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Pathways to the Polymerization of Boron Monoxide Dimer To Give Low-Density Porous Materials Containing Six-Membered Boroxine Rings

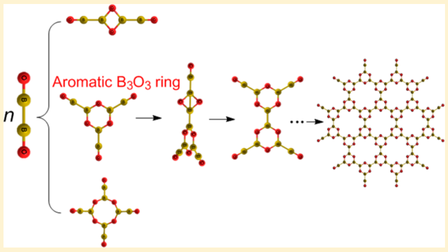
Zhong Zhang,*[†,‡] Liang Pu,[†] Qian-shu Li,[‡] and R. Bruce King*[§]

[†]College of Science, Northwest A&F University, Yangling, Shanxi 712100, P. R. China

[‡]Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, P. R. China

[§]Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, United States

S Supporting Information



ABSTRACT: Density functional theory has been used to examine the key mechanistic details of the polymerization of boron monoxide (BO) via its O≡B−B≡O dimer to give ultimately low-density porous polymeric $(BO)_n$ materials. The structures of such materials consist of planar layers of six-membered boroxine (B_3O_3) rings linked by boron−boron bonds. Initial cyclooligomerization of B_2O_2 leads to a B_4O_4 dimer with a four-membered B_2O_2 ring, a B_6O_6 trimer containing a six-membered B_3O_3 (boroxine) ring, a B_8O_8 tetramer containing an eight-membered B_4O_4 ring, and even a $B_{10}O_{10}$ pentamer containing a ten-membered B_5O_5 ring. However, an isomeric $B_{10}O_{10}$ structure containing two boroxine rings linked by a B−B bond is a much lower energy structure by ∼31 kcal/mol owing to the special stability of the aromatic boroxine rings. Rotation of the boroxine rings around the central B−B bond in this $B_{10}O_{10}$ structure has a low rotation barrier suggesting that further oligomerization to give products containing either perpendicular or planar orientations of the B_3O_3 rings is possible. However, the planar oligomers are energetically more favorable since they have fewer high-energy external BO groups bonded to the network of boroxine rings. The pendant boronyl groups are reactive sites that can be used for further polymerization. Mechanistic aspects of the further oligomerization of $(BO)_x$ systems to give a $B_{24}O_{24}$ oligomer with a naphthalene-like arrangement of boroxine rings and a $B_{84}O_{84}$ structure with a coronene-like arrangement of boroxine rings have been examined. Further polymerization of these intermediates by similar processes is predicted to lead ultimately to polymers consisting of planar networks of boroxine rings. The holes between the boroxine rings in such polymers suggests that they will be porous low-density materials. Applications of such materials as absorbents for small molecules are anticipated.

1. INTRODUCTION

The well-known allotropes of carbon, i.e., two-dimensional graphite and three-dimensional diamond, are rare examples of naturally occurring covalently bonded nonoxide polymers. Boron nitride (BN), isoelectronic with C_2, also forms analogous allotropes with graphite-like[1] and diamond-like[2] structures. In addition, molecules containing the boronyl (BO) and thioboronyl (BS) groups, such as $H_3C{-}B{\equiv}O$,[3] and $Cl{-}B{\equiv}S$,[4] are also isovalent with BN/C_2 units to the extent that the BE (E = O or S) unit can be interpreted as the BE^+ cation. This clearly is the case with Cl−B≡S which can formally be dissected into BS^+ and Cl^-. Alternatively the BO radical could be considered to be analogous to hydrogen or an alkyl radical.[5] In this connection, molecules containing BO groups, such as $B(BO)_2^-$,[6] $B_2(BO)_2^{2-}$,[7] and $C_2(BO)_2$,[8] have been observed in low temperature matrices. Furthermore, several boronyl clusters have been predicted theoretically, including the global minimum B_6O_6 having three terminal boronyl groups attached to the weak π aromatic boroxine ring by a B−B single bond.[9] The BO structural units are preserved as integral groups owing to the strong binding energy of the formal B≡O triple bonds.[10] However, such terminal boronyl groups, because of their B≡O triple bonds, provide highly reactive functionalities for further oligomerization, polymerization, and other addition reactions. Thus, organic boronyl compounds, R−B≡O, are generally unstable molecules since the reactive boronyl groups oligomerize into B_2O_2 or B_3O_3 rings.[11−13]

