Supporting information for X-ray wavefunction refinement and comprehensive structural studies on bromo-substituted analogues of 2-deoxy-D-glucose in solid state and solution

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Table S1. Crystal data and structure refinement details for investigated compounds.

Compound	2-BG	2-BM	sucrose
Empirical formula	$C_6H_{11}BrO_5$	$C_6H_{11}BrO_5$	$C_{12}H_{22}O_{11}$
Formula weight	243.055	243.055	342.302
Temperature/K	100	99.99(10)	100
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1$	$P2_1$
a/Å	6.8069(3)	8.0544(8)	7.7727(9)
b/Å	6.8839(3)	10.3670(7)	8.7216(11)
c/Å	17.1166(10)	10.0444(8)	10.8637(11)
α/°	90	90	90
β/°	90	90.784(8)	102.983(11)
γ/°	90	90	90
Volume/Å^3	802.06(7)	838.63(12)	717.63(15)
Z	4	4	2
ρ_{calc}g/cm^3	2.013	1.925	1.584
μ/mm^{-1}	6.915	6.614	0.142
F(000)	486.9	486.9	364.3
Crystal size/mm^3	0.041 × 0.04 × 0.017	0.16 × 0.049 × 0.035	nd.
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo K_α(λ=0.71073Å)
2Θ range for data collection/°	10.34 to 134.16	8.8 to 134.14°	5.38 to 58.42°
Index ranges	-8 ≤ h ≤ 7, -8 ≤ k ≤ 5, -20 ≤ l ≤ 19	-9 ≤ h ≤ 8, -12 ≤ k ≤ 12, -11 ≤ l ≤ 11	-10 ≤ h ≤ 10, -11 ≤ k ≤ 9, -14 ≤ l ≤ 14
Reflections collected	2663	11095	13618
Independent reflections	1437 [R_{int} = 0.0496, R_{sigma} = 0.0710]	2982[R(int) = 0.0626]	3318[R(int) = 0.0339]
Data/restraints/parameters	1437/3/139	2982/21/267	3318/1/400
Goodness-of-fit on F^2	0.948	1.050	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0796	R_1 = 0.0790, wR_2 = 0.2258	R_1 = 0.0238, wR_2 = 0.0395
Final R indexes [all data]	R_1 = 0.0425, wR_2 = 0.0838	R_1 = 0.0811, wR_2 = 0.2285	R_1 = 0.0289, wR_2 = 0.0410
Largest diff. peak/hole / e Å^{-3}	0.53/-0.51	2.60/-1.61	0.12/-0.14
Flack parameter	-0.06(4)	-0.01(5)	0.1(8)

Table S2. Bond lengths for 2-BG

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C2	1.955(5)	C3	O2	1.422(6)
C1	C2	1.531(7)	C4	C5	1.536(7)
C1	O1	1.377(6)	C4	O3	1.432(6)
C1	O5	1.426(6)	C5	C6	1.511(7)
C2	C3	1.518(7)	C5	O5	1.432(6)
C3	C4	1.531(7)	C6	O6	1.426(7)

Table S3. Values of valence angles for 2-BG

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	C2	113.9(4)	C5	C4	C3	109.5(4)
O5	C1	C2	107.9(4)	O3	C4	C3	109.7(4)
O5	C1	O1	109.1(4)	O3	C4	C5	107.3(4)
C1	C2	Br1	109.2(3)	C6	C5	C4	113.2(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C2	Br1	109.1(3)	O5	C5	C4	107.4(4)
C3	C2	C1	112.4(4)	O5	C5	C6	109.0(4)
C4	C3	C2	110.5(4)	O6	C6	C5	115.3(4)
O2	C3	C2	108.9(4)	C5	O5	C1	111.7(4)
O2	C3	C4	110.0(4)				

Table S4. Values of torsion angles for 2-BG

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C2	C1	O1	-62.8(4)	C1	O5	C5	C6	-167.9(4)
Br1	C2	C1	O5	175.9(3)	C2	C3	C4	C5	51.3(5)
Br1	C2	C3	C4	-170.6(3)	C2	C3	C4	O3	168.8(4)
Br1	C2	C3	O2	68.4(3)	C3	C4	C5	C6	179.7(4)
C1	C2	C3	C4	-49.3(5)	C3	C4	C5	O5	-59.9(4)
C1	C2	C3	O2	-170.2(4)	C4	C5	C6	O6	55.4(5)
C1	O5	C5	C4	69.1(4)					

Table S5. Bond lengths for 2-BM

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1A	C2A	1.950(14)	Br1B	C2B	1.960(14)
C1A	C2A	1.51(2)	C1B	C2B	1.54(2)
C1A	O1A	1.372(17)	C1B	O1B	1.402(16)
C1A	O5A	1.406(18)	C1B	O5B	1.409(16)
C2A	C3A	1.531(18)	C2B	C3B	1.509(16)
C3A	C4A	1.53(2)	C3B	C4B	1.520(19)
C3A	O3A	1.382(16)	C3B	O3B	1.407(16)
C4A	C5A	1.543(18)	C4B	C5B	1.516(18)
C4A	O4A	1.446(14)	C4B	O4B	1.433(15)
C5A	C6A	1.516(19)	C5B	C6B	1.55(2)
C5A	O5A	1.426(17)	C5B	O5B	1.405(15)
C6A	O6A	1.414(17)	C6B	O6B	1.416(18)

Table S6. Values of valence angles for 2-BM

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1A	C1A	C2A	111.3(12)	O1B	C1B	C2B	108.5(11)
O5A	C1A	C2A	111.2(11)	O5B	C1B	C2B	110.6(10)
O5A	C1A	O1A	107.7(12)	O5B	C1B	O1B	109.9(11)
C1A	C2A	Br1A	111.5(9)	C1B	C2B	Br1B	110.3(9)
C3A	C2A	Br1A	110.2(9)	C3B	C2B	Br1B	111.7(9)
C3A	C2A	C1A	110.0(12)	C3B	C2B	C1B	112.7(11)
C4A	C3A	C2A	110.6(10)	C4B	C3B	C2B	110.0(11)
O3A	C3A	C2A	111.2(11)	O3B	C3B	C2B	115.0(11)
O3A	C3A	C4A	112.0(11)	O3B	C3B	C4B	108.3(10)
C5A	C4A	C3A	114.3(11)	C5B	C4B	C3B	110.0(11)
O4A	C4A	C3A	110.8(10)	O4B	C4B	C3B	110.4(11)
O4A	C4A	C5A	108.8(11)	O4B	C4B	C5B	108.0(10)
C6A	C5A	C4A	111.7(12)	C6B	C5B	C4B	112.1(11)
O5A	C5A	C4A	111.5(11)	O5B	C5B	C4B	112.8(10)
O5A	C5A	C6A	105.4(11)	O5B	C5B	C6B	106.2(11)
O6A	C6A	C5A	110.4(11)	O6B	C6B	C5B	110.5(11)
C5A	O5A	C1A	112.0(10)	C5B	O5B	C1B	114.2(10)

