Electronic Supplementary Material (ESI) for CrystEngComm.


# Supplementary Information

# for the manuscript

## "Supramolecular interactions in boron hydrides: How non-classical bonding directs the crystal architecture"

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## S1 Computational Details

The unconstrained geometry optimisations for **1-4** were each performed at the B3LYP/6-311++G(d,p) level of approximation using the Gaussian09 software suite, starting from their experimentally determined geometries.[1] Tight convergence thresholds were imposed on these geometry optimisations with final maximum force and root-mean-square (rms) values as low as 0.000020 and 0.000008 hartrees/bohr, respectively. The subsequent topological analysis of the electron distributions and atomic properties for these systems were carried out using the AIM2000 software, while the δ values (delocalisation index) were calculated using the AIMALL package.[2,3] The electrostatic potentials superimposed on isodensity surfaces were generated from the original CIFs of **1-4** using the program CrystalExplorer, in which 'wavefunction fitting', DFT/6-311G(d,p), is performed by constraining these calculations to experimental X-ray diffraction data via Tonto.[4,5] This process leads to geometries that are in good agreement with the experimentally determined structures of these boranes, with the exception of the terminal B-H moieties which are fixed to neutron diffraction values for related B-H bonds (1.180 Å).


[1] M.J. Frisch et al. Gaussian09, Revision A.02, Gaussian Inc., Wallingford, CT (USA), 2009.

[2] F. Biegler-König, J. Schönbohm, D. Bayles, AIM2000-A program to analyse and visualize atoms in molecules, *J. Comput. Chem.*, 2001, **22**, 545.

[3] T.A. Keith, *AIMALL*, version 13.05.06, TK Gristmill Software, 2013.

[4] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, CrystalExplorer (Version 3.1), University of Western Australia, Perth, Australia, 2012.

[5] D. Jayatilaka, D.J. Grimwood, A. Lee, A. Lemay, A.J. Russel, C. Taylor, S.K. Wolff, Cassam-Chenai abd A. Whitton, *Tonto-A System for Computational Chemistry*, 2005.


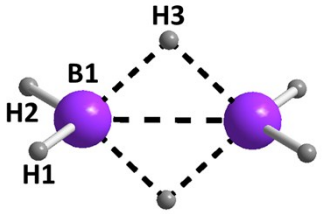


**Figure S1.** Schematic plot of **1**, with labels for the unique atoms.

**Table S1.** Salient geometrical parameters for the experimental and calculated structures of **1** (CE = CrystalExplorer).[5]

| Bond (Å) | X-Ray | Opt | CE | Angle (°) | X-Ray | Opt | CE |
|---|---|---|---|---|---|---|---|
| B1···B1[1] | 1.753(3) | 1.765 | 1.753 | B1-H3-B1[1] | 89.67(4) | 84.24 | 89.67 |
| B1-H1 | 1.102(2) | 1.186 | 1.180 | H1-B1-H2 | 124.29(6) | 121.83 | 124.29 |
| B1-H2 | 1.078(2) | 1.186 | 1.180 | H1-B1-H3 | 108.48(7) | 108.97 | 109.80 |
| B1-H3 | 1.233(2) | 1.315 | 1.233 | H2-B1-H3 | 109.52(5) | 109.10 | 109.14 |
| B1-H3[1] | 1.253(2) | 1.315 | 1.253 | | | | |
| H1···H3[2] | 2.733 | - | 2.670 | | | | |
| H2···H3[3] | 2.835 | - | 2.765 | | | | |

[1] -x,-y,-z [2] 0.5+x,-0.5+y,0.5-z [3] 0.5-x,0.5-y,0.5+z


[5] H.W. Smith, W.N. Lipscomb, *J. Chem. Phys.*, 1965, **43**, 1060.

