

# Bent Bonds ( $\tau$ ) and the Antiperiplanar Hypothesis—The Chemistry of Cyclooctatetraene and Other $C_8H_8$ Isomers

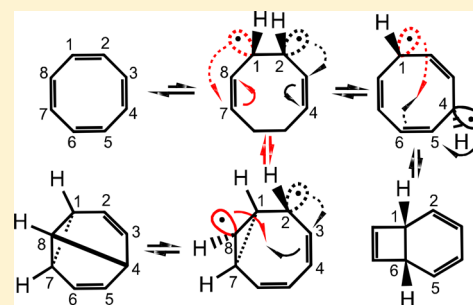
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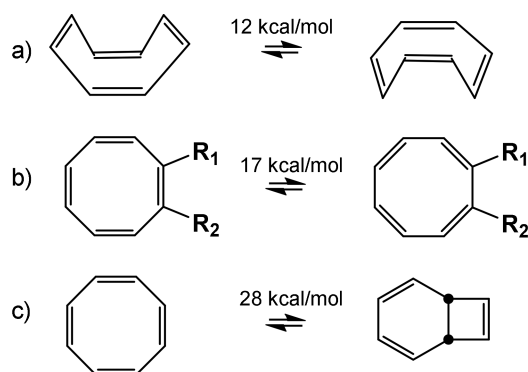
**S** Supporting Information

**ABSTRACT:** The bent bond/antiperiplanar hypothesis (BBAH) has been applied to the thermal rearrangements of cyclooctatetraene and related  $C_8H_8$  isomers. This novel orbital model shows that pyramidal singlet diradical intermediates produced from thermal vibrational states of  $C_8H_8$  isomers account for their chemical reactivity.



## INTRODUCTION

Cyclooctatetraene (COT) is capable of three fundamental structural changes referred to as ring inversion, bond shifting, and valence isomerization<sup>1,2</sup> (Figure 1). The first of these



**Figure 1.** Structural changes in cyclooctatetraene: (a) ring inversion; (b) shifting; (c) valence bond isomerization.

processes is thought to require a planar transition state and is the least energy demanding ( $\sim 12$  kcal/mol). Bond shifting is a process with a higher energy barrier ( $\sim 17$  kcal/mol), while valence isomerization of COT to bicyclo[4.2.0]-octa-2,4,7-triene (BOT) is the third dynamic process, which is necessarily disrotatory<sup>3</sup> and normally the most energy demanding option ( $\sim 28$  kcal/mol).<sup>1</sup>

In 2011, we reported<sup>4</sup> that using the Slater–Pauling bent bond model (*tau* bond,  $\tau$ -bond) in combination with the antiperiplanar hypothesis (BBAH) is a useful conceptual model to understand the conformation and reactivity of organic molecules containing carbonyl groups and double bonds. This new interpretive model in conjunction with the concept of

hyperconjugation<sup>5</sup> suggests that it is possible to have antiperiplanar electronic delocalization involving  $\tau$  bonds and that it can be applied to the Diels–Alder reaction,<sup>6</sup> [1,3]-sigmatropic alkyl thermal rearrangements,<sup>7</sup> and high-temperature isomerization of benzenoid polycyclic aromatic hydrocarbons.<sup>8</sup> We have also shown that this model can rationalize the aldol addition reaction of ketones and aldehydes containing an  $\alpha$ -alkoxy stereocenter<sup>9,10</sup> as well as the important glycosylation step in carbohydrates.<sup>9</sup> We wish now to report that the dynamic properties of COT and other  $C_8H_8$  isomers can also be readily understood through the BBAH as a simple alternative model of structure and reactivity.

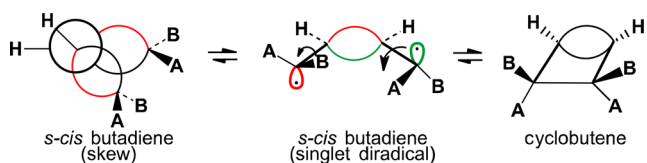
## RESULTS AND DISCUSSION

**$\tau$ -Bond Electronic Delocalization in COT.** COT exists in a tub shaped conformation and, based on its description using  $\sigma$ – $\pi$  bond orbitals, cannot have proper conjugation. With  $\tau$  bonds, the situation is however totally different because one  $\tau$  bond of each double bond is nearly antiperiplanar to a  $\tau$  bond of the neighboring olefins, allowing electronic delocalization. For example, this is illustrated in Figure 2 for the skew conformation of *s-cis* butadiene,<sup>6</sup> which shows the electronic delocalization between one  $\tau$  bond in each olefin (colored).