Table S7. Values of torsion angles for 2-BM

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1A	C2A	C1A	O1A	58.2(10)	Br1B	C2B	C1B	O1B	165.7(8)
Br1A	C2A	C1A	O5A	-61.9(10)	Br1B	C2B	C1B	O5B	-73.7(9)
Br1A	C2A	C3A	C4A	74.7(10)	Br1B	C2B	C3B	C4B	74.3(10)
Br1A	C2A	C3A	O3A	-50.4(9)	Br1B	C2B	C3B	O3B	-48.2(11)
C1A	C2A	C3A	C4A	-48.7(11)	C1B	C2B	C3B	C4B	-50.5(13)
C1A	C2A	C3A	O3A	-173.8(11)	C1B	C2B	C3B	O3B	-173.0(11)
C1A	O5A	C5A	C4A	56.8(11)	C1B	O5B	C5B	C4B	59.2(11)
C1A	O5A	C5A	C6A	178.3(12)	C1B	O5B	C5B	C6B	-177.7(11)
C2A	C3A	C4A	C5A	42.8(12)	C2B	C3B	C4B	C5B	51.3(11)
C2A	C3A	C4A	O4A	166.3(10)	C2B	C3B	C4B	O4B	170.3(11)
C3A	C4A	C5A	C6A	-163.9(11)	C3B	C4B	C5B	C6B	-175.4(11)
C3A	C4A	C5A	O5A	-46.2(11)	C3B	C4B	C5B	O5B	-55.6(11)
C4A	C5A	C6A	O6A	58.5(12)	C4B	C5B	C6B	O6B	60.1(11)

Table S8. Bond lengths for sucrose

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.4420(16)	O11	C6	1.4226(13)
O1	C6	1.4137(13)	O11	C7	1.4343(15)
O2	C2	1.4215(18)	C1	C2	1.5243(17)
O3	C3	1.4126(17)	C1	C3	1.5287(18)
O4	C4	1.4296(16)	C3	C4	1.5279(16)
O5	C5	1.4233(15)	C4	C5	1.5236(19)
O6	C7	1.4078(13)	C5	C6	1.5354(17)
O6	C11	1.4478(14)	C7	C8	1.5267(15)
O7	C12	1.423(2)	C7	C9	1.5418(15)
O8	C10	1.4206(15)	C9	C10	1.5244(16)
O9	C9	1.4032(16)	C10	C11	1.5253(18)
O10	C8	1.4239(18)	C11	C12	1.5168(16)

Table S9. Values of valence angles for sucrose

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	O1	C1	116.00(9)	C5	C6	O11	110.18(9)
C11	O6	C7	111.85(8)	O11	C7	O6	110.92(8)
C7	O11	C6	114.13(9)	C8	C7	O6	107.30(10)
C2	C1	O1	105.79(11)	C8	C7	O11	109.96(10)
C3	C1	O1	110.64(10)	C9	C7	O6	105.04(9)
C3	C1	C2	112.15(11)	C9	C7	O11	108.20(10)
C1	C2	O2	111.48(11)	C9	C7	C8	115.32(9)
C1	C3	O3	106.06(11)	C7	C8	O10	111.06(12)
C4	C3	O3	112.46(11)	C7	C9	O9	115.73(11)
C4	C3	C1	110.55(11)	C10	C9	O9	115.67(11)
C3	C4	O4	107.80(11)	C10	C9	C7	102.56(9)
C5	C4	O4	111.55(11)	C9	C10	O8	112.44(10)
C5	C4	C3	108.29(10)	C11	C10	O8	111.71(12)
C4	C5	O5	110.25(10)	C11	C10	C9	102.43(10)
C6	C5	O5	110.32(10)	C10	C11	O6	105.46(10)
C6	C5	C4	110.95(10)	C12	C11	O6	109.84(10)
O11	C6	O1	110.24(9)	C12	C11	C10	114.86(11)
C5	C6	O1	110.94(10)	C11	C12	O7	112.88(12)

Table S10. Values of torsion angles for sucrose

A B C D	Angle/°	A B C D	Angle/°
O1 C1 C2 O2	56.59(11)	O6 C11 C10 O8	147.84(9)
O1 C1 C3 O3	177.27(10)	O6 C11 C10 C9	27.28(10)
O1 C1 C3 C4	55.10(10)	O6 C11 C12 O7	69.26(12)
O1 C6 O11 C7	-108.04(11)	O7 C12 C11 C10	-49.40(13)
O1 C6 C5 O5	-177.17(10)	O8 C10 C9 O9	78.12(13)
O1 C6 C5 C4	-54.69(10)	O8 C10 C9 C7	-154.97(12)
O2 C2 C1 C3	-64.12(15)	O8 C10 C11 C12	-91.08(11)
O3 C3 C1 C2	-64.87(12)	O9 C9 C7 O11	39.17(10)
O3 C3 C4 O4	64.32(12)	O9 C9 C7 C8	-84.41(12)
O3 C3 C4 C5	-174.85(11)	O9 C9 C10 C11	-161.83(12)
O4 C4 C3 C1	-177.34(10)	O10 C8 C7 O11	-50.56(11)
O4 C4 C5 O5	-62.94(10)	O10 C8 C7 C9	72.09(12)
O4 C4 C5 C6	174.54(9)	O11 C6 C5 C4	67.67(11)
O5 C5 C4 C3	178.59(10)	O11 C7 C9 C10	-87.70(10)
O5 C5 C6 O11	-54.81(11)	C1 C3 C4 C5	-56.51(11)
O6 C7 O11 C6	44.94(10)	C3 C4 C5 C6	56.07(10)
O6 C7 C8 O10	-171.28(9)	C7 C9 C10 C11	-34.92(11)
O6 C7 C9 O9	157.70(9)	C9 C10 C11 C12	148.36(11)
O6 C7 C9 C10	30.83(10)		

Table S11. Cremer-Pople parameters for crystal structures

Compound	q_2	q_3	Q	θ [°]	φ_2 [°]
α-2-DG	0.060	0.548	0.551	6.0	256.0
β-2-DG	0.038	0.562	0.563	3.9	350.4
2-BG	0.092	0.587	0.594	9.0	335.0
2-BM (α anomer)	0.109	0.527	0.538	11.6	51.7
2-BM (β anomer)	0.019	0.532	0.533	2.2	280.4
sucrose (pentose)	0.351	-	-	-	-
sucrose (hexose)	0.052	0.556	0.558	5.3	172.6
4-BS (pentose)	0.400	-	-	-	-
4-BS (hexose)	0.116	0.588	0.599	11.2	296.1

Table S12. The geometry of hydrogen bonds in the crystal of 2-BG

D–H	A	Symmetry operation	D–H (Å)	d(D···A) (Å)	< D–H···A (°)
O1–H1A	O2	-1/2+*x*,3/2-*y*,1-*z*	0.83(7)	2.717(5)	146(8)
O2–H2A	O6	1+*x*,*y*,*z*	0.97(6)	2.702(5)	169(7)
O3–H3A	Br1	*x*,-1+*y*,*z*	0.97(7)	3.388(4)	168(5)
O6–H6	O1	*x*,-1+*y*,*z*	0.98(8)	2.810(5)	168(7)
C2–H2	O2	-1/2+*x*,3/2-*y*,1-*z*	0.981(7)	3.270(6)	129.3(5)
C5–H5	O3	1-*x*,1/2+*y*,1/2-*z*	0.981(7)	3.494(6)	165(3)
C6–H6B	O5	1-*x*,1/2+*y*,1/2-*z*	1.12(7)	3.322(6)	123(4)

