Supplementary Information (SI) for CrystEngComm.

Complete Structural and Electronic Comparison of Chiral and Racemic Ketohexoses: Hydrogen-Bond Network Topology and Interaction Strength Distribution

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Supplementary information

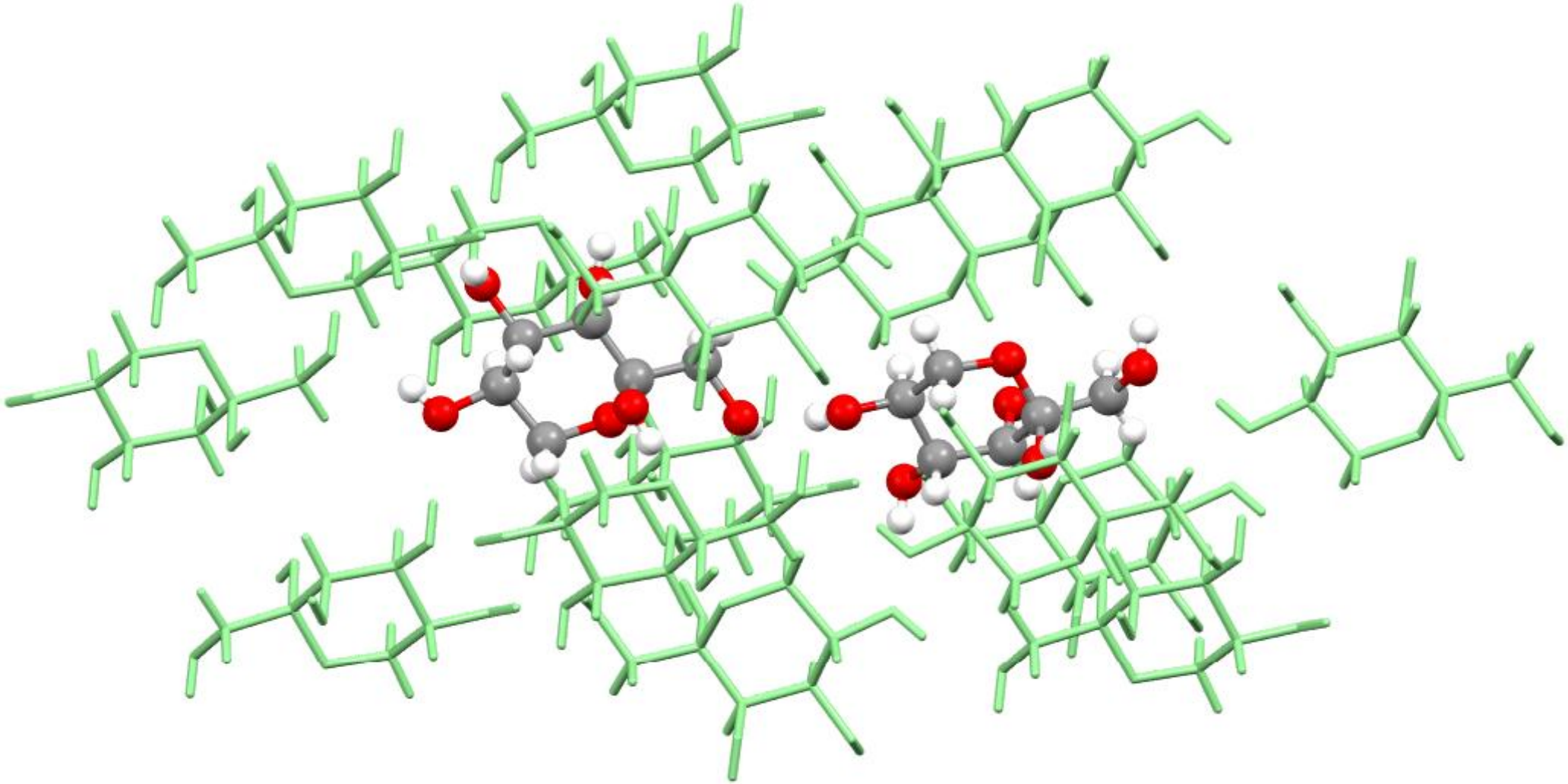
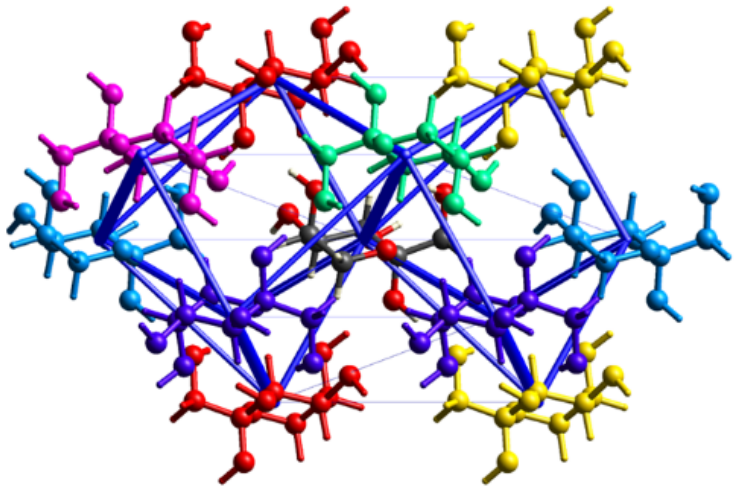
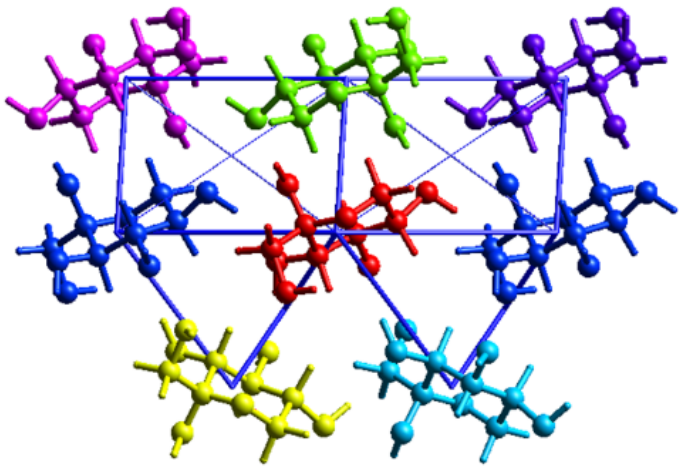


Fig. S1 Computational model of D,L-tagatose: two central molecules (one D-form and one L-form) surrounded by 15 neighboring molecules (light green).



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	-x+1/2, -y, z+1/2	5.74	HF/3-21G	-48.9	-13.9	-24.5	45.8	-43.8
	2	-x+1/2, -y, z+1/2	7.26	HF/3-21G	-55.8	-16.3	-10.3	52.0	-34.6
	2	x+1/2, -y+1/2, -z	6.3	HF/3-21G	-42.1	-11.2	-20.7	21.9	-51.1
	2	-x, y+1/2, -z+1/2	5.32	HF/3-21G	-76.9	-21.9	-33.6	58.5	-75.5
	2	x, y, z	8.08	HF/3-21G	3.7	-0.9	-8.4	2.3	-2.5
	2	x+1/2, -y+1/2, -z	6.93	HF/3-21G	-2.9	-1.5	-13.6	6.5	-11.0
	2	-x, y+1/2, -z+1/2	8.59	HF/3-21G	1.7	-0.8	-4.6	0.6	-2.4

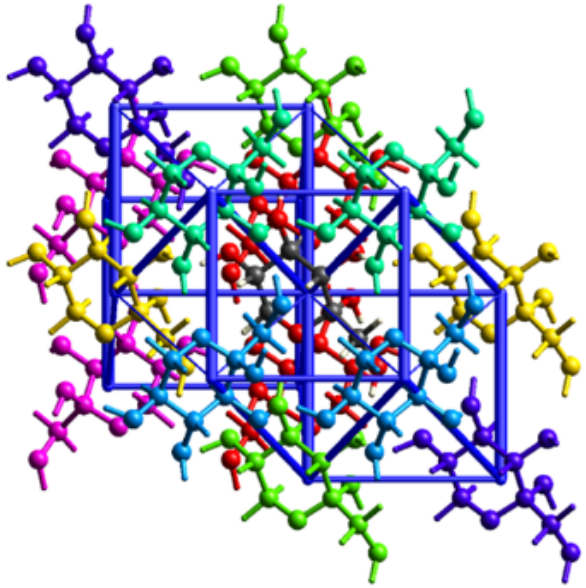
Fig. S2 Energy framework and intermolecular interaction analysis for D-fructose.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	6.29	HF/3-21G	-42.6	-12.0	-24.3	34.1	-45.5
	1	-	5.37	HF/3-21G	-38.2	-14.5	-27.1	36.9	-42.9
	1	-	8.42	HF/3-21G	-42.6	-12.0	-24.3	34.1	-45.5
	2	-x+1/2, y+1/2, -z	5.53	HF/3-21G	-49.6	-14.4	-26.5	46.8	-45.8
	2	x+1/2, -y+1/2, z	6.89	HF/3-21G	-41.1	-12.5	-18.0	29.5	-42.3
	1	-	6.24	HF/3-21G	-41.1	-12.5	-18.0	29.5	-42.3
	1	-	6.64	HF/3-21G	0.5	-0.9	-11.8	4.7	-7.0
	2	x+1/2, -y+1/2, z	7.43	HF/3-21G	0.5	-0.9	-11.8	4.7	-7.0
	1	-x, -y, -z	8.18	HF/3-21G	-3.8	-1.1	-7.5	2.1	-9.7
	1	-x, -y, -z	7.57	HF/3-21G	-11.8	-1.0	-4.0	0.2	-16.2
	1	-	8.12	HF/3-21G	-42.6	-12.0	-24.3	34.1	-45.5

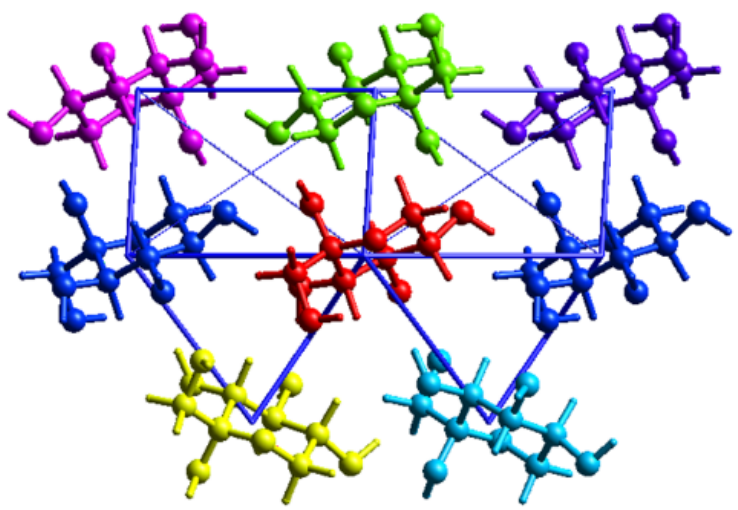
Fig. S3

Energy framework and intermolecular interaction analysis for D,L-fructose.



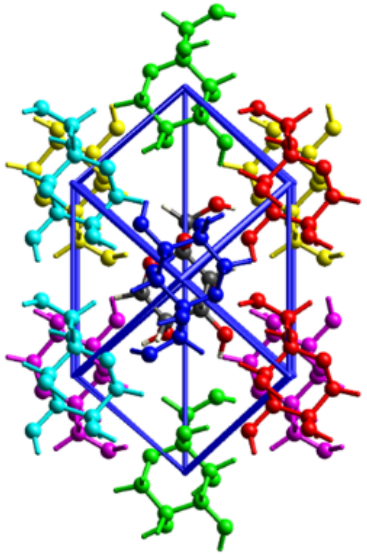
	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	-x+1/2, -y, z+1/2	5.39	HF/3-21G	-37.5	-9.8	-25.1	34.3	-39.4
	2	x, y, z	6.54	HF/3-21G	-35.4	-12.4	-23.2	29.0	-41.5
	2	x, y, z	6.31	HF/3-21G	-84.9	-23.8	-23.1	58.6	-75.3
	2	x+1/2, -y+1/2, -z	6.56	HF/3-21G	-62.4	-19.1	-15.1	46.0	-52.3
	2	x+1/2, -y+1/2, -z	6.49	HF/3-21G	-5.6	-1.6	-12.3	3.1	-15.3
	2	x, y, z	9.09	HF/3-21G	5.2	-1.6	-6.6	1.7	-0.3
	2	-x+1/2, -y, z+1/2	8.77	HF/3-21G	-4.1	-0.9	-4.9	1.4	-7.9

Fig. S4 Energy framework and intermolecular interaction analysis for L-sorbose.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	6.29	HF/3-21G	-42.6	-12.0	-24.3	34.1	-45.5
	1	-	5.37	HF/3-21G	-38.2	-14.5	-27.1	36.9	-42.9
	1	-	8.42	HF/3-21G	-42.6	-12.0	-24.3	34.1	-45.5
	2	-x+1/2, y+1/2, -z	5.53	HF/3-21G	-49.6	-14.4	-26.5	46.8	-45.8
	2	x+1/2, -y+1/2, z	6.89	HF/3-21G	-41.1	-12.5	-18.0	29.5	-42.3
	1	-	6.24	HF/3-21G	-41.1	-12.5	-18.0	29.5	-42.3
	1	-	6.64	HF/3-21G	0.5	-0.9	-11.8	4.7	-7.0
	2	x+1/2, -y+1/2, z	7.43	HF/3-21G	0.5	-0.9	-11.8	4.7	-7.0
	1	-x, -y, -z	8.18	HF/3-21G	-3.8	-1.1	-7.5	2.1	-9.7
	1	-x, -y, -z	7.57	HF/3-21G	-11.8	-1.0	-4.0	0.2	-16.2
	1	-	8.12	HF/3-21G	-42.6	-12.0	-24.3	34.1	-45.5

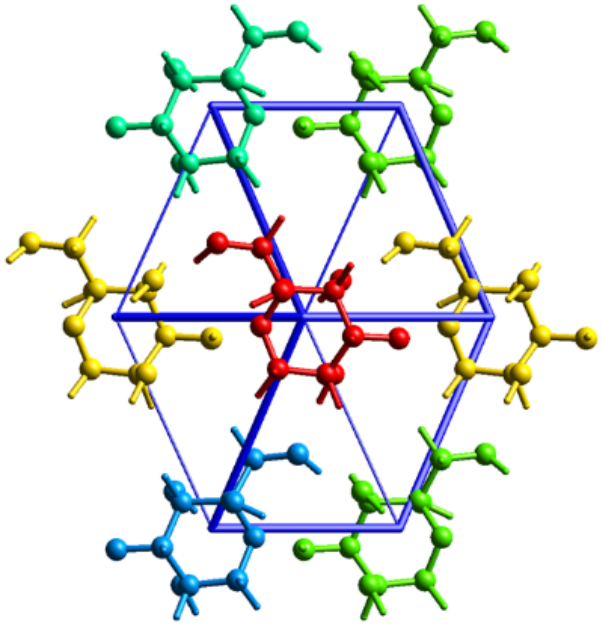
Fig. S5 Energy framework and intermolecular interaction analysis for D,L-sorbose.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	-x+1/2, -y, z+1/2	6.26	HF/3-21G	-58.1	-16.9	-19.3	42.2	-53.3
	2	x+1/2, -y+1/2, -z	6.38	HF/3-21G	-42.3	-12.5	-18.8	36.3	-38.8
	2	x, y, z	7.75	HF/3-21G	-49.3	-14.7	-14.0	40.9	-39.2
	2	-x+1/2, -y, z+1/2	6.72	HF/3-21G	-9.2	-5.4	-17.1	8.7	-21.2
	2	-x, y+1/2, -z+1/2	5.60	HF/3-21G	-3.5	-3.4	-19.0	8.2	-16.2
	2	x+1/2, -y+1/2, -z	6.48	HF/3-21G	-50.2	-15.1	-16.8	26.8	-54.4

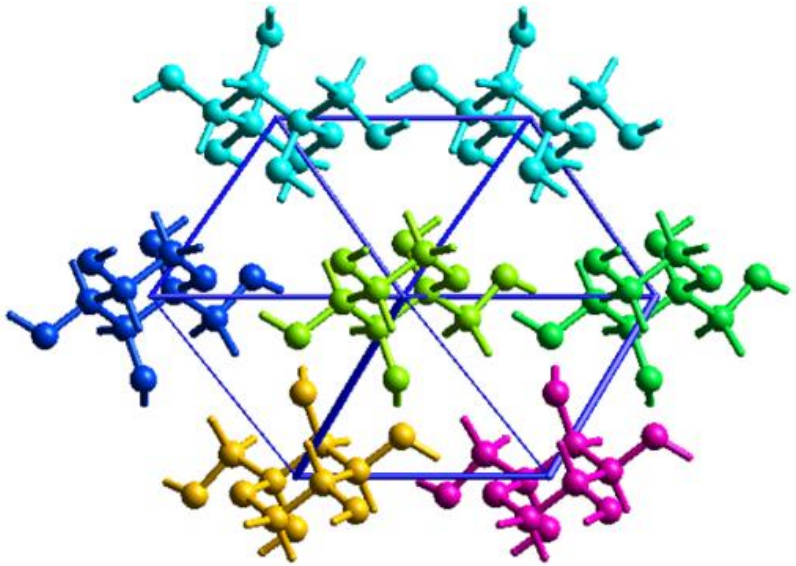
Fig. S6

Energy framework and intermolecular interaction analysis for D-psicose.



