Perfectly planar boronyl boroxine $D_{3h} B_6O_6$: A boron oxide analog of boroxine and benzene

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Inorganic benzene-like compounds such as boroxine and borazine are of interest in chemistry. Here we report on theoretical prediction of a new member of the inorganic benzene family: boronyl boroxine. This perfectly planar $D_{3h} B_6O_6$ (1, $1A_1'$) cluster is identified as the global minimum of the system at density functional theory (B3LYP) and molecular orbital theory levels, which lies at least $\sim 20$ kcal/mol lower in energy than alternative structures. It can be formulated as $B_3O_3(BO)_3$ and features a boroxol $B_3O_3$ ring as the core with three boronyl (BO) groups attached terminally, closely resembling boroxine and obtainable from the latter via isovalent BO/H substitution. Detailed bonding analyses reveal weak $\pi$ aromaticity in boronyl boroxine, rendering it a true analog to boroxine and borazine. Upon electron attachment, the slightly distorted $C_2$, $B_3O_3^-$ (2, $2A_2$) anion is also perfectly planar, and its electronic properties are calculated. A huge energy gap (4.83 eV) is predicted for $B_6O_6^-$ (2) at B3LYP level, which is characteristic of a stable closed-shell neutral cluster. Similar to benzene, boronyl boroxine is also predicted to be an effective inorganic ligand to form sandwich-type complexes, such as $D_{5d} [B_2O_3(BO)_3]_2Cr (4, 1A_2')$. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4811330]

I. INTRODUCTION

The past few years have witnessed increasing research activities in boron oxide clusters,1–18 due primarily to their novel structures and chemical bonding, and to their role in mechanistic understanding of the highly-energetic combustion processes of boron and boranes at a molecular level.19 Converging recent experimental and theoretical data have established the isovalent analogy10–14 between the boronyl (BO) group20, 21 and the H atom, which can both be considered as monovalent $\sigma$ ligands. This concept provides an unexpected link between boronyl oxide clusters and boranes,22 allowing rational design of new boron oxide clusters and boron boronyl complexes. Among boron oxide clusters characterized, the linear $D_{\infty h} B_3(BO)_2^{2-}$, triangular $D_{3h} B_3(BO)_3^{3-}$, and perfect tetrahedral $T_d B_4(BO)_4^{4-}$ form a series with a monoboron center attached with terminal boronyl ligands,10,16 akin to the simplest boranes: $BH_3$ ($n = 2–4$). The linear-chain $D_{\infty h} B_3(BO)_2^{2-}$ clusters11 are relevant to diborene $B_2H_2$ (and acetylene $C_2H_2$ as well), in which the $B_2$ core is attached by two terminal boronyl groups, one on each end. Upon changing the charge state from neutral to anion to di-anion, the formal BB bond order in the $B_2$ core varies from 2 to 2.5 to 3, marking the $B_2(BO)^{2-}$ dianion as the first global-minimum complexes with a true $B\equiv B$ triple bond. Furthermore, $\eta^2$ BO groups are characterized in $B_3(BO)_3^{1-}$ and $B_3(BO)_3^{2-}$ clusters,12 which each possesses a bridging three-center two-electron B–(BO)–B $\sigma$ bond that is similar to the $\tau$ bond in boranes.22 Based on the concept of BO/H isovalent analogy, our group has also investigated very recently the boronyl-substituted ethylenes $C_2H_{n-1}(BO)_{m}$ ($m = 1–4$) and acetylenes $C_2H_{m-n}(BO)_{n}$ ($m = 1, 2$) using density functional theory (DFT), which all prove to be stable species on their potential energy surfaces.23 Cage-like boron boronyl clusters, $B_3(BO)_{n-2}^{2-}$, $C_2B_{n-1}(BO)_{n}$, and $C_2B_{n-2}(BO)_{n}$ ($n = 5–12$), have also been studied theoretically. These are isovalent with each other and represent boronyl analogs of the closo-boranes $B_2H_2^{-}$, monocarbaboranes $CB_{n-1}H_n^-$, and dicarbaboranes $C_2B_{n-2}H_n^-$, respectively.24 Boron oxide and boron boronyl clusters that have been studied to date are relatively boron-rich,1–18 These generally contain a boron cluster core and an appropriate number of boronyl groups attached to it, either terminally or in a bridging fashion. It is anticipated that the composition ratio of B versus O should offer a critical parameter to fine-tune the electronic, structural, and bonding properties of boron oxide clusters. Novel clusters may emerge during the pursuit in this direction. In the current contribution, we report on the discovery of boronyl boroxine, $D_{3h} B_3O_6$ (1, $1A_1'$), a new member of the “inorganic benzene” family. This perfectly planar cluster is identified as the global-minimum structure on the basis of unbiased, extensive global minimum searches. It is at least $\sim 20$ kcal/mol lower in energy than alternative structures at both the B3LYP and single-point coupled-cluster with single, double, and perturbative triple excitations (CCSD(T)) levels.

