Electronic Supplementary Information

Supramolecular architectures in the reaction products of caffeine with dihalogens: crystal structures of the CT-adduct *bis*(caffeine)-diiodine and the caffeinium iodine dichloride salt.

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Table S1. Crystal data and structure refinement for (**caf**)$_2$·I_2.

Empirical formula	$C_{15.36}H_{19.2}I_2N_{7.68}O_{3.84}$
Formula weight	626.66
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	9.1739(7)
b/Å	14.8378(11)
c/Å	16.1206(13)
α/°	106.896(3)
β / °	94.066(3)
γ / °	91.916(3)
Volume/Å^3	2091.0(3)
Z	4
ρ_{calc}g/cm^3	1.991
μ/mm^{-1}	3.050
F(000)	1207.4
Crystal size/mm^3	0.16 × 0.09 × 0.02
Radiation	Mo$K\alpha$ (λ = 0.71073)
2θ range for data collection/°	4.458 to 56.726
Index ranges	$-12 \le h \le 12$, $-19 \le k \le 19$, $-21 \le l \le 21$
Reflections collected	37770
Independent reflections	10371 [R_{int} = 0.0343, R_{sigma} = 0.0328]
Data/restraints/parameters	10371/1/569
Goodness-of-fit on F^2	1.091
Final R indexes [$I \ge 2\sigma$ (I)]	R_1 = 0.0316, wR_2 = 0.0741
Final R indexes [all data]	R_1 = 0.0404, wR_2 = 0.0795
Largest diff. peak/hole / e Å^{-3}	1.15/−0.91

Table S2. Bond lengths (Å) for (**caf**)$_2$·I_2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I4	I3	2.7056(4)	N11	C19	1.412(4)
I2	I1	2.7070(3)	N11	C23	1.469(4)
N2	C1	1.334(5)	C13	C10	1.363(5)
N2	C6	1.464(5)	O4	C11	1.220(4)
N2	C2	1.381(5)	C22	N10	1.450(4)
O5	C20	1.220(4)	N3	C4	1.396(5)
N5	C13	1.352(4)	N3	C7	1.472(4)
N5	C9	1.330(5)	N3	C3	1.405(4)
O8	C27	1.208(4)	N10	C18	1.391(4)
O3	C12	1.215(4)	N10	C17	1.352(5)
O6	C19	1.221(4)	C10	C11	1.421(5)
N6	C9	1.341(4)	N16	C29	1.356(4)
N6	C10	1.395(4)	N16	C28	1.384(5)
N6	C14	1.452(4)	N16	C32	1.455(5)
N8	C13	1.377(4)	N13	C25	1.334(4)
N8	C16	1.468(4)	N13	C29	1.363(4)
N8	C12	1.370(4)	N15	C27	1.410(4)
O1	C4	1.225(4)	N15	C28	1.387(5)
O2	C3	1.223(4)	N15	C31	1.466(4)
N4	C8	1.470(4)	C1	N1	1.327(5)
N4	C4	1.371(4)	C25	N14	1.329(4)
N4	C5	1.372(4)	C5	C2	1.372(5)
N7	C12	1.409(4)	C5	N1	1.353(5)
N7	C15	1.463(4)	N14	C30	1.475(4)
N7	C11	1.410(4)	N14	C26	1.390(4)
O7	C28	1.217(4)	C2	C3	1.426(5)
N9	C21	1.353(4)	C27	C26	1.423(5)
N9	C17	1.331(5)	C29	C26	1.370(5)
N12	C24	1.464(5)	C21	C18	1.363(5)
N12	C20	1.383(4)	C19	C18	1.427(5)
N12	C21	1.366(4)	I1B	I2B	2.699(8)
N11	C20	1.388(4)	I3B	I4B	2.745(9)