Table S13. The geometry of hydrogen bonds in the crystal of 2-BM

D–H	A	Symmetry operation	D–H (Å)	d(D···A) (Å)	< D–H···A (°)
O1A–H1AA	O6B	*x*,*y*,-1+*z*	0.99(15)	2.611(14)	155(-1)
O3A–H3AA	O3B	1-*x*,1/2+*y*,-*z*	1.0(2)	2.750(13)	104(13)
O4A–H4AA	O5A	1-*x*,1/2+*y*,-*z*	0.97(13)	2.891(13)	143(-1)
O4A–H4AA	O6A	1-*x*,1/2+*y*,-*z*	0.97(13)	3.227(14)	139(11)

O6A–H6A	O1B	1-*x*,-1/2+*y*,-*z*	0.9(2)	2.861(14)	177(-1)
O6B–H6B	O5B		0.82(11)	2.815(13)	102(13)
O1B–H1BA	O3A	-1+*x*,*y*,1+*z*	0.82(13)	2.783(14)	158(10)
O3B-H3BA	O1A	-1+*x*,*y*,*z*	0.98(16)	2.724(14)	134(15)
O4B-H4BA	O4A	1-*x*,-1/2+*y*,-*z*	1.0(2)	2.646(15)	164(-1)
C6A-H6AB	Br1A	1-*x*,1/2+*y*,-*z*	1.09(13)	3.664(14)	130(9)
C2B-H2B	O6B	-1+*x*,*y*,*z*	1.09(5)	3.521(17)	172(16)
C3A-H3A	O6A	1-*x*,1/2+*y*,-*z*	1.09(6)	3.362(16)	157(11)
C4A-H4A	O6A		0.98(10)	2.914(16)	111(10)
C4B-H4B	O6B		0.98(19)	2.952(17)	1.3(12)
C6B-H6BB	O4B		1.08(13)	2.944(18)	103(10)

Table S14. The geometry of hydrogen bonds in the crystal of sucrose

D–H	A	Symmetry operation	D–H (Å)	d(D···A) (Å)	< D–H···A (°)
O2--H2	O4	-x,-1/2+y,-2-z	1.04(3)	2.8465(17)	159(3)
O3--H3	O4		0.98(3)	2.8792(18)	100(2)
O3--H3	O6	x,1+y,z	0.98(3)	2.8421(16)	121(2)
O3--H3	O2	-x,1/2+y,-2-z	0.98(3)	3.3729(18)	143(2)
O4--H4	O9	-x,1/2+y,-1-z	0.97(2)	2.8639(15)	172.6(19)
O5--H5	O7	-1+x,y,z	0.97(2)	2.8654(16)	170(2)
O7--H7	O1		1.04(3)	2.8524(14)	164(3)
O8--H8	O10	1+x,y,z	0.95(2)	2.7198(16)	166.5(18)
O9--H9	O8	1-x,1/2+y,-1-z	0.91(2)	2.8749(16)	169.7(18)
O10--H10	O5		0.94(2)	2.7818(16)	160(2)
O10--H10	O11		0.94(2)	2.7743(14)	100.1(17)
C1--H1	O8	1-x,1/2+y,-1-z	1.135(12)	3.6792(16)	163.7(10)
C2--H2A	O7		1.165(17)	3.309(2)	130.3(11)
C2--H2B	O3		1.089(17)	2.903(2)	100.6(10)
C4--H4B	O10	-x,1/2+y,-1-z	1.106(14)	3.5150(17)	163.8(12)
C6--H6	O2	-x,-1/2+y,-2-z	1.083(17)	3.3560(19)	163.8(12)
C8--H8B	O2	-x,-1/2+y,-2-z	1.070(15)	3.4690(17)	156.5(12)
C9--H9B	O5	-x,-1/2+y,-1-z	1.073(16)	3.4648(17)	158.7(11)
C10--H10B	O7		1.094(17)	2.9364(16)	105.3(10)
C12--H12A	O3	x,-1+y,z	1.109(19)	3.313(2)	124.1(11)
C12--H12B	O2	1-x,-1/2+y,-2-z	1.114(16)	3.2221(19)	120.2(11)

Table S15. The geometry of hydrogen bonds in the crystal of 4-BS (upon geometry optimization)

D–H	A	Symmetry operation	D–H (Å)	d(D···A) (Å)	< D–H···A (°)
O2--H1	O5	1/2-x,-1-y,-1/2+z	1.00	2.6494(1)	166
O3--H2	O10	-1/2+x,-1/2-y,-1-z	0.99	2.6964(1)	169
O5--H3	O7	-1/2+x,-1/2-y,-z	1.00	2.6516(1)	173
O6--H4	O2	1/2+x,-1/2-y,-1-z	0.99	2.7157(1)	173
O7--H5	O3	1+x,y,z	0.99	2.7892(1)	170
O9--H6	O1	1-x,-1/2+y,-1/2-z	0.99	3.1442(1)	123
O9--H6	O6	1-x,-1/2+y,-1/2-z	0.99	2.7462(1)	162
O10--H7	O2		0.98	2.8587(1)	162
C2--H9	Br1	-x,-1/2+y,-1/2-z	1.09	3.6773(1)	140
C3--H10	O9	1-x,1/2+y,-1/2-z	1.09	3.2959(1)	159
C5--H12	O1		1.09	2.8024(1)	100
C6--H14	Br1	-1/2+x -1/2-y ,-z	1.09	3.3149(1)	103
C10--H17	Br1	1-x,-1/2+y,-1/2-z	1.09	3.6549(1)	150
C11--H19	O4		1.09	3.3385(1)	152

Table S16. Packing indexes for investigated compounds and their relatives

compound	packing index [%]
α-2-DG	69.3
β-2-DG	68.2
2-CG	71.3
2-BG	77.4
2-IG	71.8
2-CM	70.7
2-BM	73.5
sucrose	76.3
4-BS	74.0

Table S17. Interaction energies (kJ mol^{-1}) for adjacent molecules. Only molecules having a noticeable contribution (higher than 1.0 kJ mol^{-1}) are included.