Boronyl boroxine $D_{3h} B_3O_6$ (1, $1A_1'$) can be formulated as $B_3O_3(BO)_3$: it possesses a boroxol $B_3O_3$ ring as the core with three BO groups terminally attached to three B atoms, which is structurally and chemically similar to

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boroxine (B$_2$O$_3$H$_3$)$_3$ and can be constructed from the latter via isovalent BO/H substitution. Prototypical members of the inorganic benzene family include boroxine and borazine (B$_3$N$_3$H$_6$), which have received persistent attention both experimentally and theoretically. The present work extends the chemistry of boroxine, and represents as well a new development in boronyl chemistry. Chemical bonding in boronyl boroxine is analyzed using adaptive natural density partitioning (AdNDP), natural resonance theory (NRT), and nucleus independent chemical shift (NICS). These collectively confirm that B$_6$O$_6$ (I) cluster is indeed the boron oxide analog of boroxine with σ electrons. Weak π aromaticity is revealed for B$_6$O$_6$ (I), similar to boroxine and borazine. The discrepancy between benzene and boroxene boronyl boroxine or boroxine is also analyzed. Furthermore, to explore boronyl boroxine chemistry, we have attempted to design new sandwich-type transition metal complexes, $D_3d[B_3O_5X_3]_2Cr$ (X = BO, H). In such complexes, boronyl boroxine or boroxine units, B$_3$O$_5X_3$ (X = BO, H), are utilized as robust inorganic ligands, similar to the sandwich-type complexes based on benzene or borazine.

II. THEORETICAL METHODS

DFT structural searches for the B$_6$O$_6$ cluster were conducted initially using the gradient embedded genetic algorithm (GEGA), Coalescence Kick (CK), and Basin Hopping global-minimum search programs. The candidate low-lying structures were further optimized and frequency analyses performed at the B3LYP level with the 6-311+G(d,p) basis sets, as implemented in the GAUSSIAN 03 program. The relative energies for the low-lying isomers were also refined using CCSD(T)/B3LYP geometries. Born-Oppenheimer molecular dynamics (BOMD) simulations for $D_3h$ B$_6$O$_6$ (I) were performed at 300K for 20 ps to check the dynamic behaviors using the software suite CP2K. For the sandwich-type model complexes, the Stuttgart relativistic small core basis set and effective core potential (Stuttgart RSC 1997 ECP) was employed for Cr. The NBO 5.0 program was used to calculate the natural atomic charges.

III. RESULTS

Figure 1 shows the global-minimum structure for the neutral B$_6$O$_6$ cluster, $D_3h$ (I, $1^A_1'$), as identified at both the B3LYP/6-311+G(d,p) and single-point CCSD(T) levels. Its corresponding anion structure, $C_2$, B$_6$O$_6^-$ (2, $2^A_2'$), and that of boroxine $D_3h B_3O_3H_3$ (3, $1^A_1'$) are also shown. Alternative optimized low-lying structures of B$_6$O$_6$ at the B3LYP level are depicted in Fig. 2, along with their relative energies at both B3LYP and single-point CCSD(T) levels.