Table S3. Bond angles (°) for (**caf**)$_2$·I_2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N2	C6	126.5(3)	N1	C1	N2	113.1(3)
C1	N2	C2	106.6(3)	N14	C25	N13	113.6(3)
C2	N2	C6	126.7(3)	C2	C5	N4	121.4(3)
C9	N5	C13	103.3(3)	N1	C5	N4	127.2(3)
C9	N6	C10	105.2(3)	N1	C5	C2	111.4(3)
C9	N6	C14	127.8(3)	C25	N14	C30	127.5(3)
C10	N6	C14	127.0(3)	C25	N14	C26	106.4(3)
C13	N8	C16	121.2(3)	C26	N14	C30	126.0(3)
C12	N8	C13	120.3(3)	N2	C2	C3	132.1(3)
C12	N8	C16	118.5(3)	C5	C2	N2	104.9(3)
C4	N4	C8	118.9(3)	C5	C2	C3	123.1(3)
C4	N4	C5	119.9(3)	O2	C3	N3	121.4(3)
C5	N4	C8	121.2(3)	O2	C3	C2	127.1(3)
C12	N7	C15	116.8(3)	N3	C3	C2	111.5(3)
C12	N7	C11	126.3(3)	O8	C27	N15	121.7(3)
C11	N7	C15	116.9(3)	O8	C27	C26	127.7(3)
C17	N9	C21	103.8(3)	N15	C27	C26	110.6(3)
C20	N12	C24	118.0(3)	O5	C20	N12	121.0(3)
C21	N12	C24	121.8(3)	O5	C20	N11	122.0(3)
C21	N12	C20	120.0(3)	N12	C20	N11	117.0(3)
C20	N11	C19	126.7(3)	N16	C29	N13	126.0(3)
C20	N11	C23	117.1(3)	N16	C29	C26	122.6(3)
C19	N11	C23	116.3(3)	N13	C29	C26	111.4(3)
N5	C13	N8	126.6(3)	O7	C28	N16	120.8(4)
N5	C13	C10	112.3(3)	O7	C28	N15	122.2(3)
C10	C13	N8	121.2(3)	N15	C28	N16	116.9(3)
N5	C9	N6	114.1(3)	N9	C21	N12	126.8(3)
C4	N3	C7	116.7(3)	N9	C21	C18	111.6(3)
C4	N3	C3	126.8(3)	C18	C21	N12	121.6(3)
C3	N3	C7	116.5(3)	O3	C12	N8	121.6(3)
C18	N10	C22	127.9(3)	O3	C12	N7	121.5(3)
C17	N10	C22	127.5(3)	N8	C12	N7	116.9(3)
C17	N10	C18	104.6(3)	O6	C19	N11	120.3(3)
O1	C4	N4	121.0(3)	O6	C19	C18	128.2(3)
O1	C4	N3	121.8(3)	N11	C19	C18	111.5(3)
N4	C4	N3	117.2(3)	N7	C11	C10	111.6(3)
N6	C10	C11	131.2(3)	O4	C11	N7	120.5(3)
C13	C10	N6	105.2(3)	O4	C11	C10	127.9(3)
C13	C10	C11	123.7(3)	N10	C18	C19	130.6(3)
C29	N16	C28	119.0(3)	C21	C18	N10	106.1(3)
C29	N16	C32	121.5(3)	C21	C18	C19	123.3(3)
C28	N16	C32	119.0(3)	N14	C26	C27	132.0(3)
C25	N13	C29	103.6(3)	C29	C26	N14	105.0(3)
C27	N15	C31	116.1(3)	C29	C26	C27	123.0(3)
C28	N15	C27	127.5(3)	N9	C17	N10	113.9(3)
C28	N15	C31	116.4(3)	C1	N1	C5	104.0(3)

Table S4. Crystallographic data and structure refinement details for [H**caf**][ICl_2].

Compound	[H**caf**][ICl_2]
Formula	$C_8H_{11}Cl_2IN_4O_2$
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
M.W.	393.01
a / Å	8.770(3)
b / Å	10.790(2)
c / Å	14.274(7)
α / °	90
β / °	91.77(3)
γ / °	90
V / Å^3	1350.1(8)
Z	4
D_c /g/cm^{-3}	1.934
Instrument	Enraf Nonius CAD4 diffractometer
Radiation, wavelength (Å)	Mo*K*α, 0.71073
T (K)	293(2)
μ/ mm^{-1}	2.764
Measured reflections	2372
Min. θ (°)	3.286
Max. θ (°)	24.964
Absorption correction	Psi-scan
T_{min}, T_{max}	0.810, 1.000
Independent reflections	2373
Observed reflections (I>2σ(I)	1678
Number of parameters	154
R	0.0548
*wR*2 [all data]	0.1586
GOF	1.033
Weighting scheme	$w = 1/[\sigma^2(Fo^2)+(0.0938q)^2 + 0.9846q]$ where q =

$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$
$GOF=\{\Sigma[w(Fo^2-Fc^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Table S5. Selected interatomic distances (Å) and angles (°) in [H**caf**][ICl_2].

