Crystal structure from laboratory X-ray powder diffraction data, DFT+D calculations, Hirshfeld surface analysis, and energy frameworks of 1-Benzothiophene-2-carboxylic acid

Analio J. Dugarte-Dugarte,[1] Jacco van de Streek,[2] Graciela Díaz de Delgado,[1] Alicja Rafalska-Lasocha,[3] José Miguel Delgado[1]

[1]Laboratorio de Cristalografía-LNDRX, Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela.

[2]Avant-garde Materials Simulation, Alte Str. 2, D-79249 Merzhausen, Germany

[3]Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, Krakow30-387, Poland.

Supplementary Material

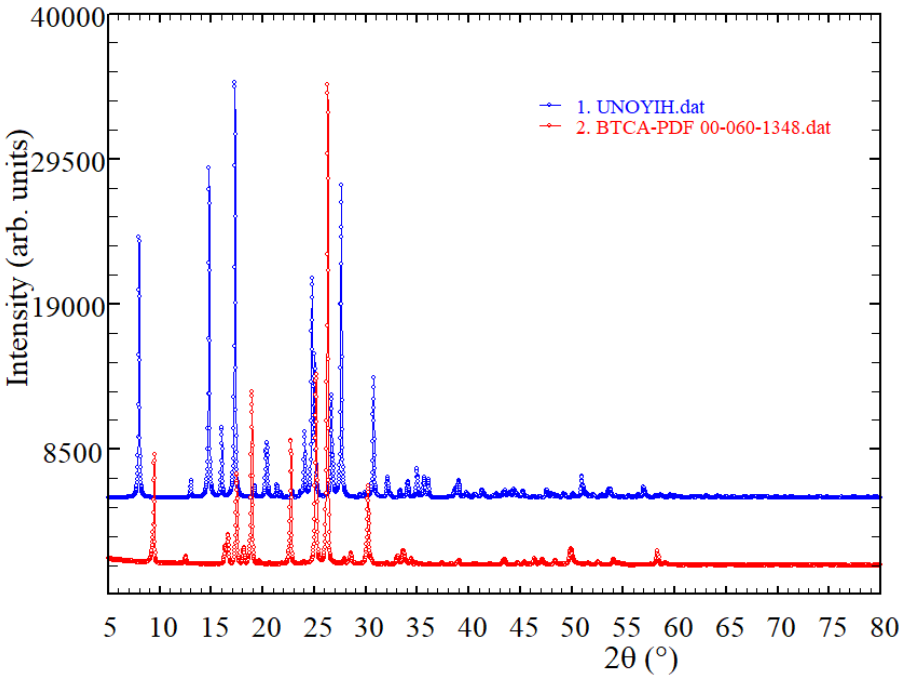


Figure S1. Superposition of the powder pattern calculated for entry UNOYIH (1-benzofuran-2-carboxylic acid) and the pattern reported in entry PDF 00-060-1348.

Table S1. X-ray powder diffraction data for form II of 1-Benzothiophene-2-carboxylic acid analyzed with NBS·AIDS86 software. Unit cell parameters: a=14.547(12), b=5.846(1), c=19.299(7) Å, β=103.88(5)°, V=1593(1) Å^3. Space group: $C2/c$ (No. 15). Figures of merit: M_{20}=26.2 and F_{30}=18.8(0 .0118, 136)

No.	$2\theta_{obs}$ (°)	d_{obs} (Å)	h	k	l	I/I_0	d_{cal} (Å)	$2\theta_{cal}$ (°)	$\Delta 2\theta$ (°)
1	9.465	9.3359	0	0	2	233	9.3679	9.433	-0.032
2	12.529	7.0590	2	0	0	21	7.0643	12.520	-0.009
3	16.383	5.4062	-1	1	0	43	5.4001	16.402	0.019
4	16.664	5.3155	-1	1	1	66	5.3202	16.650	-0.015
5	17.485	5.0678	1	1	1	191	5.0668	17.489	0.003
6	18.178	4.8762	-1	1	2	39	4.8757	18.180	0.002
7	18.949	4.6795	0	0	4	363	4.6840	18.931	-0.018
8	19.696	4.5036	1	1	2	12	4.5033	19.697	0.001
9	20.695	4.2884	-1	1	3	8	4.2836	20.719	0.023
10	22.732	3.9085	1	1	3	265	3.9114	22.715	-0.017
11	25.184	3.5333	2	0	4	399	3.5332	25.185	0.001
12	26.300	3.3858	1	1	4	1000	3.3880	26.283	-0.017
13	27.933	3.1915	-3	1	4	16	3.1909	27.938	0.006
14	28.572	3.1215	0	0	6	30	3.1226	28.562	-0.010
15	30.226	2.9543	1	1	5	166	2.9544	30.226	-0.001
16	32.062	2.7893	0	2	2	10	2.7893	32.061	0.000
17	33.139	2.7010	-2	2	0	23	2.7000	33.152	0.012
18	33.663	2.6602	-2	2	2	34	2.6601	33.664	0.001
19	34.445	2.6016	1	1	6	17	2.6019	34.441	-0.005
20	34.969	2.5638	-2	2	3	8	2.5654	34.946	-0.023
21	37.428	2.4008	-2	0	8	8	2.4016	37.415	-0.013
22	39.051	2.3047	0	2	5	14	2.3042	39.060	0.009
23	43.441	2.0814	-5	1	7	15	2.0819	43.430	-0.011
24	44.784	2.0220	4	2	3	8	2.0217	44.792	0.007
25	45.450	1.9939	-2	2	7	10	1.9944	45.439	-0.011
26	46.388	1.9558	2	2	6	17	1.9557	46.391	0.003
27	47.158	1.9256	-7	1	4	16	1.9259	47.152	-0.006
28	48.398	1.8791	1	3	2	13	1.8779	48.433	0.035
29	48.526	1.8745	0	0	10	11	1.8736	48.551	0.025
30	49.846	1.8279	0	2	8	32	1.8274	49.861	0.015
31	49.986	1.8231	-1	1	10	36	1.8225	50.003	0.017
32	52.559	1.7398	6	2	2	11	1.7392	52.578	0.019
33	54.069	1.6947	6	0	6	15	1.6949	54.061	-0.008
34	58.323	1.5808	2	2	9	32	1.5801	58.351	0.028
35	59.102	1.5618	-3	3	7	8	1.5614	59.120	0.018

