G(d,p)	-21.4	-4.4	-22.0	21.9	-31.5
-	9.24	B3LYP/6-31G(d,p)	0.1	-1.5	-19.2	9.0	-11.9
-	9.63	B3LYP/6-31G(d,p)	-2.0	-1.3	-16.2	6.0	-13.2
-x, -y, -z	17.41	B3LYP/6-31G(d,p)	-1.1	-0.2	-1.7	0.1	-2.6
-	13.83	B3LYP/6-31G(d,p)	-0.6	-0.7	-5.1	2.2	-4.2

Scale factors for benchmarked energy models See Table 1 of Turner et al., J. Phys. Chem. Lett. 5, 4249 (2014)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF HF/3-21G electron densities	0.882	0.593	0.852	0.681
CE-MP2 MP2/6-31G(d,p) electron densities	1.027	0.722	0.842	0.605
CE-B3LYP B3LYP/6-31G(d,p) electron densities	1.063	0.756	0.843	0.595

Overall Energy Profile

Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-x, -y, -z	5.20	B3LYP/6-31G(d,p)	-14.0	-3.0	-72.6	46.6	-50.7
-x, -y, -z	14.49	B3LYP/6-31G(d,p)	-3.5	-1.8	-11.0	6.7	-10.4
-	8.92	B3LYP/6-31G(d,p)	-23.8	-5.5	-28.5	29.0	-36.2
-x, -y, -z	3.24	B3LYP/6-31G(d,p)	-27.9	-3.4	-119.7	83.0	-83.7
-	9.14	B3LYP/6-31G(d,p)	-3.6	-2.8	-11.6	8.1	-10.9
-	12.48	B3LYP/6-31G(d,p)	4.7	-1.8	-13.7	8.4	-2.9
-	12.01	B3LYP/6-31G(d,p)	0.8	-0.3	-2.8	0.0	-1.7
x, y, z	17.01	B3LYP/6-31G(d,p)	- <mark>8.</mark> 5	-1.6	-4.5	6.8	-10.0
- 13.18 E		B3LYP/6-31G(d,p)	-10.6	-3.2	-15.9	12.4	-19.7
-	11.10	B3LYP/6-31G(d,p)	-6.4	-2.6	-19.9	15.6	-16.3
-	7.93	B3LYP/6-31G(d,p)	-21.4	-4.4	-22.0	21.9	-31.5
-	9.24	B3LYP/6-31G(d,p)	0.1	-1.5	-19.2	9.0	-11.9
-	9.63	B3LYP/6-31G(d,p)	-2.0	-1.3	-16.2	6.0	-13.2
-x, -y, -z	17.41	B3LYP/6-31G(d,p)	-1.1	-0.2	-1.7	0.1	-2.6
-	13.83	B3LYP/6-31G(d,p)	-0.6	-0.7	-5.1	2.2	-4.2
-x, -y, -z	6.58	B3LYP/6-31G(d,p)	-16.0	-3.1	-73.1	46.7	-53.1
-x, -y, -z	12.20	B3LYP/6-31G(d,p)	-3.9	-2.2	-17.9	15.6	-11.6
x, y, z	17.01	B3LYP/6-31G(d,p)	-10.2	-1.8	-4.7	9.6	-10.5
-x, -y, -z	4.20	B3LYP/6-31G(d,p)	-17.6	-3.7	-102.9	68.8	-67.3
-x, -y, -z	15.05	B3LYP/6-31G(d,p)	0.2	-0.6	-2.6	0.1	-2.4

Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
-x, -y, -z	6.58	B3LYP/6-31G(d,p)	-16.0	-3.1	-73.1	46.7	-53.1
-	8.92	2 B3LYP/6-31G(d,p)		-5.5	-28.5	29.0	-36.2
-	7.93	B3LYP/6-31G(d,p)	-21.4	-4.4	-22.0	21.9	-31.5
-х, -у, -z	12.20	B3LYP/6-31G(d,p)	-3.9	-2.2	-17.9	15.6	-11.6
-	9.24	B3LYP/6-31G(d,p)	0.1	-1.5	-19.2	9.0	-11.9
-	9.14	B3LYP/6-31G(d,p)	-3.6	-2.8	-11.6	8.1	-10.9
-	13.18	B3LYP/6-31G(d,p)	-10.6	-3.2	-15.9	12.4	-19.7
x, y, z	17.01	B3LYP/6-31G(d,p)	-10.2	-1.8	-4.7	9.6	-10.5
-	13.83	B3LYP/6-31G(d,p)	-0.6	-0.7	-5.1	2.2	-4.2
-х, -у, -z	4.20	B3LYP/6-31G(d,p)	-17.6	-3.7	-102.9	68.8	-67.3
-	9.63	B3LYP/6-31G(d,p)	-2.0	-1.3	-16.2	6.0	-13.2
-	12.48	B3LYP/6-31G(d,p)	4.7	-1.8	-13.7	8.4	-2.9
-	12.01	B3LYP/6-31G(d,p)	0.8	-0.3	-2.8	0.0	-1.7
-	11.10	B3LYP/6-31G(d,p)	-6.4	-2.6	-19.9	15.6	-16.3
-х, -у, -z	15.05	B3LYP/6-31G(d,p)	0.2	-0.6	-2.6	0.1	-2.4

Scale factors for benchmarked energy models See Table 1 of Turner et al., J. Phys. Chem. Lett. 5, 4249 (2014)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF HF/3-21G electron densities	0.882	0.593	0.852	0.681
CE-MP2 MP2/6-31G(d,p) electron densities	1.027	0.722	0.842	0.605
CE-B3LYP B3LYP/6-31G(d,p) electron densities	1.063	0.756	0.843	0.595

Table S6: Interaction Energies as obtained from the CrystalExplorer

Forms	E_{elec}	E _{pol}	E_{dis}	E _{repl.}	$E_{\rm tot}$	Average E _{tot}
						(kJ/mole)

	P1	-176.9	-47.3	-567.1	404.4	-461.2	-230.6
	P2	-164.9	-43.8	-550.8	385.7	-443.1	-221.55
ſ	P3	-165.3	-45.5	-565.6	396.6	-450.8	-225.4

Table S7: Energies for the intermolecular potential calculated using UNI force field.

Forms	E _{int}	Average E _{int}
	(kJ/mol)	(kJ/mol)
P1	-439.2	-219.6
P2	-409.2	-204.6
P3	-432	-216.0

Energy Frameworks Analysis



Fig. S13. Energy frameworks corresponding to the different energy components and the total interaction energy in P1



Fig. S14. Energy frameworks corresponding to the different energy components and the total interaction energy in P2



Fig. S15. Energy frameworks corresponding to the different energy components and the total interaction energy in P3

Further, to verify our observation on the striking similarity of energy frameworks for these 3D isostructural polymorphs, we have performed energy frameworks analysis on the polymorphic forms of 3-chloromandelic acid, which is also quantified as 3D isostructural polymorphs by Coles *et al.* [2]. The same procedure as above was followed for this pair of polymorphs based on their crystal geometry as deposited in CCDC (ref codes: FIZPEL – **triclinic** form, and FIZPEL01 – **monoclinic** form). The tube size and the energy threshold values were also kept same as above calculations. For both the forms, the energy frameworks based on the total energies as well as of the electrostatic and dispersion energy contributions are depicted in **Figs. S17 – S18.** Indeed, a striking similarity of energy frameworks along all the three direction is noticed between these two 3D isostructural polymorphs (**Fig. S19**). It is to be noted that the there are two symmetry independent molecules in the asymmetric unit of the **triclinic** form. This result is in high accordance with the observation made in our present study for the 3D isostructural polymorphs **P2** and **P3** (**Fig. 7**).



Fig. S16: Energy frameworks corresponding to the different energy components and the total interaction energy in triclinic form.