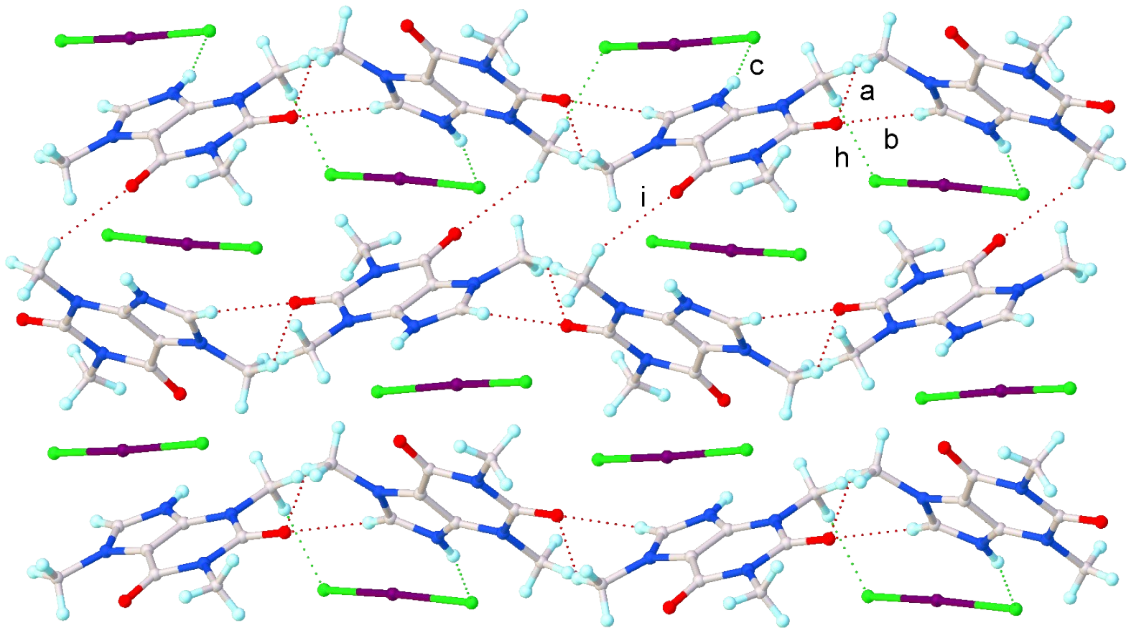
I-Cl1	2.464(3)	I-Cl2	2.656(3)
C2-O11	1.212(9)	C6-O13	1.208(10)
N1-C2	1.385(10)	N1-C6	1.402(10)
N1-C10	1.462(10)	N3-C4	1.372(8)
N3-C2	1.397(10)	N3-C12	1.463(10)
N7-C8	1.304(10)	N7-C5	1.380(9)
N7-C14	1.485(9)	N9-C8	1.340(9)
N9-C4	1.366(9)	C4-C5	1.339(10)
C5-C6	1.431(11)		

Cl1-I-Cl2	174.87(9)	N1-C2-N3	117.9(6)
C2-N1-C6	126.8(7)	C5-C4-N9	108.7(6)
C2-N1-C10	116.8(6)	C5-C4-N3	124.5(7)
C6-N1-C10	116.32(7)	N9-C4-N3	126.7(7)
C4-N3-C2	116.8(6)	C4-C5-N7	106.3(6)
C4-N3-C12	122.2(6)	C4-C5-C6	122.3(6)
C2-N3-C12	120.6(6)	N7-C5-C6	131.3(7)
C8-N7-C5	108.4(6)	O13-C6-N1	122.2(8)
C8-N7-C14	126.8(7)	O13-C6-C5	126.4(7)
C5-N7-C14	124.7(6)	N1-C6-C5	111.4(7)
C8-N9-C4	106.6(7)	N7-C8-N9	110.0(7)
O11-C2-N1	121.9(8)	O11-C2-N3	120.2(8)

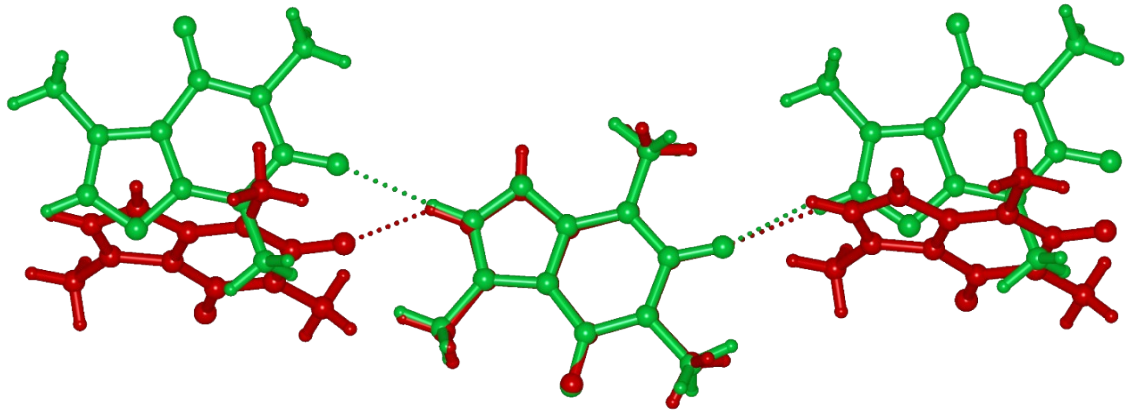
Hydrogen bonds

N9···Cl2	3.089(7)	N9-H9···Cl2^{ii}	162.8(4)
N9···O13^{ii}	3.078(9)	N9-H9···O13^{i}	95.1(4)
C10···O11	2.798(11)	C10-H10A···O11	89.4(6)
C10···O13	2.709(12)	C10-H10B···O13	105.9(6)
C12···N9	2.971(10)	C12-H12A···N9	93.3(5)
C12···O11	2.760(11)	C12-H12B···O11	102.2(6)
C14···O13	3.092(11)	C14-H14B···O13	93.1(5)
C14···O13	3.092(11)	C14-H14C···O13	93.9(5)
C12···O13^{ii}	3.357(11)	C12-H12A···O13^{ii}	139.3(5)
C8···O11^{i}	2.990(9)	C8-H8···O11^{i}	136.2(5)
C12···Cl1^{iii}	3.699(9)	C12-H12C···Cl1^{iii}	166.3(5)
C14···O11^{i}	3.224(11)	C14-H14A···O11^{i}	141.3(5)