Free monomeric boron monoxide (BO), unlike monomeric CO or even the likewise odd-electron NO molecule, is unstable under ambient conditions. Thus, boron monoxide was first detected by Mulliken in 1924[14] as a component of a gaseous mixture obtained from an electrical discharge in a BCl_3/O_2 mixture. Under ambient conditions BO exists as a polymer, synthesized by indirect methods not requiring the generation of monomeric BO. Thus, polymeric $(BO)_x$ can be obtained either by the dehydration of $B_2(OH)_4$,[15] itself obtained by the hydrolysis of B_2Cl_4 or $B_2(NMe_2)_4$, or by the high temperature reaction of B_2O_3 with elemental boron.[16] The structure of polymeric BO is unknown. However, it is assumed to have B−B

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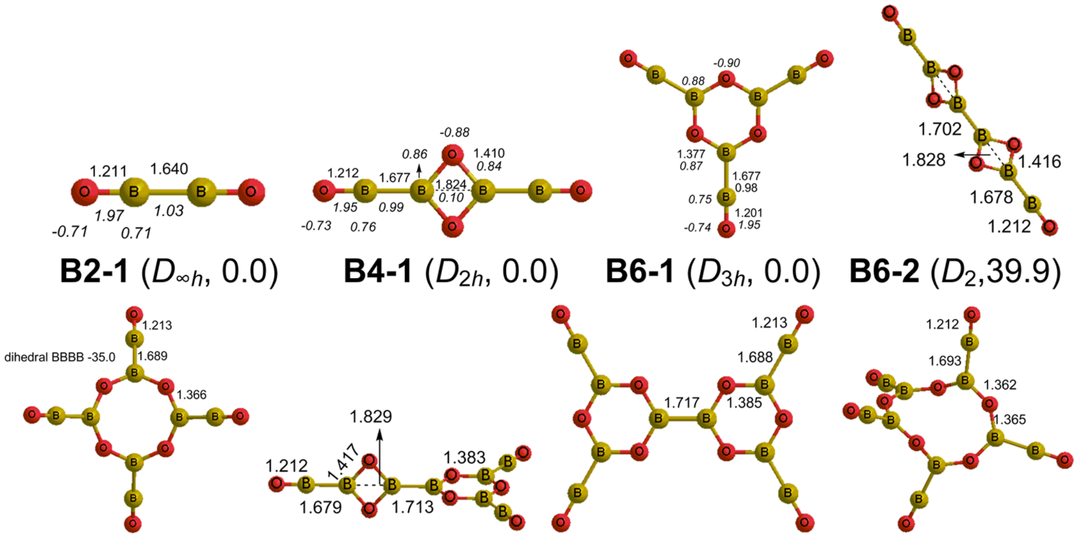

B2-1 ($D_{\infty h}$, 0.0) **B4-1** (D_{2h}, 0.0) **B6-1** (D_{3h}, 0.0) **B6-2** (D_2,39.9)

B8-1 (D_{2d}, 0.0) **B8-2** (C_{2v},3.2) **B10-1** (D_{2h},0.0) **B10-2** (C_2,31.3)

Figure 1. Selected $(B_2O_2)_n$ (n = 1, 2, 3, 4, 5) structures. The Wiberg bond indices (WBIs) as well as the natural charges are given in *italics*. Symmetry point groups and relative free energies (kcal/mol) are given in parentheses.

bonds as well as B−O bonds because of its origin from $B_2(OH)_4$ containing a B−B bond.