**Table S2.** Salient topological parameters of the electron density for the optimised structure of **1**.

| Bond | $\rho_b(r)$ (eÅ$^{-3}$) | $\nabla^2\rho_b(r)$ (eÅ$^{-3}$) | δ(A,B) |
|---|---|---|---|
| B1···B1 | - | - | 0.097 |
| B1-H1 | 1.245 | -8.042 | 0.607 |
| B1-H2 | 1.245 | -8.042 | 0.607 |
| B1-H3 | 0.833 | 1.866 | 0.348 |

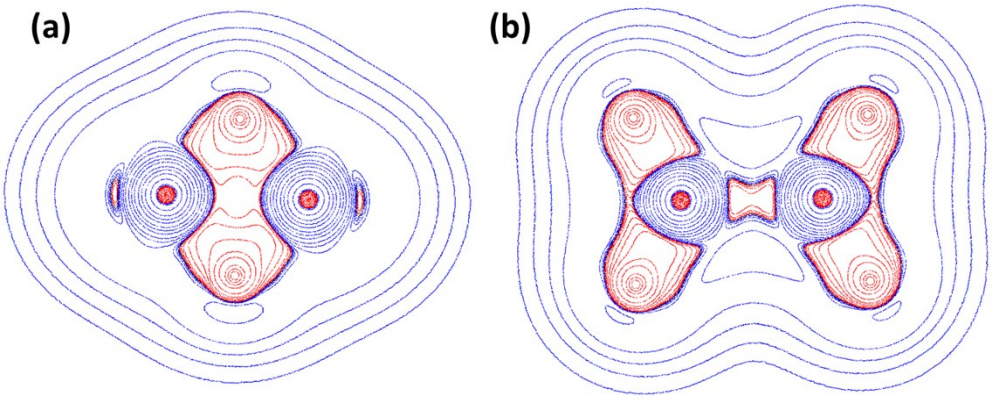


**Figure S2.** $\nabla^2\rho_b(\mathbf{r})$ plots in the plane of the B1-H3-B1 and H1-B1-B1 bonding in **1**. The positive (blue) and negative (red) contours are plotted in increments of 2.4 x 10$^{-2}$, 4.8 x 10$^{n}$, 9.6 x 10$^{n}$, and 1.9 x 10$^{n+1}$ (n = -2, -1, 0, 1, 2, and 3).

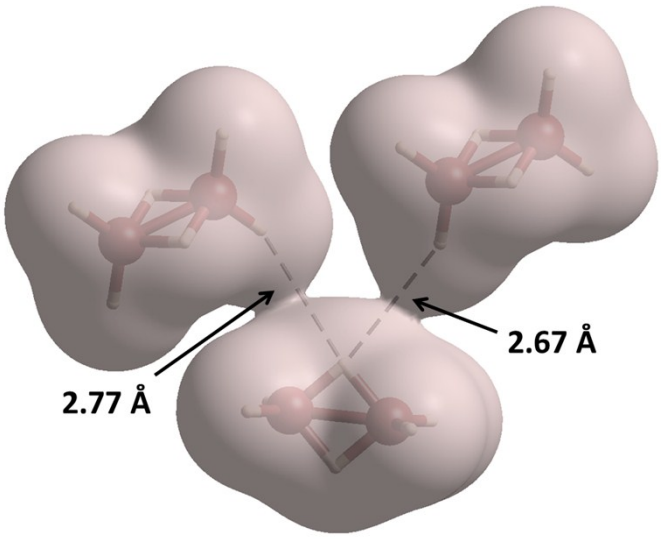


**Figure S3.** Plot of a 0.003 au isodensity surface of **1**, illustrating the maximum amount of density (~0.022 eÅ$^{-3}$) shared by each $B_2H_6$ moiety.

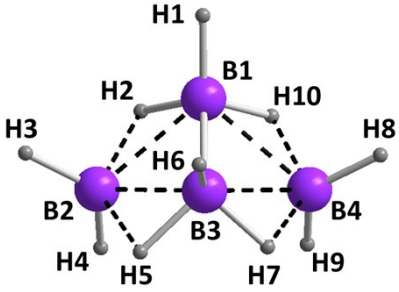


**Figure S4.** Schematic plot of **2** with labels for the unique atoms.

**Table S3.** Salient geometrical parameters for the experimental and calculated structures of **2** (CE = CrystalExplorer).[6]

