Towards the chemical control of molecular packing: syntheses and crystal structures of three *trans*-[NiL_4(NCS)$_2$] complexes

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Supplementary Material

S1. Full tables of bond lengths and angles for (I) and (II)

S2. Thermogravimetric analysis data

S3. Hirshfeld fingerprint plots

Table 1 S1. Full comparison of bond lengths (Å) and angles (°) from the X-ray crystal structure and DFT calculations for (I)

	Experimental		Experimental	DFT
Ni1—N1	2.033 (2)	Ni2—N7	2.039 (2)	2.020
Ni1—N2	2.058 (2)	Ni2—N8	2.051 (2)	2.018
Ni1—N6	2.1205 (19)	Ni2—N9	2.1207 (19)	2.172
Ni1—N5	2.1270 (18)	Ni2—N12	2.1236 (19)	2.172
Ni1—N4	2.1379 (19)	Ni2—N11	2.1384 (19)	2.166
Ni1—N3	2.1494 (18)	Ni2—N10	2.1460 (18)	2.169
N1—Ni1—N2	177.31 (8)	N7—Ni2—N8	177.68 (8)	179.5
N1—Ni1—N6	90.79 (8)	N7—Ni2—N9	89.90 (8)	89.7
N2—Ni1—N6	90.00 (7)	N8—Ni2—N9	90.54 (7)	89.9
N1—Ni1—N5	89.58 (7)	N7—Ni2—N12	90.24 (7)	90.2
N2—Ni1—N5	87.83 (7)	N8—Ni2—N12	87.47 (7)	90.0
N6—Ni1—N5	91.56 (7)	N9—Ni2—N12	91.41 (7)	89.8
N1—Ni1—N4	89.14 (7)	N7—Ni2—N11	88.37 (7)	90.3
N2—Ni1—N4	90.18 (8)	N8—Ni2—N11	91.29 (7)	90.1
N6—Ni1—N4	177.52 (8)	N9—Ni2—N11	176.80 (8)	179.9
N5—Ni1—N4	90.92 (7)	N12—Ni2—N11	91.29 (7)	90.1
N1—Ni1—N3	91.36 (7)	N7—Ni2—N10	91.46 (7)	89.8
N2—Ni1—N3	91.27 (7)	N8—Ni2—N10	90.84 (7)	90.0
N6—Ni1—N3	84.43 (7)	N9—Ni2—N10	85.39 (7)	89.9
N5—Ni1—N3	175.89 (7)	N12—Ni2—N10	176.37 (7)	179.7
N4—Ni1—N3	93.09 (7)	N11—Ni2—N10	91.96 (7)	90.2

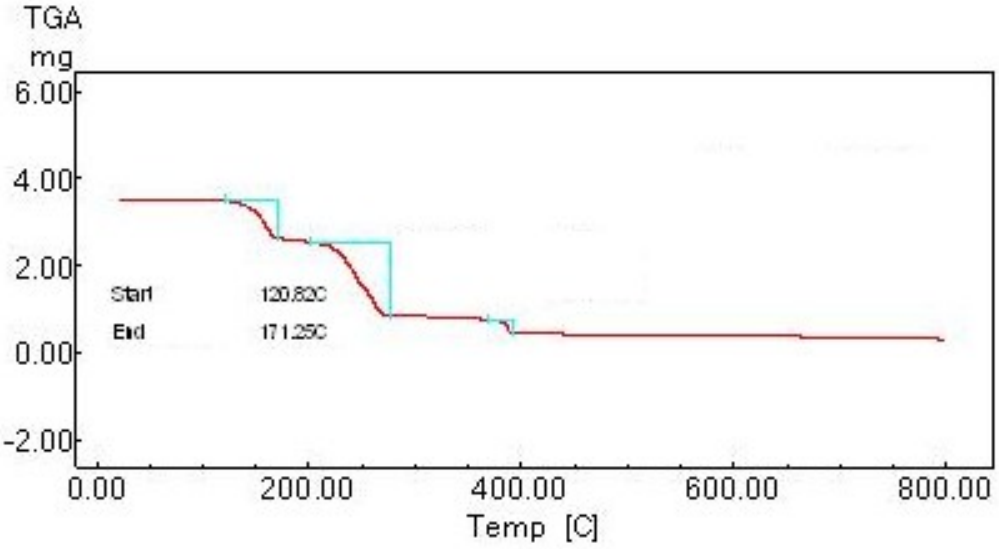
Figure 1 S1. Full comparison of bond lengths (Å) and angles (°) from the X-ray crystal structure and DFT calculations for (II)

