SUPPLEMENTARY DATA

Table 1. The relative energies, vibrational frequencies and bond lengths of $[B_5O_6(OH)_4]^-$ monomer when modelled at B3LYP/6-311++G(*d,p*) in the gas phase. Relative energies and vibrational frequencies are quoted to the nearest whole number.

Conformer[a]	Point Group	Relative Energy (kJ mol^{-1})	Lowest Vibrational Frequency (cm^{-1})	ν_{OH} (cm^{-1})	Bond Length r_{OH} (Å)
iiii	D_{2d}	0	37	3869-3870	0.962
iiio	C_1	4	35	3868-3873	0.962 (*i*) 0.961 (*o*)
oiio	C_2	8	35	3868-3873	0.962 (*i*) 0.961 (*o*)
ooii	C_{2v}	11	33	3870-3878	0.962 (*i*) 0.961 (*o*)
oooi	C_1	15	33	3868-3878	0.962 (*i*) 0.961 (*o*)
oooo	D_{2d}	22	33	3877-3878	0.961

[a] *i* and *o* relate to the position of the OH groups, where *i* denotes the OH pointing in, towards the tetrahedral B centre, and *o* denotes the OH group pointing out, away from the tetrahedral B centre.

Table 2. The relative energies, vibrational frequencies and bond lengths of $[B_5O_6(OH)_4]^-$ monomer when modelled at B3LYP/6-311++G(*d,p*) using a PCM implicit solvent model. Relative energies and vibrational frequencies are quoted to the nearest whole number.

Conformer[a]	Point Group	Relative Energy (kJ mol^{-1})	Lowest Vibrational Frequency (cm^{-1})	ν_{OH} (cm^{-1})	Bond Length r_{OH} (Å)
iiii	D_{2d}	0	33	3853	0.963
iiio	C_1	1	32	3852-3854	0.963
oiio	C_2	2	33	3853-3854	0.963
ooii	C_{2v}	2	32	3853-3855	0.963
oooi	C_1	3	31	3853-3855	0.963
oooo	D_{2d}	5	31	3854-3855	0.963

[a] *i* and *o* relate to the position of the OH groups, where *i* denotes the OH pointing in, towards the tetrahedral B centre, and *o* denotes the OH group pointing out, away from the tetrahedral B centre.

Table 3. The binding energies of $[B_5O_6(OH)_4H]_n$ polymers (n = 2, 3) when modelled at B3LYP/6-311++G(*d,p*) using neutral pentaborate monomers (formed by protonating the γ O atom distal to the H-bonding). Binding energies are quoted to the nearest whole number.

Species	Point Group	Energy of monomer (x10^3 kJ mol^{-1})	Absolute Energy of polymer (x10^3 kJ mol^{-1})	Binding Energy (kJ mol^{-1})	Energy per H-bond (kJ mol^{-1})
$[B_5O_6(OH)_4]H$ *iiii*	C_{2v}	-2311.9153	-4623.8365	0	0
$[B_5O_6(OH)_4]H$ *iiio*	C_1	-2311.9183	-4623.8305	0	0
$R_2^2(8)$ α[a]	C_{2h}	-2311.9153	-4623.9065	-76	-32
$R_2^2(8)$ α[b]	C_{2v}	-2311.9153	-6935.8843	-139	-32
$R_2^2(12)$ β[c]	C_{2h}	-2311.9183	-4623.8669	-30	-15
C(8) β	C_1	1) -2311.9153 2) -2311.9183	-4623.8457	-12	-12
$R_2^2(8)$ γ	C_{2h}	-2311.9183	-4623.8713	-34	-17

[a]This dimer was found to contain two additional O---O interactions (3.092 Å) between the protonated O atom of one monomer to the O atom within the R_2^2 (8) ring of the other monomer. [b] This molecule is a trimer which was found to have no bending of the boroxole rings on the central pentaborate unit and comprised of 4 H-bond and 2 O---O interactions. This energy of the O---O interaction (-7 kJ mol^{-1}) was evaluated from a series of simultaneous linear equations. [c] This dimer was found to contain an additional interaction between the two central O atoms (3.008 Å) within the 12-membered ring, however it's energy could not be calculated.