A. Global-minimum B$_6$O$_6$ structure

As shown in Figs. 1 and 2, the B$_6$O$_6$ (I, $1^A_1'$) state with $D_3h$ symmetry is clearly the global minimum of the system. This structure appears to be not easy, if not impossible, to conceive a priori. Indeed, for such a binary, relatively large system with six B plus six O atoms to self-assemble into this unique, highly-symmetric planar structure, some interesting chemistry has to underlie it. Yet once presented, its connection to the ternary boroxine $D_3h B_3O_3H_3$ (3, $1^A_1'$) complex is readily recognizable. The analogy suggests that B$_6$O$_6$ (I) is boronyl boroxine, which can be formulated as $B_3O_3(BO)_3$, that is, a boroxol B$_3$O$_3$ core attached with three terminal BO groups. To the best of our knowledge, a similar boron oxide core has not been definitively characterized in prior studies, although it is among the possible “guess” structures for some B$_6$O$_6^+$ cation clusters based on mass spectrometric observations. The BOMD simulations well support the high stability of B$_6$O$_6$ (I) (see Fig. S1 in the supplementary material). The root-mean-square-deviation (RMSD) and maximum deviation (MaxD) of bonds in B$_6$O$_6$ turn out to be only 0.038 and 0.077 Å (on average), respectively, at 300 K with respect to those in its minimum structure, indicating that B$_6$O$_6$ possesses a quite rigid global-minimum structure that is dynamically stable under ambient conditions. It is noted that during the BOMD simulations, we were unable to locate any structure that corresponds to a dissociated cluster, let alone any dissociated cluster that is more stable than B$_6$O$_6$ (I) itself. In fact, the cluster motif and atomic connectivity of B$_6$O$_6$ (I) do not alter in the simulations, hinting its structural robustness. We have, therefore, calculated the dissociation energies for representative reaction channels at the B3LYP level, as summarized in Table S1 in the supplementary material. Clearly, all the proposed dissociation channels are highly endothermic, and the least energy-costly channel requires an energy of ~60 kcal/mol, consistent with the thermodynamic stability of the B$_6$O$_6$ (I) cluster.

The B–O bond distance within the B$_3$O$_3$ ring in B$_6$O$_6$ (I) is remarkably similar to that in B$_3$O$_3H_3$ (3) at the B3LYP level: r$_{BO}$ = 1.38 Å in 1 versus r$_{BO}$ = 1.38 Å in 3. Also, the B=O bond distance in 1 is calculated to be r$_{BO}$ = 1.20 Å, similar to r$_{BO}$ = 1.20 Å in free BO radical, which indicates that the structural integrity of boronyl groups is well preserved. Note that the calculated structural parameters for 3 are r$_{BO}$ = 1.38 Å, r$_{B-H}$ = 1.18 Å, BOB = 121°, and BOB = 119° at B3LYP level, in close agreement with the experimental data for boroxine (r$_{BO}$ = 1.375 ± 0.002 Å, r$_{B-H}$ = 1.192 ± 0.017 Å, and BOB = 120.00 ± 0.64°). This serves as a valuable benchmark for the

![Fig. 1. Optimized structures of boronyl boroxine $(D_3h B_3O_3H_3 (3, A_1))$ and its anion $C_2$ B$_3O_3H_3^- (2, 2^A_2)$ at the B3LYP/6-311+G(d,p) level, as compared to that of boroxine $D_3h B_3O_3H_3$ (3, $1^A_1'$). The bond distances (in Å) are indicated at B3LYP and [PBE1PBE] levels. The B atom is in blue, O in red, and H in gray.](image-url)
FIG. 2. Representative isomeric structures of B$_6$O$_6$ with their relative energies (in kcal/mol) indicated at the B3LYP/6-311+G(d,p) and single-point CCSD(T)//B3LYP/6-311+G(d,p) levels. The B atom is in blue, and O is in red.

B3LYP method. The PBE1PBE calculations generated essentially the same structures (Fig. 1).

Per request of a reviewer, we have run full structural optimization at the CCSD/6-31G(d) and CCSD/6-311+G(d,p) levels and frequency analysis at the CCSD/6-31G(d) level, in order to show that the global-minimum structure 1 at B3LYP remains a true minimum at the CCSD level. The CCSD optimized structures for B$_6$O$_6$ (1) are depicted in Fig. 3. Note the bond distances at the CCSD/6-31G(d) level (1.21, 1.38, and 1.69 Å) are nearly identical to those at CCSD/6-311+G(d,p) (1.20, 1.38, and 1.69 Å), which are compared to the values of (1.20, 1.37, and 1.68 Å) and (1.20, 1.37, and 1.68 Å), respectively, at the B3LYP/6-311+G(d,p) and PBE1PBE/6-311+G(d,p) levels (Fig. 1).

