Probing the Fluxional Bonding Nature of Rapid Cope rearrangements in Bullvalene C_{10}H_{10} and Its Analogs C_{8}H_{8}, C_{9}H_{10}, and C_{8}BH_{9}

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Bullvalene C_{10}H_{10} and its analogs semibullvalene C_{8}H_{8}, barbaralane C_{9}H_{10}, and 9-Borabarbaralane C_{8}BH_{9} are prototypical fluxional molecules with rapid Cope rearrangements at finite temperatures. Detailed bonding analyses performed in this work reveal the existence of two fluxional π-bonds (2 2c-2e π → 2 3c-2e π → 2 2c-2e π) and one fluxional σ-bond (1 2c-2e σ → 1 4c-2e σ → 1 2c-2e σ) in their ground states and transition states, unveiling the universal π + σ double fluxional bonding nature of these fluctuating cage-like species. The highest occupied natural bond orbitals (HONBOs) turn out to be typical fluxional bonds dominating the dynamics of the systems. The $^{13}$C-NMR and $^1$H-NMR shielding tensors and chemical shifts of the model compound C_{8}BH_{9} are computationally predicted to facilitate future experiments.

Chemical bond is the most fundamental and important concept in chemistry. Classical bonds include localized two-center-two-electron (2c-2e) bonds and delocalized multi-center-two-electron (mc-2e, $m \geq 3$) bonds. Our group predicted the existence of fluxional σ- and π-bonds (FBs) in planar B_{18}^{−} and B_{19}^{−}, half-sandwich KB_{18}, tubular Ta@B_{20}, Ta@B_{21}, and Ta@B_{22}^{+}, and cage-like B_{39}^{−} in four recent papers. Multicenter FBs in these fluctuating boron nanoclusters form and break constantly in concerted mechanisms at room temperatures. It is these FBs that facilitate the fluxional behaviors of these electron-deficient boron-based nanoclusters which possess energy barriers lower than the differences of the corresponding zero-point energy corrections. However, boron nanoclusters are known to be unstable in air and moisture and have hitherto been observed and characterized in gas phase only. Fluxional bonds in stable systems beyond boron which fluctuate rapidly and reversibly at finite temperatures remain to be explored in chemistry.

Prototypical fluxional molecules in organic chemistry include the norcaradiene-cycloheptatriene system, various annulenes, and homotropilidenes. Bridged homotropilidenes with degenerate valence-bond tautomerisms, such as the cage-like bullvalene C_{10}H_{10}, semibullvalene C_{8}H_{8}, barbaralane C_{9}H_{10}, and 9-borabarbaralane C_{8}BH_{9}, are of particular interest which exhibit reversible fluxionalities in rapid Cope rearrangements through a transition state with a bis-homoaromatic array of orbitals. A topological analysis of experimental electron densities of the ground-state C_{8}H_{8} bullvalene was reported in 1996. C_{10}H_{10}, C_{9}H_{10}, and C_{8}H_{8} have the experimental free energy barriers of $\Delta G^\circ = 12.8$ kcal/mol at 100 °C, 5.5 kcal/mol at $-143$ °C, and 7.8 kcal/mol at $-77$ °C in NMR measurements, respectively, while the model compound C_{8}BH_{9} has the calculated $\Delta G^\circ = 10.36$ kcal/mol at 27 °C. Semibullvalene C_{8}H_{8} has proven to have the lowest fluxional energy barrier, fastest rearrangement rate, and lowest fluctuating temperature in the series. Despite their differences in compositions and ground state structures, cage-like C_{10}H_{10}, C_{8}H_{8}, and C_{8}BH_{9} have similar transition state structures in rapid Cope rearrangements which have obvious multicenter bonding characteristics. However, the specific bonding patterns and fluxional bonding nature which facilitate the fluctuating behaviors of these intriguing molecules still remain unknown to date in both theory and experiments.