Table S2. Atomic coordinates and isotropic displacement parameters for BTCA refined with the Rietveld method.

Atom	*x*	*y*	*z*	U(eq)[Å^2]
S1	0.3415(4)	0.4296(8)	0.13131(17)	0.072(3)
O1	0.3814(4)	-0.1112(9)	0.0240(2)	0.072(3)
O2	0.4603(5)	0.2078(11)	0.0436(2)	0.072(3)
C1	0.1141(3)	0.5013(8)	0.2094(3)	0.100(4)
C2	0.0639(3)	0.3020(8)	0.1827(3)	0.100(4)
C3	0.0980(3)	0.1469(8)	0.1391(3)	0.100(4)
C4	0.1863(3)	0.1916(8)	0.1245(2)	0.100(4)
C5	0.2357(3)	0.3999(8)	0.1535(3)	0.100(4)
C6	0.1989(3)	0.5529(8)	0.1942(3)	0.100(4)
C7	0.2379(3)	0.0610(7)	0.0840(2)	0.100(4)
C8	0.3218(3)	0.1671(7)	0.0841(2)	0.100(4)
C9	0.3924(3)	0.0929(7)	0.05001(17)	0.100(4)
H1	0.0879(6)	0.6052(14)	0.2367(5)	0.120(4)
H1A	0.4317(5)	-0.1448(16)	0.0027(3)	0.087(4)
H2	0.0047(5)	0.2742(16)	0.1932(6)	0.120(4)
H3	0.0641(6)	0.0112(15)	0.1216(6)	0.120(4)
H6	0.2327(6)	0.6854(13)	0.2128(5)	0.120(4)
H7	0.2187(6)	-0.0801(13)	0.0613(5)	0.120(4)

Table S3. Bond distances and angles for BTCA.

Experimental	
Bond	**Distance (Å)**
S1–C5	1.714(7)
S1–C8	1.775(6)
O1–C9	1.292(6)
O2–C9	1.231(8)
O1–H1A	0.948(9)
C1–C2	1.409(7)
C1–C6	1.377(7)
C2–C3	1.410(7)
C3–C4	1.413(6)
C4–C5	1.459(7)
C4–C7	1.434(6)
C5–C6	1.385(7)
C7–C8	1.377(6)
C8–C9	1.422(6)

Experimental	
Atoms	**Angle**
C5-S1-C8	89.8(3)
C9-O1-H1A	108.9(8)
C2-C1-C6	121.4(5)
C1-C2-C3	121.6(4)
C2-C3-C4	118.3(4)
C3-C4-C7	129.7(4)
C5-C4-C7	112.2(4)
C3-C4-C5	118.1(4)
S1-C5-C4	112.5(4)
C4-C5-C6	122.3(4)
S1-C5-C6	125.2(4)
C1-C6-C5	118.3(4)
C4-C7-C8	110.3(4)