Although BO is unstable as a monomeric species, Braunschweig and co-workers[17] have recently shown that BO can be stabilized by complexation with a transition metal in a metal boronyl complex, synthesized by indirect methods not requiring the generation of unstable BO. Thus, the platinum boronyl complex $(Cy_3P)_2Pt(BO)Br$ with a terminal BO group can be obtained by the reaction of $(Cy_3P)_2Pt$ with $Me_3SiOBBr_2$ with concurrent elimination of Me_3SiBr. Subsequently, the trinuclear ruthenium complex $[Cp^*Ru]_3(\mu_2\text{-}H)_2(\mu_3\text{-}H)(CPh)(\mu_3\text{-}BO)$ with a μ_3-BO group bridging an Ru_3 triangle was obtained by Suzuki and co-workers from the direct reaction of $[Cp^*Ru]_3(\mu_2\text{-}H)_2(\mu_3\text{-}H)_2(Ph)(\mu_3\text{-}BH)$ with H_2O.[18] Complexation of boron monoxide with platinum as a terminal ligand in $(Cy_3P)_2Pt(BO)Br$ does not completely prevent its susceptibility toward oligomerization. Thus, debromination of $(Cy_3P)_2Pt(BO)Br$ using the Ag^+ cation leads to cyclodimerization of the BO ligand to give $[(Cy_3P)_2Pt_2(B_2O_2)]^{2+}$ containing a cyclic B_2O_2 ligand bridging the two Pt atoms.[19]

Possible structures for $(BO)_x$ polymers have recently been investigated by Claeyssens and co-workers[20] using density functional theory. Their study focused on possible $(BO)_x$ polymer structures containing six-membered B_4O_2/B_3O_3 rings originating from condensation polymerization by the dehydration of diboronic acid, $B_2(OH)_4$.[15] No suggestions were provided by Claeyssens and co-workers[20] was given regarding possible mechanistic details of obtaining such $(BO)_x$ polymers from low molecular weight boron oxide species.

An alternative route to polymeric $(BO)_x$ is the addition polymerization of boron monoxide. Since BO is a paramagnetic species with an odd number of electrons, the first stage of its polymerization is likely to be its dimerization to B_2O_2 (biboronyl) with an even number of electrons. We have now used density functional theory to predict that the further polymerization of B_2O_2 can lead to low-density polymers constructed from planar networks of boroxine (B_3O_3) rings. Such polymeric $(BO)_x$ networks differ from the networks previously suggested by the previous density functional study[20] that contain nonplanar B_4O_2 rings. The formation of such B_4O_2 rings is expected to occur from the dehydration of $B_2(OH)_4$ in the reported[15] synthesis of $(BO)_x$. Our studies reported here consider not only the thermodynamics and kinetics of the further oligomerization of B_2O_2 to higher B_nO_n oligomers but also the mechanisms of such processes. The results show that the cyclotrimer of B_2O_2 with a $B_3O_3(BO)_3$ triboronylboroxine structure rather than the cyclodimer or cyclotetramer is the dominant initial B_2O_2 oligomerization product owing to the aromaticity of the central B_3O_3 ring. In fact, the cyclotrimerization of O≡B−B≡O involving one of the B≡O triple bonds can be viewed as analogous to the cyclotrimerization of acetylene to give benzene.[21] Furthermore, the $B_3O_3(BO)_3$ trimer arising from this initial process can further oligomerize by using its three terminal boronyls as sites for further reactivity. This leads ultimately to polymers having graphene-like structures in which the carbon atoms of graphene are replaced by planar B_3O_3 boroxine rings. Recently, planar B_3O_3 boroxine rings have been found in B_2O_3 polymers connected by flexible B−O−B motifs in several different forms.[22,23] Such polymers are likely to be novel low-density porous materials owing to cavities between the boroxine rings in their structures.