Compound	N	Symmetry operation	R	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
2-BG	2	x+1/2, -y+1/2, -z	5.15	-71.9	-12.8	-30.7	89.9	-56.7
	2	x, y, z	6.88	-58.3	-12.2	-23.7	84.3	-39.3
	2	-x, y+1/2, -z+1/2	8.14	-9.8	-2.0	-21.1	19.2	-18.3
	2	-x, y+1/2, -z+1/2	5.93	-10.6	-2.3	-20.9	18.5	-19.8
	2	x, y, z	6.81	-53.4	-13.0	-19.5	67.9	-41.1
	2	x+1/2, -y+1/2, -z	8.58	-0.4	-0.3	-3.3	0.9	-2.9
	2	x+1/2, -y+1/2, -z	8.62	-3.0	-0.4	-2.2	0.0	-5.4
	2	x, y, z	9.68	-4.7	-0.3	-1.0	0.0	-6.1
	1	-x+1/2, -y, z+1/2	9.51	-0.2	-0.0	-0.9	0.0	-1.1
2-BM	1	-	12.11	-0.9	-0.1	-0.3	0.0	-1.3
	1	-	10.19	-1.2	-0.1	-1.2	0.0	-2.5
	0	-x, y+1/2, -z	6.53	-13.7	-2.1	-15.5	16.0	-15.3
	0	-x, y+1/2, -z	6.72	-61.1	-10.5	-21.6	90.4	-2.8
	1	-	7.04	-44.8	-11.4	-14.3	53.6	-16.9
	1	-	6.44	-38.6	-9.7	-30.4	63.4	-15.3
	1	-	6.41	-45.3	-10.4	-23.2	71.9	-7.0
	0	x, y, z	8.05	-11.3	-2.8	-9.2	11.0	-12.3
	1	-	7.04	-110.4	-22.6	-21.3	137.8	-16.5
	1	-	5.93	-82.2	-17.8	-24.9	103.0	-21.9
	1	-	7.48	-5.8	-1.1	-3.9	0.3	-10.5
	1	-	7.74	-3.7	-0.9	-6.1	0.7	-10
	1	-	10.61	-2.9	-0.1	-0.5	0.0	-3.5
	1	-	11.18	-1.2	-0.1	-0.4	0.0	-1.7
	1	-	10.00	-1.5	-0.1	-1.0	0.0	-2.6
	1	-	12.37	-1.0	-0.0	-0.1	0.0	-1.1
	2	-x, y+1/2, -z	5.99	-44.9	-12.2	-30.8	55.8	-32.1
	2	x, y, z	8.05	-1.4	-1.7	-11.9	8.2	-6.8
	1	-x, y+1/2, -z	16.35	-1.1	-0.0	-0.0	0.0	-1.1
	2	x, y, z	14.43	-1.1	-0.0	-0.0	0.0	-1.1
	2	x, y, z	10.37	-4.4	-0.2	-0.4	0.0	-5
	2	-x, y+1/2, -z	7.24	-6.2	-1.7	-8.7	5.1	-11.5
	2	-x, y+1/2, -z	15.84	-1.3	-0.0	-0.0	0.0	-1.3
	2	x, y, z	13.13	-1.8	-0.1	-0.1	0.0	-2
4-BS	2	x, y, z	10.45	-35.6	-8.2	-16.1	53.1	-24.9
	2	-x, y+1/2, -z+1/2	9.37	-9.4	-1.1	-11.7	14.5	-12.0
	2	x+1/2, -y+1/2, -z	8.38	-67.2	-13.4	-31.9	101.4	-46.2
	2	-x, y+1/2, -z+1/2	6.41	-86.8	-16.7	-56.6	105.0	-88.5
	2	-x+1/2, -y, z+1/2	7.77	-65.3	-16.6	-29.3	82.3	-56.0
	2	x+1/2, -y+1/2, -z	8.30	-97.6	-24.4	-31.7	120.7	-74.3
	2	-x+1/2, -y, z+1/2	11.09	-8.2	-2.1	-11.6	7.7	-15.6
	2	-x+1/2, -y, z+1/2	9.93	-0.4	-0.1	-2.2	0.0	-2.4
	2	-x, y+1/2, -z+1/2	14.59	-1.8	-0.1	-0.6	0.0	-2.4
	2	x+1/2, -y+1/2, -z	12.68	-0.7	-0.0	-0.6	0.0	-1.2
	2	x, y, z	12.56	-1.9	-0.1	-0.7	0.0	-2.8
	2	-x+1/2, -y, z+1/2	12.69	-0.8	-0.0	-0.5	0.0	-1.4
Sucrose	2	-x, y+1/2, -z	7.22	-78.4	-17.5	-48.3	104.4	-73.4
	2	-x, y+1/2, -z	9.82	-3.7	-0.9	-12.1	10.4	-8.7

	2	x, y, z	8.72	-7.3	-1.7	-17.5	12.9	-16.2
	2	-x, y+1/2, -z	7.44	-61.9	-15.6	-36.0	63.9	-68.8
	2	x, y, z	7.77	-110.8	-28.0	-32.8	121.8	-91.2
	2	-x, y+1/2, -z	7.86	-42.9	-10.1	-29.2	61.3	-40.4
	2	x, y, z	10.86	-3.0	-0.5	-1.8	0.0	-5.1
	2	x, y, z	11.68	0.8	-0.3	-3.7	0.7	-2.1
	2	-x, y+1/2, -z	13.03	-1.7	-0.1	-0.4	0.0	-2.3
	2	x, y, z	11.85	-1.9	-0.1	-0.7	0.0	-2.6
	2	-x, y+1/2, -z	11.34	-0.2	-0.2	-1.1	0.0	-1.3

Table S18. Conformational analysis of the brominated analogues of 2-DG in an aqueous solution and in the solid state compared to parent compounds

Comp.	Crystal state					Aqueous solution					
	Torsion angle		H···H distance		C5-C6 / O6-H6 rotamers	Torsion angle		H···H distance		C5-C6 (*gt*/gg/*tg*)/ O6-H6 (*g*/*t*) [c] rotameric equilibria [%]	anomeric equilibrium (α/β) [%]
	angle	[˚]	H···H	[Å]		angle [b]	[˚]	H···H	[Å]		
α-2-BG	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	-	-	-	-	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+63 +172 -176 +180 nd nd - -	H1 H2 H1 H3	2.5 3.4	42/48/10 nd	34/66
β-2-BG	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+177.55 -156.82 +157.40 +177.03 +43.74 -71.15 -63.92 +151.95	H1 H2 H1 H3 H1 H4 H1 H5 H2 H3 H2 H5 H3 H5 H4 H5 H5 H6' H6 H6'	2.90 2.90 3.90 2.10 2.96 3.66 2.61 2.92 2.51 1.77	*gg*/*gauche*	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	-175 +178 +174 +180 nd nd - -	H1 H2 H1 H3 H1 H4 H1 H5 H2 H3 H2 H5 H3 H5 H4 H5 H5 H6' H6 H6'	2.8 2.4 3.4 2.2 2.5 3.1 2.3 2.5 2.6 1.8	55/35/11 nd	
α-2-BM	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	-53.86 -55.92 +173.65 -174.93 +75.46 -58.76 -176.11 -132.22	H1 H2 H2 H3 H3 H5	2.36 2.41 2.52	*gg*/*trans*	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	-75 -53 +174 +174 nd nd - -	H1 H2 H2 H3 H3 H5	2.5 2.4 2.4	50/46/4 nd	47/53
β-2-BM	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+70.84 -57.23 +158.32 -164.49 +52.90 -42.28 -62.84 -130.30	H1 H2 H1 H3 H1 H5 H2 H3 H3 H5 H5 H6 H5 H6' H6 H6'	2.48 2.75 2.30 2.79 2.75 2.39 2.46 1.48	*gg*/*cis*	H1-C1-C2-H2 H2-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+70 -53 -175 -179 nd nd - -	H1 H2 H1 H3 H1 H5 H2 H3 H3 H5 H5 H6 H5 H6' H6 H6'	2.4 2.4 2.3 2.3 2.5 2.5 3.1 1.8	60/30/10 nd	
α-2-DG [c]	H1-C1-C2-H2 H1-C1-C2-H2' H2-C2-C3-H3 H2'-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	-68.7 +49.0 -52.9 -170.6 +175.0 -178.6 +85.0 -157.1 +81.9 -119.6	H1 H2 H1 H2' H2 H2' H2 H3 H2' H4 H3 H5 H6 H6'	2.41 2.30 1.60 2.33 2.61 2.53 1.60	*gt*/[a]	H1-C1-C2-H2 H1-C1-C2-H2' H2-C2-C3-H3 H2'-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+58 nd -56 +180 -175 -179 nd nd - -	H1 H2 H1 H2' H2 H2' H2 H3 H2' H4 H3 H5 H6 H6'	2.5 2.5 1.8 2.5 2.6 2.5 1.8	45/45/10 nd	49/51
β -2-DG [c]	H1-C1-C2-H2 H1-C1-C2-H2' H2-C2-C3-H3 H2'-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+54.8 +174.9 -51.1 -170.7 +170.6 -177.1 +58.0 -61.8 -64.8 +157.4	H1 H2 H1 H2' H1 H3 H1 H5 H2 H2' H2 H3 H2' H4 H4 H6 H5 H6 H5 H6' H6 H6'	2.43 3.03 2.65 2.39 1.76 2.39 2.66 3.12 2.42 2.45 1.77	*gg*/*trans*	H1-C1-C2-H2 H1-C1-C2-H2' H2-C2-C3-H3 H2'-C2-C3-H3 H3-C3-C4-H4 H4-C4-C5-H5 H5-C5-C6-H6 H5-C5-C6-H6' O5-C5-C6-O6 (*ω*) C5-C6-O6-H06 (*θ*)	+59 +179 -56 +180 -175 -179 nd nd - -	H1 H2 H1 H2' H1 H3 H1 H5 H2 H2' H2 H3 H2' H4 H4 H6 H5 H6 H5 H6' H6 H6'	2.4 3.4 2.4 2.2 1.8 2.4 2.5 2.5 2.2 2.5 1.8	60/30/10 nd	