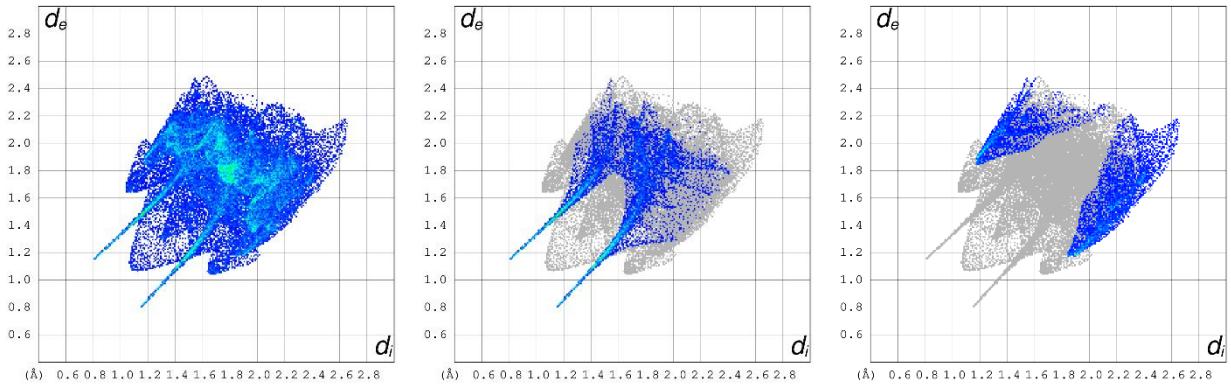
C1–H1	0.946(10)
C2–H2	0.951(9)
C3–H3	0.955(10)
C6–H6	0.944(10)
C7–H7	0.946(9)

S1-C8-C9	117.2(4)
C7-C8-C9	127.6(4)
S1-C8-C7	115.2(4)
O1-C9-C8	115.3(4)
O2-C9-C8	125.1(5)
O1-C9-O2	119.6(5)
C2-C1-H1	119.4(7)
C6-C1-H1	119.1(7)
C1-C2-H2	119.0(8)
C3-C2-H2	119.4(8)
C2-C3-H3	121.3(7)
C4-C3-H3	120.4(7)
C1-C6-H6	121.1(7)
C5-C6-H6	120.6(7)
C4-C7-H7	125.6(7)
C8-C7-H7	124.1(7)

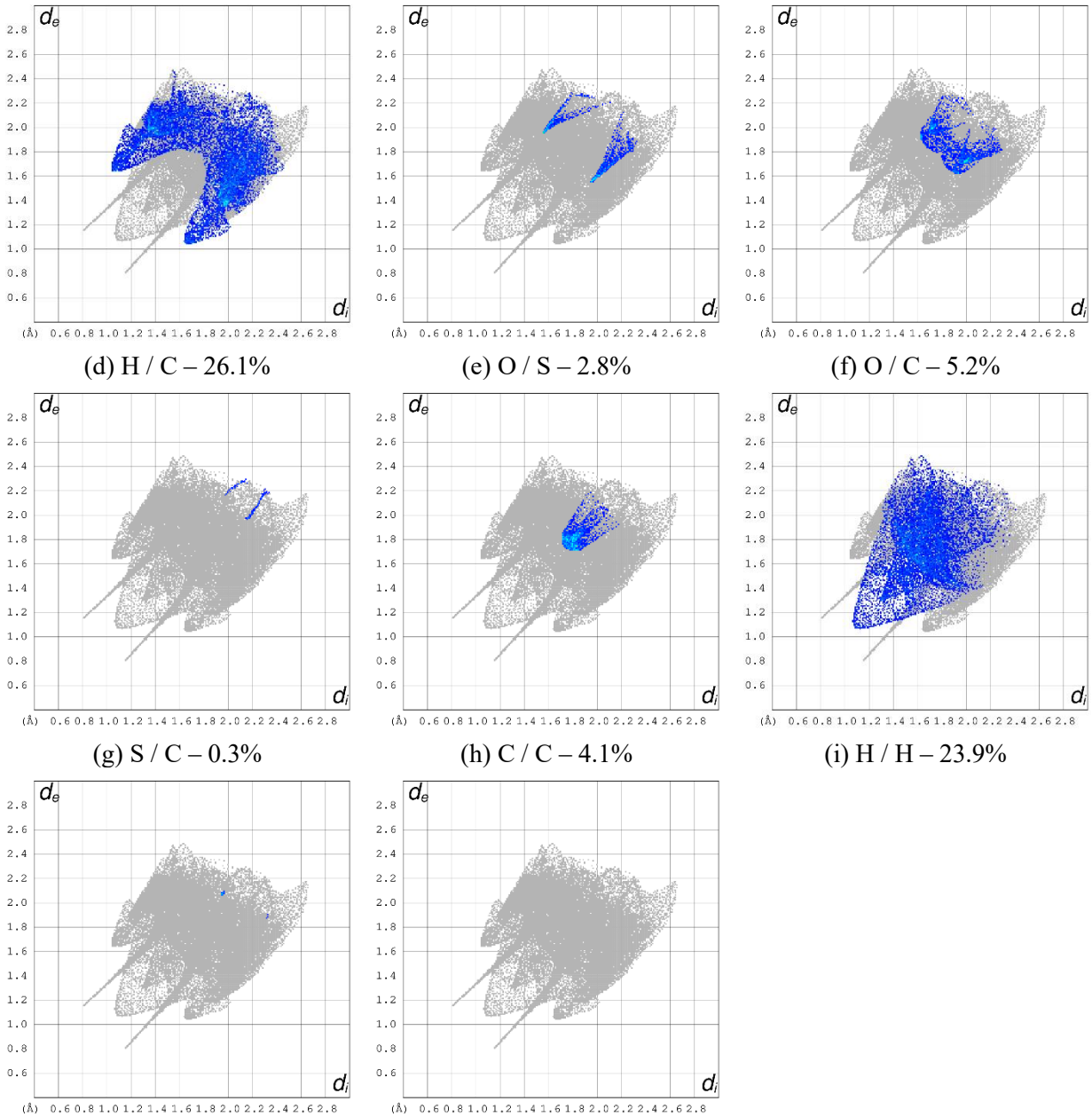
Interatomic distance classified as unusual by the Mogul geometry analysis.