The minimum vibrational frequency at the CCSD/6-31G(d) level is 62 cm$^{-1}$, due to the out-of-plane bending of terminal BO groups. This is comparable to those of 62 and 61 cm$^{-1}$ at the B3LYP/6-311+G(d,p) and PBE1PBE/6-311+G(d,p) levels, respectively. All three levels of theory thus concordantly confirm B$_6$O$_6$ (1) as a true minimum. In addition, we note that B$_6$O$_6$ (1) is also a true minimum at the MP2/6-311+G(d,p) level, with a minimum vibrational frequency of 62 cm$^{-1}$. Frequency analysis at the CCSD/6-311+G(d,p) level appears to be too costly for us to pursue at present.

FIG. 3. Optimized structures of boronyl boroxine D$_{3h}$ B$_6$O$_6$ (1, $^1A_1'$) at the CCSD/6-31G(d) and [CCSD]6-311+G(d,p) levels. The B atom is in blue, and O is in red.


### IV. DISCUSSION

#### A. Boronyl boroxine: A boron oxide analog of boroxine and benzene

Boroxine $D_{3h}$ $\text{B}_3\text{O}_3\text{H}_3$ ($3, ^1A_1'$) as an inorganic analog of benzene in terms of geometry and formal topology of the π molecular orbitals (MOs) has been well known.\(^{25-30}\) The same is true for boronyl boroxine, $D_{3h}$ $\text{B}_3\text{O}_3(\text{BO})_3$ ($1, ^1A_1'$). As shown in Fig. 4 (top panel), there exist three global π MOs in 1: HOMO–11 ($\pi_{a''}$) and the degenerate HOMO–8 ($\pi'$) orbitals, which are six-center two-electron (6c-2e) in nature as well, similar to benzene (Fig. 4; bottom panel). Thus, boronyl boroxine formally conforms to the ($4n + 2$) Hückel rule, rendering it π aromaticity as a new inorganic benzene. However, just as the situation in boroxine and borazine, the main difference in π electron distribution in 1 with respect to benzene is that the π electrons are heavily located on the three oxygen centers in the $\text{B}_3\text{O}_3$ boroxol ring, as clearly indicated in the π electron localization functions (π ELFs; Fig. 5),\(^{34,55}\) in contrast to the true six-centered delocalization in benzene. Natural bond orbital (NBO) analyses also indicate that B–O bonds in the $\text{B}_3\text{O}_3$ boroxol cores and the circular delocalization (and hence aromaticity) in 1 and 3 should be substantially reduced.

To further elucidate the nature of bonding, we performed the AdNDP analysis\(^34\) for $\text{B}_3\text{O}_3(\text{BO})_3$ (1). The results are straightforward and easy to interpret (Fig. 6). Of the 54 valence electrons in total, 12 are for the O 2s/2p lone pairs, either terminal or bridging; 18 are for three terminal B=O triple bonds; 6 are for three B–BO single bonds; and 12 are for six B–O bonds in $\text{B}_3\text{O}_3$ ring. The remaining six electrons are delocalized to form three 6c-2e π bonds (bottom row; Fig. 6), which have the same pattern as that revealed from MO analysis (Fig. 4). It is interesting to point out that although the three O atoms contribute the most to the three 6c-2e π bonds, the AdNDP analyses indicate that the π system cannot be further localized into three 1c-2e lone pairs over the three O atoms in the core. This result shows that the relatively small contribution from the three $2p$, atomic orbitals, that is, the covalent nature of B–O π bonding, plays a critical role in defining the nature of delocalized π system. The covalent nature is also apparent in the gas-phase BO radical.