The BBAH further implies that *s-cis* butadiene, which is necessarily higher in energy, has a singlet diradical equivalent in which the two radicals are partly pyramidal and *anti* to each other, allowing for stereoelectronically aligned antiperiplanar delocalization with an adjacent  $\tau$  bond. Each radical in the singlet intermediate is thus conjugated with a different  $\tau$  bond. Furthermore, each radical should retain a degree of conjugation at the transition state for an eventual thermal ring closure.

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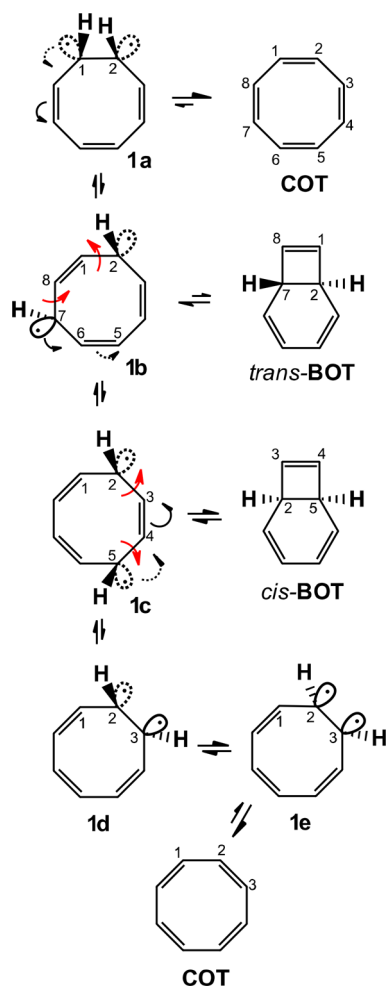
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**Figure 2.** Electronic delocalization in *s-cis* butadiene and conrotatory cyclization.

Thus, the formation of cyclobutene must therefore occur through the equivalent of a conrotatory process (Figure 2). It is thus possible to interpret the chemical reactivity of pyramidal singlet diradical intermediates by applying the BBAH.<sup>7,8</sup>

Molecular models show that each butadiene segment in COT exists in a skew conformation similar to that of butadiene so the BBAH can be used to account for its reactivity. Indeed, COT can lead to the formation of the pyramidal diradical intermediate **1a**, which is a thermally induced vibrationally excited state (Figure 3). By a proper antiperiplanar



**Figure 3.** Bond shifting and valence isomerization of COT.

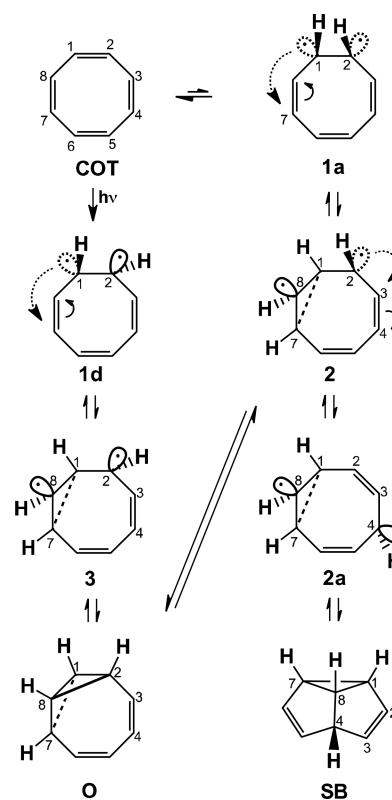
delocalization pathway, structure **1a** can be converted to **1b**, then to **1c**, and finally to **1d**. Interestingly, structure **1d** cannot readily form a double bond between  $C_2$  and  $C_3$  because the two radicals are *anti* to each other and cannot overlap. To reform COT, there must be a radical inversion at  $C_2$  (or  $C_3$ ) in **1d** to reach diradical **1e**. As a result, the bond shifting process, which leads to the COT isomer with an olefin between  $C_2$  and  $C_3$ ,

implies a loss of electronic delocalization at the radical inversion transition state. This bond shifting event is known experimentally to have a higher energy barrier ( $\sim 17$  kcal/mol) than the inversion of the tub shaped conformation ( $\sim 12$  kcal/mol), which takes place through an antiaromatic planar transition state.

