Electronic Supplementary Material (ESI) for CrystEngComm.

Effect of substituents in novel bioactive tavaborole derivatives on intermolecular interactions hierarchy

Electronic Supplementary Information

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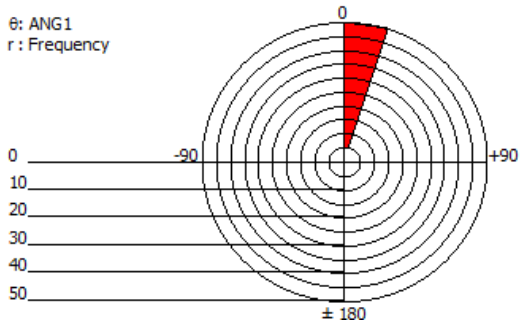


Figure S 1: Crystallographic Structure Database analysis results for observed fold angle in the 9-membered ring of benzoxaborole derivatives

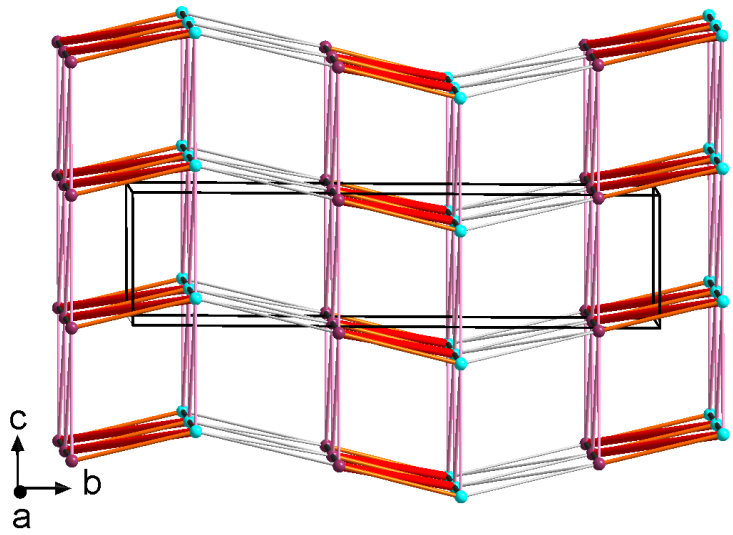


*Figure S 2: Large supramolecular synthon graph for **Bx** ($P2_1$)*