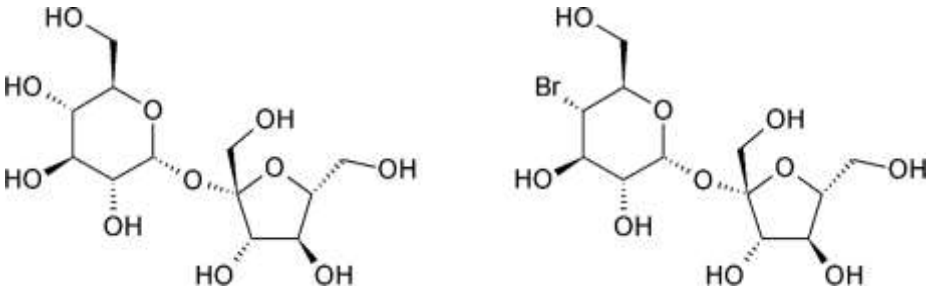
[a] conformation between cis and trans conformers

[b] for torsion angles H5-C5-C6-H6 and H5-C5-C6-H6' their values could not be determined for the each rotamer using available NMR data. In the case of *ω* angle following values were assumed: -60˚ (±5), -60˚ (±5), -180˚ (±5) for the rotamers *gg*, *gt*, *tg*, respectively. The value of *θ* was assumed to be either 60˚ or 180 ˚(±) for *cis* and *gauche* conformers respectively.

[c] data taken from [ziemniak 2021]

Table S19. ^{1}H-^{13}C HSQC and ^{1}H NMR data for halogenated analogues of 2-DG and the parental compound. NMR shifts values are measured in ppm and *J*-coupling constants in Hz

Compound	H1; C1 $J_{1,2}$	H2; C2 $J_{2,3}$	H3; C3 $J_{3,4}$	H4; C4 $J_{4,5}$	H5; C5 $J_{5,6R}$; $J_{5,6S}$	H6; H6'; C6 $J_{6,6}$
α-2-BG	5.27; 94.27 3.3	3.96; 54.81 10.8	3.76; 74.83 9.3	3.34; 72.75 10.0	3.92; 73.94 5.2; 2.4	3.52-3.68 nd
β-2-BG	4.81; 97.48 8.7	3.42; 57.54 9.9	3.72; 78.36 9.6	3.18; 72.38 9.8	3.52; 78.00 6.1; 2.3	3.52-3.68 nd
α-2-BM	5.35; 96.12 1.3	4.18; 57.47 3.8	3.98; 70.40 9.5	3.53; 69.33 15.1	3.90; 75.13 5.7; 2.3	3.53-3.80 nd
β-2-BM	93.58; 4.81 1.2	4.43; 62.09 3.6	3.70; 73.40 9.4	3.44; 68.99 9.6	3.22; 78.88 6.7; 2.5	3.53-3.80 nd



Scheme S1. Structural formulae of sucrose (left) and 4-BS (right).

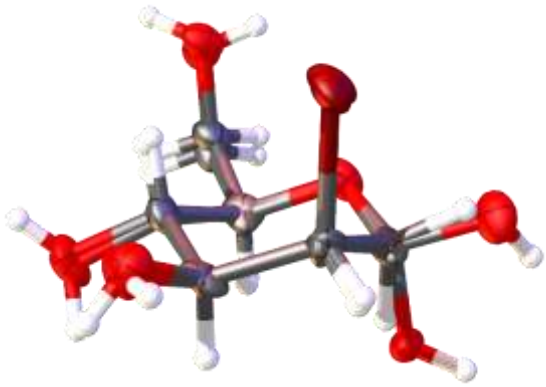


Figure S1. Superimposed structures of 2-BG molecules existing in its asymmetric unit (RMSD = 0.494).

