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It was recently reported that boron monoxide (BO) is formed through the cross-linking of  $B_4O_2$  structural building units. Multiple theoretical phases agree with this description. Using pycnometry, multidimensional  $^{17}O$  NMR spectroscopy, and plane-wave DFT calculations we determined the likely polymorph to be a one-dimensional polymer initially proposed in 1955.

Among the binary oxides, boron monoxide (BO) is perhaps unique in having evaded attempts to determine its structure for nearly a century. The material was initially reported in 1940,<sup>1,2</sup> however, the first synthesis for the preparation of a single-phase BO material was described in 1955 by Wartik and Apple.<sup>3</sup> Their synthesis employed the condensation of tetrahydroxydiboron ( $B_2(OH)_4$ , Fig. 1) at high temperature and while it was soon discovered that the boron–boron bonds were preserved in the resulting material,<sup>4,5</sup> the long-range structure was never determined. Several potential model structures were reported,<sup>6–8</sup> most exhaustively by Claeysen *et al.*,<sup>9</sup> however, none were supported by experimental evidence.

Recently, some of us applied multidimensional  $^{11}B$  NMR spectroscopy to revisit this structural conundrum.<sup>10</sup> Key observations included (1) the detection of a single crystallographically unique boron site; (2) observation of symmetry-amplified  $^{11}B$ – $^{11}B$  *J* couplings;<sup>11–13</sup> (3) observation of the collinearity of closest B–B bonds from  $^{11}B$ – $^{11}B$  triple-quantum correlations; and (4) observation of diffraction signals that suggested the formation of a layered structure. The work strongly suggested that the main structural building unit was a  $B_4O_2$  ring with local  $D_{2h}$  symmetry.<sup>10</sup> This agrees with the isolation of a  $B_4O_2(OH)_4$  intermediate by Carmalt *et al.*<sup>14</sup> Owing to the observed diffraction patterns we proposed that the material

## Boron monoxide is a one-dimensional polymer

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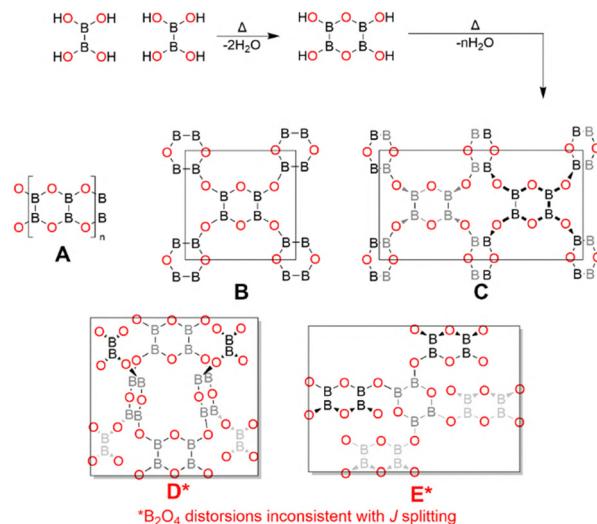


Fig. 1 The synthesis of BO involves the condensation of  $B_2(OH)_4$  to form structural building units composed of a six-membered  $B_4O_2$  rings that then interlink into a polymeric material. The structural building units can organize into either one-dimensional (A), two-dimensional (B) and (C), or three-dimensional (D) and (E) structures. Three-dimensional structures (D) and (E) feature twisting of the  $B_2O_4$  moieties, which is inconsistent with the observation of symmetry-amplified *J* splittings. Darker shades indicate moieties in the foreground.

was two-dimensional, which could have important practical implications;<sup>15–21</sup> however, a great deal of uncertainty on the structure remained.  $B_4O_2$  rings may cross-link in a number of patterns, as evident from the structures compiled by Claeysen and listed in Fig. 1.<sup>9</sup> We thus sought to apply  $^{17}O$  NMR spectroscopy to further narrow the possible structures for BO. While most materials are indistinguishable from  $^{11}B$  NMR (with the exception of structure D and E, which do not have local  $D_{2h}$  symmetry), structure A features a single unique  $^{17}O$  site while the others feature intraring and interring oxygens that may be distinguishable. All five models further differ in their B–B–O–B dihedral angles that could be probed using  $^{17}O\{^{11}B\}$  heteronuclear correlation.