	Expt.		**Expt.**		**Expt.**	**DFT**
Ni1—N2	2.042 (3)	Ni2—N7	2.036 (3)	Ni3—N13^{i}	2.039 (3)	2.017
Ni1—N1	2.060 (3)	Ni2—N8	2.040 (3)	Ni3—N13	2.039 (3)	2.019
Ni1—N4	2.112 (3)	Ni2—N12	2.100 (3)	Ni3—N15	2.127 (3)	2.171
Ni1—N5	2.133 (3)	Ni2—N11	2.124 (3)	Ni3—N15^{i}	2.127 (3)	2.172
Ni1—N6	2.139 (3)	Ni2—N10	2.162 (3)	Ni3—N14	2.207 (3)	2.170
Ni1—N3	2.154 (3)	Ni2—N9	2.172 (3)	Ni3—N14^{i}	2.207 (3)	2.171
N2—Ni1—N1	177.90 (11)	N7—Ni2—N8	179.63(13)	N13^{i}—Ni3—N13	180	179.8
N2—Ni1—N4	90.28 (11)	N7—Ni2—N12	90.69(12)	N13^{i}—Ni3—N15	89.65 (11)	89.8
N1—Ni1—N4	87.62 (11)	N8—Ni2—N12	88.97(11)	N13—Ni3—N15	90.35 (11)	90.0
N2—Ni1—N5	89.97 (11)	N7—Ni2—N11	90.27(11)	N13^{i}—Ni3—N15^{i}	90.35 (11)	90.1
N1—Ni1—N5	90.11 (11)	N8—Ni2—N11	89.86(11)	N13—Ni3—N15^{i}	89.65 (11)	89.9
N4—Ni1—N5	93.72 (11)	N12—Ni2—N11	90.07(11)	N15—Ni3—N15^{i}	180	90.0
N2—Ni1—N6	92.05 (11)	N7—Ni2—N10	90.64(12)	N13^{i}—Ni3—N14	89.46 (11)	90.3
N1—Ni1—N6	90.04 (11)	N8—Ni2—N10	89.70(12)	N13—Ni3—N14	90.54 (11)	90.1
N4—Ni1—N6	177.65 (11)	N12—Ni2—N10	177.92(11)	N15—Ni3—N14	86.23 (10)	179.9
N5—Ni1—N6	86.49 (11)	N11—Ni2—N10	88.32(10)	N15^{i}—Ni3—N14	93.77 (10)	90.1
N2—Ni1—N3	89.31 (11)	N7—Ni2—N9	88.48(11)	N13^{i}—Ni3—N14^{i}	90.53 (11)	89.8
N1—Ni1—N3	90.87 (11)	N8—Ni2—N9	91.38(11)	N13—Ni3—N14^{i}	89.47 (11)	90.1
N4—Ni1—N3	93.19 (10)	N12—Ni2—N9	89.61(10)	N15—Ni3—N14^{i}	93.77 (10)	90.0
N5—Ni1—N3	173.06 (10)	N11—Ni2—N9	178.71(11)	N15^{i}—Ni3—N14^{i}	86.23 (10)	179.9
N6—Ni1—N3	86.63 (11)	N10—Ni2—N9	92.02(10)	N14—Ni3—N14^{i}	180	90.0