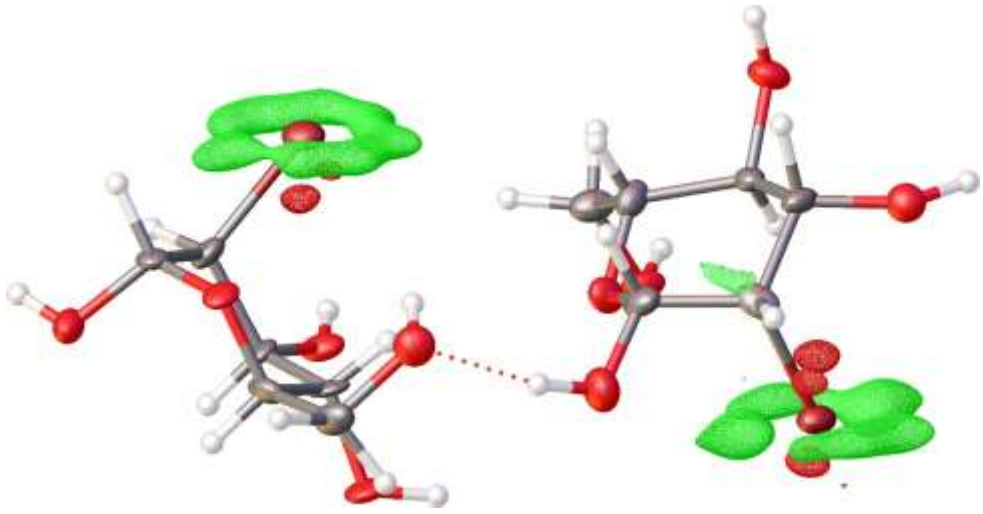


Figure S2. Residual experimental density for 2-BM

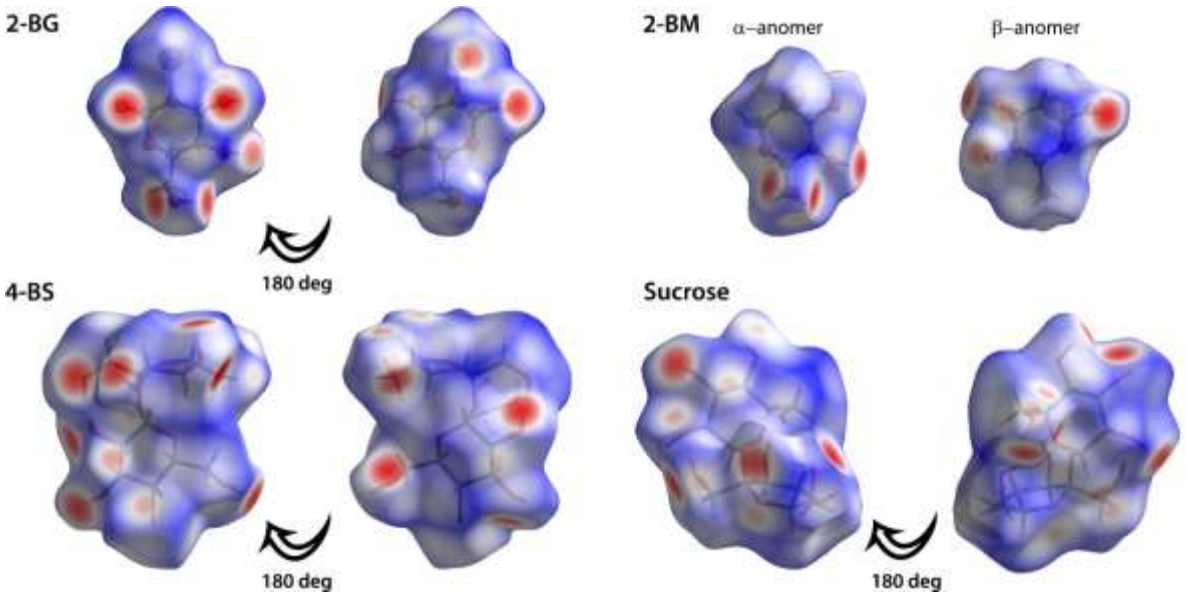


Figure S3. Hirshfeld surfaces mapped onto d_e. Intermolecular contacts which are closer than the sum of their Van der Waals radii are highlighted in red on the surface, whereas longer contacts are blue. Contacts having similar lengths to the radii sum are depicted as white.

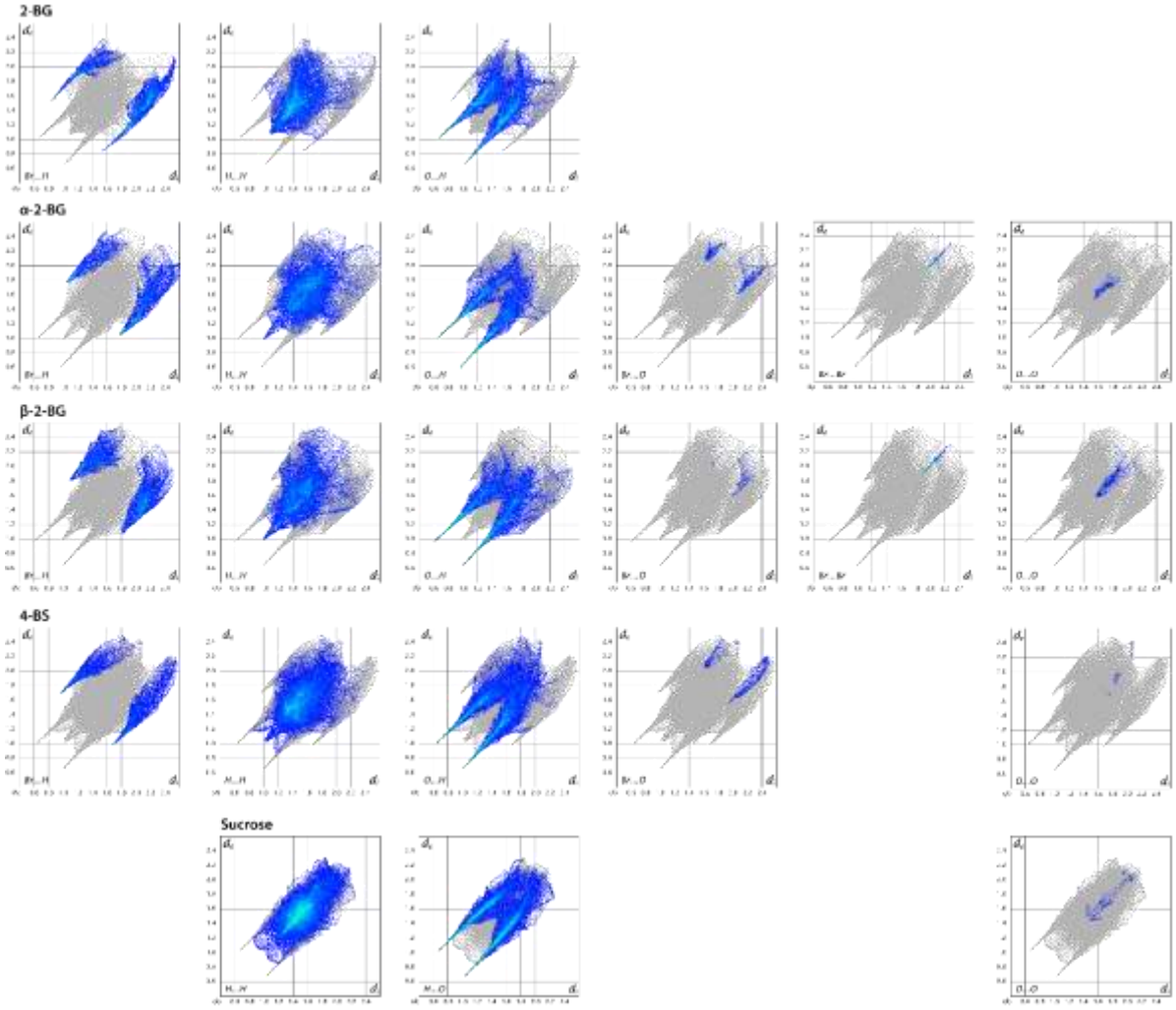


Figure S4. Contribution of different X-X contacts for each crystal lattice discussed in the article.