Bond	Observed (Å)	DFT-D Optimized (Å)	Calculated average (Å)	Z–score	No. of structures
C4–C5	1.459(7)	1.427	1.408(2)	2.616	536
C8–C9	1.422(6)	1.460	1.474(23)	2.205	138

Hirshfeld surface analysis



(a) All (b) H / O – 22.5% (c) H / S – 14.9%



(d) H / C – 26.1% (e) O / S – 2.8% (f) O / C – 5.2%

(g) S / C – 0.3% (h) C / C – 4.1% (i) H / H – 23.9%

(j) O / O – 0.1% (k) S / S 0% (l)

Figure S2. Fingerprint plots for BTCA-Form II. (a) all contacts, (b) H···O contacts, (c) H···S contacts, (d) H···C contacts, (e) O···S contacts, (f) O···C contacts, (g) S···C contacts, (h) C···C contacts, (i) H···H contacts, (j) O···O contacts, (k) S···S contacts. The percent of surface area included is shown for each plot (99.8%).

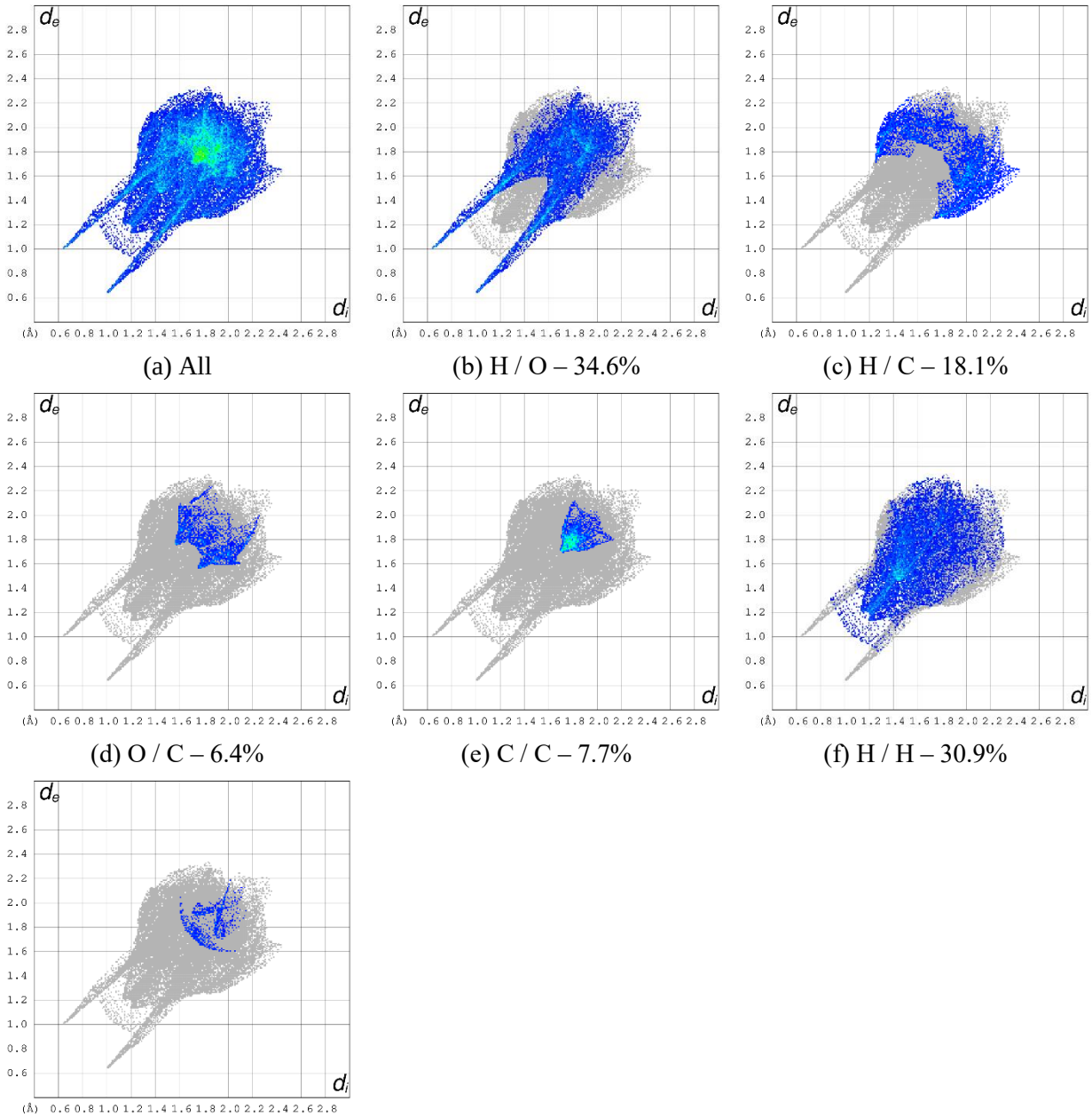
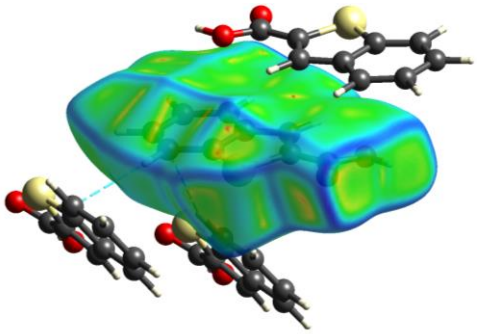


