



Fluxional Bonds in Planar B_{19}^- , Tubular $Ta@B_{20}^-$, and Cage-Like B_{39}^-

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Based on detailed bonding analyses on the fluxional behaviors of planar B_{19}^- , tubular $Ta@B_{20}^-$, and cage-like B_{39}^- , we propose the concept of fluxional bonds in boron nanoclusters as an

extension of the classical localized bonds and delocalized bonds in chemistry. © 2018 Wiley Periodicals, Inc.

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Introduction

Boron has a strong propensity to form delocalized multi-center-two-electron (mc-2e) bonds in both bulk allotropes and polyhedral molecules due to its prototypical electron-deficiency.^[1,2] Persistent joint photoelectron spectroscopy (PES) and first-principles theory investigations on small monoanionic boron clusters in the past decade have unveiled a rich landscape from planar or quasi-planar $B_n^{-/0}$ ($n = 3-30, 33-38$) to cage-like borospherenes $D_{2d} B_{40}^{-/0}$ and $C_3/C_2 B_{39}^-$ which are all characterized with delocalized multicenter σ and π bonds.^[2-12] Delocalized bonds have also been reported in metal-doped boron clusters.^[13-16] In particular, the experimentally observed perfectly planar $C_{2v} B_{11}^- (B_2@B_9^-)$,^[17,18] $C_{2v} B_{13}^+ (B_3@B_{10}^+)$,^[19-21] $C_{2v} B_{15}^+ (B_4@B_{11}^+)$,^[22,23] and $C_{2v} B_{19}^- (B@B_5@B_{13}^-)$ ^[24-26] have been proposed to be molecular Wankel motors with almost barrier-free pseudo-rotations between the inner ring and outer bearing. A recent joint infrared photodissociation (IR-PD) and first-principles theory investigation provided the first spectroscopic evidence that can be associated with the internal quasi-rotation of the B_3 inner ring inside a B_{10} outer bearing in B_{13}^+ .^[20] Quasi-planar $C_s B_{18}^{2-} (B@B_5@B_{12}^-)$ ^[27] and perfectly planar $C_{2v} B_{20}^{2-} (B@B_6@B_{13}^{2-})$ ^[28] have also been theoretically predicted to be Wankel motors. Such planar concentric double-ring boron nanoclusters $B@B_n@B_m^{-/0/+}$ (with or without a central B atom) exhibit almost barrier-free pseudo-rotations between the B_n inner ring ($n = 2-6$) and B_m outer ring ($m = 9-13$) at room temperature, with $n \times m$ equivalent global minima (GMs) and $n \times m$ equivalent transition states (TSs) on the flat potential energy surface of the system. For examples, $B_{13}^+ (B_3@B_{10}^+)$ with the energy barrier of $\Delta E_a \approx 0.1$ kcal/mol possesses 30 equivalent C_{2v} GMs and 30 equivalent C_{2v} TSs in a full circle, with the rotation angle of 12° in each step,^[21] while $B_{11}^- (B_2@B_9^-)$ with $\Delta E_a \approx 0.35$ kcal/mol has 18 equivalent GMs and 18 equivalent TSs on the potential energy surface, with the rotation angle of 20° in each step.^[18] Fluxional behaviors have also been reported in transition-metal-doped tubular molecular rotor $Ta@B_{20}^-$ which has the highest coordination number of CN = 20 observed in experiments to date.^[29] A W-X-M structural transformation mechanism was proposed to interpret the

fluxional behaviors of cage-like borospherene B_{39}^- ,^[5,30] with the global minima $C_3 B_{39}^-$ and second lowest-lying minimum $C_2 B_{39}^-$ observed in PES measurements and two intermediates $M_1 (C_7 B_{39}^-)$ and $M_2 (C_7 B_{39}^-)$ and three transition states $TS_1 (C_7 B_{39}^-)$, $TS_2 (C_7 B_{39}^-)$, $TS_3 (C_7 B_{39}^-)$ predicted at first-principles theory.^[30] The four cage-like true minima of B_{39}^- (C_3 , M_1 , M_2 , and C_2) with relative energies smaller than 3.0 kcal/mol are expected to coexist in experiments at room temperature.^[30]

Chemical bond is the most fundamental concept in chemistry. Bonding determines the structures and dynamics of molecules. To further explore the bonding nature of the above mentioned fluxional boron nanoclusters, we perform herein a detailed bonding analysis on the fluxional behaviors of planar B_{19}^- , tubular $Ta@B_{20}^-$, and cage-like B_{39}^- and propose the concept of fluxional bonds in these experimentally observed boron nanoclusters.