On the other hand, singlet diradical intermediates **1b** and **1c** can lead to BOT valence isomers. Because of its diradical geometry, the cyclization through **1b** must be a conrotatory process that can only form the highly strained *trans*-BOT, which is not observed experimentally. On the other hand, cyclization through diradical **1c** can take place through a disrotatory mode to produce the *cis*-BOT, which is experimentally observed. Indeed, close examination of a molecular model of the tub shaped conformation of **1** shows that the  $C_5$  and  $C_2$  radicals in intermediate **1c** are *syn* oriented and can undergo a disrotatory closure to the *cis*-BOT isomer. This analysis is in complete agreement with our previous work based on the BBAH orbital model.<sup>4,6a,7,8</sup>

In summary, the tub shaped stereostructure of COT leads to thermally induced singlet diradical intermediates **1a,b,c,d**. The highly strained *trans*-BOT could be formed from the conrotatory closure of **1b**, but the lower energy *cis*-BOT valence isomer is much more easily produced from the disrotatory closure of **1c**. Singlet diradical **1d** allows the bond shifting process in COT to occur but only through a radical inversion and intermediacy of **1e**.

Other transformations of COT are known. For instance, COT can form semibullvalene (SB) under thermal and photochemical conditions (Figure 4). **1a** corresponds to a singlet diradical of COT, whereas **1d** is one of its excited states via radical inversion. **1a** can be converted to diradical **2**<sup>7,8</sup> and

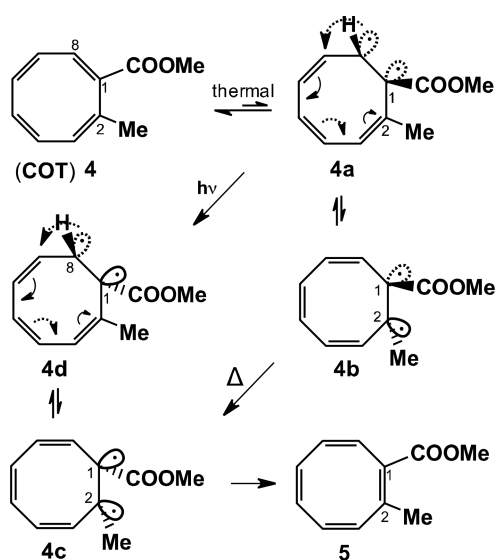


**Figure 4.** Thermal and photochemical conversion of COT to semibullvalene (SB).

the corresponding diradical **2a**, which has its radicals at C<sub>4</sub> and C<sub>8</sub> *syn* to each other and can form the C<sub>4</sub>–C<sub>8</sub> bond, resulting in **SB**. Under photochemical conditions, **COT** corresponds to diradical **1d**, which can form octavalene (**O**) through diradical **3**.<sup>7,8</sup> Now, strained octavalene (**O**), under thermal conditions, can cleave the C<sub>2</sub>–C<sub>8</sub> bond with a radical inversion at C<sub>2</sub>, producing diradical **2**, which can lead to **SB** through *syn* diradical **2a**. It has been further reported that octavalene (**O**) gives **COT** in boiling benzene, reinforcing the above analysis.<sup>11</sup> Detailed computational studies on the thermal and photo-induced transformations of **COT** have been reported,<sup>2f,g</sup> including a two-photon mechanism for the latter process. Our model is compatible with these studies, and a concordance between the models is described in the [Supporting Information](#).