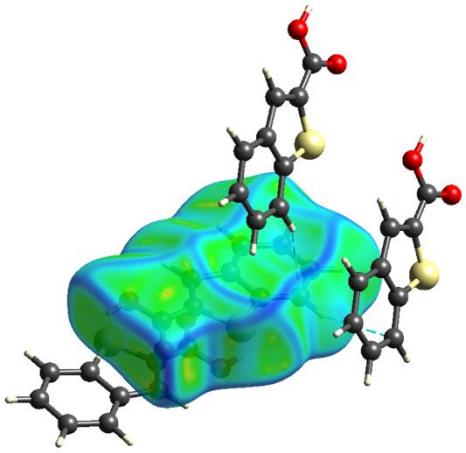
Figure S3. Fingerprint plots for BFCA. (a) all contacts, (b) H···O contacts, (c) H···C contacts, (d) O···C contacts, (e) C···C contacts, (f) H···H contacts, (g) O···O contacts. The percent of surface area included is shown for each plot. (100%).

The curvedness plot for BTCA-Form II (figure S4(a)) shows a large flat surface on the top part of the molecule, consistent with the π···π interactions observed. The other side displays a concave area (figure S4(b)) due to the C—H···π interaction with a neighboring molecule. The shape index

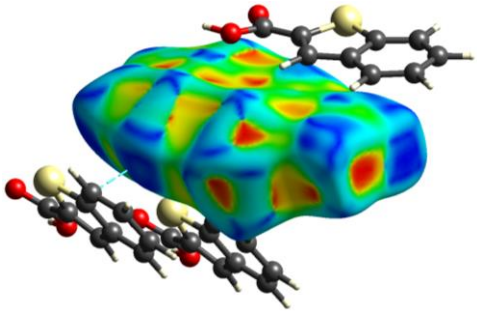
plots in figure S4(c)-(d) display contiguous red and blue triangular regions indicative of the π···π interactions as well as red concave regions associated to the C—H···π contacts. On the other hand, the curvedness and shape index plots of BTCA-Form I (Sagaama and Issaoui, 2020) and BFCA (Figure S4(e)-(h)) display flat surfaces and complementary red and blue regions on both sides of the molecule due to the offset π···π stacking pattern.



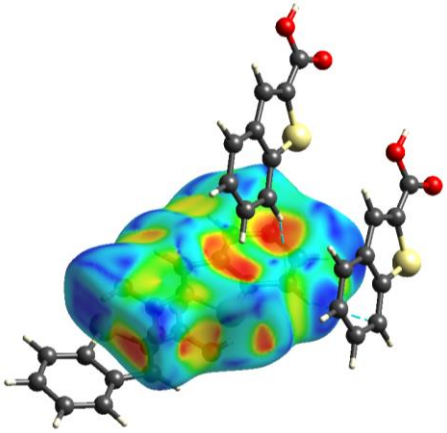
(a)



(b)



(c)



(d)

