SUPPLEMENTARY MATERIAL

5-Iodo-1-Arylpyrazoles as Potential Benchmarks for Investigating the Tuning of the Halogen Bonding

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Crystallographic data

Table 1S. Bond distances and angles.

Compound **1**			
C1-C2	1.374(6)	C9-C10	1.415(4)
C1-C6	1.368(6)	C9-C13	1.479(5)
C2-C3	1.380(5)	C10-C11	1.489(5)
C3-C4	1.377(5)	C10-N2	1.338(4)
C4-C5	1.381(5)	C11-O3	1.192(4)
C4-N1	1.451(4)	C11-O4	1.324(4)
C5-C6	1.394(5)	C12-O4	1.452(5)
C5-C7	1.502(5)	C13-O1	1.200(4)
C8-C9	1.378(5)	C13-O2	1.323(4)
C8-I1	2.074(3)	C14-O2	1.442(4)
C8-N1	1.357(4)	N1-N2	1.363(4)
C6-C1-C2	121.0(4)	C9-C10-C11	129.5(3)
C1-C2-C3	118.9(4)	N2-C10-C9	111.8(3)
C4-C3-C2	119.5(4)	N2-C10-C11	118.3(3)
C3-C4-C5	122.8(4)	O3-C11-C10	123.2(3)
C3-C4-N1	117.8(3)	O3-C11-O4	124.3(4)
C5-C4-N1	119.4(3)	O4-C11-C10	112.4(3)
C4-C5-C6	116.3(4)	O1-C13-C9	123.7(3)
C4-C5-C7	122.4(4)	O1-C13-O2	124.1(3)
C6-C5-C7	121.3(4)	O2-C13-C9	112.1(3)
C1-C6-C5	121.6(4)	C8-N1-C4	128.5(3)
C9-C8-I1	130.7(2)	C8-N1-N2	112.1(3)
N1-C8-C9	107.3(3)	N2-N1-C4	119.4(2)
N1-C8-I1	121.8(2)	C10-N2-N1	104.4(2)
C8-C9-C10	104.4(3)	C13-O2-C14	115.6(3)
C8-C9-C13	125.2(3)	C11-O4-C12	115.1(3)
C10-C9-C13	130.4(3)		
Compound **2**			
C1-C2	1.381(8)	C10-C11	1.417(7)
C1-C6	1.401(8)	C10-C14	1.467(8)
C1-C8	1.506(8)	C11-C12	1.495(7)
C2-C3	1.379(8)	C11-N2	1.331(7)
C3-C4	1.374(7)	C12-O1	1.192(6)
C4-C5	1.395(7)	C12-O2	1.304(7)
C4-N1	1.426(7)	C13-O2	1.453(5)
C5-C6	1.391(8)	C14-O3	1.203(6)
C5-C7	1.514(8)	C14-O4	1.329(7)
C9-C10	1.366(7)	C15-O4	1.448(7)
C9-I1	2.072(5)	N1-N2	1.364(5)

C9-N1	1.356(7)		
C2-C1-C6	117.5(7)	C11-C10-C14	128.8(6)
C2-C1-C8	123.1(7)	C10-C11-C12	130.6(6)
C6-C1-C8	119.4(7)	N2-C11-C10	111.7(5)
C3-C2-C1	121.4(6)	N2-C11-C12	117.6(5)
C4-C3-C2	120.0(6)	O1-C12-C11	122.3(6)
C3-C4-C5	121.2(6)	O1-C12-O2	125.8(5)
C3-C4-N1	118.5(6)	O2-C12-C11	111.9(5)
C5-C4-N1	120.2(6)	O3-C14-C10	124.7(6)
C4-C5-C7	121.0(6)	O3-C14-O4	123.3(7)
C6-C5-C4	117.4(6)	O4-C14-C10	112.0(6)
C6-C5-C7	121.5(6)	C9-N1-C4	129.2(4)
C5-C6-C1	122.4(6)	C9-N1-N2	111.1(5)
C10-C9-I1	131.5(5)	N2-N1-C4	119.4(5)
N1-C9-C10	108.2(5)	C11-N2-N1	104.9(4)
N1-C9-I1	120.2(4)	C12-O2-C13	115.4(5)
C9-C10-C11	104.1(6)	C14-O4-C15	116.4(5)
C9-C10-C14	127.1(5)		