Theoretical Procedure

The previously reported GM and TS states of B_{19}^- , B_{39}^- , and $Ta@B_{20}^-$ were fully re-optimized at the hybrid density functional theory (DFT) level of PBE0^[31] with the basis set of 6-311 + G(d) ^[32] for boron implemented in Gaussian 09 program ^[33] and Stuttgart relativistic small-core pseudopotential for Ta. ^[34,35] Frequency checks were performed to make sure the optimized structures are true GMs or TSs. The simulated PES spectra of B_{19}^- and B_{39}^- were obtained using the time-dependent DFT approach (TD-DFT).^[36] Detailed bonding analyses were performed using the adaptive natural density partitioning (AdNDP) ^[37] method which recovers both the localized and delocalized bonding elements of the concerned systems. AdNDP has been successfully applied to a wide range of boron and boron-based nanoclusters.^[2-16] The reaction rate

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constant k from a true minimum to its transition state neighbor was calculated using Eyring standard transition state theory.^[38]

Results and Discussions

Fluxional bonds in planar B_{19}^- and B_{15}^+

We re-analyzed and compared the AdNDP bonding patterns of C_{2v} GM and its transition state C_{2v} TS of B_{19}^- [25,26] in Figure 1a. The GM and TS possess the negligible energy

difference of $\Delta E_a = 0.02$ kcal/mol at CCSD(T)^[26] which is smaller than the difference of the corresponding zero-point corrections ($\Delta ZPE = 0.07$ kcal/mol at PBE0). Our bonding patterns are slightly different from that reported in Ref. 24. But they agree well with the electron localization function (ELF)^[39] maps of the GM and TS shown in Figure 1a (with the bifurcation values of $ELF_\sigma = 0.8$), possess higher occupation numbers, and more importantly, better reflect the fluxional bonding nature of the planar concentric double-ring system, as discussed in details below. Besides the 13 localized 2c-2e σ bonds on the periphery,