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To this aim, we enriched  $\text{B}_2(\text{OH})_4$  with  $^{17}\text{O}$  to prepare an  $^{17}\text{O}$ -enriched BO material. Enrichment of tetrahydroxydiboron by direct  $^{17}\text{O}$  exchange with water proved ineffective due to its poor solubility and slow decomposition to form boric acid, a non-isolable impurity. We therefore instead produced tetramethoxydiboron as previously described,<sup>22</sup> which then hydrolyzed with an excess of  $^{17}\text{O}$ -enriched water (39.9%) to yield pure  $\text{B}_2(^{17}\text{OH})_4$ . From liquid-state  $^{17}\text{O}$  NMR, we estimate the enrichment level to be  $\sim 3.9\%$  (Fig. S5). Synthesis of  $\text{B}^{17}\text{O}$  was then carried out in the usual fashion by the self-condensation of  $\text{B}_2(^{17}\text{OH})_4$  at 200 °C, see SI for further details.

We acquired  $^{11}\text{B}$  and  $^{17}\text{O}$  multiple-quantum (MQ) magic-angle spinning (MAS) NMR spectra of the resulting material (Fig. 2).<sup>23–25</sup> As expected,<sup>10</sup> we observed a single  $^{11}\text{B}$  resonance with an isotropic ( $\delta_{\text{iso}}$ ) chemical shift of 35.1 ppm, a quadrupolar coupling constant ( $C_Q$ ) of 3.5 MHz, and a quadrupolar asymmetry parameter ( $\eta$ ) of 0.5. The  $^{17}\text{O}$  MQMAS spectrum was equally simple, being described with a single site ( $\delta_{\text{iso}} = 178$  ppm;  $C_Q = 3.8$  MHz;  $\eta = 0.7$ , see Table 1). These parameters were obtained by fitting the MAS lineshape and the MQMAS shift simultaneously using dmfit.<sup>26</sup>

Immediately, these results strongly suggest the formation of structure **A** (see Fig. 1), which uniquely features only one type of chemically distinct oxygen site. We then performed plane-wave density functional theory (DFT) calculations to predict the  $^{11}\text{B}$  and  $^{17}\text{O}$  chemical shifts and electric field gradient (EFG) tensor<sup>27,28</sup> so that they may be compared with experiment. We found that the  $^{17}\text{O}$  chemical shifts of sites within ring structures were highly sensitive to the method used, and as such a monomer correction<sup>29</sup> was applied using the resolution of identity second-order Møller-Plesset perturbation theory method (RI-MP2) for all calculated  $^{17}\text{O}$  chemical shifts. The results are listed in Table 1. There is a clear distinction between the intraring ( $\delta_{\text{iso}} = 200$ –225 ppm) and interring oxygen species ( $\delta_{\text{iso}} = 150$ –165 ppm) suggesting that structure **B**–**F** are inconsistent with the  $^{17}\text{O}$  NMR observations.

The differences between the various model are perhaps most clearly depicted by comparing experimental and computed  $^{17}\text{O}\{^{11}\text{B}\}$  dipolar heteronuclear multiple-quantum correlation

**Table 1** Experimentally-determined and computed BO NMR parameters and densities

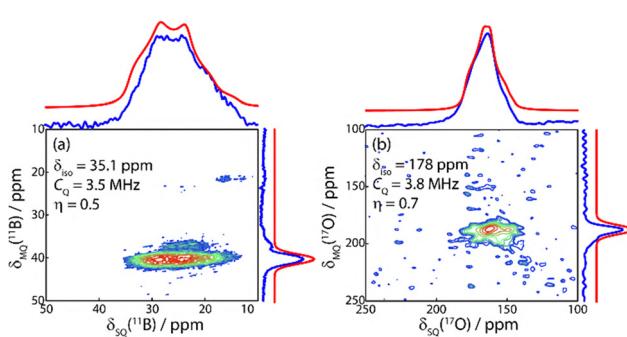
	$\rho/\text{g cm}^{-3}$	Site	$\delta_{\text{iso}}/\text{ppm}$	$ C_Q /\text{MHz}$	$\eta$
Expt.	$2.08 \pm 0.13$	B	$35 \pm 1$	$3.5 \pm 0.1$	$0.5 \pm 0.2$
<b>A</b> <sup>a</sup>	2.05	O	$178 \pm 2$	$3.8 \pm 0.1$	$0.7 \pm 0.1$
		B	33.8	3.90	0.32
<b>B</b>	1.53	O	203.9	4.73	0.52
		B	28.2	3.86	0.44
<b>C</b>	1.44	$\text{O}_{\text{intra}}$	223.1	5.16	0.35
		$\text{O}_{\text{inter}}$	149.8	6.87	0.51
<b>D</b>	0.84	B	25.5	3.65	0.50
		B	31.0	3.95	0.38
<b>E</b>	1.35	$\text{O}_{\text{intra}}$	217.0	4.84	0.50
		$\text{O}_{\text{intra}}$	219.4	4.48	0.66
<b>F</b>	0.84	$\text{O}_{\text{inter}}$	161.3	5.03	0.81
		B	31.7	3.97	0.38
<b>G</b>	0.84	B	25.5	5.66	0.95
		$\text{O}_{\text{intra}}$	215.9	4.48	0.70
<b>H</b>	0.84	$\text{O}_{\text{intra}}$	205.4	4.31	0.40
		$\text{O}_{\text{inter}}$	163.2	4.79	0.30
<b>I</b>	0.84	$\text{O}_{\text{inter}}$	162.2	4.84	0.36
		B	30.9	4.28	0.64
<b>J</b>	0.84	B	27.7	6.18	0.94
		$\text{O}_{\text{intra}}$	213.6	4.60	0.63
<b>K</b>	0.84	$\text{O}_{\text{intra}}$	218.8	4.67	0.26
		$\text{O}_{\text{inter}}$	153.6	4.81	0.95