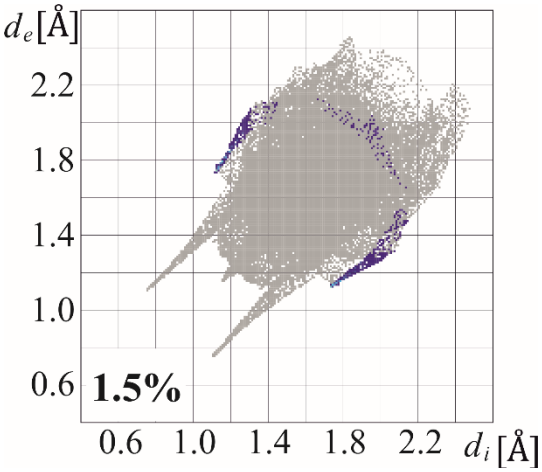


*Figure S 3: Resolved fingerprint plots of H···B weak interactions in **TvO***

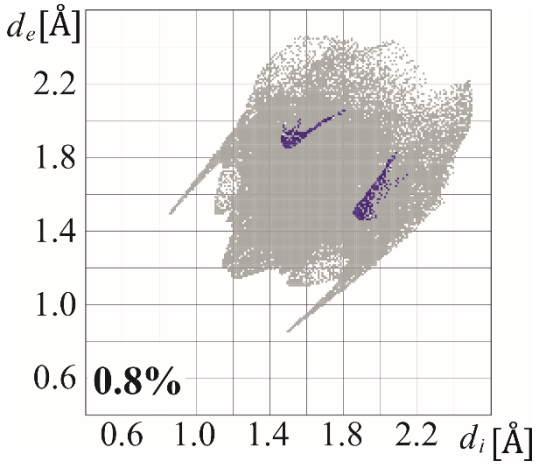


*Figure S 4: Resolved fingerprint plots of B···O weak interactions in **TvS***

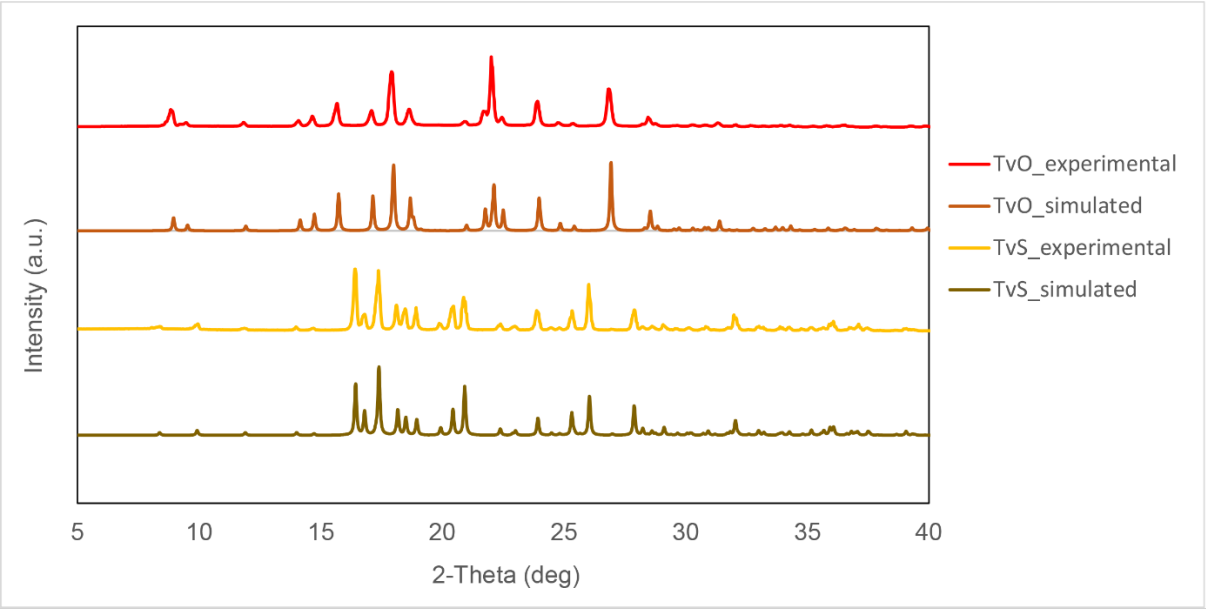


*Figure S 5: Powder X-ray diffraction studies of **TvO** and **TvS**: simulated powder patterns from single crystal data and experimental diffractograms for bulk samples.*

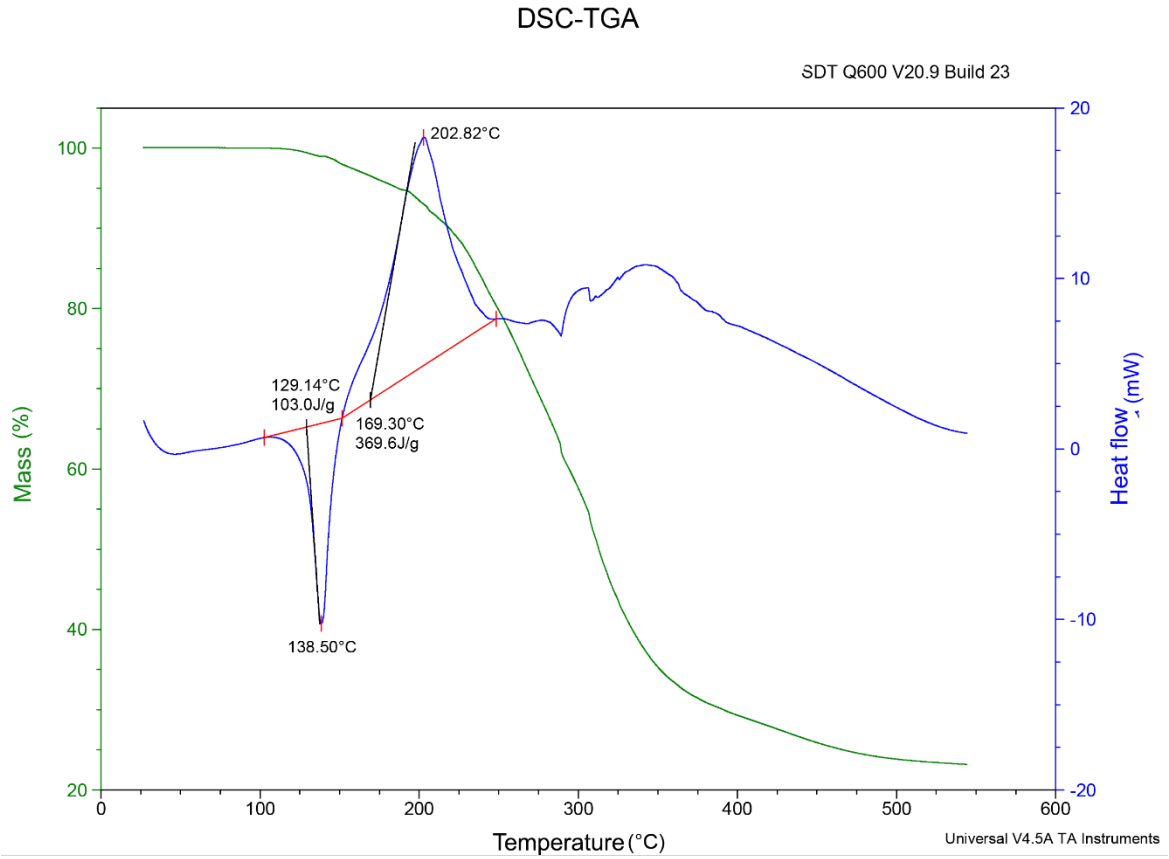


*Figure S 6: DSC-TGA analysis of **TvO** under pure nitrogen flow at 100.0 ml/min.*

