

**supporting- Existence of untypical halogen-involved interactions in crystal packings:
A statistical and first-principles study**

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CSD SEARCH

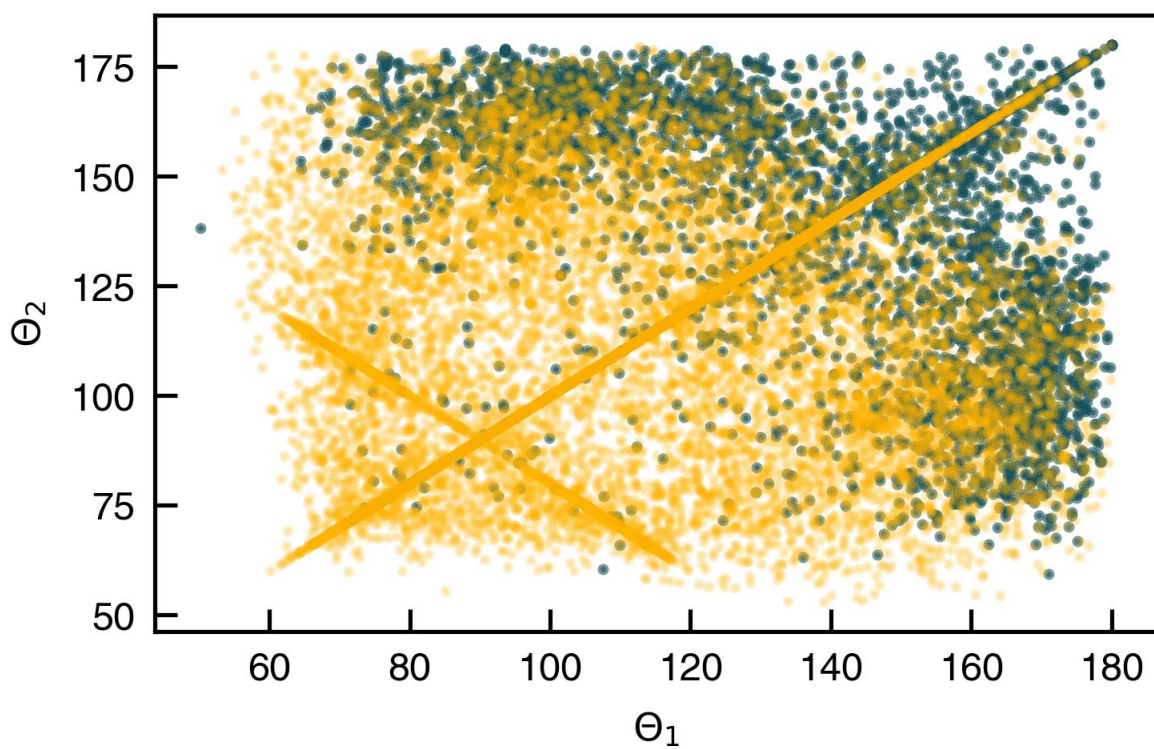


Figure 1: Scatter plot for searching at up to 10% more than the sum of the van der Waals radii of (C-Br...Br-C) which covers the (Br...Br < 4.07Å) range. Blue points stand for contacts with less than the sum of the van der Waals radii and golden points stand for contacts with up to 10% more than the sum of the van der Waals radii.

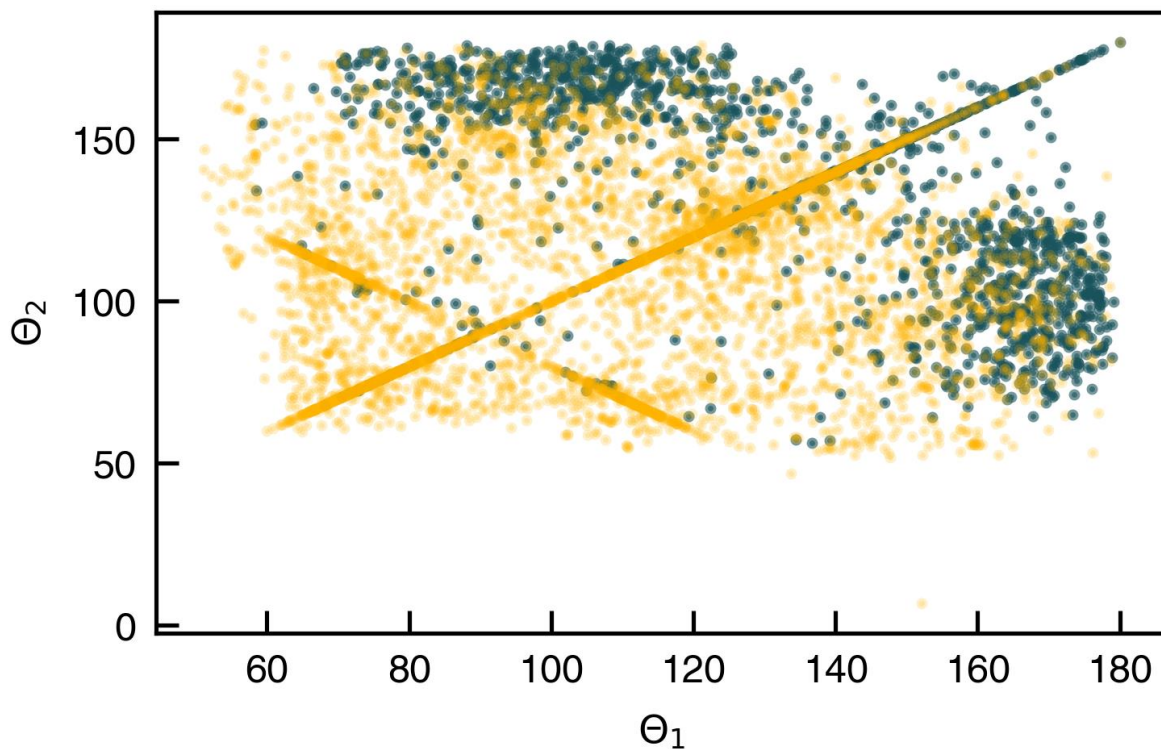


Figure 2: Scatter plot for searching at up to 10% more than the sum of the van der Waals radii of (C-I \cdots I-C) which covers the (I \cdots I < 4.36Å) range. Blue points stand for contacts with less than the sum of the van der Waals radii and golden points stand for contacts with up to 10% more than the sum of the van der Waals radii.

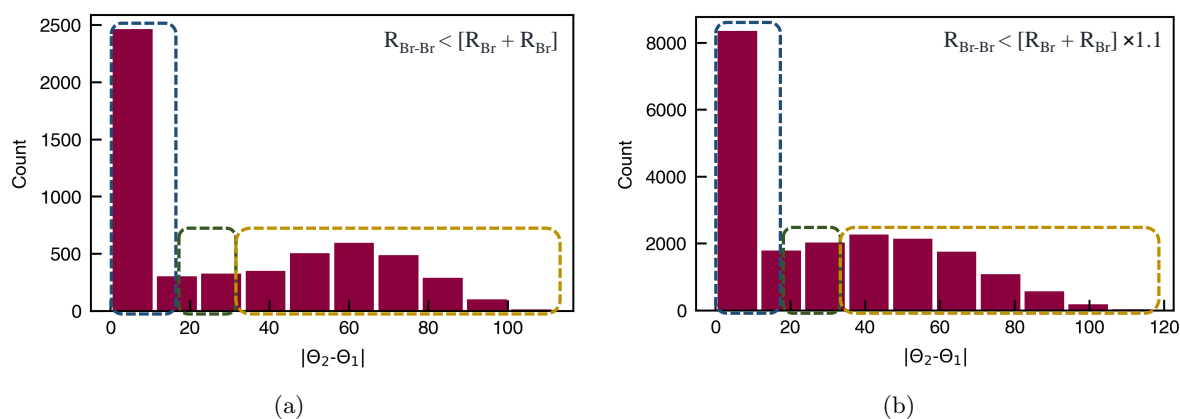


Figure 3: Bar chart of (C-Br \cdots Br-C) (a) searching at less than the sum of the van der Waals radii which covers the (Br \cdots Br < 3.70Å) range (b) Bar chart of (C-Br \cdots Br-C) for searching at up to 10% more than the sum of the van der Waals radii of (Br \cdots Br) which covers the (Br \cdots Br < 4.07Å) range. The domain with the golden dots line indicates type II interaction, the domain with the blue dots line indicates type I and the domain with the green dots line indicate quasi-type I interactions.

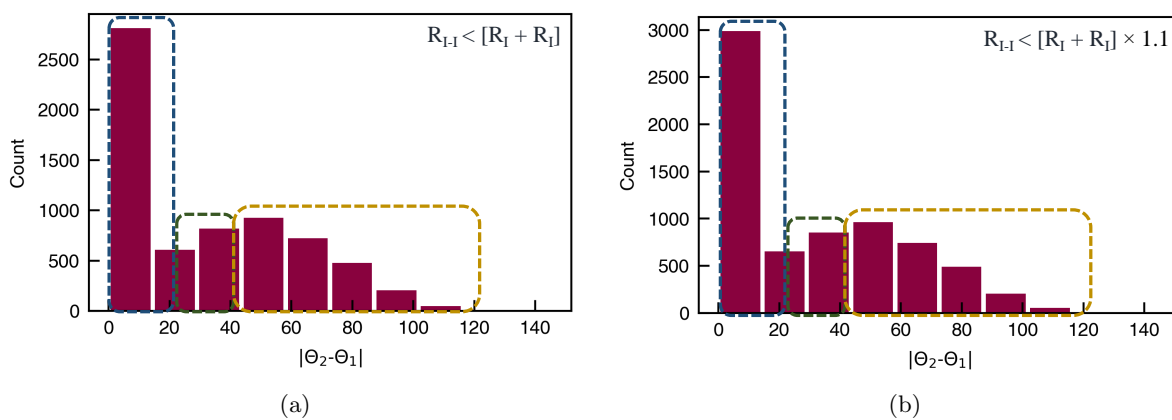


Figure 4: Bar chart of (C-I...I-C) (a) searching at less than the sum of the van der Waals radii which covers the (I...I $< 3.96\text{\AA}$) range (b) Bar chart of (C-I...I-C) for searching at up to 10% more than the sum of the van der Waals radii of (I...I) which covers the (I...I $< 4.36\text{\AA}$) range. The domain with the golden dots line indicates type II interaction, the domain with the blue dots line indicates type I and the domain with the green dots line indicate quasi-type I interactions.

COUPLES PICTURES

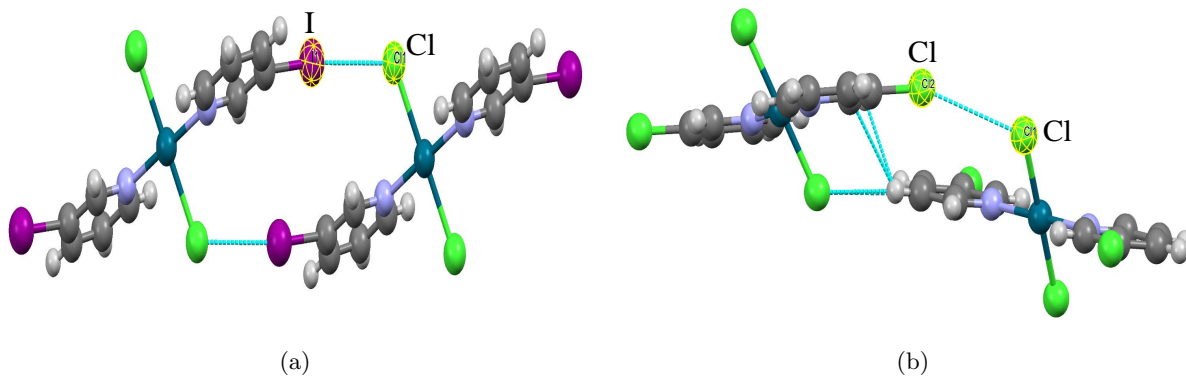


Figure 5: Dimers contain halogen-involved interactions of cop4; (a) cop4-I dimer involved I...Cl interaction (b) cop2-Cl dimer involved Cl...Cl interaction

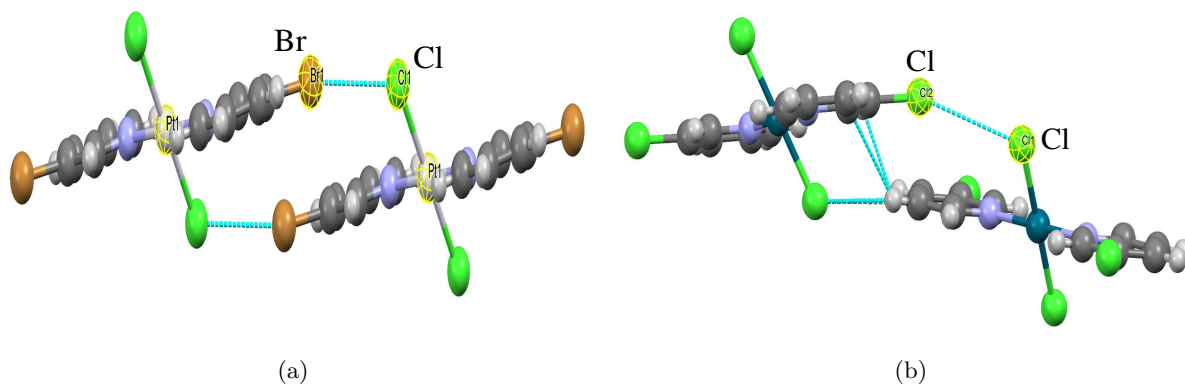


Figure 6: Dimers contain halogen-involved interactions of cop5; (a) cop5-Br dimer involved Br \cdots Cl interaction (b) cop5-Cl dimer involved Cl \cdots Cl interaction

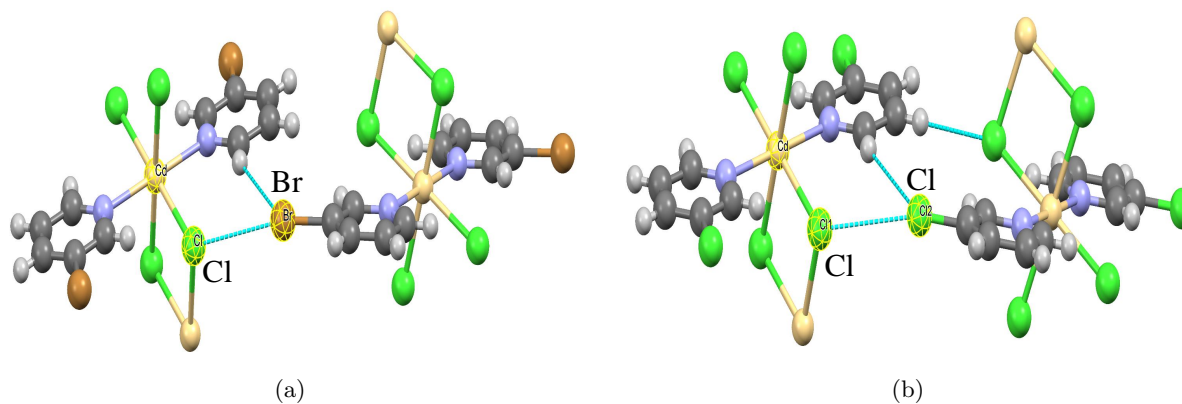


Figure 7: Dimers with halogen-involved interactions of cop6; (a) cop6-Br dimer involved Br \cdots Cl interaction (b) cop6-Cl dimer involved Cl \cdots Cl interactions

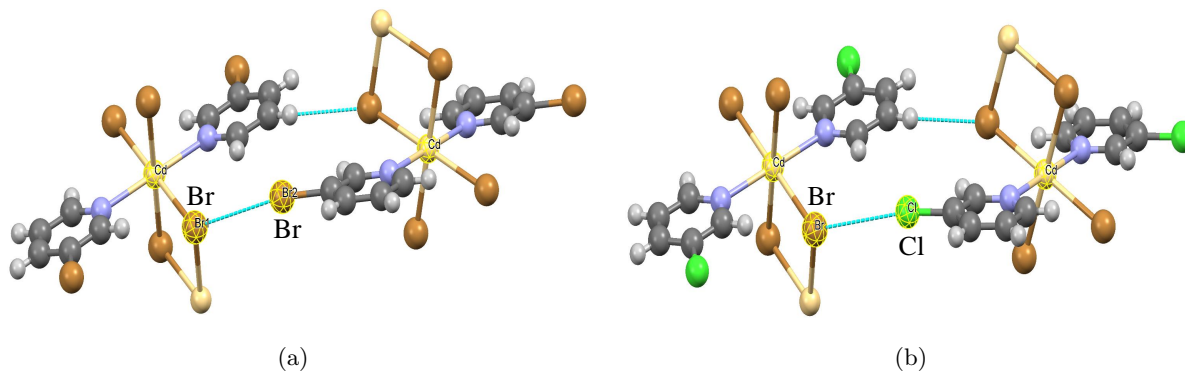


Figure 8: Dimers with halogen-involved interactions of cop7; (a) cop7-Br dimer involved Br \cdots Br interaction (b) cop7-Cl dimer involved Br \cdots Cl interaction

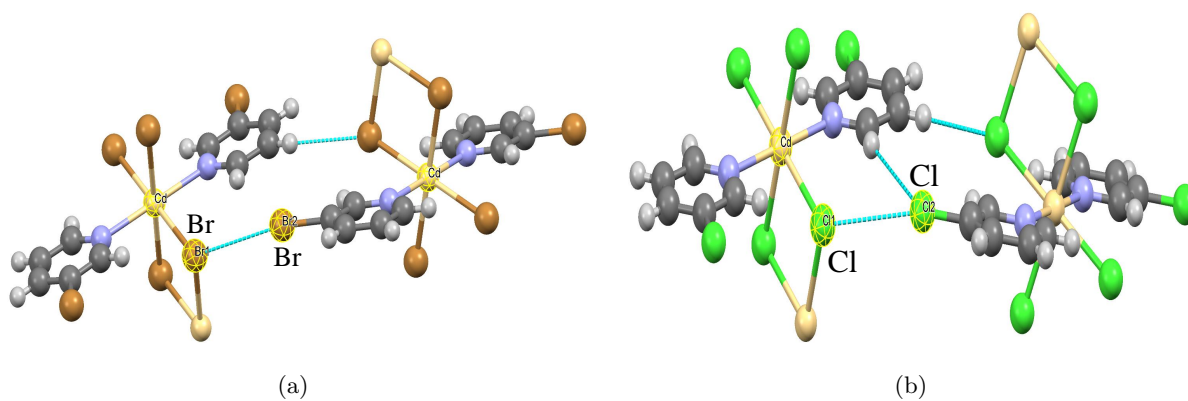


Figure 9: Dimers with halogen-involved interactions of cop8; (a) cop8-Br dimer involved Br \cdots Br interaction (b) cop8-Cl dimer involved Cl \cdots Cl interaction

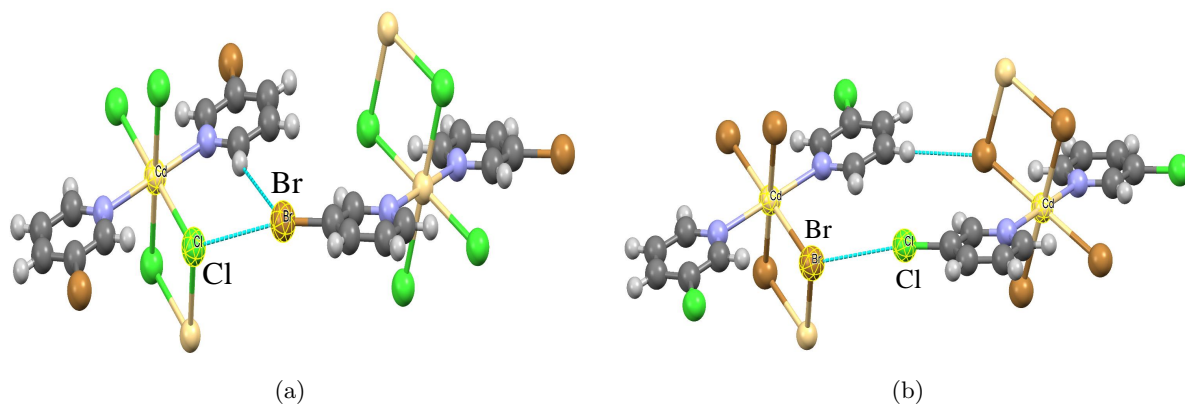


Figure 10: Dimers with halogen-involved interactions of cop9; (a) cop9-Br dimer involved Br \cdots Cl interaction (b) cop9-Cl dimer involved Br \cdots Cl interaction