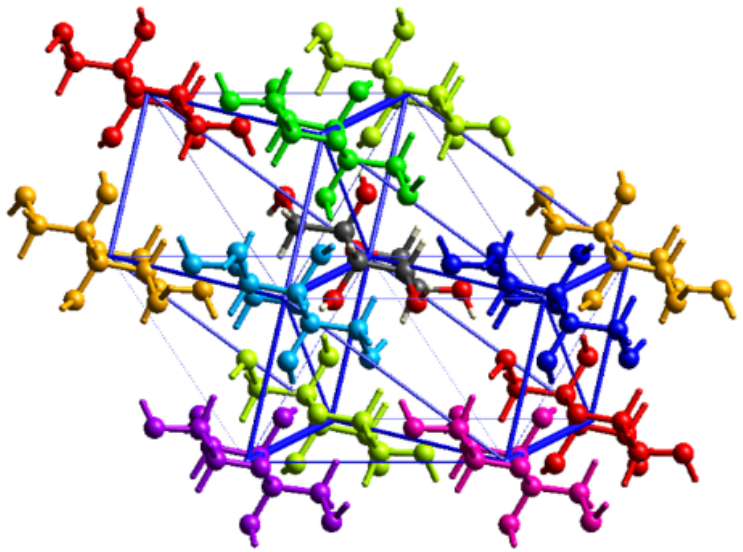
	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	5.36	HF/3-21G	-12.4	-6.0	-22.5	18.9	-21.6
	2	x+1/2, -y+1/2, z	6.33	HF/3-21G	-56.1	-17.9	-20.1	44.8	-50.6
	2	-x, -y, z+1/2	6.91	HF/3-21G	-6.9	-2.7	-13.0	4.7	-16.7
	2	-x+1/2, y+1/2, z+1/2	7.45	HF/3-21G	-56.9	-17.4	-12.7	40.0	-48.2
	2	-x+1/2, y+1/2, z+1/2	7.45	HF/3-21G	0.1	-1.6	-10.2	3.8	-7.0
	2	x+1/2, -y+1/2, z	6.15	HF/3-21G	-65.7	-17.2	-20.5	58.4	-49.2
	1	-x, -y, z+1/2	8.61	HF/3-21G	-6.6	-0.7	-1.8	0.0	-8.7

Fig. S7 Energy framework and intermolecular interaction analysis for D,L-psicose.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x+1/2, -y+1/2, -z	5.42	HF/3-21G	-33.0	-8.9	-28.7	33.6	-38.1
	2	-x, y+1/2, -z+1/2	6.05	HF/3-21G	-63.9	-23.1	-22.9	51.1	-59.2
	2	x, y, z	6.50	HF/3-21G	-45.8	-12.2	-24.6	41.8	-42.8
	2	x, y, z	6.22	HF/3-21G	-44.5	-15.2	-23.0	42.2	-41.7
	2	x+1/2, -y+1/2, -z	8.81	HF/3-21G	-3.6	-0.6	-3.4	0.4	-6.7
	2	x, y, z	9.00	HF/3-21G	-35.7	-8.8	-7.7	19.7	-33.0
	2	x+1/2, -y+1/2, -z	8.10	HF/3-21G	1.5	-0.3	-3.3	0.1	-1.5
	2	-x, y+1/2, -z+1/2	6.60	HF/3-21G	-5.6	-4.2	-12.0	3.8	-16.2

Fig. S8 Energy framework and intermolecular interaction analysis for D-tagatose.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, -y+1/2, z+1/2	8.65	HF/3-21G	-47.0	-13.1	-9.4	42.7	-30.2
	2	x, y, z	8.11	HF/3-21G	-4.6	-1.4	-6.1	1.7	-9.7
	2	x, -y+1/2, z+1/2	5.32	HF/3-21G	-51.0	-14.4	-22.2	42.8	-46.7
	1	-x, -y, -z	5.56	HF/3-21G	-22.3	-5.0	-22.1	15.4	-33.4
	1	-x, -y, -z	6.97	HF/3-21G	-0.2	-0.7	-9.2	1.3	-8.0
	2	-x, y+1/2, -z+1/2	5.61	HF/3-21G	-93.3	-29.2	-30.0	79.8	-76.5
	2	-x, y+1/2, -z+1/2	7.34	HF/3-21G	-51.2	-15.7	-15.6	47.7	-37.8
	1	-x, -y, -z	8.43	HF/3-21G	-4.7	-0.3	-1.6	0.0	-6.4
	1	-x, -y, -z	8.62	HF/3-21G	-0.1	-0.4	-3.2	0.0	-3.3

Fig. S9 Energy framework and intermolecular interaction analysis for D,L-tagatose.

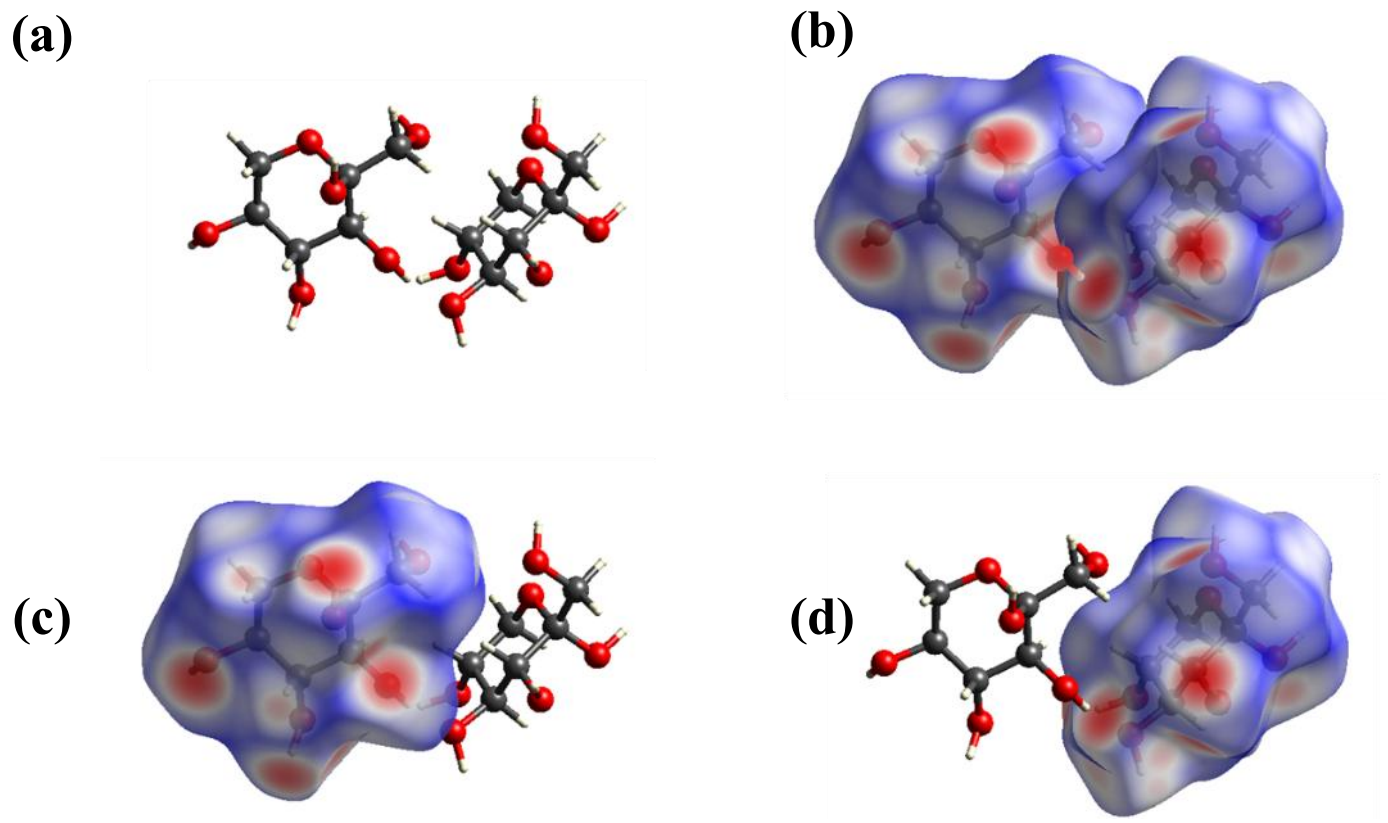


Fig. S10

Hirshfeld surface analysis of D,L-sorbose. (a) Molecular structure of D,L-sorbose. (b) Hirshfeld surface analysis for the entire D,L-sorbose crystal. (c) Hirshfeld surface of the D-enantiomer in D,L-sorbose. (d) Hirshfeld surface of the L-enantiomer in D,L-sorbose.

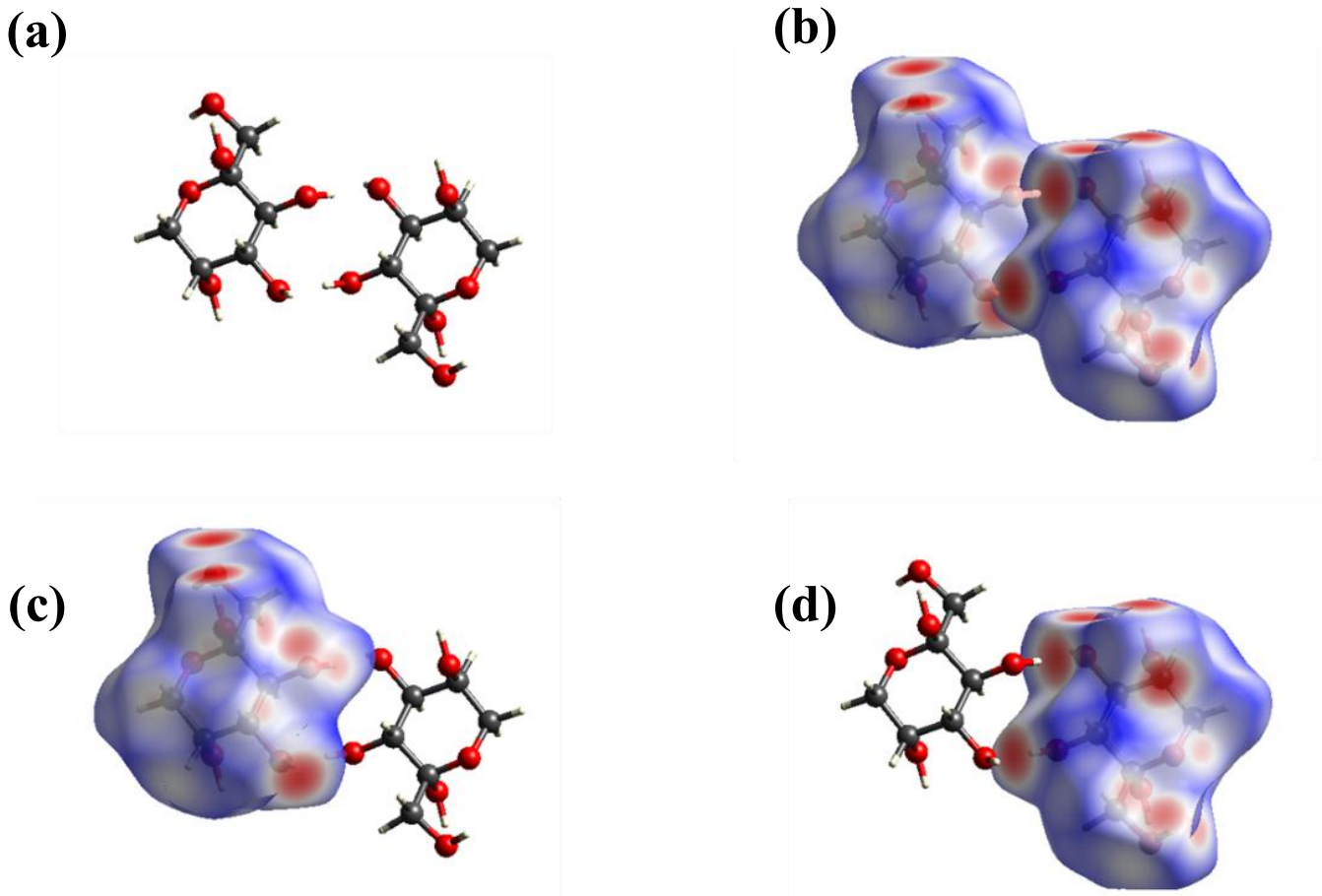


Fig. S11 Hirshfeld surface analysis of D,L-fructose. (a) Molecular structure of D,L-fructose. (b) Hirshfeld surface analysis for the entire D,L-fructose crystal. (c) Hirshfeld surface of the D-enantiomer in D,L-fructose. (d) Hirshfeld surface of the L-enantiomer in D,L-fructose.

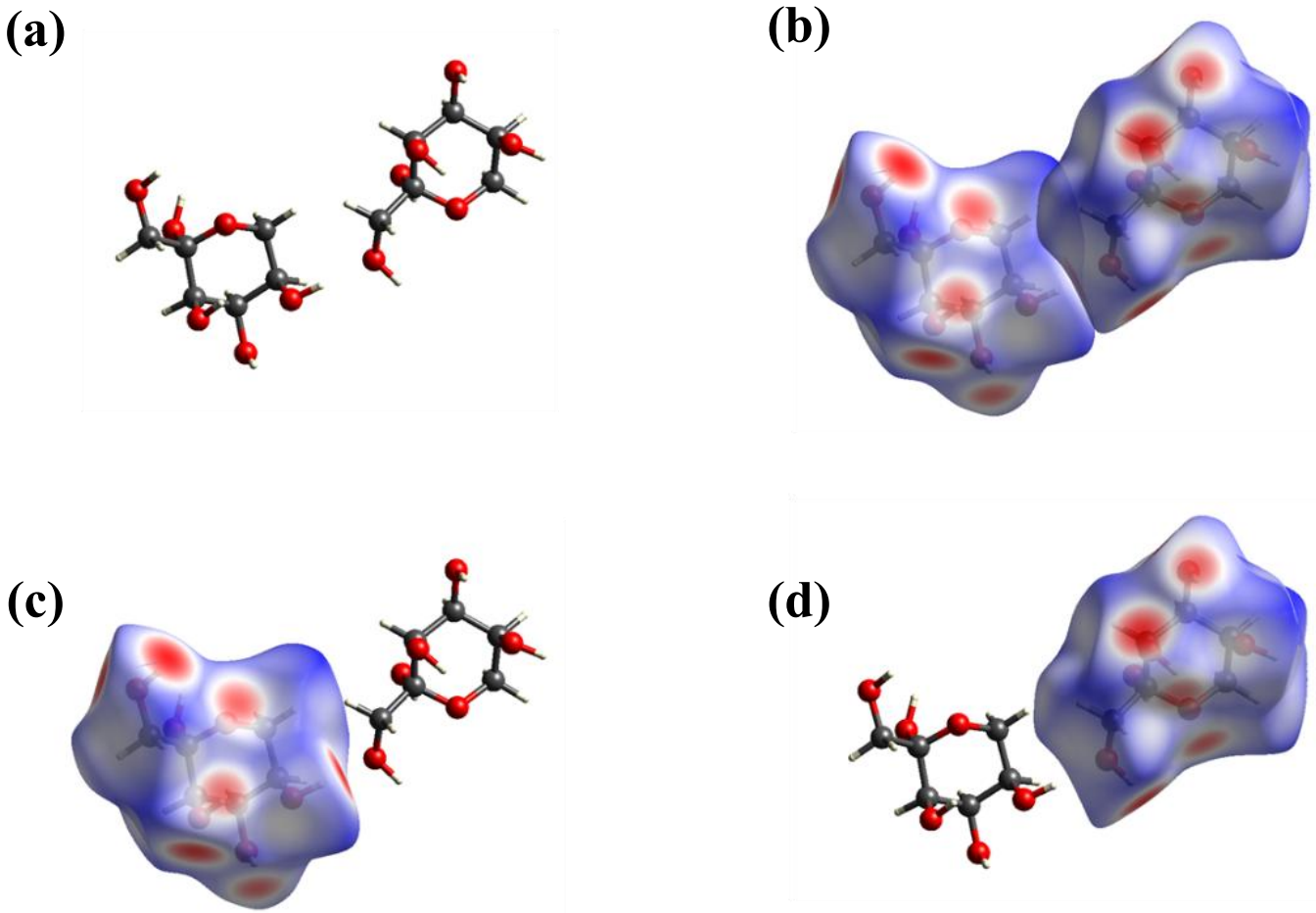


Fig. S12

Hirshfeld surface analysis of D,L-psicse. (a) Molecular structure of D,L-psicose. (b) Hirshfeld surface analysis for the entire D,L-psicose crystal. (c) Hirshfeld surface of the D-enantiomer in D,L-psicose. (d) Hirshfeld surface of the L-enantiomer in D,L-psicose.

