

## Supplementary information

### 1,3-Diborata-2,4-diphosponiocyclobutane-1,3-diyls Communicate through a para-Phenyl Linker

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#### X-Ray Structure Determination 3b

A purple thin plate fragment (0.16 x 0.13 x 0.02 mm<sup>3</sup>) was used for the single crystal x-ray diffraction study of C<sub>26</sub>H<sub>44</sub>B<sub>2</sub>P<sub>2</sub> (sample gb367I2a). The crystal was coated with paratone oil and mounted on to a cryo-loop pin. X-ray intensity data were collected at 100(2) K on a Bruker APEX2 (version 2.0-22)<sup>1</sup> platform-CCD x-ray diffractometer system (Mo-radiation,  $\lambda = 0.71073 \text{ \AA}$ , 50KV/30mA power). The CCD detector was placed at a distance of 6.1000 cm from the crystal.

A total of 500 frames were collected (60 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (version V7.23A)<sup>2</sup> and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 5367 reflections at a maximum  $2\theta$  angle of  $40.36^\circ$  (1.03  $\text{\AA}$  resolution), of which 2421 were independent reflections ( $R_{\text{int}} = 0.0559$ ,  $R_{\text{sig}} = 0.0807$ , redundancy = 2.2, completeness = 92.8%) and 1731 (71.5%) reflections were greater than  $2\sigma(I)$ . The unit cell parameters were,  $\mathbf{a} = 23.670(16) \text{ \AA}$ ,  $\mathbf{b} = 8.918(6) \text{ \AA}$ ,  $\mathbf{c} = 25.608(17) \text{ \AA}$ ,  $\beta = 90.142(19)^\circ$ ,  $V = 5406(6) \text{ \AA}^3$ ,  $Z = 8$ , calculated density  $D_c = 1.082 \text{ g/cm}^3$ . Absorption corrections were applied (absorption coefficient  $\mu = 0.172 \text{ mm}^{-1}$ ; max/min transmission = 0.9966/0.9731) to the raw intensity data using the SADABS program (version 2004/1).<sup>3</sup>

The Bruker SHELXTL software package (Version 6.14)<sup>4</sup> was used for phase determination and structure refinement. The distribution of intensities ( $E^2 - 1 = 0.869$ ) and systematic absent reflections indicated two possible space groups, I2/a and Ia. The space group I2/a (#15) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified, including the disordered atoms. There was one disordered molecule of C<sub>26</sub>H<sub>44</sub>B<sub>2</sub>P<sub>2</sub> present in the asymmetry unit of the unit cell. The restraints, SADI, DELU, SIMU, and EADP were used to model the disorder groups (-C[CH<sub>3</sub>]<sub>3</sub>, -CH[CH<sub>3</sub>]<sub>2</sub>). The minor component of the -CH[CH<sub>3</sub>]<sub>2</sub> groups were refined with isotropic model. The structure was modeled as a pseudo-merohedral monoclinic twin that emulates the orthorhombic [TWIN 1 0 0, 0 -1 0, 0 0 -1, BASF = 0.5566,  $\beta = 90.142(19)^\circ$ ] system. It is very important to note that the data collected for this structure was of poor quality (high

<sup>1</sup> APEX 2, version 2.0-22, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.

<sup>2</sup> SAINT, version V7.23A, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

<sup>3</sup> SADABS, version 2004/1, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.

<sup>4</sup> SHELXTL, version 6.14, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.

su and low maximum  $2\theta$  angle of  $40.36^\circ$ . Even though the data quality was poor, the basic structure connectivity information of this compound is accurate.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F^2$ . The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at  $R1 = 0.0520$ ,  $wR2 = 0.1029$ , with intensity  $I > 2\sigma(I)$ . The largest peak/hole in the final difference map was  $0.254/-0.248 \text{ e}/\text{\AA}^3$ .

### X-Ray Structure Determination of 7a

A colorless fragment of a prism ( $0.51 \times 0.43 \times 0.24 \text{ mm}^3$ ) was used for the single crystal x-ray diffraction study of  $\text{C}_{40}\text{H}_{82}\text{B}_4\text{P}_4$  (sample gb101m; A24). The crystal was coated with paratone oil and mounted on to a glass fiber. X-ray intensity data were collected at 223(2) K on a Bruker SMART 1000 platform-CCD x-ray diffractometer system (Mo-radiation,  $\lambda = 0.71073 \text{ \AA}$ , 50KV/40mA power)<sup>5</sup> The CCD detector was placed at a distance of 4.9690 cm from the crystal.

A total of 1818 frames were collected for a sphere of reflections (with scan width of  $0.3^\circ$  in  $\omega$  and  $\phi$  angles of  $0^\circ$ ,  $120^\circ$ , and  $240^\circ$  for every 606, 606, and 606 frames, respectively, 10sec/frame exposure time). The frames were integrated using the Bruker SAINT software package<sup>6</sup> and using a narrow-frame integration algorithm. Based on a triclinic crystal system, the integrated frames yielded a total of 9909 reflections at a maximum  $2\theta$  angle of  $52.74^\circ$  ( $0.80 \text{ \AA}$  resolution), of which 4917 were independent reflections ( $R_{\text{int}} = 0.0182$ ,  $R_{\text{sig}} = 0.0235$ , redundancy = 2.0, completeness = 99.1%) and 4296 (87.4%) reflections were greater than  $2\sigma(I)$ . The unit cell parameters were,  $\mathbf{a} = 9.6416(14) \text{ \AA}$ ,  $\mathbf{b} = 9.9192(15) \text{ \AA}$ ,  $\mathbf{c} = 15.161(2) \text{ \AA}$ ,  $\alpha = 99.409(2)^\circ$ ,  $\beta = 99.848(2)^\circ$ ,  $\gamma = 117.657(2)^\circ$ ,  $V = 1215.4(3) \text{ \AA}^3$ ,  $Z = 1$ , calculated density  $D_c = 0.998 \text{ g/cm}^3$ . Absorption corrections were applied (absorption coefficient  $\mu = 0.179 \text{ mm}^{-1}$ ; max/min transmission = 0.9583/0.9142) to the raw intensity data using the SADABS program within the SAINT software.<sup>6</sup>