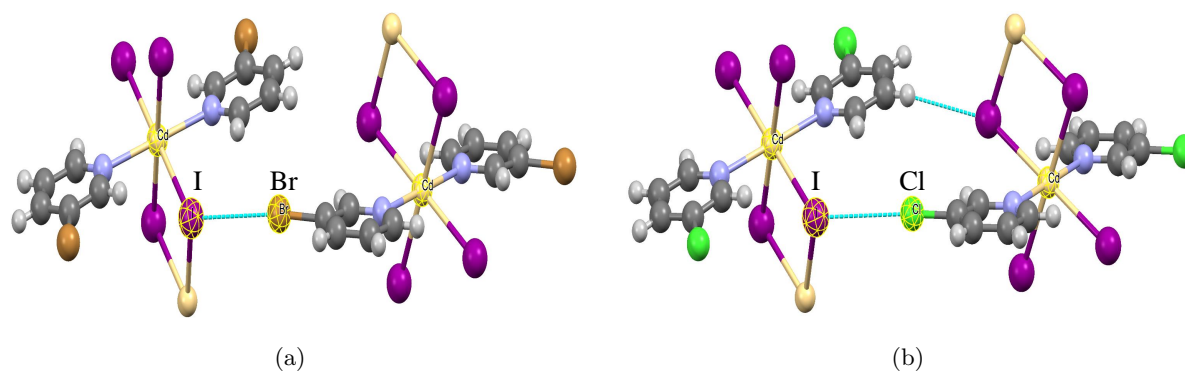


Figure 11: Dimers with halogen-involved interactions of cop10; (a) cop10-Br dimer involved Br \cdots Br interaction (b) cop10-Cl dimer involved Cl \cdots Cl interaction

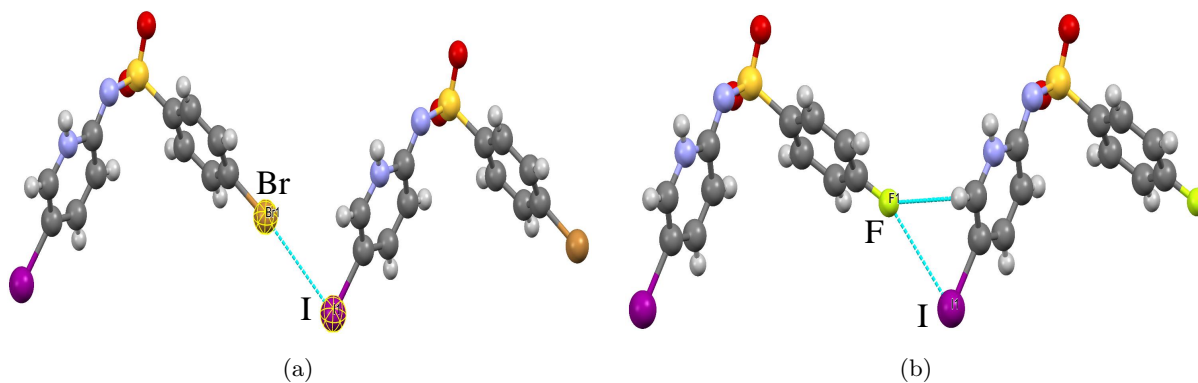


Figure 12: Dimers with halogen-involved interactions of cop11; (a) cop11-Br dimer involved Br \cdots I interaction (b) cop11-F dimer involved F \cdots I interaction

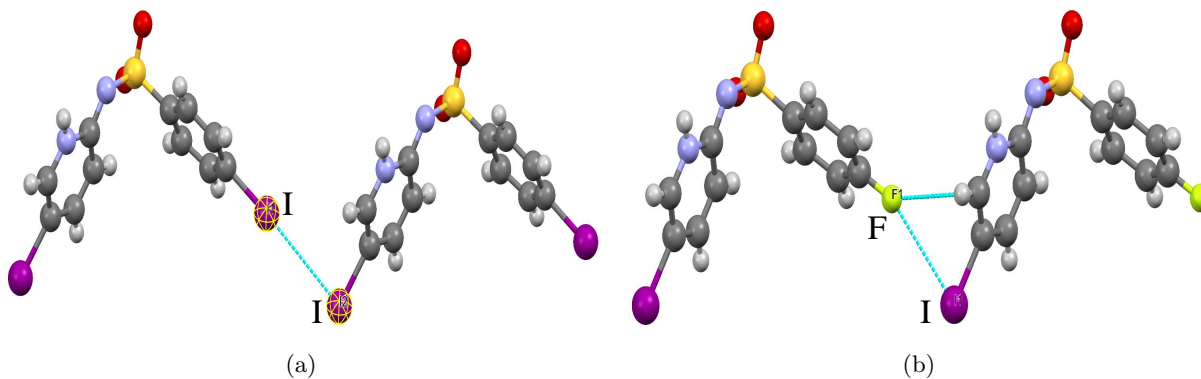


Figure 13: Dimers with halogen-involved interactions of cop12; (a) cop12-I dimer involved I \cdots I interaction (b) cop12-F dimer involved I \cdots F interaction

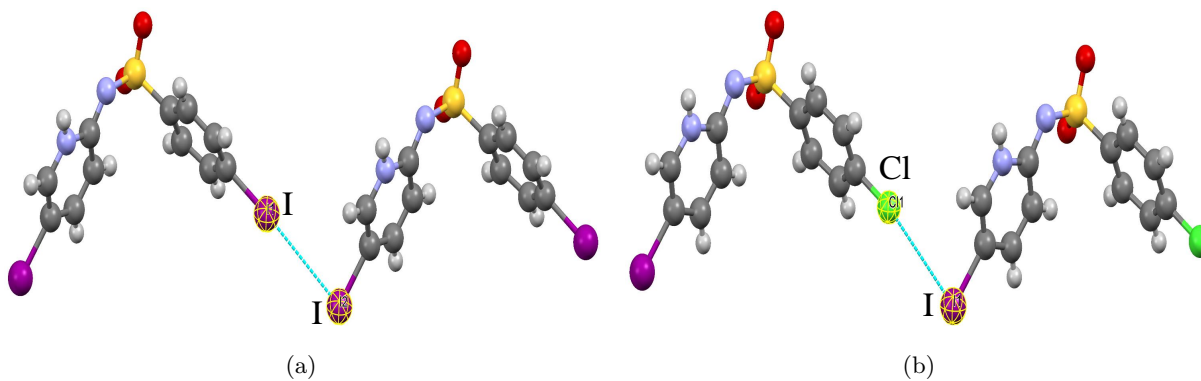


Figure 14: Dimers with halogen-involved interactions of cop13; (a) cop13-I dimer involved I \cdots I interaction (b) cop13-F dimer involved I \cdots F interaction

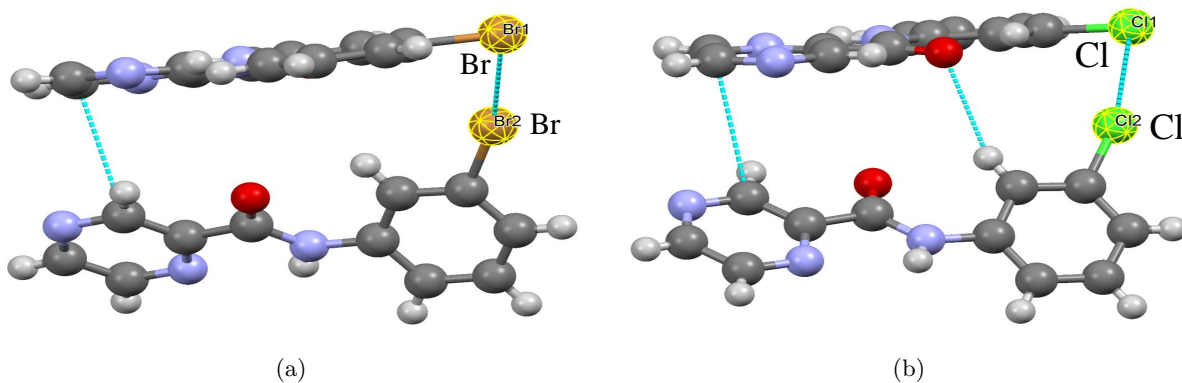


Figure 15: Dimers with halogen-involved interactions of cop14; (a) cop14-Br dimer involved Br \cdots Br interaction (b) cop14-Cl dimer involved Cl \cdots Cl interaction

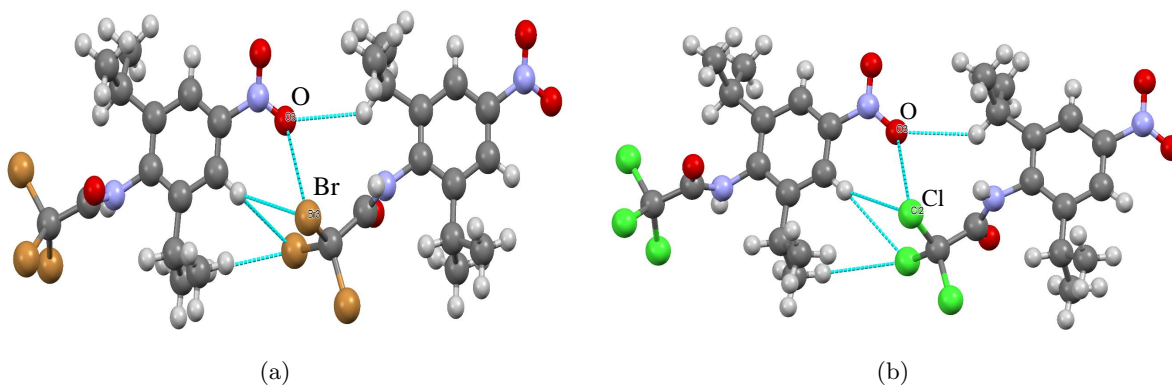


Figure 16: Dimers with halogen-involved interactions of cop15; (a) cop15-Br dimer involved Br \cdots O interaction (b) cop15-Cl dimer involved Cl \cdots O interaction

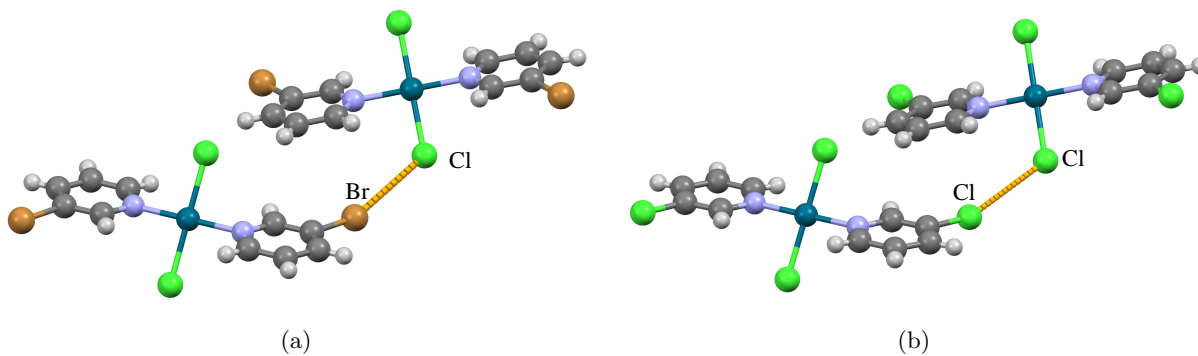


Figure 17: Dimers with halogen-involved interactions of cop16; (a) cop16-Br dimer involved Br \cdots Cl interaction (b) cop16-Cl dimer involved Cl \cdots Cl interaction

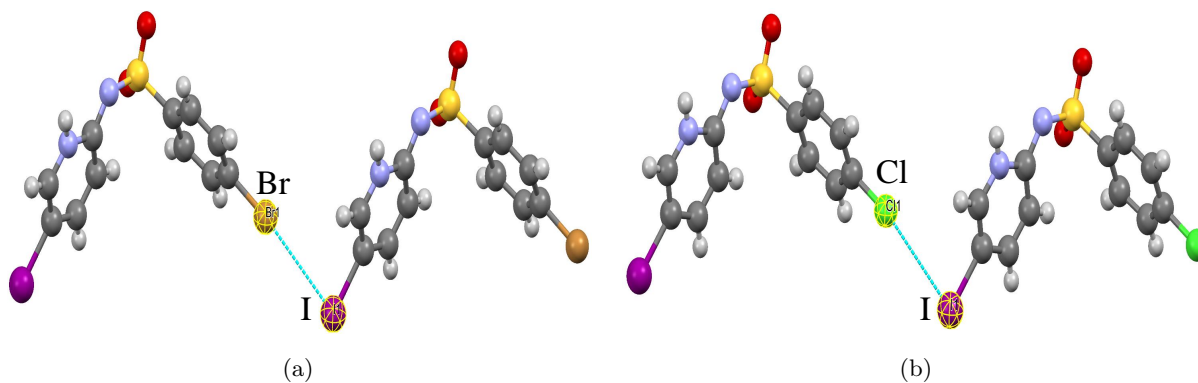


Figure 18: Dimers with halogen-involved interactions of cop17; (a) cop17-Br dimer involved Br \cdots I interaction (b) cop17-Cl dimer involved Cl \cdots I interaction

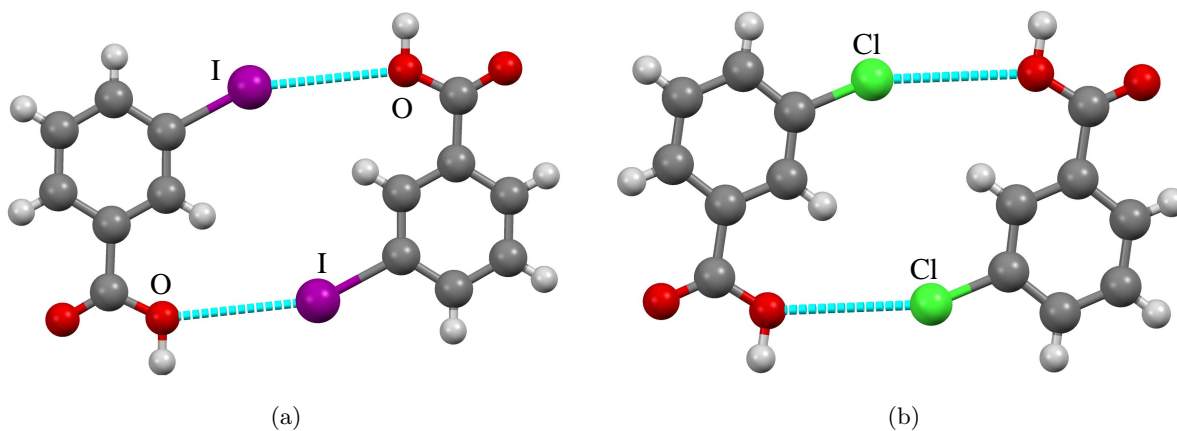


Figure 19: Dimers with halogen-involved interactions of cop18; (a) cop18-I dimer involved I \cdots O interaction (b) cop18-Cl dimer involved Cl \cdots O interaction

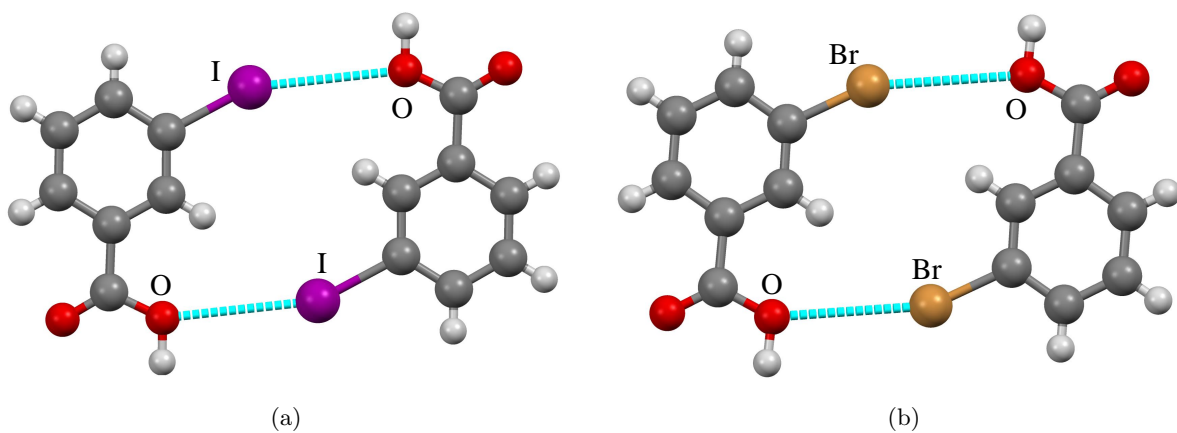


Figure 20: Dimers with halogen-involved interactions of cop19; (a) cop19-I dimer involved I \cdots O interaction (b) cop19-Br dimer involved Br \cdots O interaction

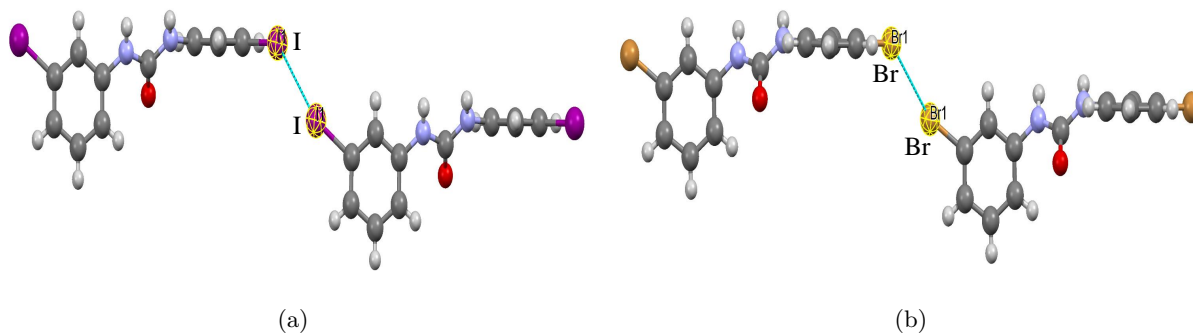


Figure 21: Dimers with halogen-involved interactions of cop20; (a) cop20-I dimer involved I \cdots I interaction (b) cop20-Br dimer involved Br \cdots Br interaction

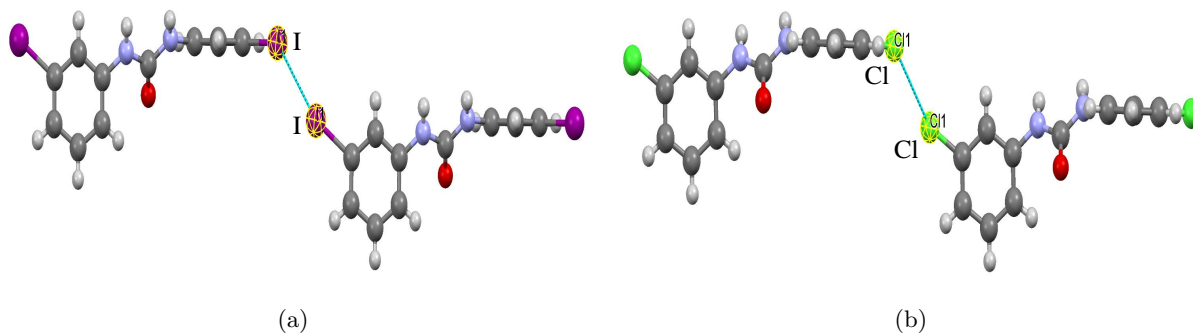


Figure 22: Dimers with halogen-involved interactions of cop21; (a) cop21-I dimer involved I \cdots I interaction (b) cop21-Cl dimer involved Cl \cdots Cl interaction

HIRSHFELD FINGERPRINTS

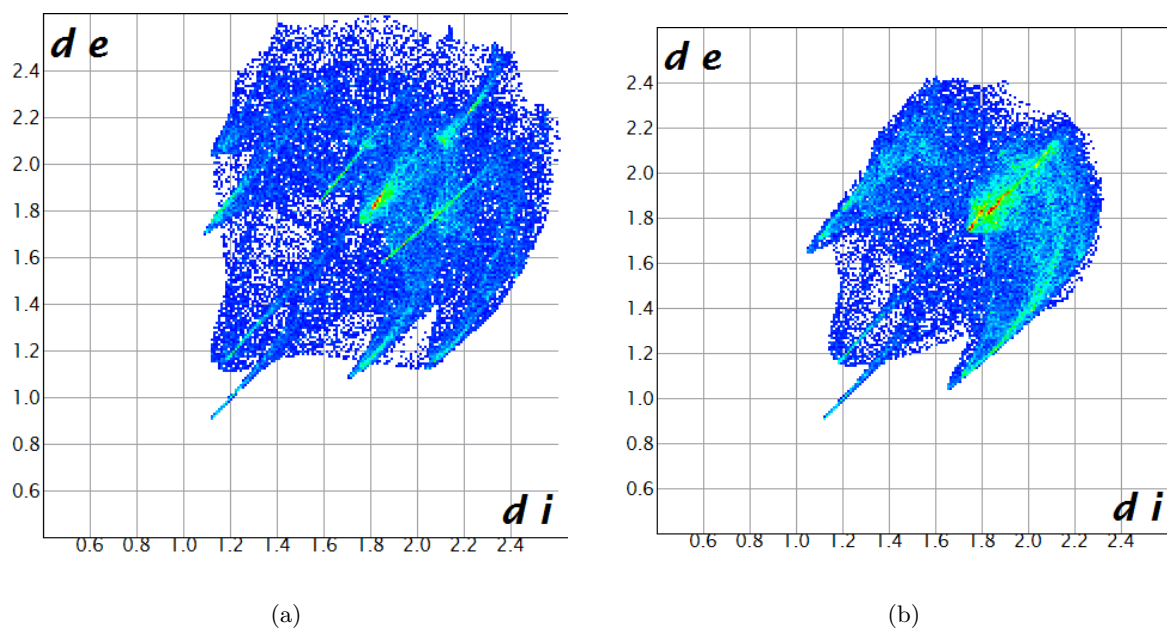


Figure 23: Hirshfeld fingerprint plots for (a) Cop4-I and (b) cop4-cl. The dissimilarity index of the two structures is $x = 3.1$