2. THEORETICAL METHODS

Computations were performed using the popular B3LYP method, which is a hybrid HF/DFT method combining the three-parameter Becke functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[24,25] All computations were performed using double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for boron and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(B) = 0.70$ and $\alpha_d(O) = 0.85$ to the standard Huzinaga−Dunning contracted DZ sets.[26−28]

The geometries of all structures were fully optimized using the B3LYP/DZP method. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. All of the computations were carried out with the Gaussian 09 program,[29] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[30] while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence. The reported free energies (ΔG) were obtained by applying zero point energy corrections to the initially

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obtained ΔH values. The Wiberg bond indices (WBIs)[31] were obtained from the orthogonal natural atom orbitals (NAO)[32] in the natural bond orbital (NBO)[33] calculations.

The optimized structures are listed in Figure 1−6. A given B_nO_n structure is designated as **B*n*−*m*** where ***n*** is the number of boron atoms (the same as the number of oxygen atoms) and ***m*** orders the structures according to their relative free energies. Thus, the lowest energy structure of B_6O_6 is designated **B6−1**.

3. RESULTS AND DISCUSSION

3.1. Oligomers $(B_2O_2)_n$ (*n* = 2, 3, 4, 5). The B_2O_2 and $OB-C_2-BO$ molecules can be generated in low temperature matrices and thus are potential monomers for polymerization under mild conditions below room temperature.[10,34] We therefore chose the reactive B_2O_2 molecule as the starting point for the formation of $(BO)_x$ polymers. In this connection, we predict two BO radicals[34] to dimerize exothermally into B_2O_2 by releasing free energy of 107.6 kcal/mol. The global minimum B_2O_2 structure contains two boronyl groups connected by a B−B single bond of length 1.640 Å (Figure 1). The predicted B−O distances of 1.211 Å, as determined by X-ray crystallography, are the same as the experimental B−O distance of 1.210 Å in the stable $(Cy_3P)_2Pt(BO)Br$ complex.[17] The natural charges on the boron and oxygen atoms are predicted to be 0.71 and −0.71, respectively, consistent with the highly polarized B≡O bonds for easy protonation.[18] The interesting B_2O_2 molecule is formally derived from the known $B_2(OH)_4$ by loss of two water molecules and thus may be regarded as the anhydride of $B_2(OH)_4$. However, such double dehydration of $B_2(OH)_4$ to give O≡B−B≡O is strongly thermodynamically disfavored with a predicted very large free energy of 65.6 kcal/mol required for this process (Figure S4 in the SI). Instead dehydration of $B_2(OH)_4$ is likely to generate a polymeric cyclic anhydride containing a chain of fused B_4O_2 rings rather than monomeric O≡B−B≡O. Such a polymeric cyclic anhydride with B_4O_2 rings is the basis of the $(BO)_x$ polymer studies suggested in a recent DFT study.[20] Thus, experimental realization of the polymerization processes discussed in this paper to give the porous $(BO)_x$ cannot use $B_2(OH)_4$ as a starting point. Instead experimental methods must be developed to generate B_2O_2 (O≡B−B≡O) as a reactive intermediate using other boron sources.