Table 4. The binding energies, dimerization type and bond lengths of $[B_5O_6(OH)_4]_2^{2-}$ dimers when modelled at B3LYP/6-311++G(*d,p*) using a PCM implicit solvent model. Binding energies are quoted to the nearest whole number.

Dimerization reciprocal position	Point Group	Dimerization type	Number of H-bonds	Binding Energy (kJ mol^{-1})	Interatomic distance (Å)	
					r_{O---H}	r_{OH---O}
α	C_i	$R_2^2(8)$	2	-21	1.773	2.755
β	C_1	$R_2^2(12)$	2	-10	1.973	2.941[a]
β	C_1	C(8)	1	-16	1.846	2.814
γ	C_{2h}	$R_2^2(8)$	2	-16	1.849	2.825

[a] This dimer was found to contain an additional interaction between the two central O atoms (3.043 Å) within the 12-membered ring.

Table 5. The frequencies and bond lengths of the OH bonds of $[B_5O_6(OH)_4]_2^{2-}$ dimers when modelled at B3LYP/6-311++G(*d,p*) using a PCM implicit solvent model. Frequencies are quoted to the nearest whole number.

Reciprocal dimer	Interacting Bond Length r_{OH} (Å)	Non-interacting Bond Length r_{OH} (Å)	Lowest Vibrational Frequency (cm^{-1})	Number of interacting OH	ν_{OH} (interacting) (cm^{-1})	ν_{OH} (non-interacting) (cm^{-1})
α $R_2^2(8)$	0.983	0.963	11	2	3422-3451	3851-3854
β $R_2^2(12)$	0.974	0.963	8	2	3635-3638	3851-3853
β C(8)	0.975	a) 0.963 b) 0.964[a]	4	1	a)3596 b) 3589[a]	3852-3853
γ $R_2^2(8)$	0.976	0.963	7	2	3563-3581	3853-3854

[a] Proton accepting OH

Table 6. The geometries of the dimerization motifs of $[B_5O_6(OH)_4]_2^{2-}$ dimers when modelled at B3LYP/6-311++G(*d,p*) using a PCM implicit solvent model.

Reciprocal dimer	Interatomic distance r_{O---H} (Å)	OH^b---O^c angle (°)	BOH^b angle (°)	BO^c---H^b angle (°)
α $R_2^2(8)$	1.773	178.14	113.92	121.70
β $R_2^2(12)$	1.973	171.83	113.05	125.23
β[a] $R_2^2(12)$	1.973	172.93	113.00	124.86
β C(8)	1.846	171.52	114.27	128.96
γ $R_2^2(8)$	1.849	178.08	114.57	124.61

[a] The β $R_2^2(12)$ dimer was found to be asymmetric, [b] donor atom, [c] acceptor atom.

Table 7. A summary of the electron density and bond character of $[B_5O_6(OH)_4]_2^{2-}$ dimers found in QTAIM analysis.

Atomic Units (a.u.)								
Reciprocal dimer	Bond	ρ_b [b]	λ_1 [c]	λ_2 [c]	λ_3 [c]	$\nabla^2(\rho_b)$ [d]	Character [e]	ε [f]
α $R_2^2(8)$	O-H*	0.336	-1.683	-1.673	1.013	-2.342	A	0.006
	O---H	0.037	-0.060	-0.056	0.237	0.121	B	0.058
β $R_2^2(12)$	O-H*	0.347	-1.736	-1.723	1.019	-2.440	A	0.007
	O---H	0.022	-0.030	-0.028	-0.140	0.082	B	0.087
	O---O	0.008	-0.007	-0.006	-0.039	0.026	B	0.142
β[a] $R_2^2(12)$	O-H*	0.347	-1.735	-1.723	1.019	-2.439	A	0.007
	O---H	0.022	-0.030	-0.028	0.140	0.082	B	0.085
β C(8)	O-H*	0.345	-1.734	-1.722	1.031	-2.425	A	0.007
	O---H	0.030	-0.045	-0.042	0.196	0.109	B	0.059
γ $R_2^2(8)$	O-H*	0.344	-1.726	-1.714	1.027	-2.413	A	0.007
	O---H	0.030	-0.046	-0.043	0.195	0.106	B	0.066

[a] The β $R_2^2(12)$ dimer was found to be asymmetric but close to the idealized C_2 symmetry, [b] Electron density at the BCP, [c] Eigenvalues of Hessian, [d] Laplacian of the electron density at the BCP, [e] A = covalent, highly polar, B = "closed-shell", [f] Bond ellipticity, * Atom involved in hydrogen bonding.