| Bond (Å) | X-Ray | Opt | CE | Angle (°) | X-Ray | Opt | CE |
|---|---|---|---|---|---|---|---|
| B1-B3 | 1.709(4) | 1.721 | 1.709 | B1···B2···B3 | 55.38 | 55.09 | 55.38 |
| B1···B2 | 1.845(3) | 1.860 | 1.845 | B2···B3···B4 | 99.47 | 98.79 | 99.47 |
| B1···B4 | 1.843(7) | 1.861 | 1.843 | B3···B4···B1 | 55.33 | 55.07 | 55.33 |
| B3···B2 | 1.833(5) | 1.860 | 1.833 | B4···B1···B2 | 98.89 | 98.78 | 98.89 |
| B3···B4 | 1.838(4) | 1.861 | 1.838 | B1-H2···B2 | 91.76 | 88.08 | 91.76 |
| B1-H1 | 1.157(4) | 1.181 | 1.180 | B2···H5-B3 | 89.30 | 88.07 | 89.30 |
| B1-H2 | 1.129(3) | 1.257 | 1.129 | B3-H7···B4 | 95.09 | 88.14 | 95.05 |
| B1-H10 | 1.173(3) | 1.257 | 1.173 | B1-H10···B4 | 95.97 | 88.14 | 95.97 |
| B2···H2 | 1.424(4) | 1.414 | 1.424 | H1-B1-H2 | 109.94 | 111.23 | 109.94 |
| B2-H3 | 1.137(3) | 1.186 | 1.180 | H1-B1-H10 | 112.66 | 111.27 | 112.66 |
| B2-H4 | 1.086(4) | 1.192 | 1.180 | H2-B1-H10 | 96.74 | 93.82 | 96.74 |
| B2···H5 | 1.413(3) | 1.415 | 1.413 | H2···B2-H3 | 104.01 | 104.72 | 104.01 |
| B3-H5 | 1.185(2) | 1.257 | 1.185 | H2···B2-H4 | 96.29 | 95.80 | 96.29 |
| B3-H6 | 1.063(2) | 1.181 | 1.180 | H2···B2···H5 | 130.64 | 137.73 | 130.64 |
| B3-H7 | 1.141(4) | 1.257 | 1.141 | H3-B2-H4 | 126.74 | 119.02 | 126.74 |
| B4···H7 | 1.344(4) | 1.413 | 1.344 | H3-B2···H5 | 108.62 | 104.67 | 108.62 |
| B4-H8 | 1.118(2) | 1.186 | 1.180 | H4-B2···H5 | 92.86 | 95.80 | 92.86 |
| B4-H9 | 1.023(3) | 1.192 | 1.180 | H5-B3-H6 | 108.30 | 111.21 | 108.30 |
| B4···H10 | 1.304(3) | 1.414 | 1.304 | H5-B3-H7 | 92.34 | 93.86 | 92.34 |
| H1···H1[1] | 2.714 | - | 2.671 | H6-B3-H7 | 117.57 | 111.26 | 117.57 |
| H1···H5[2] | 2.615 | - | 2.599 | H7···B4-H8 | 107.82 | 104.78 | 107.82 |
| H1···H8[3] | 2.707 | - | 2.635 | H7···B4-H9 | 95.51 | 95.77 | 95.51 |
| H2···H9[4] | 2.896 | - | 2.768 | H7···B4···H10 | 130.66 | 137.61 | 130.66 |
| H3···H7[5] | 2.606 | - | 2.575 | H8-B4-H9 | 125.33 | 119.01 | 125.33 |
| H3···H10[6] | 2.644 | - | 2.616 | H8-B4···H10 | 102.79 | 104.78 | 102.79 |
| H4···H6[7] | 2.760 | - | 2.647 | H9-B4···H10 | 97.24 | 95.74 | 97.24 |
| H4···H9[4] | 2.912 | - | 2.711 | | | | |
| H4···H10[4] | 2.728 | - | 2.649 | | | | |
| H6···H9[2] | 2.739 | - | 2.522 | | | | |

[1]1-x,1-y,1-z; [2]0.5+x,0.5-y,0.5+z; [3]1-x,1-y,-z; [4]-x,1-y,-z
[5]x,y,1+z; [6]0.5-x,-0.5+y,0.5-z; [7]-0.5+x,0.5-y,-0.5+z

[6] E.B. Moore Jr., R.E. Dickerson, W.N. Lipscomb, *J. Chem. Phys.*, 1957, **27**, 209.