We aim to tackle the problem at first-principles theory level in this work. Detailed bonding analyses reveal a universal bonding pattern with two fluxional π-bonds and one fluxional σ-bond in the ground states and transition states of the C_{10}H_{10}, C_{8}H_{8}, C_{9}H_{10}, and C_{8}BH_{9} series, unveiling the σ + π double fluxional bonding nature of...
the C3-C4 bond and C5-C6 bond. These transition states with two weak C-C interactions (C1-C2 and C5-C6) on the top and at the bottom of the C8 octahedron are at the critical points of Cope intramolecular rearrangements, where the original C1-C2 single bond forms the GS. The C1-C2 single bond with rC1–C2 = 1.53–1.59 Å on the top in the C2v C8H8 GS has been elongated to rC1–C2 = 3.50–3.55 Å = 1.92–2.04 Å in the C2v TSs. The calculated C1–C2 and C5–C6 distances in the C2v TSs appear to be about 0.5 Å longer than the sum of the bond covalent radii of two carbon atoms (rC–C = 1.50 Å)10, indicating that the C1–C2 and C5–C6 interactions across the two long edges in the C2v TSs are much weaker than a usual C-C single bond. Such C-C distances also appear to be much longer than the C-C single bond (1.579 Å) observed between the two inverted carbon atoms in propellane44. The calculated distances of rC1–C2 = 2.9–3.2 Å in C2v TSs (2, 5, 8, 11) clearly show that there exists no bonding interaction between C3–C4. These transition states with two weak C-C interactions (C1–C2 and C5–C6) on the top and at the bottom of the C8 octahedron are at the critical points of Cope intramolecular rearrangements, where the original C1-C2 single bond forms the GS. While the C5-C6 σ-interaction in GS’ is to be formed simultaneously in the same process and vice versa. The three carbon atoms (1–6) in the front of the C8 TSs can be divided into two equivalent groups weakly bonded together, with two effective parallel C=C=C multicenter bonds (C1=C3=C5 and C2=C4=C6) along the two long edges of the C8 octahedron and two weak C-C interactions (C1–C2 and C5–C6) on the top and at the bottom between them. C8H10, C8H8, C9H10, and C8BH9 possess the calculated free energy barriers of 11.2, 9.0, 10.2, and 14.0 kcal/mol higher in energy than their ground states at CCSD(T)//PBE0 level at 298 K, respectively. Such energy barriers appear to be much higher than that previously reported in boron nanoclusters1–4. This can be qualitatively understood based on the fact that, due to its prototypical electron-deficiency, boron has the strong propensity to form delocalized σ and π bonds in highly reactive boron nanoclusters with extremely small energy barriers45, while the fluxional processes in 1, 4, 7, and 10 possess much higher energy barriers because they involve the formations and breakages of C-C interactions in stable organic species. The C1-C2 single bond with rC1–C2 = 1.53–1.59 Å on the top in the C2v C8H8 GS has been elongated to rC1–C2 = 3.50–3.55 Å = 1.92–2.04 Å in the C2v TSs. 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delocalized 4c-2e $\sigma$-bond is a $\sigma + \pi$ mixture between two sets of titled $p_z$-$p_z$ pair interactions, with the major contribution from a head-to-head $\sigma$-overlap and minor contribution from a shoulder-by-shoulder $\pi$-overlap. An opposite process occurs from $C_{2v}$ TS to the second minimum $C_{3v}$ $G_S'$. Thus, as clearly shown in Fig. 3a, in a full fluxional process $C_{3v}$ $G_S \rightarrow C_{2v}$ TS $\rightarrow C_{3v}$ $G_S' \rightarrow C_{2v}$ TS $' \rightarrow C_{3v}$ $G_S$, $C_{10}H_{10}$ undergoes a $\pi$-fluctuation of $2 \text{2c-2e} \pi$ (HONBOs) $\rightarrow 2 \text{3c-2e} \pi$ (HONBO-2) $\rightarrow 2 \text{2c-2e} \pi'$ (HONBOs) $\rightarrow 2 \text{3c-2e} \pi$ (HONBOs) $\rightarrow 2 \text{2c-2e} \pi$ (HONBOs) $\rightarrow 2 \text{3c-2e} \pi$ (HONBO-2) $\rightarrow 2 \text{2c-2e} \pi$ (HONBOs) and a $\sigma$-fluctuation of $1 \text{2c-2e} \sigma$ (HONBO-1) $\rightarrow 1 \text{4c-2e} \sigma$ (HONBO) $\rightarrow 1 \text{2c-2e} \sigma'$ (HONBO-1) $\rightarrow 1 \text{4c-2e} \sigma'$ (HONBO) $\rightarrow 1 \text{2c-2e} \sigma$ (HONBO-1) simultaneously in a concerted mechanism. Such a bonding fluctuation

**Figure 1.** Optimized structures of the ground states ($G_S$/$G_S'$) and transition states ($T_S$) of (a) $C_{10}H_{10}$ (b) $C_8H_8$, (c) $C_9H_{10}$, and (d) $C_8BH_9$, with the lowest vibrational frequencies $\nu_{\min}$ and relative energies $\Delta E_a$ indicated at PBE0 and CCSD(T) levels, respectively. Typical calculated C-C bond lengths are indicated in Å.
process occurs randomly in three equivalent directions perpendicular to the three equivalent C₇ heptagons around the C₃ molecular axis in both C₃v GS and GS', generating 10!/3 equivalent isomers (~1.2 million) in total for C₁₀H₁₀, making all the ten H atoms magnetically equivalent with one signal observed in NMR measurements above 100 °C¹⁵.