<sup>a</sup> Calculation performed on the *Immm* polymorph.<sup>9</sup>

(D-HMQC)<sup>30</sup> spectra (Fig. 3) that depend on the  $^{11}\text{B}$  and  $^{17}\text{O}$  EFG tensors (including their relative orientations) in addition to the chemical shifts. We acquired such a spectrum using rotational-echo double-resonance (REDOR) recoupling,<sup>31</sup> applied at the  $^{11}\text{B}$  frequency, and  $^{17}\text{O}$  detection.<sup>32,33</sup> Owing to the strong  $^{11}\text{B}$ – $^{11}\text{B}$  homonuclear dipolar interactions and the low  $^{17}\text{O}$  concentration,  $^{11}\text{B}$ -detection was not feasible. DFT-predicted  $^{17}\text{O}\{^{11}\text{B}\}$  correlation spectra were calculated using SIMPSON<sup>34,35</sup> with the parameters listed in Table 1, Euler angles calculated using MagresView ver. 1.6.2 (Table S2),<sup>36</sup> and assuming a 100% efficient magnetization transfer. Clearly only structure **A** yields a correlation spectrum in close agreement with that measured experimentally, with the others having clearly defined intraring and interring correlations. Three-dimensional structures **D** and **E** feature ring distortions that disagree with prior  $J$  coupling measurements.<sup>10,11</sup> These distortions further dramatically increase the magnitude of the  $^{11}\text{B}$  quadrupolar interactions beyond that observed experimentally. Comparisons between the 1D Hahn echo NMR spectra and the five models are also shown in Fig. S2.

To further confirm that structure **A** is the correct polymorph for the BO materials produced by the condensation of  $\text{B}_2(\text{OH})_4$ , we performed pycnometry measurements to determine the density of the material. As described by Claeysens,<sup>9</sup> and as listed in Table 1, the polymorphs differ greatly in their densities, with structure **A** being the densest at a predicted  $2.08 \text{ g cm}^{-3}$ . We measured a density of  $2.08 \pm 0.13$ , which is within error of the predicted value for **A**, and far denser than structures **B**–**E**.

It thus seems that structure **A**, a one-dimensional polymer, is indeed the correct model for BO, however, this does not explain the peculiar X-ray reflections that pointed to a two-dimensional material. Claeysens predicted four different



**Fig. 2**  $^{11}\text{B}$  (a) and  $^{17}\text{O}$  (b) 2D MQMAS NMR spectra. There is one well-defined site present for both  $^{11}\text{B}$  and  $^{17}\text{O}$ , suggesting a structure containing only a single crystallographically unique site for each element. Sum projections (blue) are overlaid with a fit to a single site with the listed chemical shift and EFG tensor parameters (red).

