

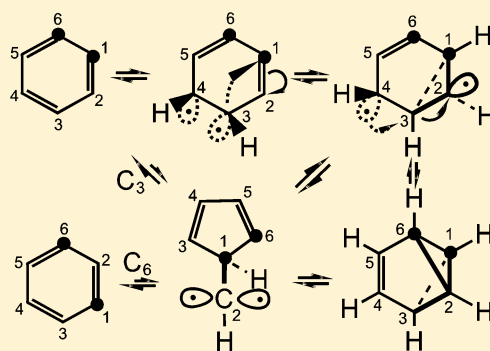
High-Temperature Isomerization of Benzenoid Polycyclic Aromatic Hydrocarbons. Analysis through the Bent Bond and Antiperiplanar Hypothesis Orbital Model

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Supporting Information

ABSTRACT: L. T. Scott has discovered the 1,2-swapping of carbon and hydrogen atoms which is known to take place on benzenoid aromatics (up to ~1000 °C range). For example, ¹³C-1-naphthalene is specifically converted to ¹³C-2-naphthalene, and there is evidence that this occurs through the formation of benzofulvene and a naphthalene–carbene intermediate. Application of the bent bond/antiperiplanar hypothesis leads to the postulate that higher in energy pyramidal singlet diradical intermediates can be used to propose a mechanism that rationalizes various atom rearrangements on benzenoid aromatics and related isomeric compounds.



The specific 1,2-swapping of carbon and hydrogen atoms at high temperature (≥ 1000 °C) on benzenoid aromatic hydrocarbons was discovered by Scott and co-workers.¹ One of their initial investigations² reported the selective thermal isomerization of ¹³C-1-labeled naphthalene **1** to produce ¹³C-2 isomer **2** without any appearance of the ¹³C-8a isomer **3** (Figure 1). This intriguing novel thermal isomerization of

was then postulated that the benzene isomerization must be taking place through the intermediate formation of the isomeric benzvalene **7**, a hypothesis supported by the thermal isomerization of *d*-1,*d*-2-benzvalene, which gave 1,2-deuteriobenzene quantitatively.⁴

It was thus believed that the carbon isomerization of naphthalene must be occurring through an intermediate having a bicyclo[1.1.0]butane unit similar to that found in benzvalene. The known thermal isomerization of azulene to naphthalene was also thought to occur through the same benzvalene type of intermediate.⁵ However, Scott found that flash vacuum pyrolysis (FVP) of ¹³C-8a-azulene **8** gave not only ¹³C-8a-naphthalene **3** but also isomers **1** and **2**. This result clearly indicated that other intermediates must be involved in the thermal isomerization of **1** and **8**.⁶

Although the benzvalene pathway is believed¹ to apply only to benzene and closely related aromatics, it is inconsistent with experimental data for the 1,2-swapping of carbon in larger polycyclic benzenoid hydrocarbons.⁷ The presently accepted mechanism^{7,8} for the 1,2-swapping of carbon in naphthalene and other benzenoid aromatic hydrocarbons at high temperature is shown in Figure 2. The isomerization of carbenes to alkenes by the 1,2-shift of hydrogen and carbon atoms is known.⁹ The experimental evidence⁸ supported by calculation⁷ suggests that the transformation of **1** to **2** occurs through the intermediate formation of naphthalene–carbenes **9a–d** and the isomeric benzofulvenes **10a,b**. Indeed, FVP of benzofulvene gives naphthalene as the sole product. Further support for this