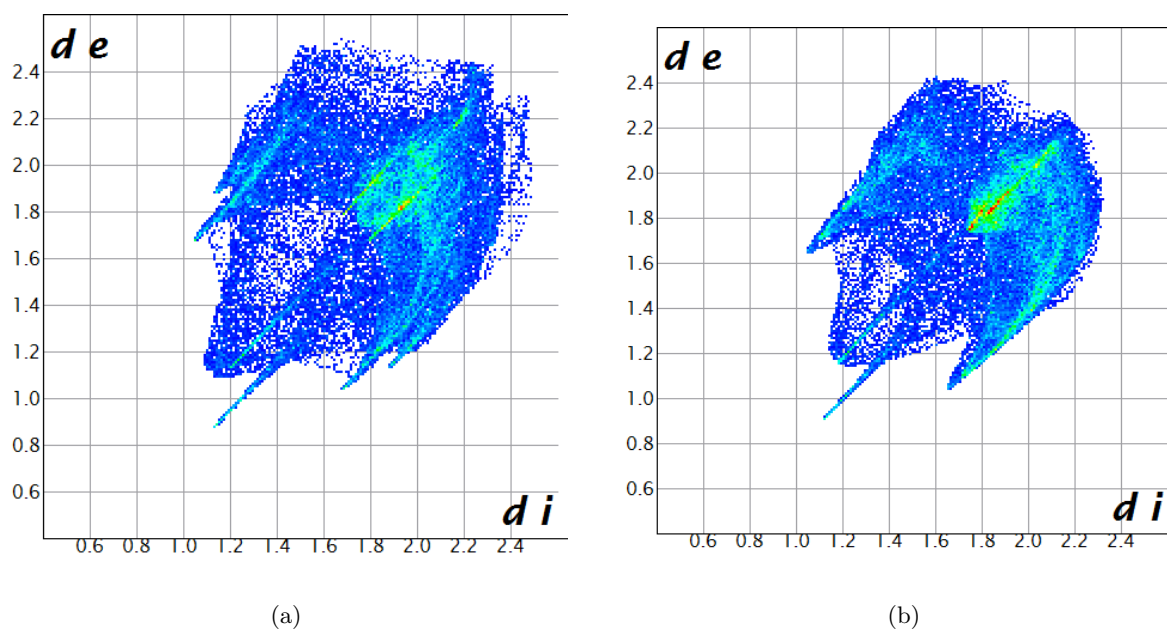


Figure 24: Hirshfeld fingerprint plots for (a) Cop5-Br and (b) cop5-Cl. The dissimilarity index of the two structures is $x = 2.6$

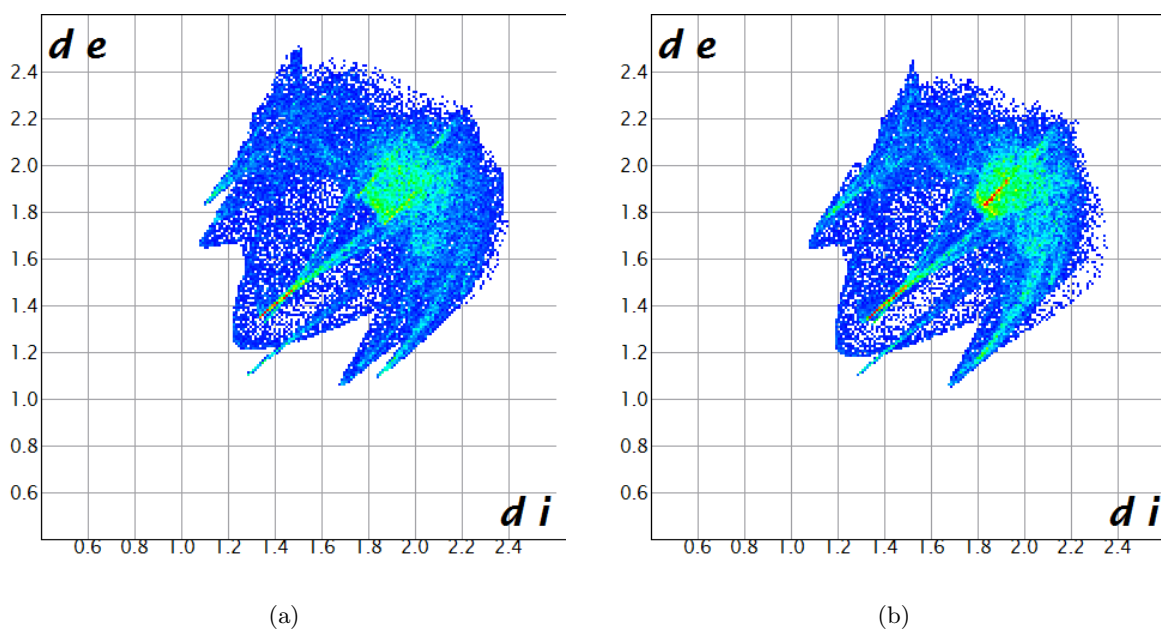


Figure 25: Hirshfeld fingerprint plots for (a) Cop6-Br and (b) cop6-Cl. The dissimilarity index of the two structures is $x = 0.4$

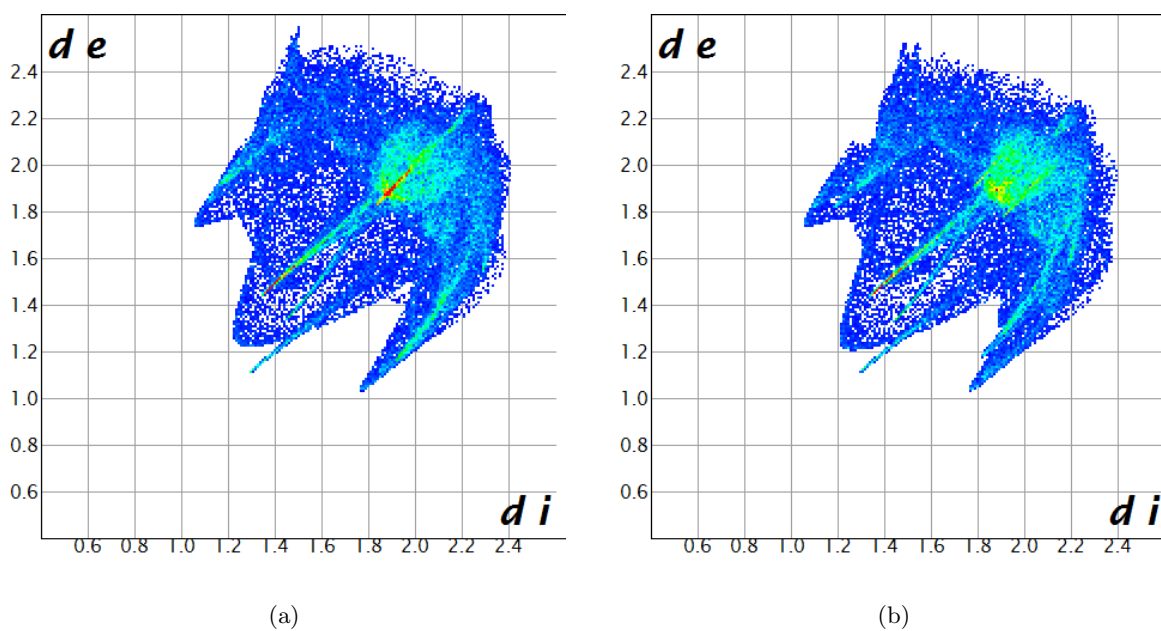


Figure 26: Hirshfeld fingerprint plots for (a) Cop7-Br and (b) cop7-Cl. The dissimilarity index of the two structures is $x = 0.5$

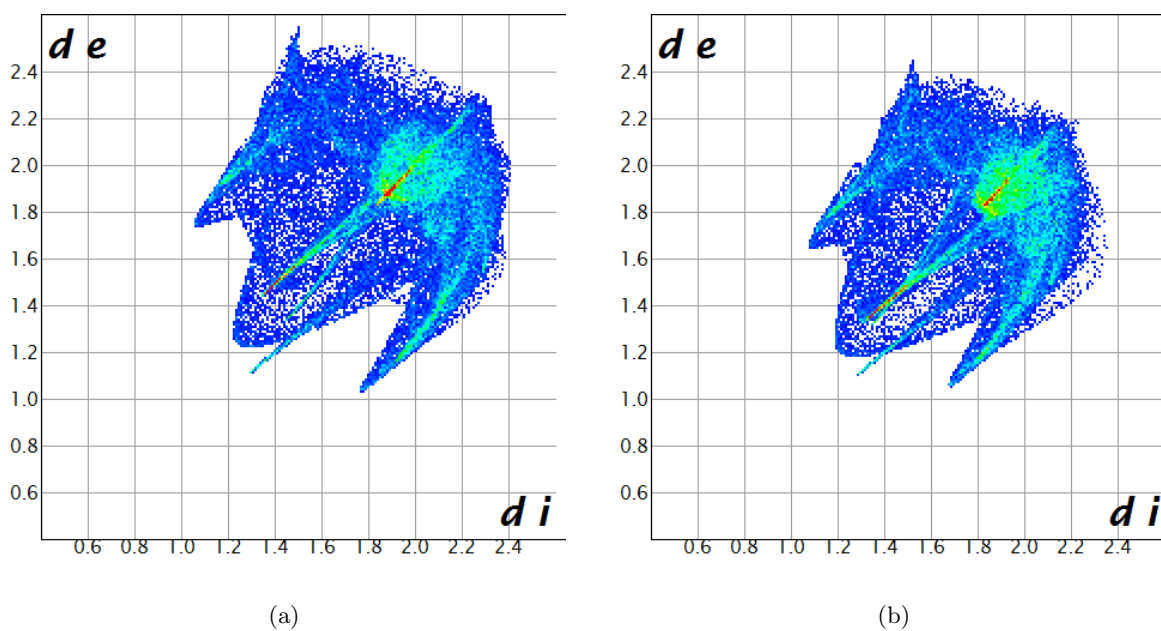


Figure 27: Hirshfeld fingerprint plots for (a) Cop8-Br and (b) cop8-Cl. The dissimilarity index of the two structures is $x = 0.4$

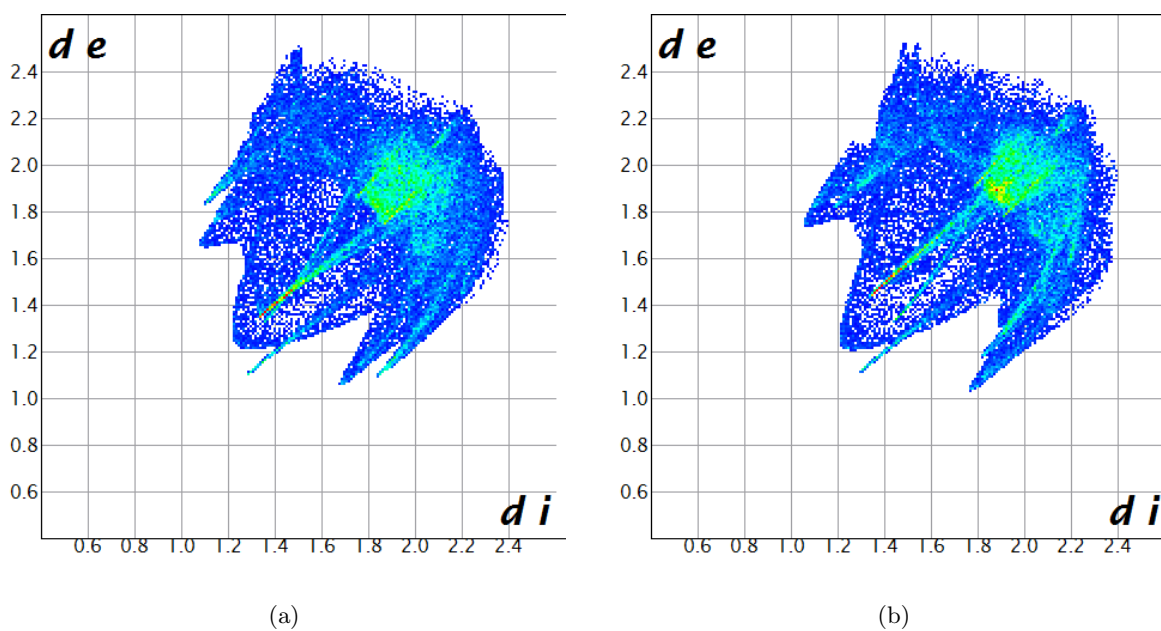


Figure 28: Hirshfeld fingerprint plots for (a) Cop9-Br and (b) cop9-Cl. The dissimilarity index of the two structures is $x = 0.4$

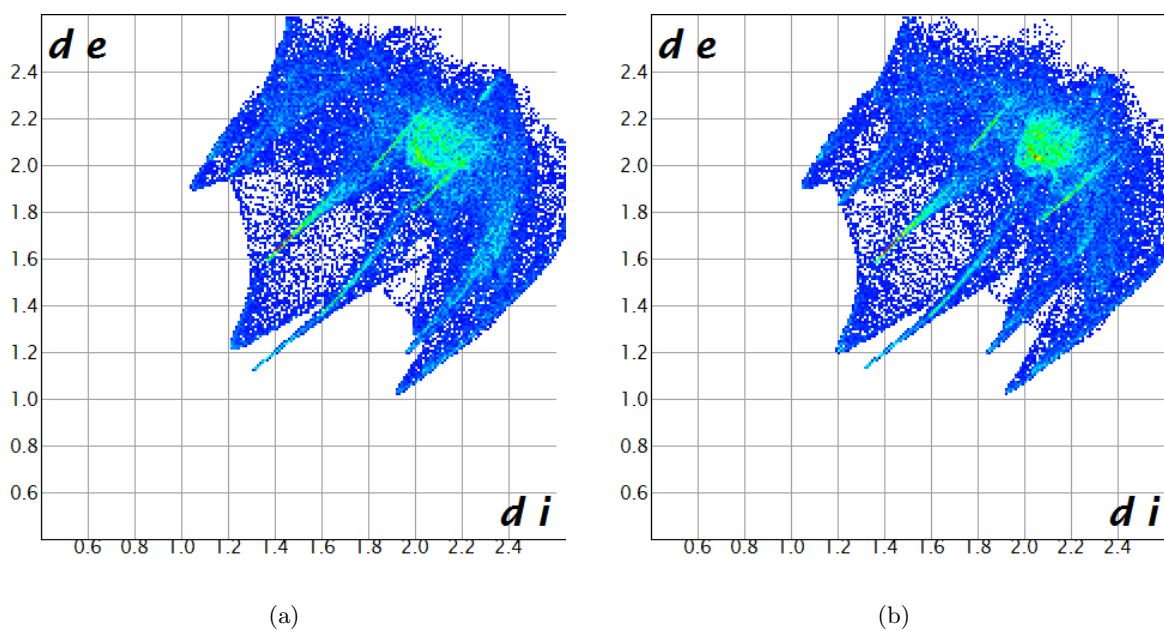


Figure 29: Hirshfeld fingerprint plots for (a) Cop10-Br and (b) cop10-Cl. The dissimilarity index of the two structures is $x = 0.4$

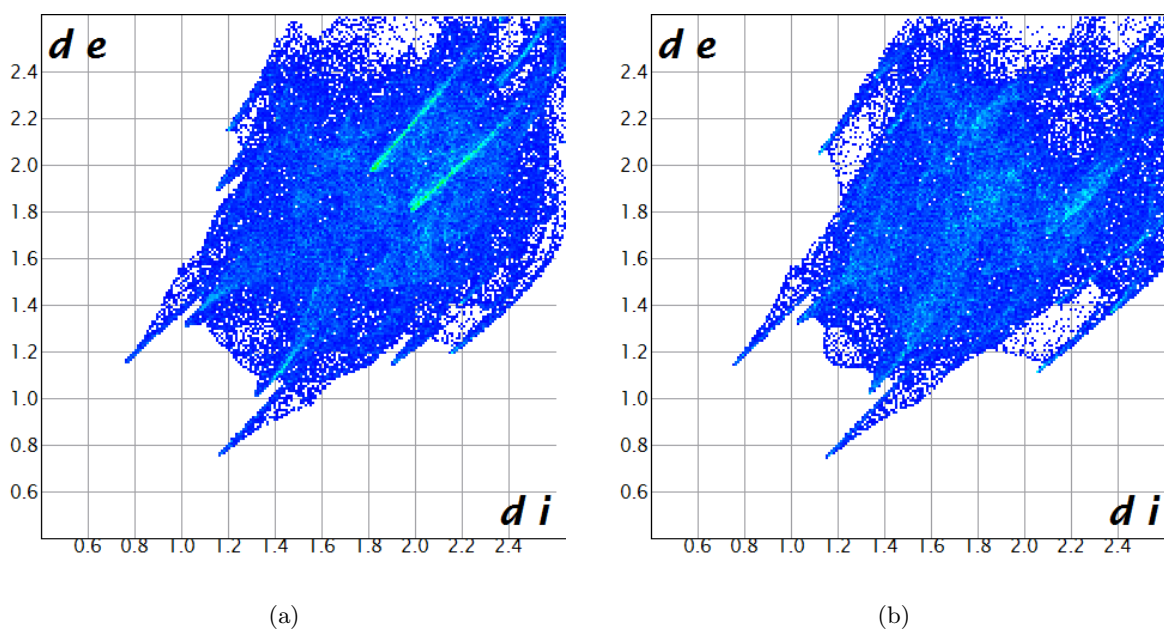


Figure 30: Hirshfeld fingerprint plots for (a) Cop11-Br and (b) cop11-F. The dissimilarity index of the two structures is $x = 6.1$

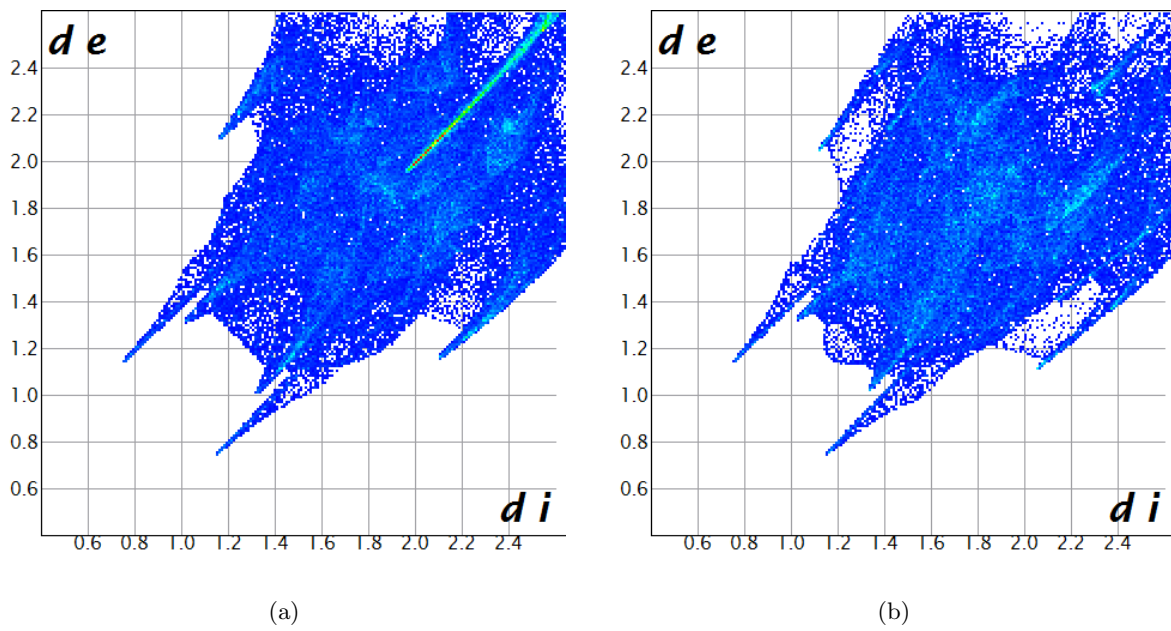


Figure 31: Hirshfeld fingerprint plots for (a) Cop12-I and (b) cop12-F. The dissimilarity index of the two structures is $x = 6.8$