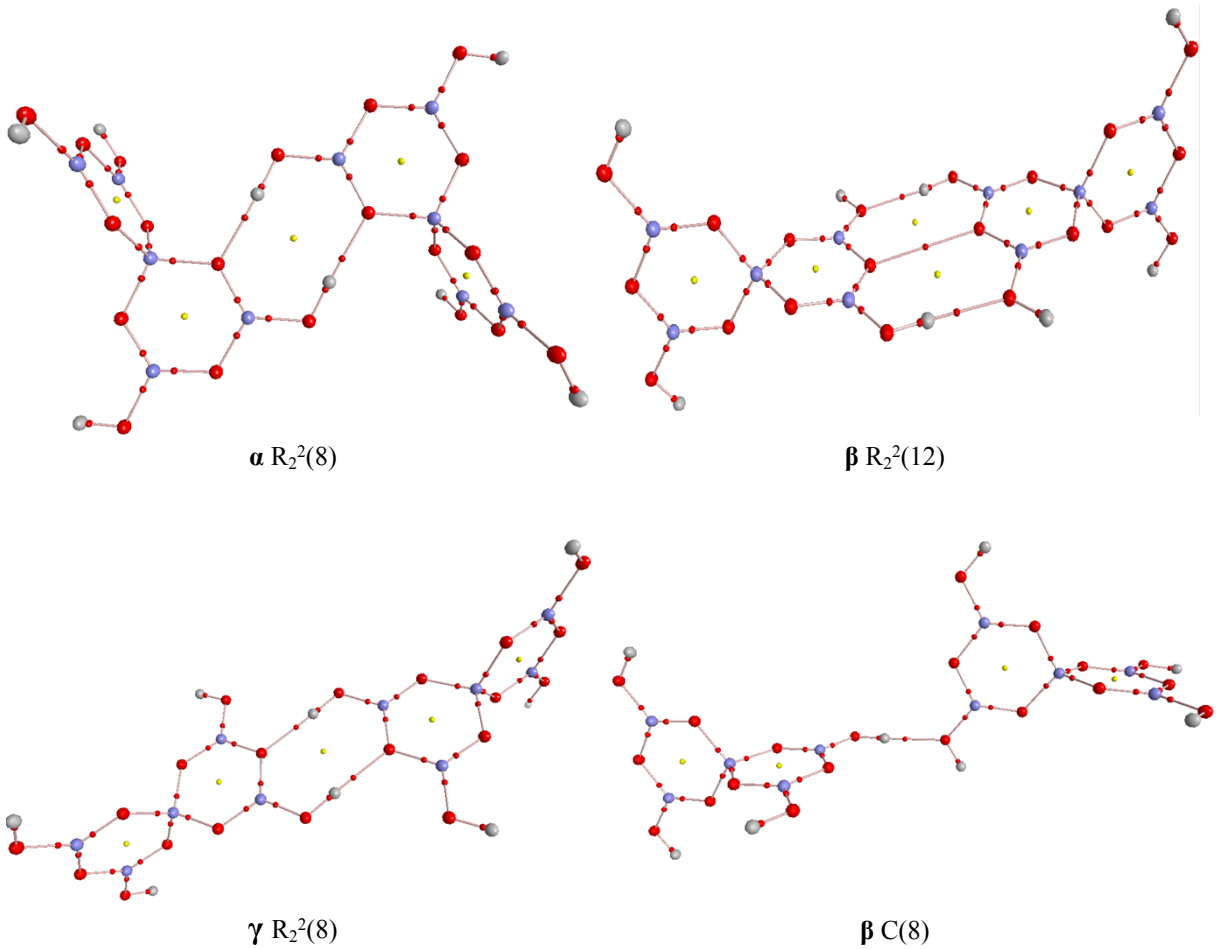

Figure 1. The four dimerization types of $[B_5O_6(OH)_6]_2^{2-}$ under QTAIM analysis. Any BCPs (small red balls), RCPs (small yellow balls) and bond paths are displayed. H---O and O---O interactions are indicated.