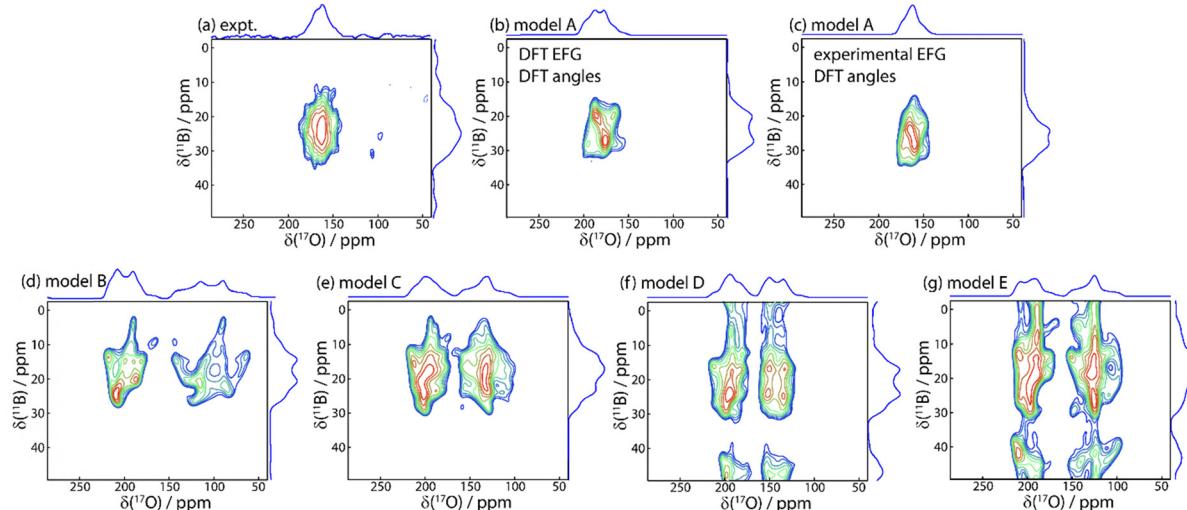


Fig. 3 Experimental (a) and calculated (b)–(g)  $^{17}\text{O}\{^{11}\text{B}\}$  D-HMQC 2D correlation spectra. Simulations were performed using the periodic DFT-calculated chemical shifts and EFG tensor parameters for the structures indicated on the Figure. For the simulation shown in (c), the Euler angles from the DFT calculations were used together with the experimentally-determined EFG tensor parameters and chemical shifts.

packing arrangements for the polymers in **A**,<sup>9</sup> which lead to very different diffraction patterns (Fig. 4), none of which agree with the experimental result. If we randomize the stacking arrangement in a  $1 \times 1 \times 10$  *P1* supercell,<sup>10</sup> however, we do reproduce a similar powder pattern as that predicted for structure **B**. There are still differences with the experiment, however, and a broader study of the stacking faults may be required to fully understand the diffraction pattern.

To conclude, density measurements and  $^{17}\text{O}\{^{11}\text{B}\}$  solid-state NMR experiments were used to narrow the potential structural candidates for boron monoxide (BO), which was earlier shown to be made of interconnected  $\text{B}_4\text{O}_2$  rings. We discovered that the material was, in fact, not a two-dimensional nanomaterial but instead was composed of one-dimensional polymers composed of fused  $\text{B}_4\text{O}_2$  rings. Interestingly, this exact model

was initially suggested by Wartick and Apple in 1955 when the material was first prepared.<sup>3</sup> We were nevertheless unable to narrow the possibilities for a space group, with the material seeming to lack long-range order. Learning about the long-range order of the material will require methods that are sensitive to such length scales, such as scanning tunneling microscopy.<sup>37</sup>

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

Raw data for this study are available at <https://doi.org/10.5281/zenodo.1688429>.

Supplementary information (SI): synthesis details, solution-phase NMR data, differential scanning calorimetry,  $^{11}\text{B}$  J-resolved NMR data, thermogravimetric analysis, infrared spectroscopy, and further calculation details. See DOI: <https://doi.org/10.1039/d5cc04723d>.

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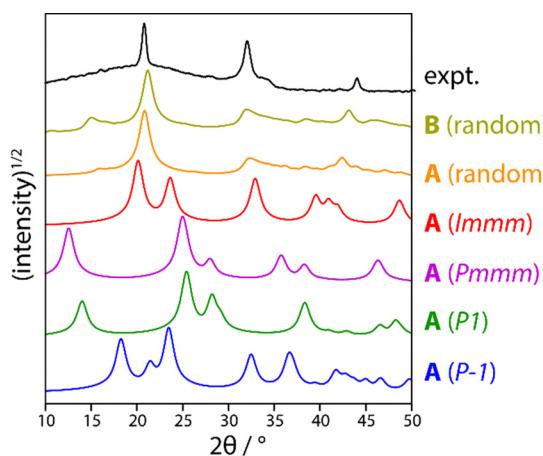


Fig. 4 Comparison of the experimentally-measured PXRD pattern to those predicted using different polymorphs of model **A**, as indicated on the Figure, including turbostratic models of **A** and **B**. None of the predicted patterns agree with the experimental measurement, suggesting that some degree of random stacking is common.

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