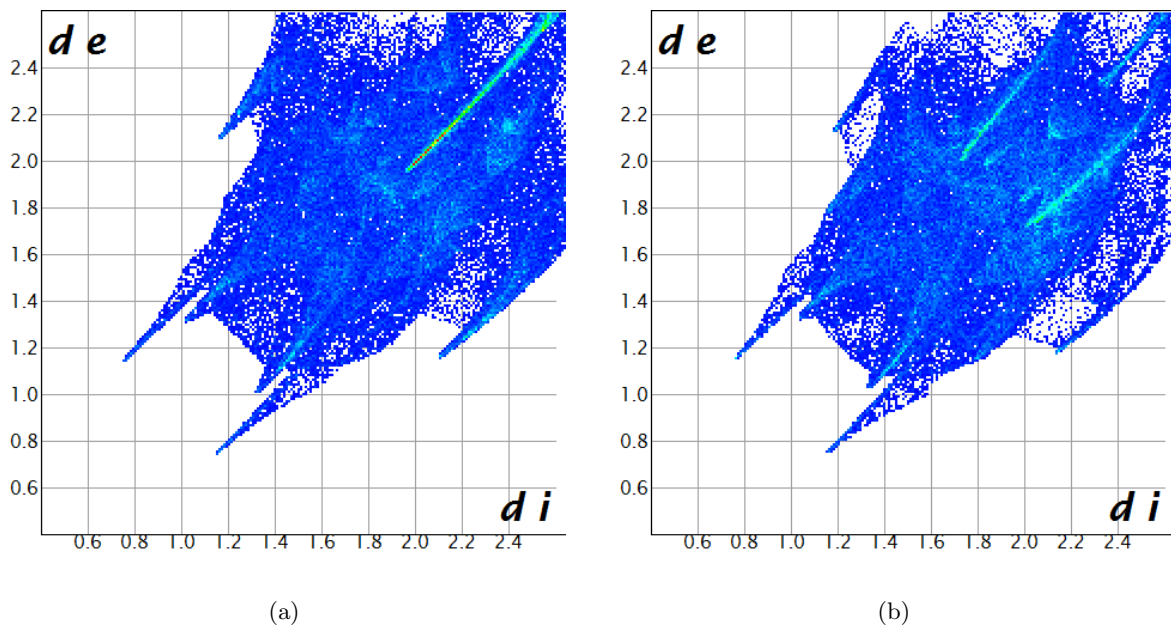


Figure 32: Hirshfeld fingerprint plots for (a) Cop13-I and (b) cop13-Cl. The dissimilarity index of the two structures is $x = 2.1$

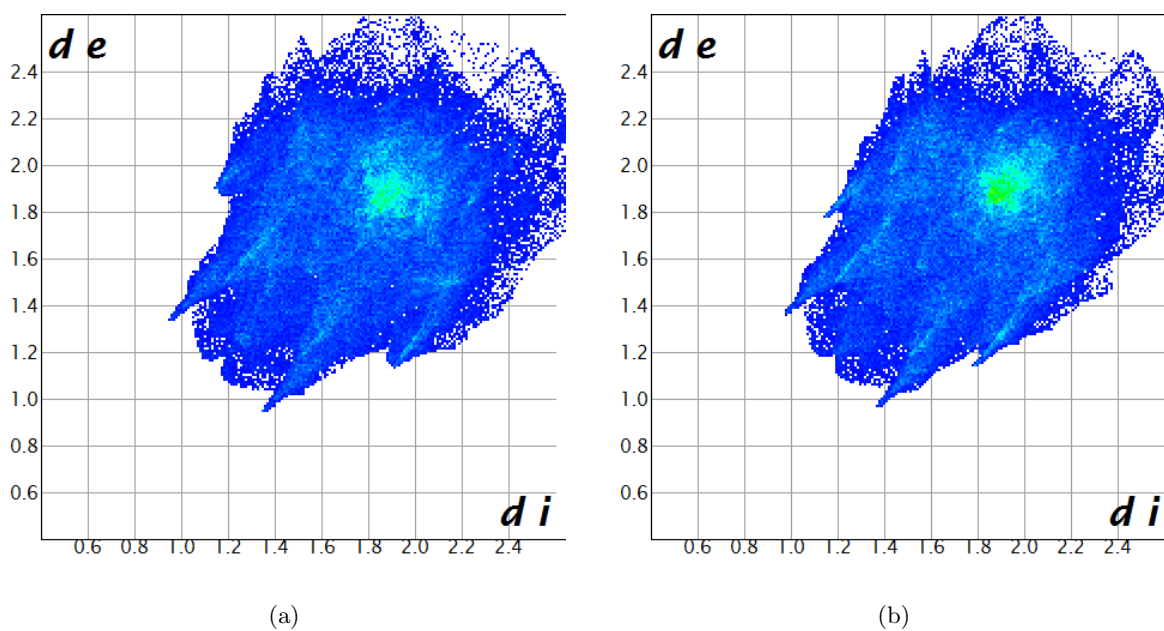


Figure 33: Hirshfeld fingerprint plots for (a) Cop14-Br and (b) cop14-Cl. The dissimilarity index of the two structures is $x = 1.6$

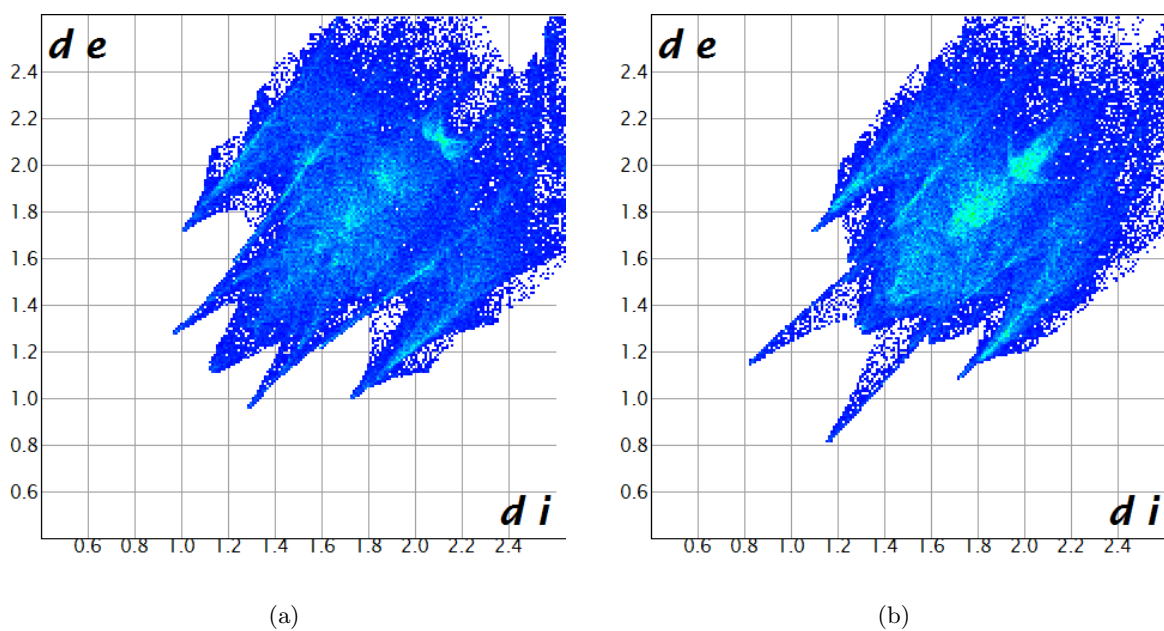


Figure 34: Hirshfeld fingerprint plots for (a) Cop15-Br and (b) cop15-Cl. The dissimilarity index of the two structures is $x = 4.7$

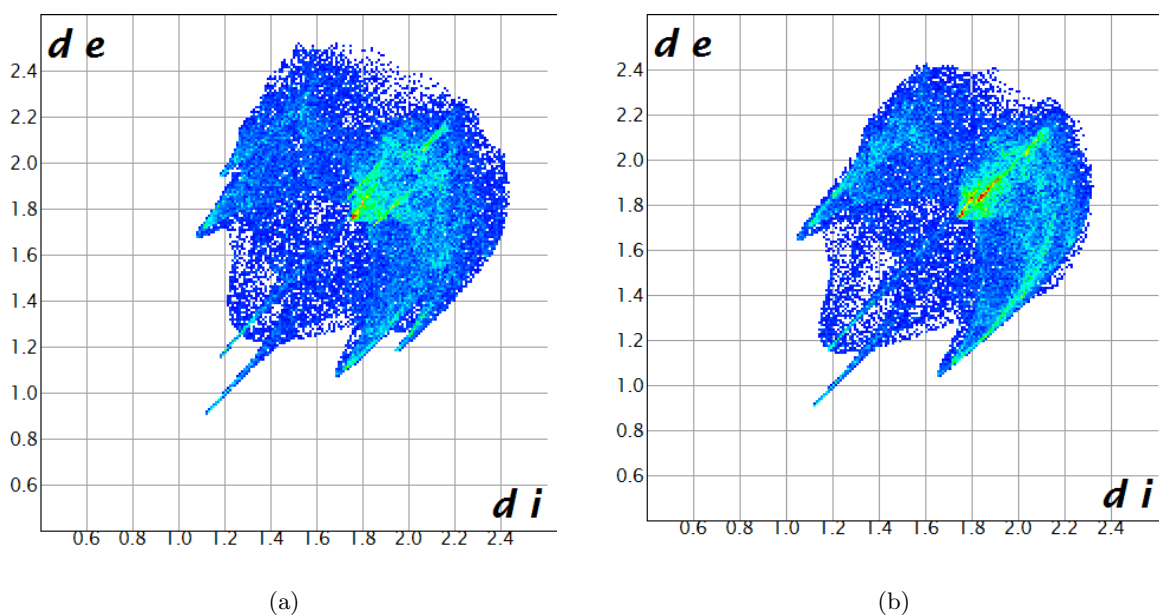


Figure 35: Hirshfeld fingerprint plots for (a) Cop16-Br and (b) cop16-Cl. The dissimilarity index of the two structures is $x = 0.4$

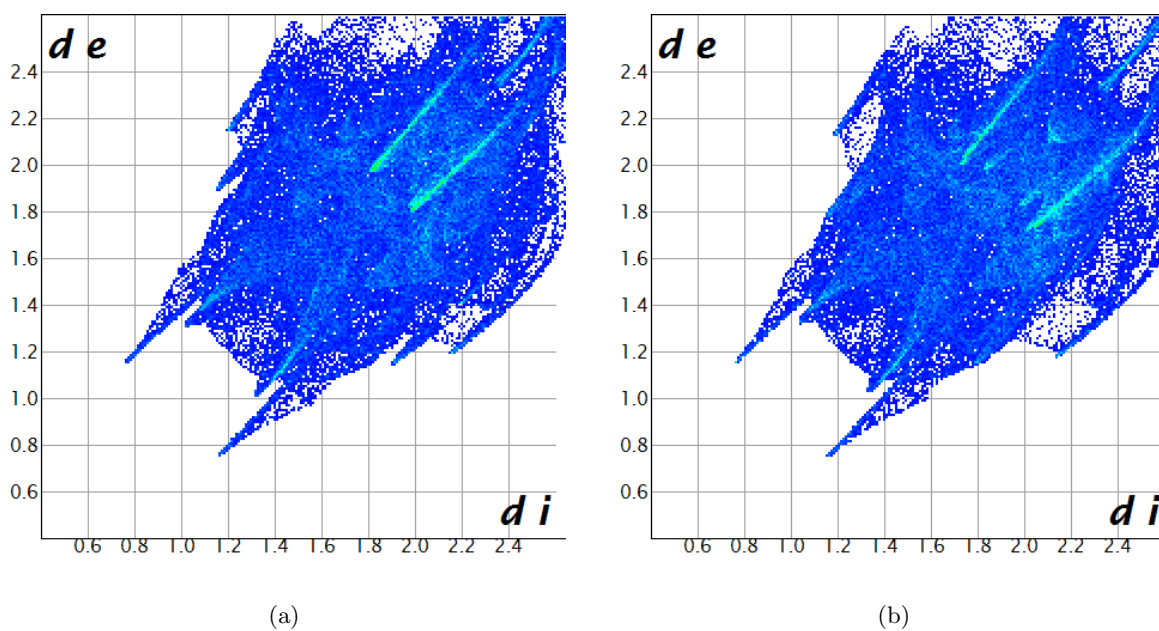


Figure 36: Hirshfeld fingerprint plots for (a) Cop17-Br and (b) cop17-Cl. The dissimilarity index of the two structures is $x = 0.4$

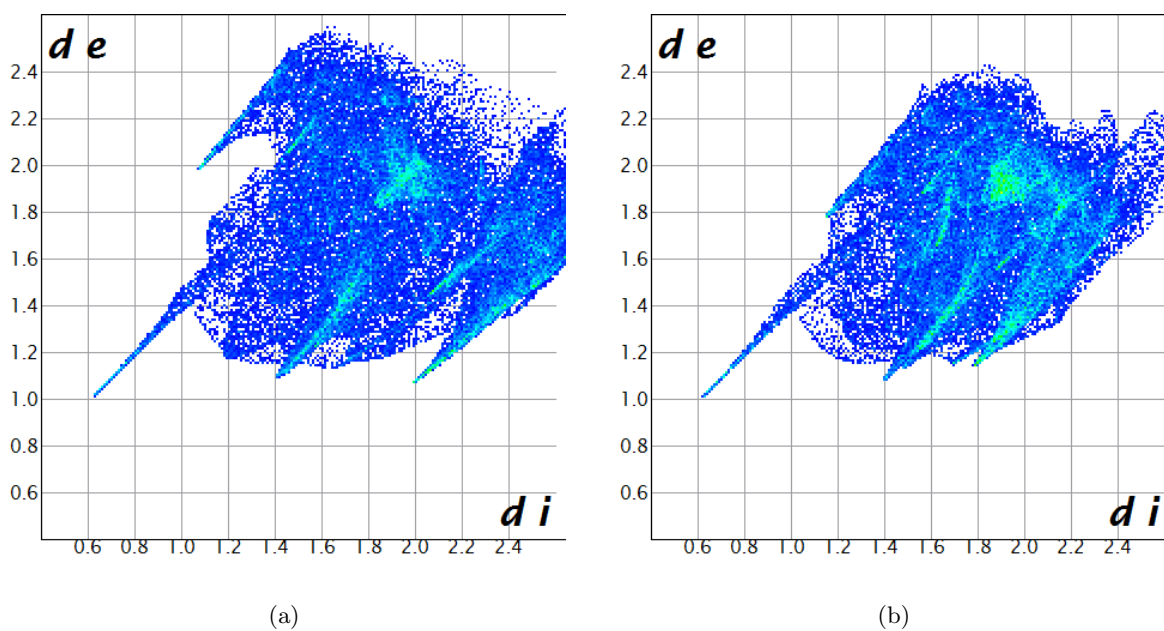


Figure 37: Hirshfeld fingerprint plots for (a) Cop18-I and (b) cop18-Cl. The dissimilarity index of the two structures is $x = 7.4$

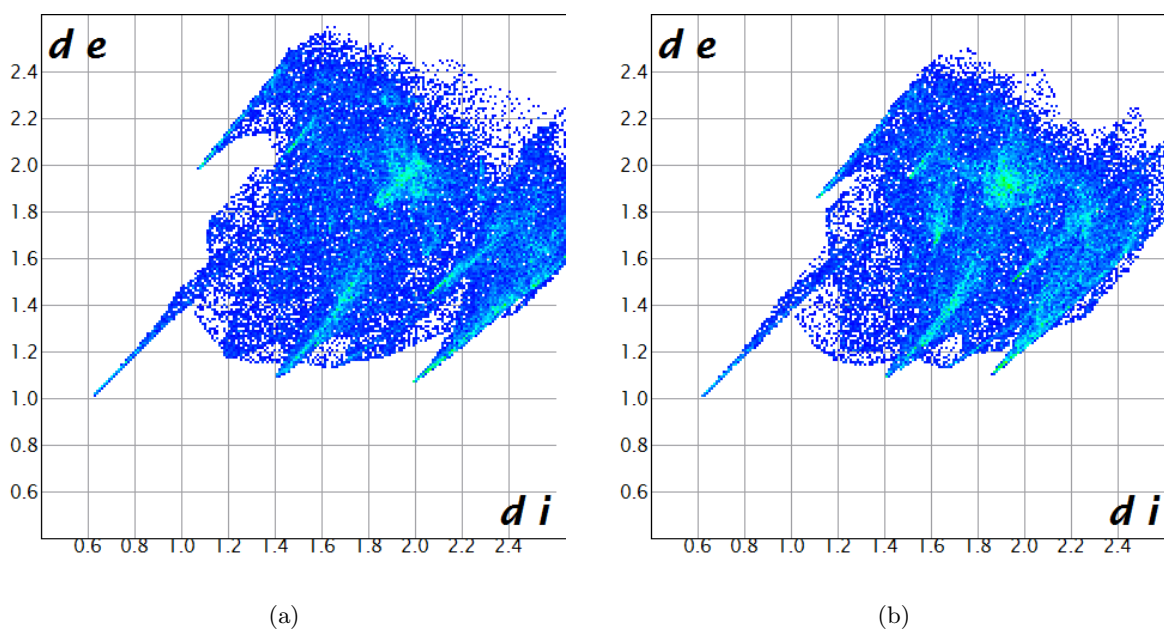


Figure 38: Hirshfeld fingerprint plots for (a) Cop19-I and (b) cop19-Br. The dissimilarity index of the two structures is $x = 4.3$

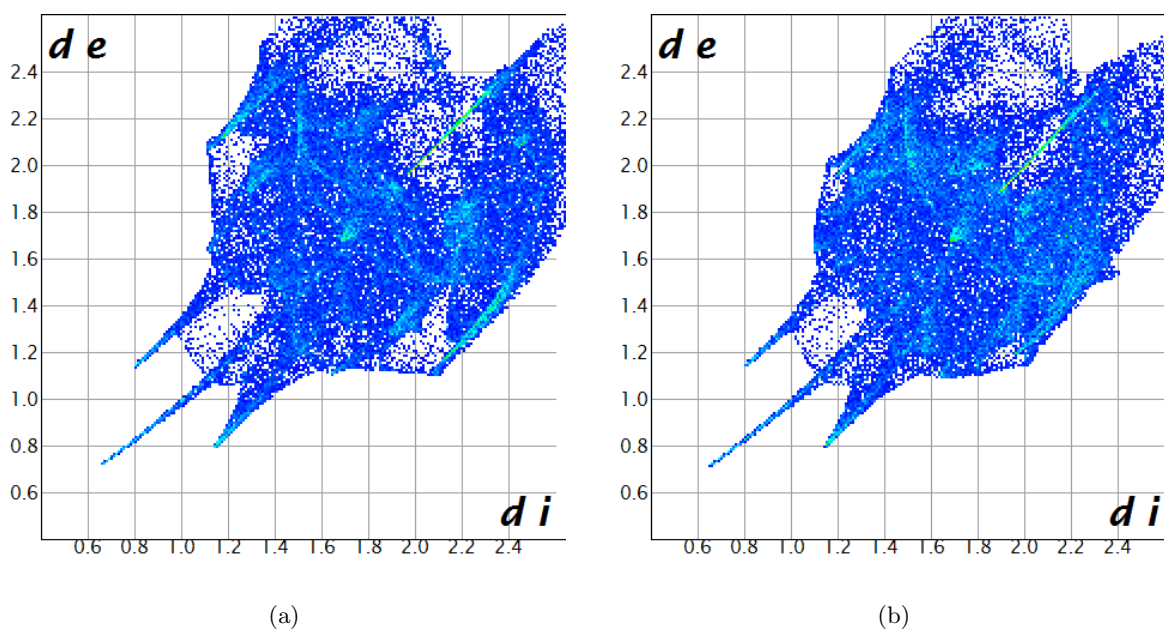


Figure 39: Hirshfeld fingerprint plots for (a) Cop20-I and (b) cop20-Br. The dissimilarity index of the two structures is $x = 4.7$

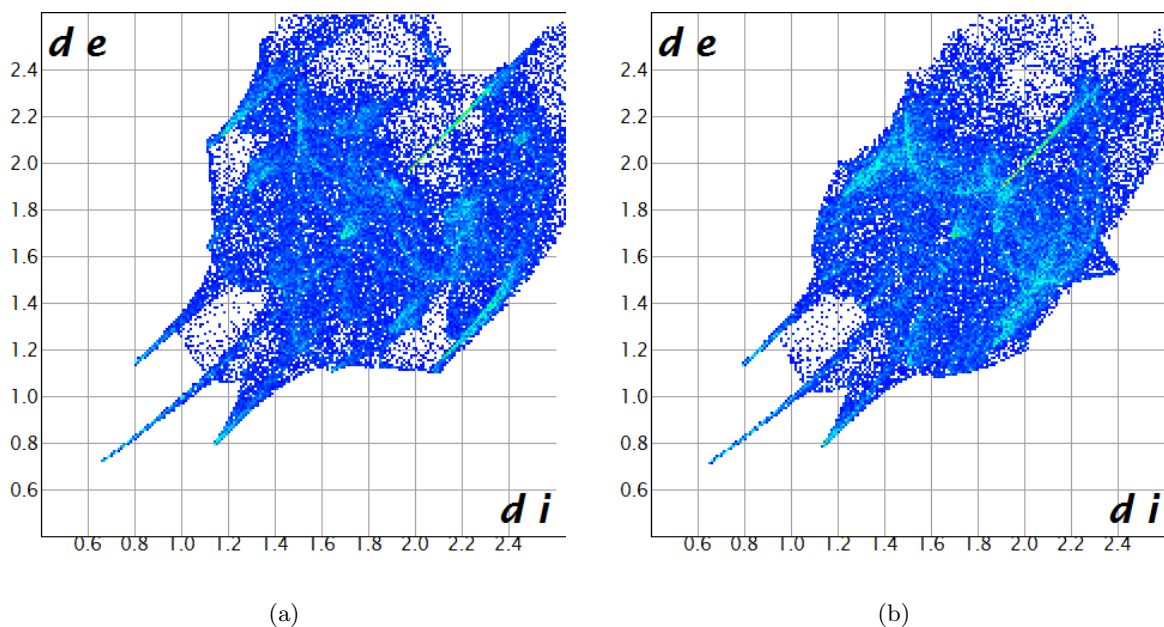


Figure 40: Hirshfeld fingerprint plots for (a) Cop21-I and (b) cop21-Cl. The dissimilarity index of the two structures is $x = 4.8$