#### B. NRT and NICS analyses

Natural resonance theory (NRT) is used to shed further light on the difference between benzene and its inorganic analogs: boronyl boroxine $\text{B}_3\text{O}_3(\text{BO})_3$ (1) and boroxine $\text{B}_3\text{O}_3\text{H}_3$ (3). The results are shown in the supplementary material (Fig. S2).\(^53\) Clearly, boronyl boroxine has the leading resonance structure with conjugated π bonds (62%), which shows a gradual increase to 68% and 82%, respectively, in boroxine and benzene. On the other hand, the percentage of the resonance structure with localization of lone pairs on the electronegative atoms decreases from boronyl boroxine (22%) to boroxine (21%), and to benzene (8%). Both trends are consistent with the reduction of electron delocalization (and aromaticity) from benzene to boroxine and...
FIG. 6. AdNDP bonding pattern of boronyl boroxine $D_3h B_3O_6 (1, 1A_1')$. The occupation numbers (ONs) are indicated.

boronyl boroxine, where the latter two have roughly the same properties.

NICS is widely used to quantify the extent of aromaticity, and a negative NICS value denotes aromaticity.\(^{39, 40}\) NICS\(_{zz}(1)\) appears to be a better indicator of \(\pi\) aromaticity for planar molecules. The calculated NICS\(_{zz}(1)\) values for $B_3O_3(BO)_3 (1)$ and $B_3O_3H_3 (3)$ are $-2.8$ and $-3.4$ ppm at the molecular center, respectively (Table I). These are negative but relatively small values, which indicate weak \(\pi\) aromaticity in the inorganic benzene species. For comparison, the prototypical aromatic benzene has a NICS\(_{zz}(1)\) value of $-29.7$ ppm at the same level. Overall, the NICS results are qualitatively in line with those of NRT and ELF analyses, confirming boronyl boroxine as a close analog of boroxine, which are both inorganic benzene species.

C. Possible implication of boronyl boroxine on vitreous $B_2O_3$

Boronyl boroxine $D_{3h} B_3O_3(BO)_3 (1, 1A_1')$ is simple in structure, yet it contains all critical structural and bonding elements in glassy bulk $B_2O_3$ and high temperature $B_2O_3$ liquids: the six-membered $B_3O_3$ boroxol ring and the terminal BO groups. Amorphous $B_2O_3$ bulk materials have remained structurally controversial and challenging to model, but it is generally thought that boroxol $B_2O_3$ ring constitutes a large fraction of them, probably up to 75%.\(^{56}\) On the other hand, it has long been speculated that the network in $B_2O_3$ liquids is terminated by boronyl groups, whose population increases with temperature.\(^{57}\)

The intrinsic stability of boronyl boroxine as a robust gas-phase cluster hints that boroxol $B_3O_3$ ring is likely the preferred structural building block for boron oxides, which aggregates and networks to form the vitreous $B_2O_3$ materials. The potency for this relatively small cluster to develop a boroxol $B_3O_3$ ring core structure that dominates the glassy and liquid $B_2O_3$ phases is remarkable, and indeed surprising. Boronyl boroxine and similar larger clusters may thus be interesting molecules to mimic the microscopic, short-range structures of amorphous $B_2O_3$ glasses and liquids, and to model their nucleation and growth.

D. Predicted electronic properties for boronyl boroxine and its anion

To aid future experimental characterizations of boronyl boroxine and its anion, we report herein their calculated electronic properties. Ionization potentials (IPs) are calculated at B3LYP/6-311+G(d,p) level for boronyl boroxine $B_3O_3(BO)_3 (1)$, boroxine $B_3O_3H_3 (3)$, and benzene, which are 12.22,
11.87, and 9.28 eV, respectively (Table I). Boronyl boroxine is thus predicted to have an IP that is comparable to and slightly greater than boroxine, which are both substantially higher than that of benzene (by ~2.6–2.9 eV), suggesting that boronyl boroxine is a relatively stable neutral species. These IP values at B3LYP appear to be quite reliable, in light of the fact that the calculated IP for benzene is in excellent agreement with the most recent, accurate experimental data (9.24384 ± 0.00006 eV).58

