Supplementary Information (SI) for CrystEngComm.
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Supplementary Information

for

Structural determinants of H-bonded layer and ribbon formation in crystals of α-, β-, and γ-substituted primary amides

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Table S1 Crystallographic and structure refinement information for **Ia-c**

Parameter	Compound		
	Ia	**Ib**	**Ic**
Empirical formula	C_4H_9NO	$C_5H_{11}NO$	$C_8H_{17}NO$
Formula weight	87.12	101.15	143.22
m.p. (°C)	129.5(2)	128.5(2)	126.3(1)
T, K	215	215	200
Radiation (λ), Å	0.71073	0.71073	0.71073
Crystal size, mm	0.15×0.16×0.50	0.25×0.2×0.15	0.3×0.06×0.06
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$C2/c$	P-1
a, Å	10.240(9)	22.649(15)	5.0331(12)
b, Å	6.055(5)	6.262(4)	7.9540(19)
c, Å	9.734(8)	9.768(6)	12.550(3)
α, deg.	90	90	98.921(6)
β, deg.	108.636(17)	100.597(9)	101.549(4)
γ, deg.	90	90	99.419(4)
V, Å^3	571.9(8)	1361.7(15)	476.4(2)
Z	4	8	2
d_c, g/cm^3	1.012	0.987	0.999
μ, mm^{-1}	0.073	0.068	0.065
F(000)	192	448	160
θ range for data collection, deg.	2.10 to 27.07	1.83 to 26.02	1.69 to 26.02
Reflections collected	4386	7312	7975
Independent reflections	1258	1339	1859
R_{int}	0.0519	0.0622	0.0289
Absorption correction	none	semi-empirical	semi-empirical
Refined variables	65	74	121
R_1 [$I > 2\sigma(I)$]	0.0582	0.0751	0.0769
wR_2 [$I > 2\sigma(I)$]	0.1783	0.2165	0.2151
R_1 (all data)	0.0645	0.1108	0.1178
wR_2 (all data)	0.1892	0.2485	0.2454
Goodness-of-fit on F^2	1.079	1.047	1.069
Largest diff. peak and hole, *e*/Å^3	0.25 and -0.23	0.27 and -0.21	0.22 and -0.20
A- and B-level CheckCIF alerts	None	B[1]	B[2]

[1] "Calculated Density Less Than 1.0 gcm-3" (authors' response: The calculated density value is correct); [2] "Calculated Density Less Than 1.0 gcm-3" (authors' response: The calculated density value is correct).

Table S2 Intermolecular N-H…O hydrogen bonds (Å and deg.) in crystal structures of **Ia-c**

Compound	D - H…A	d(D - H)	d(H…A)	d(D…A)	∠(D - H…A)
Ia	N(1) - H(1A)…O(1)[1]	0.78(2)	2.14(2)	2.904(2)	168(2)
	N(1) - H(1B)…O(1)[2]	0.85(2)	2.12(2)	2.968(3)	174(2)
Ib	N(1) - H(1A)…O(1)[3]	0.88(3)	2.08(3)	2.961(4)	176(3)
	N(1) - H(1B)…O(1)[4]	0.76(3)	2.11(3)	2.862(3)	170(3)
Ic	N(1) - H(1A)…O(1)[5]	0.80(3)	2.10(3)	2.868(2)	160(3)

D - proton donor; A - proton acceptor.
Symmetry transformations used to generate equivalent atoms: [1] *x*, -*y*+1/2, *z*+1/2; [2] -*x*+1, -*y*, -*z*+1; [3] -*x*+1/2, -*y*+1/2, -*z*+1; [4] *x*, -*y*+1, *z*+1/2; [5] *x*+1, *y*, *z*.