Table I: Geometric Parameters of π -involved interactions in couples

Couple	Interaction	C-C Distance (\AA)	P-P($^\circ$)	P-CC ($^\circ$)
cop4-I	$\pi_{\text{Pyridine}} \cdots \pi_{\text{Pyridine}}$	4.15	0.0	28.30, 28.30
cop4-Cl	$\pi_{\text{Pyridine}} \cdots \pi_{\text{Pyridine}}$	3.91	0.0	24.45, 24.47
cop5-Br	$\pi_{\text{Pyridine}} \cdots \pi_{\text{Pyridine}}$	3.97	0.0	23.68, 26.97
cop5-Cl	$\pi_{\text{Pyridine}} \cdots \pi_{\text{Pyridine}}$	3.91	0.0	24.45, 24.47

cop6-Br	π Pyridine $\cdots\pi$ Pyridine	3.85	0.0	21.23, 21.49
cop6-Cl	π Pyridine $\cdots\pi$ Pyridine	3.81	0.0	20.79, 20.92
cop7-Br	π Pyridine $\cdots\pi$ Pyridine	3.94	0.0	20.45, 20.70
cop7-Cl	π Pyridine $\cdots\pi$ Pyridine	3.91	0.0	20.26, 19.66
cop8-Br	π Pyridine $\cdots\pi$ Pyridine	3.94	0.0	20.45, 20.70
cop8-Cl	π Pyridine $\cdots\pi$ Pyridine	3.81	0.0	20.79, 20.92
cop9-Br	π Pyridine $\cdots\pi$ Pyridine	3.85	0.0	21.23, 21.49
cop9-Cl	π Pyridine $\cdots\pi$ Pyridine	3.91	0.0	20.26, 19.66
cop10-Br	π Pyridine $\cdots\pi$ Pyridine	4.14	0.0	19.02, 18.41
cop10-Cl	π Pyridine $\cdots\pi$ Pyridine	4.13	0.0	17.94, 18.30
cop11-Br	π Pyridine $\cdots\pi$ Pyridine	5.56	0.0	47.31, 46.91
cop11-F	π Pyridine $\cdots\pi$ Pyridine	6.01	0.0	49.36, 49.94
cop12-I	π Pyridine $\cdots\pi$ Pyridine	5.68	0.0	47.99, 47.97
cop12-F	π Pyridine $\cdots\pi$ Pyridine	6.01	0.0	49.36, 49.94
cop13-I	π Pyridine $\cdots\pi$ Pyridine	5.68	0.0	47.99, 47.97
cop13-Cl	π Pyridine $\cdots\pi$ Pyridine	5.58	0.0	46.50, 47.19
cop14-Br	π Phenyl $\cdots\pi$ Pyrazine	3.95	7.31	27.15, 28.37
cop14-Cl	π Phenyl $\cdots\pi$ Pyrazine	3.94	6.11	26.05, 27.15
cop16-Br	π Pyridine $\cdots\pi$ Pyridine	3.95	0.0	24.41, 24.80
cop16-Cl	π Pyridine $\cdots\pi$ Pyridine	3.91	0.0	24.45, 24.47
cop17-Br	π Pyridine $\cdots\pi$ Pyridine	5.56	0.0	47.31, 46.91
cop17-Cl	π Pyridine $\cdots\pi$ Pyridine	5.58	0.0	46.50, 47.19
cop18-I	π Acridine $\cdots\pi$ Acridine	4.20	0.0	16.37, 16.55
cop18-Cl	π Acridine $\cdots\pi$ Acridine	3.82	0.33	15.55, 15.55
cop19-I	π Acridine $\cdots\pi$ Acridine	4.20	0.0	16.37, 16.55
cop19-Br	π Acridine $\cdots\pi$ Acridine	3.97	0.35	14.72, 14.72
cop18-I	π Phenyl $\cdots\pi$ Phenyl	5.50	0.0	55.44, 55.44
cop18-Cl	π Phenyl $\cdots\pi$ Phenyl	5.25	0.0	50.50, 50.50
cop19-I	π Phenyl $\cdots\pi$ Phenyl	5.50	0.0	55.44, 55.44
cop19-Br	π Phenyl $\cdots\pi$ Phenyl	5.32	0.00	52.75, 52.75
cop20-I	π Phenyl $\cdots\pi$ Phenyl	4.57	0.0	47.39, 43.43
cop20-Br	π Phenyl $\cdots\pi$ Phenyl	4.56	0.0	43.62, 43.55
cop21-I	π Phenyl $\cdots\pi$ Phenyl	4.57	0.0	47.39, 43.43
cop21-Cl	π Phenyl $\cdots\pi$ Phenyl	4.56	0.0	43.36, 43.34

Table II: Geometric Parameters of $C - H \cdots \pi$ and $C - X \cdots \pi$ interactions in couples

Couple	Interaction	$d_{centroid}$ (Å)	d_{plane} (Å)	d_{offset} (Å)	α (°)	β (°)
cop1-I	$C - H_{Naphthalene} \cdots \pi Naphthalene$	2.83	2.69	0.88	74.03	127.50
cop1-Br	$C - H_{Naphthalene} \cdots \pi Naphthalene$	3.83	2.66	2.57	51.07	129.07
cop2-I	$C - H_{Naphthalene} \cdots \pi Naphthalene$	2.83	2.69	0.88	74.03	127.50
cop2-Cl	$C - H_{Naphthalene} \cdots \pi Naphthalene$	3.71	2.69	2.55	51.07	128.56
cop3-I	$C - H_{Naphthalene} \cdots \pi Naphthalene$	2.83	2.69	0.88	74.03	127.50
cop3-F	$C - H_{Naphthalene} \cdots \pi Naphthalene$	3.70	2.69	2.54	50.91	129.59
cop1-I	$C - H_{Naphthalene} \cdots \pi Phenyl$	3.42	2.72	2.07	52.68	131.85
cop1-Br	$C - H_{Naphthalene} \cdots \pi Phenyl$	2.76	2.70	0.57	87.29	138.63
cop2-I	$C - H_{Naphthalene} \cdots \pi Phenyl$	3.42	2.72	2.07	52.68	131.85
cop2-Cl	$C - H_{Naphthalene} \cdots \pi Phenyl$	2.72	2.67	0.57	87.26	138.66
cop3-I	$C - H_{Naphthalene} \cdots \pi Phenyl$	3.42	2.72	2.07	52.68	131.85
cop3-F	$C - H_{Naphthalene} \cdots \pi Phenyl$	2.71	2.67	0.46	79.89	138.68
cop15-Br	$C - Br \cdots \pi Phenyl$	3.68	3.61	0.71	80.25	152.24
cop15-Cl	$C - Cl \cdots \pi Phenyl$	3.37	3.33	0.52	82.30	147.26

GEOMETRIC PARAMETERS OF COUPLES

Table III: Geometric Parameters and percent of halogen-involved interactions for cop4-21

Couple	Interaction	Distance(Å)	Contribution(%)	vdW radii changes (%)	Θ_1	Θ_2
cop4-I	I...Cl	3.38	3.9	-9.38	169	121
cop4-Cl	Cl...Cl	3.59	4.3	+2.57	159	121
cop5-Br	Br...Cl	3.43	3.2	-4.72	166	126
cop5-Cl	Cl...Cl	3.59	4.3	+2.57	159	121
cop6-Br	Br...Cl	3.57	2.4	-0.83	164	111
cop6-Cl	Cl...Cl	3.61	4.4	+3.14	164	111
cop7-Br	Br...Br	3.62	5.0	-2.16	166	110
cop7-Cl	Br...Cl	3.65	2.2	+4.28	167	110
cop8-Br	Br...Br	3.62	5.0	-2.16	166	110
cop8-Cl	Cl...Cl	3.61	4.4	+3.14	164	111
cop9-Br	Br...Cl	3.57	2.4	-0.83	164	111
cop9-Cl	Br...Cl	3.65	2.2	+4.28	167	110
cop10-Br	I...Br	3.75	2.7	-2.09	169	109
cop10-Cl	I...Cl	3.80	2.6	+1.88	171	109
cop11-Br	Br...I	3.74	7.5	-2.35	80	172
cop11-F	F...I	3.51	3.8	+1.74	69	159
cop12-I	I...I	3.87	8.8	-2.28	83	175
cop12-F	F...I	3.51	3.8	+1.74	69	159
cop13-I	I...I	3.87	8.8	-2.28	83	175
cop13-Cl	I...Cl	3.73	6.5	+0.01	78	169
cop14-Br	Br...Br	3.58	0.3	-3.24	90	156
cop14-Cl	Cl...Cl	3.52	0.1	+0.57	92	156
cop15-Br	Br...O	3.26	6.0	-3.26	91	118
cop15-Cl	Cl...O	3.44	4.2	+5.20	91	130
cop16-Br	Br...Cl	3.53	2.4	-1.94	158	121
cop16-Cl	Cl...Cl	3.59	4.3	+2.57	159	121
cop17-Br	Br...I	3.74	7.5	-2.35	80	172
cop17-Cl	Cl...I	3.73	6.5	+0.01	78	169
cop18-I	I...O	3.46	3.3	-1.14	157	147
cop18-Cl	Cl...O	3.39	3.6	+3.67	154	141
cop19-I	I...O	3.46	3.3	-1.14	157	147
cop19-Br	Br...O	3.41	4.1	+1.19	156	145
cop20-I	I...I	3.88	3.4	-2.02	140	140
cop20-Br	Br...Br	3.74	3.2	+1.08	138	138
cop21-I	I...I	3.88	3.4	-2.02	140	140
cop21-Cl	Cl...Cl	3.75	3.0	+7.14	136	136

RELAXED HIRSHFELD FINGERPRINTS

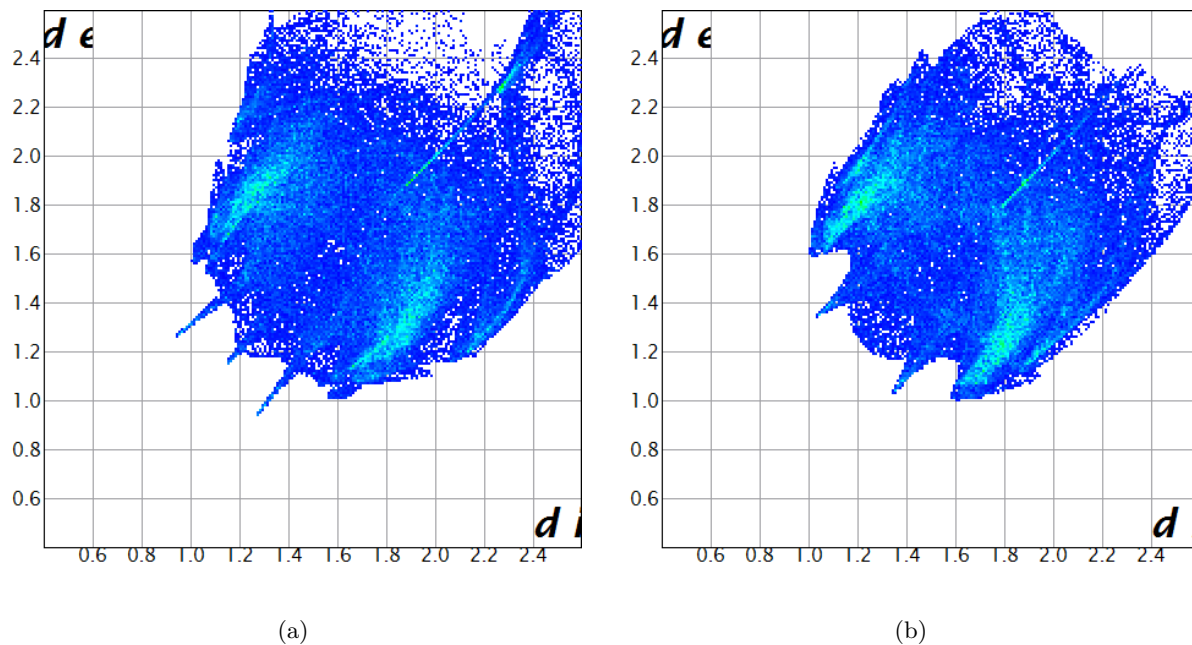


Figure 41: Hirshfeld fingerprint plots of relaxed structures for (a) Cop1-I-relaxed and (b) cop1-Br-relaxed

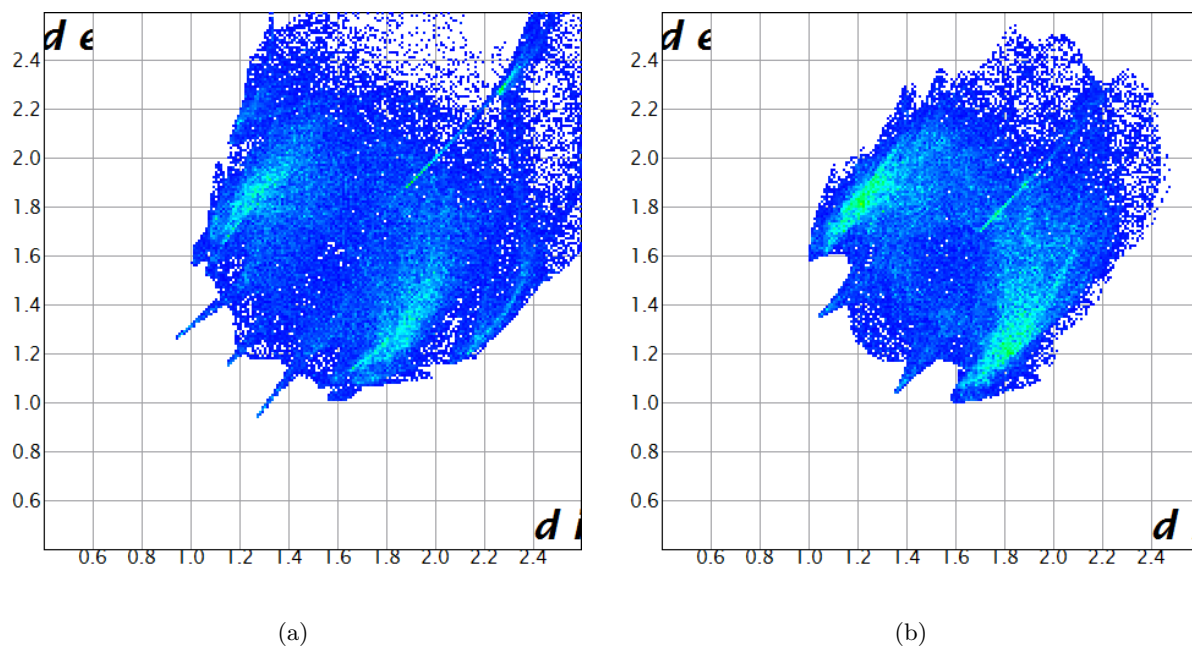


Figure 42: Hirshfeld fingerprint plots of relaxed structures for (a) Cop2-I-relaxed and (b) cop2-Cl-relaxed

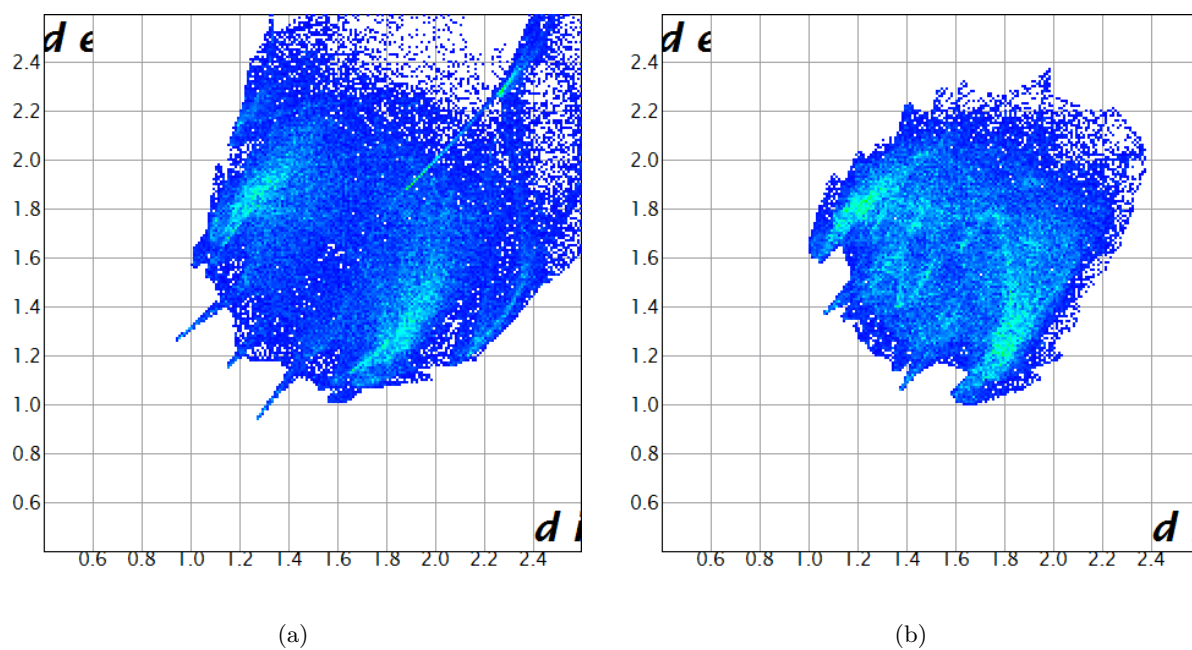


Figure 43: Hirshfeld fingerprint plots of relaxed structures for (a) Cop3-I-relaxed and (b) cop3-F-relaxed

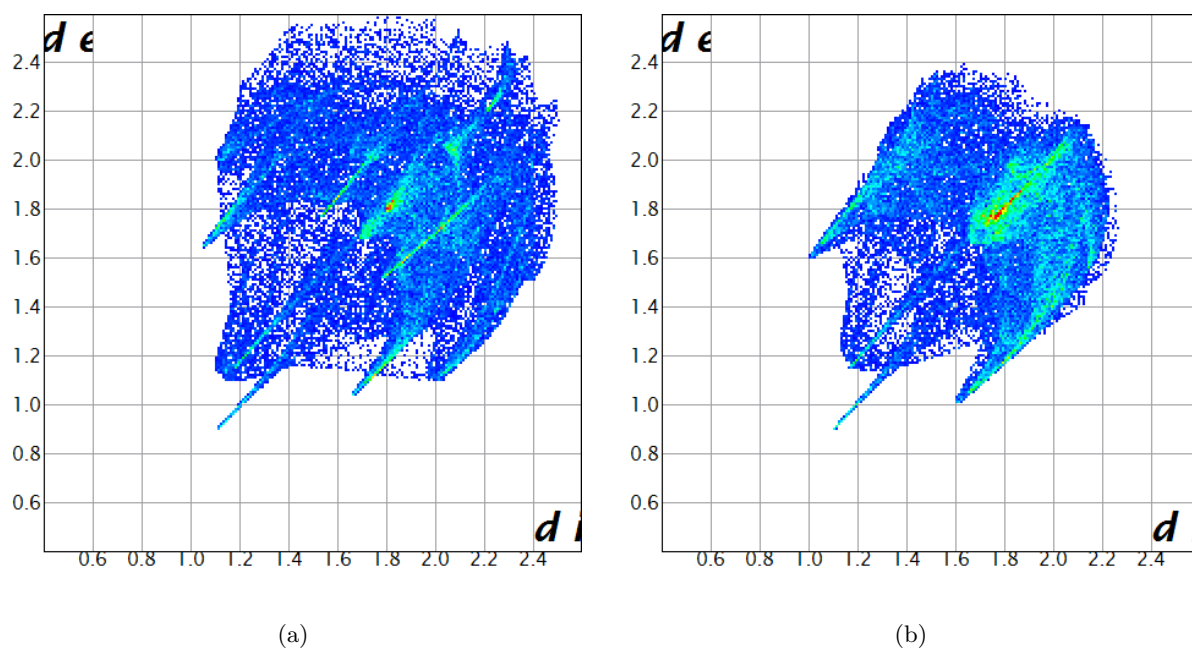


Figure 44: Hirshfeld fingerprint plots of relaxed structures for (a) Cop4-I-relaxed and (b) cop4-Cl-relaxed