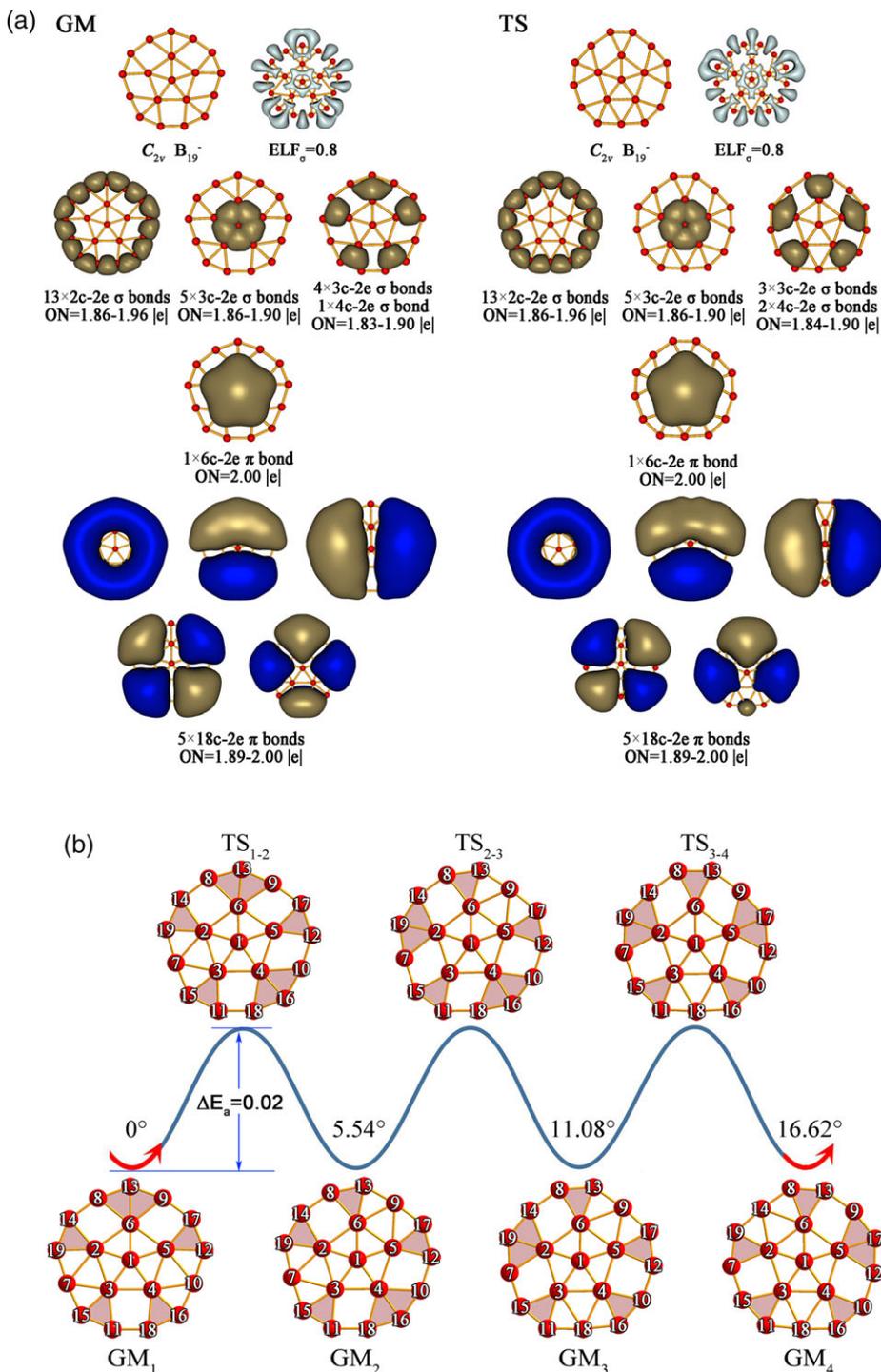


Figure 1. (a) AdNDP bonding patterns of the C_{2v} GM and C_{2v} TS of B_{19}^- and (b) bonding fluctuations in B_{19}^- with a rotational angle of 5.54° between two neighboring GMs, with the energy barrier ΔE_a indicated in kcal/mol. The electron localization function maps of the GM and TS are also depicted in (a) for comparison, with the bifurcation values ELF_σ indicated. The fluxional 3c-2e σ bonds and 4c-2e σ bonds are highlighted in pink. [Color figure can be viewed at wileyonlinelibrary.com] [Color figure can be viewed at wileyonlinelibrary.com]

there exist two sets of delocalized σ -systems in the GM, one with 5 3c-2e σ bonds on the inner B_6 pentagonal unit and the other with 4 3c-2e σ bonds plus 1 4c-2e σ bond between B_6 pentagon and the B_{13} outer ring. C_{2v} GM is thus σ dually aromatic. Meanwhile, there have two sets of delocalized π -systems over the σ -skeleton, including 1 6c-2e π bond over the B_6 pentagon at the center and 5 18c-2e π bonds over the molecular disk between the B_6 pentagon and the B_{13} outer bearing (note the central B is not included). It is therefore π dually aromatic. C_{2v} GM thus possesses an overall fourfold concentric $\sigma + \pi$ aromaticity. Interestingly and importantly, as shown in Figure 1b, both the two π -systems over the B_6 pentagon (1 6c-2e π bond) and between the inner and outer rings (5 18c-2e π bonds) and the inner σ -system on the B_6 pentagon (5 3c-2e σ bonds) are well inherited in C_{2v} TS from C_{2v} GM. The main changes occur in the second aromatic σ -system between the inner B_6 pentagon and outer B_{13} ring where the 4 3c-2e σ bonds plus 1 4c-2e σ bond in the GM have been transferred to 3 3c-2e σ bonds plus 2 4c-2e σ bonds in the TS. A reversed process occurs from TS to GM. Such a 4 3c-2e σ + 1 4c-2e σ \rightarrow 3 3c-2e σ + 2 4c-2e σ \rightarrow 4 3c-2e σ + 1 4c-2e bonding transformation in the GM \rightarrow TS \rightarrow GM fluctuation process can be clearly seen from Figure 1b. For example, the electron densities on the 4 3c-2e σ bonds on B2B14B19, B3B15B11, B4B18B16, and B5B12B17 and 1 4c-2e σ bond on B6B9B13B8 in GM₁ have migrated to 3 3c-2e σ bonds on B2B14B19, B3B15B11, and B5B12B17 and 2 4c-2e σ bonds on B4B18B16B10 and B6B9B13B8 in TS₁₋₂, from where the σ -system is transferred to 4 3c-2e σ bonds plus 1 4c-2e σ bond in the second global minimum GM₂, in a rotational angle of 5.54°. In such a fluxional process, both the locations of the delocalized σ bonds and numbers of boron centers involved in the multicenter bonds between the inner B_6 pentagon and outer B_{13} ring are changed in a collective mode. The authors propose the tentative name of "fluxional bonds" to describe such migratory multicenter bonds which form and break constantly in a concerted mechanism under certain condition (Supporting Information Video-1), as an extension of the traditional localized bonds and delocalized bonds in chemistry.^[40]