**Table S4.** Salient topological parameters of the electron density for the optimised structure of **2**.

| Bond | $\rho_b(r)$ (eÅ$^{-3}$) | $\nabla^2\rho_b(r)$ (eÅ$^{-3}$) | δ(A,B) |
|---|---|---|---|
| B1-B3 | 0.905 | -5.453 | 0.524 |
| B1···B2 | - | - | 0.151 |
| B1···B4 | - | - | 0.151 |
| B3···B2 | - | - | 0.151 |
| B3···B4 | - | - | 0.151 |
| B1-H1 | 1.233 | -6.735 | 0.670 |
| B1-H2 | 0.928 | 1.755 | 0.473 |
| B1-H10 | 0.927 | 1.764 | 0.473 |
| B2···H2 | 0.698 | 0.139 | 0.310 |
| B2-H3 | 1.247 | -8.030 | 0.615 |
| B2-H4 | 1.226 | -7.674 | 0.593 |
| B2···H5 | 0.697 | 0.132 | 0.309 |
| B3-H5 | 0.928 | 1.748 | 0.474 |
| B3-H6 | 1.233 | -6.733 | 0.670 |
| B3-H7 | 0.927 | 1.771 | 0.474 |
| B4···H7 | 0.698 | 0.181 | 0.310 |
| B4-H8 | 1.247 | -8.031 | 0.616 |
| B4-H9 | 1.225 | -7.674 | 0.593 |
| B4···H10 | 0.697 | 0.173 | 0.310 |

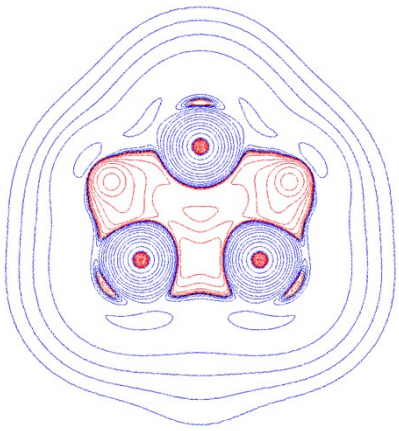

**Figure S5.** $\nabla^2\rho_b(\mathbf{r})$ plot in the plane of the B1-B2-B3 bonding in **2**. The positive (blue) and negative (red) contours are plotted in increments of 2.4 x $10^{-2}$, 4.8 x $10^{n}$, 9.6 x $10^{n}$, and 1.9 x $10^{n+1}$ (n = -2, -1, 0, 1, 2, and 3).

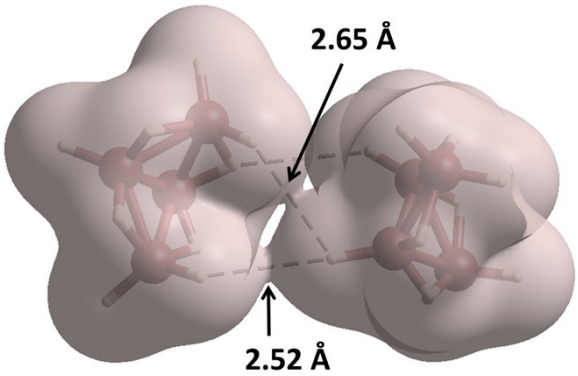


**Figure S6.** Plot of a 0.004 au isodensity surface of **2**, illustrating the maximum amount of density (~0.027 eÅ$^{-3}$) shared for selected B-H···H-B interactions.

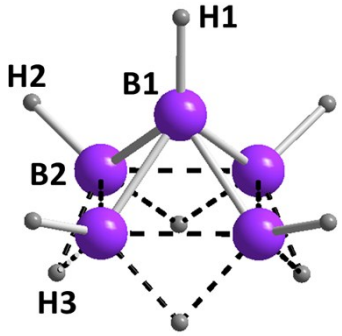


**Figure S7.** Schematic plot of **3** with labels for the unique atoms.

**Table S5.** Salient geometrical parameters for the experimental and calculated structures of **3** (CE = CrystalExplorer).[7]