Compound 3

Br1-C1	1.895(7)	C9-C10	1.403(8)
C1-C2	1.372(11)	C9-C13	1.469(9)
C1-C6	1.361(10)	C10-C11	1.488(9)
C2-C3	1.378(10)	C10-N2	1.321(8)
C3-C4	1.365(9)	C11-O3	1.204(8)
C4-C5	1.361(10)	C11-O4	1.313(8)
C4-N1	1.432(8)	C12-O4	1.443(8)
C5-C6	1.407(9)	C13-O1	1.184(8)
C5-C7	1.511(9)	C13-O2	1.322(7)
C8-C9	1.382(9)	C14-O2	1.445(8)
C8-I1	2.071(6)	N1-N2	1.356(6)
C8-N1	1.348(8)		

C2-C1-Br1	118.8(6)	C10-C9-C13	128.6(6)
C6-C1-Br1	118.4(6)	C9-C10-C11	127.8(6)
C6-C1-C2	122.8(7)	N2-C10-C9	112.8(5)
C1-C2-C3	118.5(7)	N2-C10-C11	119.3(6)
C4-C3-C2	119.3(8)	O3-C11-C10	122.5(6)
C3-C4-N1	117.9(7)	O3-C11-O4	125.4(6)
C5-C4-C3	122.6(7)	O4-C11-C10	112.1(6)
C5-C4-N1	119.5(6)	O1-C13-C9	124.5(6)
C4-C5-C6	118.4(6)	O1-C13-O2	123.6(7)
C4-C5-C7	122.8(7)	O2-C13-C9	111.9(6)
C6-C5-C7	118.8(7)	C8-N1-C4	128.6(5)
C1-C6-C5	118.4(7)	C8-N1-N2	111.2(5)

C9-C8-I1	129.3(5)	N2-N1-C4	120.1(5)
N1-C8-C9	108.1(5)	C10-N2-N1	104.8(5)
N1-C8-I1	122.5(5)	C13-O2-C14	116.6(6)
C8-C9-C10	103.1(6)	C11-O4-C12	116.1(6)
C8-C9-C13	128.3(6)		

Compound 4

Br1-C1	1.892(5)	C9-N1	1.365(6)
C1-C2	1.364(7)	C10-C11	1.394(7)
C1-C6	1.387(7)	C10-C14	1.486(7)
C2-C3	1.380(7)	C11-C12	1.484(7)
C3-C4	1.380(7)	C11-N2	1.327(6)
C4-C5	1.376(7)	C12-O1	1.180(6)
C4-N1	1.438(6)	C12-O2	1.314(6)
C5-C6	1.372(7)	C13-O2	1.447(6)
C5-C7	1.514(7)	C14-O3	1.184(6)
C7-C8	1.486(7)	C14-O4	1.323(6)
C9-C10	1.368(7)	C15-O4	1.442(7)
C9-I1	2.056(5)	N1-N2	1.365(5)

C2-C1-Br1	119.6(4)	C9-C10-C14	123.6(5)
C2-C1-C6	122.0(5)	C11-C10-C14	130.7(5)
C6-C1-Br1	118.4(4)	C10-C11-C12	129.3(5)
C1-C2-C3	118.6(5)	N2-C11-C10	112.2(5)
C2-C3-C4	118.8(5)	N2-C11-C12	118.2(5)
C3-C4-N1	116.9(5)	O1-C12-C11	123.2(6)
C5-C4-C3	123.2(5)	O1-C12-O2	124.4(5)
C5-C4-N1	119.9(5)	O2-C12-C11	112.3(5)
C4-C5-C7	120.5(5)	O3-C14-C10	125.4(5)
C6-C5-C4	117.2(5)	O3-C14-O4	124.3(6)
C6-C5-C7	122.2(5)	O4-C14-C10	110.3(5)
C5-C6-C1	120.1(5)	C9-N1-C4	128.2(4)
C8-C7-C5	117.4(5)	C9-N1-N2	112.0(4)
C10-C9-I1	132.6(4)	N2-N1-C4	119.7(4)
N1-C9-C10	106.2(5)	C11-N2-N1	104.0(4)
N1-C9-I1	121.1(4)	C12-O2-C13	116.0(5)
C9-C10-C11	105.5(5)	C14-O4-C15	116.1(5)

Compound 5

Br1-C1	1.906(4)	C10-N1	1.347(5)
C1-C2	1.380(5)	C11-C12	1.406(5)
C1-C6	1.378(5)	C11-C15	1.466(5)
C2-C3	1.387(5)	C12-C13	1.499(5)
C3-C4	1.378(5)	C12-N2	1.333(5)
C4-C5	1.388(5)	C13-O3	1.196(5)
C4-N1	1.438(5)	C13-O4	1.315(5)