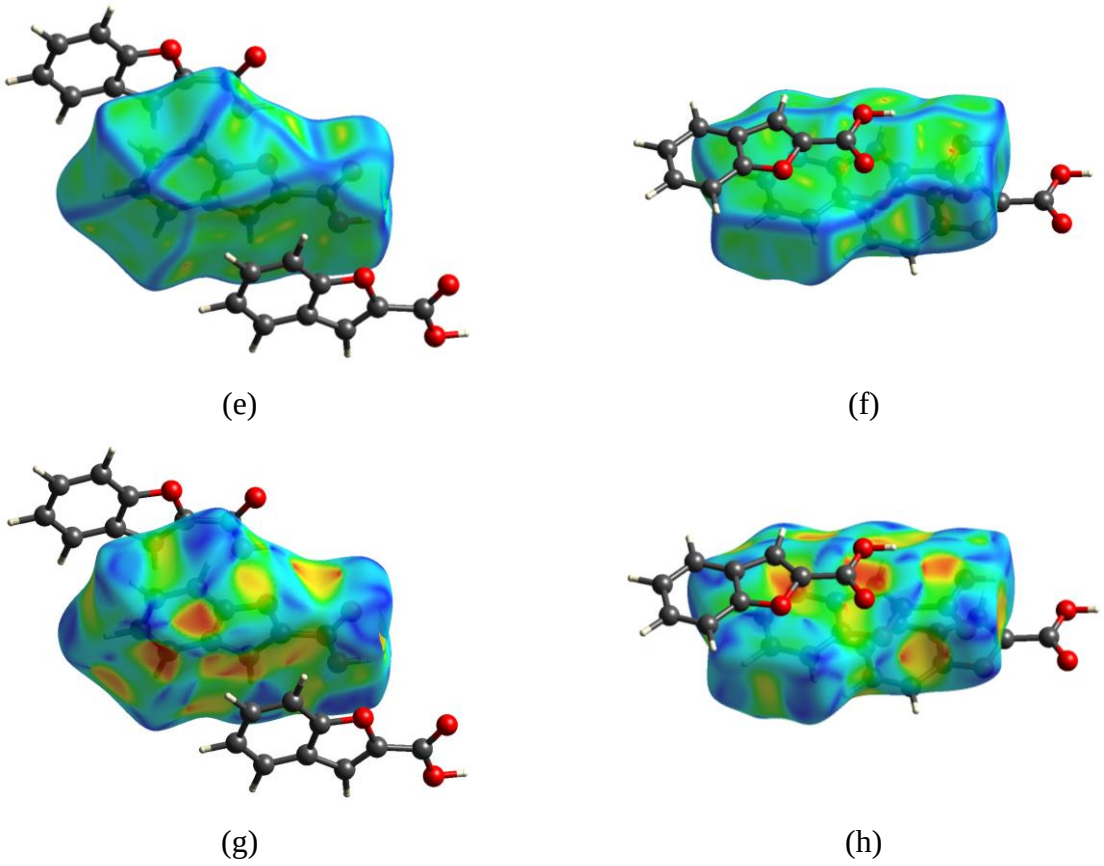
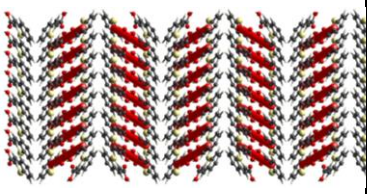
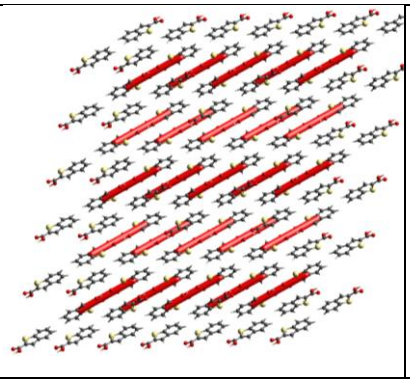
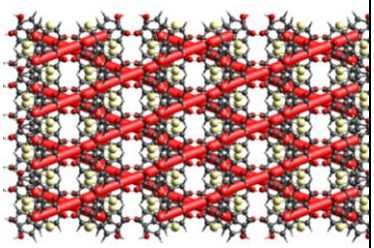


Figure S4. Hirshfeld surfaces mapped over the curvedness and shape-index for BTCA-Form II (a-d) and BFCA (e-h).