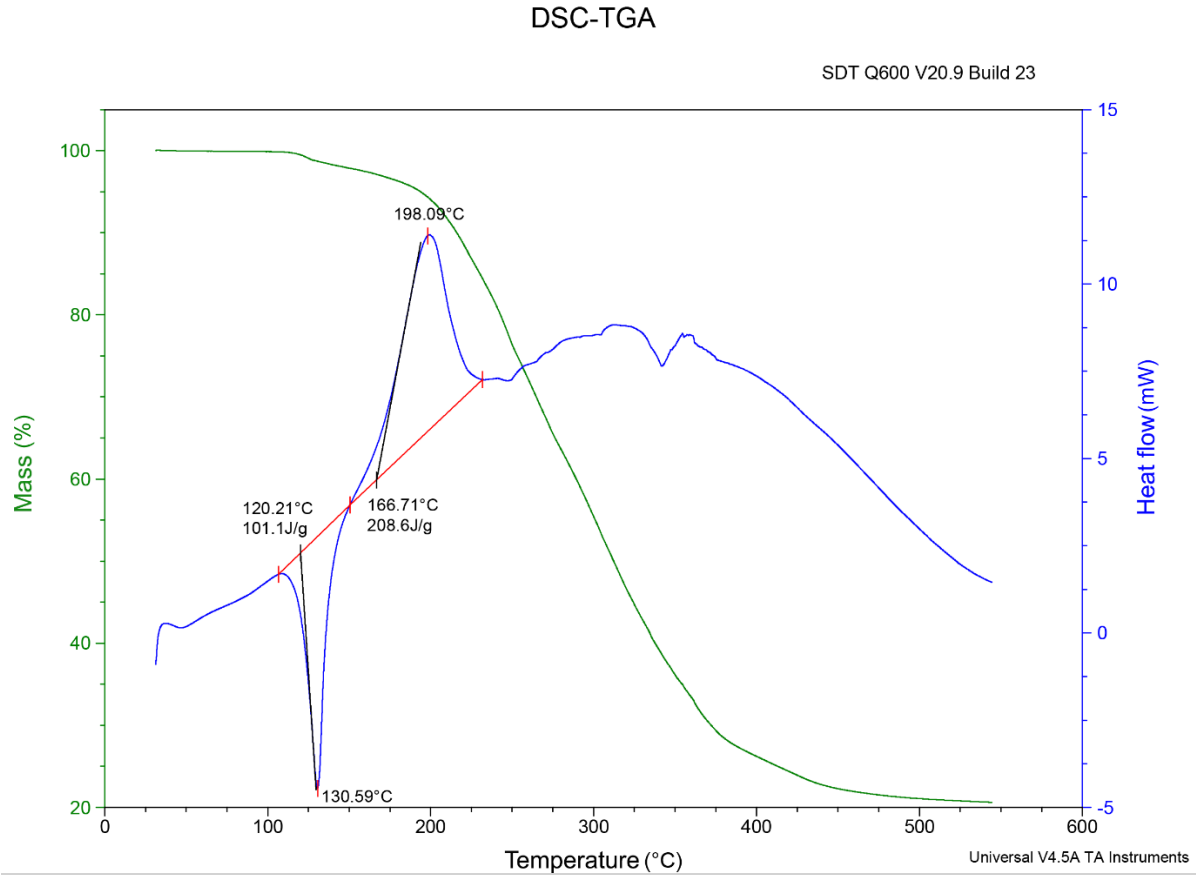


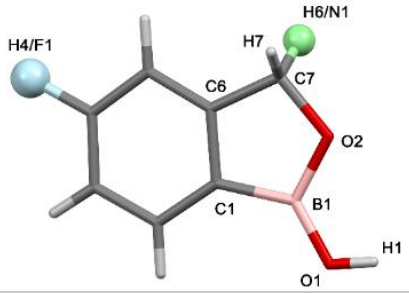
*Figure S 7: DSC-TGA analysis of **TvO** under pure nitrogen flow at 100.0 ml/min.*

2. Supplementary Tables

For previously determined structures[1–6] the numbering scheme was changed to be consistent with TvO and TvS

2.1. Geometrical parameters of the molecules

*Table S 1: Selected bond lengths [Å] and angles [°] for the analysed compounds. [a] Defined as an acute angle between least-square planes (S = P*X + Q*Y + R*Z) of 6-membered benzene ring and 5-membered oxaborole ring*