Fig. S17: Energy frameworks corresponding to the different energy components and the total interaction energy in **monoclinic** form.



- Fig. S18: Energy framework of total interaction energy of the 3D isostructural polymorphs of 3chloromendelic acid.
- **Table S8:** Different energy components and the total lattice energies of three forms as derived from

 PIXEL calculation. Energy listed here are per molecules in the asymmetric unit.

Forms	E(Coulomb)	E(Polarization)	E(Dispersion)	E(Repulsion)	Total <i>E</i> (Latt.)	
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	kJ/mol	
P1	-68.3	-26.3	-185.1	132.4	-147.3	
P2	-63.0	-24.3	-183.8	127.5	-143.6	
P3	-65.0	-24.8	-183.6	130.4	-143.0	

Forms	E(crystal)	E(molecule)	Ζ	E(Lattice)	E(Latt.)	Average E(Latt.)
	Hartree	Hartree		Hartree	kJ/mol	kJ/mol
P1	-4264.1	-2131.9	2	-0.1762	-462.6	-231.3
P2	-4264.1	-2131.9	2	-0.1745	-458.3	-229.1
Р3	-4264.1	-2131.9	2	-0.1739	-456.7	-228.3

Table S9: Lattice energies of three forms as derived from Crystal14 calculation.

• Thermal characterization

For Differential scanning calorimetry, the amples were kept in an Aluminium crucible with accurate measured weight (**Bulk**: 3.39mg, **P1**: 2.09mg, **P2**: 2.42mg and **P3**: 1.09mg).

	Bulk				P1		P2			P3		
Cycles	Phase #	Peak (°C)	ΔH (J/g)	Phase #	Peak (°C)	ΔH (J/g)	Phase #	Peak (°C)	ΔH (J/g)	Phase #	Peak (°C)	ΔH (J/g)
First	1	154.42	16.71	1	152.78	14.96	1	156.39	16.47	1	153.84	16.40
Heating	2	179.91	-146.31	2	178.09	-135.69	2	179.45	-141.46	2	179.43	-155.28
First Cooling	1	128.66	128.03	1	105.06 to 123.62	-	1	131.95	123.95	1	123.28	130.53
Second	1	159.27	-112.65	1	151.50	-69.19	1	158.02	-72.00	1	158.34	-77.67
Heating	2	161.87	104.19	2	155.73	47.31	2	160.24	69.30	2	160.01	74.05
	3	180.39	-147.79	3	174.13	-84.06	3	179.36	-139.47	3	179.43	-155.28
Second Cooling	1	127.72	123.67	1	98.72 to 107.69	-	1	121.88	115.99	1	124.93	127.88

Table S10: DSC phase changes for Bulk, P1, P2 and P3 at 2 °C/min.

140°C

125°C

75°C

30°C













185°C





200°C



208°C





190°C



160°C











175°C

120°C

155°C

180°C

130°C

135°C

140°C

150°C







25°C

30°C

Hot stage microscopy (HSM) images

60°C

90°C

Ρ1

P2









110°C











120°C

130°C

135°C











155°C

177°C

160°C

165°C

170°C

175°C







190°C

210°C





220°C









140°C

90°C

30°C

P3



25°C









110°C





130°C



140°C

150°C

175 °C

160°C

180°C

165°C

135°C



190°C



200°C

170°C

210°C

220°C

230°C

250°C





S19: HSM images Fig. of polymorphs P1, P2 and P3.



30°C



Fig. S20: Showing the comparison of observed PXRD patterns of forms P1, P2 and P3. The variations in peak positions across the polymorphs are pointed by the arrows.

- References :
- 1. A. M. Asiri, S. A. Khan, K. W. Tan and S. W. Ng, Acta Crystallogr., 2010, E66, o1733.
- 2. S. J. Coles, T. L. Threlfall and G. J. Tizzard, Cryst. Growth Des., 2014, 14, 1623.