Similarly, a π-fluctuation of 2 2c-2e π (HONBOs) → 2 3c-2e π (HONBO-1) → 2 2c-2e π (HONBOs) and a σ-fluctuation of 1 2c-2e σ (HONBO-3) → 1 4c-2e σ (HONBO) → 1 2c-2e σ (HONBO-3) occurs in C₈BH₉ in a full fluxional circle (Fig. 3b). The two AdNDP π bonds and one AdNDP σ bond of C₁₀H₁₀ and C₈BH₉ have their origin from the two CMO π orbitals and one CMO σ orbital in them in both the ground state and transition state, as shown in Fig. S1, well supporting the AdNDP bonding patterns presented in Figs. 2 and 3. As shown in Fig. S3, C₈H₈ and C₉H₁₀ also exhibit two similar fluxional π bonds (2 2c-2e π → 2 3c-2e π → 2 2c-2e π) and one fluxional σ-bond (1 2c-2e σ → 1 4c-2e σ → 1 2c-2e σ) in reversible Cope rearrangements. However, different from C₃v C₁₀H₁₀ which possesses three equivalent fluctuating directions, C₈H₈, C₉H₁₀, and C₈BH₉ have their origin from the two CMO π orbitals and one CMO σ orbital in them in both the ground state and transition state, as shown in Fig. S1, well supporting the AdNDP bonding patterns presented in Figs. 2 and 3. As shown in Fig. S3, C₈H₈, C₉H₁₀, and C₈BH₉ all have π-HONBOs, while the C₃v TSs possess σ-HONBOs (Fig. 2 and S2). Such a natural bond orbital energy order renders low stability and high reactivity to the C₃v TSs.

Figure 2. AdNDP natural bond orbital energy levels and bonding patterns of the ground states (GSs/GSs') and transition states (TSs) of (a) C₁₀H₁₀ and (b) C₈BH₉ at PBE0/6-311 + G (d) level, with the two fluxional π-bonds and one fluxional σ-bond interlinked by arrowed lines from GS, TS, to GS'.
The calculated electron numbers from the involved C atoms to the fluxional 3c-2e π-bonds and fluxional 4c-2e σ-bond in Table 1 indicate that, in the C\textsubscript{2v} transition states of these fluxional molecules, the two central C atoms (C3 and C4) on the two long edges each contribute one electron to the respective 3c-2e π bond over C1=3=C5 or C2=C4=C6, while the four C atoms on the top (C1 and C2) and at the bottom (C5 and C6) each contribute approximately half an electron. Meanwhile, the four C atoms on the top (C1 and C2) and at the bottom (C5 and C6) each contribute half an electron to the delocalized 4c-2e σ-bond, forming a half σ-bond on the top over C1--C2 and a half σ-bond at the bottom over C5--C6. The two separated half σ-bonds over C1--C2 and C5--C6 are antibonding in nature. As shown in Figs. 3a,b and S3a,b and Video S1, the two fluxional π-bonds and one fluxional σ-bond in each species fluctuate up and down in opposite directions indicated by red arrows. The ON values represent the calculated occupation numbers of corresponding bonds.

![Diagram](https://www.nature.com/scientificreports/)
requirement to convert GS and GS' backward and forward in a continuously and reversibly fluctuating process (Figs. 3 and S3).

NMR shielding constants. NMR has proved to be a powerful tool for the determination of the energy barriers and rate constants of molecules with fluxional bonds in rapid Cope rearrangements. The calculated absolute 13C- and 1H-NMR shielding tensors $\delta$ and chemical shifts $\Delta\delta$ relative to tetramethylsilane (TMS) are tabulated for $C_{3v}$ $C_{10}H_{10}$ (1) and $C_{2v}$ $C_{8}BH_{9}$ (11) in Table 2 in ppm. Our calculated 13C and 1H chemical shifts ($\Delta\delta$) of $C_{10}H_{10}$ (1) at $-59.9^\circ$C and $-59.2^\circ$C are cited in square brackets for comparison, respectively.

