# Electronic Supporting Information for

# **Boric Acid as Supramolecular Graphite**

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#### **Experimental Procedures**

**Crystallization:** Saturated solutions were prepared by dissolving 15–20 mg of commercially available boric acid (**BA**) (Aldrich, 99+%) in 100 mL of boiling deionized water or dimethyl sulfoxide (DMSO). Best quality single crystals (*c.a.* 2 mm x 0.5 mm x 0.2 mm) suitable for single crystal x-ray diffraction (SCXRD) and qualitative and quantitative tests were obtained after 10-15 days.

Single Crystal X-ray Diffraction (SCXRD): Here we are reporting a slightly improved SCXRD data of boric acid (BA). The X-ray diffraction data for the crystal was collected at 100 K on SuperNova (dual, Cu/Mo at zero, Eos) diffractometer using monochromatic  $MoK_{\alpha}$  radiation ( $\lambda = 0.71073$  Å. Structure was solved by Using Olex2<sup>[1]</sup> in the Superflip<sup>[2]</sup> structure solution program by charge flipping and refined with the least squares minimization SHELXL refinement programme.<sup>[3]</sup>

**Powder X-ray Diffraction (PXRD):** The PXRD patterns were collected on a Rigaku SmartLab with a  $CuK\alpha$  radiation (1.540 Å). The tube voltage and amperage were set at 40 kV and 50 mA respectively. Each sample was scanned between 10 and 50° 20 with a step size of 0.02°. The instrument was previously calibrated using a silicon standard.

**Energy Frameworks Calculations:** Energy calculations pertaining to intermolecular interactions were performed using the software suite *CrystalExplorer17.5*<sup>[4]</sup> based on HF/3-21G molecular wave-functions calculated using .cif files of the crystals (**BA**). Pairwise interaction energies between molecules were calculated considering a radius of 3.8 Å from centroid of a molecule to an atom (of another molecule) belonging to its nearest neighbour. The "energy frameworks" were constructed based on the crystal symmetry and total intermolecular interaction energy (E\_tot), which includes electrostatic (E\_ele), polarization (E\_pol), dispersion (E\_dis), and exchange-repulsion components (E\_rep) with scale factors of 1.019, 0.651, 0.901 and 0.811, respectively. Where E\_total =  $1.0019E_ele + 0.651E_pol + 0.901E_disp + 0.811E_rep$ .

**Nanoindentation:** Nanoindentation experiments have been performed on the single crystals of **BA** using the TI Premier from Hysitron, Minneapolis, USA, equipped with an in-situ Scanning Probe Microscope (SPM). A diamond Berkovich tip (three-sided pyramidal tip with a total included plane-edge angle of  $142.3^{\circ}$ ) of radius ~150 nm was employed to determine the hardness (*H*) and elastic modulus (*E*) of the crystals. The *H* and *E* were extracted using the standard Oliver-Pharr (O&P) method.<sup>[5]</sup> The complete details of the method can be found elsewhere.<sup>[6]</sup>

Single crystals were glued down to a coverslip using a spread drop of cyanoacrylate adhesive (fevikwik) and the coverslip were the further mounted on steel stub prior to the experiments. To ease sample preparation prior to scanning probe microscopy (SPM) imaging after nanoindentation, some crystals were directly mounted and indented on a round shaped steel stub. Horizontal and vertical sample tilts and sample roughness were assessed using in situ scanning probe microscopy (SPM), using the Berkovich tip.

Crystals of boric acid (**BA**) have hexagonal morphology with non-equal side faces. Here, (011) is the face with largest surface area as compared to the other side faces i.e., (001) and (010). This can be clearly visualized in the face-indexed images of the crystal as presented in Supplementary Figure S3. That is why we chose to perform indentation on (011) face for extracting data without much difficulty. On the other hand, obtaining reliable data from narrow faces is challenging and may cause significant errors, often due to tilting issues. Hence, we did not attempt to perform nanoindentation on (001) and (010) side faces as they were too small and risky.

### **Results and Discussion**

1. Sheared crystal images:



**Figure S1.** Optical (a) and scanning electron microscopic (SEM) (b) images of multiple stages of shearing on several single crystals of boric acid (**BA**).