The next higher boron monoxide oligomer, namely B_4O_4, was found to exhibit structure **B4−1** having a central B_2O_2 ring with external BO groups bonded to both ring boron atoms (Figure 1). Our predicted B−O bond distances of 1.410 Å in the B_2O_2 ring are almost identical to the experimentally known B_2O_2 ring in $[(Cy_3P)_2Pt_2(B_2O_2)]^{2+}$ with an average B−O distance of 1.413 Å.[19] The equivalent B−O bonds in the B_2O_2 ring of **B4−1** are formal single bonds, as suggested by their Wiberg bond indices of 0.84 close to unity. Thus, the relatively short nonbonding B···B distance in **B4−1** of 1.824 Å originates mainly from the four-membered B_2O_2 ring structure and repulsion of the lone pairs on the two oxygen atoms, analogous to the Si_2O_2 ring.[35] Formation of **B4−1** arises from dimerization of two B_2O_2 molecules by the positively charged boron atom and the negatively charged oxygen atom in a B≡O bond of one B_2O_2 molecule attracting the oxygen and boron atoms, respectively, in a B≡O bond of the other B_2O_2 molecule. The predicted exothermicity of this dimerization process liberating free energy of 23.7 kcal/mol can be related to the reactivity of the polarized π bonds in boronyl groups. This dimerization of B_2O_2 is also kinetically feasible because of the small activation free energy of 13.7 kcal/mol (Figure 2). However, B_4O_4 (Figure 2) is not expected to be a viable molecule for two reasons. First, the lowest energy B_4O_4 structure still has two highly energetic B≡O bonds, which could drive B_4O_4 into a linear polymer with alternating B−B single bonds and B_2O_2 rings. However, a linear polymer of this type was shown by Claeyssens and co-workers in their DFT study[20] to be a structure of such high energy not to be chemically realizable. In addition, the B_2O_2 ring is potentially an unstable motif, since the strained and more polarized four-membered ring might be a driving force for further oligomerization to form larger rings. Considerations similar to those discussed above lead to two different structures to be considered for B_6O_6. The lowest energy structure, i.e., **B6−1** (Figure 1), has a B_3O_3 ring with six B−O bonds and three external boronyl groups bonded to the ring boron atoms. The B−O bond distances in the six-membered ring are found to be 1.377 Å, which is 0.03 Å shorter than those in B_4O_4. This bond shortening is attributed to the aromaticity[5] stabilizing the six-membered ring as well as the smaller steric repulsion in the larger ring. Structure **B6−1** arises from the addition of B_2O_2 to B_4O_4 by using a polarized boronyl group in B_2O_2 to attack the more polarized B_2O_2 ring in B_4O_4. The reported reaction free energy of −62.0 kcal/mol and activation free energy of 11.5 kcal/mol for this process obviously suggest the easy formation of **B6−1**. These B_6O_6 formation mechanisms from B_2O_2 are nearly unaffected in dichloromethane and water solvents (Figure S5 in the SI). The second B_6O_6 structure **B6−2** (Figure 1), has two B_2O_2 fragments joined by a B−B single bond (1.702 Å), which is elongated owing to the repulsion of the two B_2O_2 rings. However, **B6−2** is predicted to lie 39.9 kcal/mol in energy above the global minimum **B6−1** and thus is not likely to be chemically significant.

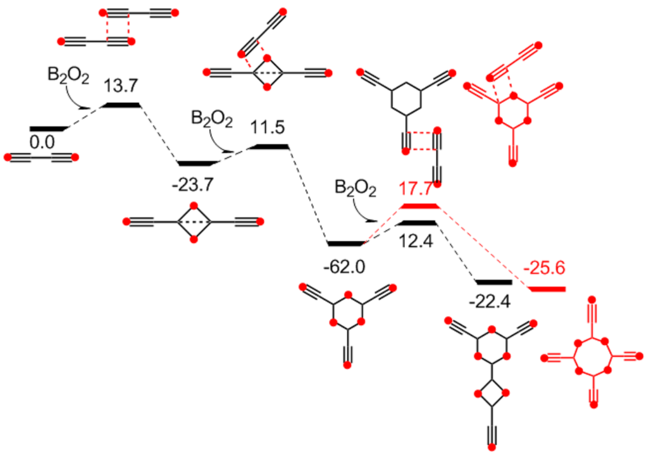

Figure 2. Predicted B_2O_2 cyclooligomerization mechanisms as far as B_8O_8. In Figures 2, 5, and 6, the oxygen atoms are indicated by red dots.

The highly energetic boronyl groups in B_6O_6 also can add to the boronyl groups in a B_2O_2 molecule thereby leading to B_8O_8 structures either with an eight-membered B_4O_4 ring (**B8−1**) or with a six-membered B_3O_3 ring linked to a four-membered B_2O_2 ring by a B−B bond (Figure 1). The lower energy of these B_8O_8 structures (**B8−1**) has a bent eight-membered B_4O_4 ring with a pendant BO group bonded to each of the four ring boron atoms. The second B_8O_8 structure **B8−2**, lying only 3.2 kcal/mol above **B8−1**, has a six-membered B_3O_3 ring bonded to a four-membered B_2O_2 ring by a B−B bond. In **B8−2**, the planes of the B_3O_3 and B_2O_2 rings are perpendicular. The slightly higher energy B_8O_8 structure **B8−2** is kinetically favored over **B8−1**, since the predicted 12.4 kcal/mol activation free energy for formation of **B8−2** is 5.3 kcal/mol lower than that of **B8−1**.