Table S3 Crystallographic and structure refinement information for **IIa-c**

Parameter	Compound			
	IIa	**IIb**	**SAWHAC**[1]	**IIc**
Empirical formula	$C_{10}H_{13}NO$	C_8H_9NO	C_8H_9NO	$C_{10}H_{13}NO$
Formula weight	163.21	135.16	135.16	163.21
m.p. (°C)	85.2(3)	159.6(1)	Unknown	162.2(2)
T, K	100	215	150	100
Radiation (λ), Å	0.71073	0.71073	Unknown	0.71073
Crystal size, mm	0.25×0.2×0.2	0.2×0.2×0.1	Unknown	0.48×0.35×0.17
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/c$
a, Å	16.33(1)	19.433(9)	19.400(3)	14.598(4)
b, Å	6.118(4)	11.133(5)	11.111(2)	6.159(2)
c, Å	8.926(6)	27.95(1)	27.612(5)	10.129(3)
α, deg.	90	90	90	90
β, deg.	90.79(1)	90.386(6)	90.277(3)	105.121(4)
γ, deg.	90	90	90	90
V, Å^3	892(1)	6047(5)	5952	879.1(5)
Z	4	32	32	4
d_c, g/cm^3	1.216	1.188	1.207	1.233
μ, mm^{-1}	0.079	0.079	Unknown	0.080
F(000)	352	2304	Unknown	352
θ range for data collection, deg.	2.49 to 22.98	1.46 to 26.02	Unknown	2.89 to 31.09
Reflections collected	2580	33209	Unknown	13467
Independent reflections	1118	5953	Unknown	2807
R_{int}	0.0313	0.1094	Unknown	0.0245
Absorption correction	semi-empirical	multi scan	Unknown	semi-empirical
Refined variables	115	393	Unknown	119
R_1 [$I > 2\sigma(I)$]	0.0725	0.0653	0.0699	0.0366
wR_2 [$I > 2\sigma(I)$]	0.2095	0.1433	Unknown	0.0989
R_1 (all data)	0.0837	0.1804	Unknown	0.0391
wR_2 (all data)	0.2137	0.1897	Unknown	0.1015
Goodness-of-fit on F^2	0.990	0.975	Unknown	1.057
Largest diff. peak and hole, *e*/Å^3	0.22 and -0.17	0.16 and -0.18	Unknown	0.41 and -0.22
A- and B-level CheckCIF alerts	A[2], A[3], B[4], B[5]	None	Unknown	None

[1] for comparison, information for the previously deposited structure of **IIb**[10] (reference code SAWHAC) is shown.
[2] "The value of sine(theta_max)/wavelength is less than 0.550. Calculated sin(theta_max)/wavelength = 0.5495"; [3] "_diffrn_measured_fraction_theta_full value Low"; [4] "Small Aver Phenyl C-C Dist C5-C10"; [5] "Missing FCF Refl Between Thmin & STh/L= 0.550" (authors' response: These 4 alerts are interrelated. The best crystal of available ones was of poor quality and unstable, therefore the collected data were of low completeness and resolution).

Table S4 Intermolecular N-H…O hydrogen bonds (Å and deg.) in crystal structures of **IIa-c**

Compound	D - H…A	d(D - H)	d(H…A)	d(D…A)	∠(D - H…A)
IIa	N(1) - H(1A)…O(1)[1]	0.85(2)	1.98(3)	2.810(5)	163(5)
	N(1) - H(1B)…O(1)[2]	0.86(2)	2.02(2)	2.867(5)	169(5)
IIb	N(1A) - H(1AA)…O(1C)	0.97(4)	1.88(4)	2.852(4)	172(3)
	N(1A) - H(1AB)…O(1A)[3]	0.89(4)	2.04(4)	2.918(4)	172(3)
	N(1B) - H(1BA)…O(1B)[4]	0.94(3)	1.93(3)	2.863(4)	170(3)
	N(1B) - H(1BB)…O(1D)	0.91(2)	1.95(3)	2.829(3)	162(3)
	N(1C) - H(1CA)…O(1C)[5]	0.97(3)	1.92(3)	2.886(4)	170(3)
	N(1C) - H(1CB)…O(1B)[6]	0.84(3)	2.00(3)	2.817(4)	164(3)
	N(1D) - H(1DA)…O(1A)[7]	0.84(3)	2.08(3)	2.869(4)	156(3)
	N(1D) - H(1DB)…O(1D)[8]	0.97(4)	1.91(4)	2.887(4)	179(4)
SAWHAC*	N(1) - H(1A)…O(1)[9]	0.88	2.00	2.882	175.3
	N(1) - H(1B)…O(4)[10]	0.88	1.96	2.800	158.1
	N(2) - H(2C)…O(2)[11]	0.88	2.01	2.887	171.0
	N(2) - H(2D)…O(3)[12]	0.88	2.02	2.855	158.4
	N(3) - H(3A)…O(3)[13]	0.88	2.03	2.902	173.0
	N(3) - H(3B)…O(1)	0.88	1.99	2.839	163.2
	N(4) - H(4A)…O(4)[14]	0.88	1.99	2.864	173.3
	N(4) - H(4B)…O(2)	0.88	1.97	2.809	158.1
IIc	N(1) - H(1A)…O(1)[15]	0.88(1)	2.12(1)	2.974(1)	164(1)
	N(1) - H(1B)…O(1)[16]	0.90(1)	2.09(1)	2.981(1)	176(1)