| Bond (Å) | X-Ray | Opt | CE | Angle (°) | X-Ray | Opt | CE |
|---|---|---|---|---|---|---|---|
| B1-B2 | 1.659(18) | 1.695 | 1.659 | B1-B2···B2 | 57.71 | 57.96 | 57.71 |
| B2···B2 | 1.772(15) | 1.798 | 1.772 | H1-B1-B2 | 130.94 | 131.38 | 130.94 |
| B1-H1 | 1.21(5) | 1.178 | 1.180 | H2-B2-B1 | 114.75 | 131.74 | 114.75 |
| B2-H2 | 1.20(5) | 1.180 | 1.180 | B2···H3···B2 | 82.27 | 83.81 | 82.27 |
| B2-H3 | 1.35(5) | 1.346 | 1.347 | H2-B2···H3 | 117.41 | 108.07 | 117.41 |
| H1···H3[1] | 2.59 | - | 2.617 | | | | |
| H2···H2[2] | 2.46 | - | 2.503 | | | | |

[1]-x,-y,1+z; [2]1-x,-y,z

[7] W.J. Dulmage, W.N. Lipscomb, *Acta Cryst.*, 1952, **5**, 260.

**Table S6.** Salient topological parameters of the electron density for the optimised structure of **3**.

| Bond | $\rho_b(r)$ (eÅ$^{-3}$) | $\nabla^2\rho_b(r)$ (eÅ$^{-3}$) | δ(A,B) |
|---|---|---|---|
| B1-B2 | 0.913 | -3.979 | 0.524 |
| B2···B2 | - | - | 0.283 |
| B1-H1 | 1.201 | -5.472 | 0.752 |
| B2-H2 | 1.248 | -7.820 | 0.688 |
| B2-H3 | 0.804 | 0.295 | 0.403 |

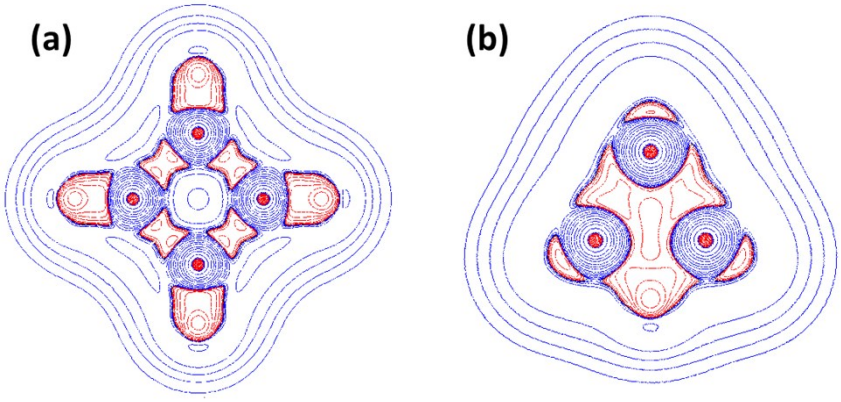


**Figure S8.** $\nabla^2\rho_b(\mathbf{r})$ plots in the plane of the B2-B2-B2 and B2-B1-B2 bonding in **3**. The positive (blue) and negative (red) contours are plotted in increments of 2.4 x $10^{-2}$, 4.8 x $10^{n}$, 9.6 x $10^{n}$, and 1.9 x $10^{n+1}$ (n = -2, -1, 0, 1, 2, and 3).

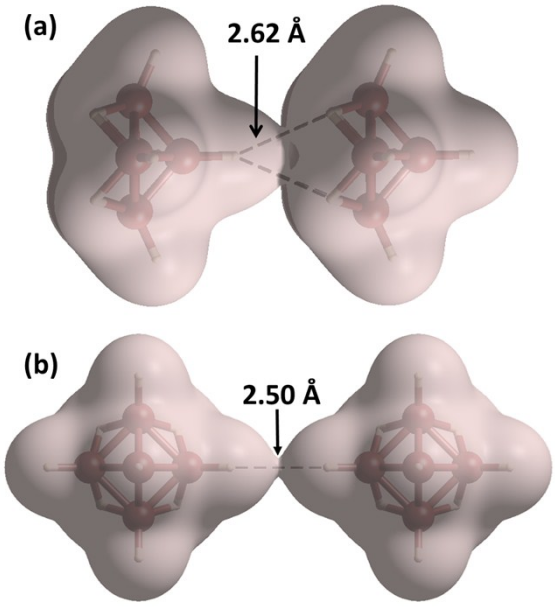


**Figure S9.** Plots of a 0.004 au isodensity surface for **3**, illustrating the maximum amount of density (~0.027 eÅ$^{-3}$) for (a) heteropolar B-H···H-B interactions and (b) homopolar B-H···H-B interactions between each $B_5H_9$ moiety.