Table 1. Calculated electron numbers from specific carbon atoms (1–6) contributed to the respective fluxional 3c-2e $\pi$-bonds and fluxional 4c-2e $\sigma$-bond in the transition states $C_{2v}$ $C_{10}H_{10}$ (2) and $C_{2v}$ $C_{8}BH_{9}$ (11) at PBE0/6-311+G(d) level.

| TSS | Atoms | 3c-2e $\pi$-bonds | 4c-2e $\sigma$-bond |
|-----|-------|-------------------|-------------------|
| C$_{2v}$ $C_{10}H_{10}$ | C1(C2) | 0.47 | 0.49 |
| | C3(C4) | 1.02 | — |
| | C5(C6) | 0.47 | 0.49 |
| C$_{2v}$ $C_{8}BH_{9}$ | C1(C2) | 0.45 | 0.49 |
| | C3(C4) | 1.03 | — |
| | C5(C6) | 0.45 | 0.49 |

Table 2. Calculated absolute 13C-NMR and 1H-NMR shielding tensors $\delta$ and chemical shifts $\Delta\delta$ with TMS as internal reference in $C_{3v}$ $C_{10}H_{10}$ (1) and $C_{2v}$ $C_{8}BH_{9}$ (11) at PBE0/6-311+G(d) level. The experimental 13C and 1H chemical shifts ($\Delta\delta$) of $C_{10}H_{10}$ (1) at $-59.9^\circ$C and $-59.2^\circ$C are cited in square brackets for comparison, respectively.

|       | 13C-NMR $\delta$/ppm | 13C-NMR $\Delta\delta$/ppm | 1H-NMR $\delta$/ppm | 1H-NMR $\Delta\delta$/ppm |
|-------|-----------------------|-----------------------------|---------------------|-----------------------------|
| $C_{3v}$ $C_{10}H_{10}$ (1) | 54.62 (3) | 130.39 (3) [128.5] | 25.33 (3) | 5.07 (3) [5.70] |
| | 54.72 (3) | 130.29 (3) [128.3] | 25.48 (3) | 4.92 (3) [5.62] |
| | 152.27 (1) | 32.75 (1) [31.0] | 28.99 (1) | 1.41 (1) [2.13] |
| | 162.74 (3) | 22.28 (3) [21.0] | 29.02 (3) | 1.38 (3) [2.07] |
| $C_{2v}$ $C_{8}BH_{9}$ (11) (298 K) | 55.23 (2) | 129.78 (2) [128.4] | 23.04 (1) | 7.36 (1) [7.13] |
| | 60.28 (2) | 124.73 (2) | 25.49 (2) | 4.92 (2) |
| | 144.08 (2) | 41.01 (2) | 25.75 (2) | 4.65 (2) |
| | 144.77 (1) | 40.24 (1) | 27.85 (1) | 2.56 (1) |
| | 160.20 (1) | 24.82 (1) | 28.41 (2) | 1.99 (2) |
| | | | 29.19 (1) | 1.22 (1) |

In summary, detailed AdNDP bonding analyses performed in this work reveal the existence of two fluxional $\pi$-bonds and one fluxional $\sigma$-bond in bullvalene $C_{10}H_{10}$ and its analogs $C_{8}H_{8}$, $C_{9}H_{10}$, and $C_{8}BH_{9}$. These fluxional bonds form and break constantly and reversibly in rapid Cope rearrangements at finite temperatures. Such a universal $\pi + \sigma$ double fluxional bonding pattern reflects both the structural characteristics and fluxional bonding nature of these rapidly fluctuating species. Their HONBOs with the highest relative energies and reactivity belong to typical fluxional bonds which dominate the dynamics of the systems. The fluxional behaviors of these organic molecules are different in nature from that of the classical fluxional molecules like iron pentacarbonyl (Fe(CO)$_5$), phosphorus pentfluoride (PF$_5$), and dimethylformamide (CH$_3$)$_2$NC(O)H which undergo Berry pseudo-rotations via bond bending, swing, or stretching of localized 2c-2e $\sigma$ bonds without the breaks or formations of chemical bonds involved in the fluxional process. Explorations of fluxional bonds in more complicated intramolecular rearrangements known in chemistry are currently underway.

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S.-D. Li, H.-G. Lu and Y.-B. Wu designed the research. Y.-Y. Ma, M. Yan, H.-R. Li and X.-X. Tian performed the calculations. All authors contributed to the interpretation and discussion of the data and participated in the preparation of the manuscript.

Competing interests
The authors declare no competing interests.

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