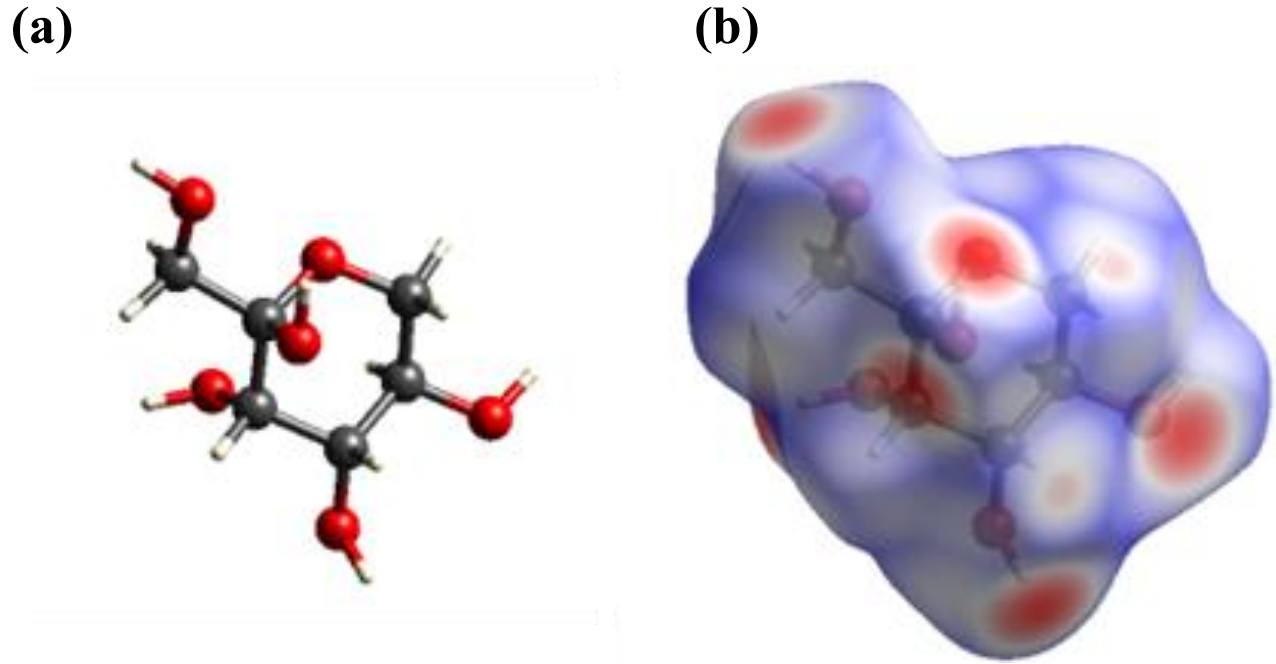


Fig. S13

Hirshfeld surface analysis of D-tagatose. (a) Molecular structure of D-tagatose. (b) Hirshfeld surface analysis for the entire D-tagatose crystal.

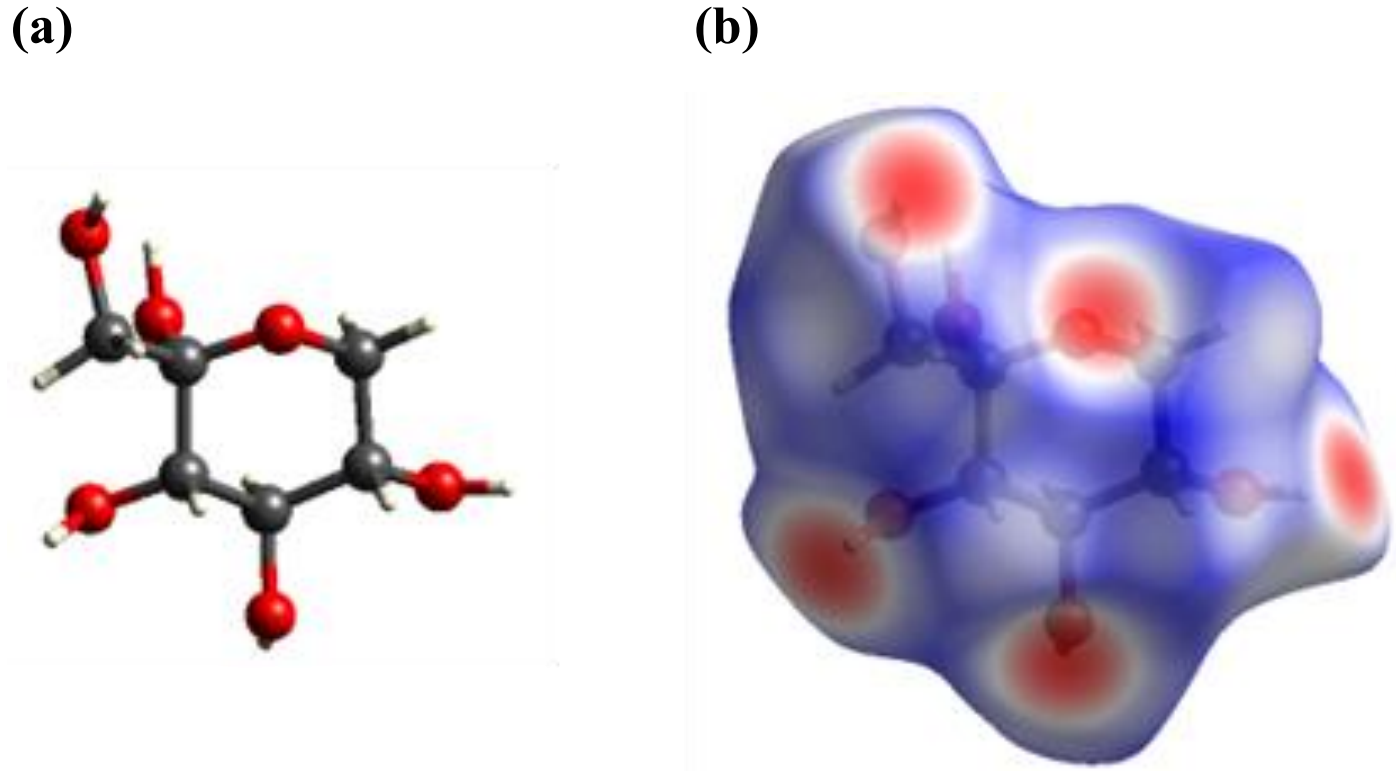


Fig. S14 Hirshfeld surface analysis of L-sorbose. (a) Molecular structure of L-sorbose. (b) Hirshfeld surface analysis for the entire L-sorbose crystal.

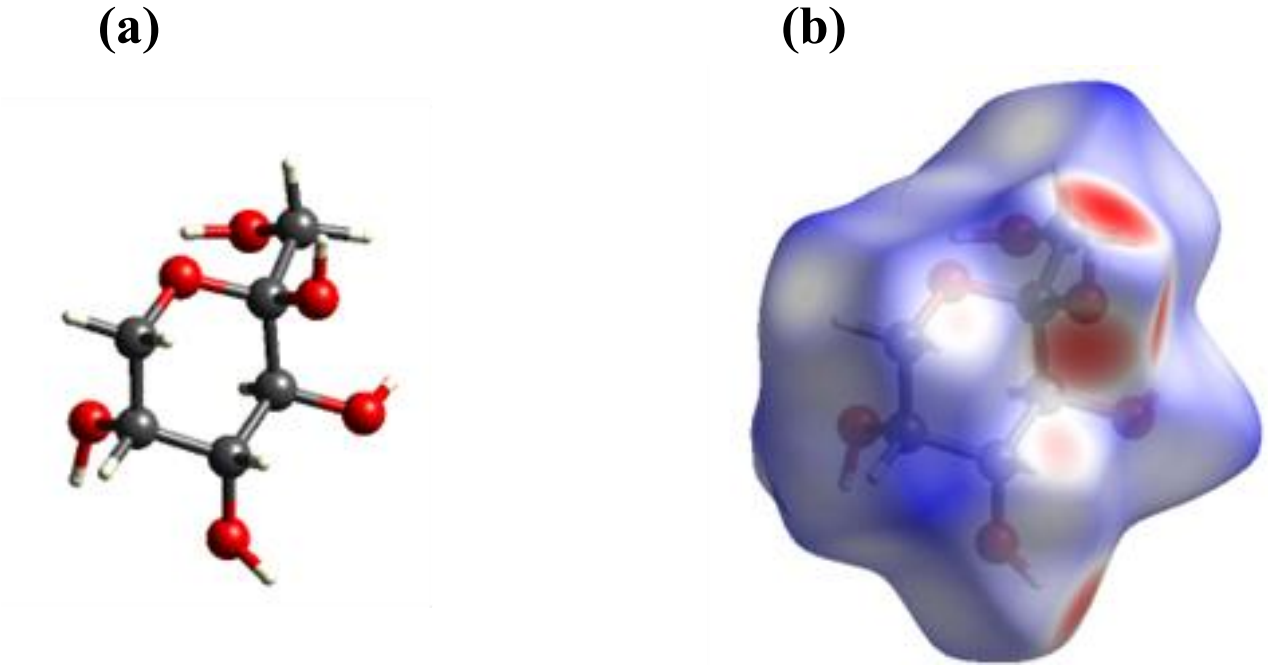


Fig. S15 Hirshfeld surface analysis of D-fructose. (a) Molecular structure of D-fructose. (b) Hirshfeld surface analysis for the entire D-fructose crystal.

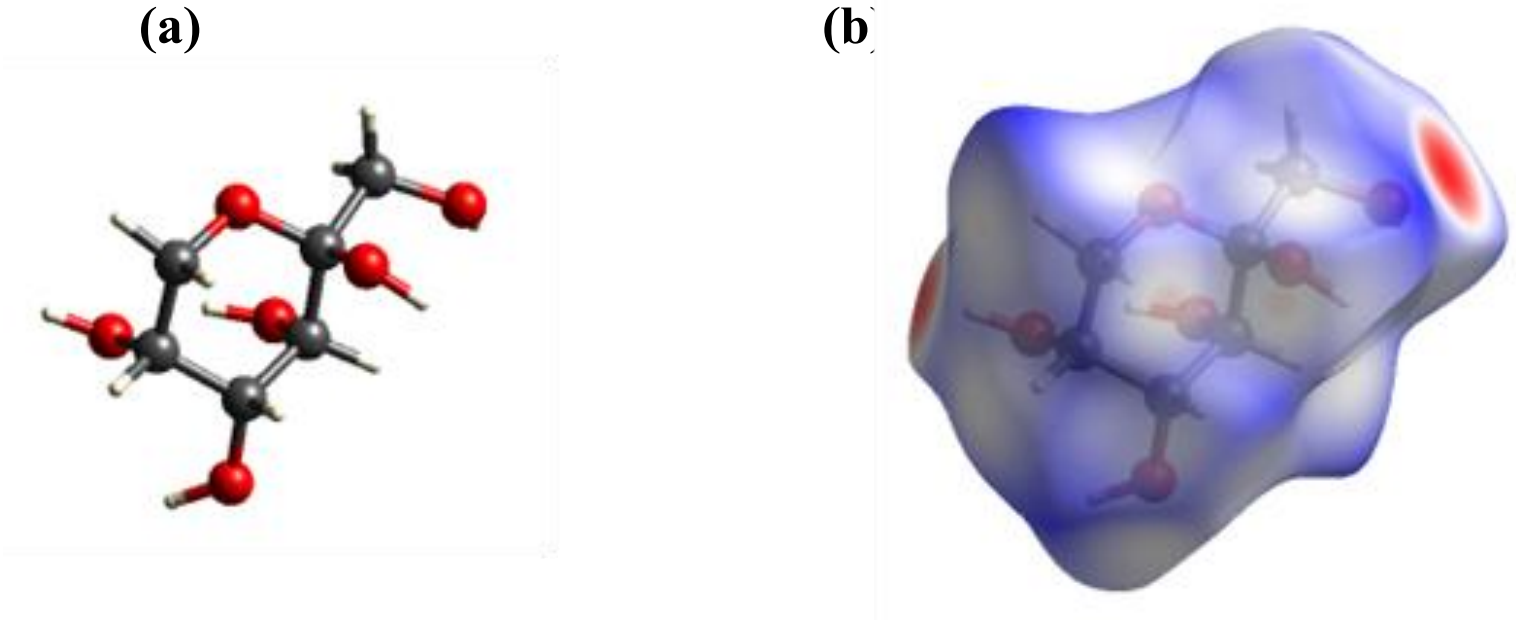


Fig. S16 Hirshfeld surface analysis of D-psicose. (a) Molecular structure of D-psicose. (b) Hirshfeld surface analysis for the entire D-psicose crystal.

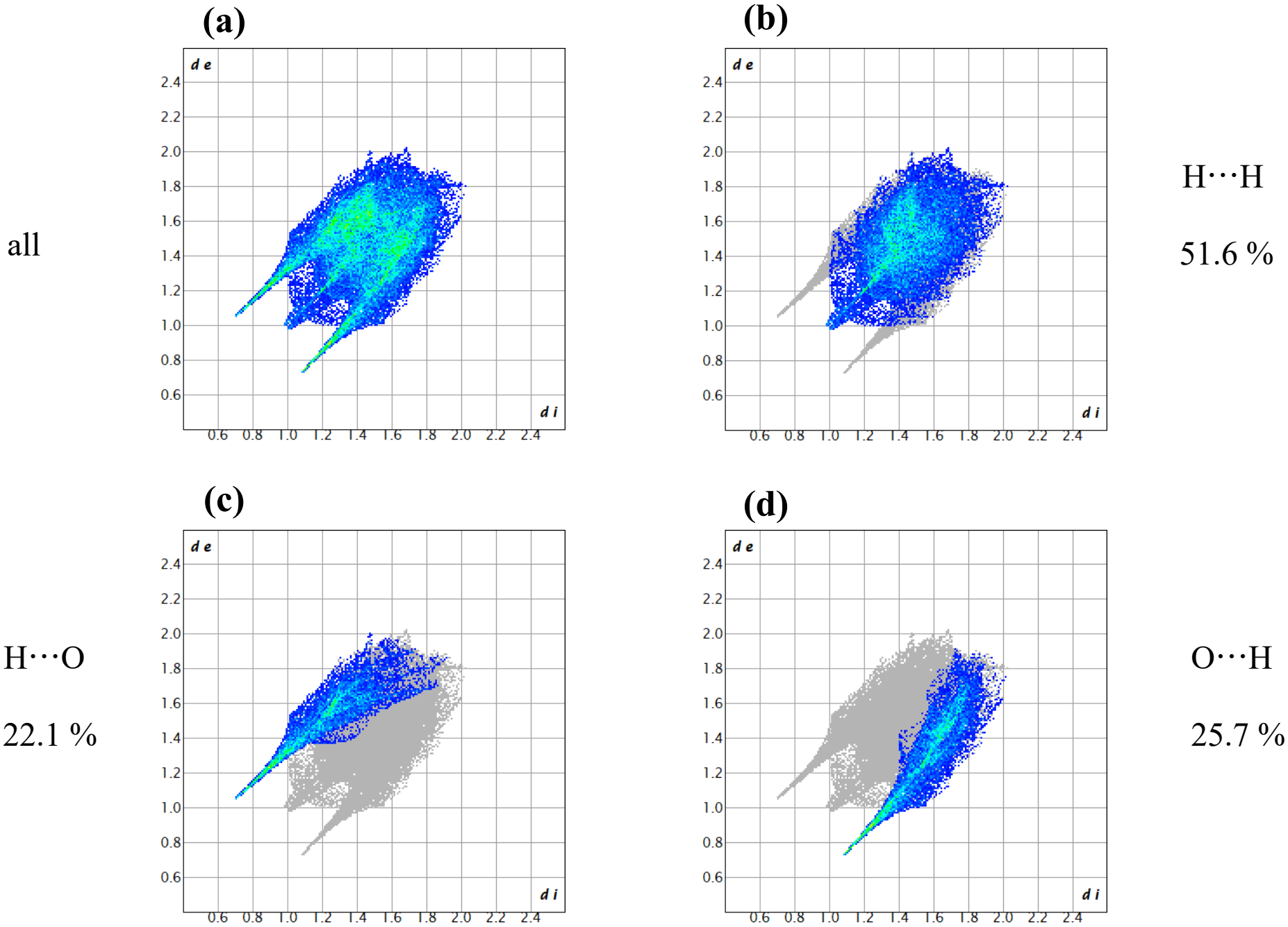


Fig. S17 2D fingerprint plots for the D-enantiomer of D,L-sorbose.