Bond [Å]/ Angle [°]	Bx (*P*-1)		Bx ($P2_1$)		Tv		BxO	BxS	TvO	TvS
	a	b	a	b	100 K	298 K				
O1-H1	1.02(7)	0.92(8)	0.90(5)	0.84(4)	0.83(2)	0.82	0.86(3)	0.76(2)	0.834(1)	0.79(3)
B1-O1	1.372(8)	1.351(8)	1.352(4)	1.348(5)	1.349(1)	1.346(1)	1.353(2)	1.342(2)	1.342(1)	1.349(2)
B1-O2	1.407(8)	1.412(8)	1.401(5)	1.406(5)	1.393(1)	1.388(1)	1.394(2)	1.387(2)	1.375(1)	1.372(2)
B1-C1	1.49(1)	1.54(1)	1.550(6)	1.560(6)	1.553(1)	1.546(2)	1.565(3)	1.552(3)	1.557(1)	1.550(3)
C1-C6	1.405(8)	1.407(8)	1.406(4)	1.399(5)	1.395(1)	1.393(1)	1.406(2)	1.394(3)	1.388(1)	1.388(3)
C6-C7	1.517(9)	1.501(9)	1.508(5)	1.512(5)	1.503(1)	1.501(2)	1.517(2)	1.512(2)	1.508(1)	1.508(2)
C7-O2	1.457(7)	1.448(8)	1.456(4)	1.453(4)	1.447(1)	1.446(1)	1.488(2)	1.491(2)	1.462(1)	1.469(2)
C7-N1	-	-	-	-	-	-	1.438(2)	1.433(2)	1.429(1)	1.428(2)
B1-O1-H1	115(4)	117(4)	111(3)	111(3)	115.1(1)	109	115.1(1)	117.3(1)	115.7(1)	115.9(1)
O1-B1-O2	118.3(6)	121.5(6)	121.9(4)	122.3(4)	121.52(1)	121.51(1)	122.88(1)	122.96(1)	123.96(1)	124.01(1)
C1-B1-O1	118.3(6)	130.5(6)	130.1(3)	129.9(4)	130.26(1)	130.24(1)	128.84(1)	128.67(1)	127.06(1)	126.95(1)
C1-B1-O2	110.5(5)	108.1(5)	108.0(3)	107.8(3)	108.22(1)	108.25(1)	108.28(1)	108.39(1)	108.96(1)	109.06(1)

C7-O2-B1	108.5(5)	110.0(5)	111.0(3)	110.3(3)	110.47(9)	110.42(1)	110.92(1)	110.84(1)	110.23(9)	110.29(1)
Fold [a]	0.8(3)	0.7(4)	0.74(1)	0.92(1)	1.89(6)	1.54(8)	1.66(8)	2.63(9)	0.29(6)	0.33(9)

2.2. Hydrogen bonds geometry

Table S 2: Hydrogen bonds geometry for the analysed compounds based on calculations in Platon program[7–9]