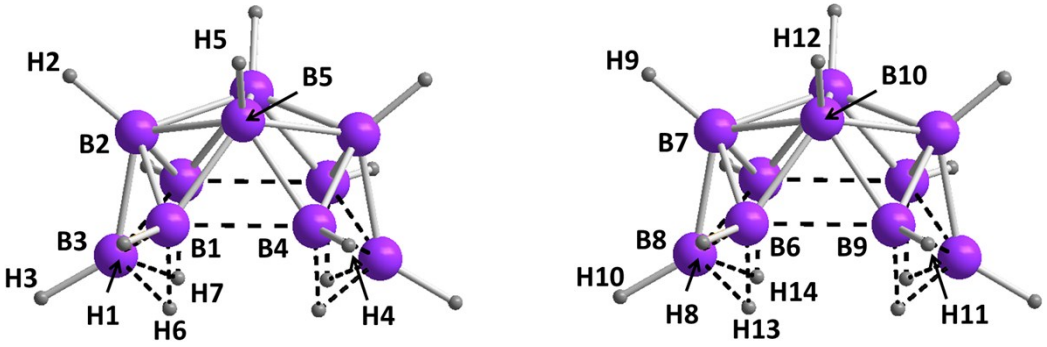


**Figure S10.** Schematic plot of **4** with labels for the unique atoms.

**Table S7.** Salient geometrical parameters for the experimental and calculated structures of **4** (CE = CrystalExplorer).[8]