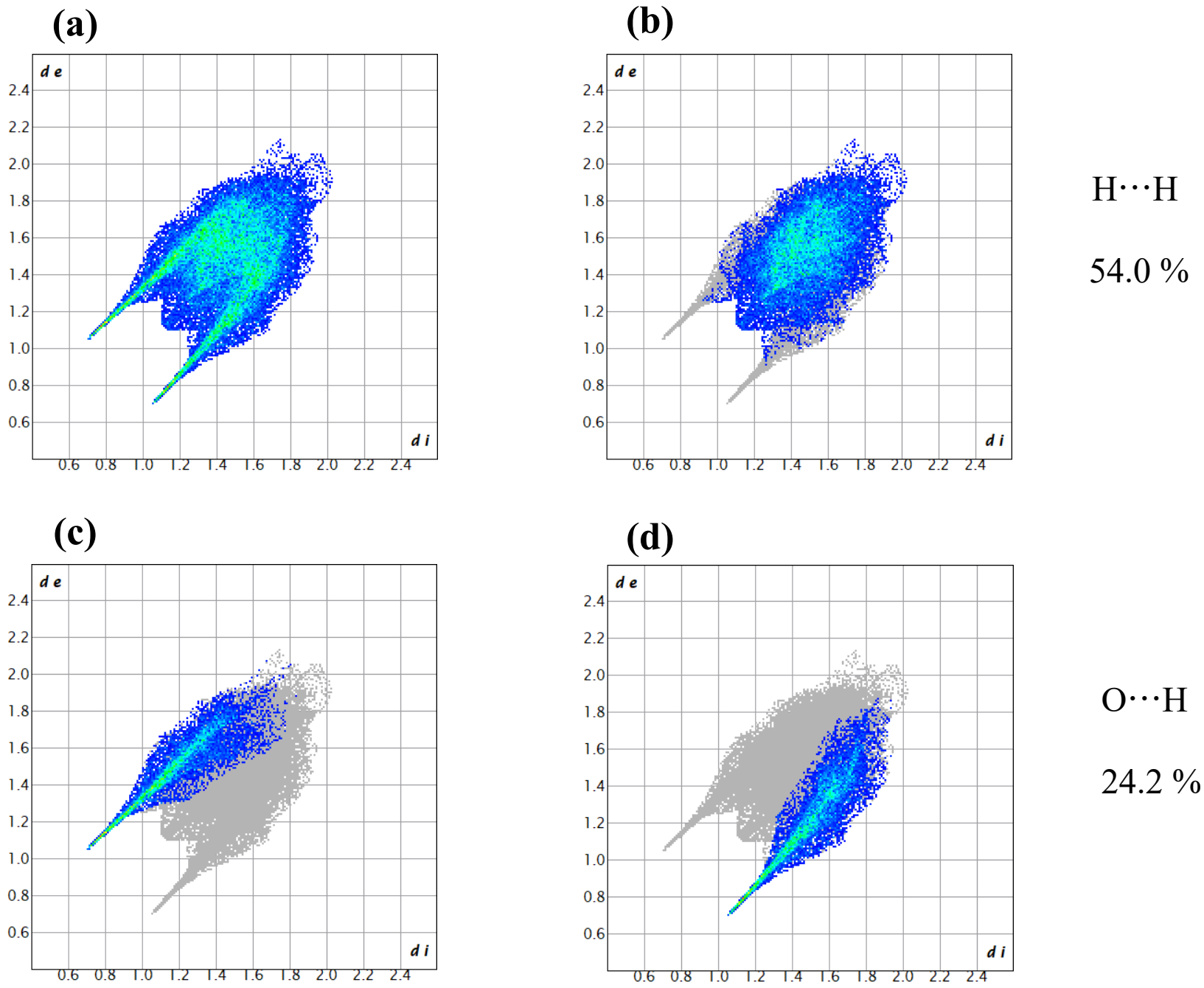


Fig. S18 2D fingerprint plots for the D-enantiomer of D,L-fructose.

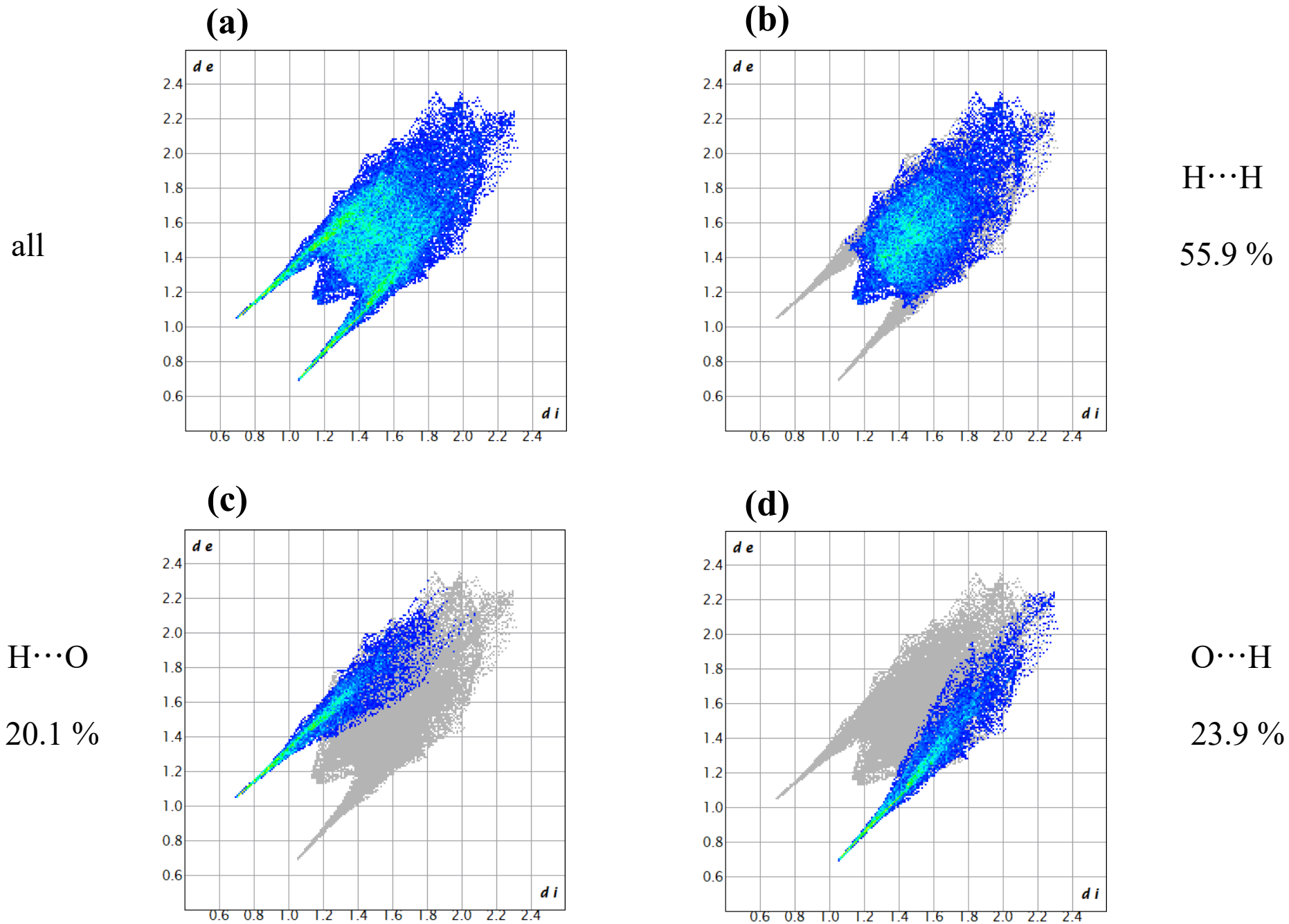


Fig. S19

2D fingerprint plots for the D-enantiomer of D,L-psicose.

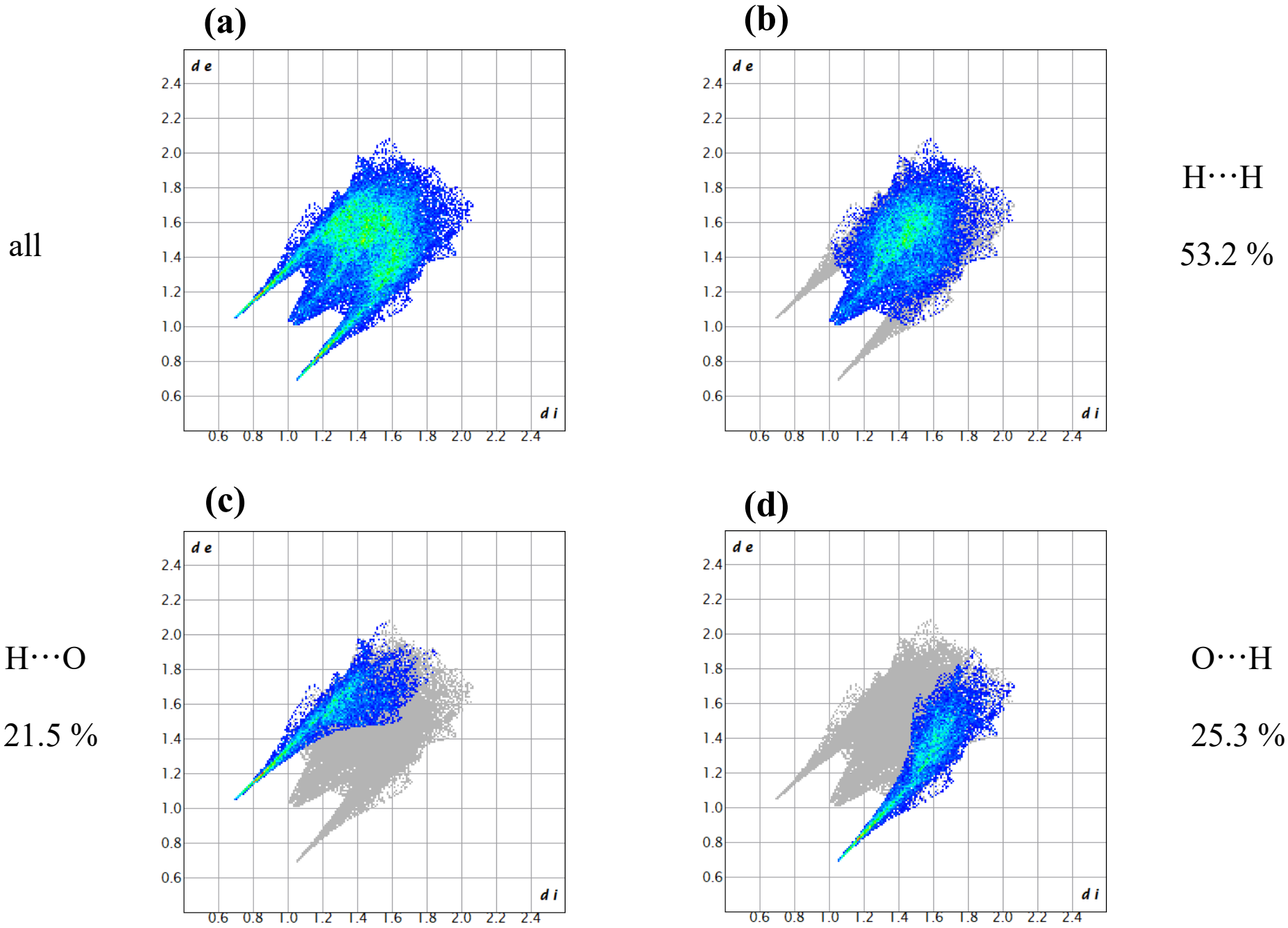
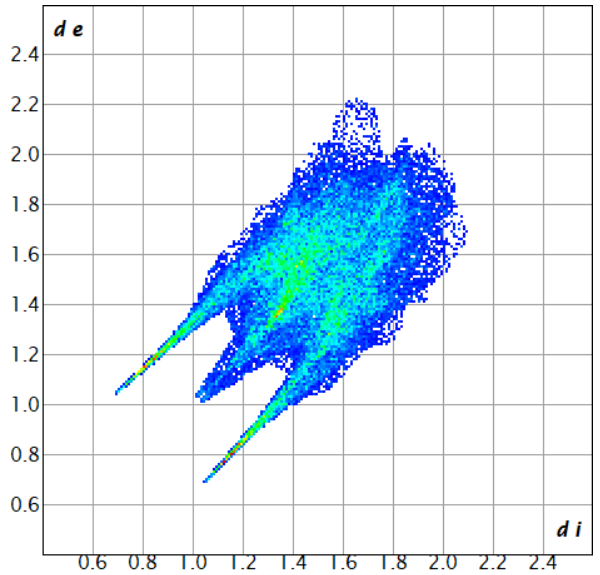
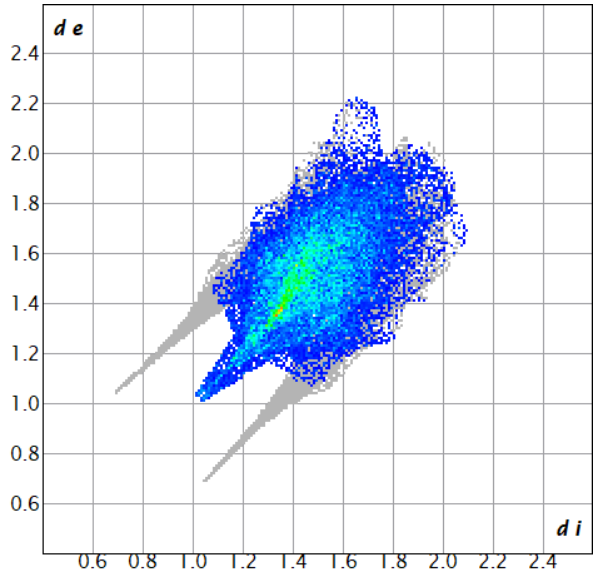


Fig. S20 2D fingerprint plots for D-tagatose.

all



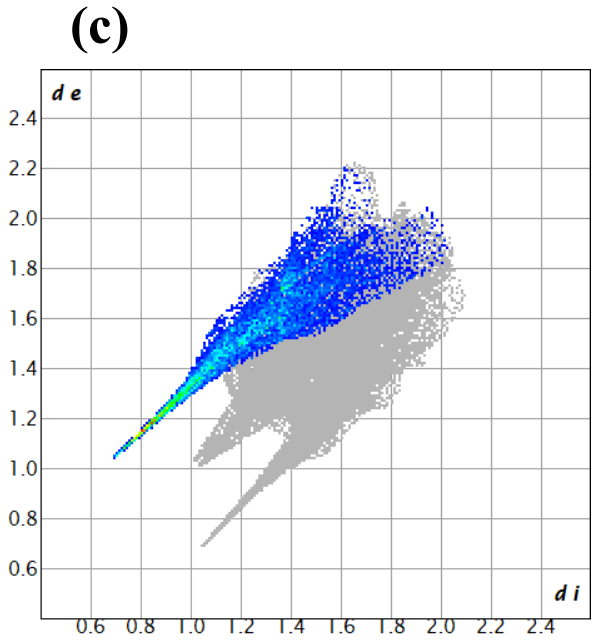


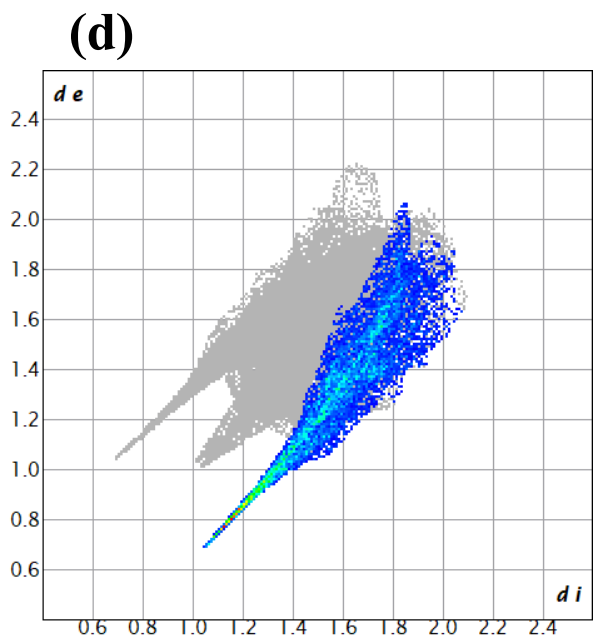
H···H

53.4 %

H···O

21.1 %



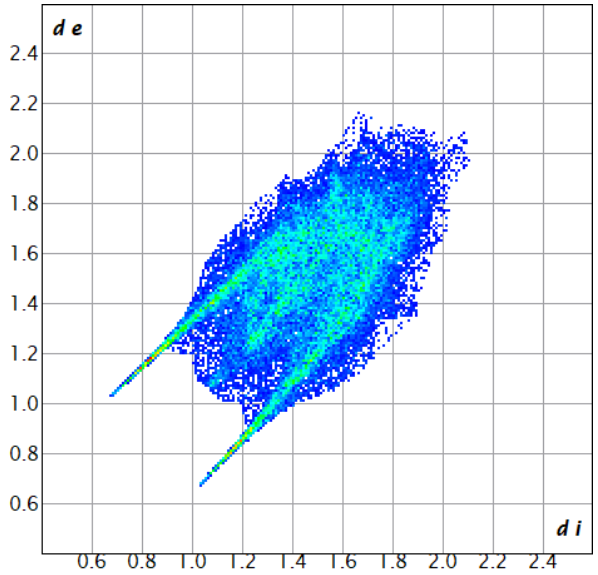


O···H

24.4 %

Fig. S21 2D fingerprint plots for L-sorbose

(a)