### 2. Powder X-ray diffraction (PXRD):



**Figure S2.** Comparison of the powder X-ray diffraction (PXRD) patterns (red) collected from the bulk crystals of **BA** and the simulated patterns (black) evaluated from the corresponding SCXRD data collected at 100K.



## 2. Face indexing of single crystal of BA:

**Figure S3.** Face indexed images of **BA** crystal in different orientations with nice correlation with crystal faces observed in the Bravais–Friedel–Donnay–Harker (BFDH) morphology of the crystal.



**Figure S4.** The Bravais–Friedel–Donnay–Harker (BFDH) morphology obtained from Mercury (a) and a clear sheared crystal of **BA** with nice correlation with direction of shearing.

## 4. ORTEP and crystallographic parameters table:



**Figure S5.** ORTEP diagram of single crystal of **BA** with 50% of thermal ellipsoid probability with extended connections.

Table S1: Crystallographic parameters of single crystal of BA

Temperature (K)	167 (90)
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Formula	H <sub>3</sub> BO <sub>3</sub>
Formula Weight	61.83
Crystal System	triclinic
Space group	<i>P</i> -1
a(Å)	6.3573(3)
$b(\text{\AA})$	7.0201(4)
$c(\text{\AA})$	7.0339(4)
$V(\text{\AA}^3)$	263.17(3)
$\alpha(^{o})$	119.810(5)
β(°)	92.530(4)
γ(°)	101.447(4)
Ζ	4
$D_{\rm c}({\rm g~cm^{-3}})$	1.561
$\mu (\mathrm{mm}^{-1})$	0.161
θ range (°)	3.31 - 26.36
Reflections collected	34998
Unique reflections	1060
R <sub>int</sub>	0.0773
GoF (obs/all)	1.082
$R_{\rm F}^{\rm obs}$ ( $I > 2\sigma({\rm I})$ )	0.0578
$wR_{\rm F}^{\rm all}$	0.1680
$\Delta \rho_{min} / \Delta \rho_{max} \ (e {\rm \AA}^{-3})$	0.46/-0.31
CCDC No.	2392298

Table S2: Hydrogen bonding information

Hydrogen bonds	Bond distance (Å, D…A)	Bond angles (°)
O1 - H1…O4	1.86(2)	172.3(16)
O2 - H2…O6	1.877(18)	174.2(17)
O3 - H3…O5	1.90(4)	176(3)
O4 - H4…O2	1.88(3)	174(3)

O5 - H5…O1	1.921(18)	174.8(17)
O6 - H6···O3	1.85(2)	170.9(10)

5. Energy frameworks analysis:



**Figure S6.** Energy frameworks analysis performed by *CrystalExplorer* 17.5 using basis set **HF/3-21G**. (a) Illustration of a hexagon formed by strong hydrogen bonding interactions with specifying total energy values and (b) and ethe hexagon with total energy tubes without molecules. (c) Stacking of molecules along crystallographic *a*-axis depicting anisotropic interactions between intralayer and interlayers interactions and the corresponding calculated energy tables. Environments around both symmetry independent unique molecules in the asymmetric unit are shown.



**Figure S7.** Anisotropic interaction energies. Stacking of consecutive hexagons along crystallographic *a*-axis illustrating the anisotropic total energy tubes with molecules (a), without molecules (b) and energy values (c).



6. Nanoindentation:

**Figure S8.** Analysis of nanomechanical tests on (011) of **BA**. Representative *P*-*h* curves at 5 mN load (a) and with variable load ranging from 1-5 mN indentation load (b). Corresponding histograms of extracted reduced modulus (c) and hardness (d) obtained from several indentation on multiple crystals. Optical images of one representative crystal (e) and two dimensional (2D) scanning probe microscopic (SPM) post-indent impression profiles (f,g).



**Figure S9.** Optical images and post-indent SPM imaging analysis. (a) Optical image of **BA** crystal with marked (yellow arrows) possible shearing direction of layers. (b) Post-indent SPM images of BA (011) resulting from Berkovich indents at load of 5 mN. Layer shearing is happened exactly parallel to (100), shown by yellow double headed lines with nice correlation of directions between optical and SPM images. (c) SPM image before applying 5 mN load. Optical image (d) and 2D SPM image (e) demonstrating the same correlation at 1 mN load for another set of crystal.