* for comparison, information for the previously deposited structure of **IIb**[10] (reference code SAWHAC) is also shown.

D - proton donor; A - proton acceptor.

Symmetry transformations used to generate equivalent atoms: [1] *x*, -*y*+1/2, *z*-1/2; [2] -*x*+1, *y*-1/2, -*z*+1/2; [3] -*x*+1/2, -*y*+1/2, -*z*; [4] -*x*+1, -*y*+1, -*z*; [5] -*x*, -*y*+1, -*z*; [6] *x*-1/2, *y*+1, *z*; [7] *x*, *y*+1, *z*; [8] -*x*+1/2, -*y*+3/2, -*z*; [9] -*x*+1, -*y*+1, -*z*+1; [10] *x*, *y*-1, *z*; [11] -*x*+1/2, -*y*+3/2, -*z*+1; [12] *x*-1/2, *y*-1/2, *z*; [13] -*x*+3/2, -*y*+3/2, -*z*-1; [14] -*x*+1, -*y*+2, -*z*-1; [15] *x*, -*y*+1/2, *z*-1/2; [16] -*x*+1, -*y*+1, -*z*+1.

Table S5 Weak intermolecular C-H…O and C-H…N hydrogen bonds (Å and deg.) in crystal structures of **IIa** and **IIc**

Compound	D - H…A	d(D - H)	d(H…A)	d(D…A)	∠(D - H…A)
IIa	C(2) - H(2B)…N(1)	0.990	2.768	3.675	152.41
IIc	C(8) - H(8C)…O(1)	0.980	2.577	3.532	166.19

D - proton donor; A - proton acceptor.
Symmetry transformations used to generate equivalent atoms:

Table S6 C-H…π interactions (Å and deg.) in crystal structures of **IIb** and **IIc**

Compound	C-H…C(Ph)	d(H…π plane)	d(H…π centroid)	∠(C - H…π centroid)
IIb	C(4B)-H(4B)…C(6D)[2]	2.871	3.235	155.80
SAWHAC[1]	C(32-H(36)…C(14)[2]	2.834	3.196	155.53
IIc	C(9)-H(9C)…C(6)[3]	2.838	2.961	143.16

[1] for comparison, information for the previously deposited structure of **IIb**[10] (reference code SAWHAC) is also shown; [2] edge-to-face aromatic interaction between two phenyl groups; [3] interaction between methyl group and phenyl group.

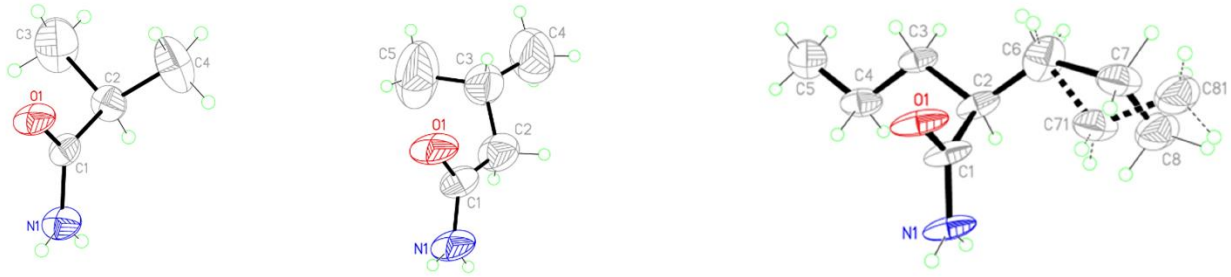

Fig. S1 Molecular structures of **Ia** (left), **Ib** (center), and **Ic** (right). The minor positions for the disordered fragments are shown by dashed lines. Atoms are shown as thermal ellipsoids (50% probability level).