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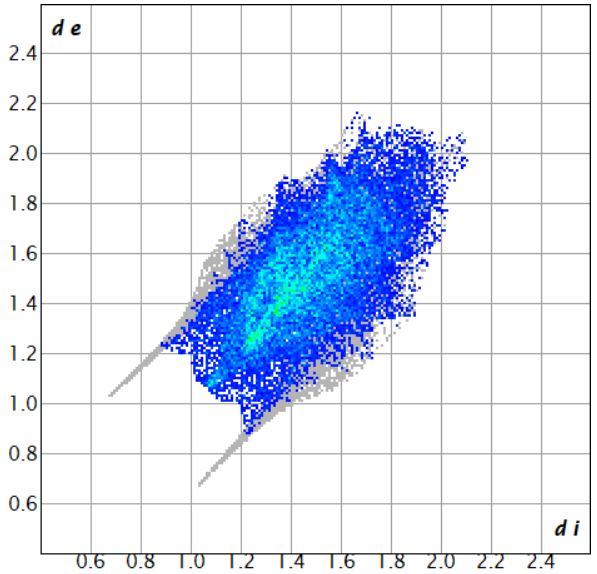
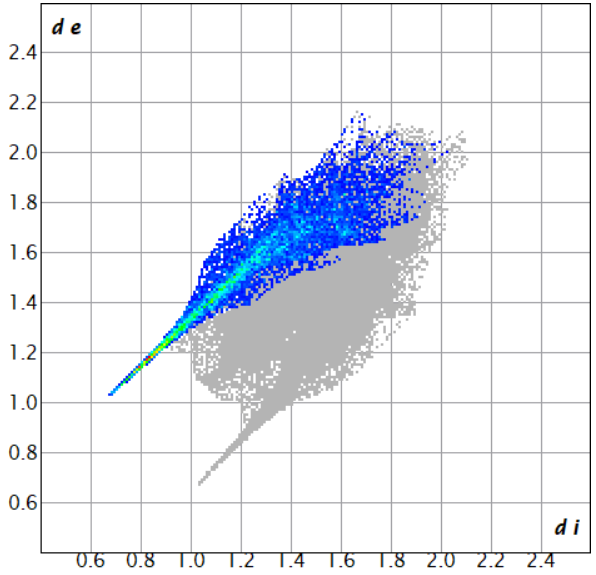
(b)



H···H

53.0 %

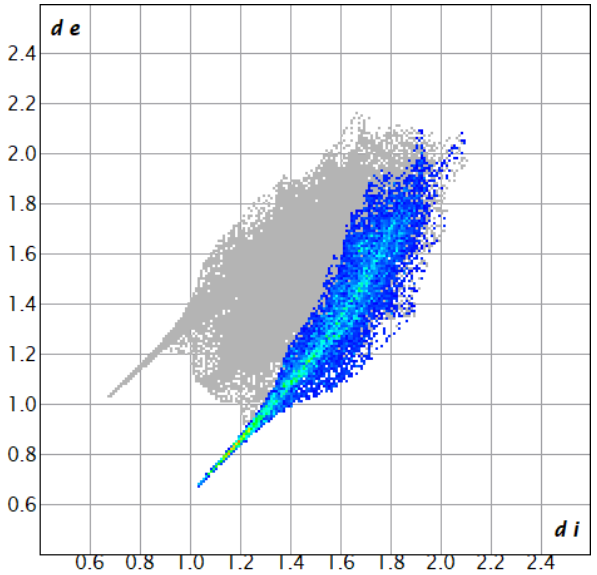
(c)



H···O

21.6 %

(d)

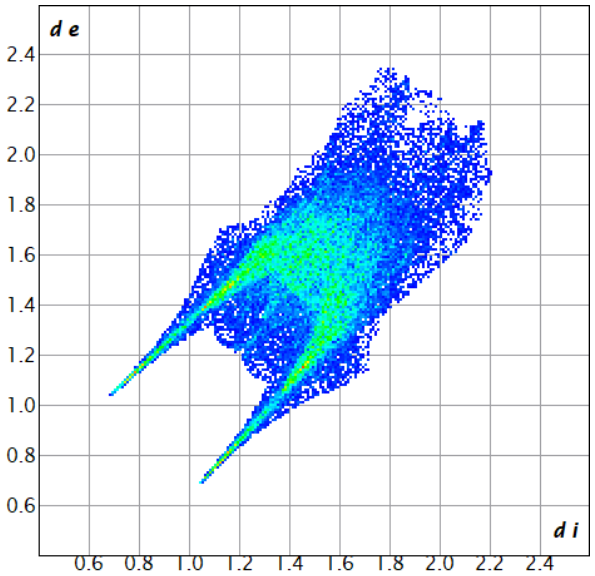


O···H

25.4 %

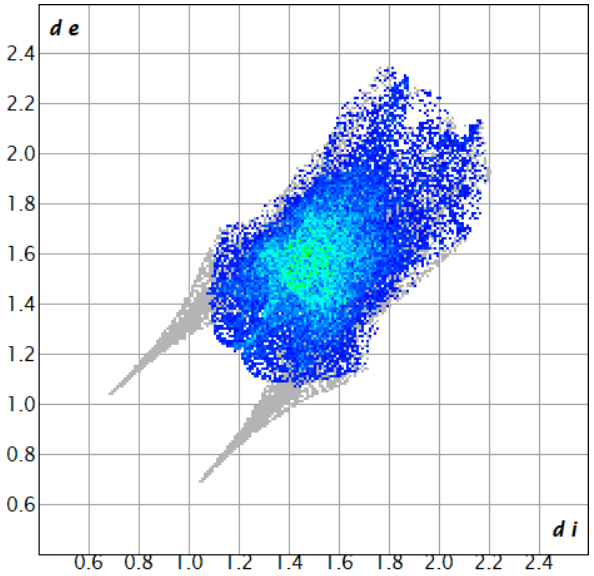
Fig. S22 2D fingerprint plots for fructose.

(a)



all

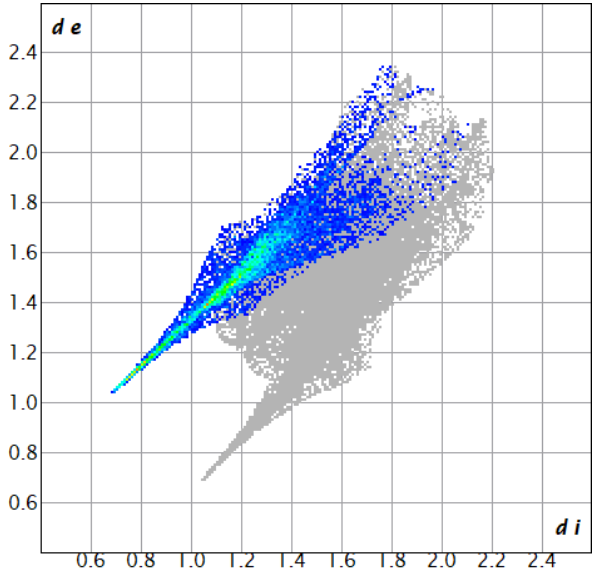
(b)



H···H

53.6 %

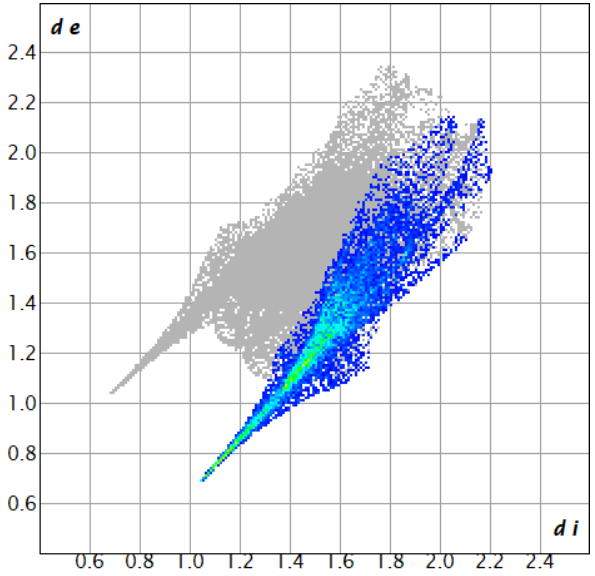
(c)



H···O

21.9 %

(d)

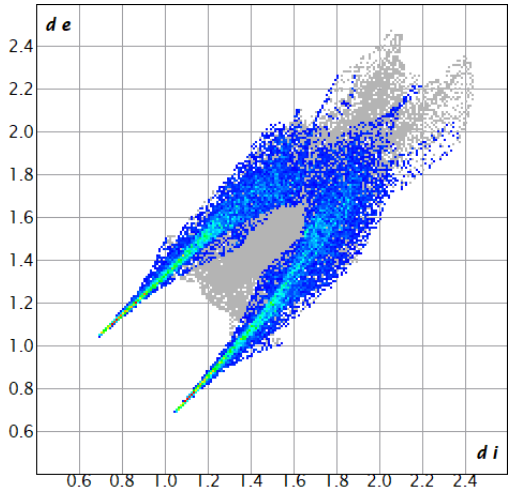


O···H

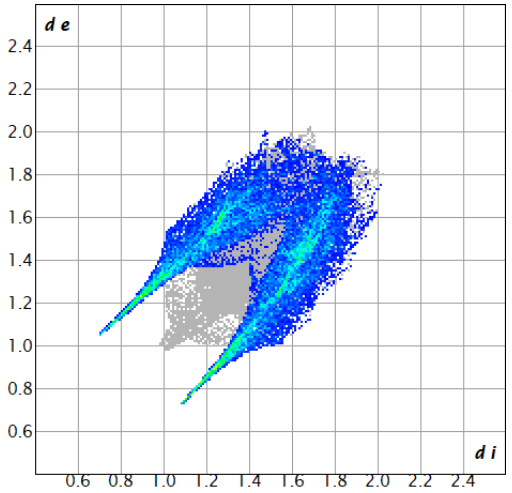
24.4 %

Fig. S23 2D fingerprint plots for D-psicose.

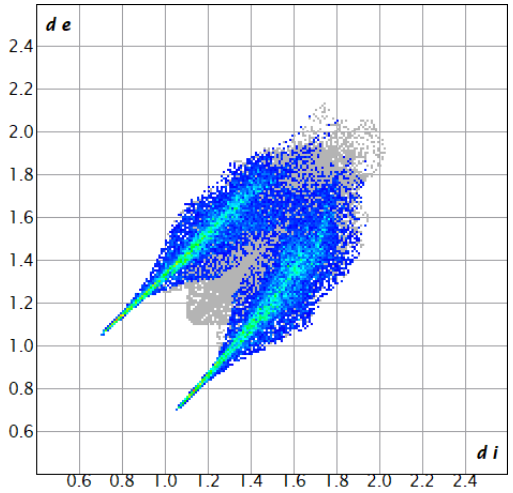
(a) tagatose



(b) sorbose



(c) fructose



(d) psicose

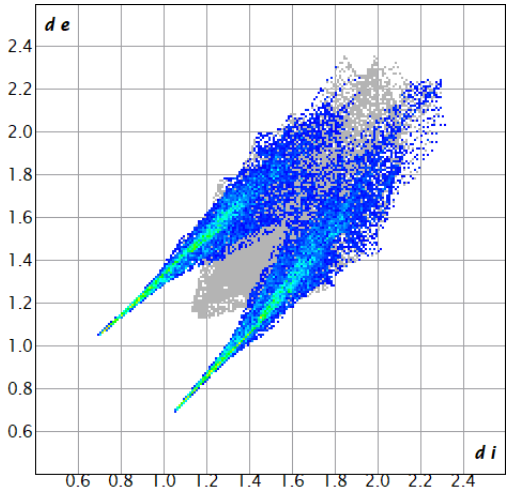
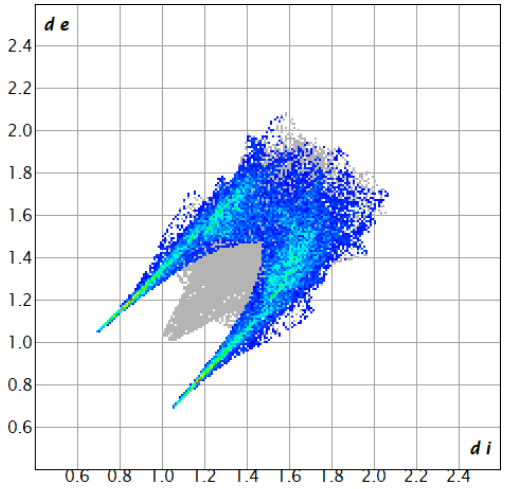
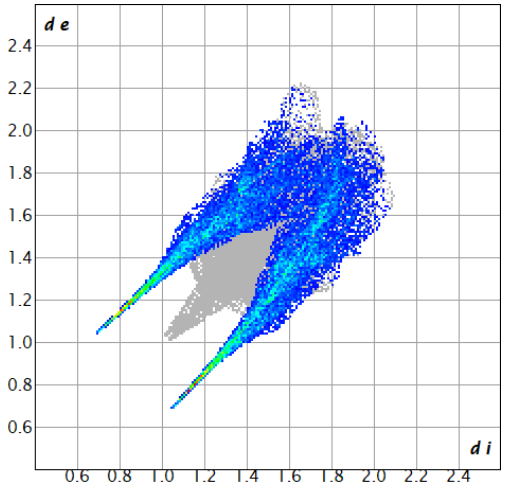


Fig. S24 2D fingerprint plots for racemic.