**Figure S10.** Optical images and post-indent SPM imaging analysis. (a,b) Optical image of **BA** crystal captured at different magnifications with marked (yellow lines) possible shearing direction of (100) layers. (c) Pre- and post-indent SPM images of **BA** (011) resulting from Berkovich indents at different loads of 3 mN (upper panel), 1-4 mN (middle panel), and 5 mN & 1-4 mN (bottom panel). Layer striations were occurred exactly parallel to (100), shown by yellow double headed arrows with nice correlation of directions between optical and SPM images.



**Figure S11.** Analysis of nanomechanical tests on (100) of **BA**. Representative *P*-*h* curves resulting from indentation at variable loads ranging from 500  $\mu$ N to 9 mN loads (a), Optical image of BA (100) with visible indent impressions (b) and typical multiple *P*-*h* curves obtained from 6 mN indentation load (c). Corresponding histograms of extracted reduced modulus (d) and hardness (f) obtained from several indentation on multiple crystals. (g) Two-dimensional (2D) scanning probe microscopic (SPM) post-indent impression profiles resulting from different loads at 3 mN, 4 mN and 6 mN (left to right) and their corresponding three-dimensional (3D) impression profiles.



**Figure S12.** Comparison of nanomechanical tests on (011) and (100) of **BA**. Representative *P*-*h* curves resulting from range of loads from 500  $\mu$ N to 5 mN on (011) (a) and (100) (c), (b) optical images of BA crystals mounted on (011) (top) and (100) (bottom). Post-indent 2D SPM image on (011) obtained under the load of 5mN (d) and corresponding height profile of impression [drawn along the black line in (d)] demonstrating no significant 'pile-up' on (011) (e). Post-indent 2D SPM image of impression [drawn along the red line in (f)] demonstrating significant 'pile-up' on (100) (g).



**Figure S13.** Before and after indent optical images of different crystal of **BA** mounted on (100) (a) and 2D SPM image profiles obtained after applying indentation load of 1 mN (b).



**Figure S14.** Scattered plot the extracted reduced modulus (*E*r) and hardness with respect to contact depths ( $h_c$ ), obtained from indentation tests on (011) (a), (100) (b) and comparison of *E*r resulting from (011) and (100) (c) of multiple **BA** crystals.



**Figure S15.** Table of intermolecular interaction energies estimated for **CAF-2I4NA** system using HF/3-21G model. Both the total energy (E(tot)) and electrostatic (E(ele)), polarization (E(pol)), dispersion (E(dis)), and exchange-repulsion (E(rep)) components of the energy are listed. *R* indicated the distance between centers of mass of the pair of molecules. Environment around both CAF and 2I4NA molecules in the asymmetric unit are shown.



**Figure S16.** Table of intermolecular interaction energies estimated for **CAF-CNB** system using HF/3-21G model. Both the total energy (E(tot)) and electrostatic (E(ele)), polarization (E(pol)), dispersion (E(dis)), and exchange-repulsion (E(rep)) components of the energy are listed. *R* indicated the distance between centers of mass of the pair of molecules. Environment around both CAF and CNB molecules in the asymmetric unit are shown.



**Figure S17.** Table of intermolecular interaction energies estimated for **THP-PIC** system using HF/3-21G model. Both the total energy (E(tot)) and electrostatic (E(ele)), polarization (E(pol)), dispersion (E(dis)), and exchange-repulsion (E(rep)) components of the energy are listed. *R* indicated the distance between centers of mass of the pair of molecules. Environment around both THP and PIC molecules in the asymmetric unit are shown.



**Figure S18.** Table of intermolecular interaction energies estimated for **3NBA-4hydroxybenzamide** system using HF/3-21G model. Both the total energy (E(tot)) and electrostatic (E(ele)), polarization (E(pol)), dispersion (E(dis)), and exchange-repulsion (E(rep)) components of the energy are listed. *R* indicated the distance between centers of mass of the pair of molecules. Environment around both 3NBA and 4-Hydroxybenzamide molecules in the asymmetric unit are shown.

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