Fig. S2 Superimposed molecular structures of free **Ic** from our study (magenta; the conformation with partial occupancy of 0.45) and **Ic** in a cocrystal with triflusal[26] (blue). Hydrogen atoms are omitted for clarity.

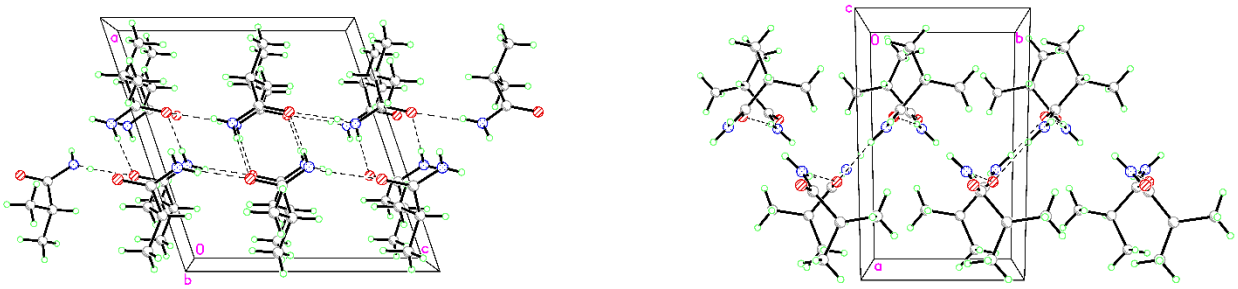

Fig. S3 Crystal packing in **Ia** along the *b* axis (left) and along the *c* axis (right). Hydrogens attached to carbons are omitted for clarity.

