ESI

Theoretical Investigation of various aspects of Two Dimensional holey Boroxine, B3O3

Computational Details:

SIESTA code has the capability of making a cocktail of various functionals to be employed in the calculations[1, 2]. In this regard, we combine GGA with the LDA to make a hybrid functional, though it is not in the true spirit of the hybrid since the exact Hartree-Fock exchange is absent[3, 4]. The exchange energy is built by taking 50% of each functional, whereas, 25-75% GGA-LDA is used to define the correlation part. For AIMD simulations, we use both the hybrid and vdW-DF level by employing a 2x2 supercell. The heat treatment is performed at 300K and 600 K where the heat-bath is controlled by the Nosé–Hoover thermostat with NVT ensemble. The VASP calculations were carried out with a kinetic energy cutoff of 500 eV[5-7]. The forces and energy convergence criteria are set as 0.01 eV/Å and 10^{-6} eV, respectively. We use Methfessel-Paxton smearing with 0.05-0.001 eV smearing width since we also report various properties of graphene/graphite for the comparison[8]. Spin polarization is turned on in each and every case.

We also calculate the formation energy of B_3O_3 monolayer by taking the energy of one O from O_2 molecule as a chemical potential using the equation given in the main text. At PBE-D3 level, the formation energy of B_3O_3 monolayer is -5.03 eV/atom. With the same definition, the formation energy at PBE-D2 and hybrid levelsare -5.023 and -5.38 eV/atom, respectively. For completeness, the cohesive energy of O2 molecule is -3.377, -3.374, and -3.385 eV/atom at PBE-D3, PBE-D2, and hybrid level, respectively. The vulnerability of SIESTA's results to BSSE is a known fact, therefore, the energetics from SIESTA cannot be trusted. Yet we see a reasonable agreement between hybrid and PBE-D2/PBE-D3 values.

Table 1: Structural parameters (in Å), charge transfer, band gaps and cohesive strengths at various levels of study. On an average, charge accumulation on O atoms is equal to the charge depletion on B atoms.

	Lattice parameter *a* (Å)	**d_{BB} (Å)**	**d_{BO} (Å)**	**d_{OO} (Å)**	***Charge |e|**	**Band-gap (eV)**	**Cohesive energy (eV/atom)**
GGA	7.83	1.73	1.39	6.28	0.15	3.66	
vdW-DF	7.89	1.74	1.39	6.33	0.15	3.80	
Hybrid	7.81	1.72	1.38	6.27	0.15	3.66	-7.08
PBE-D2	7.83	1.72	1.39	6.28	1.96	3.57	-6.71
PBE-D3	7.82	1.72	1.39	6.27	1.96	3.57	-6.72
M06-L	7.78	1.71	1.38	6.21	0.4	3.90	-6.3
HSEH1PBE	7.80	1.72	1.38	6.24	0.4	5.30	