Energy frameworks calculations

E_{ele}			

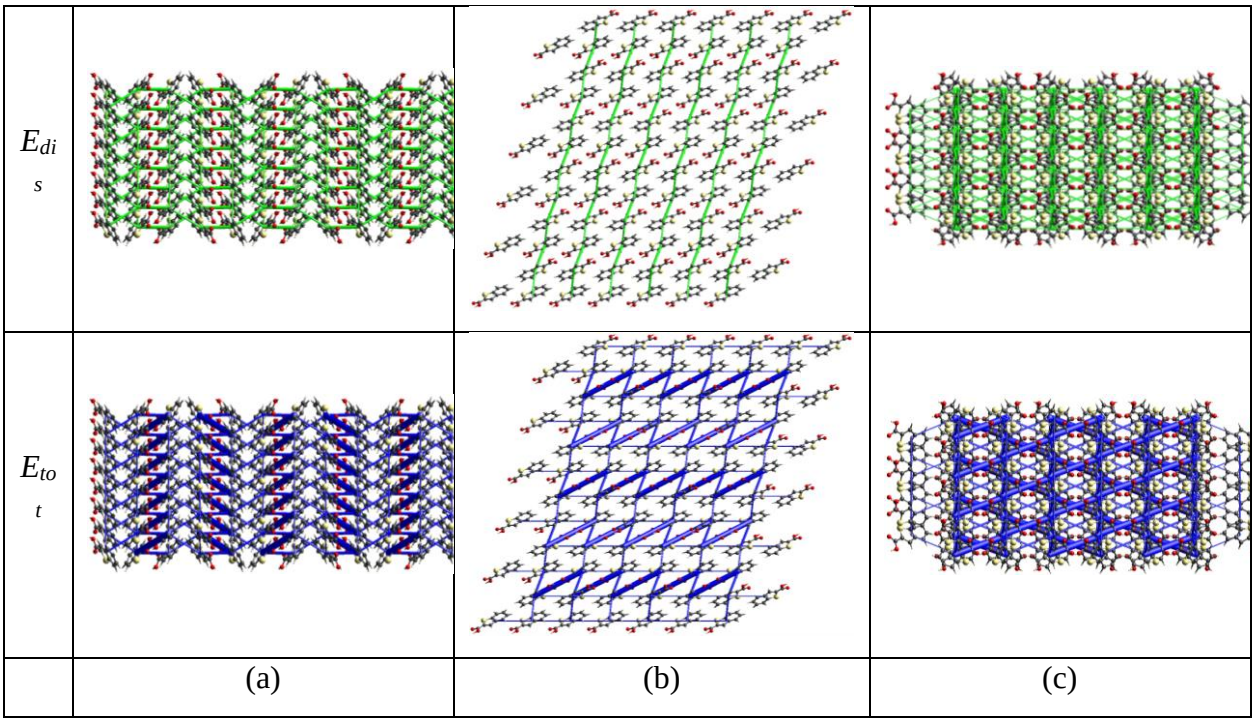


Figure S5. Energy frameworks calculated for BTCA-Form II (a) viewed along the **a**-axis, (b) along the **b**-axis and (c) along the **c**-axis. Energy contributions are represented within 3 *x* 3 *x* 3 unit cells. The cylinders radii were scaled to 80 arbitrary units with a cut-off value of 10 kJ mol^{-1}. E_{ele}, E_{dis}, and E_{tot} are represented (top to bottom) in red, green, and blue, respectively.

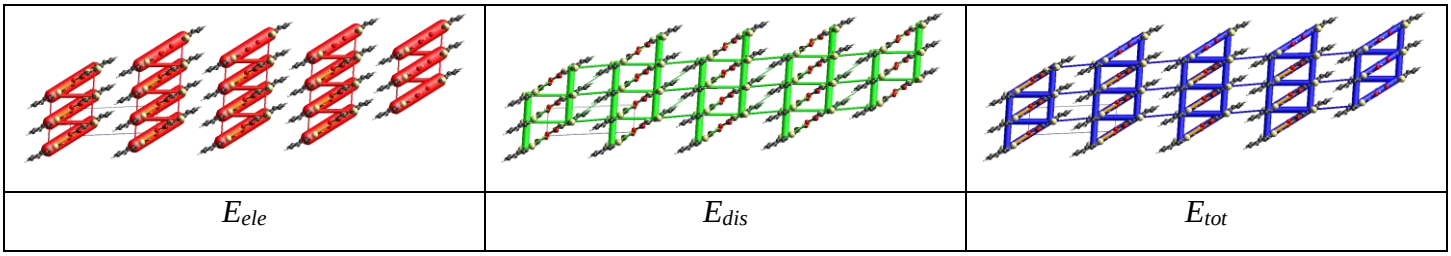
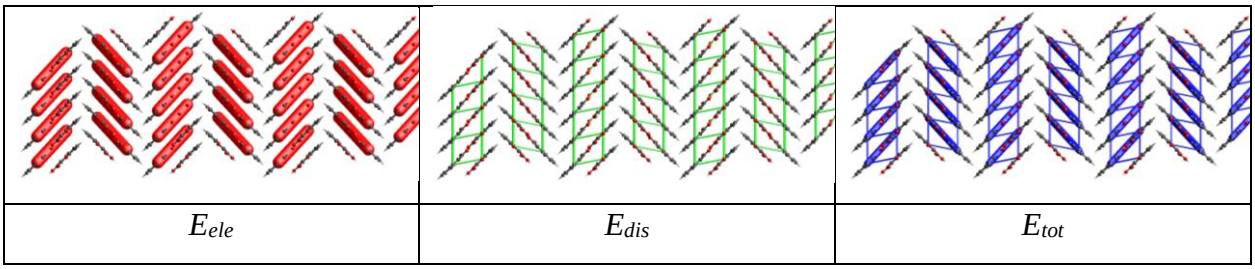


Figure S6. Energy frameworks calculated for BTCA-Form I viewed along the **b**-axis. Energy contributions are represented within 3 *x* 5 *x* 5 unit cells. The cylinders radii were scaled to 80 arbitrary units with a cut-off value of 10 kJ mol^{-1}. E_{ele}, E_{dis}, and E_{tot} are represented (left to right) in red, green, and blue, respectively.