| Bond (Å) | X-Ray | Opt | CE | Angle (°) | X-Ray | Opt | CE |
|---|---|---|---|---|---|---|---|
| **Molecule 1** | | | | | | | |
| B1-B2 | 1.792(2) | 1.792 | 1.791 | B1-B2-B3 | 61.06 | 61.19 | 61.07 |
| B1-B3 | 1.790(2) | 1.790 | 1.790 | B1-B2-B5 | 58.53 | 58.59 | 58.52 |
| B1-B4 | 1.988(2) | 1.991 | 1.988 | B1-B5-B4 | 69.22 | 69.35 | 69.17 |
| B1-B5 | 1.749(2) | 1.750 | 1.749 | B2-B3-B4 | 61.14 | 61.27 | 61.23 |
| B2-B3 | 1.731(2) | 1.724 | 1.731 | B2-B4-B5 | 60.54 | 60.52 | 60.46 |
| B2-B4 | 1.787(3) | 1.792 | 1.789 | B2-B5-B5 | 60.22 | 60.00 | 60.01 |
| B2-B5 | 1.787(2) | 1.785 | 1.787 | B1-H6-B3 | 83.76 | 84.87 | 83.76 |
| B3-B4 | 1.782(3) | 1.790 | 1.780 | B3-H7-B4 | 83.79 | 84.88 | 83.83 |
| B4-B5 | 1.751(2) | 1.750 | 1.753 | | | | |
| B5-B5 | 1.779(3) | 1.785 | 1.779 | | | | |
| B1-H1 | 1.186(3) | 1.181 | 1.180 | | | | |
| B2-H2 | 1.186(3) | 1.181 | 1.180 | | | | |
| B3-H3 | 1.177(5) | 1.180 | 1.180 | | | | |
| B4-H4 | 1.190(4) | 1.181 | 1.180 | | | | |
| B5-H5 | 1.191(10) | 1.183 | 1.180 | | | | |
| B1-H6 | 1.327(4) | 1.318 | 1.328 | | | | |
| B3-H6 | 1.354(2) | 1.335 | 1.354 | | | | |
| B3-H7 | 1.344(4) | 1.335 | 1.344 | | | | |
| B4-H7 | 1.324(4) | 1.318 | 1.321 | | | | |
| H1···H9[1] | 2.650 | - | 2.657 | | | | |
| H1···H10[2] | 2.569 | - | 2.574 | | | | |
| H1···H12[3] | 2.593 | - | 2.602 | | | | |
| H2···H3[4] | 2.585 | - | 2.589 | | | | |
| H2···H8[3] | 2.677 | - | 2.684 | | | | |
| H3···H4[5] | 2.787 | - | 2.789 | | | | |
| H3···H8[6] | 2.552 | - | 2.551 | | | | |
| H4···H12[1] | 2.554 | - | 2.569 | | | | |
| H4···H13[2] | 2.653 | - | 2.660 | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H5···H6[4] | 2.405 | - | 2.411 | | | | |
| H5···H7[7] | 2.413 | - | 2.419 | | | | |
| H5···H8[2] | 2.565 | - | 2.572 | | | | |
| H5···H11[3] | 2.574 | - | 2.588 | | | | |
| H6···H11[6] | 2.617 | - | 2.624 | | | | |
| **Molecule 2** | | | | | | | |
| B6-B7 | 1.792(3) | - | 1.792 | B6-B7-B8 | 61.08 | - | 61.08 |
| B6-B8 | 1.792(2) | - | 1.792 | B6-B7-B10 | 58.57 | - | 58.57 |
| B6-B9 | 1.986(2) | - | 1.986 | B6-B10-B9 | 69.05 | - | 69.05 |
| B6-B10 | 1.750(2) | - | 1.750 | B7-B8-B9 | 61.08 | - | 61.08 |
| B7-B8 | 1.733(2) | - | 1.733 | B7-B9-B10 | 60.49 | - | 60.49 |
| B7-B9 | 1.787(3) | - | 1.783 | B7-B10-B10 | 60.23 | - | 60.23 |
| B7-B10 | 1.784(2) | - | 1.784 | B6-H13-B8 | 84.33 | - | 84.33 |
| B8-B9 | 1.783(3) | - | 1.783 | B8-H14-B9 | 83.60 | - | 83.60 |
| B9-B10 | 1.755(2) | - | 1.755 | | | | |
| B10-B10 | 1.772(3) | - | 1.771 | | | | |
| B6-H8 | 1.183(3) | - | 1.180 | | | | |
| B7-H9 | 1.185(3) | - | 1.180 | | | | |
| B8-H10 | 1.183(4) | - | 1.180 | | | | |
| B9-H11 | 1.190(5) | - | 1.180 | | | | |
| B10-H12 | 1.193(3) | - | 1.180 | | | | |
| B6-H13 | 1.321(4) | - | 1.321 | | | | |
| B8-H13 | 1.349(4) | - | 1.349 | | | | |
| B8-H14 | 1.346(4) | - | 1.346 | | | | |
| B9-H14 | 1.329(4) | - | 1.329 | | | | |
| H9···H10[8] | 2.568 | - | 2.573 | | | | |
| H9···H10[9] | 2.783 | - | 2.787 | | | | |
| H12···H13[8] | 2.415 | - | 2.422 | | | | |
| H12···H14[10] | 2.410 | - | 2.413 | | | | |

[1]-0.5+x,1+y,-z; [2]-0.5+x,1+y,1-z; [3]x,1+y,z; [4]x,y,1+z; [5]0.5+x,y,-z; [6]x,1+y,-1+z; [7]-x,0.5-y,1+z; [8]x,y,-1+z; [9]1-x,-1-y,1-z; [10]0.5-x,-1-y,-1+z

[8] R. Brill, H. Dietrich, H. Dierks, *Acta Cryst.*, 1971, **B27**, 2003.

**Table S8.** Salient topological parameters of the electron density for the optimised structure of **4**.

| Bond | $\rho_b(r)$ (eÅ$^{-3}$) | $\nabla^2\rho_b(r)$ (eÅ$^{-3}$) | δ(A,B) |
|---|---|---|---|
| B1-B2 | 0.790 | -2.731 | 0.428 |
| B1-B3 | - | - | 0.271 |
| B1-B4 | - | - | 0.364 |
| B1-B5 | 0.801 | -3.166 | 0.500 |
| B2-B3 | 0.871 | -4.153 | 0.512 |
| B2-B4 | 0.790 | -2.731 | 0.428 |
| B2-B5 | 0.781 | -2.730 | 0.430 |
| B3-B4 | - | - | 0.270 |