Symmetry codes: ^{i} = x−1/2, 1/2−y, 1/2+z; ^{ii} = 3/2−x, y−1/2, 1/2−z; ^{iii} = x+1/2, 1/2−y,z−1/2



(**A**)



(**B**)

Figure S1. (A) Perspective view of the crystal structure of [H**caf**][ICl_2] seen along [100] direction; (B) overlap of successive caffein molecules/caffeinium ions as found in the ribbons of (**caf**)$_2$·I_2 and [H**caf**][ICl_2], respectively.

	D–H···A	$d_{H\cdots A}$	$d_{D\cdots A}$	$d_{D\cdots H}$	$\alpha_{D-H\cdots A}$
a	C8^{i}–H8^{i}···O11	2.248(6)	2.989(10)	0.93	136.2(5)
b	C14^{i}–H14A'···O11	2.418(6)	3.224(11)	0.96	141.3(5)
c	N9–H9···Cl2	2.256(3)	3.089(7)	0.86	162.8(4)
h	C12–H12C···Cl1^{i}	2.759(3)	3.699(9)	0.96	166.3(6)
i	C12^{ii}–H12A^{ii}···O13	2.571(6)	3.358(10)	0.96	139.3(5)

Symmetry code: ^{i} = 1/2+*x*, 1/2−*y*, −1/2+*z*; ^{ii} = 3/2−*x*, 1/2+*y*, 1/2−*z*.

Consecutive cations are also bridged by ICl_2^- anions through N(9)–H···Cl2 and C(3)–H···Cl1 interactions involving the N(9)–H group of the imidazolium ring and a C–H of the methyl group in position 3 (see Figure 1 in the text for labelling scheme, interactions *c* and *h* in Figure S1). Based on Jeffrey's classification[1] of the energy of a hydrogen bond in relation to its length, we can deduce that Cl2 forms a 'moderate' hydrogen bond with the N(9)–H donor, associated with energies in the range of 4 to 15 kcal/mol. In contrast, Cl1 forms a 'weak' hydrogen bond with the C–H donor, associated with energies of less than 4 kcal/mol.[2] Ribbons of interacting [H**caf**]$^+$ cations and ICl_2^- anions stack along the [010] direction and are interconnected by C–H···O hydrogen bonds involving the C(6)=O group and a C–H of the methyl group in position 3 (Figure 1 in the text for labelling scheme, interaction *i* in Figure S1).

1. "Moderate" hydrogen bonds are associated with X···A bond distances in the range 2.5 - 3.2 Å and energies in the range 4 - 15 kcal /mol, while "weak" hydrogen bonds are associated with distances > 3.2 Å and energies < 4 kcal /mol, according to Jeffrey's classification, G. A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, Oxford, 1997.
2. T. Steiner, *Angew. Chem. Int. Ed.,* 2002, **41**, 48–76.