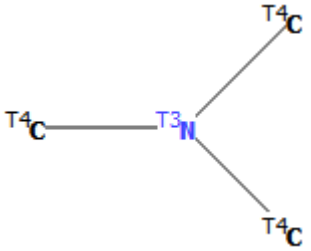
Compound	D	H	A	d(D-H) [Å]	d(H-A) [Å]	d(D-A) [Å]	D-H-A [°]	Symmetry
Bx *(P-1)*	O1	H1	O2	1.02(7)	1.74(7)	2.752(7)	177(9)	2-x,2-y,-z
	O1'	H1'	O2'	0.92(8)	1.84(7)	2.757(7)	172(7)	3-x,2-y,1-z
	C7	H6	O1	0.99(1)	2.745(7)	3.648(7)	152.0(7)	x,-1+y,z
	C7	H7	O1	1.00(1)	2.656(7)	3.285(7)	121.6(6)	-1+x,-1+y,z
	C7	H7	O1	1.00(1)	2.699(8)	3.464(8)	134.4(5)	1-x,2-y,-z
	C7’	H6’	O1’	1.00(1)	2.624(7)	3.283(7)	124.2(6)	-1+x,-1+y,z
	C7’	H6’	O1’	1.00(1)	2.721(8)	3.475(8)	133.3(5)	2-x,2-y,1-z
	C7’	H7’	O1’	0.99(1)	2.749(8)	3.641(8)	150.1(7)	x,-1+y,z
	C4	C4	C3’	0.96(1)	2.824(1)		143.9(7)	-1+x,y,z
Bx *($P2_1$)*	O1	H1	O2'	0.90(5)	1.88(5)	2.767(3)	172(5)	-x,1/2+y,-z
	O1'	H1'	O2	0.84(4)	1.92(4)	2.758(4)	178(5)	-x,-1/2+y,-z
	C7	H6	O1	0.97	2.74	3.257(4)	151	x,y,1+z
	C7	H7	O1	0.97	2.63	3.257(4)	123	1+x,y,1+z
	C7	H7	O1’	0.97	2.67	3.417(5)	134	1-x,1/2+y,-z
	C7’	H6’	O1	0.97	2.71	3.451(5)	133	1-x,-1/2+y,-z
	C7’	H7’	O1’	0.97	2.75	3.272(4)	149	x,y,1+z
	C4	H4	C3’	0.93	2.83		143	1+x,y,z
	C3’	H3’	C3	0.93	2.85		161	
Tv *(100K)*	O1	H1	O2	0.83(2)	1.93(2)	2.762(3)	175(2)	2-x,2-y,1-z
	C7	H7	O1	0.99	2.55	3.533(5)	172	x,-1+y,z
	C7	H6	O1	0.99	2.55	3.218(1)	155	-1+x,-1+y,z
	C3	H3	F1	0.95	2.58	3.478(5)	157	-x,2-y,2-z
Tv *(297K)*	O1	H1	O2	0.82	1.96	2.774(4)	175	-x,-y,1-z
	C7	H7	O1	1.00	2.67	3.298(1)	150	-1+x,y,z
	C7	H6	O1	0.97	2.73	3.298(1)	118	1+x,1+y,z
	C3	H3	F1	0.93	2.65	3.532(4)	158	2-x,-y,-z
BxO	O1	H1	O2	0.86(3)	1.94(3)	2.797(1)	172(2)	1-x,2-y,-z
	C7	H7	O1	1.00	2.67	3.575(2)	150	-1+x,y,z
	C11	H11A	O3	0.99	2.64	3.309(2)	125	-x,2-y,1-z
	C5	H5	O3	0.95	2.60	3.440(2)	147	-x,1-y,1-z
BxS	O1	H1	O2	0.76(2)	1.97(2)	2.7284(6)	174(3)	2-x,1-y,-z
	C5	H5	S1	0.95	2.83	3.6090(8)	140	1-x,-y,-z
	C7	H7	O1	1.00	2.56	3.500(2)	157	x,-1+y,z
	C11	H11A	O1	0.99	2.69	3.548(2)	145	x,1+y,z
	C10	H10A	S1	0.99	3.00	3.868	147	3/2-x,1/2+y,1/2-z
TvO	O1	H1	O3	0.83(1)	1.971(8)	2.7613(3)	158.6(8)	1-x,2-y,1-z
	C2	H2	O1	0.93	2.51	3.3979(6)	159	2-x,1-y,1-z
	C8	H8A	F1	0.97	2.60	3.253(1)	160	1-x,1-y,-z
	C10	H10B	F1	0.97	2.66	3.573(1)	156	-x,1-y,-z
	C11	H11B	O1	0.97	2.98	3.831(1)	147	-1+x,y,z
TvS	O1	H1	S1	0.79(3)	2.56(3)	3.3336(4)	169(2)	1-x, -1/2+y, 1/2-z

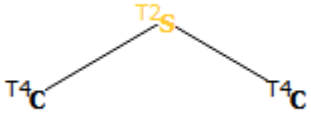
C7	H7	O1	0.99(1)	2.840(1)	3.766(2)	119.20(1)	x,-1+y,z
C11	H11B	O1	0.97	2.74	3.679(2)	165	x,1+y,z
C10	H10A	O2	0.97	2.71	3.391(2)	127	1-x, -1/2+y, 1/2-z
C10	H10B	F1	0.97	2.75	3.653(1)	156	2-x,1-y,1-z

2.3. Hydrogen Bond Propensity Calculations [10,11]

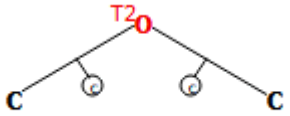
Defined search fragments:

BO 

al_tert_amine_1 

al_al_thioether_1 

BOH 

cyclic_ether_1 

Legend:

Tn = atom makes *n* bonds
H_n = *n* bonded hydrogen atoms

Table S 3: Predicted intermolecular hydrogen bond propensities of ***Bx*** *(P-1)*

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O2 of BOH	O1 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	observed
O2 of BOH	O3 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	
O4 of BOH	O1 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	
O4 of BOH	O3 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	observed
O2 of BOH	O2 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	
O2 of BOH	O4 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	
O4 of BOH	O2 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	
O4 of BOH	O4 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	

*Table S 4: Predicted intermolecular hydrogen bond propensities of **Bx** ($P2_1$)*

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O2 of BOH	O1 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	
O2 of BOH	O3 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	observed
O4 of BOH	O1 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	observed
O4 of BOH	O3 of BO	3.00	36.94	42.63	0.55	0.55	0.67	0.58	0.76	-	
O2 of BOH	O2 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	
O2 of BOH	O4 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	
O4 of BOH	O2 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	
O4 of BOH	O4 of BOH	3.00	36.94	36.94	0.55	0.55	0.47	0.34	0.60	-	

*Table S 5: Predicted intermolecular hydrogen bond propensities of **Tv***

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O2 of BOH	O1 of BO	1.50	36.94	42.71	0.50	0.50	0.67	0.58	0.74	60.2	observed
O2 of BOH	O2 of BOH	1.50	36.94	36.94	0.50	0.50	0.46	0.34	0.59	39.1	