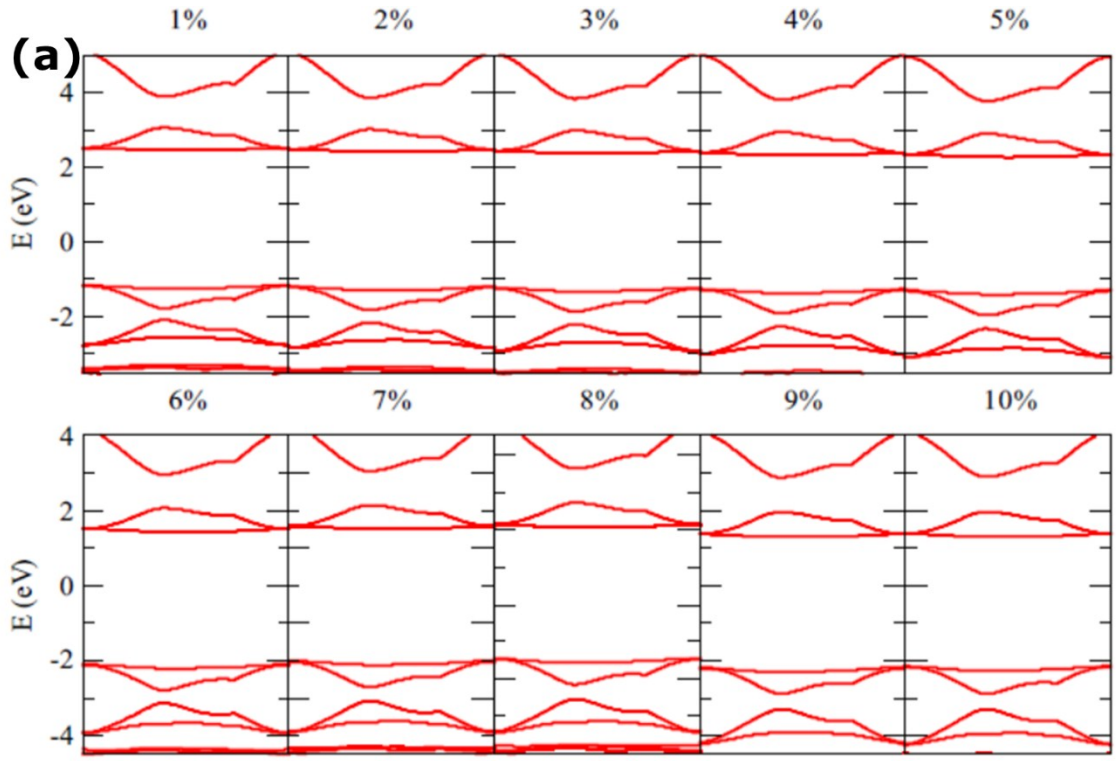
**Hirshfeld and Voronoi analyses in SIESTA, Bader in VASP, and Mulliken in Gaussian*

Table S2 : Structural and energetics data at various levels of theory

	Relative energy (meV)	***IIE* (meV/atom)**	**E_{exf} (meV/A^2)**	**Interlayer separation, *h,h1/h2* (Å)**
PBE-D2				
B_3O_3	1100			
AA-bilayer	870	9.6		3.55
AB-bilayer	650	18.73		3.138/3.25
AB2-bilayer	570	22.13		2.97/3.2

AA-bulk	550	22.83	5.1	3.11
AB-bulk	85	42.34	9.5	3.0/3.0
AB2-bulk	0	45.88	10.37	2.97/3.0
Graphene-bilayer		25		3.33
Graphite		55.9	21	3.21
vdW-DF				
B_3O_3	1732			
AA-bilayer	1082	27		3.56
AB-bilayer	984	31		3.33/3.52
AB2-bilayer	856	36.5		3.03/3.33
AA-bulk	456	53	11.8	3.6
AB-bulk	103	68	15	3.27/3.27
AB2-bulk	0	72	16	3.16/3.16
Hybrid				
B_3O_3	798			
AA-bilayer	565	9.7		3.5
AB-bilayer	460	14.1		3.32/3.45
AB2-bilayer	358	18.3		3.04/3.3
AA-bulk	375	17	4	3.6
AB-bulk	88	29	6.7	3.21/3.21
AB2-bulk	0	33	7.5	3.09/3.14
Graphene-		17.5		3.35