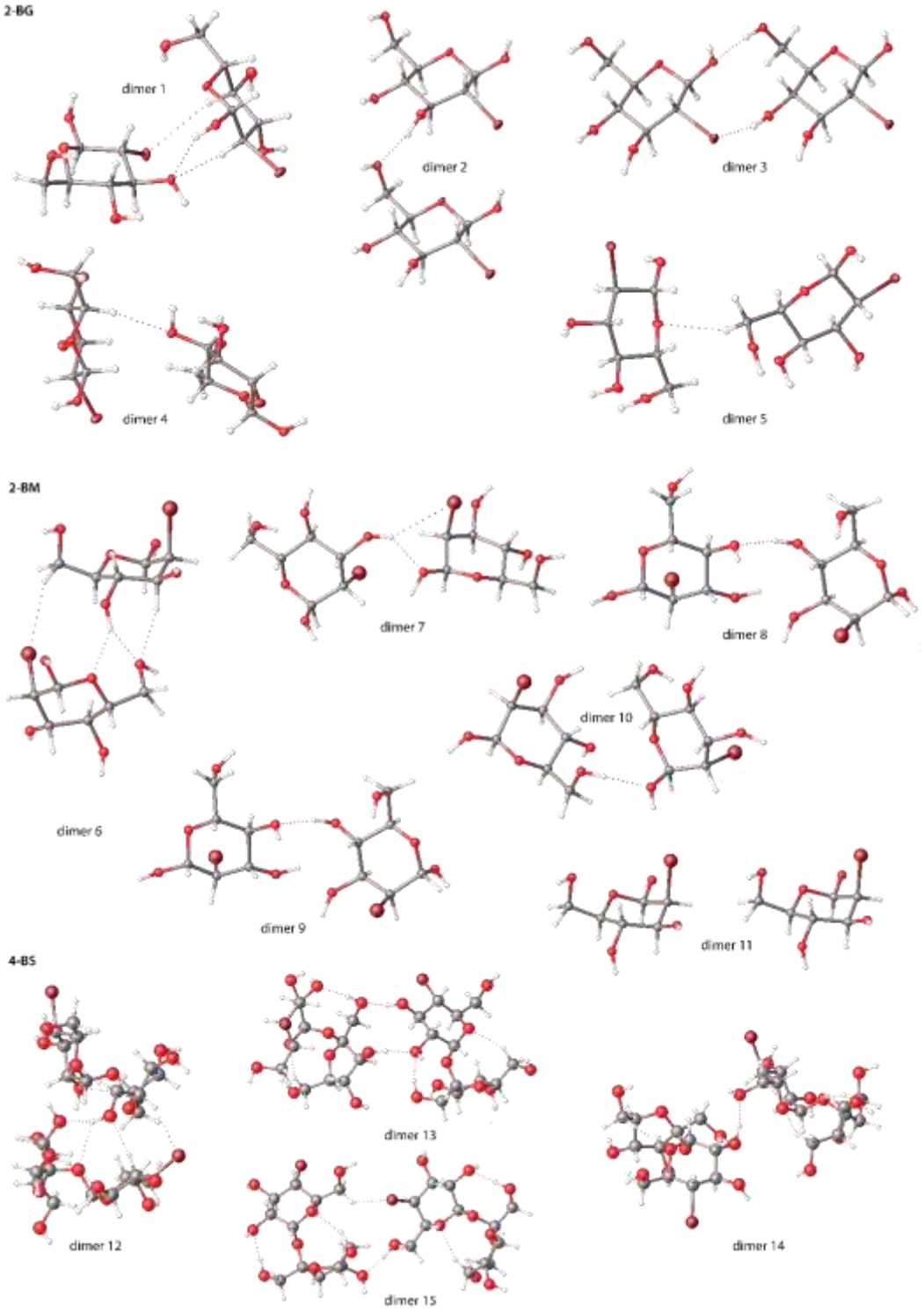


Figure S5. Dimers of 2-BG, 2-BM and 4-BS discussed in the text

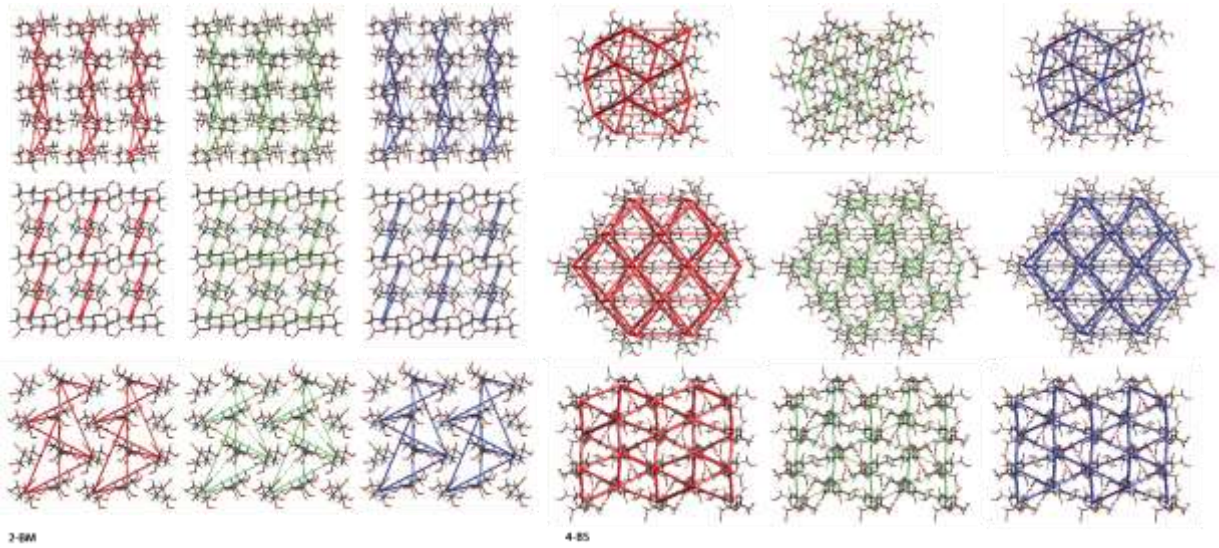


Figure S6. Energy frameworks for **2-BM** and **4-BS** crystals viewed along axes *a* (top), *b* (middle) and *c* (bottom) showing electrostatic (red) and dispersion (green) components, and the total interaction energy (blue).

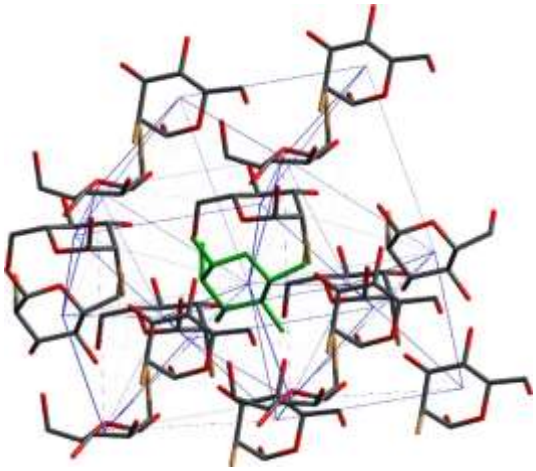


Figure S7. Energy framework of total interaction energy for a small cluster of 2-BM molecules. Weaker interactions are also included and the cut-off is 3.0 kJ mol^{-1}