At elevated temperature (350–450 °C), the most relevant conversions of isomeric dimethyl-COTs are those of the 1,2-dimethyl isomer into its 1,4-dimethyl isomer and of the 1,5-dimethyl isomer into its 1,4-dimethyl isomer. These conversions are believed to involve **BOT** intermediates and Diels–Alder and retro-Diels–Alder processes.<sup>12</sup>

It is also known that **COT**-ester **4** can be transformed into its bond shifted isomer **5** under thermal or photochemical conditions ([Figure 5](#)). The thermal isomerization can be

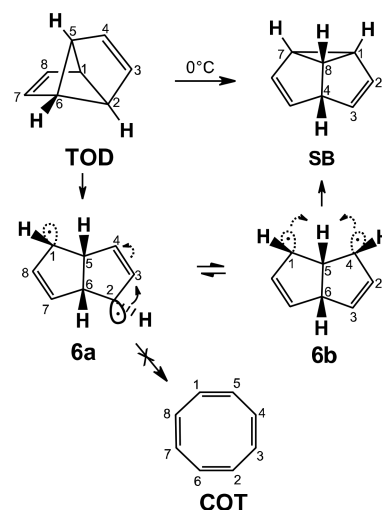


**Figure 5.** Thermal and photochemical bond shifting in **COT**.

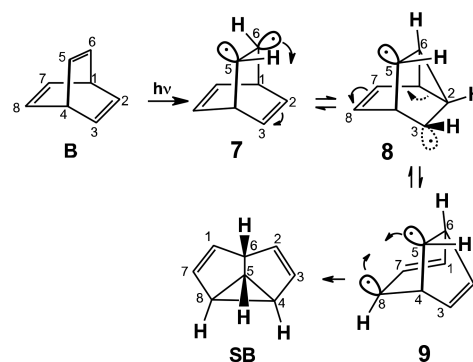
rationalized by invoking singlet diradical **4a** and the corresponding **4b**. Diradical **4b** cannot readily form a double bond between C<sub>1</sub> and C<sub>2</sub> and must therefore undergo radical inversion at C<sub>1</sub> to attain *syn* diradical **4c**, leading to bond shifted isomer **5**. Under photochemical conditions, radical inversion takes place on **4a** to form **4d**, which leads directly to *syn* diradical **4c** and the bond shifted **5**.<sup>13</sup>

The strained hydrocarbon tricyclo[3.3.0.0<sup>2,6</sup>]-octa-3,7-diene (**TOD**) gives **SB** rapidly at 0 °C ([Figure 6](#)). This can occur by cleaving the C<sub>1</sub>–C<sub>2</sub> bond with radical inversion at C<sub>2</sub> to give diradical **6a**, leading to diradical **6b** and **SB**. In principle, cleavage of the C<sub>5</sub>–C<sub>6</sub> bond in **6a** could lead to **COT**, but this is not observed because the radicals at C<sub>1</sub> and C<sub>2</sub> in **6a** are not properly aligned antiperiplanar to cleave the C<sub>5</sub>–C<sub>6</sub> bond.<sup>14</sup>

Photosensitized irradiation of bicyclo[2.2.2]octa-2,5,7-triene (barrelene, **B**) produces semibullvalene (**SB**) ([Figure 7](#)). There is experimental evidence that this reaction involves a triplet



**Figure 6.** Thermal conversion of tricyclo[3.3.0.0<sup>2,6</sup>]-octa-3,7-diene **TOD** into semibullvalene (**SB**).



**Figure 7.** Photochemical conversion of barrelene (**B**) to semibullvalene (**SB**).

followed by the formation of two intermediates according to Zimmerman.<sup>15</sup> Following the BBAH orbital model, this can be explained by the formation of diradical **7** and the formation of cyclopropane diradical **8** which, after radical inversion at C<sub>3</sub>, is antiperiplanar to the C<sub>1</sub>–C<sub>2</sub> bond for a stereoelectronically aligned bond cleavage to form diradical **9** and yield product **SB**. This reaction corresponds to the di- $\pi$ -methane rearrangement of Zimmerman.

Finally, when heated at 400–600 °C in a flow system, **COT** produces 3,8-dihydropentalene (**11**) presumably<sup>16</sup> via bicyclo[3.3.0]octadienyl intermediate **10** which must then undergo several 1,2-hydrogen shifts ([Figure 8](#)). The BBAH orbital model suggests that the singlet diradical **1c** of **COT** can form diradical **12**, which has the proper stereoelectronic alignment to produce intermediate **13** by a 1,2-hydrogen shift followed by two consecutive 1,5-hydrogen shifts to finally lead to **11**.