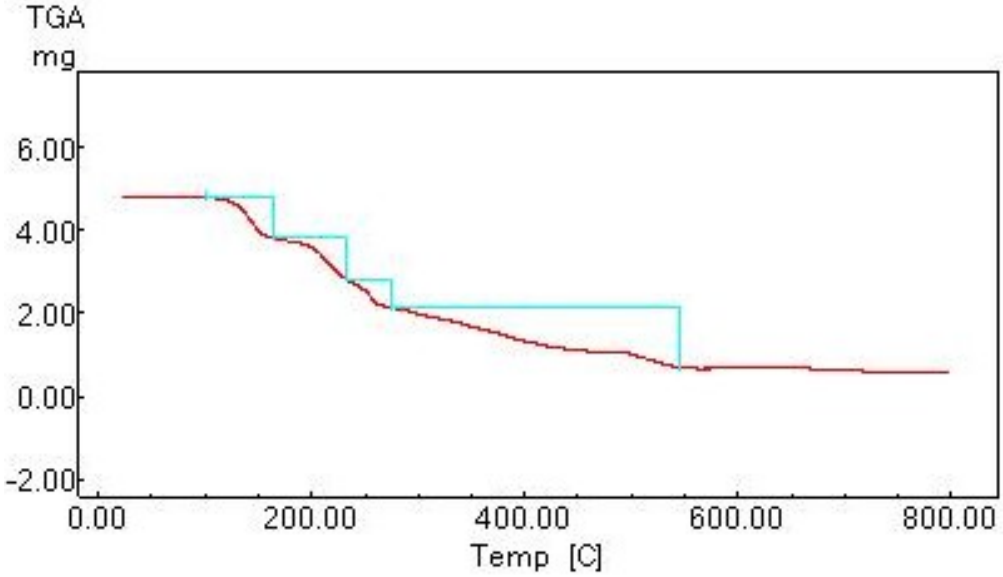
Symmetry code: (i) $-x+1, -y, -z+1$.

S2. TGA Thermograms

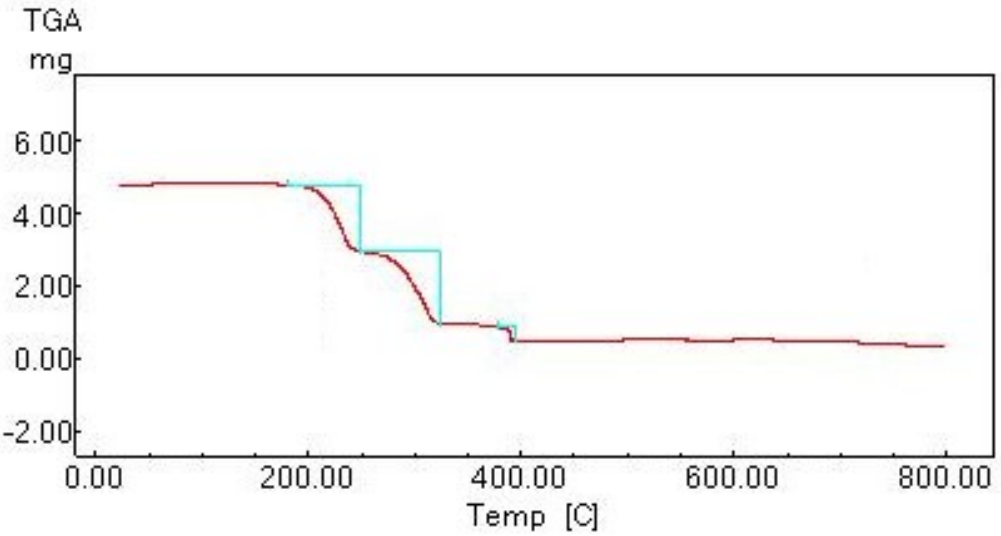
(I)



(II)

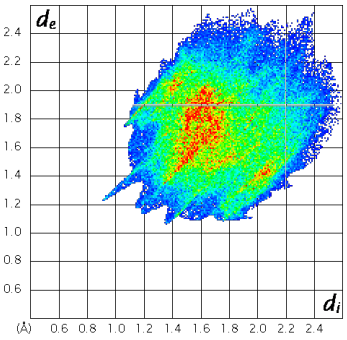


(III)

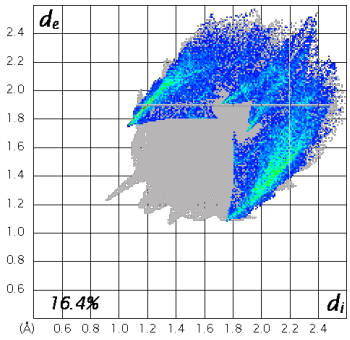


S3. Hirshfeld analysis for (I): two independent units

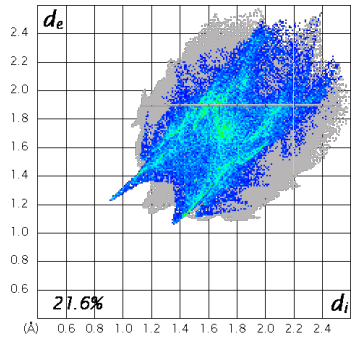
(I): Unit 1



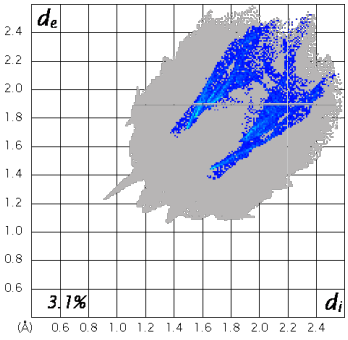
Contacts with H (92.0%)