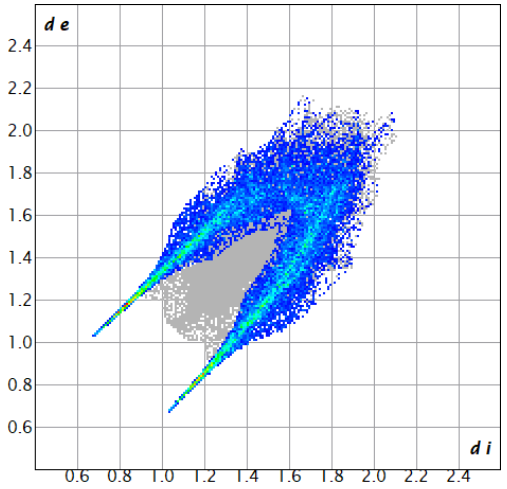
(a) tagatose



(b) sorbose



(c) fructose



(d) psicose

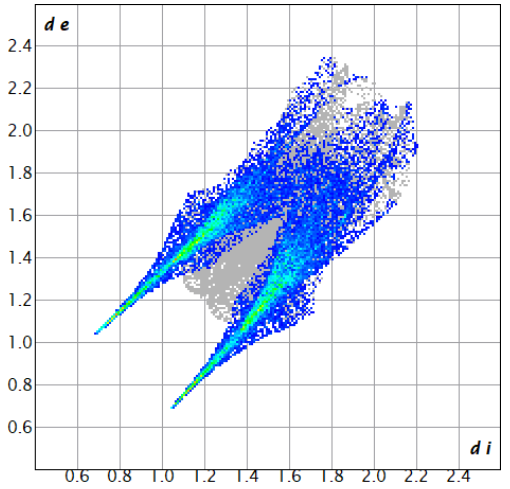


Fig. S25 2D fingerprint plots for chiral

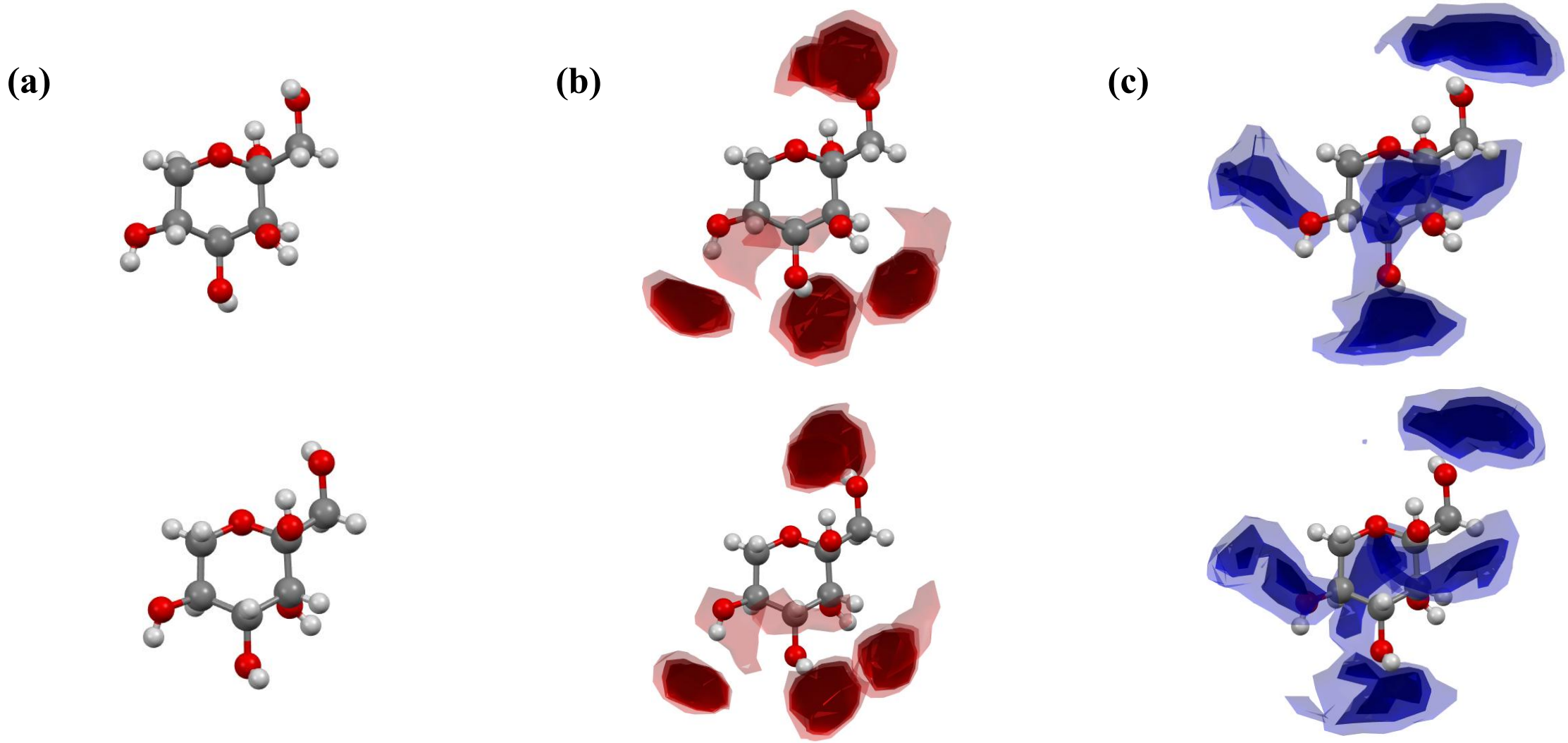


Fig. S26 FIMs analysis results for D,L-tagatose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding). In panels (a)–(c), results for the L-form are shown in the upper part, and those for the D-form are shown in the lower part.

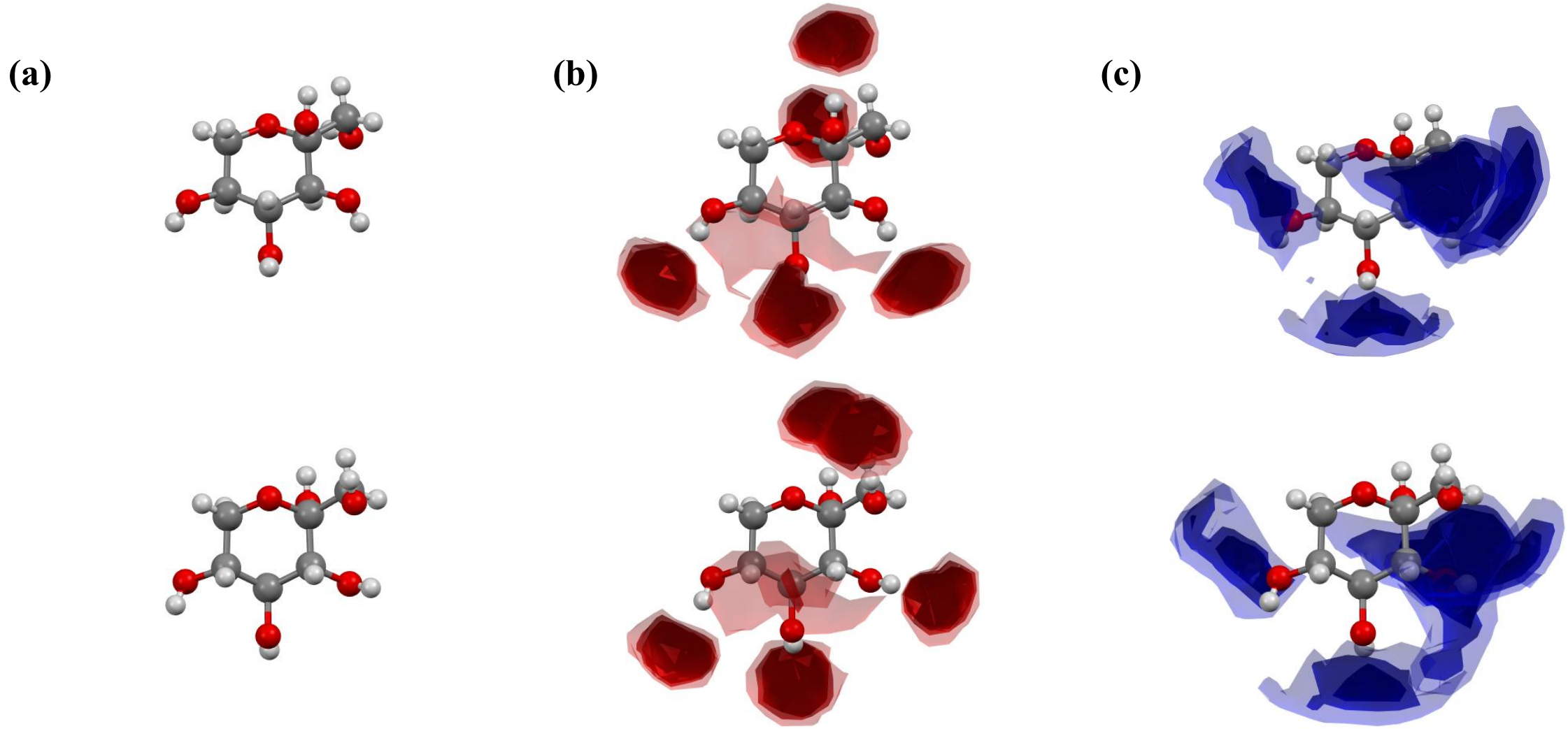


Fig. S27 FIMs analysis results for D,L-sorbose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding). In panels (a)–(c), results for the L-form are shown in the upper part, and those for the D-form are shown in the lower part.

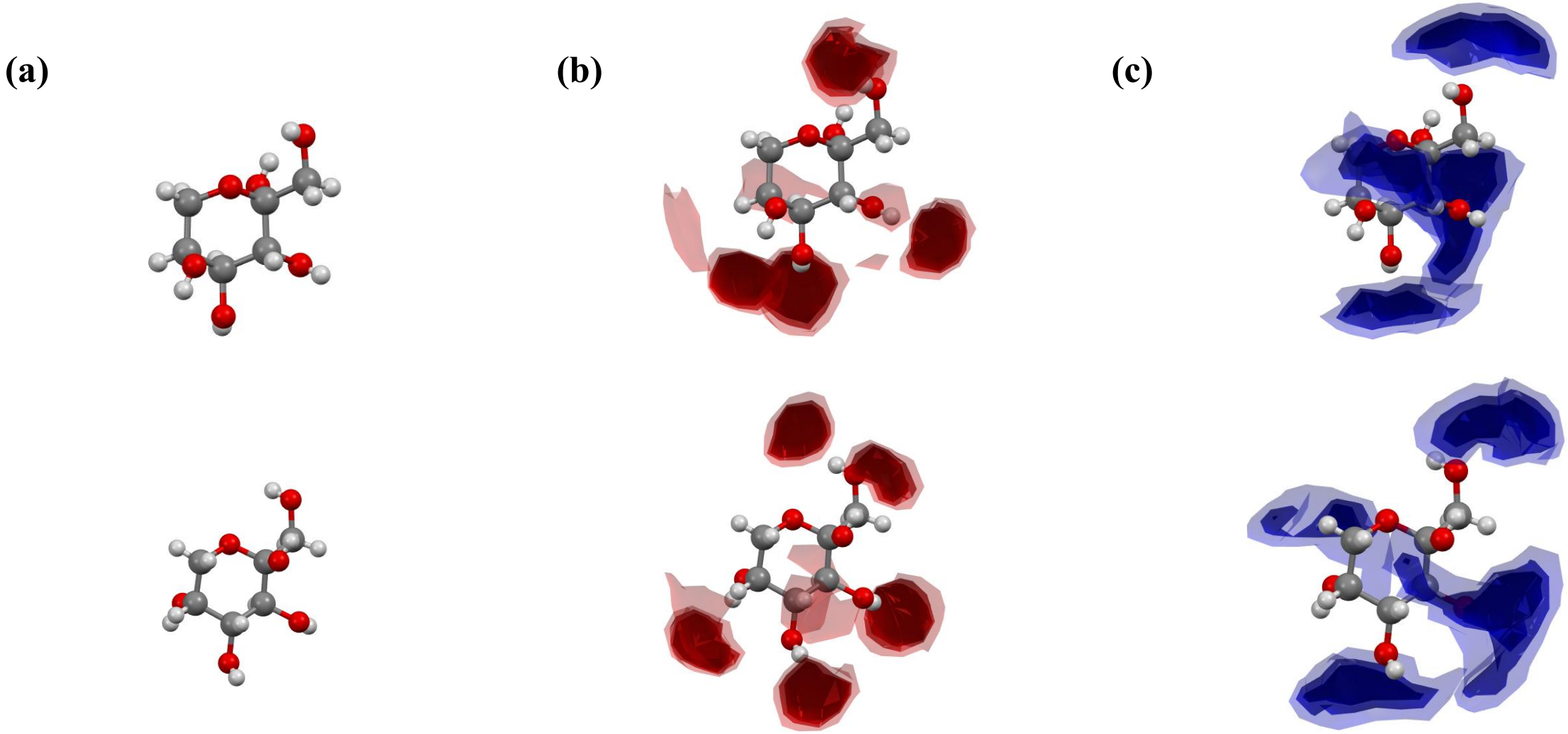


Fig. S28 FIMs analysis results for D,L-fructose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding). In panels (a)–(c), results for the L-form are shown in the upper part, and those for the D-form are shown in the lower part.

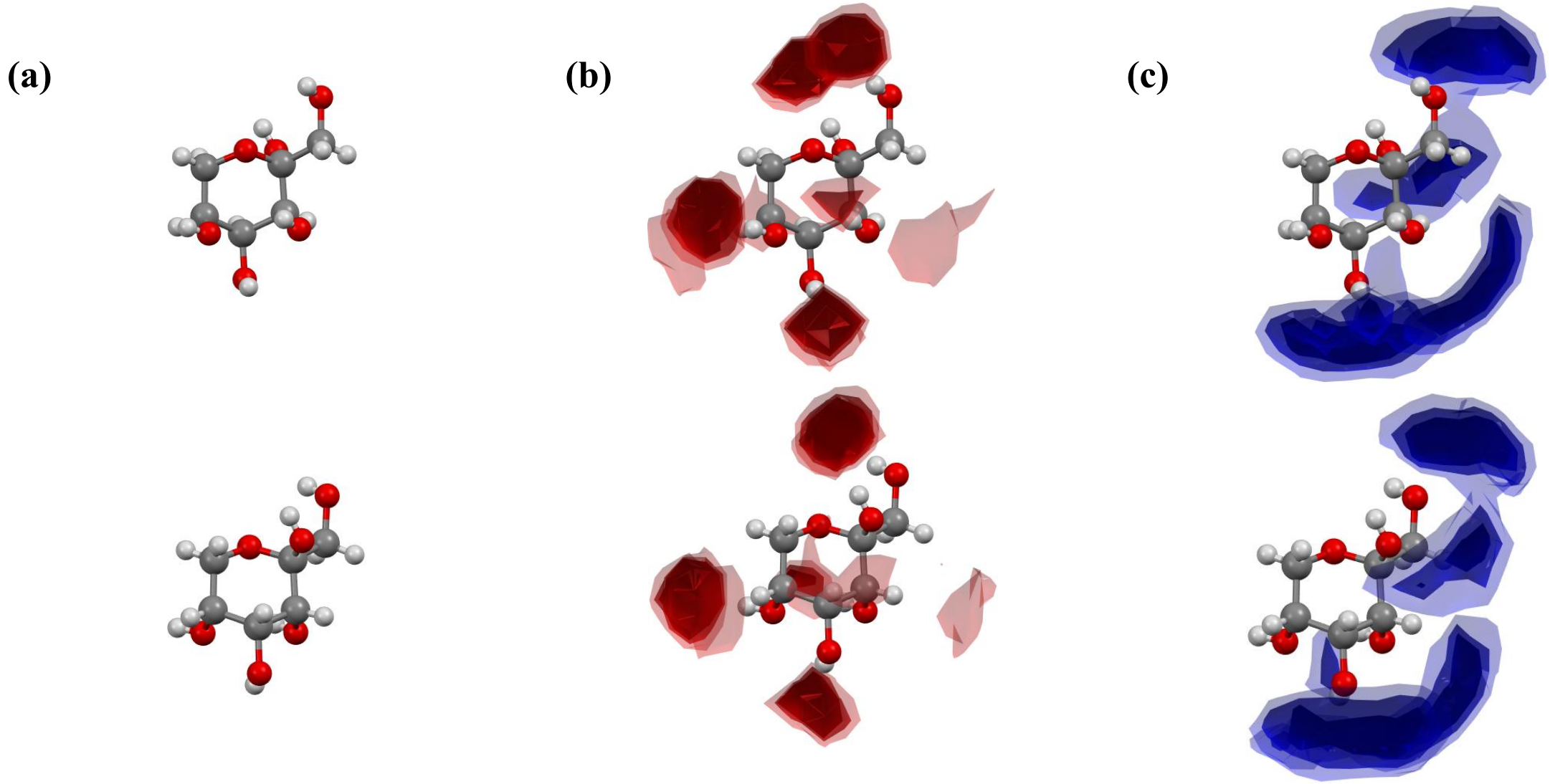


Fig. S29 FIMs analysis results for D,L-psicose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding). In panels (a)–(c), results for the L-form are shown in the upper part, and those for the D-form are shown in the lower part.