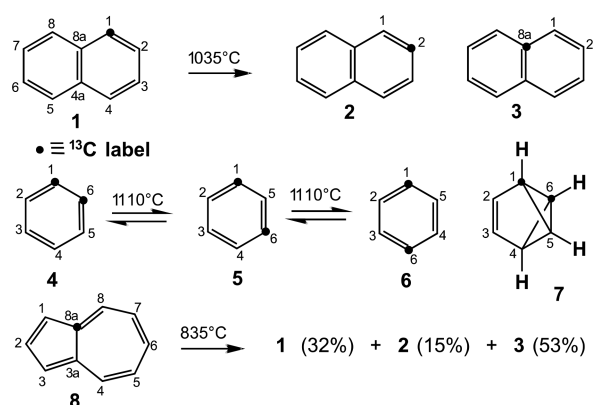


Figure 1. ¹³C carbon isomerization of naphthalene, benzene, and azulene.

aromatic compounds was also shown to be general (azulene, benzene, pyrene, etc.). As the laws of nature apply at all temperatures,¹ the next step was to figure out the mechanism of these fascinating rearrangements. Accordingly, Scott³ showed that ¹³C-1,2-benzene **4** gives ¹³C-1,3-benzene **5**, which in turn produces ¹³C-1,4-benzene **6** by consecutive 1,2 carbon swaps. It

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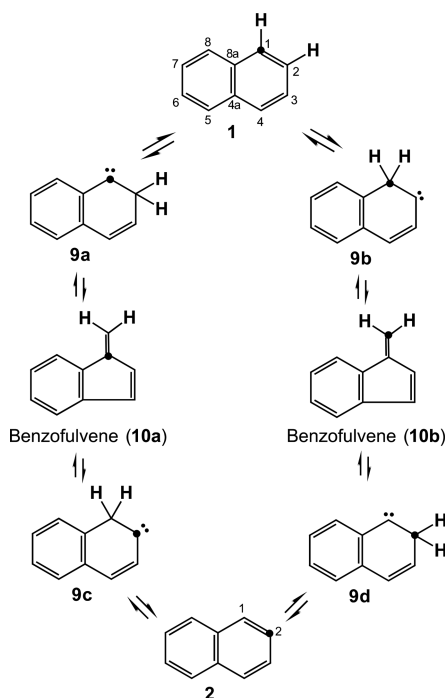


Figure 2. Scott mechanism for the 1,2-swapping of carbon atoms in naphthalene.

mechanism comes from experiments on doubly labeled naphthalene, demonstrating that the 1,2-swapping of hydrogen atoms occurs faster than that of carbon atoms.¹

To date, only the standard σ - π orbital model for double bonds has been used to interpret these thermal isomerization reactions.¹ Since 2011, we have been advancing the “BBA hypothesis”, which is founded on the Slater–Pauling bent bond model (*tau*-bonds, τ -bonds), and the antiperiplanar hypothesis as a useful conceptual model to understand electronic delocalization and the ensuing chemical reactivity.¹⁰ For example, Figure 3 shows the τ -bond models of ethylene and

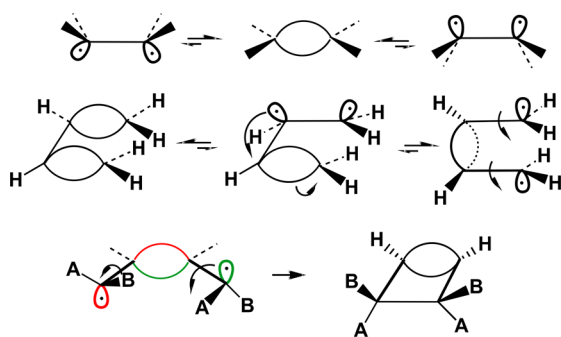


Figure 3. *Tau* bond description of ethylene and *s-cis* butadiene and their corresponding singlet diradical intermediates. Conrotatory ring closure.

the *s-cis* conformation of butadiene. It also shows their corresponding singlet diradical intermediates which are necessarily higher in energy. For the case of butadiene, the BBA hypothesis implies that the singlet doubly allylic diradical intermediate must be pyramidal and oriented *anti* in order to enable antiperiplanar electronic delocalization with an adjacent τ -bond. Each radical is thus conjugated with a different τ bond. In addition, each radical should remain conjugated at the transition state level for an eventual thermal ring closure. For

example, the formation of a cyclobutene must therefore occur through the equivalent of a conrotatory process as illustrated.^{10a}

We have applied the BBA hypothesis to the thermal rearrangements of polyaromatic compounds and, when analyzing these reactions in terms of pyramidal singlet diradical intermediates, found that it readily accounted for these reactions which occur at temperature over 1000 °C. We now report that the BBA hypothesis can provide a basis of understanding of how these carbon atom shifts and skeletal rearrangements take place in such a highly specific manner.