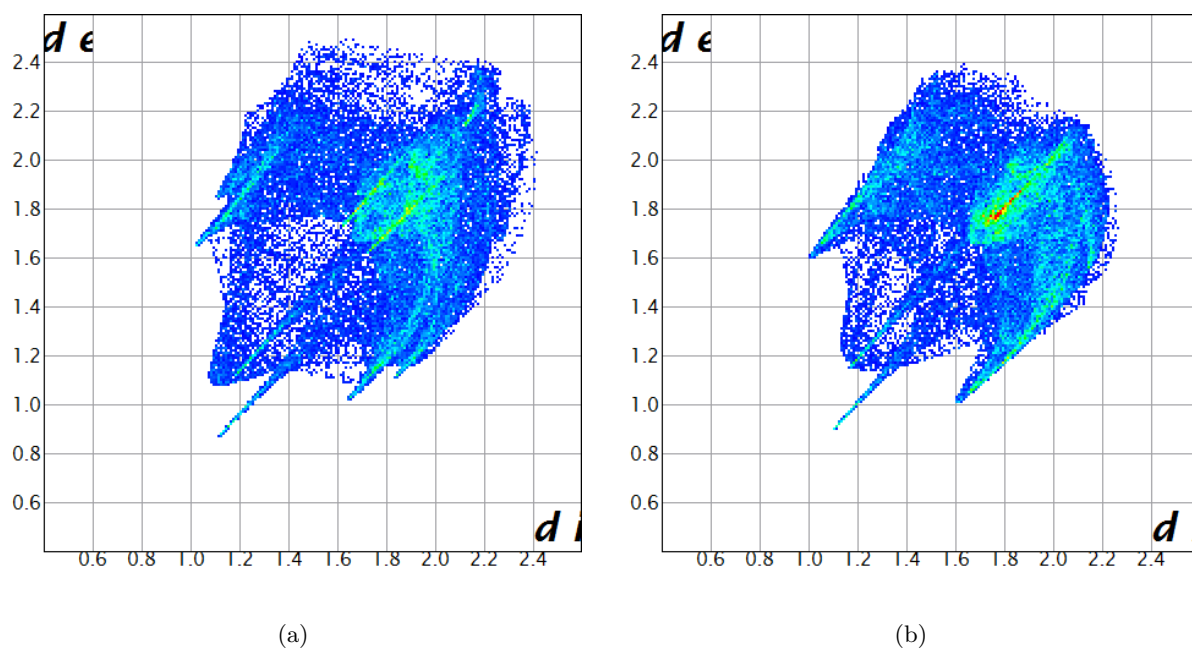


Figure 45: Hirshfeld fingerprint plots of relaxed structures for (a) Cop5-Br-relaxed and (b) cop5-Cl-relaxed

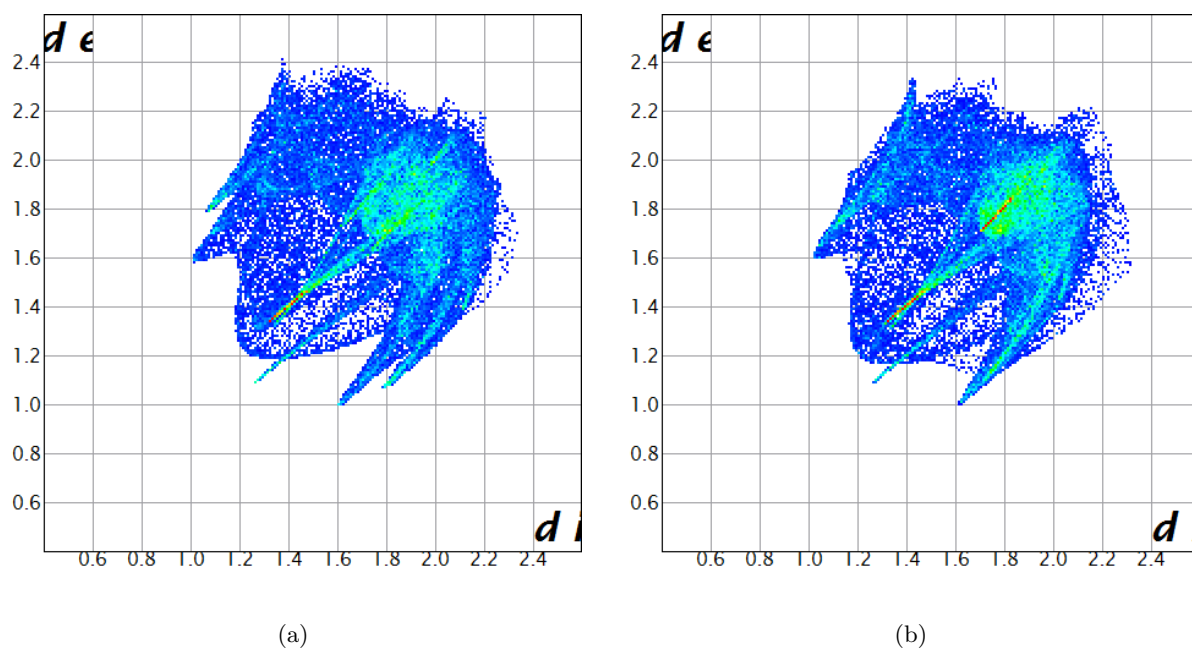


Figure 46: Hirshfeld fingerprint plots of relaxed structures for (a) Cop6-Br-relaxed and (b) cop6-Cl-relaxed

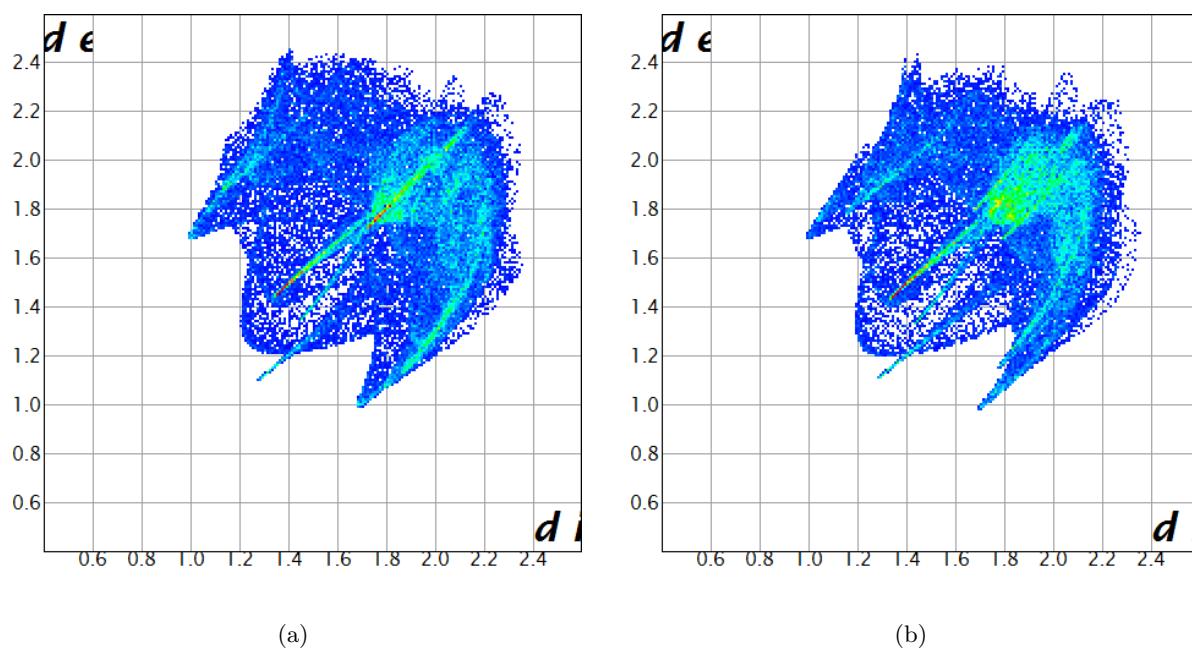


Figure 47: Hirshfeld fingerprint plots of relaxed structures for (a) Cop7-Br-relaxed and (b) cop7-Cl-relaxed

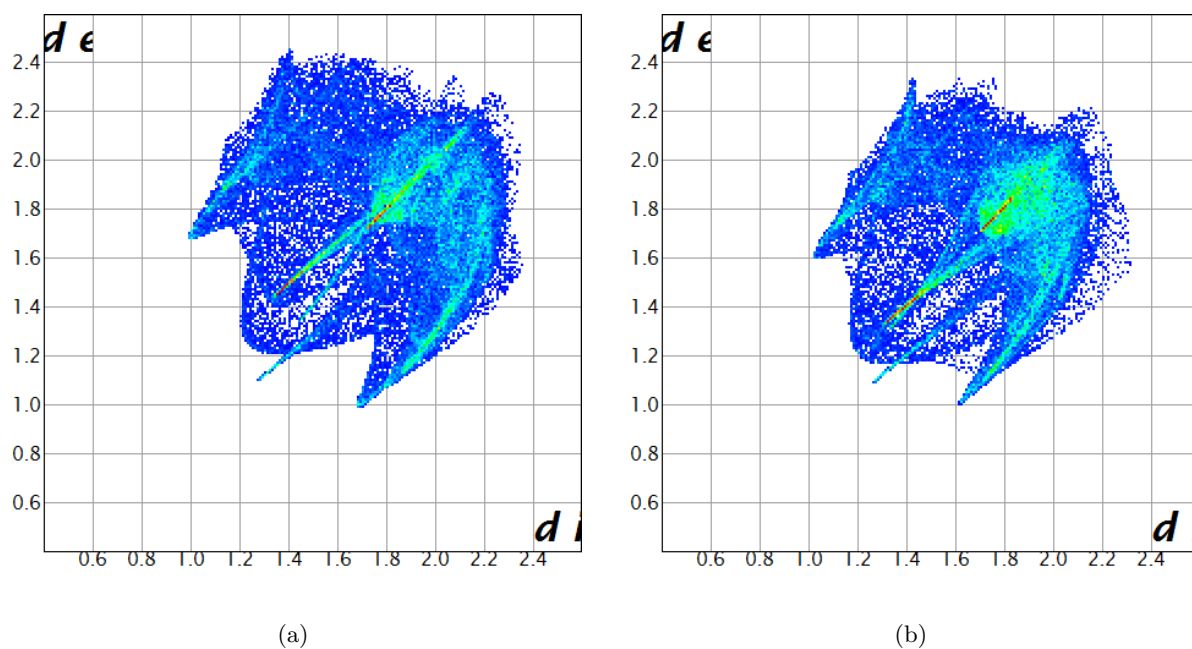


Figure 48: Hirshfeld fingerprint plots of relaxed structures for (a) Cop8-Br-relaxed and (b) cop8-Cl-relaxed

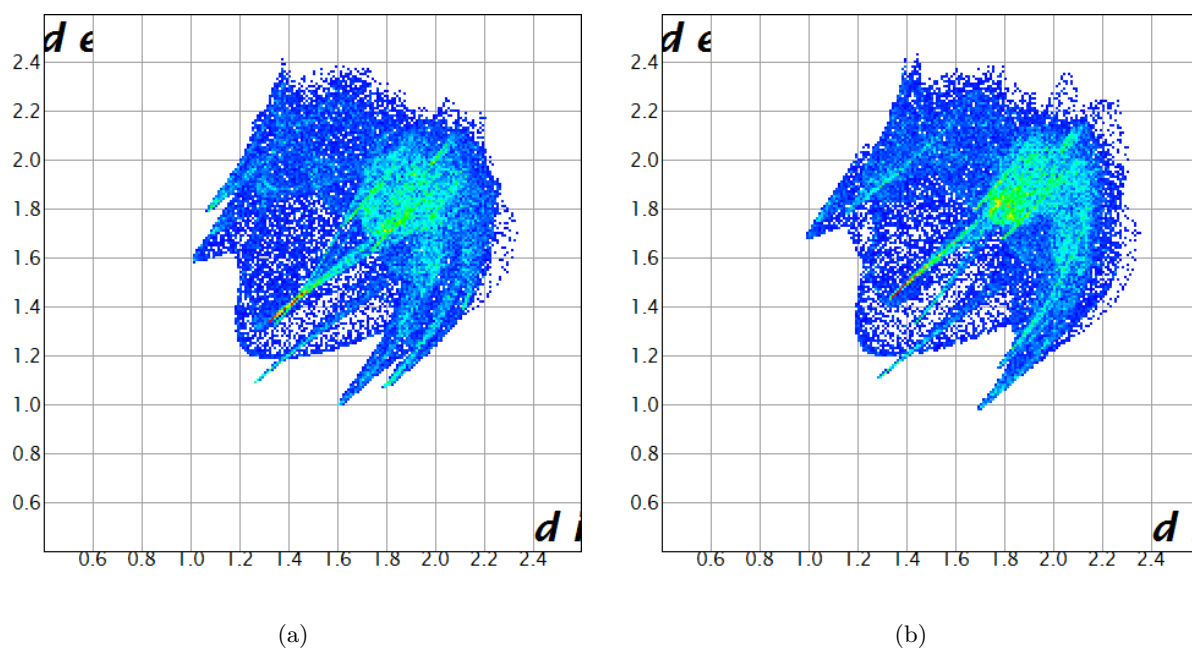


Figure 49: Hirshfeld fingerprint plots of relaxed structures for (a) Cop9-Br-relaxed and (b) cop9-Cl-relaxed

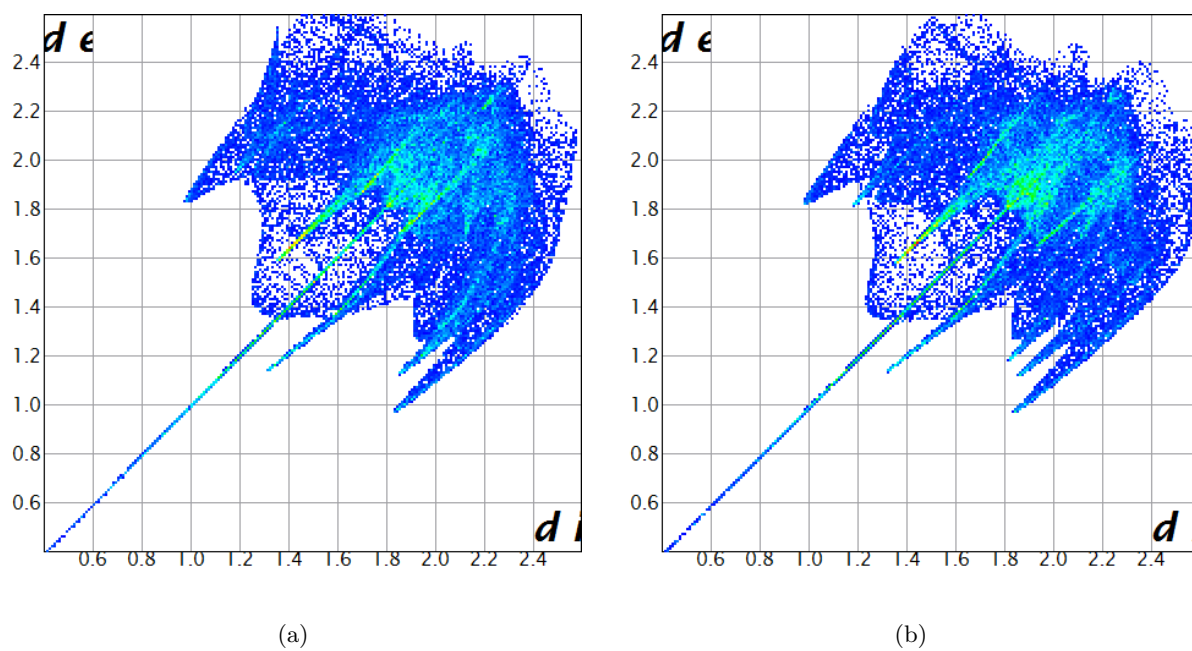


Figure 50: Hirshfeld fingerprint plots of relaxed structures for (a) Cop10-Br-relaxed and (b) cop10-Cl-relaxed

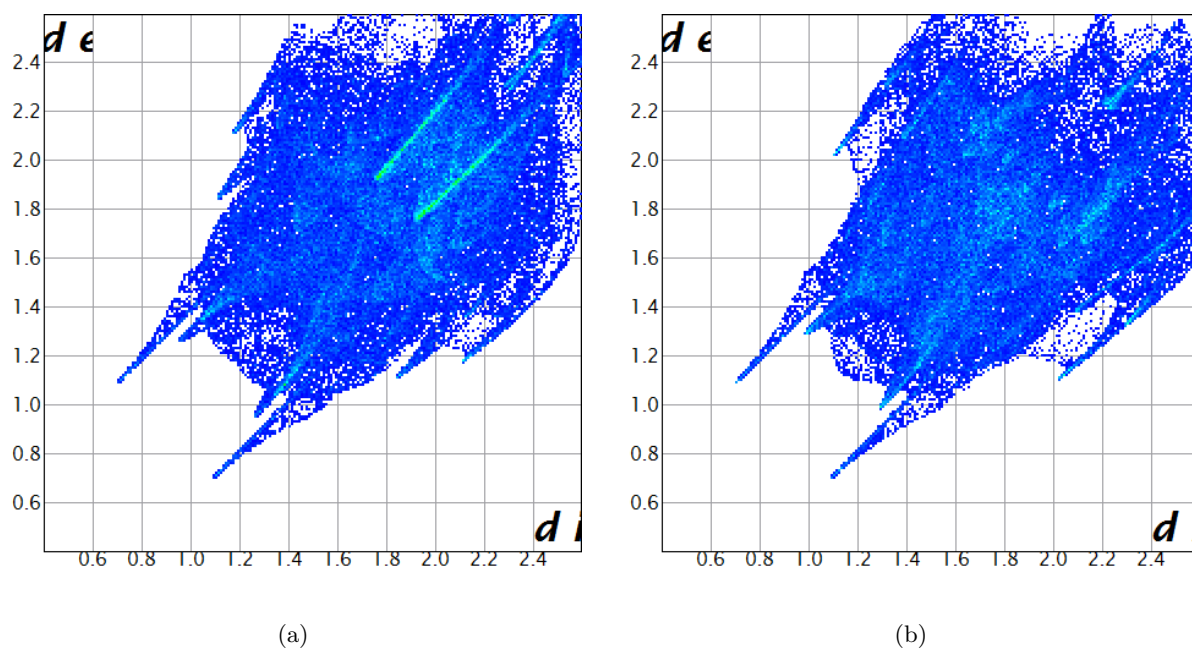


Figure 51: Hirshfeld fingerprint plots of relaxed structures for (a) Cop11-Br-relaxed and (b) cop11-F-relaxed

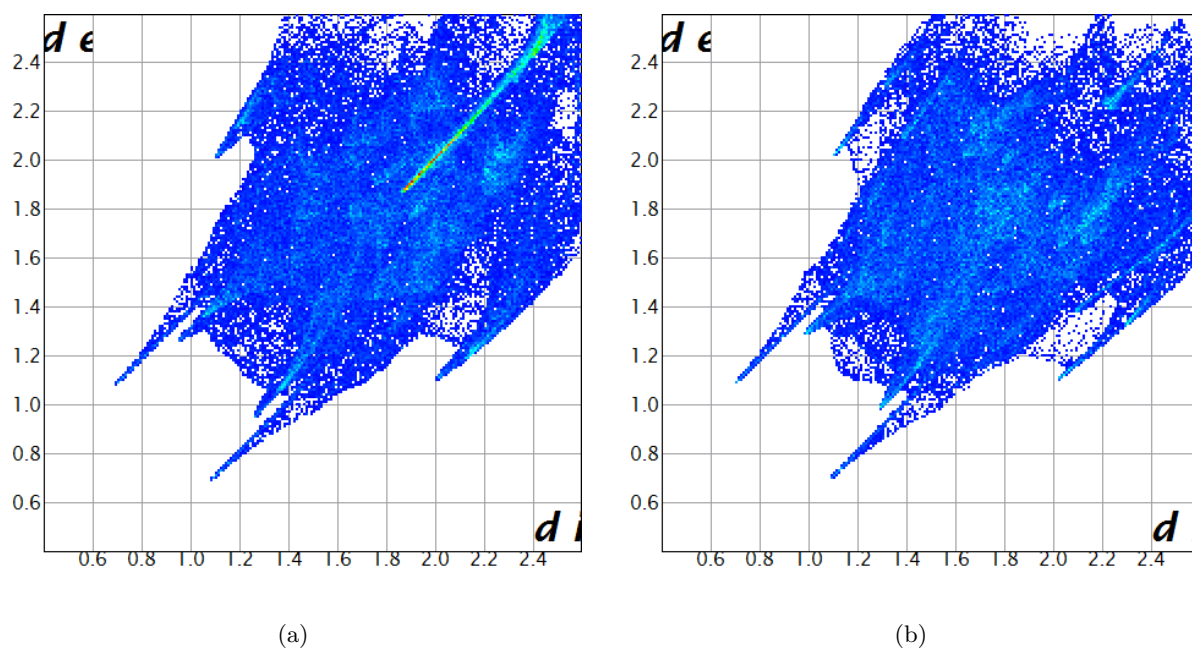


Figure 52: Hirshfeld fingerprint plots of relaxed structures for (a) Cop12-I-relaxed and (b) cop12-F-relaxed