The B_8O_8 structure **B8−2** is a key intermediate for further oligomerization to the lowest energy $B_{10}O_{10}$ structure **B10−1** containing two aromatic B_3O_3 rings (Figure 1). Unlike the two benzene rings in biphenyl,[36] the two B_3O_3 boroxine rings in **B10−1** are coplanar. However, the rotation barrier of two boroxine rings around the B−B single bond connecting the two rings is predicted to be ∼0.3 kcal/mol, indicating free rotation. Addition of B_2O_2 to the B_8O_8 structure **B8−2** gives a $B_{10}O_{10}$ structure **B10−2** (Figure 1) containing a ten-membered B_5O_5 ring. However, this structure is found to have a relative free energy of 31.3 kcal/mol above **B10−1**.

3.2. Larger Oligomers. The $B_{10}O_{10}$ structure **B10−1** has isomers with two boroxine rings perpendicular to each other lying 0.3 kcal/mol below **B10−1** (Figure 3). Therefore, further oligomerization can lead to two different $B_{18}O_{18}$ structures, namely planar **B18−1** and perpendicular **B18−2** (Figure 4). The $B_{18}O_{18}$ structure **B18−1** with four coplanar B_3O_3 rings is slightly favored over the nonplanar $B_{18}O_{18}$ structure **B18−2** with the outer three B_3O_3 rings each perpendicular to the central B_3O_3 ring (Figure 4) because of the smaller relative free energy of −3.2 kcal/mol. However, the naphthalene-like planar $B_{42}O_{42}$ structure (**B42−1**) is predicted to lie 81.9 kcal/mol below the perpendicular $B_{42}O_{42}$ structure **B42−2** (Figure 4), since the planar **B42−1** has nine highly energetic external boronyl groups whereas the perpendicular **B42−2** structure has ten such external boronyls (Figure 4). For this reason, the planar two-dimensional structure is more stable than the diamond structure. We also optimized a coronene-like $B_{84}O_{84}$ structure (**B84−1** in Figure 4), which is a stoichiometric dimer of **B42−1** with a dimerization free energy of −160.5 kcal/mol (Figure 4). We therefore predict such B_2O_2 polymers to be viable. A major reason for the viability of such boron oxide polymers appears to be the aromaticity of the B_3O_3 rings.

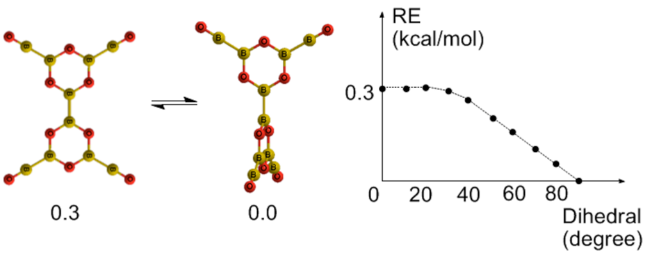

Figure 3. Rotation potential energy surface of the $B_{10}O_{10}$ structure **B10−1**. Relative free energies and relative electronic energies are given in kcal/mol.

The B_6O_6 unit also can be regarded as a basic building block for the formation of polymers with boroxine rings. As shown in Figure 5, this channel is slightly more favorable than the B_2O_2 channel (Figure 2) since the former one has smaller activation free energies.