■ BENZENE, DEWAR BENZENE, AND BENZVALENE

The antiperiplanar hypothesis when combined with τ -bonds allows one to account for observed chemical reactivities that are not readily apparent when using traditional interpretive models. Let us begin by a re-examination of the thermal isomerization of benzene (Figure 4).^{10a} The corresponding high energy

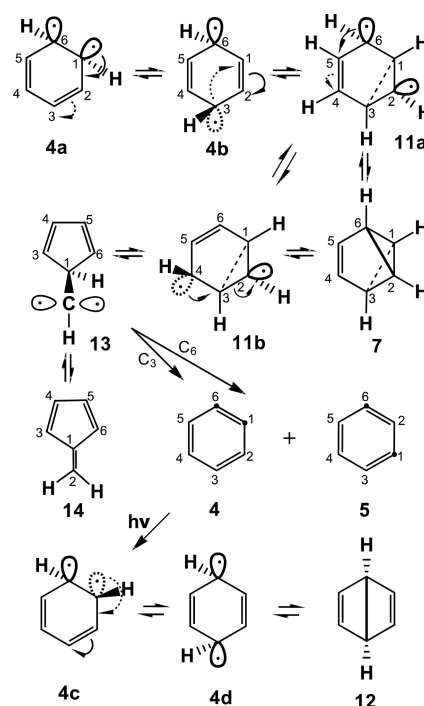


Figure 4. Benzene, benzvalene, and Dewar benzene interconversion.

pyramidal singlet diradical intermediate of benzene corresponds to 4a. The benzene diradical 4a represents a vibrationally excited benzene in which two *ortho*-hydrogen atoms have been bent out-of-plane in the same direction.¹¹ Diradical 4a can also be converted into diradical 4b via an antiperiplanar delocalization. The two radicals in 4b being on opposite faces can only lead to the formation of *syn* cyclopropane diradical 11a but are not properly oriented to form Dewar benzene 12 (vide infra). The diradical recombination in intermediate 11a is poised to only produce the higher energy benzvalene 7. Therefore, incorporating the stereoelectronic component of the BBA hypothesis affords a clear reaction pathway for the formation of benzvalene and, as will be shown next, for the observed 1,2-carbon atom shifts.

We assume here that homolytic bond cleavage of benzvalene (7) at C_2 - C_6 (or the equivalent C_1 - C_6 , C_1 - C_3 , or C_2 - C_3) with retention of configuration at C_6 yielding 11a will have a kinetic propensity to reform 7 in light of its diradical geometry,

alignment, and proximity.^{12,13} Cleavage of **7** with inversion at C₂ can be eliminated because a cyclopropyl radical inversion is too high in energy.¹⁴ Furthermore, cleavage of **7** with inversion at C₆ will lead to a diradical (**11c**, not shown) which will give back benzvalene by forming a bond between C₂ and C₄. In addition, diradical **11a** is conjugated with diradical **11b**. Now, diradical **11b** has the allyl radical at C₄ to be antiperiplanar to the C₂–C₃ bond, leading to bond cleavage and formation of cyclopentadiene carbene **13**. Carbene **13** can either undergo a well-known [1,2]-hydrogen shift to form fulvene **14** or a 1,2-carbon swap at C₃ (or C₆) to form benzene. This model is consistent with the FVP of ¹³C-1,2-benzene (**4**) to produce first isomer **5**, which then gives **6** (Figure 1). Furthermore, the formation of benzvalene (**7**) may not be an intermediate in the 1,2-carbon swap mechanism.¹⁵