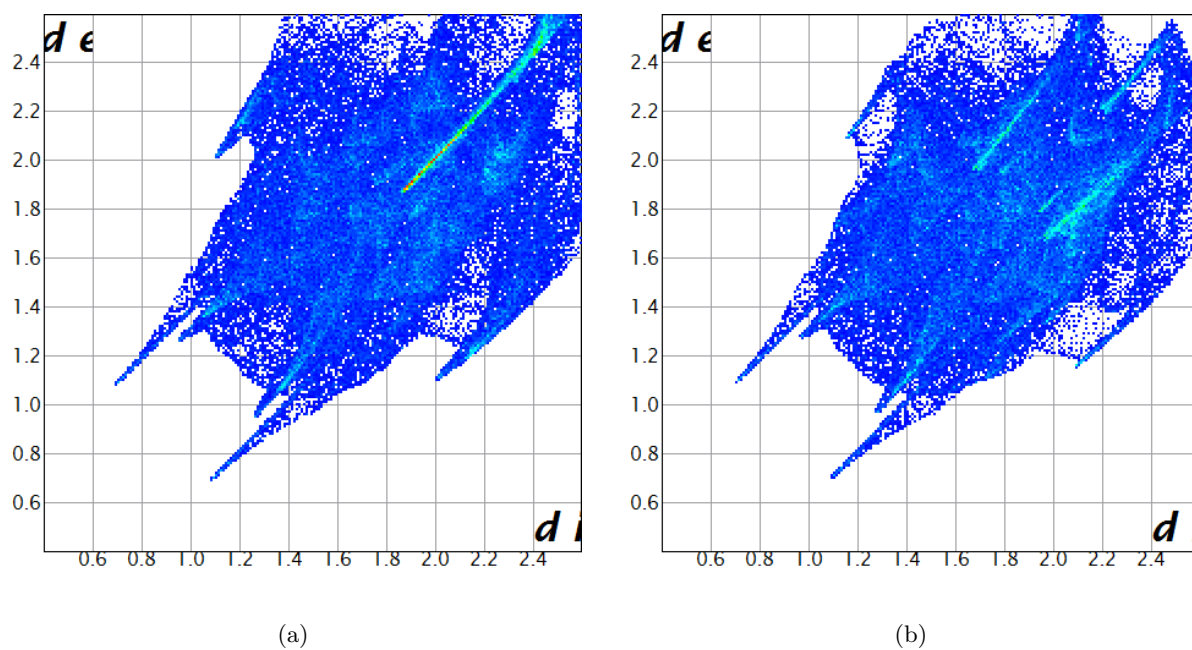


Figure 53: Hirshfeld fingerprint plots of relaxed structures for (a) Cop13-I-relaxed and (b) cop13-Cl-relaxed

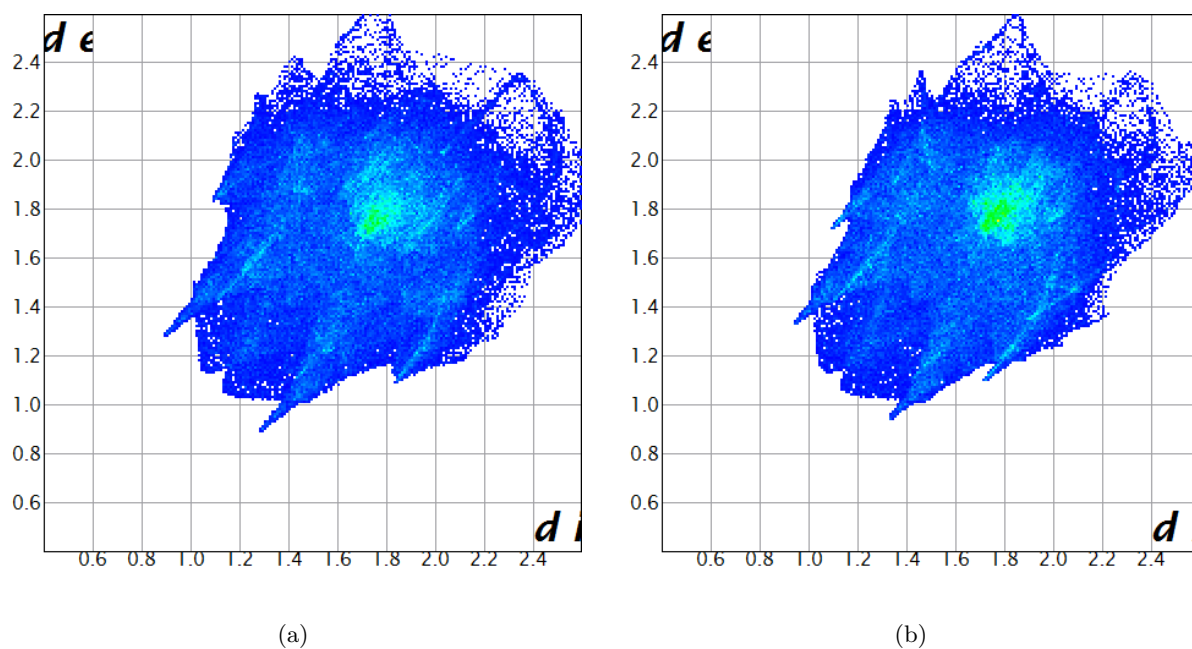


Figure 54: Hirshfeld fingerprint plots of relaxed structures for (a) Cop14-Br-relaxed and (b) cop14-Cl-relaxed

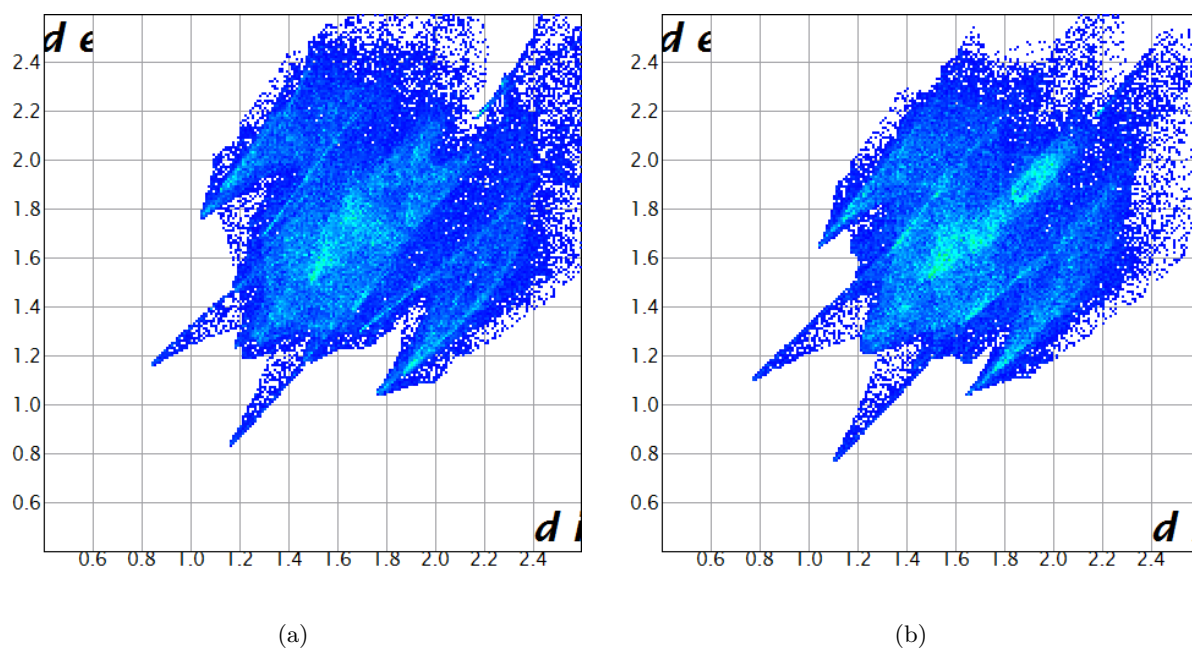


Figure 55: Hirshfeld fingerprint plots of relaxed structures for (a) Cop15-Br-relaxed and (b) cop15-Cl-relaxed

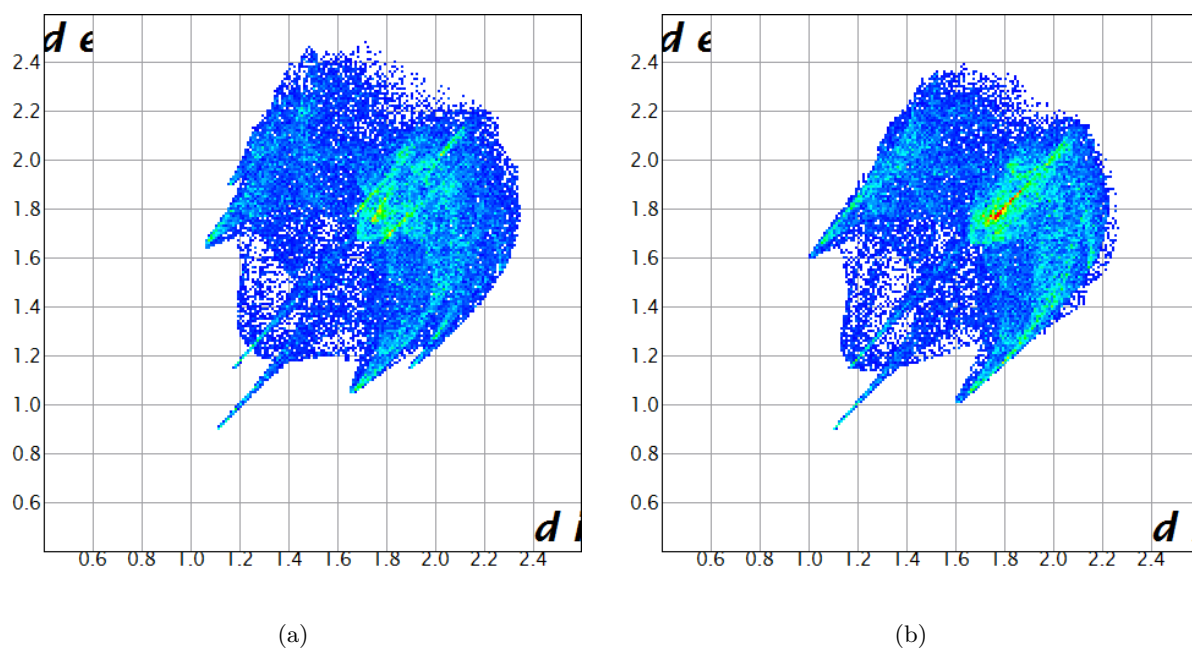


Figure 56: Hirshfeld fingerprint plots of relaxed structures for (a) Cop16-Br-relaxed and (b) cop16-Cl-relaxed

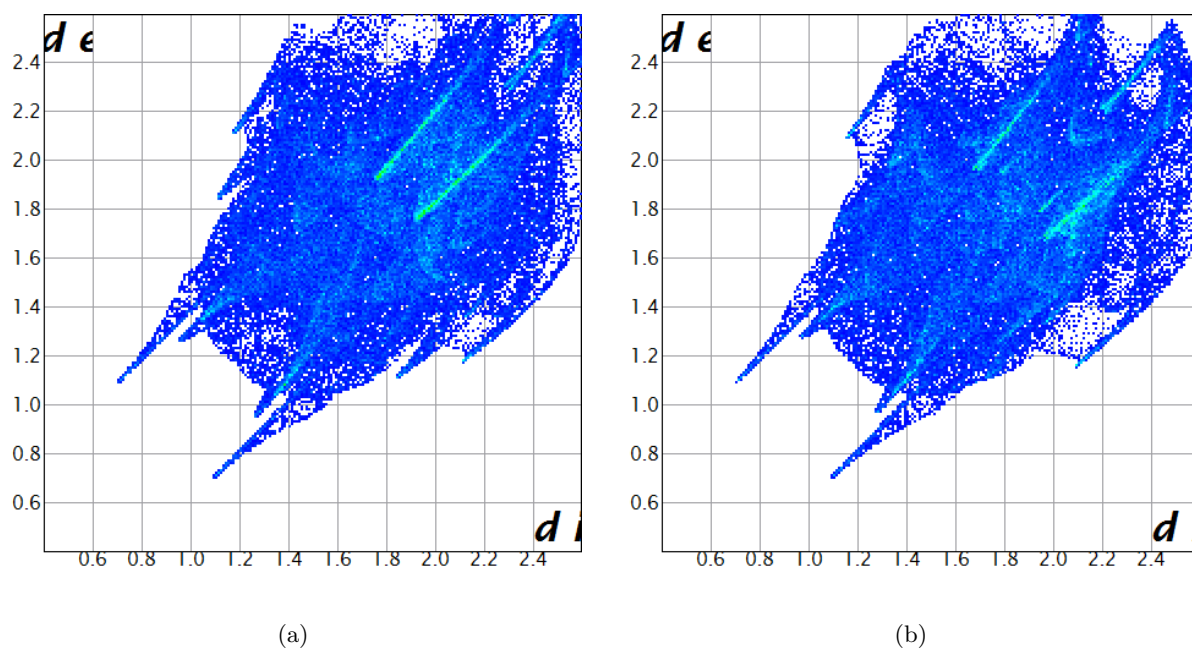


Figure 57: Hirshfeld fingerprint plots of relaxed structures for (a) Cop17-Br-relaxed and (b) cop17-Cl-relaxed

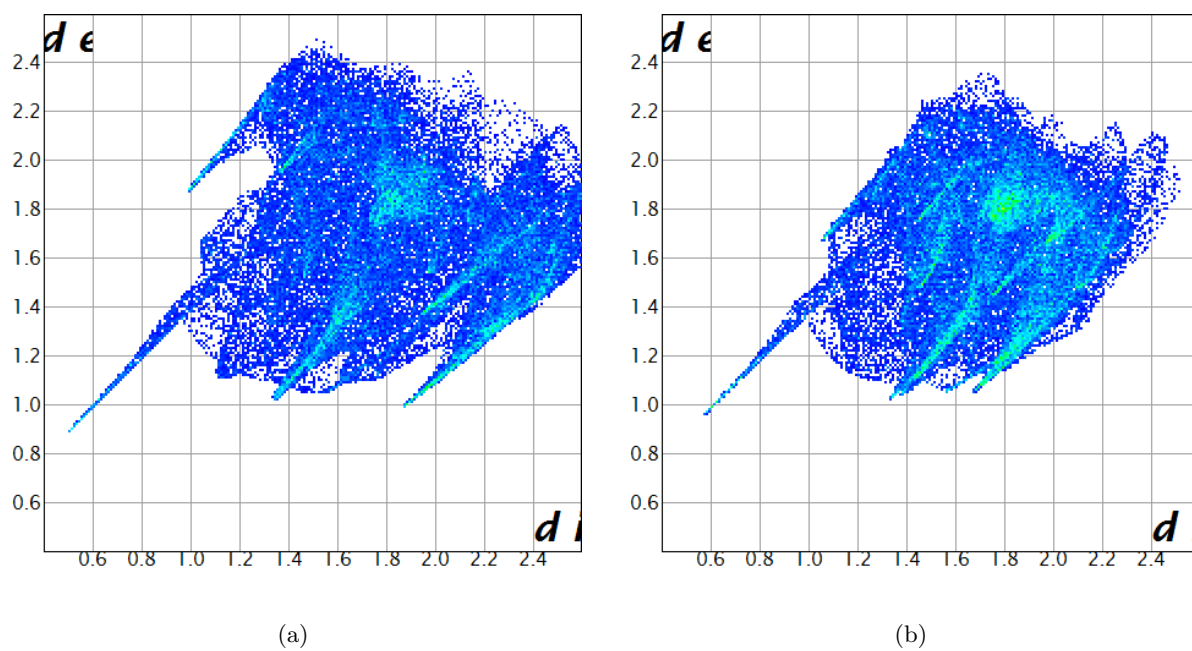


Figure 58: Hirshfeld fingerprint plots of relaxed structures for (a) Cop18-I-relaxed and (b) cop18-Cl-relaxed

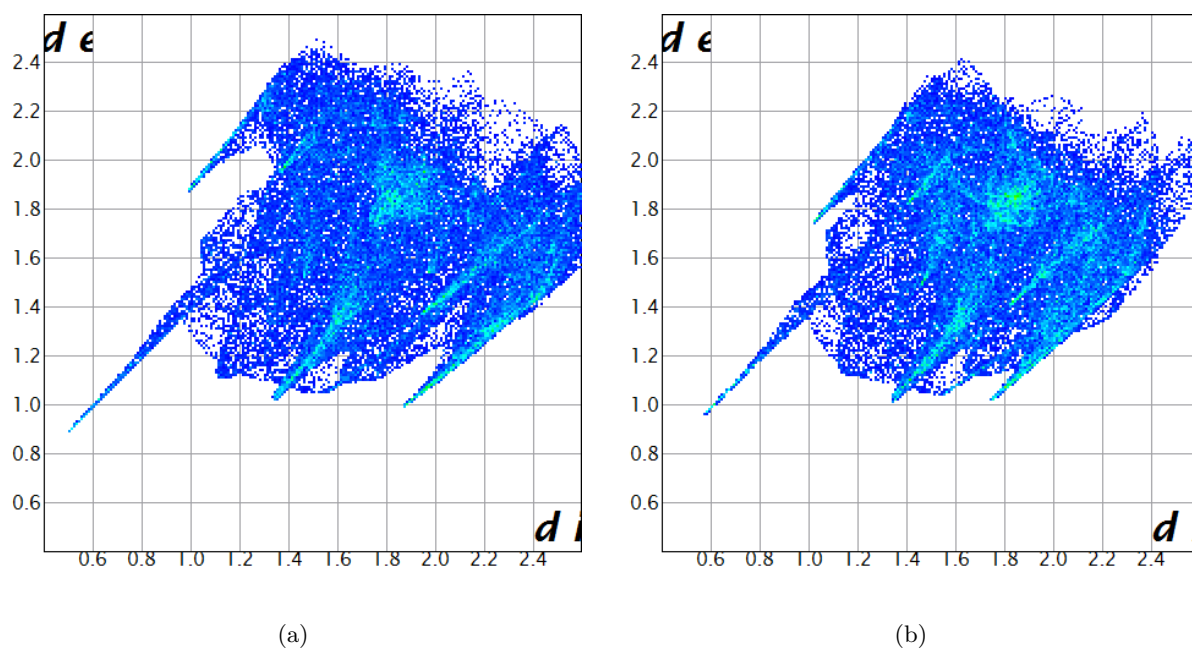


Figure 59: Hirshfeld fingerprint plots of relaxed structures for (a) Cop19-I-relaxed and (b) cop19-Br-relaxed

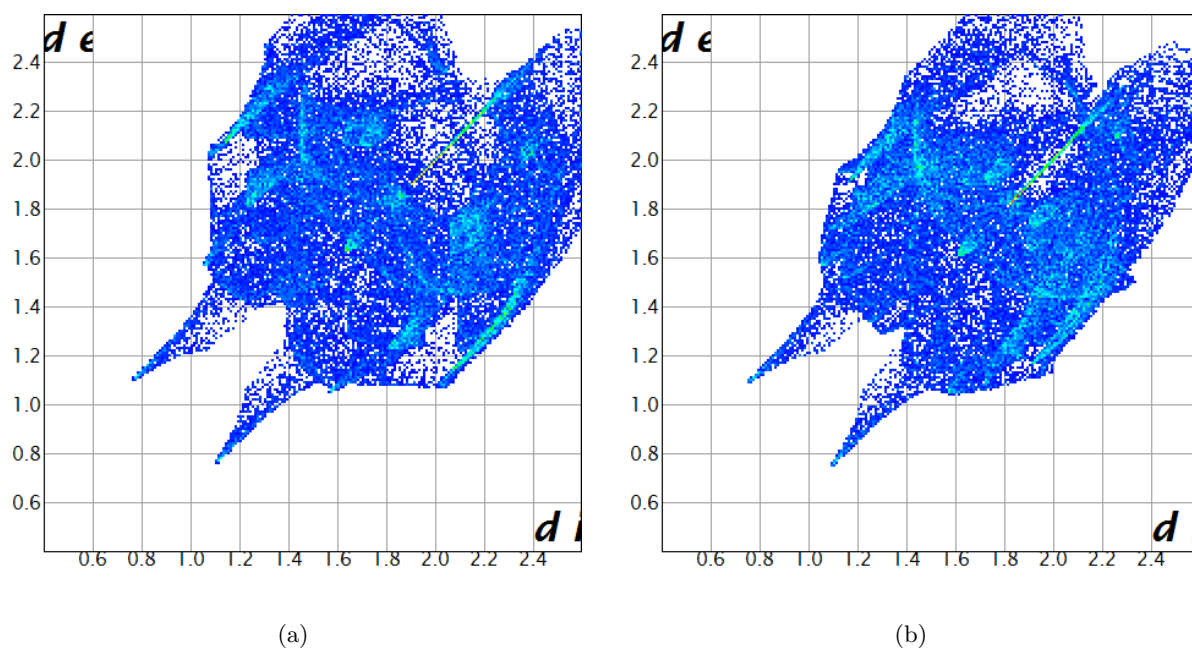


Figure 60: Hirshfeld fingerprint plots of relaxed structures for (a) Cop20-I-relaxed and (b) cop20-Br-relaxed