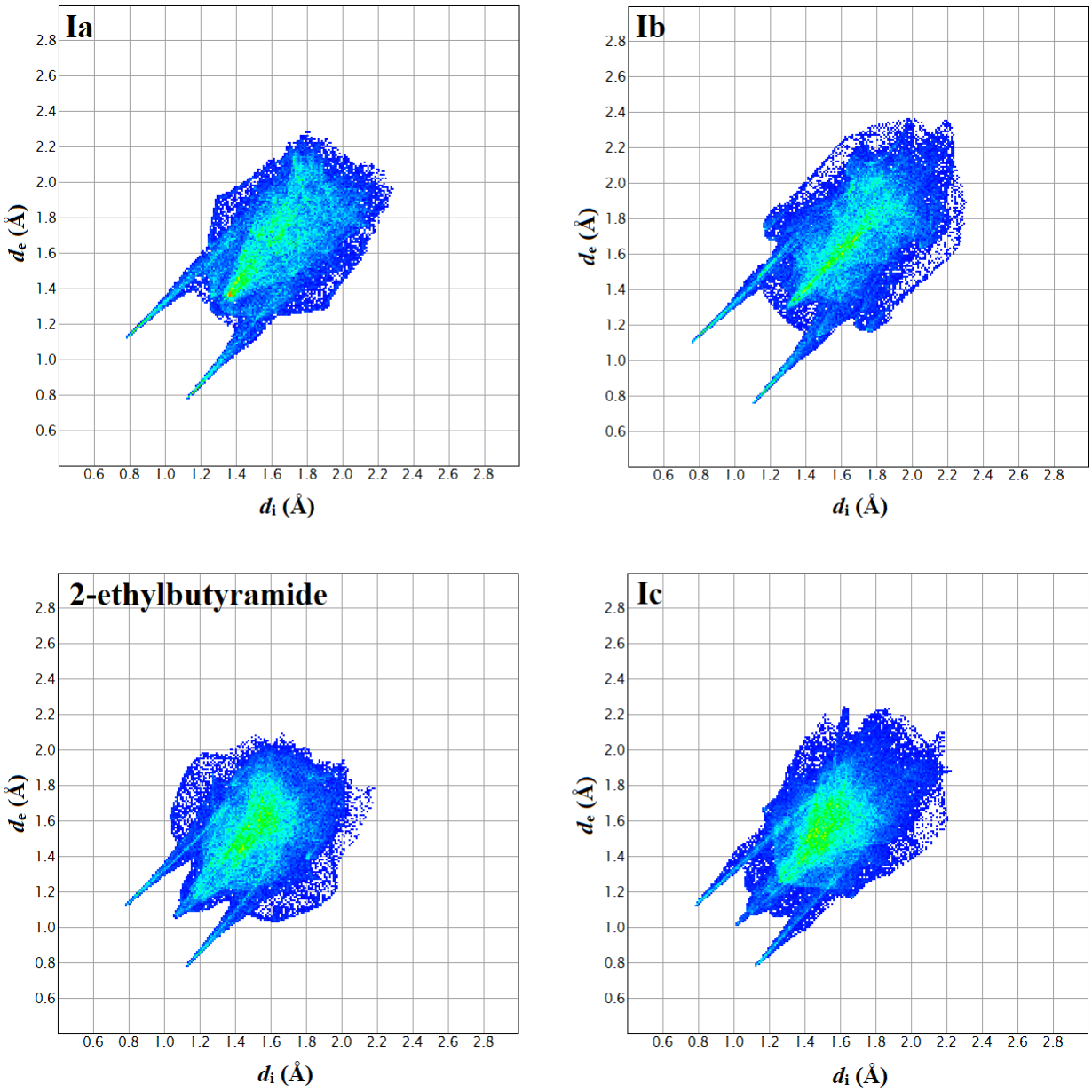

Fig. S4 Hirshfeld fingerprint plots for **Ia**, **Ib**, and **Ic**. For comparison, a fingerprint plot for the structurally related compound, 2-ethylbutyramide,[25] is also shown.

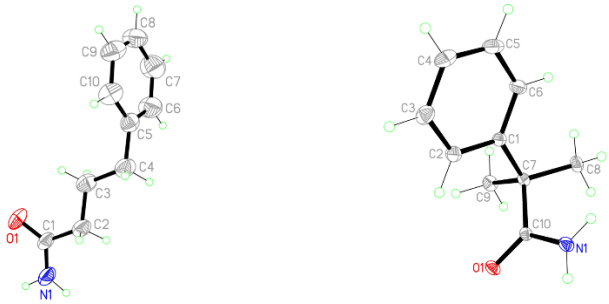

Fig. S5 Molecular structures of **IIa** (left) and **IIc** (right). Atoms are shown as thermal ellipsoids (50% probability level).

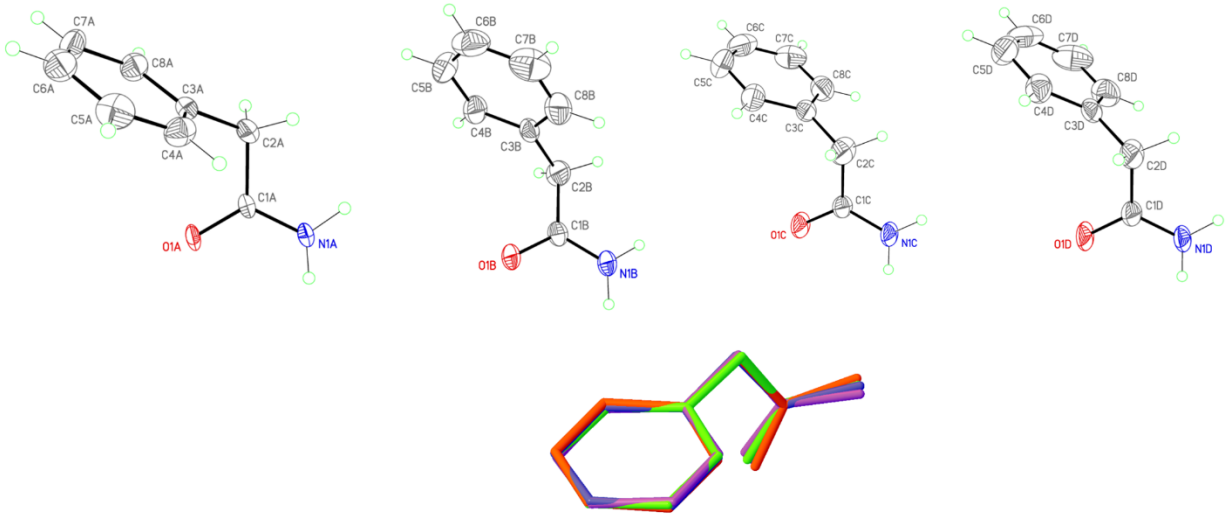

Fig. S6 Molecular structures of four molecules of **IIb**. Atoms are shown as thermal ellipsoids (50% probability level). The lower panel shown the superimposed structures with hydrogen atoms omitted for clarity.