C5-C6	1.401(5)	C14-O4	1.457(4)
C5-C7	1.524(5)	C15-O1	1.204(4)
C7-C8	1.519(6)	C15-O2	1.341(4)
C7-C9	1.515(5)	C16-O2	1.447(4)
C10-C11	1.383(5)	N1-N2	1.367(4)
C10-I1	2.065(4)		

C2-C1-Br1	119.7(3)	C10-C11-C12	103.6(3)
C6-C1-Br1	118.5(3)	C10-C11-C15	126.7(3)
C6-C1-C2	121.8(4)	C12-C11-C15	129.5(4)
C1-C2-C3	118.5(4)	C11-C12-C13	128.2(4)
C4-C3-C2	119.6(4)	N2-C12-C11	112.7(3)
C3-C4-C5	122.9(4)	N2-C12-C13	119.1(3)
C3-C4-N1	118.0(3)	O3-C13-C12	122.8(4)
C5-C4-N1	119.1(3)	O3-C13-O4	125.2(4)
C4-C5-C6	116.8(4)	O4-C13-C12	112.0(4)
C4-C5-C7	122.6(3)	O1-C15-C11	124.8(4)
C6-C5-C7	120.5(3)	O1-C15-O2	124.1(4)
C1-C6-C5	120.4(4)	O2-C15-C11	111.2(3)
C8-C7-C5	110.7(3)	C10-N1-C4	127.6(3)
C9-C7-C5	111.8(3)	C10-N1-N2	111.9(3)
C9-C7-C8	111.8(4)	N2-N1-C4	120.3(3)
C11-C10-I1	129.9(3)	C12-N2-N1	104.0(3)
N1-C10-C11	107.8(3)	C15-O2-C16	115.1(3)
N1-C10-I1	122.2(3)	C13-O4-C14	115.2(3)

Compound 6

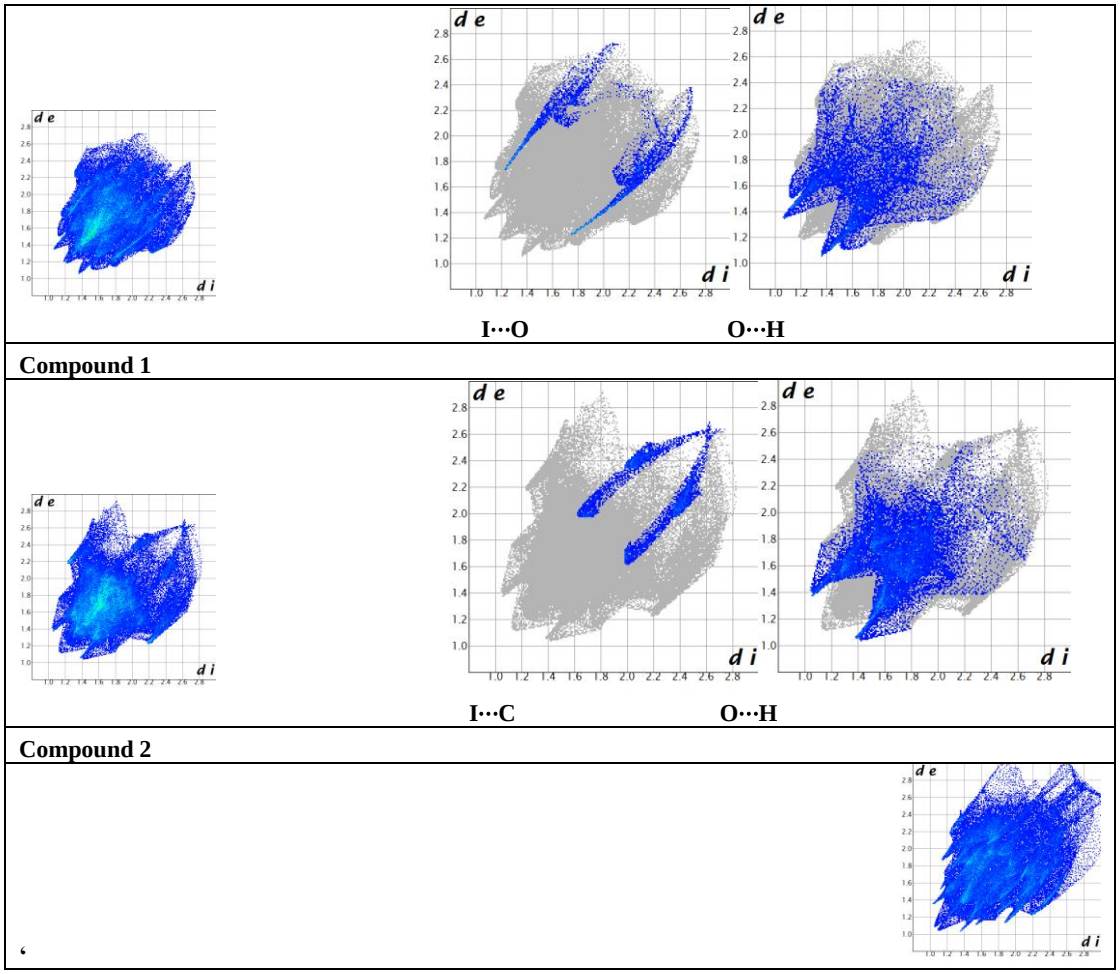
Br1-C1	1.897(6)	C8-C9	1.397(8)
C1-C2	1.379(11)	C8-C12	1.471(8)
C1-C6	1.358(10)	C9-C10	1.501(8)
C2-C3	1.370(9)	C9-N2	1.323(7)
C3-C4	1.380(9)	C10-O1	1.175(8)
C4-C5	1.382(9)	C10-O2	1.315(8)
C4-N1	1.438(7)	C11-O2	1.461(8)
C5-C6	1.380(8)	C12-O3	1.184(7)
C5-Cl1	1.721(7)	C12-O4	1.303(7)
C7-C8	1.356(8)	C13-O4	1.428(8)
C7-I1	2.062(6)	N1-N2	1.357(6)
C7-N1	1.349(7)		