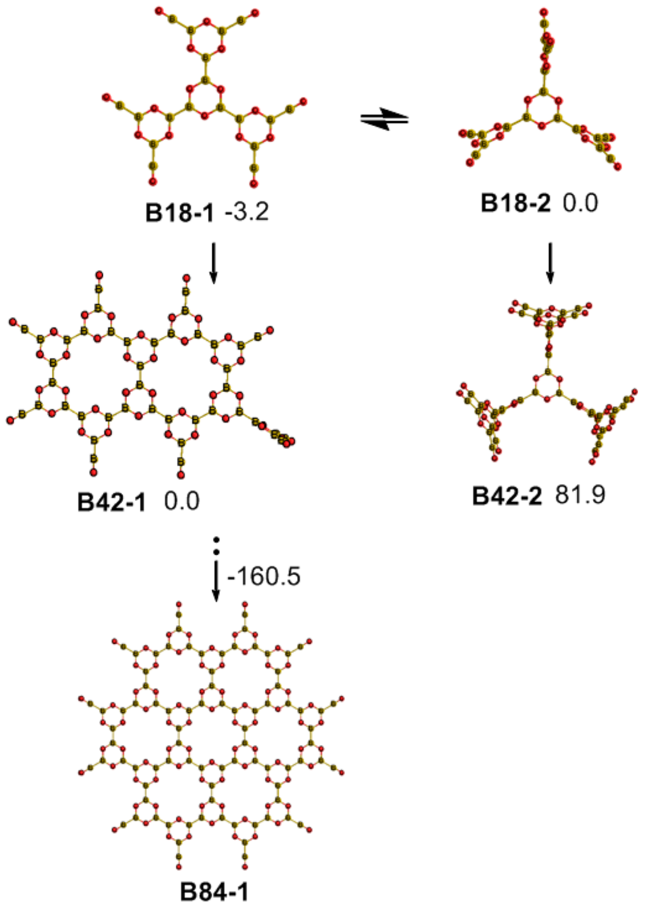

Figure 4. Calculated structures of larger $(BO)_n$ polymers.

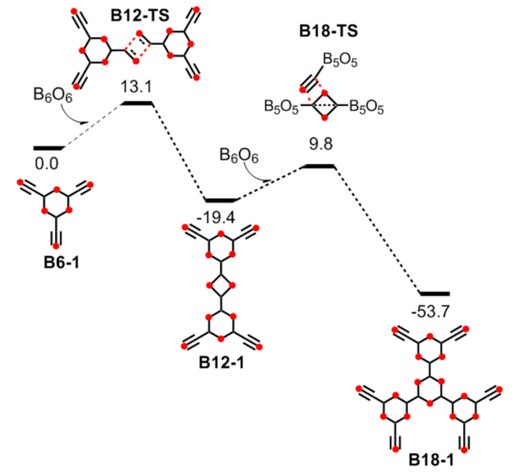

Figure 5. Mechanisms for the formation of $(B_6O_6)_m$ derivatives.

The above results show that formation of a two-dimensional polymer from the polymerization of boron monoxide via B_2O_2 and B_6O_6 intermediates is energetically viable. Another key question is whether the smaller planar benzene-like $B_{24}O_{24}$ intermediate with a central hexagon of connected boroxine rings is kinetically viable. A $B_{22}O_{22}$ structure was chosen as the starting point (**B22** in Figure 6). Two different channels were investigated (Figure 6). In the lower channel (black) the initial $B_{22}O_{22}$ structure isomerizes to the more stable structure **B22a** with a B_2O_2 ring originating from dimerization of two boronyls in $B_{22}O_{22}$. Conversion of **B22** to **B22a** reduces the number of high-energy external boronyl groups from seven to five. The predicted activation free energy of 13.1 kcal/mol suggests the viability of the formation of the planar **B22a** structure. The B_2O_2 ring in **B22a** then can add an additional B_2O_2 unit, leading to the benzene-like planar $B_{24}O_{24}$ structure **B24**. For