As we have previously reported,^{10a} other diradical intermediates such as *anti* **4c** and *syn* **4d** cannot be obtained from **4a** and **4b** while respecting the BBA hypothesis under thermal conditions because they require a radical inversion that would disrupt the aromatic resonance. However, diradicals **4c,d** can be generated by a photochemically induced radical inversion^{9a} in benzene and can lead to the formation of Dewar benzene **12** from the *syn* diradical orientation in **4d**. Thus, the BBA hypothesis accounts for the relative kinetic stability of Dewar benzene **12** compared to benzene because there is an energy barrier for a radical inversion to take place from **4c,d** to **4a,b** prior to isomerization.^{10a}

This analysis is in complete agreement with the ¹³C-double-label benzene experiment reported by Scott (**4** → **5** → **6**) and makes the assumption that benzene leads to intermediate **11b** indirectly through **11a** or through the intermediate formation of benzvalene (**7**) to produce carbene **13** from **11b**.¹² This stereocontrolled pathway thus suggests that it is necessary to go through fulvene–carbene **13**, which allows the 1,2-swapping of carbon atoms. It also means that the alternative pathway in which benzene undergoes directly a 1,2-shift of a hydrogen atom producing a benzene–carbene (similar to naphthalene carbene **9** in Figure 2) in order to allow the 1,2-shift of carbon atoms to form fulvene as an intermediate may not correspond to reality. The real key intermediate would be fulvene–carbene **13** from benzene, but that does not prevent the interconversion of **13** and **14** from taking place.

■ NAPHTHALENE, BENZOFULVENE, AND AZULENE

As shown in Figure 2, Scott¹ has suggested that the 1,2-swapping of ¹³C-1-naphthalene (**1**) to ¹³C-2-naphthalene (**2**) takes place through the intermediate formation of a naphthalene–carbene (**9**) and benzofulvene (**10**). He also noted that the ¹³C-8a-naphthalene (**3**) was not observed in these pyrolyses. On the other hand, he also showed that the thermal isomerization of ¹³C-8a-azulene (**8**) not only produces naphthalenes **1** and **2** but also ¹³C-8a-naphthalene (**3**).

In addition, the thermal isomerization of ¹³C and deuterated label naphthalene **15** gave rapidly deuterated isomer **16** and more slowly isomers **17** and **18** (Figure 5).

Finally, he also observed that ¹³C-1,2-naphthalene **19** does not isomerize into the ¹³C-1,3-naphthalene isomer **20** and explains this result by mentioning that this isomerization would temporarily destroy aromaticity in both rings. Interestingly, all these results can be rationalized if one takes into account the BBAH orbital model just described.

Naphthalene (**1**) through diradical intermediate **1a** in which the two radicals are *anti* oriented can lead to the *syn* diradical

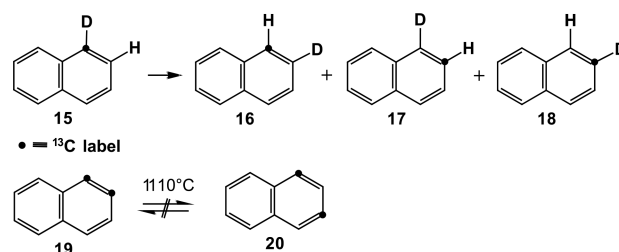


Figure 5. ¹³C and deuterated naphthalene thermolysis.

intermediate **21a** to produce benzobicyclobutane **22** (Figure 6). Cleavage of **22** with retention of configuration at C₄ gives back