*Table S 6: Predicted intermolecular hydrogen bond propensities of **BxO***

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O1 of BOH	O2 of BO	2.00	43.02	68.51	0.33	0.33	0.60	0.51	0.69	-	observed
O1 of BOH	O1 of BOH	2.00	43.02	43.02	0.33	0.33	0.58	0.48	0.67	-	
O1 of BOH	O3 of cyclic_ether_1	2.00	43.02	43.30	0.33	0.33	0.27	0.20	0.35	-	
O1 of BOH	N1 of al_tert_amine_1	4.00	43.02	73.20	0.33	0.33	0.24	0.20	0.30	-	

*Table S 7: Predicted intermolecular hydrogen bond propensities of **BxS***

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O1 of BOH	O1 of BOH	2.00	43.02	43.02	0.33	0.33	0.64	0.56	0.71	-	
O1 of BOH	O2 of BO	2.00	43.02	68.69	0.33	0.33	0.61	0.53	0.68	-	observed
O1 of BOH	N1 of al_tert_amine_1	4.00	43.02	73.62	0.33	0.33	0.27	0.21	0.34	-	
O1 of BOH	S1 of al_al_thioether_1	2.00	43.02	43.30	0.33	0.33	0.09	0.08	0.10	-	

*Table S 8: Predicted intermolecular hydrogen bond propensities of **TvO***

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O1 of BOH	O2 of BO	2.00	43.02	68.60	0.32	0.32	0.61	0.52	0.70	-	
O1 of BOH	O1 of BOH	2.00	43.02	43.02	0.32	0.32	0.59	0.49	0.68	-	
O1 of BOH	O3 of cyclic_ether_1	2.00	43.02	43.30	0.32	0.32	0.27	0.20	0.36	-	observed
O1 of BOH	N1 of al_tert_amine_1	4.00	43.02	73.28	0.32	0.32	0.25	0.20	0.31	-	

*Table S 9: Predicted intermolecular hydrogen bond propensities of **TvS***

Donor	Acceptor	Competition	Donor steric density	Acceptor steric density	Donor aromaticity	Acceptor aromaticity	Propensity	Lower bound	Upper bound	Frequency	Observed Inter-?
O1 of BOH	O1 of BOH	2.00	43.02	43.02	0.32	0.32	0.65	0.57	0.72	-	
O1 of BOH	O2 of BO	2.00	43.02	68.77	0.32	0.32	0.61	0.54	0.68	-	
O1 of BOH	N1 of al_tert_amine_1	4.00	43.02	73.70	0.32	0.32	0.27	0.21	0.34	-	
O1 of BOH	S1 of al_al_thioether_1	2.00	43.02	43.30	0.32	0.32	0.09	0.08	0.10	-	observed

2.4. Aromatic interactions geometry

2.4.1. X···π interactions

*Table S 10: Important X···π interactions found in the analysed compounds. [a] Cg = centre of gravity of an aromatic ring found by Platon automatic search for rings[7–9], **Cg1** – 5-membered ring, **Cg2** – 6-membered ring, **Cg3** – 9-membered ring. [b] an angle between Cg-X vector and a normal to the Cg ring plane*

Compound	Y-X···π bond	Distance X···Cg [a] [Å]	Gamma [b] [°]	Y-X···π angle [Å]	Symmetry
Bx *(P-1), a-b*	C3-H3'···C3	2.866(1)	-	160.8(7)	-
Bx *($P2_1$), a*	C4-H4···C3'	2.83	-	143.00	1+x,y,z
Bx *($P2_1$), b*	C12-H11···C5	2.85	-	161.00	-
Tv *(100K)*	C4-F1···Cg2	3.591(1)	15.40	74.39(6)	-1+x, y, z
	C4-F1···Cg3	3.892(1)	26.85	62.55(6)	-1+x, y, z
Tv *(297K)*	C4-F1···Cg2	3.644(1)	12.84	77.10(9)	1+x, y, z
	C4-F1···Cg3	3.911(1)	24.52	65.20(8)	1+x, y, z
BxO	C9-H10b···Cg2	2.84	11.65	146.00	1-x, 1-y, 1-z
BxS	C9-H9B···Cg2	2.84	14.88	141.00	1-x,1-y,-z
	C2-H2···Cg2	2.74	9.89	136.00	3/2-x,1/2+y,-1/2-z
TvO	C4-F1···Cg3	3.785(1)	20.75	109.63(8)	1-x,1-y,-z
TvS	C4-F1···Cg2	3.519(1)	6.66	91.50(1)	2-x,1-y,1-z

2.4.2. π···π interactions

*Table S 11: Important π···π interactions found in the analysed compounds. [a] Cg = centre of gravity of an aromatic ring found by Platon automatic search for rings[7–9], **Cg1** – 5-membered ring, **Cg2** – 6-membered ring, **Cg3** – 9-membered ring. [b] an angle between Cg(I) and Cg(J) vector and normal to plane J, [c] a distance between Cg(I) and perpendicular projection of Cg(J) on ring (I)*