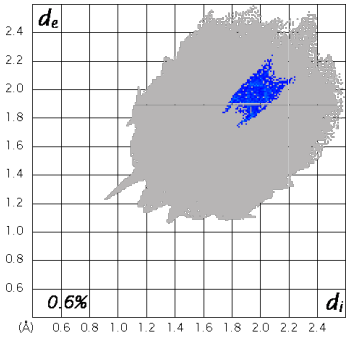
Contacts with S (16.4%)



Contacts with O (21.6%)

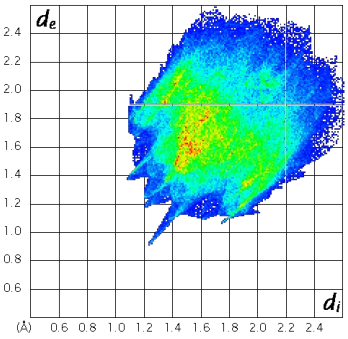


C…O contacts (3.1%)

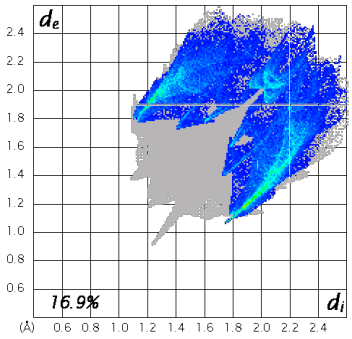


C…C contacts (0.6%)

(I): Unit 2



Contacts with H (92.6%)



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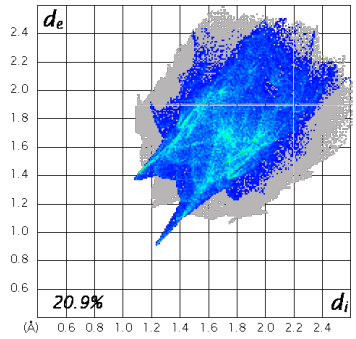
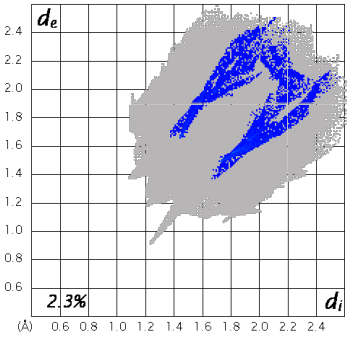
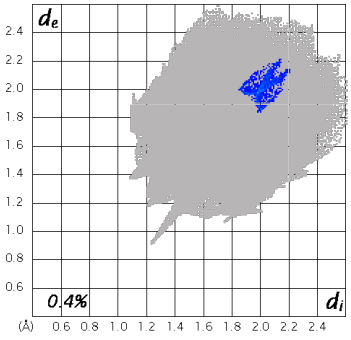


Contacts with O (20.9%)



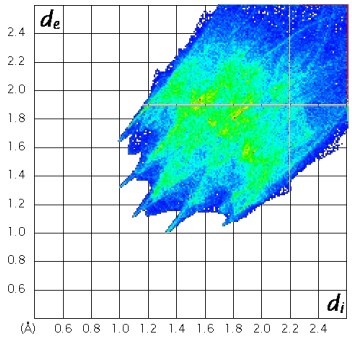
C…O contacts (2.3%)



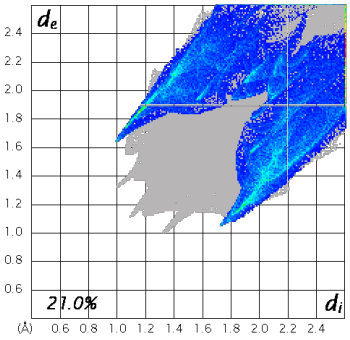
C…C contacts (0.4%)