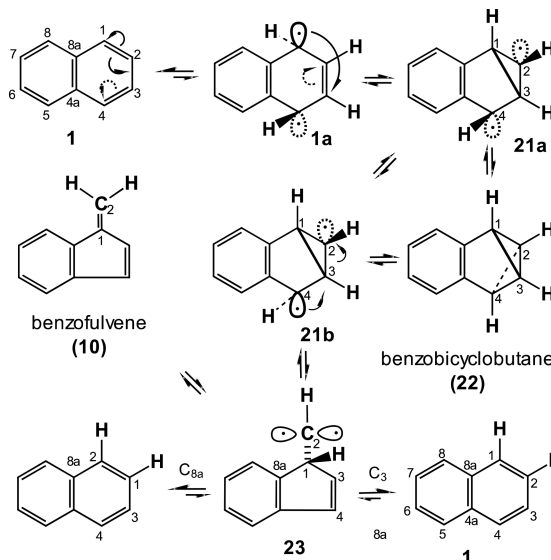


Figure 6. 1,2-Swapping in naphthalene can take place only at C₁ and C₂.

21a and with inversion,^{12,13} the isomeric diradical **21b**. We assume here that cleavage of **22** with inversion in a cyclopropyl radical is too high in energy. Diradical **21b** is now properly oriented to cleave the C₂–C₃ bond to form the benzofulvene–carbene **23**.

Of course, it is also conceivable that diradical **21a** could undergo an inversion of the benzylic radical at C₄ to yield diradical **21b** directly. As in the case of benzene, carbene **23** can now yield either benzofulvene **10** by hydrogen shift or naphthalene with 1,2-transposition of carbons at C_{8a} or C₃ as shown in Figure 6.

Contrary to the case of benzene, the diradical intermediate **21c** can be written but is not important (compared to **21a**) because the aromatic resonance energy is lost in both rings (Figure 7). Otherwise, **21c** would have led to carbene **24** allowing the 2,3-swapping of carbon atoms in ¹³C-1,2-naphthalene. Scott¹ has previously explained the absence of C₂ to C₃ interconversion in naphthalene due to the loss of aromaticity in both rings (Figure 7).

The mechanism shown in Figure 6 is in complete agreement with experimental results on naphthalene assuming the rapid hydrogen exchange at C₁ and C₂ occurring between **23** and benzofulvene (**10**). It shows that there can be carbon exchange only between C₁ and C₂ and no exchange between C₁ and C_{8a} or between C₂ and C₃ as shown in Figure 7. The mechanism in Figure 6 is, however, different from the one shown in Figure 2

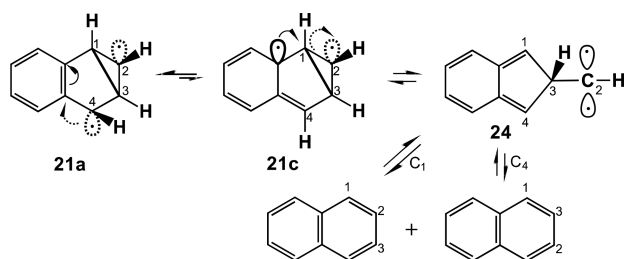


Figure 7. 2,3-Swapping of carbon atom not observed in naphthalene.

because the carbene intermediate **23** has a benzofulvene basic structure rather than the naphthalene–carbene **9** shown in Figure 2.

By taking into consideration singlet pyramidal diradical intermediates of azulene, it becomes possible to understand why ^{13}C -8a-azulene led to the formation of the three isomeric ^{13}C -label naphthalenes **1–3** as shown in Figure 1, azulene (**8**) through singlet diradical intermediate **8a** can form the bicyclobutane intermediate **26** through cyclopropane diradical **25** (Figure 8). Intermediate **26** can then produce