| | | | |
|---|---|---|---|
| B4-B5 | 0.801 | -3.164 | 0.500 |
| B5-B5 | 0.782 | -2.187 | 0.465 |
| B1-H1 | 1.256 | -7.944 | 0.700 |
| B2-H2 | 1.231 | -6.674 | 0.734 |
| B3-H3 | 1.262 | -8.406 | 0.675 |
| B4-H4 | 1.256 | -7.945 | 0.698 |
| B5-H5 | 1.234 | -7.069 | 0.724 |
| B1-H6 | 0.817 | 2.068 | 0.425 |
| B3-H6 | 0.839 | -0.631 | 0.412 |
| B3-H7 | 0.839 | -0.630 | 0.412 |
| B4-H7 | 0.817 | 2.069 | 0.425 |

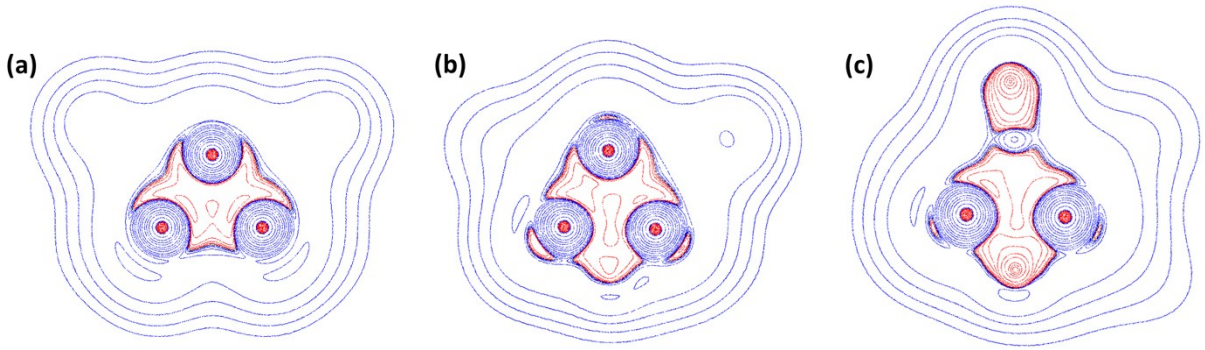


**Figure S11.** $\nabla^2\rho_b(\mathbf{r})$ plots in the plane of the B1-B5-B4, B1-B2-B3, and B1-H6-B3 bonding in **4**. The positive (blue) and negative (red) contours are plotted in increments of 2.4 x $10^{-2}$, 4.8 x $10^{n}$, 9.6 x $10^{n}$, and 1.9 x $10^{n+1}$ (n = -2, -1, 0, 1, 2, and 3).

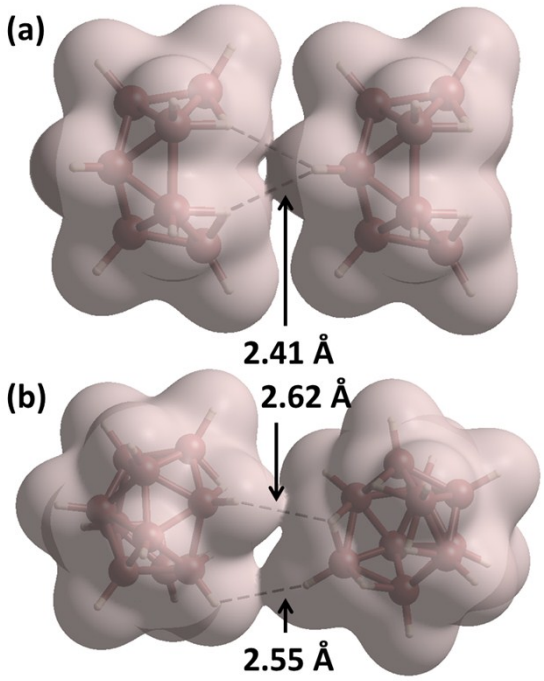


**Figure S12.** Plots of (a) 0.0055 au and (b) 0.004 au isodensity surfaces for **4**, illustrating the maximum amount of density (~0.037 and 0.027 eÅ$^{-3}$, respectively) shared for selected B-H···H-B interactions.