Compound	Cg···Cg bond	Distance Cg···Cg [a] [Å]	Gamma [b] [°]	Slippage [c] [Å]	Symmetry
Bx *(P-1), a*	Cg1···Cg2	3.698(4)	16.7	1.099	1+x, y, z
Bx *(P-1), b*	Cg1'···Cg2'	3.705(4)	17.0	1.126	1+x, y, z
Bx *(P21), a*	Cg1···Cg2	3.683(2)	16.8	1.109	-1+x, y, z
Bx *(P21), b*	Cg1'···Cg2'	3.686(2)	16.9	1.127	-1+x, y, z
Tv *(100K)*	Cg1···Cg3	3.5442(7)	14.6	0.947	1+x, y, z
Tv *(297K)*	Cg1···Cg2	3.6658(9)	16.0	1.016	-1+x, y, z
BxO	Cg3···Cg3	3.768(1)	22.9	1.467	1-x,1-y,-z
BxS	-	-	-	-	-
TvO	Cg1···Cg1	3.905(1)	30.0	1.955	1-x,1-y,1-z
TvS	Cg2···Cg2	4.493(1)	39.2	2.838	2-x,2-y,1-z

2.4.3. Aromatic Analyzer calculation results [12]

*Table S 12: Results of Aromatic Analyzer calculations for **Bx** (P-1), molecule a*

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.53	0	8.2	Strong
5.47	71.63	6.2	Moderate
6.16	0	5.5	Moderate
5.6	71.63	5.2	Moderate
6.8	0	3.5	Moderate

*Table S 13 Results of Aromatic Analyzer calculations for **Bx** (P-1), molecule b*

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.53	0	8.1	Strong
5.47	71.63	6.2	Moderate
6.16	0	5.6	Moderate
5.6	71.63	5.2	Moderate
6.8	0	3.4	Moderate

*Table S 14: Results of Aromatic Analyzer calculations for **Bx** ($P2_1$)*

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.54	0	8.2	Strong
5.43	72.87	6.2	Moderate
6.14	0	5.6	Moderate
5.56	72.87	5.2	Moderate
6.78	0	3.4	Moderate

*Table S 15: Results of Aromatic Analyzer calculations for **Tv** (100K)*

Distance (Å)	Relative Orientation (°)	Score	Assessment
3.88	0	10	Strong
5.79	0	6.3	Moderate
6.31	0	4.9	Moderate
6.74	0	3.7	Moderate
6.78	0	3.2	Moderate

*Table S 16: Results of Aromatic Analyzer calculations for **Tv** (298K)*

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.03	0	9.6	Strong
5.85	0	6.1	Moderate
6.32	0	4.8	Moderate
6.81	0	3.4	Moderate
6.84	0	3.1	Moderate

*Table S 17: Results of Aromatic Analyzer calculations for **BxO***

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.06	0	9.8	Strong
5.99	0	6	Moderate

*Table S 18: Results of Aromatic Analyzer calculations for **BxS***

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.72	52.59	8.5	Strong
6.02	0	5.9	Moderate

*Table S 19: Results of Aromatic Analyzer calculations for **TvO***

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.75	0	7.5	Strong
5.5	0	6	Moderate
6.12	0	5.1	Moderate

*Table S 20: Results of Aromatic Analyzer calculations for **TvS***

Distance (Å)	Relative Orientation (°)	Score	Assessment
4.49	0	8.3	Strong
6.27	0	4.9	Moderate

2.5. Calculated interaction energies

Interaction energies have been calculated using CrystalExplorer21 software (version 21.5)[13] using CE-B3LYP ... B3LYP/6-31G(d,p) electron densities energy model. Total energies (E_{tot}) are the sum of the four energy components, scaled appropriately with scale factors for benchmarked energy models according
to Mackenzie et al.[14]:

$$E_{tot} = E_{ele} \times k_{ele} + E_{pol} \times k_{pol} + E_{dis} \times k_{dis} + E_{rep} \times k_{rep}$$

E_{ele} electrostatic energy, E_{pol} polarization energy, E_{dis} dispersion energy, E_{rep} repulsion energy

k_{ele} 1.057, k_{pol} 0.74, k_{disp} 0.871 and k_{rep} 0.618

*Table S 21: Interaction Energies [kJ/mol] for compound **Bx** (P-1), Molecules a and b have approximately the same energy values. [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	3-x,2-y, 1-z	7.1	-85	-18	-16	95	-58
2	1+x, y, z	4.5	-2	-1	-29	14	-20
1	2-x, 2-y, 1-z	5.4	-4	-1	-19	11	-15
2	1+x, 1+y, z	6.2	-4	-1	-14	9	-11
2	x, 1+ y, z	6.8	-4	-1	-13	10	-10

*Table S 22: Interaction Energies [kJ/mol] for compound **Bx** ($P2_1$), Molecules a and b have approximately the same energy values. [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	-	7.1	-83	-17	-16	95	-56
2	1+x, y, z	4.5	-2	-1	-29	14	-19
1	-	5.4	-5	-1	-21	13	-17
2	1+x, y, 1+z	6.1	-4	-1	-14	10	-11
2	x, y, 1+z	6.8	-5	-2	-13	11	-11