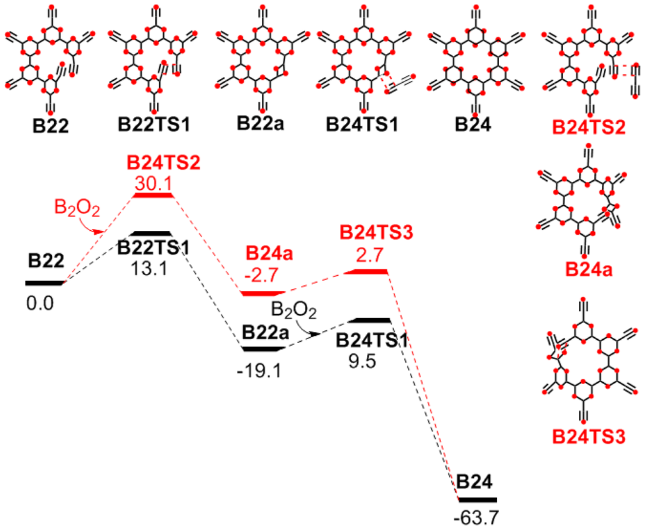

Figure 6. Predicted formation mechanisms for benzene-like planar $B_{24}O_{24}$.

this step, the predicted activation free energy of 9.5 kcal/mol indicates a faster reaction rate than the earlier isomerization step. Thus, the isomerization of **B22** to **B22a** is the rate-determining step in the lower (black) channel of the conversion of **B22** to **B24**. The alternative upper (red) channel in Figure 6 starts with the **B22** structure adding a B_2O_2 unit to give a $B_{24}O_{24}$ structure with a four-membered B_2O_2 ring. However, the transition state for this process (**B24TS2**) is predicted to have an extremely high activation free energy of 30.1 kcal/mol. Thus, formation of the planar $B_{24}O_{24}$ structure **B24** from a $B_{22}O_{22}$ structure **B22** appears first to involve isomerization of the $B_{22}O_{22}$ to a more favorable structure **B22a** before adding a B_2O_2 fragment to generate **B24**.

4. SUMMARY

The polarized π bonds in boronyl groups make B_2O_2 highly reactive toward cyclooligomerization leading to a B_4O_4 dimer containing a four-membered B_2O_2 ring, a B_6O_6 trimer containing a six-membered B_3O_3 (boroxine) ring, a B_8O_8 tetramer containing an eight-membered B_4O_4 ring, and even a $B_{10}O_{10}$ pentamer containing a ten-membered B_5O_5 ring. However, an isomeric $B_{10}O_{10}$ structure containing two boroxine rings linked by a B—B bond is a much lower energy structure by ~31 kcal/mol owing to the special stability of the aromatic boroxine rings. Rotation of the boroxine rings around the central B—B bond in this $B_{10}O_{10}$ structure has a low activation barrier suggesting that further oligomerization to give products containing either perpendicular or planar orientations of the B_3O_3 rings is possible. However, the planar oligomers are energetically more favorable since they have fewer high-energy external BO groups bonded to the network of boroxine rings. The pendant boronyl groups in such oligomers are reactive sites that can be used for further polymerization. Mechanistic aspects of the further oligomerization of $(BO)_x$ systems to give a $B_{24}O_{24}$ oligomer with a naphthalene-like arrangement of boroxine rings and a $B_{84}O_{84}$ with a coronene-like arrangement of boroxine rings have been examined. Further polymerizations of these intermediates by similar processes are predicted to lead ultimately to polymers consisting of planar graphene-like networks of boroxine rings. The holes between the boroxine rings in such polymeric structures suggest that they will be porous low-density materials. Applications of such materials as absorbents for small molecules are anticipated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1: Full list of the predicted local minima structures. Figure S2: All reported transition state structures. Figure S3: Some important orbital interactions for **B4TS**, **B6TS**, and **B8TS1**. Figure S4: Predicted $B_2(OH)_4$ structures. Figure S5: Solvent effects on the formation of B_6O_6 structures. Tables S1−S28: Theoretical Cartesian coordinates for local minima structures (18 structures) as well as transition state structures (10 structures). Complete Gaussian 09 reference (ref 29).This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: rbking@chem.uga.edu (R.B.K.).
*E-mail: zhangzhong6@126.com (Z.Z.).

Notes

The authors declare no competing financial interest.

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