The Bruker SHELXTL (Version 6.14) software package<sup>4</sup> was used for phase determination and structure refinement. There were no systematic absent reflections. The distribution of intensities ( $E^2 - 1 = 0.909$ ) indicated two possible space groups, P1 and P-1. The space group P-1 was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified, including two of the disordered  $-\text{CH}[\text{CH}_3]_2$  groups that were attached to the two P-atoms. There was half a disordered-molecule of  $\text{C}_{40}\text{H}_{82}\text{B}_4\text{P}_4$  present in the asymmetry unit of the unit cell. The molecule was located on the inversion center. The two disordered- $\text{CH}[\text{CH}_3]_2$  groups site occupancy ratios were 76%/24%. (Isotropic refinement model of the minor component of the two disordered- $\text{CH}[\text{CH}_3]_2$  groups caused the three carbon atoms to be planar. Hence, the anisotropic refinement model of

<sup>5</sup> SMART Software Reference Manual, Version 5.054, Bruker AXS Inc., Madison, Wisconsin, USA.

<sup>6</sup> SAINT Software Reference Manual, Version 5.02, Bruker AXS Inc., Madison, Wisconsin, USA.

the minor component was used even though C15 had unusual thermal ellipsoid, indicating further disorder which could not be modeled successfully).

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F^2$ . All H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. The refinement converged at  $R1 = 0.0388$ ,  $wR2 = 0.1079$ , with intensity,  $I > 2\sigma(I)$ . The largest peak/hole in the final difference map was  $0.323/-0.167 \text{ e}/\text{\AA}^3$ .

### X-Ray Structure Determination 7b

A colorless fragment of a prism ( $0.35 \times 0.25 \times 0.14 \text{ mm}^3$ ) was used for the single crystal x-ray diffraction study of  $\text{C}_{39}\text{H}_{80}\text{B}_4\text{P}_4$  (sample gb231m; A-50). The crystal was coated with paratone oil and mounted on to a glass fiber. X-ray intensity data were collected at 218(2) K on a Bruker SMART 1000 platform-CCD x-ray diffractometer system (Mo-radiation,  $\lambda = 0.71073 \text{ \AA}$ , 50KV/40mA power).<sup>5</sup> The CCD detector was placed at a distance of 4.1770 cm from the crystal.

A total of 1818 frames were collected for a sphere of reflections (with scan width of  $0.3^\circ$  in  $\omega$  and  $\phi$  angles of  $0^\circ$ ,  $90^\circ$ , and  $180^\circ$ , for every 606 frames, 30sec/frame exposure time). The frames were integrated using the Bruker SAINT software package<sup>6</sup> and using a narrow-frame integration algorithm. Based on a monoclinic crystal system, the integrated frames yielded a total of 41048 reflections at a maximum  $2\theta$  angle of  $52.74^\circ$  ( $0.80 \text{ \AA}$  resolution), of which 9606 were independent reflections ( $R_{\text{int}} = 0.0548$ ,  $R_{\text{sig}} = 0.0501$ , redundancy = 4.3, completeness = 99.9%) and 6245 (65.0%) reflections were greater than  $2\sigma(I)$ . The unit cell parameters were,  $\mathbf{a} = 17.184(2) \text{ \AA}$ ,  $\mathbf{b} = 9.8153(12) \text{ \AA}$ ,  $\mathbf{c} = 28.413(3) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 101.509(4)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 4696.0(10) \text{ \AA}^3$ ,  $Z = 4$ , calculated density  $D_c = 1.013 \text{ g/cm}^3$ . Absorption corrections were applied (absorption coefficient  $\mu = 0.184 \text{ mm}^{-1}$ ; max/min transmission = 0.9746/0.9383) to the raw intensity data using the SADABS program in the SAINT software.<sup>6</sup>

The Bruker SHELXTL (Version 6.14) software package<sup>4</sup> was used for phase determination and structure refinement. The distribution of intensities ( $E^2 - 1 = 0.971$ ) and systematic absent reflections indicated one possible space group,  $P2(1)/c$ . The space group  $P2(1)/c$  (#14) was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified, including the disordered atoms. There was one disordered molecule of  $\text{C}_{39}\text{H}_{80}\text{B}_4\text{P}_4$  present in the asymmetry unit of the unit cell. Two of the  $-\text{CH}[\text{CH}_3]_2$  groups attached to P1 and P2, the  $-\text{CH}_3$  group attached to C18 of the aromatic ring were modeled with disorder. The disordered-site occupancy ratio was 66/34% where the minor component was refined as isotropic model.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F^2$ . All H-atoms were included in the refinement in calculated positions riding on the atoms they were attached. The refinement converged at  $R1 = 0.0588$ ,  $wR2 = 0.1387$ , with

intensity,  $I > 2\sigma(I)$ . The largest peak/hole in the final difference map was 0.495/-0.381  $e/\text{\AA}^3$ .