With one electron attached, the C₂₂, B₂O₃(OBO)₃⁻ (2, 2′A₂) anion cluster is produced (Fig. 1). The extra electron in 2 occupies one of the degenerate LUMO (ẽ) orbitals of 1, resulting in a slight Jahn–Teller distortion in the anion from the perfect D₃h structure. The terminal BO groups in 2 retain their boronyl nature (r₁ = 1.21–1.22 Å). The ground-state adiabatic and vertical detachment energies (ADE and VDE) of 2 are predicted at B3LYP/6-311+G(d,p) level to be ADE = 1.82 eV and VDE = 2.03 eV, where the ADE also represents electron affinity (EA) of 1 (Table I). The simulated photoelectron spectrum based on B3LYP/6-311+G(d,p) and time-dependent DFT (TDDFT)59,60 calculations are depicted in Fig. S3 in the supplementary material,53 which exhibits a huge energy gap between its ground-state band (X) and first excited-state band (A), amounting to 4.83 eV at the TDDFT level. The X–A gap of an anion is a rough reflection of the HOMO-LUMO gap of a closed-shell neutral species. Thus, the simulated photoelectron spectrum further suggests that B₂O₃ (1) is an extraordinarily stable species. Indeed, B3LYP calculation yields a huge HOMO-LUMO energy gap of 7.05 eV for 1 (Table I). For comparison, the calculated C₆₀ molecule has an X–A energy gap of 1.62 eV as revealed from the photoelectron spectrum of C₆₀ anion.51

It is well known that the EA calculation for an anion is challenging for the DFT methods, including B3LYP. This is true for a stable neutral cluster with a large HOMO-LUMO gap, such as boronyl boroxine (1). To address this technical issue, we have run further calculations. First, we checked the EA at B3LYP using the augmented Dunning’s all-electron basis sets (aug-cc-pVTZ) that include diffuse functions, which many believe can better handle an anion. We also calculated the EA using different functionals. The results thus obtained are 1.78 eV at B3LYP/aug-cc-pVTZ and 1.81 eV at PBE1PBE/6-311+G(d,p), which are nearly identical to that at B3LYP/6-311+G(d,p). Second, we checked the EA at more sophisticated MO theory levels. The calculated EA values are 1.11 eV at MP2/6-311+G(d,p), 1.17 eV at CCSD(T)/B3LYP/6-311+G(d,p), 1.17 eV at CCSD(T)/PBE1PBE/6-311+G(d,p), and 1.16 eV at CCSD(T)/MP2/6-311+G(d,p). These numbers are remarkably consistent with each other within 0.06 eV, and should be considered to be more reliable than the DFT results. The 0.3–0.6 eV discrepancy between DFT and MO theory in the EAs of boronyl boroxine and boroxine is another example that demonstrates the limitation of DFT methods in certain cases. In summary, the recommended EA for boronyl boroxine D₃h B₂O₃(OBO)₃⁻ (1, 1′A₁) based on MO theory calculations is 1.1–1.2 eV, which should be compared with further experimental data.

For comparison, the calculated EA values for boroxine (3) are ~0.85 eV at CCSD(T)/B3LYP/6-311+G(d,p) level, whereas benzene is known to have a negative EA. Thus for the species discussed here, the photoelectron spectroscopy technique is probably suitable only for characterizations of boronyl boroxine and its anion. Note that the EA of 1 is much higher than that of 3 due to the fact that the terminal BO ligand is more electronegative than H, resulting in electrostatic stabilization in 1 relative to 3 by ~2 eV at CCSD(T) level (~0.7 eV per BO group). A similar effect was observed in our previous studies on Au₂(BO) versus Au₂H, where the former species has a higher EA (4.32 eV) than the latter (3.55 eV).62,63

E. Sandwich-type complexes containing B₂O₃X₃ (X = BO, H) units

Motivated by the intriguing electronic and magnetic properties of multidecker organometallic sandwich clusters and their infinite one-dimensional molecular wires, a series of recent works has explored the use of D₆h C₆H₆ and D₃h B₃N₃H₆ as ligands to form multidecker sandwich molecular wires.54–56 It is thus of interest as well to pursue sandwich-type transition metal complexes by using D₆h B₂O₃(OBO)₃ (1) and D₃h B₂O₃H₃ (3) as ligands. Figure 7 shows the optimized structures of D₆h [B₂O₃(OBO)₃]Cr (4) and D₃h [B₂O₃H₃]Cr (5) sandwich complexes at the B3LYP level, in which two 1 and 3 ligands, respectively, sandwich one Cr atom from the opposite ends along the threefold axis of the systems, forming staggered D₆h complexes with the Cr–B distances of rₐₐ = 2.26 and 2.25 Å in 4 and 5, respectively. These distances are slightly longer than that in D₆h [C₆H₆]Cr (6): rₐₐ = 2.17 Å. Note that different from the eclipsed 6 sandwich complex,52,64 the staggered D₆h complexes 4 and 5 are true minimum with the lowest vibrational frequency of 25 and 80 cm⁻¹, respectively. The corresponding eclipsed D₆h structures of [B₂O₃X₃]Cr (X = BO, H) turn out to be transition states with one imaginary frequency due to the electrostatic repulsion between the two ligands, similar to the situation in [B₃N₃H₆]₂M.67,68