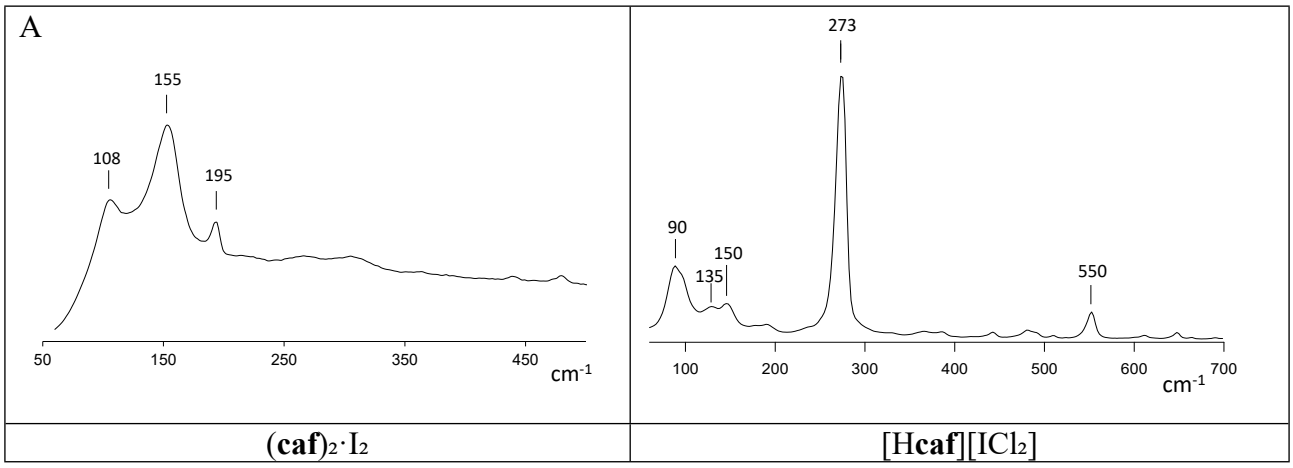


Figure S2. Solid-state FT-Raman spectra of the compounds (**caf**)$_2$·I$_2$ (left) and [H**caf**][ICl$_2$] (right).

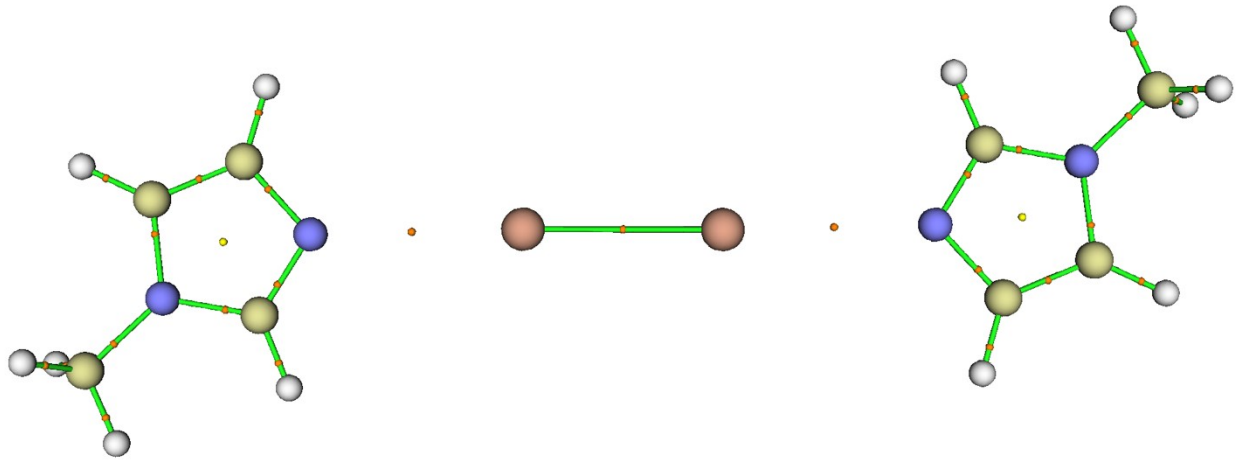


Figure S3. Bond Critical Points (BCPs) calculated for the model compound (MMI)$_2$·I$_2$ at QTAIM/DFT level. BCP types: (3,–1) red, (3, +1) yellow.

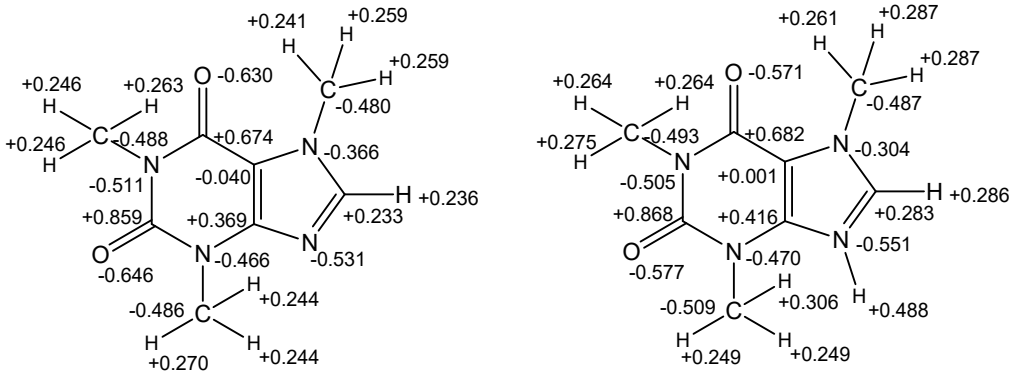


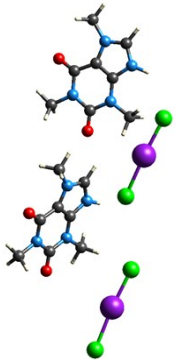
Figure S4. Electron density calculated at DFT level for caffeine (left) and caffeinium cation (right).