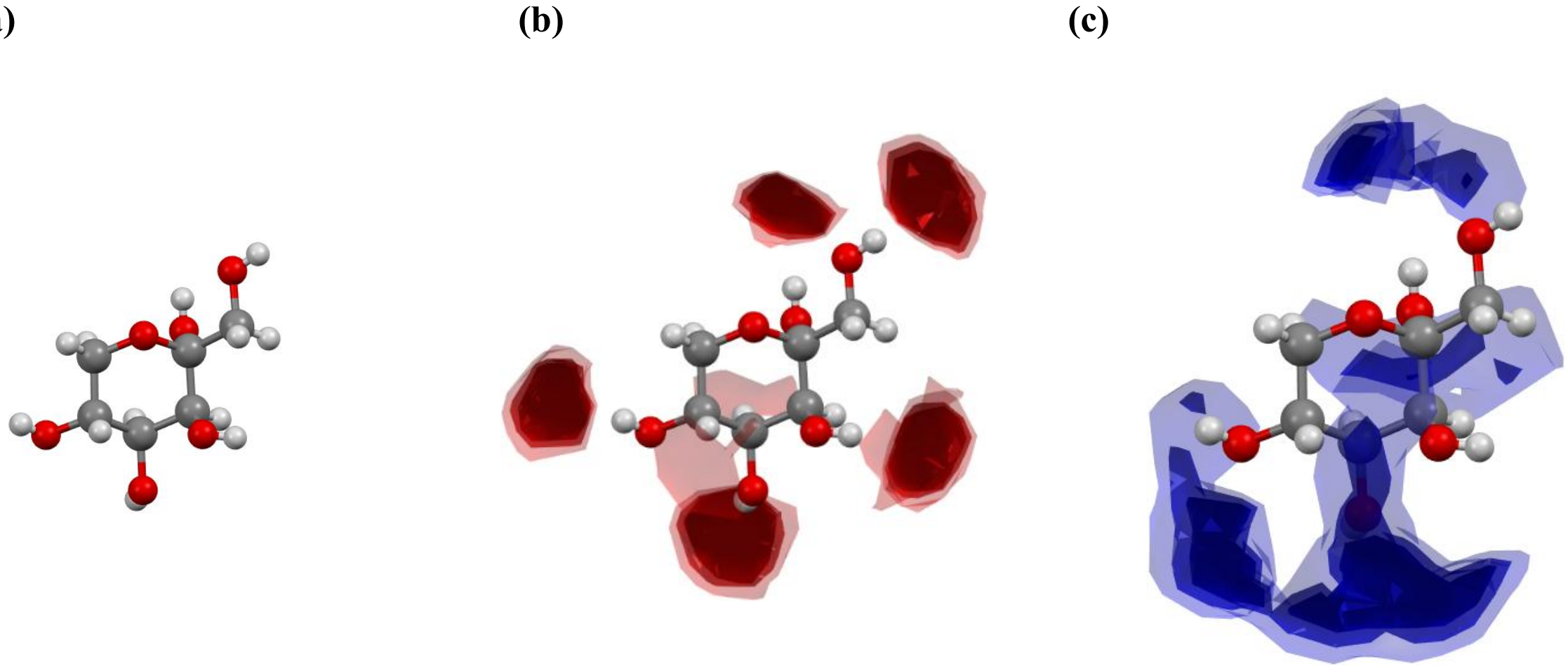


Fig. S30 FIMs analysis results for D-tagatose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding).

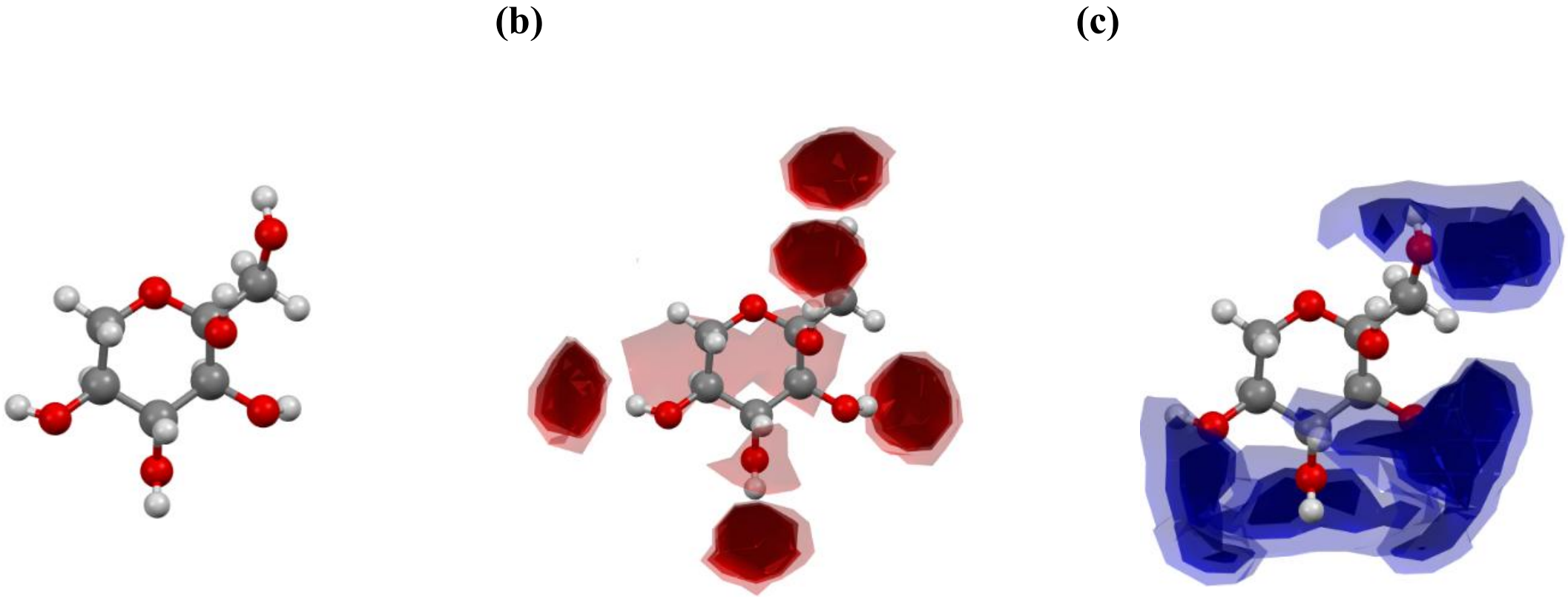


Fig. S31 FIMs analysis results for L-sotbose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding).

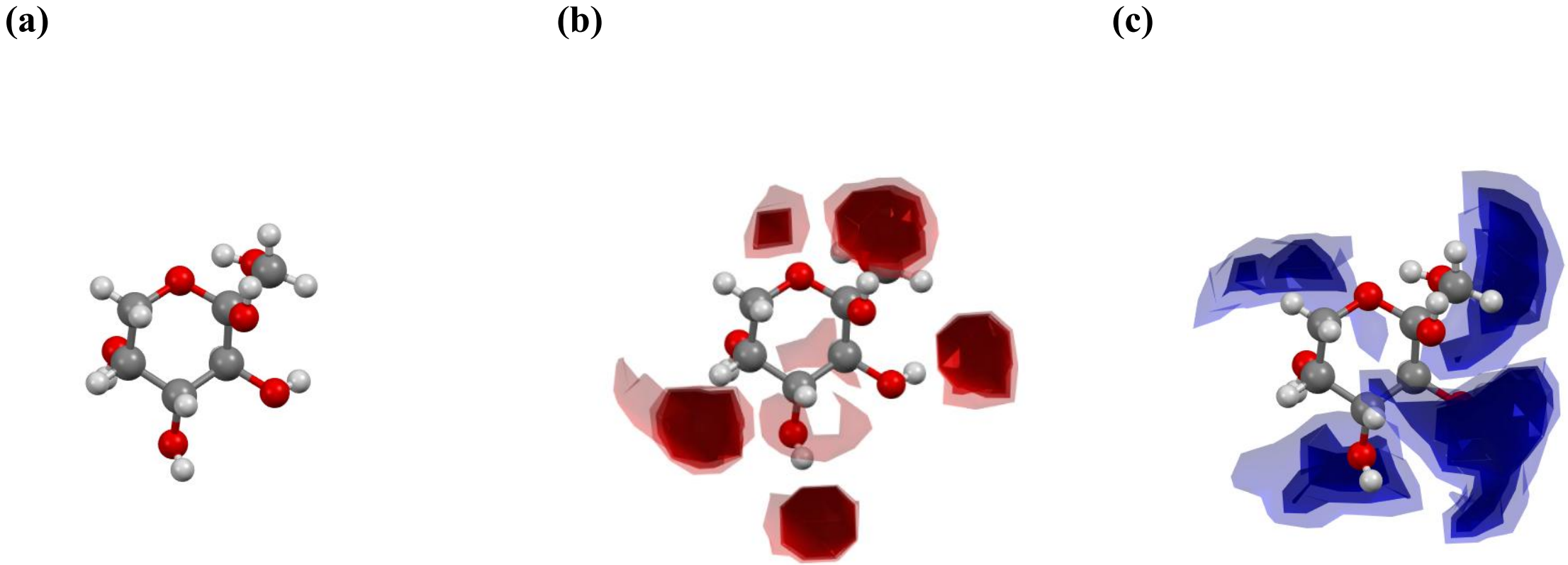


Fig. S32 FIMs analysis results for D-fructose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding).

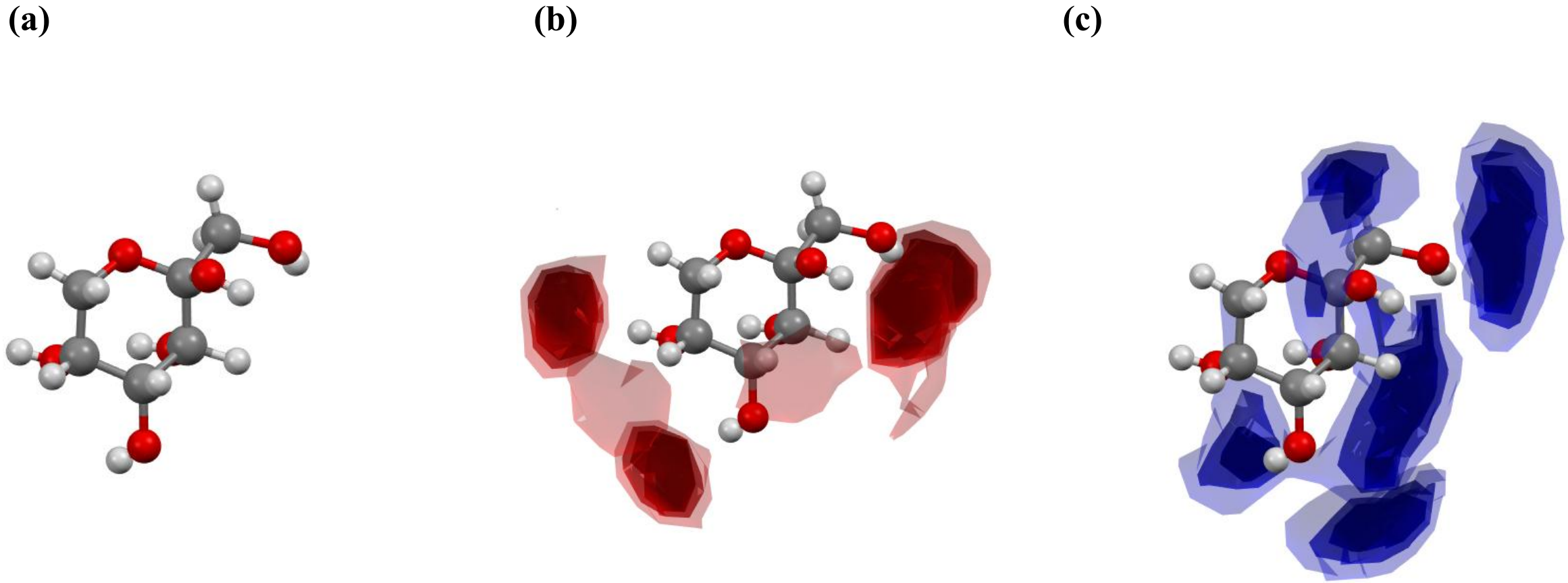


Fig. S33 FIMs analysis results for D-psicose. (a) Molecular structure. (b) Full interaction map (acceptor-type hydrogen bonding). (c) Full interaction map (donor-type hydrogen bonding).

Table S1 Cell parameters of the four ketohexose chiral forms.

	D-fructose	D-psicose	D-tagatose	L-sorbose
Formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)
a [Å]	8.0818 (4)	8.693 (2)	6.22010 (10)	6.545 (2)
b [Å]	9.1394 (4)	11.185 (4)	6.50220 (10)	18.062 (7)
c [Å]	9.9546 (5)	7.745 (2)	17.6629 (4)	6.310 (2)
α [º]	90	90	90	90
β [º]	90	90	90	90
γ [º]	90	90	90	90
Cell Volume [Å³]	735.275	753.056	714.364	745.942
Z	4	4	4	4
Z′	1	1	1	1
R-Factor [%]	2.03	4.3	2.47	3.7

Table S2 Cell parameters of the four ketohexose racemic forms.

	D,L-fructose	D,L-psicose	D,L-tagatose	D,L-sorbose
Formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Crystal System	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space Group	$P\bar{1}$ (#2)	$Pna2_1$ (#33)	$P2_1/c$ (#14)	$P2_1/a$ (#14)
a [Å]	5.43124 (19)	11.2629(5)	8.11340 (10)	12.8152 (3)
b [Å]	7.2727 (3)	5.3552(3)	9.4936 (2)	6.29489 (13)
c [Å]	10.1342 (4)	12.6538(6)	10.4731 (2)	18.9482 (4)
α [º]	69.120 (2)	90	90	90
β [º]	83.907 (2)	90	103.067 (7)	108.3472 (12)
γ [º]	78.381 (2)	90	90	90
Cell Volume [Å³]	366.088	763.215	785.806	1450.85
Z	2	4	4	8
Z′	1	1	2	2
R-Factor [%]	3.68	4.75	3.77	4.42

Table S3 Comparison of densities between chiral and racemic forms of monosaccharides. (Δ = racemic − Chiral)

Compound	chiral	racemic	Δdensity
psicose	1.588	1.567	-0.021
fructose	1.627	1.634	0.007
allose	1.593	1.618	0.043
arabinose	1.627	1.655	0.025
fucose	1.484	1.504	0.020

Table S4 Hydrogen-bond pairs forming the Interaction frames in D-fructose.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1 − O3	O3 − O5	−	−	dimer
O2	O2 − O1	O1 − O3	O4 − O2	−	triangular
O2	O2 − O1	O2 − O1	O5 − O2	O5 − O2	square
O2	O2 − O1	O5 − O2	O5 − O2	O4 − O2	square
O3	O3 − O5	O1 − O3	−	−	dimer
O4	O4 − O2	O3 − O5	O5 − O2	−	triangular
O5	−	−	−	−	−
O6	−	−	−	−	−

Table S5 Hydrogen-bond pairs forming the Interaction frames in D,L-fructose, centered on the D molecule.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1(#D) − O3(#D)	O4(#D) − O5(#D)	−	−	dimer
O2	O2(#D) − O1(#L)	O2(#L) − O1(#D)	−	−	dimer
O3	O3(#D) − O4(#L)	O3(#L) − O4(#D)	−	−	dimer
O4	O4(#D) − O5(#D)	O1(#D) − O3(#D)	−	−	dimer
O5	O5(#D) − O4(#L)	O5(#L) − O4(#D)	−	−	dimer
O6	−	−	−	−	−

Table S6 Hydrogen-bond pairs forming the Interaction frames in L-sorbose.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1 − O3	O4 − O6	−	−	dimer
O2	O2 − O5	O4 − O6	O2 − O5	−	triangular
O3	O3 − O4	O3 − O4	O5 − O2	−	triangular
O3	O3 − O4	O5 − O2	O3 − O4	−	triangular
O4	O4 − O6	O1 − O3	−	−	dimer
O5	O5 − O2	O3 − O4	O3 − O4	−	triangular
O6	−	−	−	−	−

Table S7 Hydrogen-bond pairs forming the Interaction frames in D,L-sorbose, centered on the L molecule.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1(#L) − O4(#L)	O4(#L) − O6(#L)	−	−	dimer
O2	O2(#L) − O5(#L)	O4(#L) − O6(#L)	O2(#L) − O5(#L)	−	triangular
O3	O3(#L) − O4(#D)	O3(#D) − O4(#D)	O5(#D) − O3(#L)	−	triangular
O3	O3(#L) − O4(#D)	O5(#D) − O3(#L)	O3(#L) − O2(#L)	−	triangular
O4	O4(#L) − O6(#L)	O1(#L) − O4(#L)	−	−	dimer
O5	O5(#L) − O3(#D)	O3(#D) − O4(#L)	O3(#L) − O4(#L)	−	triangular
O6	−	−	−	−	−

Table S8 Hydrogen-bond pairs forming the Interaction frames in D-psicose.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1 − O6	O5 − O3	O4 − O1	−	triangle
O1	O1 − O6	O1 − O6	O5 − O3	O5 − O3	square
O1	O1 − O6	O2 − O4	O2 − O4	O5 − O3	square
O2	O2 − O4	O2 − O4	O4 − O1	−	triangular
O2	O2 − O4	O4 − O1	O2 − O4	−	triangular
O3	O3 − O2	O2 − O4	O4 − O1	O1 − O6	square
O3	O3 − O2	O4 − O1	O2 − O4	O1 − O6	square
O4	O4 − O1	O1 − O6	O5 − O3	−	triangular
O4	O4 − O1	O2 − O4	O2 − O4	−	triangular
O5	O5 − O3	O3 − O1	O1 − O6	−	triangular
O6	−	−	−	−	−

Table S9 Hydrogen-bond pairs forming the Interaction frames in D,L-psicose, centered on the D molecule.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1(#D) − O3(#L)	O4(#L) − O6(#D)	−	−	dimer
O2	O2(#D) − O4(#L)	O4(#L) − O6(#D)	O3(#D) − O2(#D)	−	triangular
O3	O3(#D) − O2(#D)	O2(#D) − O4(#L)	O4(#L) − O6(#D)	−	triangular
O4	O4(#D) − O6(#L)	O1(#L) − O3(#D)	−	−	dimer
O5	−	−	−	−	
O6	−	−	−	−	−

Table S10 Hydrogen-bond pairs forming the Interaction frames in D-tagatose.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1 − O5	O4 − O6	O5 − O2	−	triangular
O1	O1 − O5	O5 − O2	O4 − O6	−	triangular
O2	O2 − O5	O4 − O6	O2 − O5	−	triangular
O2	O2 − O5	O2 − O5	O4 − O6	−	triangular
O3	O3 − O4	O3 − O4	O5 − O2	−	triangular
O3	O3 − O4	O5 − O2	O3 − O4	−	triangular
O4	O4 − O6	O1 − O5	O5 − O2	−	triangular
O4	O4 − O6	O2 − O5	O2 − O5	−	triangular
O4	O4 − O6	O5 − O2	O1 − O5	−	triangular
O5	O5 − O2	O1 − O5	O4 − O6	−	triangular
O5	O5 − O2	O3 − O4	O3 − O4	−	triangular
O5	O5 − O2	O4 − O6	O1 − O5	−	triangular
O6	−	−	−	−	−

Table S11 Hydrogen-bond pairs forming the Interaction frames in D,L-tagatose, centered on the D molecule.