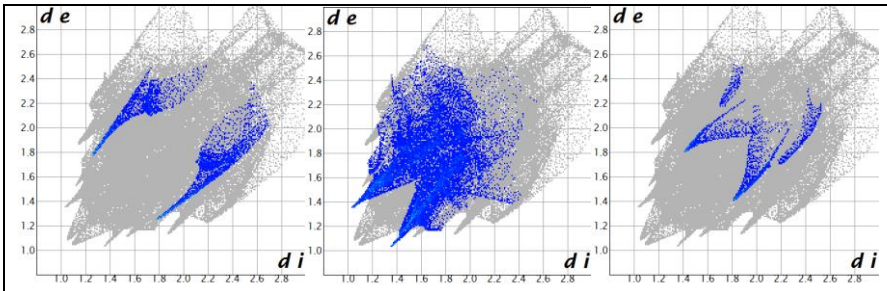
C2-C1-Br1	119.3(6)	C9-C8-C12	128.8(6)
C6-C1-Br1	119.3(6)	C8-C9-C10	128.8(5)
C6-C1-C2	121.4(6)	N2-C9-C8	112.4(5)
C3-C2-C1	120.0(7)	N2-C9-C10	118.4(5)
C2-C3-C4	119.3(7)	O1-C10-C9	124.2(6)
C3-C4-C5	119.9(6)	O1-C10-O2	125.1(6)

C3-C4-N1	118.9(6)	O2-C10-C9	110.6(5)
C5-C4-N1	121.2(6)	O3-C12-C8	123.9(6)
C4-C5-Cl1	119.7(5)	O3-C12-O4	122.9(6)
C6-C5-C4	120.5(6)	O4-C12-C8	113.2(5)
C6-C5-Cl1	119.8(6)	C7-N1-C4	128.3(5)
C1-C6-C5	118.9(7)	C7-N1-N2	111.4(5)
C8-C7-I1	131.0(4)	N2-N1-C4	120.1(5)
N1-C7-C8	107.8(5)	C9-N2-N1	104.1(5)
N1-C7-I1	121.0(4)	C10-O2-C11	116.7(6)
C7-C8-C9	104.2(5)	C12-O4-C13	117.6(5)
C7-C8-C12	127.0(6)		

1. Fingerprint plots

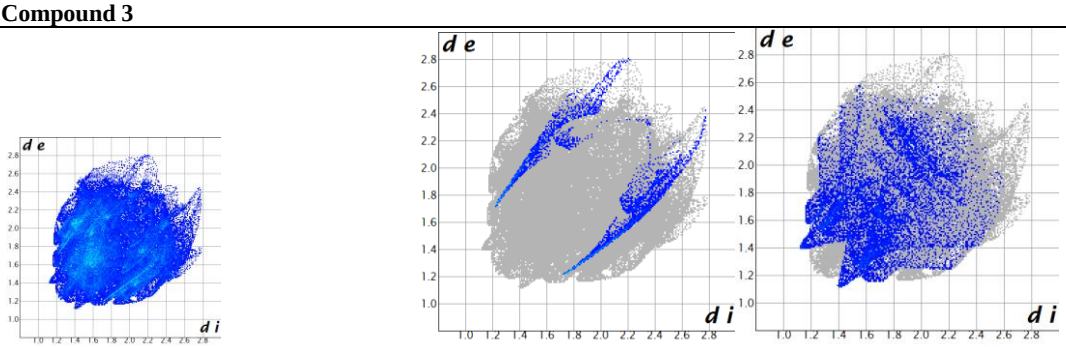
Table 2S. Fingerprint plots showing the most important intermolecular interactions: halogen bonds and hydrogen bonds.