bilayer				
Graphite		35	13	3.35



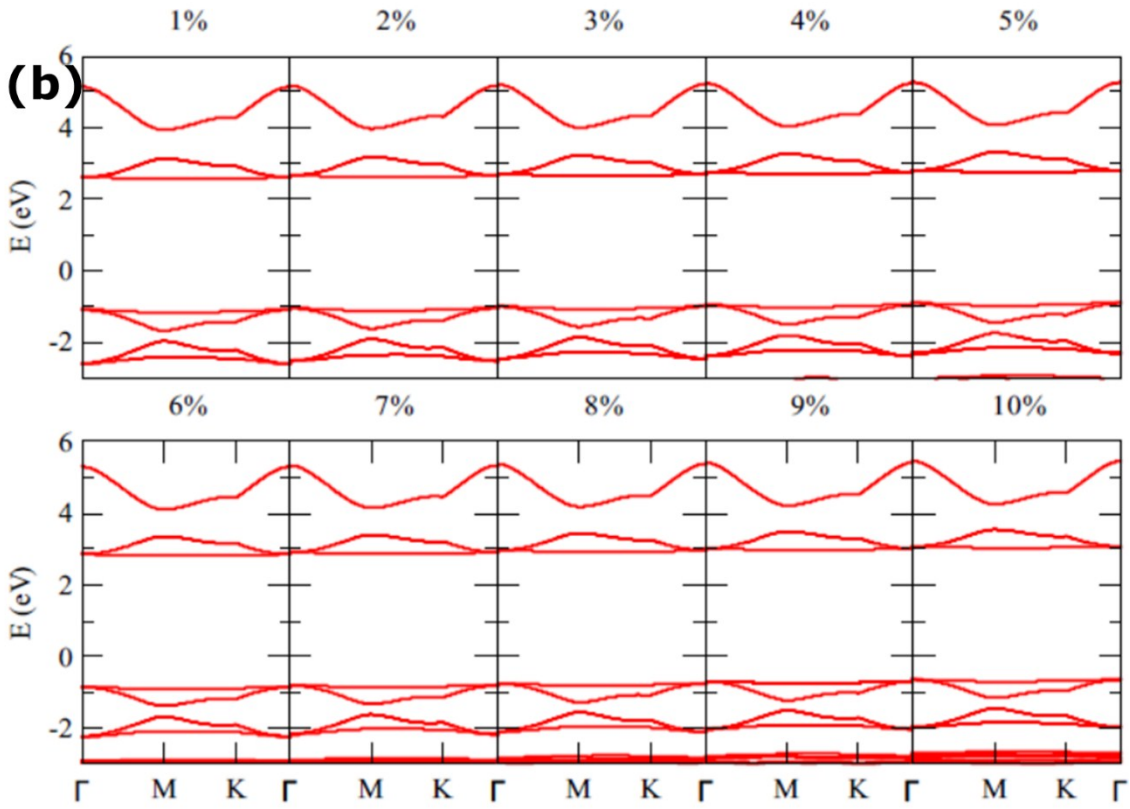


Figure S1: Electronic band structure of B3O3 monolayer with biaxial strain, (a) compression and (b) expansion

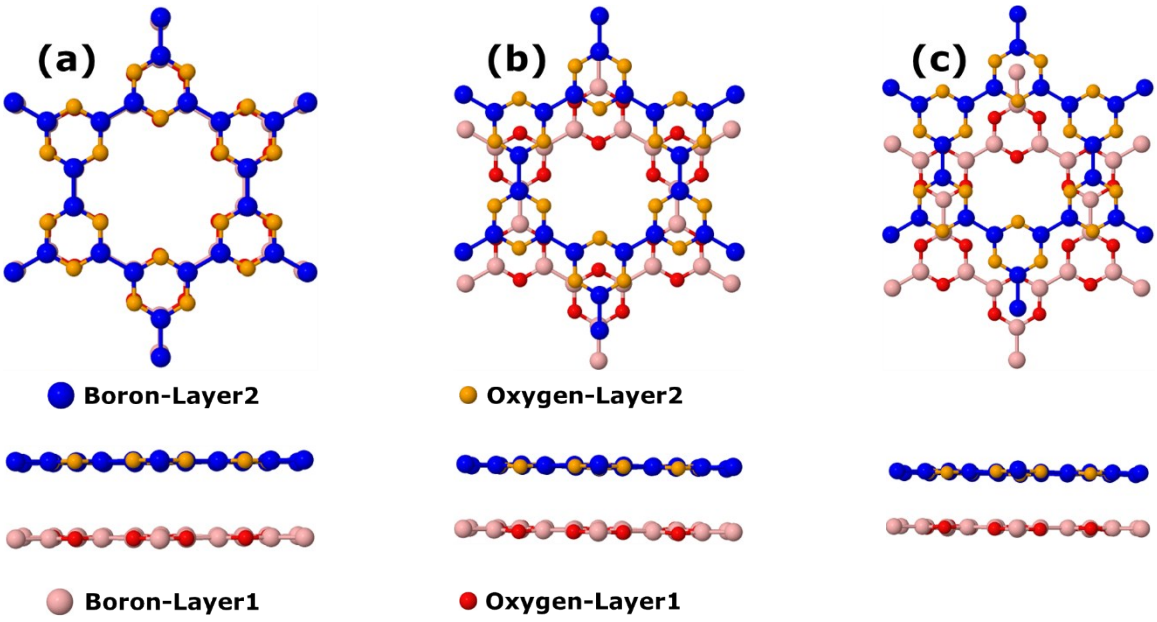


Figure S2: Geometric structures of bilayer B3O3 in (a) AA, (b) AB, and (C) AB2 stacking.