S3. Hirshfeld analysis for (II): three independent units

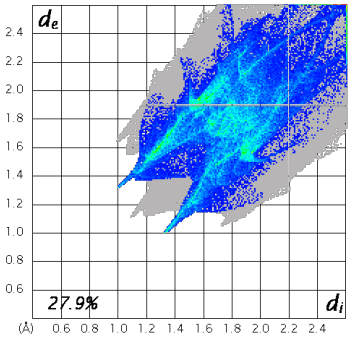
(II): Unit 1



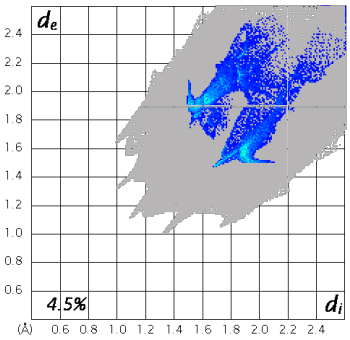
Contacts with H (88.0%)



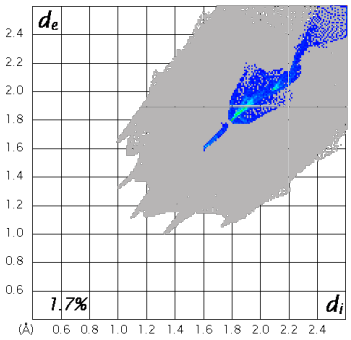
Contacts with S (21.0%)



Contacts with O (27.9%)

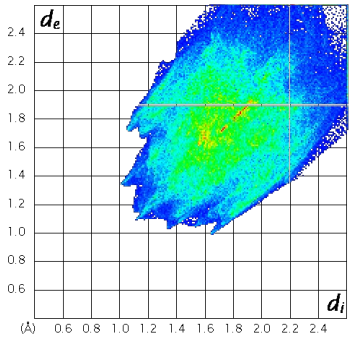


C…C contacts (4.5%)

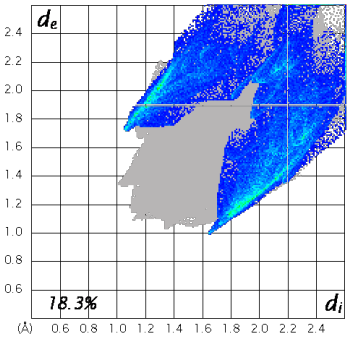


C…O contacts (1.7%)

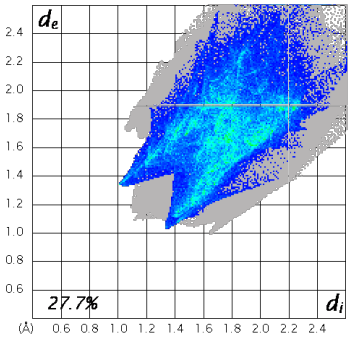
(II): Unit 2



Contacts with H (87.7%)



Contacts with S (18.3%)



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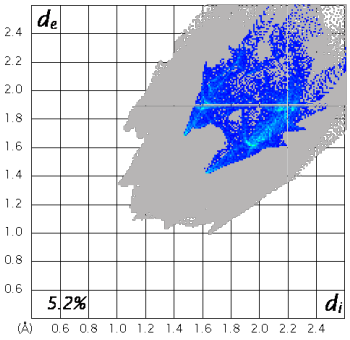
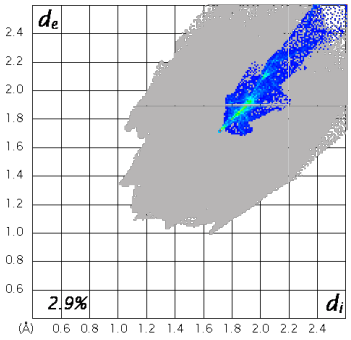
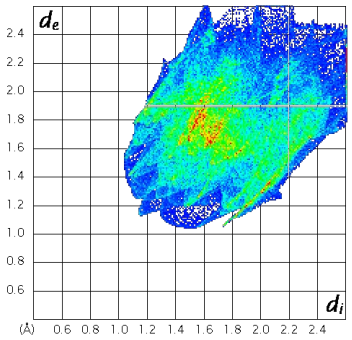


C…O contacts (5.2%)

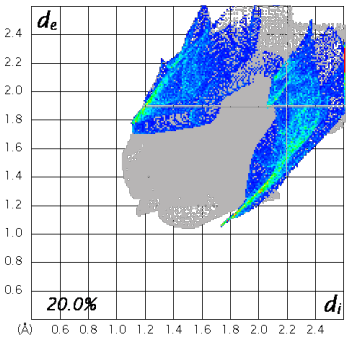


C…C contacts (2.9%)