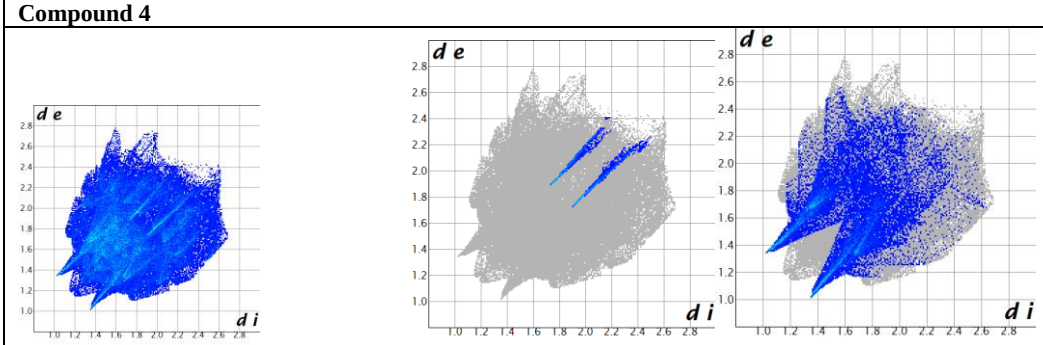
I···O O···H Br···O

Compound 3



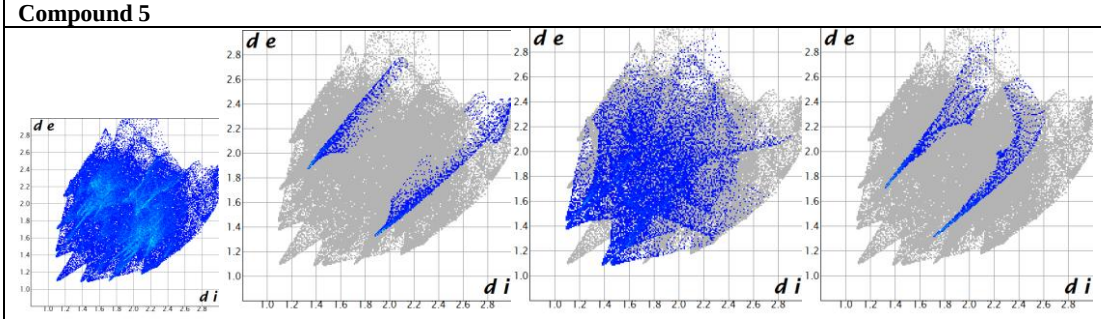
I···O O···H

Compound 4

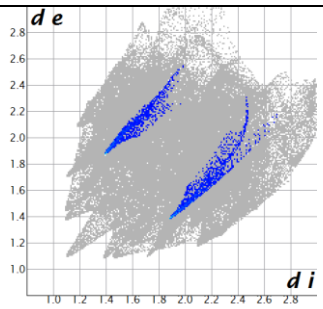


I···Br O···H

Compound 5

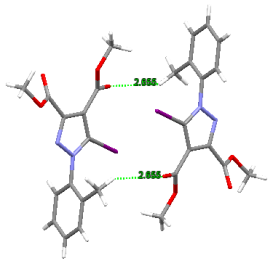
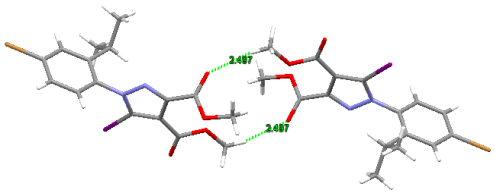


I···O O···H Br···O

 **I···N**
Compound 6

2. Energy calculations

Table 3S. Selected hydrogen bonded dimers and calculated energies.

	
1S -54.9 kJ/mol/dimer (-27.45 kJ/mole/O···H interaction)	**5S -36.57 kJ/mol (-18.29 kJ/mole/O···H interaction)**

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