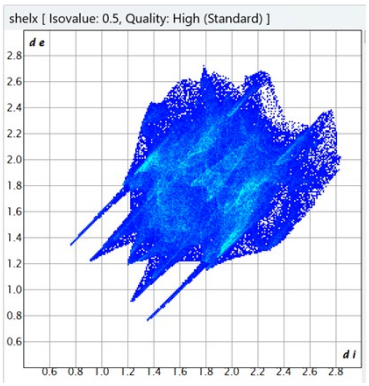
Hirshfeld surface analysis: normalized contact distance function, d_{norm},

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}}$$ eq. 1

where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms inside (i) and outside (e) of the surface; di and d_e are the distances between the point on the surface and the nearest atoms present inside and outside of the surface, respectively.[1]

1. (a) M. A. Spackman, D. Jayatilaka, *CrystEngComm*, 2009, **11**, 19-32, (b) J. J. McKinnon, D. Jayatilaka, M. A. Spackman, *Chem. Commun*., 2007, 3814–3816





All atoms (100%)

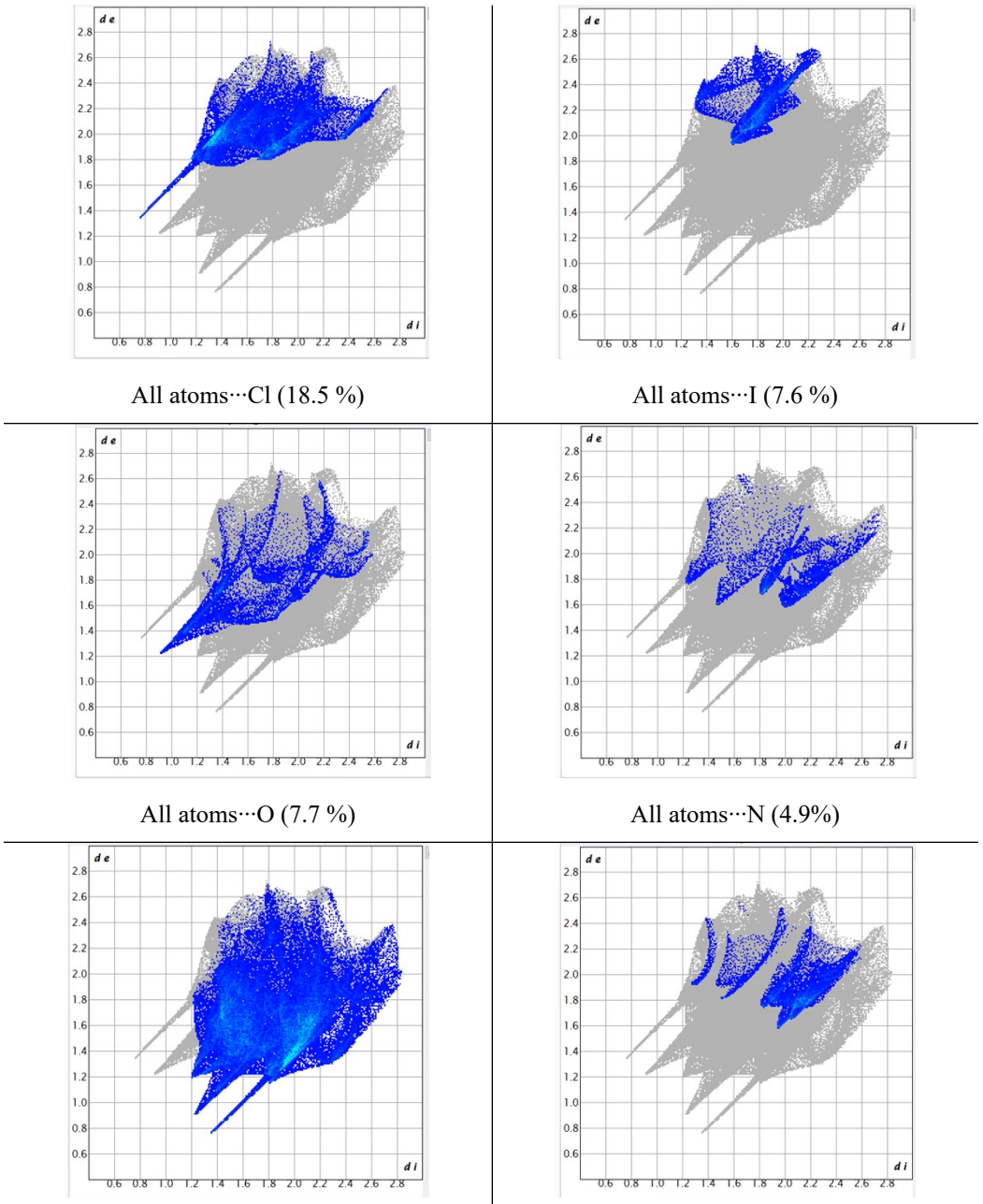


Figure S5. 2D fingerprint plots for [H**caf**][ICl_2] showing percentage of interaction between each atom and all the other atoms in the molecule.