The D₆h → D₃h rotatory transition for [B₂O₃(OBO)₃]Cr and [B₂O₃H₃]Cr has an energy barrier of 18.91 and 10.11 kcal/mol, respectively, suggesting that boronyl boroxine based sandwich complex 4 is more robust against rotatory transition relative to its boroxine counterpart 5.

It is worth noting that both B₂O₃(OBO)₃ and B₂O₃H₃ units in the D₆h sandwich complexes are structurally well preserved. For instance, the B–O bond distances in the...
B$_2$O$_3$ ring in 4 and 5 are 1.40 Å, well comparable to 1.38 Å in 1 and 3. Also, B=O bond distance in 4 is 1.20 Å, nearly identical to that either in 1 or the gas-phase BO radical. NBO analyses show that the 4 and 5 sandwich complexes exhibit only slight charge separation as follows: [B$_3$O$_3$(BO)$_3$]$^{−0.14}_{0.14}$, [B$_3$O$_3$(BO)$_3$]$^{−0.14}_{0.14}$, and [B$_3$O$_3$(H)$_3$]$^{−0.10}_{0.10}$, [B$_3$O$_3$(H)$_3$]$^{−0.10}_{0.10}$]. We also note that both sandwich 4 and 5 complexes possess sizeable HOMOLUMO gaps: 3.22 eV for 4 and 3.70 eV for 5 at the B3LYP level (Table I), suggesting that these complexes are stable species thermodynamically. Preliminary calculations also indicate that such complexes can be extended to form triple-decker sandwich-type structures and to include other transition metal centers.

V. CONCLUSIONS

We report on theoretical prediction of boronyl boroxine, $D_{3h}$ B$_2$O$_3$(BO)$_3$(1, 1$A'$), which represents a new member of the “inorganic benzene” family. This perfectly planar cluster is identified as the global minimum, via the gradient embedded genetic algorithm, the Coalescence Kick, and the Basin Hopping global-minimum searches. It lies closely resembles boroxine lower in energy than the nearest alternative structure at both $\sim$Hopping global-minimum searches. It lies identified as the global minimum, via the gradient embedded genetic algorithm (GEGA) and the Coalescence Kick (CK) global-minimum search and the adaptive natural density partitioning (AdNDP) programs, and Professor Jun Li for the Basin Hopping global-minimum search program. This work was supported by the National Natural Science Foundation of China (Grant Nos. 20873117 and 21243004).

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44M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 03, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 2003.


49The CP2K developers group, 2000–2011, see http://cp2k.berlios.de/.


51Stuttgart RSC 1997 ECP basis sets used in this work and the related references therein can be obtained at https://bse.pnl.gov/bse/portal.
See supplementary material at http://dx.doi.org/10.1063/1.4811330 for the calculated dissociation energies for $D_{3h}$ $\text{B}_3\text{O}_3(\text{BO})_3$ (1) at the B3LYP/6-311+G(d,p) level (Table SI); molecular dynamic simulations of $D_{3h}$ $\text{B}_3\text{O}_3(\text{BO})_3$ (1) at 300K (Figure S1); main resonant structures as revealed from natural resonance theory (NRT) analyses for $D_{3h}$ $\text{B}_3\text{O}_3(\text{BO})_3$ (1), as compared with those for $D_{3h}$ $\text{B}_3\text{H}_3$ (3) and benzene (Figure S2); and simulated photoelectron spectrum of $\text{B}_3\text{O}_3(\text{BO})_3^-$ (2) based on TDDFT calculations (Figure S3).