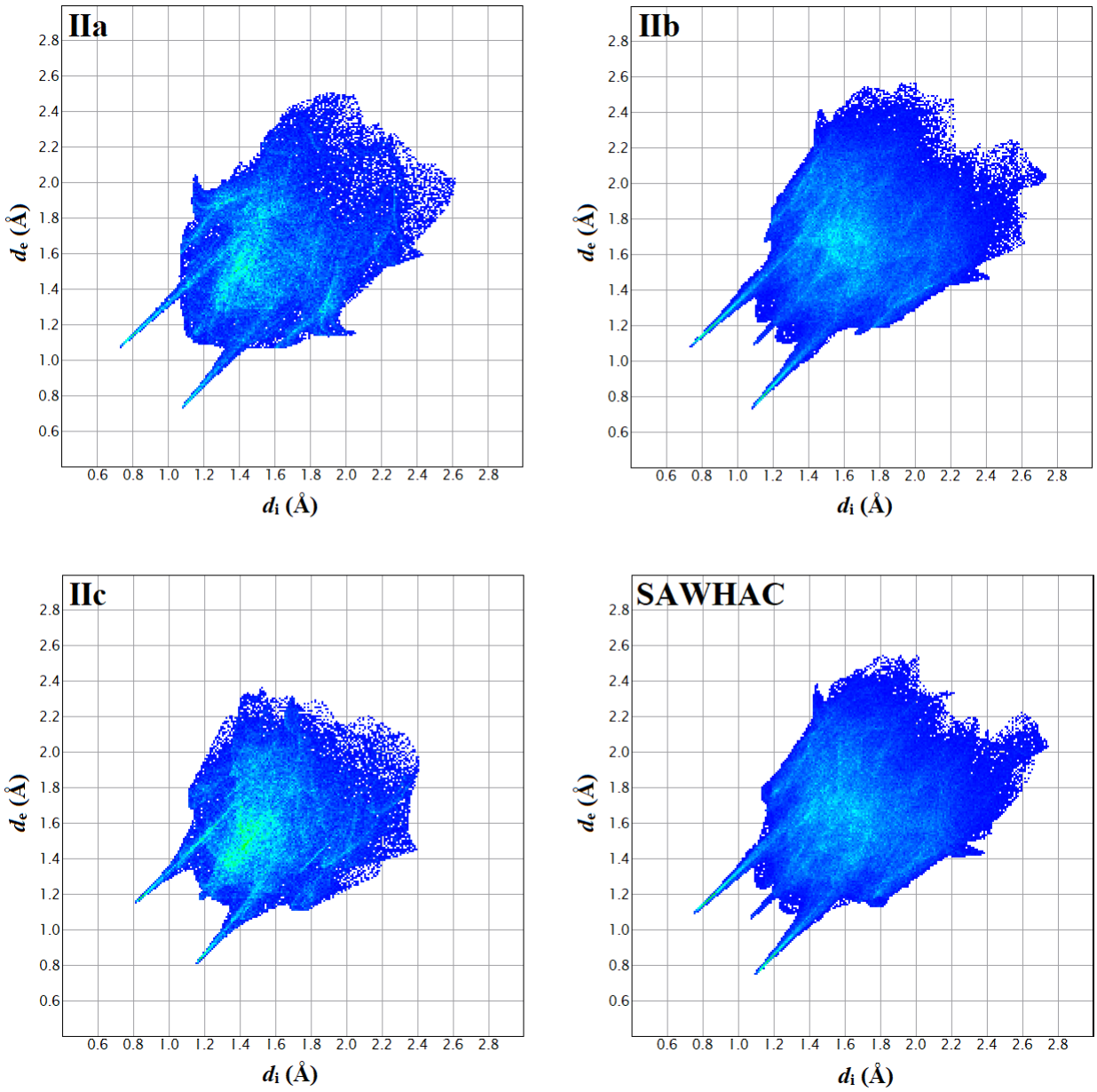

Fig. S7 Hirshfeld fingerprint plots for **IIa**, **IIb**, and **IIc**. For comparison, a fingerprint plot for the previously deposited structure of **IIb**[10] (reference code SAWHAC) is also shown.