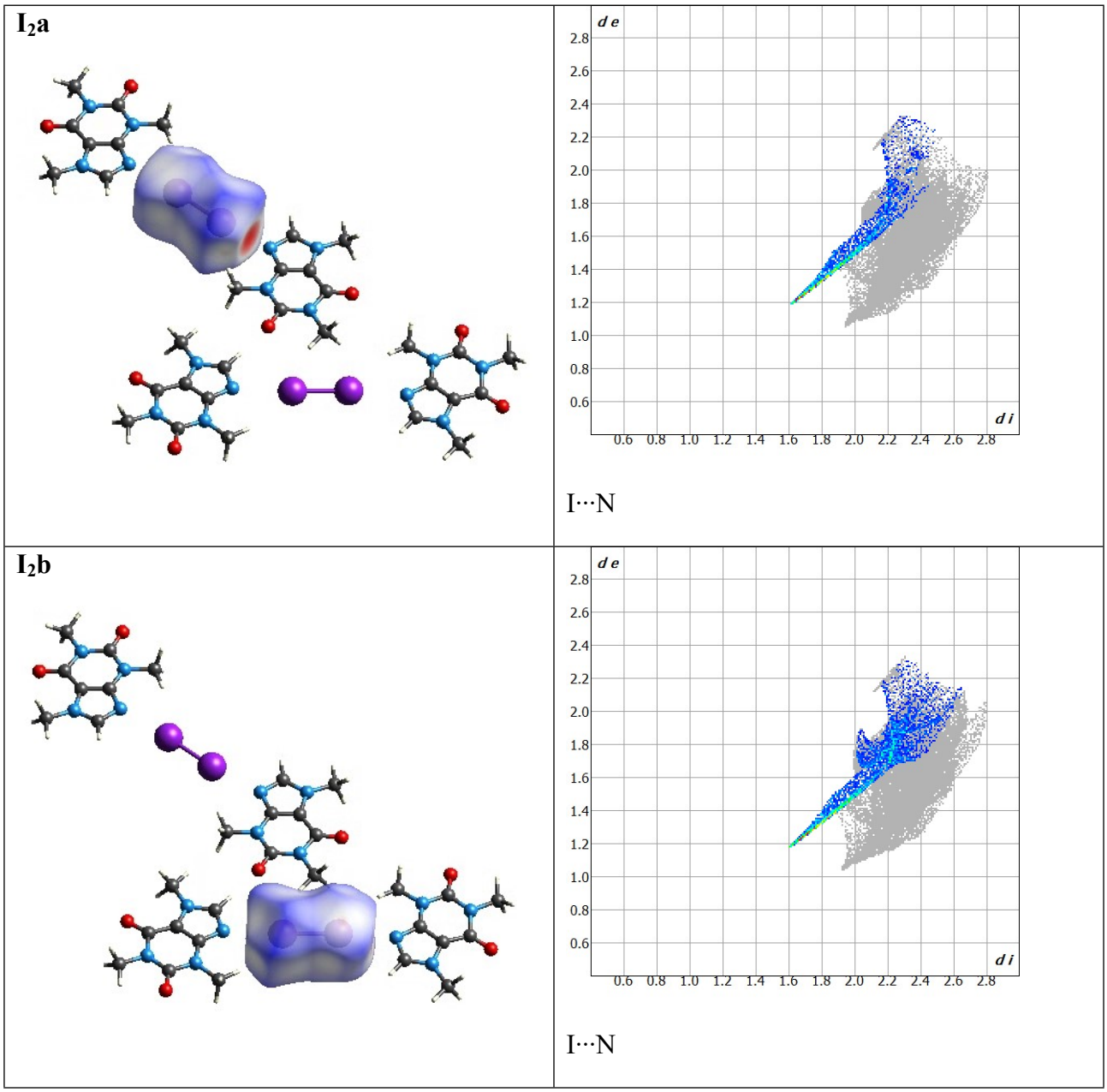


Figure S6. Hirshfeld surfaces mapped over d_{norm} for the two crystallographically independent iodine molecules (I2a and I2b) of (**caf**)$_2$·I$_2$ (left), and the corresponding 2D fingerprint plots decomposed to show the I···N contacts (right).