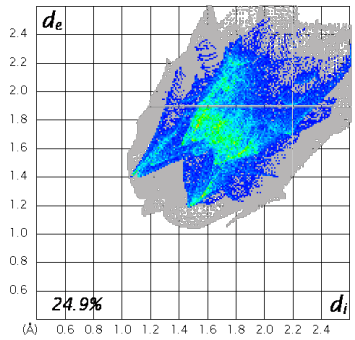
(II): Unit 3



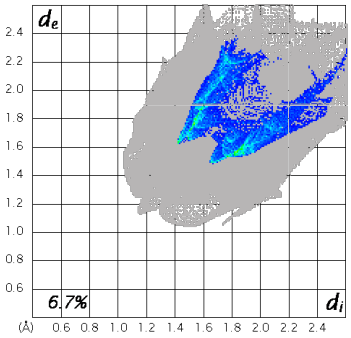
Contacts with H (86.4%)



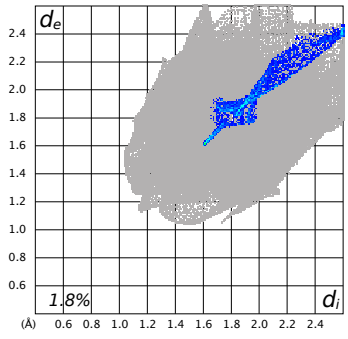
Contacts with S (20.0%)



Contacts with O (24.9%)

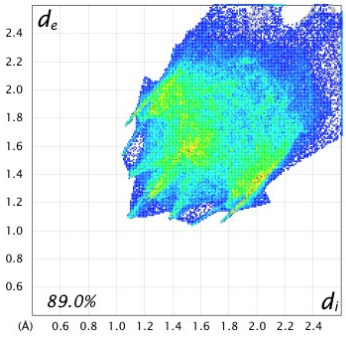


C…O contacts (6.7%)

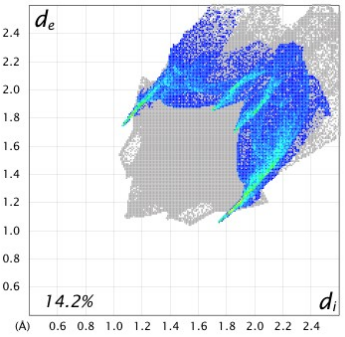


C…C contacts (1.8%)

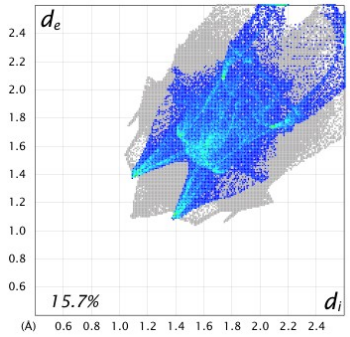
S3. Hirshfeld analysis for (III) one independent units



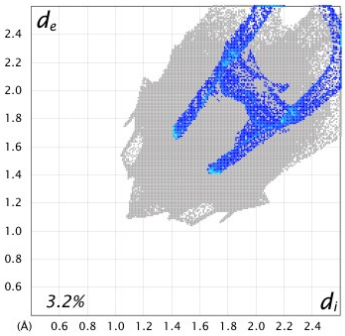
Contacts with H (89.0%)



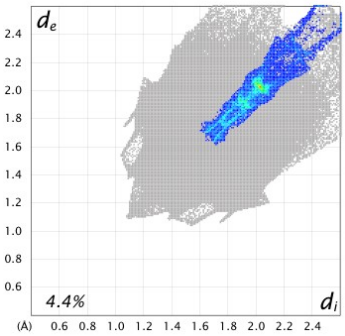
Contacts with S (14.2%)



Contacts with O (15.7%)