The authors also compared the simulated PES spectra of C_{2v} GM and C_{2v} TS of B_{19}^- at PBE0 level in Supporting Information Figure S1. Intriguingly, the simulated PES spectra of C_{2v} GM and C_{2v} TS appear to be practically the same, both matching the main spectroscopic features of the measured PES of B_{19}^- equally well (Supporting Information Fig.S1 and Ref. 17). This observation provides spectroscopic evidence for the pseudo-rotation of the B_6 pentagonal unit inside B_{13} outer bearing, suggesting the existence of fluxional bonds in B_{19}^- , similar to the situation observed in B_{13}^+ in IR-PD measurements.^[20] B_{19}^- is the first planar boron monoanion with fluxional bonds observed in PES measurements.^[2-16,24]

Previous bonding analysis by our group indicates that, in the experimentally observed σ -aromatic/ π -antiaromatic C_{2v} B_{15}^+ , there exist both fluxional σ and π bonds which migrate simultaneously and continuously between the inner B_4 rhombus and outer B_{11} bearing, facilitating the dynamic fluxionality of the system at 500 K with the rotational energy barrier of 1.66 kcal/mol.^[22,23]

Fluxional bonds in tubular Ta@B₂₀⁻

The tubular C_5 GM and tubular C_5 TS of Ta@B₂₀⁻ obtained at PBE0 level in this work agree well with that reported in Ref. 29. A detailed comparison of their AdNDP bonding patterns is presented in Supporting Information Figure S2 which indicates that major bonding changes occur on the top of the B_{18} double-ring tube involving the B_2 bar and boron atoms on the top B_9 ring, with 2 4c-2e σ bonds in the C_5 GM transferred to 2 3c-2e σ bonds in the C_5 TS during the structural pseudo-rotation, while all the other σ and π bonds remain basically unchanged. For instance, the 2 4c-2e σ bonds on two rhombuses B1B9B8B7 and B2B3B11B10 in GM₁ have been changed into 2 3c-2e σ bonds on two triangles B1B9B8 and B2B3B11 in C_5 TS₁₋₂, from where the 2 3c-2e σ bonds are transferred to 2 4c-2e σ bonds on two rhombuses B1B10B9B8 and B2B4B3B11 in GM₂ (Figure 2). Such a 2 4c-2e σ \rightarrow 2 3c-2e σ \rightarrow 2 4c-2e σ bonding