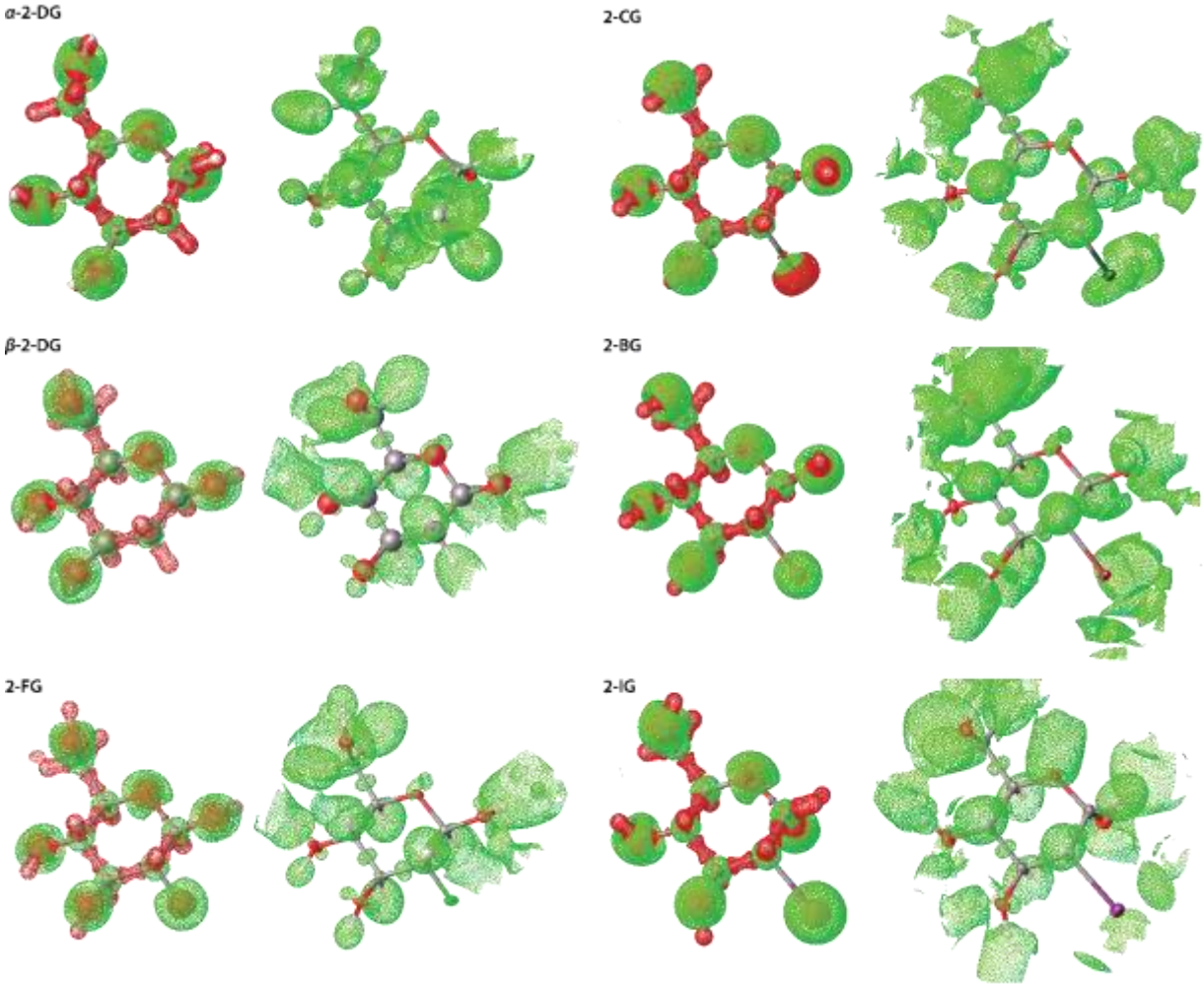
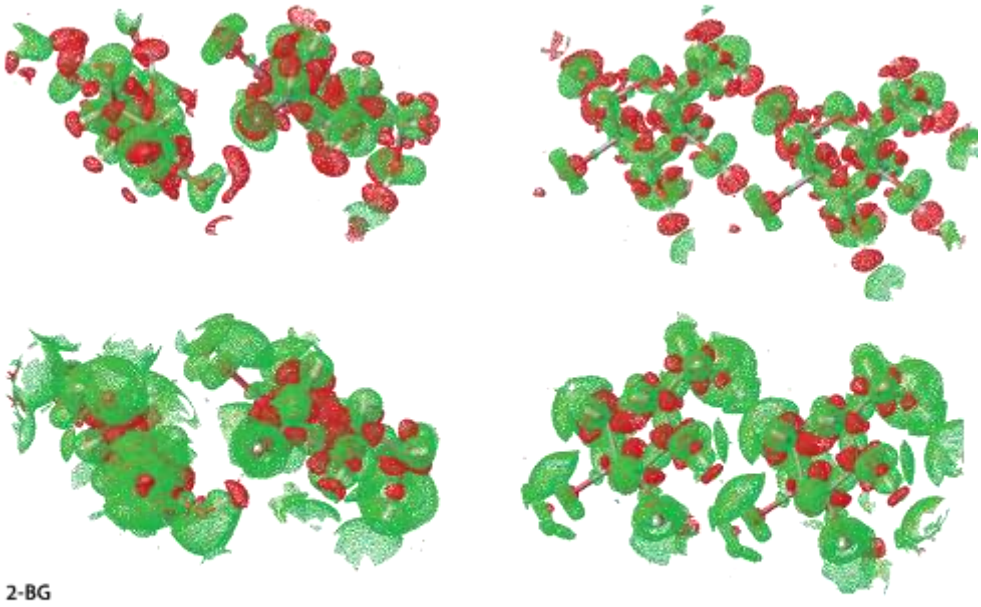
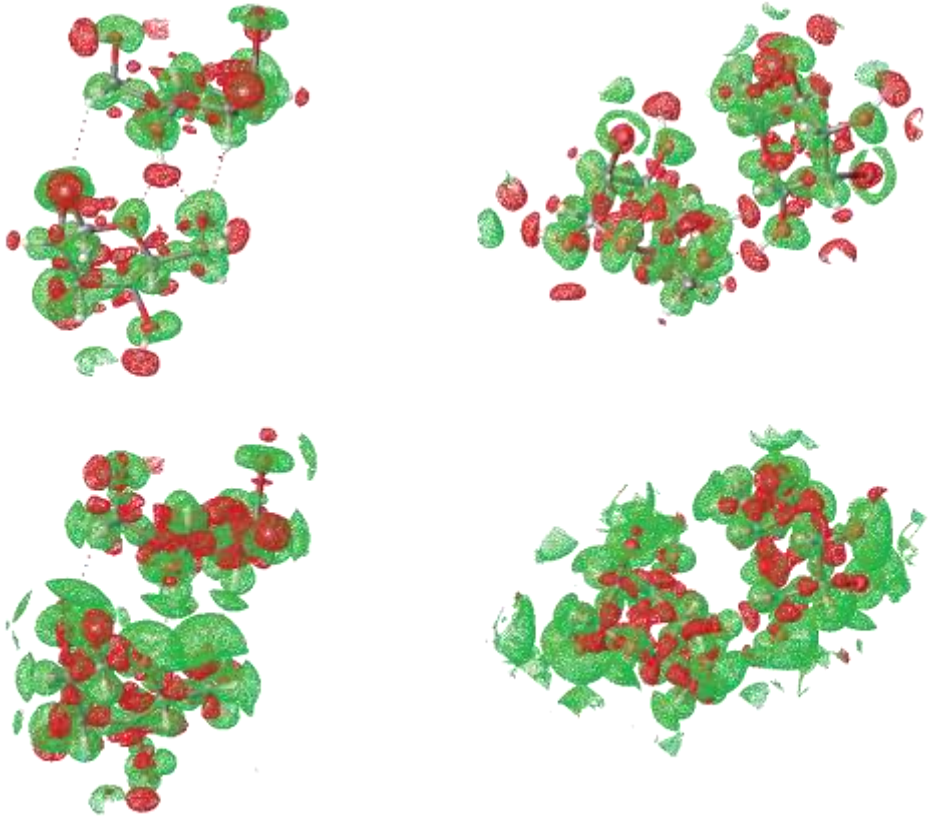


Figure S8. ED Laplacian and ELI for selected dimers of 2-DG and its halogenated derivatives. Contour levels are 0.8 e A^{-5} and 2.2 Y_D for Laplacian and ELI-D respectively.



2-BG



2-BM

Figure S9. Experimental (top) and static (bottom) deformation densities isosurfaces for selected dimers of **2-BM** and **2-BG**. Contour level is 0.095 *e* A^{-3} for both density maps.