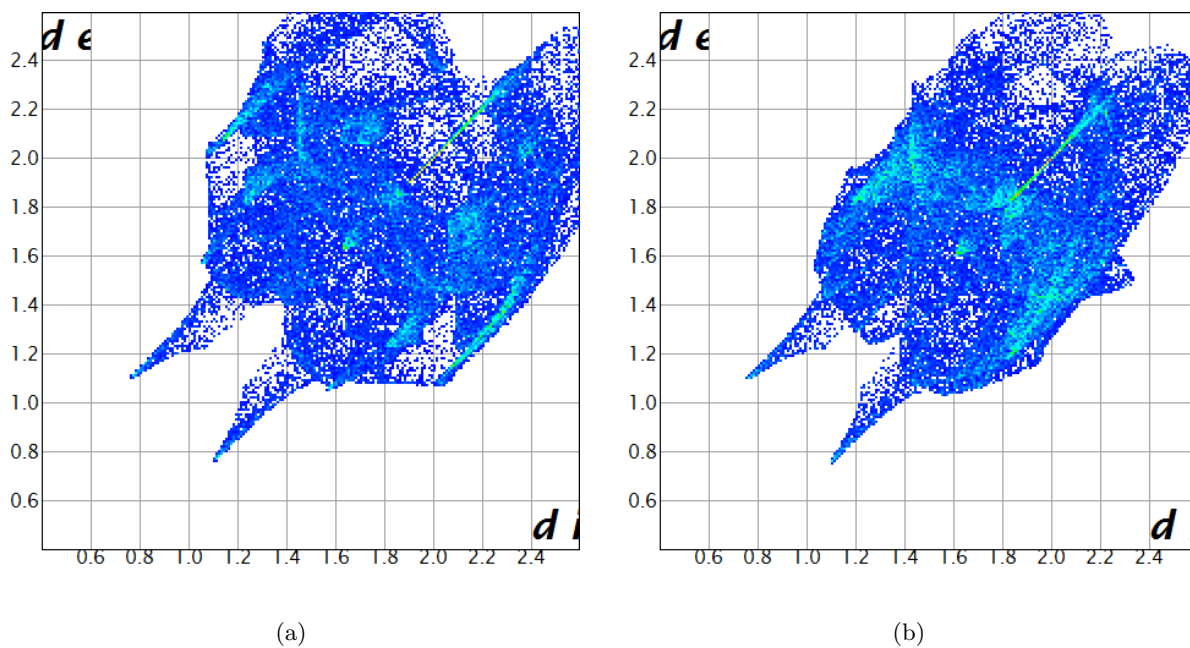


Figure 61: Hirshfeld fingerprint plots of relaxed structures for (a) Cop21-I-relaxed and (b) cop21-Cl-relaxed

Table IV: Geometric Parameters and percent of halogen-involved interactions for experimental and relaxed structures of cop1-cop21

Couple	$R_1 - X_1$ (Å)	$R_2 - X_2$ (Å)	Interaction Distance (Å)	Hirshfeld(%)	Θ_1	Θ_2
cop1-I	2.09	2.09	3.91	2.7	140	140
cop1-I-relaxed	2.11	2.11	3.75	3.3	141	141
cop1-Br	1.90	1.90	3.77	1.3	129	129
cop1-Br-relaxed	1.91	1.91	3.60	1.3	129	129
cop2-I	2.09	2.09	3.91	2.7	140	140
cop2-I-relaxed	2.11	2.11	3.75	3.3	141	141
cop2-Cl	1.75	1.75	3.61	1.2	129	129
cop2-Cl-relaxed	1.75	1.75	3.42	1.3	130	130
cop3-I	2.09	2.09	3.91	2.7	140	140
cop3-I-relaxed	2.11	2.11	3.75	3.3	141	141
cop3-F	1.36	1.36	3.55	0.7	127	127
cop3-F-relaxed	1.37	1.37	3.27	0.8	129	129
cop4-I	2.32	2.09	3.38	3.9	169	121
cop4-I-relaxed	2.34	2.10	3.32	4.2	170	119
cop4-Cl	2.31	1.74	3.59	4.3	159	121
cop4-Cl-relaxed	2.33	1.73	3.53	4.5	161	121
cop5-Br	2.31	1.89	3.43	3.2	166	126
cop5-Br-relaxed	2.33	1.91	3.37	3.3	168	125
cop5-Cl	2.31	1.74	3.59	4.3	159	121
cop5-Cl-relaxed	2.33	1.73	3.53	4.5	161	121
cop6-Br	2.66	1.89	3.57	2.4	164	111
cop6-Br-relaxed	2.68	1.91	3.39	2.7	166	103
cop6-Cl	2.64	1.74	3.61	4.4	164	111
cop6-Cl-relaxed	2.67	1.73	3.43	4.3	165	109
cop7-Br	2.76	1.89	3.62	5.0	166	110
cop7-Br-relaxed	2.80	1.90	3.46	4.9	167	106
cop7-Cl	2.75	1.73	3.65	2.2	167	110
cop7-Cl-relaxed	2.79	1.74	3.48	2.6	167	107
cop8-Br	2.76	1.89	3.62	5.0	166	110
cop8-Br-relaxed	2.80	1.90	3.46	4.9	167	106
cop8-Cl	2.64	1.74	3.61	4.4	164	111

cop8-Cl-relaxed	2.67	1.73	3.43	4.3	165	109
cop9-Br	2.66	1.89	3.57	2.4	164	111
cop9-Br-relaxed	2.68	1.91	3.39	2.7	166	103
cop9-Cl	2.75	1.73	3.65	2.2	167	110
cop9-Cl-relaxed	2.79	1.74	3.48	2.6	167	107
cop10-Br	2.92	1.88	3.75	2.7	169	109
cop10-Br-relaxed	3.02	1.91	3.56	3.4	170	101
cop10-Cl	2.91	1.73	3.80	2.6	171	109
cop10-Cl-relaxed	3.01	1.74	3.58	3.4	172	101
cop11-Br	2.09	1.91	3.74	7.5	80	172
cop11-Br-relaxed	2.10	1.92	3.69	8.6	81	173
cop11-F	2.09	1.36	3.51	3.8	69	159
cop11-F-relaxed	2.10	1.37	3.48	5.1	69	158
cop12-I	2.07	2.10	3.87	8.8	83	175
cop12-I-relaxed	2.10	2.12	3.74	11.1	81	177
cop12-F	2.09	1.36	3.51	3.8	69	159
cop12-F-relaxed	2.10	1.37	3.48	5.1	69	158
cop13-I	2.07	2.10	3.87	8.8	83	175
cop13-I-relaxed	2.10	2.12	3.74	11.1	81	177
cop13-Cl	2.09	1.74	3.73	6.5	78	169
cop13-Cl-relaxed	2.10	1.75	3.64	7.4	76	171
cop14-Br	1.90	1.90	3.58	0.3	90	156
cop14-Br-relaxed	1.92	1.92	3.49	0.3	89	157
cop14-Cl	1.78	1.78	3.52	0.1	92	156
cop14-Cl-relaxed	1.75	1.75	3.41	0.1	91	157
cop15-Br	1.17	1.90	3.26	6.0	91	118
cop15-Br-relaxed	1.24	1.97	3.40	5.2	85	112
cop15-Cl	1.21	1.77	3.44	4.2	91	130
cop15-Cl-relaxed	1.24	1.80	3.39	4.2	91	119
cop16-Br	2.32	1.89	3.53	2.4	158	121
cop16-Br-relaxed	2.34	1.90	3.45	2.4	160	121
cop16-Cl	2.31	1.74	3.59	4.3	159	121
cop16-Cl-relaxed	2.33	1.73	3.53	4.5	161	121
cop17-Br	2.09	1.91	3.74	7.5	80	172
cop17-Br-relaxed	2.10	1.92	3.69	8.6	80	172
cop17-Cl	2.09	1.74	3.73	6.5	78	169
cop17-Cl-relaxed	2.10	1.75	3.64	7.4	76	171
cop18-I	1.31	2.09	3.46	3.3	157	147
cop18-I-relaxed	1.32	2.11	3.34	3.8	158	146
cop18-Cl	1.30	1.74	3.39	3.6	154	141
cop18-Cl-relaxed	1.31	1.75	3.22	4.1	156	141
cop19-I	1.31	2.09	3.46	3.3	157	147
cop19-I-relaxed	1.32	2.11	3.34	3.8	158	146
cop19-Br	1.31	1.90	3.41	4.1	156	145
cop19-Br-relaxed	1.32	1.92	3.25	4.1	158	144
cop20-I	2.10	2.10	3.88	3.4	140	140
cop20-I-relaxed	2.11	2.11	3.81	3.9	140	144
cop20-Br	1.90	1.90	3.74	3.2	138	138
cop20-Br-relaxed	1.92	1.92	3.67	3.7	138	138
cop21-I	2.10	2.10	3.88	3.4	140	140
cop21-I-relaxed	2.11	2.11	3.81	3.9	140	144
cop21-Cl	1.74	1.74	3.75	3.0	136	136
cop21-Cl-relaxed	1.75	1.75	3.68	3.4	135	135

QTAIM

Table V: Topological Properties of electron and Energy density at BCP Between two Atoms Involved in halogen-involved Interaction in cop4-cop21

Couple	Basis Set	Functional	ρ_{BCP}	$\nabla^2\rho_{BCP}$	G_{BCP}	V_{BCP}	H_{BCP}	$ V_{BCP} /G_{BCP}$
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cop4-I	Def2-TZVP	WB97X-D	0.0120	0.0369	0.0078	-0.0064	0.0014	0.8205
	Def2-TZVP	M062-X	0.0120	0.0378	0.0081	-0.0067	0.0014	0.8272
cop4-Cl	Def2-TZVP	WB97X-D	0.0055	0.0192	0.0036	-0.0025	0.0011	0.6944
	Def2-TZVP	M062-X	0.0056	0.0192	0.0037	-0.0026	0.0011	0.7027
cop5-Br	Def2-TZVP	WB97X-D	0.0088	0.0292	0.0059	-0.0046	0.0013	0.7797
	Def2-TZVP	M062-X	0.0089	0.0302	0.0061	-0.0048	0.0013	0.7869
cop5-Cl	Def2-TZVP	WB97X-D	0.0055	0.0192	0.0036	-0.0025	0.0011	0.6944
	Def2-TZVP	M062-X	0.0056	0.0192	0.0037	-0.0026	0.0011	0.7027
cop6-Br	Def2-TZVP	WB97X-D	0.0068	0.0223	0.0044	-0.0033	0.0011	0.7500
	Def2-TZVP	M062-X	0.0070	0.0230	0.0046	-0.0034	0.0012	0.7391
cop6-Cl	Def2-TZVP	WB97X-D	0.0051	0.0181	0.0034	-0.0023	0.0011	0.6765
	Def2-TZVP	M062-X	0.0052	0.0182	0.0035	-0.0024	0.0011	0.6857
cop7-Br	Def2-TZVP	WB97X-D	0.0075	0.0228	0.0047	-0.0037	0.0010	0.7872
	Def2-TZVP	M062-X	0.0077	0.0237	0.0049	-0.0038	0.0011	0.7755
cop7-Cl	Def2-TZVP	WB97X-D	0.0058	0.0199	0.0038	-0.0027	0.0011	0.7105
	Def2-TZVP	M062-X	0.0060	0.0202	0.0039	-0.0027	0.0011	0.7180
cop8-Br	Def2-TZVP	WB97X-D	0.0075	0.0228	0.0047	-0.0037	0.0010	0.7872
	Def2-TZVP	M062-X	0.0077	0.0237	0.0049	-0.0038	0.0011	0.7755
cop8-Cl	Def2-TZVP	WB97X-D	0.0051	0.0181	0.0034	-0.0023	0.0011	0.6765
	Def2-TZVP	M062-X	0.0052	0.0182	0.0035	-0.0024	0.0011	0.6857
cop9-Br	Def2-TZVP	WB97X-D	0.0068	0.0223	0.0044	-0.0033	0.0011	0.7500
	Def2-TZVP	M062-X	0.0070	0.0230	0.0046	-0.0034	0.0012	0.7391
cop9-Cl	Def2-TZVP	WB97X-D	0.0058	0.0199	0.0038	-0.0027	0.0011	0.7105
	Def2-TZVP	M062-X	0.0060	0.0202	0.0039	-0.0027	0.0011	0.7180
cop10-Br	Def2-TZVP	WB97X-D	0.0077	0.0210	0.0044	-0.0035	0.0009	0.7954
	Def2-TZVP	M062-X	0.0077	0.0219	0.0046	-0.0036	0.0010	0.7826
cop10-Cl	Def2-TZVP	WB97X-D	0.0057	0.0179	0.0035	-0.0024	0.0011	0.6857
	Def2-TZVP	M062-X	0.0057	0.0181	0.0035	-0.0025	0.0010	0.7143
cop11-Br	Def2-TZVP	WB97X-D	0.0079	0.0221	0.0047	-0.0038	0.0009	0.8085
	Def2-TZVP	M062-X	0.0080	0.0223	0.0049	-0.0039	0.0010	0.7959
cop11-F	Def2-TZVP	WB97X-D	0.0053	0.0210	0.0040	-0.0028	0.0012	0.7000
	Def2-TZVP	M062-X	0.0054	0.0215	0.0042	-0.0030	0.0012	0.7143
cop12-I	Def2-TZVP	WB97X-D	0.0079	0.0207	0.0044	-0.0036	0.0008	0.8182
	Def2-TZVP	M062-X	0.0080	0.0214	0.0045	-0.0037	0.0008	0.8222
cop12-F	Def2-TZVP	WB97X-D	0.0053	0.0210	0.0040	-0.0028	0.0012	0.7000
	Def2-TZVP	M062-X	0.0054	0.0215	0.0042	-0.0030	0.0012	0.7143
cop13-I	Def2-TZVP	WB97X-D	0.0079	0.0207	0.0044	-0.0036	0.0008	0.8182
	Def2-TZVP	M062-X	0.0080	0.0214	0.0045	-0.0037	0.0008	0.8222
cop13-Cl	Def2-TZVP	WB97X-D	0.0066	0.0211	0.0042	-0.0031	0.0011	0.7381
	Def2-TZVP	M062-X	0.0067	0.0214	0.0043	-0.0032	0.0011	0.7442
cop14-Br	Def2-TZVP	WB97X-D	0.0085	0.0259	0.0054	-0.0044	0.0010	0.8148
	Def2-TZVP	M062-X	0.0087	0.0268	0.0056	-0.0046	0.0010	0.8214
cop14-Cl	Def2-TZVP	WB97X-D	0.0062	0.0229	0.0043	-0.0030	0.0013	0.6977
	Def2-TZVP	M062-X	0.0063	0.0229	0.0044	-0.0031	0.0013	0.7045
cop15-Br	Def2-TZVP	WB97X-D	0.0085	0.0312	0.0063	-0.0048	0.0015	0.7619
	Def2-TZVP	M062-X	0.0087	0.0319	0.0065	-0.0051	0.0014	0.7846
cop15-Cl	Def2-TZVP	WB97X-D	0.0048	0.0185	0.0035	-0.0023	0.0012	0.6571
	Def2-TZVP	M062-X	0.0049	0.0187	0.0035	-0.0024	0.0011	0.6857
cop16-Br	Def2-TZVP	WB97X-D	0.0076	0.0243	0.0049	-0.0037	0.0012	0.7551
	Def2-TZVP	M062-X	0.0077	0.0259	0.0050	-0.0038	0.0012	0.7600
cop16-Cl	Def2-TZVP	WB97X-D	0.0055	0.0192	0.0036	-0.0025	0.0011	0.6944
	Def2-TZVP	M062-X	0.0056	0.0192	0.0037	-0.0026	0.0011	0.7027
cop17-Br	Def2-TZVP	WB97X-D	0.0079	0.0221	0.0047	-0.0038	0.0009	0.8085
	Def2-TZVP	M062-X	0.0080	0.0223	0.0049	-0.0039	0.0010	0.7959
cop17-Cl	Def2-TZVP	WB97X-D	0.0066	0.0211	0.0042	-0.0031	0.0011	0.7381
	Def2-TZVP	M062-X	0.0067	0.0214	0.0043	-0.0032	0.0011	0.7442
cop18-I	Def2-TZVP	WB97X-D	0.0062	0.0222	0.0044	-0.0032	0.0012	0.7272
	Def2-TZVP	M062-X	0.0064	0.0229	0.0046	-0.0034	0.0012	0.7391
cop18-Cl	Def2-TZVP	WB97X-D	0.0044	0.0148	0.0034	-0.0022	0.0012	0.6470
	Def2-TZVP	M062-X	0.0046	0.0150	0.0036	-0.0023	0.0013	0.6389
cop19-I	Def2-TZVP	WB97X-D	0.0062	0.0222	0.0044	-0.0032	0.0012	0.7272
	Def2-TZVP	M062-X	0.0064	0.0229	0.0046	-0.0034	0.0012	0.7391

cop19-Br	Def2-TZVP	WB97X-D	0.0053	0.0205	0.0040	-0.0028	0.0012	0.7000
	Def2-TZVP	M062-X	0.0055	0.0210	0.0041	-0.0029	0.0012	0.7073
cop20-I	Def2-TZVP	WB97X-D	0.0080	0.0196	0.0042	-0.0035	0.0007	0.8333
	Def2-TZVP	M062-X	0.0082	0.0201	0.0044	-0.0036	0.0008	0.8181
cop20-Br	Def2-TZVP	WB97X-D	0.0062	0.0189	0.0038	-0.0029	0.0009	0.7632
	Def2-TZVP	M062-X	0.0064	0.0195	0.0040	-0.0030	0.0010	0.7500
cop21-I	Def2-TZVP	WB97X-D	0.0080	0.0196	0.0042	-0.0035	0.0007	0.8333
	Def2-TZVP	M062-X	0.0082	0.0201	0.0044	-0.0036	0.0008	0.8181
cop21-Cl	Def2-TZVP	WB97X-D	0.0038	0.0135	0.0025	-0.0016	0.0009	0.6400
	Def2-TZVP	M062-X	0.0039	0.0139	0.0027	-0.0017	0.0010	0.6296

EDA

Table VI: The interaction energy and its components based on EDA analysis for cop4-cop21-all energy units is (Kj/mol)

Couple	Functional	Basis set	ΔE_{int}	ΔE_{elstat}	ΔE_{pauli}	ΔE_{orb}	ΔE_{disp}
cop4-I-dimer	B3LYP-D	TZP	-44.13	-65.20	87.66	-34.04	-32.55
cop4-Cl-dimer	B3LYP-D	TZP	-31.32	-26.02	30.96	-12.49	-23.77
cop5-Br-dimer	B3LYP-D	TZP	-32.96	-32.38	44.56	-19.21	-25.93
cop5-Cl-dimer	B3LYP-D	TZP	-31.32	-26.02	30.96	-12.49	-23.77
cop6-Br-dimer	B3LYP-D	TZP	-15.92	-9.60	15.55	-8.69	-13.18
cop6-Cl-dimer	B3LYP-D	TZP	-9.36	-3.52	9.50	-4.88	-10.46
cop7-Br-dimer	B3LYP-D	TZP	-15.52	-10.47	16.68	-8.94	-12.80
cop7-Cl-dimer	B3LYP-D	TZP	-9.29	-4.99	10.49	-4.92	-9.87
cop8-Br-dimer	B3LYP-D	TZP	-15.52	-10.47	16.68	-8.94	-12.80
cop8-Cl-dimer	B3LYP-D	TZP	-9.36	-3.52	9.50	-4.88	-10.46
cop9-Br-dimer	B3LYP-D	TZP	-15.92	-9.60	15.55	-8.69	-13.18
cop9-Cl-dimer	B3LYP-D	TZP	-9.29	-4.99	10.49	-4.92	-9.87
cop10-Br-dimer	B3LYP-D	TZP	-13.35	-11.18	17.04	-8.27	-10.94
cop10-Cl-dimer	B3LYP-D	TZP	-7.42	-5.41	10.26	-4.00	-8.27
cop11-Br-dimer	B3LYP-D	TZP	-8.12	-8.36	17.31	-6.14	-10.93
cop11-F-dimer	B3LYP-D	TZP	-8.46	-5.16	9.88	-2.89	-10.29
cop12-I-dimer	B3LYP-D	TZP	-9.03	-9.88	19.87	-6.44	-12.58
cop12-F-dimer	B3LYP-D	TZP	-8.46	-5.16	9.88	-2.89	-10.29
cop13-I-dimer	B3LYP-D	TZP	-9.03	-9.88	19.87	-6.44	-12.58
cop13-Cl-dimer	B3LYP-D	TZP	-5.14	-5.62	13.12	-3.66	-8.98
cop14-Br-dimer	B3LYP-D	TZP	-33.26	-22.23	39.18	-12.16	-38.04
cop14-Cl-dimer	B3LYP-D	TZP	-30.53	-16.97	28.92	-8.61	-33.87
cop15-Br-dimer	B3LYP-D	TZP	-29.42	-27.55	48.43	-12.01	-38.29
cop15-Cl-dimer	B3LYP-D	TZP	-27.14	-17.38	22.06	-7.13	-24.69
cop16-Br-dimer	B3LYP-D	TZP	-38.29	-32.74	37.59	-16.38	-26.75
cop16-Cl-dimer	B3LYP-D	TZP	-31.32	-26.02	30.96	-12.49	-23.77
cop17-Br-dimer	B3LYP-D	TZP	-8.12	-8.36	17.31	-6.14	-10.93
cop17-Cl-dimer	B3LYP-D	TZP	-5.14	-5.62	13.12	-3.66	-8.98
cop18-I-dimer	B3LYP-D	TZP	-15.84	-14.32	26.54	-6.33	-21.72
cop18-Cl-dimer	B3LYP-D	TZP	-10.74	-7.80	12.20	-2.92	-12.22
cop19-I-dimer	B3LYP-D	TZP	-15.84	-14.32	26.54	-6.33	-21.72
cop19-Br-dimer	B3LYP-D	TZP	-15.41	-10.48	16.79	-5.48	-16.25
cop20-I-dimer	B3LYP-D	TZP	-3.37	-9.17	18.25	-4.71	-7.75
cop20-Br-dimer	B3LYP-D	TZP	-4.21	-4.07	8.36	-3.08	-5.42
cop21-I-dimer	B3LYP-D	TZP	-3.37	-9.17	18.25	-4.71	-7.75
cop21-Cl-dimer	B3LYP-D	TZP	-1.52	-0.93	3.43	-0.88	-3.13