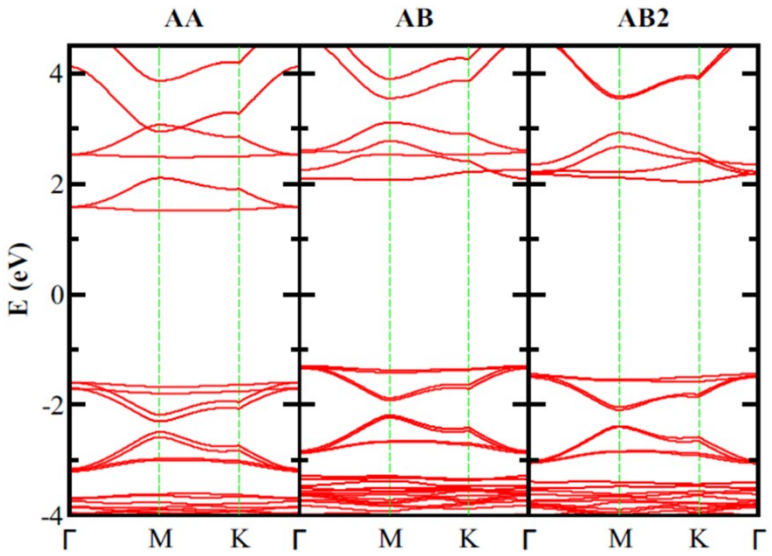
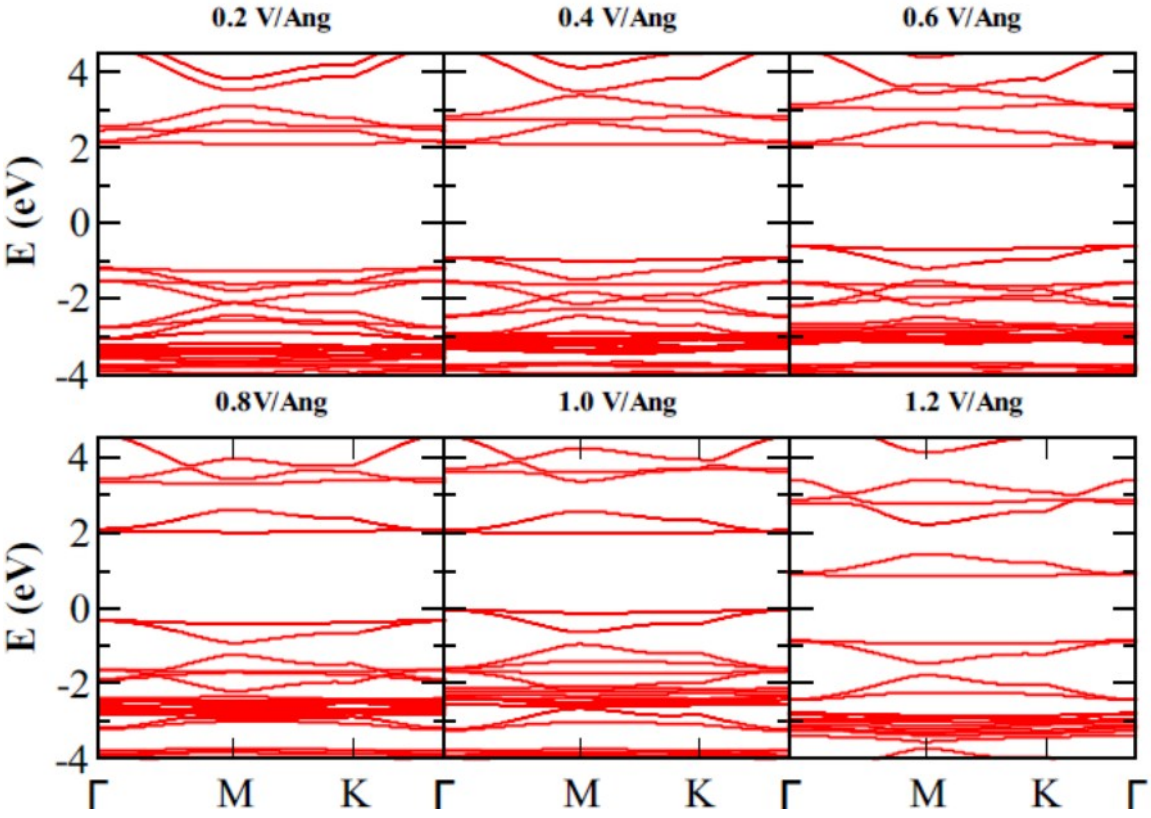