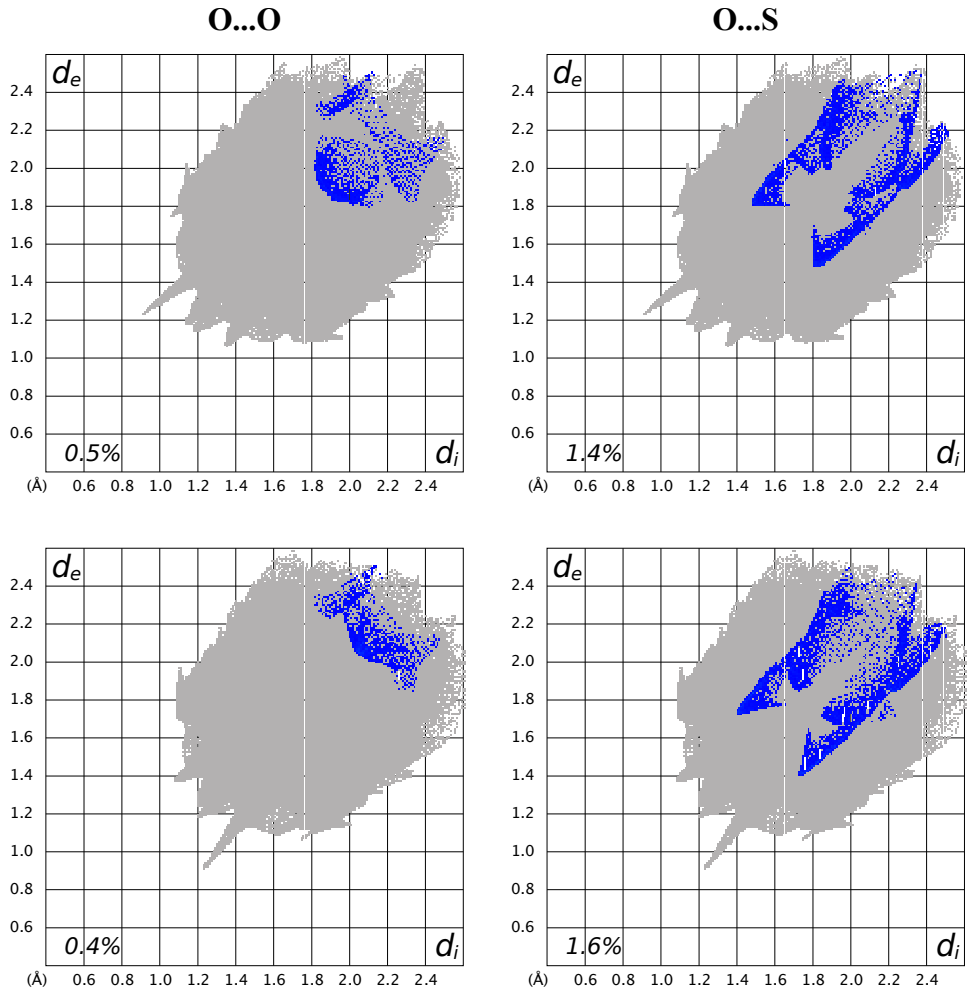
C…O contacts (3.2%)



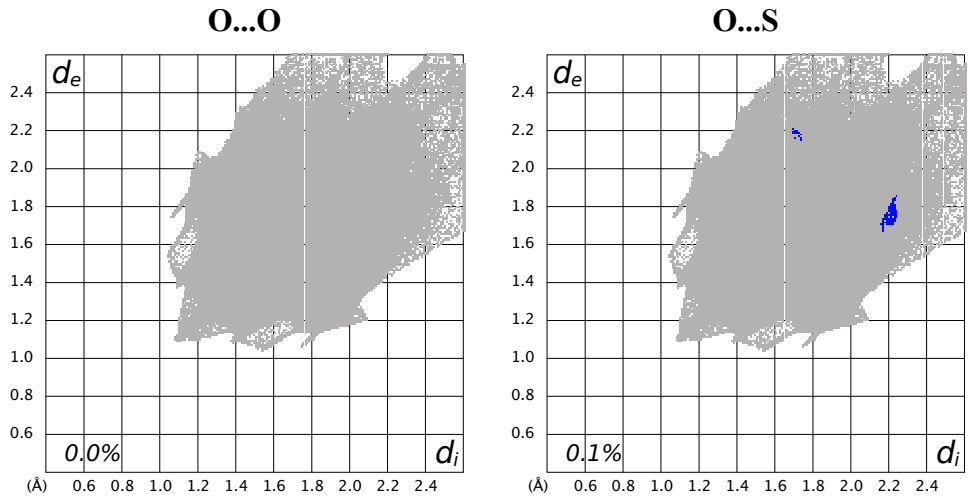
C…C contacts (4.4%)

S3. Hirshfeld analysis: O...O and O...S intermolecular contacts

Compound (I)



Compound (III)



Compound (II)