Now, addition of two electrons to **1c** forms a dianion of **COT** ([Figure 9](#)), which is known to be flat and aromatic, abiding by the  $4n + 2$  Hückel rule.<sup>17</sup> This flat **COT** dianion can be completely electronically delocalized in a cyclic manner, producing a ring current as shown in [Figure 9](#) in which the dianions alternate between *trans* (*T*) and *cis* (*C*) geometries.

Schleyer and co-workers have analyzed **COT** on the basis of the  $\sigma$ - $\pi$  orbital model.<sup>2c</sup> They concluded the following: “*D*<sub>2d</sub> **COT** is far from being an unconjugated polyene model devoid of important  $\pi$  interactions. Instead, “two-fold” (double) hyper-

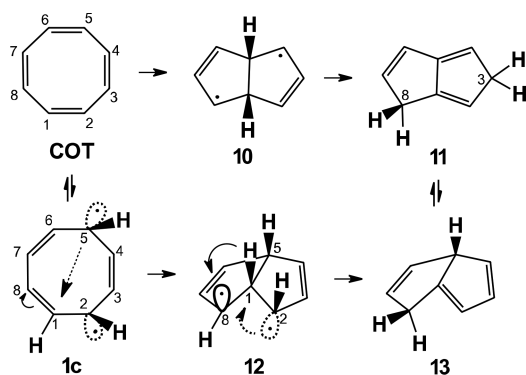


Figure 8. Thermal conversion of COT to 3,8-dihydropentalene (11).

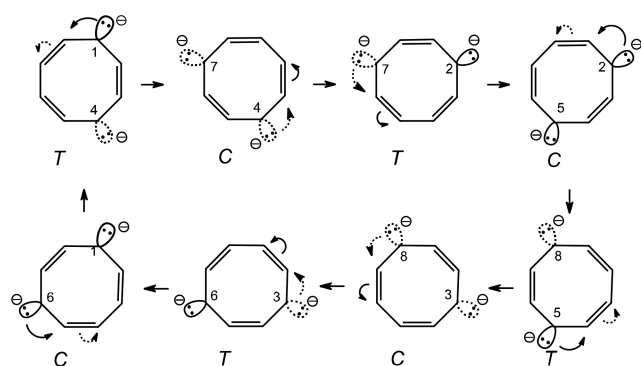


Figure 9. Ring current in aromatic cyclooctatetraene dianion.

conjugative interactions across the twisted C–C bonds of  $D_{2d}$  COT stabilize its twisted conformation considerably and compensate for the reduction in  $\pi$  conjugation relative to  $D_{4h}$  COT". They proposed that "two-way double hyperconjugation is operative in COT, butadiene and many other molecules with non-planar equilibrium structure". Our work based on the BBAH presents a general and simpler interpretive model for nonplanar conjugation based on the stereoelectronic alignment and delocalization of  $\tau$  orbitals.

## SUMMARY

The Slater–Pauling bent bond model ( $\tau$ ,  $\tau$  bond) used in combination with the antiperiplanar hypothesis (BBAH) leads to pyramidal "singlet" diradical intermediates under thermal and photochemical conditions, respectively, that allow one to rationalize the inherent chemical reactivity of an ever-widening range of reactions. For example, this new model can explain the dynamic properties of the following  $C_8H_8$  isomers: (a) the ring inversion, bond shifting, and valence bond isomerization of cyclooctatetraene (COT); (b) the conversion of COT into semibullvalene (SB) under thermal conditions or through photochemical conditions forming octovalene (O), which then yields SB thermally; (c) the bond shifting isomerization of COT-ester 4 under both thermal and photochemical conditions; (d) the thermal isomerization of tricyclo-[3.3.0.0<sup>2,6</sup>]-octa-3,7-diene (TOD) into SB; (e) the photochemical conversion of barrelene (B) into SB; (f) the thermal isomerization of COT to 3,8-dehydropentalene (11) at  $\geq 400$  °C; and finally (g) the ring current of the flat aromatic COT dianion.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00809.

Concordance of the COT isomerization and conversion to SB with that of the work reported in refs 2f and g (PDF)

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### Notes

The authors declare no competing financial interest.

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