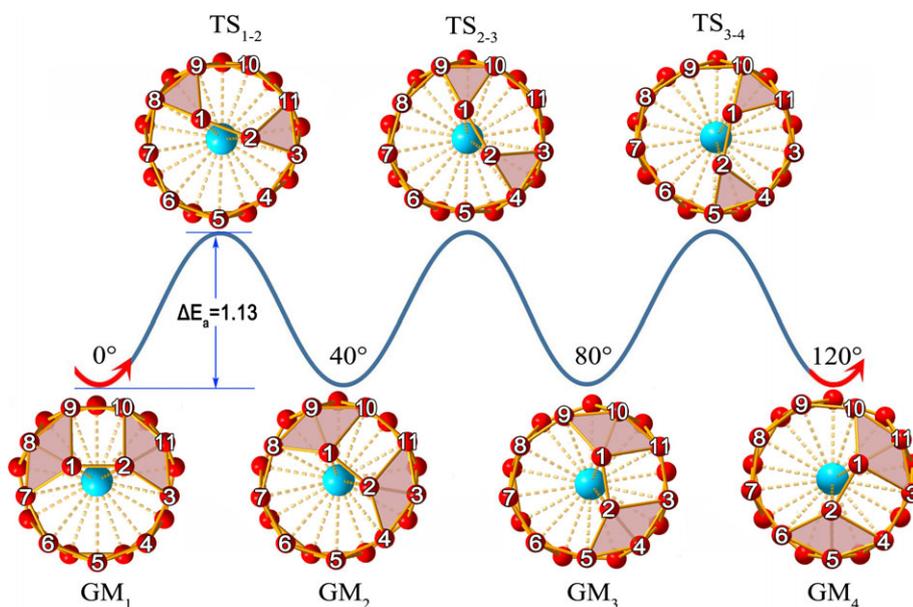


Figure 2. Fluxional bonds in tubular molecular rotor Ta@B₂₀⁻ with the rotational angle of 40° between neighboring GMs, with the energy barrier ΔE_a indicated in kcal/mol. The 3c-2e σ bonds and 4c-2e σ bonds formed atop the B_{18} double-ring tube are highlighted in pink. [Color figure can be viewed at wileyonlinelibrary.com] [Color figure can be viewed at wileyonlinelibrary.com]

fluctuation repeats itself during the pseudo-rotation of the B_2 unit atop the B_{18} double-ring tube with an energy barrier of 1.13 kcal/mol.^[29] It is noticed that both the C_5 GM and C_5 TS can reproduce the main PES features of $Ta@B_{20}^-$ equally well (Supporting Information Fig.S3 and Ref. 29), evidencing the pseudo-rotational behaviors of the system and existence of fluxional bonds in tubular $Ta@B_{20}^-$.

Fluxional bonds in cage-like B_{39}^-

The four true minima of B_{39}^- ($C_3 B_{39}^-$, M_1 ($C_1 B_{39}^-$), M_2 ($C_1 B_{39}^-$), and $C_2 B_{39}^-$) and three transition states between them TS_1 ($C_1 B_{39}^-$), TS_2 ($C_1 B_{39}^-$), and TS_3 ($C_1 B_{39}^-$) are collectively depicted in Figure 3, with their relative energies (<4.0 kcal/mol) indicated.^[5,30] B_{39}^- fluctuates almost freely from $C_2 B_{39}^-$ to $C_3 B_{39}^-$ at 300 K ($C_2 \rightarrow TS_3 \rightarrow M_2 \rightarrow TS_2 \rightarrow M_1 \rightarrow TS_1 \rightarrow C_3$) via the concerted mechanism of W-X-M transformation.^[30] We analyzed the AdNDP patterns of all these species and found that major bonding changes occur at the three B_5 active sites W, X, and M which correspond to the bonding fluctuation process of 3 3c-2e σ bonds (W) \rightarrow 2 3c-2e σ bonds plus 1 5c-2e σ bond (X) \rightarrow 3 3c-2e σ bonds (M) (Fig. 3b). Such fluxional bonds are expected to also exist in the molecular dynamics of B_{40} as a nano-bubble at

1400 K.^[41] We notice that similar to $C_3 B_{39}^-$ and $C_2 B_{39}^-$, the simulated PES spectra of the two intermediate states M_1 and M_2 with the relative energies of 2.84 and 2.68 kcal/mol also regenerate the major spectroscopic features of the measured PES of B_{39}^- reasonably well (Supporting Information Fig.S4 and Ref. 5). They could have been buried in the measured broad PES features of B_{39}^- ,^[5] again suggesting that M_1 and M_2 may coexist as minor isomers with the two lowest-lying $C_3 B_{39}^-$ and $C_2 B_{39}^-$ in PES experiments. Fluxional B_{39}^- is the only monoanion boron cluster observed to date which possesses a cage-like ground-state structure.^[2-9] Fluxional bonds help to stabilize cage-like B_{39}^- monoanions, similar to the situations in planar molecular Wankel motors B_{11}^- ,^[17,18] B_{13}^+ ,^[19-21] B_{15}^+ ,^[22,23] and B_{19}^- .^[24-26] We also calculated the rate constants k for the rate-determining steps of B_{39}^- and found that $k \approx 8.98 \times 10^9 \text{ s}^{-1}$ for the reaction of $C_3 \rightarrow TS_1$ with the energy barrier of $\Delta E_a = 3.89$ kcal/mol and $k \approx 1.84 \times 10^{11} \text{ s}^{-1}$ for the reaction of $C_2 \rightarrow TS_3$ with $\Delta E_a = 2.11$ kcal/mol at 300 K, suggesting that the second lowest-lying $C_2 B_{39}^-$ has a much higher fluxional reaction rate than the ground-state $C_3 B_{39}^-$ at room temperature. This agrees with the observation that $C_3 B_{39}^-$ is the major species observed in PES measurements while $C_2 B_{39}^-$ is a minor isomer.^[5]