	Step 1	Step 2	Step 3	Step 4	Interaction frame
O1	O1(#D) − O4(#D)	O3(#D) − O6(#D)	−	−	dimer
O2	O2(#D) − O3(#L)	O1(#L) − O4(#L)	O4(#L) − O5(#L)	O5(#L) − O1(#D)	square
O2	O2(#D) − O3(#L)	O5(#L) − O1(#D)	O1(#D) − O4(#D)	O4(#D) − O5(#D)	square
O3	O3(#D) − O6(#D)	O1(#D) − O4(#D)	−	−	dimer
O4	O4(#D) − O5(#D)	O5(#D) − O1(#L)	O4(#L) − O5(#L)	O5(#L) − O1(#D)	square
O4	O4(#D) − O5(#D)	O1(#D) − O4(#D)	O1(#D) − O4(#D)	O4(#D) − O5(#D)	square
O5	O5(#D) − O1(#L)	O1(#L) − O4(#L)	O4(#L) − O5(#L)	O2(#L) − O3(#D)	square
O5	O5(#D) − O1(#L)	O2(#L) − O3(#D)	O1(#D) − O4(#D)	O4(#D) − O5(#D)	square
O6	−	−	−	−	−

Table S12 Donor-type intermolecular hydrogen bonds in D,L-tagatose, D,L-sorbose, D,L-fructose, and D,L-psicose: experimental bond distances (Å), hydrogen bond angles (°), and calculated Bond Overlap Populations (BOP).

Compound	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)	BOP (electrons)
D,L-tagatose(#L)	O1-H1···O4 (#L) (#L)	0.820	1.99	2.78	163.4	0.0290
	O2-H2···O3 (#L) (#D)	0.820	1.91	2.70	163.0	0.0323
	O3-H3···O6 (#L) (#L)	0.820	1.89	2.69	163.1	0.0351
	O4-H4···O5 (#L) (#L)	0.820	1.91	2.73	176.4	0.0354
	O5-H5···O1 (#L) (#D)	0.820	1.91	2.71	162.9	0.0341
D,L-tagatose(#D)	O1-H1···O4 (#D) (#D)	0.820	1.99	2.78	163.4	0.0300
	O2-H2···O3 (#D) (#L)	0.820	1.91	2.70	163.0	0.0327
	O3-H3···O6 (#D) (#D)	0.820	1.89	2.69	163.1	0.0366
	O4-H4···O5 (#D) (#D)	0.820	1.91	2.73	176.4	0.0324
	O5-H5…O1 (#D) (#L)	0.820	1.91	2.71	162.9	0.0399
D,L-sorbose (#L)	O1−H1···O4 (#L) (#L)	0.820	2.37	3.17	166.8	0.0050
	O2−H2···O5 (#L) (#L)	0.820	1.96	2.76	164.4	0.0278
	O3−H3···O4 (#L) (#D)	0.820	1.99	2.81	172.3	0.0283
	O4−H4···O6 (#L) (#L)	0.820	2.11	2.92	170.3	0.0199
	O5−H5···O3 (#L) (#D)	0.820	2.10	2.87	156.0	0.0157
D,L-sorbose (#D)	O1−H1···O3 (#D) (#D)	0.820	2.14	2.92	158.5	0.0185
	O2−H2···O5 (#D) (#D)	0.820	2.01	2.81	169.3	0.0241
	O3−H3···O4 (#D) (#D)	0.820	1.93	2.75	172.0	0.0315
	O4−H4···O6 (#D) (#D)	0.820	2.25	3.05	165.4	0.0119

	O5−H5···O3 (#D) (#L)	0.820	2.29	3.06	157.9	0.0095
D,L-fructose(#L)	O1-H1···O3 (#L) (#L)	0.820	2.28	2.92	135.0	0.0074
	O2-H2···O1 (#L) (#D)	0.820	1.93	2.72	161.0	0.0295
	O3-H3···O4 (#L) (#D)	0.820	1.96	2.78	177.2	0.0317
	O4-H4···O5 (#L) (#L)	0.820	2.01	2.79	158.4	0.0215
	O5-H5···O4 (#L) (#D)	0.820	2.05	2.84	162.5	0.0206
D,L-fructose(#D)	O1-H1···O3 (#D) (#D)	0.820	2.28	2.92	135.0	0.0076
	O2-H2···O1 (#D) (#L)	0.820	1.93	2.72	161.0	0.283
	O3-H3···O4 (#D) (#L)	0.820	1.96	2.78	177.3	0.0321
	O4-H4···O5 (#D) (#D)	0.820	2.01	2.79	158.4	0.0243
	O5-H5···O4 (#D) (#L)	0.820	2.05	2.84	162.5	0.0238
D,L-psicose(#L)	O1-H1···O3 (#L) (#D)	0.820	1.91	2.72	168.2	0.0337
	O2-H2···O4 (#L) (#D)	0.820	1.92	2.72	166.1	0.0334
	O3-H3···O2 (#L) (#L)	0.820	2.20	2.87	140.4	0.0102
	O4-H4···O6 (#L) (#D)	0.820	2.14	2.83	141.0	0.0140
	O5-H5···O1 (#L) (#D)	0.820	1.94	2.75	169.0	0.0284
D,L-psicose(#D)	O1-H1···O3 (#D) (#L)	0.820	1.91	2.72	168.2	0.0335
	O2-H2···O4 (#D) (#L)	0.820	1.92	2.72	166.1	0.0370
	O3-H3···O2 (#D) (#D)	0.820	2.20	2.87	140.4	0.0104
	O4-H4···O6 (#D) (#L)	0.820	2.14	2.83	141.0	0.0129
	O5-H5···O1 (#D) (#L)	0.820	1.94	2.75	169.0	0.0312

Table S13 Donor-type intermolecular hydrogen bonds in D-tagatose, L-sorbose, D-fructose, and D-psicose: experimental bond distances (Å), hydrogen bond angles (°), and calculated Bond Overlap Populations (BOP).

Compound	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)	BOP (electrons)
D-tagatose	O1-H1···O5	0.829	2.09	2.79	141.6	0.0191
	O2-H2···O5	0.805	2.10	2.85	154.8	0.0205
	O3-H3···O4	0.826	1.90	2.72	172.6	0.0358
	O4-H4···O6	0.810	1.96	2.77	175.1	0.0328
	O5-H5···O2	0.810	2.02	2.82	170.7	0.0260
D-tagatose (2)	O1-H1···O5	0.829	2.09	2.79	141.6	0.0184
	O2-H2···O5	0.805	2.10	2.85	154.8	0.0183
	O3-H3···O4	0.826	1.90	2.72	172.6	0.0408
	O4-H4···O6	0.810	1.96	2.77	175.1	0.0353
	O5-H5···O2	0.810	2.02	2.82	170.7	0.0245
L-sorbose	O1−H1···O3	0.917	1.87	2.77	166.8	0.0363
	O2−H2···O5	0.968	1.88	2.80	157.2	0.0427
	O3−H3···O4	0.974	1.75	2.72	175.7	0.0605
	O4−H4···O6	0.941	1.93	2.86	168.4	0.0409
	O5−H5···O2	0.962	1.95	2.89	162.8	0.0367
	O5−H5···O3	0.962	2.58	3.18	120.4	0.0420
L-sorbose (2)	O1−H1···O3	0.917	1.87	2.77	166.8	0.0411
	O2−H2···O5	0.968	1.88	2.80	157.2	0.0606
	O3−H3···O4	0.974	1.75	2.72	175.7	0.0394
	O4−H4···O6	0.941	1.93	2.86	168.4	0.0350
	O5−H5···O2	0.962	1.95	2.89	162.8	0.0363
	O5−H5···O3	0.962	2.58	3.18	120.4	0.0427
D-fructose	O1−H1···O3	0.825	2.03	2.81	156.1	0.0220
	O2−H2···O1	0.875	1.81	2.65	159.7	0.0469
	O3−H3···O5	0.812	2.09	2.89	172.1	0.0223
	O4−H4···O2	0.817	2.14	2.93	161.8	0.0153
	O5-H5···O2	0.847	1.94	2.78	168.2	0.0262
D-fructose (2)	O1−H1···O3	0.825	2.03	2.81	156.1	0.0261
	O2−H2···O1	0.875	1.81	2.65	159.7	0.0425
	O3−H3···O5	0.812	2.09	2.89	172.1	0.0203
	O4−H4···O2	0.817	2.14	2.93	161.8	0.0159
	O5-H5···O2	0.847	1.94	2.78	168.2	0.0304
D-psicose	O1-H1···O6	0.743	2.03	2.75	160.5	0.0222
	O2-H2···O4	0.807	1.95	2.73	162.8	0.0273
	O3-H3···O5	0.735	2.64	3.15	128.0	0.0154
	O4-H4···O1	0.685	2.06	2.74	171.5	0.0179
	O5-H5···O3	0.839	2.04	2.87	173.5	0.0234

D-psicose (2)	O1−H1···O6	0.743	2.03	2.75	160.5	0.0228
	O2−H2···O4	0.807	1.95	2.73	162.8	0.0283
	O3−H3···O2	0.735	2.64	3.15	128.0	0.0169
	O4−H4···O1	0.685	2.06	2.74	171.5	0.0208
	O5−H5···O3	0.839	2.04	2.87	173.5	0.0241

Table S14 Contribution ratios of intermolecular interactions in racemic ketohexoses.

Compound	H…O(donor)[%]	H…H[%]	O…H(Acceptor)[%]	O…O[%]	all…all[%]
D,L-fructose(#L)	21.6	54.0	24.2	0.2	100
D,L-fructose(#D)	21.6	54.0	24.2	0.2	100
D,L-psicose(#L)	20.1	55.9	23.9	0.1	100
D,L-psicose(#D)	20.1	55.9	23.9	0.1	100
D,L-tagatose(#L)	19.1	58.0	22.7	0.2	100
D,L-tagatose(#D)	19.0	58.0	22.8	0.2	100
D,L-sorbose(#L)	22.1	51.6	25.7	0.6	100
D,L-sorbose(#D)	22.1	51.6	25.7	0.6	100

Table S15 Contribution ratios of intermolecular interactions in chiral ketohexoses.

Compound	H···O(donor)[%]	H···H[%]	O···H(Acceptor)[%]	O···O[%]	all···all[%]
D-fructose	21.6	53.0	25.4	0.0	100
D-psicose	20.4	56.7	22.8	0.1	100
D-tagatose	21.5	53.2	25.3	0.0	100
L-sorbose	21.1	53.4	24.4	1.1	100

Table S16 FIMs analysis results for D,L-tagatose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D,L-tagatose (#L)	O1-O4	O4-O1
	(#L) (#L)	(#L) (#L)
	O2-O3	O3-O2
	(#L) (#D)	(#D) (#L)
	O3-O6	O6-O3
	(#L) (#L)	(#L) (#L)
	O4-O5	O5-O4
	(#L) (#L)	(#L) (#L)
	O5-O1	O1-O5
	(#L) (#D)	(#D) (#L)
D,L-tagatose (#D)	O1-O4	O4-O1
	(#D) (#D)	(#D) (#D)
	O2-O3	O3-O2
	(#D) (#L)	(#L) (#D)
	O3-O6	O6-O3
	(#D) (#D)	(#D) (#D)
	O4-O5	O5-O4
	(#D) (#D)	(#D) (#D)
	O5-O1	O1-O5
	(#D) (#L)	(#L) (#D)

Table S17 FIMs analysis results for D,L-sorbose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D,L-sorbose (#L)	O1-O4	O4-O1
	(#L) (#L)	(#L) (#L)
	O2-O5	O5-O2
	(#L) (#L)	(#L) (#L)
	O3-O4	O4-O3
	(#L) (#D)	(#D) (#L)
	O4-O6	O6-O4
	(#L) (#L)	(#L) (#L)
	O5-O2	O2-O5
	(#L) (#D)	(#D) (#L)
	O5-O3	O3-O5
	(#L) (#D)	(#D) (#L)
D,L-sorbose (#D)	O1-O3	O3-O1
	(#D) (#D)	(#D) (#D)
	O1-O4	O4-O1
	(#D) (#D)	(#D) (#D)
	O2-O5	O5-O2
	(#D) (#D)	(#D) (#D)
	O3-O4	O4-O3
	(#D) (#D)	(#D) (#D)
	O4-O1	O1-O4
	(#D) (#D)	(#D) (#D)
	O4-O6	O6-O4
	(#D) (#D)	(#D) (#D)
	O5-O2	O2-O5
	(#D) (#L)	(#L) (#D)
	O5-O3	O3-O5
	(#D) (#L)	(#L) (#D)

Table S18 FIMs analysis results for D,L-fructose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D,L-fructose (#L)	O1-O2 (#L) (#L)	O2-O1 (#L) (#L)
	O1-O3 (#L) (#L)	O3-O1 (#L) (#L)
	O2-O1 (#L) (#D)	O1-O2 (#D) (#L)
	O3-O4 (#L) (#D)	O4-O3 (#D) (#L)
	O4-O5 (#L) (#L)	O5-O4 (#L) (#L)
	O5-O4 (#L) (#D)	O4-O5 (#D) (#L)
D,L-fructose (#D)	O1-O2 (#D) (#D)	O2-O1 (#D) (#D)
	O1-O3 (#D) (#D)	O3-O1 (#D) (#D)
	O2-O1 (#D) (#L)	O1-O2 (#L) (#D)
	O3-O4 (#D) (#L)	O4-O3 (#L) (#D)
	O4-O5 (#D) (#D)	O5-O4 (#D) (#D)
	O5-O4 (#D) (#L)	O4-O5 (#L) (#D)

Table S19 FIMs analysis results for D,L-psicose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D,L-psicose (#L)	O1-O3 (#L) (#D)	O3-O1 (#D) (#L)
	O2-O4 (#L) (#D)	O4-O2 (#D) (#L)
	O3-O2 (#L) (#L)	O2-O3 (#L) (#L)
	O4-O6 (#L) (#D)	O6-O4 (#D) (#L)
	O5-O1 (#L) (#D)	O1-O5 (#D) (#L)
D,L-psicose (#D)	O1-O3 (#D) (#L)	O3-O1 (#L) (#D)
	O2-O4 (#D) (#L)	O4-O2 (#L) (#D)
	O3-O2 (#D) (#D)	O2-O3 (#D) (#D)
	O4-O6 (#D) (#L)	O6-O4 (#L) (#D)
	O5-O1 (#D) (#L)	O1-O5 (#L) (#D)

Table S20 FIMs analysis results for D-tagatose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D-tagatose	O1-O5	O5-O1
	O2-O5	O5-O2
	O3-O4	O4-O3
	O4-O6	O6-O4
	O5-O2	O2-O5

Table S21 FIMs analysis results for L-sorbose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
L-sorbose	O1-O3	O3-O1
	O2-O5	O5-O2
	O3-O4	O4-O3
	O4-O6	O6-O4
	O5-O2	O2-O5
	O5-O3	O3-O5

Table S22 FIMs analysis results for D-fructose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D-fructose	O1-O3	O3-O1
	O2-O1	O1-O2
	O3-O5	O5-O3
	O3-O6	O6-O3
	O4-O2	O2-O4
	O5-O2	O2-O5

Table S23 FIMs analysis results for D-psicose. Ideal hydrogen-bonding pairs are shown in black, while non-ideal hydrogen-bonding pairs are shown in red.

compound	Hydrogen bond pairs	
	Donor	Acceptor
D-psicose	O1-O6	O6-O1
	O2-O4	O4-O2
	O3-O2	O2-O3
	O4-O1	O1-O4
	O5-O3	O3-O5