E_{ele}	E_{dis}	E_{tot}

Figure S7. Energy frameworks calculated for BFCA viewed down the **c**-axis represented within 2 *x* 1 *x* 3 unit cells. The cylinders radii were scaled to 80 arbitrary units with a cut-off value of 10 kJ mol^{-1}. E_{ele}, E_{dis}, and E_{tot} are represented (left to right) in red, green, and blue, respectively.

Tables S3, S4, S5. Interaction Energies (kJ/mol) for BTCA Forms II and I and for BFCA.
- R is the distance between molecular centroids (mean atomic position) in Å.
- Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

Table S4. Interaction Energies for BTCA-Form II.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	x+1/2, y+1/2, z	7.88	B3LYP/6-31G(d,p)	-8.1	-2.2	-9.4	11.6	-11.2
	1	-x, y, -z+1/2	10.43	B3LYP/6-31G(d,p)	-2.5	-0.5	-11.1	12.3	-5.1
	1	x+1/2, y+1/2, z	7.88	B3LYP/6-31G(d,p)	0.5	-0.9	-11.3	3.9	-7.6
	0	-x+1/2, -y+1/2, -z	7.43	B3LYP/6-31G(d,p)	-0.2	-0.8	-9.3	6.1	-5.2
	0	-x, -y, -z	9.46	B3LYP/6-31G(d,p)	-70.3	-13.4	-9.1	46.5	-63.5
	1	x, y, z	5.85	B3LYP/6-31G(d,p)	-4.9	-0.8	-15.9	9.0	-14.1
	0	-x+1/2, -y+1/2, -z	4.41	B3LYP/6-31G(d,p)	-8.1	-1.9	-34.8	19.8	-28.1
	2	-x+1/2, y+1/2, -z+1/2	6.08	B3LYP/6-31G(d,p)	-8.6	-0.9	-24.5	20.2	-18.7
				TOTALS	-102.2	-21.4	-125.4	129.4	-153.5

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Table S5 Interaction energies calculated for BTCA-Form I

	N	Symop	R	Electron density	E_ele	E_pol	E_dis	E_rep	E_tot
	0	x, y, z	3.89	B3LYP/6-31G(d,p)	-12.5	-7.4	-75.7	36.7	-61.9
	0	-x, -y, -z	8.36	B3LYP/6-31G(d,p)	1.7	-0.6	-6.6	0.9	-3.8
	0	-x, -y, -z	8.73	B3LYP/6-31G(d,p)	-0.4	-0.1	-6.9	3.5	-4.4
	0	x, y, z	8.58	B3LYP/6-31G(d,p)	-0.6	-0.5	-7.0	1.8	-6.0
	0	-x, -y, -z	5.79	B3LYP/6-31G(d,p)	-37.5	-9.7	-30.1	25.8	-57.2
	0	-x, -y, -z	10.90	B3LYP/6-31G(d,p)	-2.0	-0.1	-10.4	9.8	-5.2
	0	-x, -y, -z	9.07	B3LYP/6-31G(d,p)	-120.1	-25.5	-13.3	156.0	-61.0
	0	x, y, z	7.89	B3LYP/6-31G(d,p)	-5.7	-2.0	-14.5	13.1	-12.1
	0	-x, -y, -z	7.10	B3LYP/6-31G(d,p)	-9.1	-1.2	-21.7	22.7	-15.4
	0	-x, -y, -z	7.04	B3LYP/6-31G(d,p)	24.4	-8.5	-15.4	38.0	29.5
	0	-x, -y, -z	9.85	B3LYP/6-31G(d,p)	-2.3	-0.3	-9.3	4.4	-8.1
				TOTALS	-164.1	-55.9	-210.9	312.7	-205.6

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Table S6. Interaction Energies for BFCA.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	6.97	B3LYP/6-31G(d,p)	-8.8	-2.2	-9.8	3.4	-17.4
	1	x, y, z	4.75	B3LYP/6-31G(d,p)	-0.2	-0.9	-33.8	18.0	-19.2
	0	x+1/2, -y+1/2, z+1/2	7.37	B3LYP/6-31G(d,p)	-1.1	-0.4	-10.6	6.9	-6.5
	1	x, y, z	7.17	B3LYP/6-31G(d,p)	-8.3	-3.3	-9.0	6.1	-15.2
	0	x+1/2, -y+1/2, z+1/2	7.62	B3LYP/6-31G(d,p)	-0.6	-0.6	-9.5	4.6	-6.5
	1	-x, -y, -z	5.47	B3LYP/6-31G(d,p)	-1.5	-0.7	-18.1	9.8	-11.8
	0	x, y, z	9.03	B3LYP/6-31G(d,p)	0.4	-0.8	-2.6	0.2	-2.3
	1	-x, -y, -z	9.04	B3LYP/6-31G(d,p)	-131.3	-35.9	-12.8	157.4	-79.4
	0	-x, -y, -z	7.45	B3LYP/6-31G(d,p)	0.3	-0.9	-9.2	8.9	-2.9
				TOTALS	-151.1	-45.7	-115.4	215.3	-161.2

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618