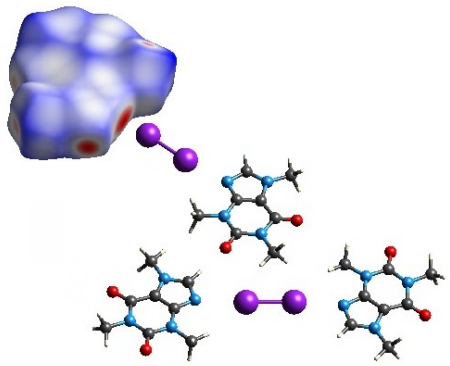
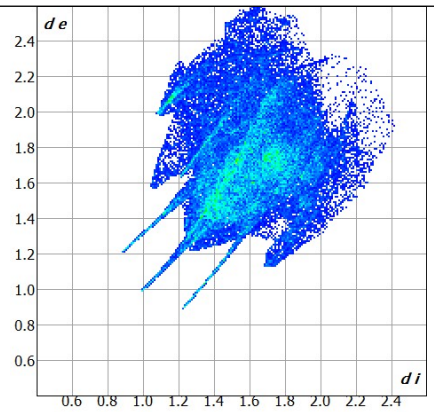
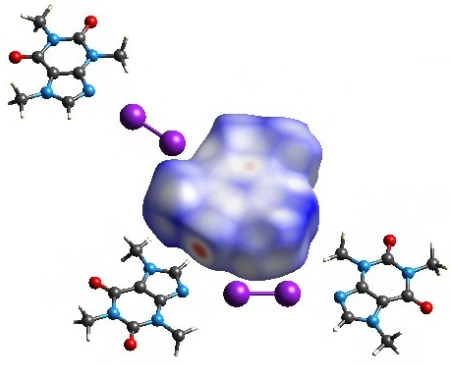
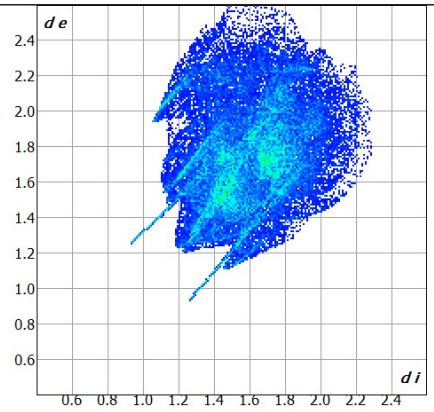
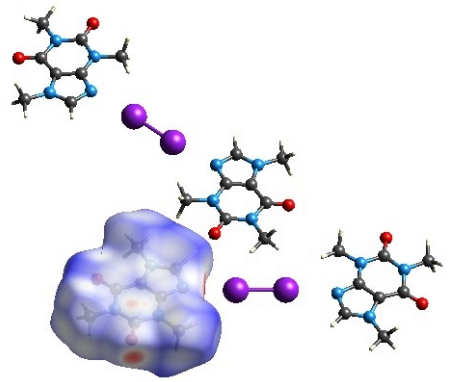
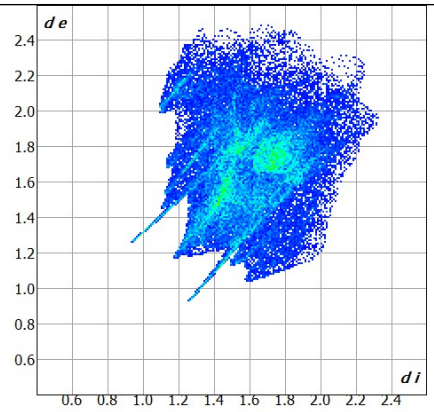
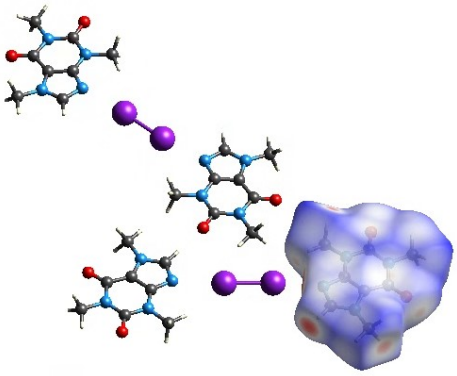
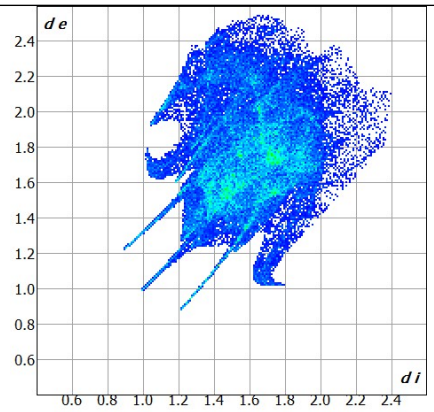
caf-a1 			%
		All···N	5.8
		All···O	10.9
		All···C	7.0
		All···H	64.9
		All···I	11.5
caf-a2 			%
		All···N	7.3
		All···O	10.9
		All···C	6.9
		All···H	61.8
		All···I	13.1
caf-b1 			%
		All···N	6.9
		All···O	14.1
		All···C	9.9
		All···H	62.7
		All···I	6.4
caf-b2 			%
		All···N	6.9
		All···O	13.2
		All···C	8.5
		All···H	59.2
		All···I	12.1

Figure S7. Hirshfeld surfaces mapped over d_{norm} for the four independent caffeine molecules of (**caf**)$_2$·I_2 (left), and the corresponding full 2D fingerprint plots (right). Percentage contributions to the Hirshfeld surface are reported for contacts involving atoms inside the HS and selected external atoms (N, O, C, H, I).