*Table S 23: Interaction Energies [kJ/mol] for compound **Tv** (100K). [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	2-x, 2-y, 1-z	8.0	-83.2	-17.2	-16.0	94.4	-56.2
2	1+x, y, z	3.9	-3.7	-1.0	-44.0	25.7	-27.1
2	x, -1+y, z	6.8	-6.9	-1.9	-14.6	12.6	-13.7
2	-1+x, -1+y, z	6.3	-6.6	-1.1	-11.2	9.4	-11.8
1	1-x, 2-y, 2-z	8.5	-5.2	-0.5	-8.1	7.7	-8.2
1	-x, 2-y, 2-z	7.3	-1.7	-0.2	-11.2	5.8	-8.1

*Table S 24: Interaction Energies [kJ/mol] for compound **Tv** (298K). [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	2-x, 2-y, 1-z	8.0	-78.9	-16.1	-16	90.8	-53.2
2	1+x, y, z	4.0	-1.6	-0.8	-37.8	17.2	-24.6

2	x, -1+y, z	6.8	-6.3	-1.7	-12.6	9.1	-13.3
2	-1+x, -1+y, z	6.3	-5.6	-1	-10.7	7.6	-11.3
1	-x, 2-y, 2-z	8.5	-4.7	-0.5	-7.5	6.2	-8.0

*Table S 25: Interaction Energies [kJ/mol] for compound **BxO**. [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	1-x, 2-y, -z	6.9	-80.2	-16.9	-25.8	89.7	-64.4
1	-x, 1-y, 1-z	6.6	-15.7	-2.3	-41.9	33.7	-34.0
1	1-x, 1-y, -z	6.8	-2.1	-1.4	-41.8	22.6	-25.7
1	1-x, 1-y, 1-z	5.8	-6.8	-1.7	-37.8	26.6	-24.9
2	1+x, y, z	6.0	-5.5	-1.3	-30.7	17.7	-22.6

*Table S 26: Interaction Energies [kJ/mol] for compound **BxS**. [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	2-x, 1-y, -z	6.9	-95.2	-20.9	-29.3	118.8	-68.2
1	1-x, 1-y, -z	5.6	-10.1	-1.8	-41.0	30.8	-28.7
1	1-x, -y, -z	6.4	-18.9	-2.8	-34.8	40.9	-27.1
2	x, 1+y, z	6.0	-7.9	-1.4	-32.0	21.2	-24.1
2	3/2-x, -1/2+y, -1/2-z	8.2	-3.9	-1.0	-25.7	15.9	-17.4
2	3/2-x, 1/2+y, 1/2-z	9.5	-2.6	-0.6	-10.9	6.7	-8.5
1	2-x, 1-y, -z	7.5	-0.4	-0.1	-6.2	0.1	-5.8

*Table S 27: Interaction Energies [kJ/mol] for compound **TvO**. [a] the distance between molecular centroids (mean atomic position) in Å.*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
1	1-x, 2-y, 1-z	6.8	-79.0	-16.8	-33.0	85.5	-72.0
1	1-x, 1-y, 1-z	6.2	-6.5	-1.0	-40.8	20.0	-30.8
1	1-x, 1-y, -z	6.6	-3.9	-1.1	-29.6	13.7	-22.1
2	1+x, y, z	6.1	-2.8	-1.1	-28.8	12.4	-21.2
1	-x, 1-y, -z	8.8	-4.0	-0.4	-15.9	9.9	-12.2
1	2-x, 1-y, 1-z	6.9	-2.1	-0.8	-16.4	8.6	-11.8
1	1-x, 2-y, 1-z	9.3	-10.1	-2.1	-11.0	17.6	-10.9

*Table S 28: Interaction Energies [kJ/mol] for compound **TvS**. [a] the distance between molecular centroids (mean atomic position) in Å*

N	Symmetry operation	R [a]	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
2	-x, y+1/2, -z+1/2	7.5	-31.8	-5.2	-22.1	40.7	-31.5
1	2-x, 1-y, 1-z	6.8	-2.7	-1.1	-34.6	16.2	-23.8
2	x, 1+y, z	6.3	-5.7	-1.3	-27.9	15.0	-22.0
2	2-x, 1/2+y, 1/2-z	7.5	-2.7	-1.2	-19.2	8.9	-15.0
1	2-x, 2-y, 1-z	7.0	-2.9	-0.9	-18.3	8.0	-14.7
1	1-x, 2-y, 1-z	8.9	-4.9	-1.0	-10.8	8.7	-10.0

Table S 29: Total lattice energies [kJ/mol] for all the analysed structures

Compound	$E_{lattice}$
Bx (*P*-1)	-94
Bx(*P*21*/*)	-88.5
Tv (100K)	-78.7
Tv (293K)	-74.2
BxO	-132.8
BxS	-131.6
TvO	-127.3
TvS	-119.1

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