Figure S3: Bilayer B3O3 band structures at hybrid level of theory



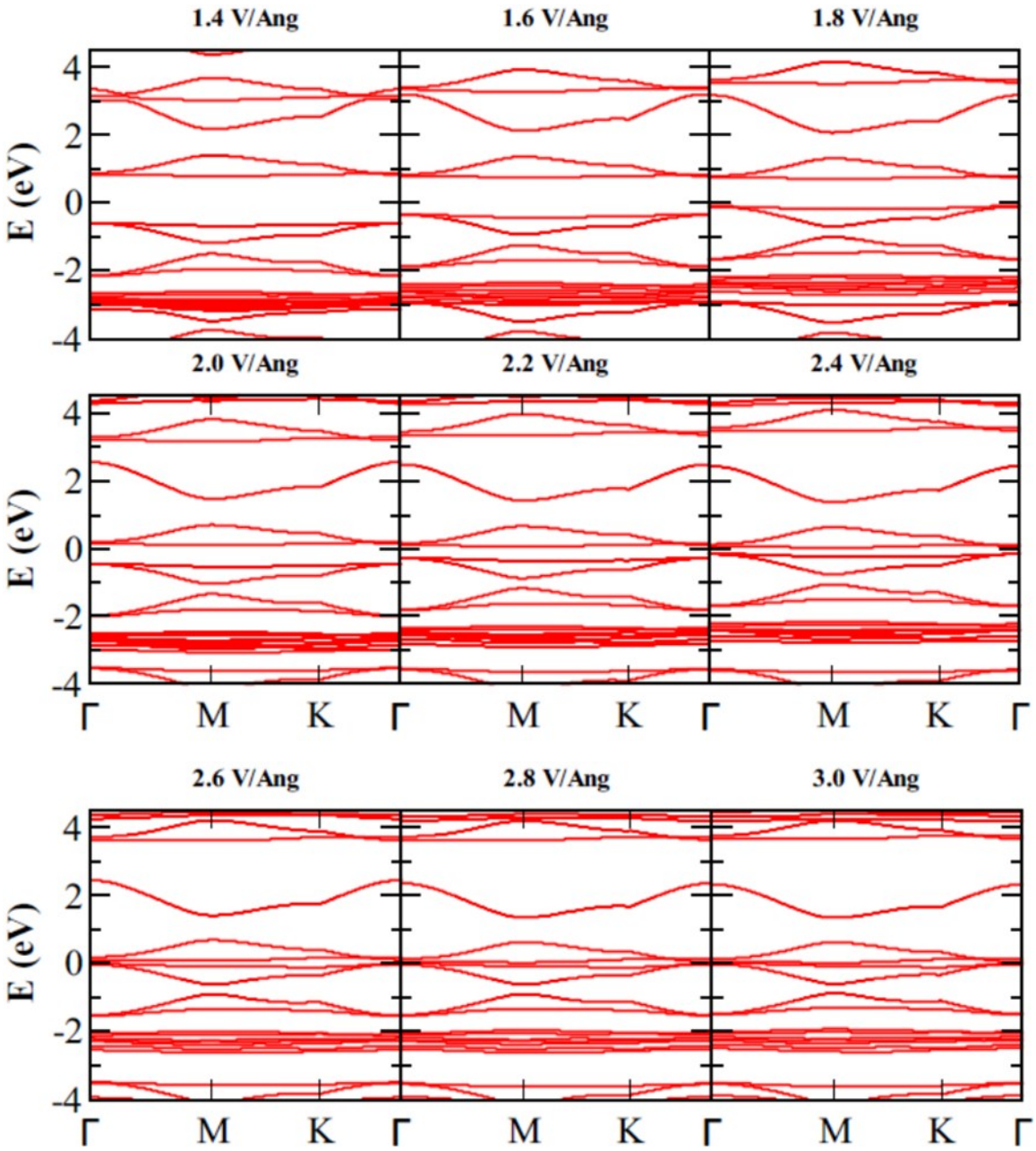


Figure S4: Electronic band structures of AB2 stacked bilayer B3O3 in the presence of external electric field

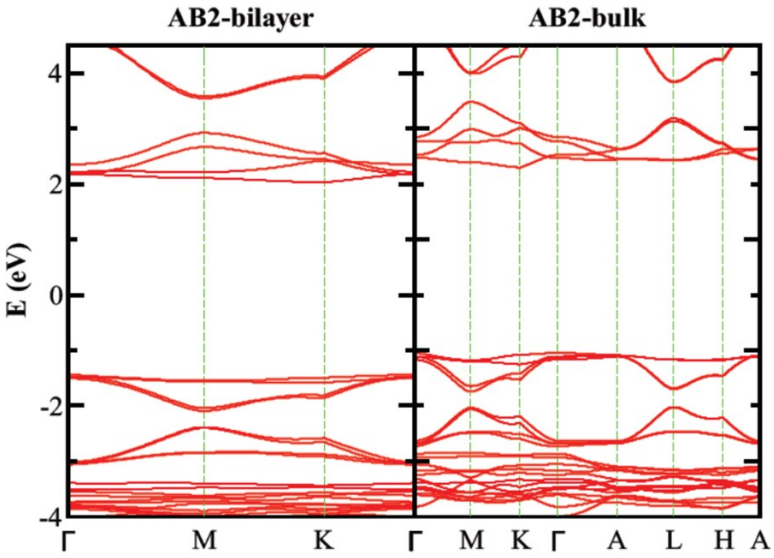


Figure S5: Comparison of the band structures of bilayer and bulk B3O3 at hybrid level of theory

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#======================================================================

# CRYSTAL DATA

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_cell_length_a                         7.82000
_cell_length_b                         7.82000
_cell_length_c                         20.00000
_cell_angle_alpha                      90
_cell_angle_beta                       90
_cell_angle_gamma                      120.00
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1

loop_
_space_group_symop_operation_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_B_iso_or_equiv
   _atom_site_type_symbol
   B1         1.0     0.640757      0.972400      0.149790     Biso  1.000000 B
   B2         1.0     0.331130      0.972395      0.150143     Biso  1.000000 B
   B3         1.0     0.331131      0.662809      0.150149     Biso  1.000000 B
   B4         1.0     0.204228      0.408949      0.150141     Biso  1.000000 B
   B5         1.0     0.894609      0.099345      0.149779     Biso  1.000000 B
   B6         1.0     0.204243      0.099371      0.150136     Biso  1.000000 B
   O1         1.0     0.536195      0.767330      0.149853     Biso  1.000000 O
   O2         1.0     0.536183      0.072900      0.149842     Biso  1.000000 O
   O3         1.0     0.230582      0.767334      0.150399     Biso  1.000000 O
   O4         1.0     0.999154      0.304403      0.149835     Biso  1.000000 O
   O5         1.0     0.999176      0.998851      0.149827     Biso  1.000000 O
   O6         1.0     0.304767      0.304424      0.150395     Biso  1.000000 O
```

Cif file of monolayer B3O3 at PBE-D3 level. VESTA software is used for the conversion.[9]

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