Conclusions

Based on detailed bonding analyses, the authors present in this work the concept of fluxional bonds in planar B_{19}^- , tubular $Ta@B_{20}^-$, and cage-like B_{39}^- which form and break constantly on the extremely flat potential energy surfaces of the systems. It is the fluxional multicenter σ or π bonds that facilitate the almost barrier-free fluxional behaviors of these electron-deficient clusters in concerted mechanisms (i.e., fluxional bonds fluctuate in collective modes). Systems with fluxional bonds may exhibit spectroscopic line-broadening in experiments. It requires low temperatures and high resolutions to distinguish the close-lying coexisting isomers in spectroscopic experiments, as demonstrated in the measured IR-PD spectrum of B_{13}^+ ^[20] and PES spectra of B_{19}^- ^[24] and B_{39}^- .^[5] Such prototypical electron-deficient boron nanoclusters are different from classical fluxional molecules like iron pentacarbonyl ($Fe(CO)_5$), phosphorus pentafluoride (PF_5), and dimethylformamide ($CH_3)_2NC(O)H$ which undergo Berry pseudo-rotations via bond bending, swing, or stretching of localized 2c-2e σ bonds.^[42-44] Fluxional bonds evolving with times could exist in other systems beyond boron with delocalized bonds under certain conditions and may have important applications in molecular dynamics, catalytic mechanisms, and electronics nanomaterials.

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Keywords: fluxional bonds · AdNDP · bonding patterns · structures · first-principles theory

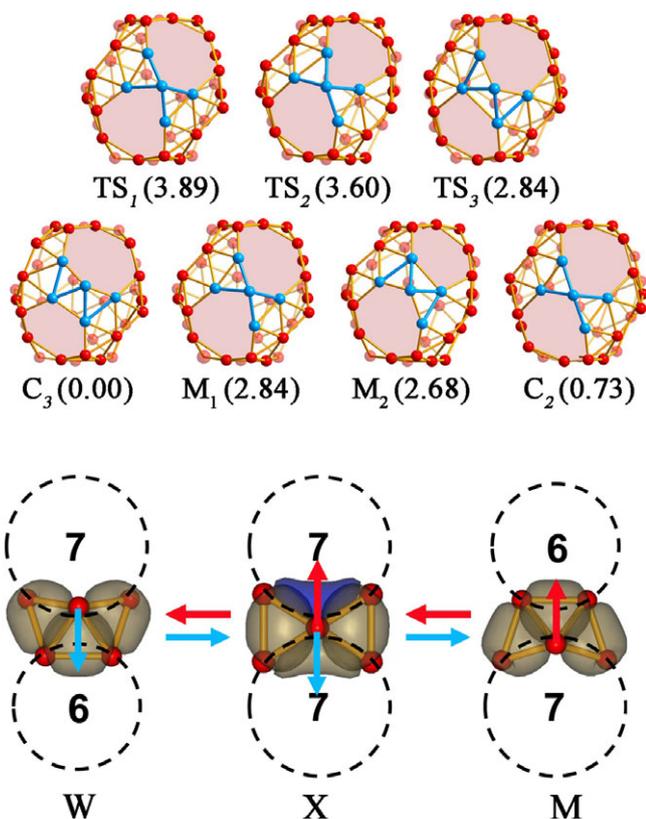


Figure 3. (a) The four true minima (C_3 , C_2 , M_1 , and M_2) of B_{39}^- and three transition states (TS_1 , TS_2 , and TS_3) between them, with their energies relative to the global minimum $C_3 B_{39}^-$ indicated in kcal/mol.^[23] The active B_5 W, X, and M sites in the front of the cages are highlighted in blue. (b) W-X-M transformation of borospherenes, with the 3c-2e σ bonds and 5c-2e σ bond highlighted in the W-, X-, and M-shaped B_5 units. [Color figure can be viewed at wileyonlinelibrary.com] [Color figure can be viewed at wileyonlinelibrary.com]

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 Additional Supporting Information may be found in the online version of this article.

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- More detailed information can be found online at <http://www.ch.ic.ac.uk/rzepa/bpr/>.

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