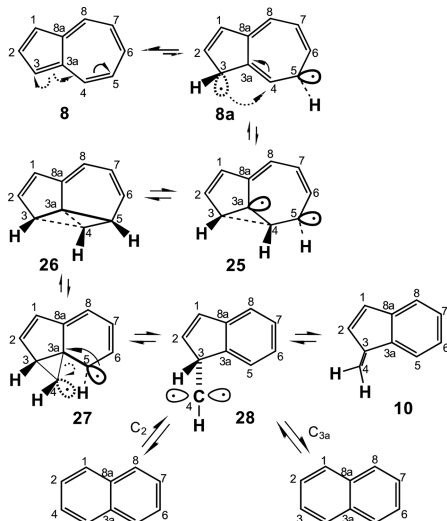


Figure 8. ^{13}C -4-Azulene thermolysis to ^{13}C -1-naphthalene.

carbene **28** through cyclopropyl diradical **27**. Carbenes **28** can now produce benzofulvene (**10**) or naphthalene. The 1,2-swapping of carbon atom in naphthalene is illustrated by the numbering of carbon atoms.

It can be seen that if C_{3a} or C_{8a} are labeled, the benzofulvene or the naphthalene ^{13}C label at C_{3a} (or C_{8a}) will remain unchanged. Of course, the cleavage of the C_{3a} – C_5 bond can also take place in **26**, but it will go back to **25** and azulene while retaining the ^{13}C atom at the $3a$ or C_{8a} position. Now it remains to examine how the ^{13}C -label naphthalenes **1** and **2** can be obtained from ^{13}C -8a-azulene (**8**).

This can be achieved by considering a new singlet diradical intermediate which is available because there are three conjugated olefins in the cycloheptane ring of azulene. The BBAH model indicates that azulene can lead to the singlet diradical intermediate **8b** in which the two radicals at C_{3a} and C_8 are *syn* (Figure 9). As a result, the cyclopropane intermediate **29** can be formed. Interestingly, its corresponding singlet diradical intermediate **29a** can be written, and it has the radical at C_3 antiperiplanar to the C_{3a} – C_{8a} bond and can thus

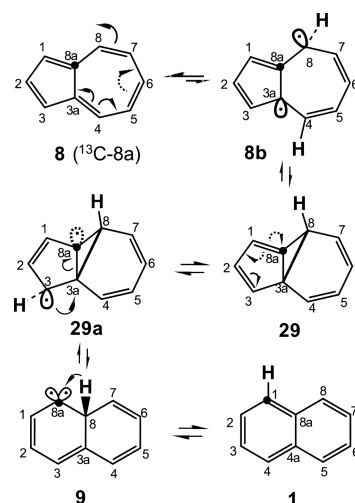


Figure 9. Thermolysis ^{13}C -8a-azulene to ^{13}C -1-naphthalene.

generate a naphthalene–carbene at C_{8a} (**9**) as previously postulated by Scott (Figure 2). Thus, a 1,2-shift of the hydrogen atom from C_8 to C_{8a} can take place to produce ^{13}C -1-naphthalene (**1**). This analysis thus shows that ^{13}C -8a-azulene (**8**) can produce ^{13}C -1-naphthalene **1**, which in turn can produce $^{13}\text{C}_2$ -naphthalene (**2**). Indeed, as indicated in Figure 6, if there is a ^{13}C -label at C_1 in **1**, it follows that there is a ^{13}C label at C_1 in carbene **23** that can produce $^{13}\text{C}_2$ -naphthalene by a 1,2-transposition of carbon $8a$ from C_1 to C_2 . Thus, azulene can lead to the three isomeric ^{13}C -naphthalene isomers **1–3** because it can react through two different singlet diradical intermediates **8a** and **8b**.

■ $\text{C}_{10}\text{H}_{10}$ AND C_{10}H_8 CARBON ISOMERIZATION

The thermal and photochemical interconversions of several $\text{C}_{10}\text{H}_{10}$ skeletal isomers have been studied in detail by several investigators.¹⁶ It was thus of interest to see if the known interconversion described in Figure 10 can be rationalized while considering the BBAH.

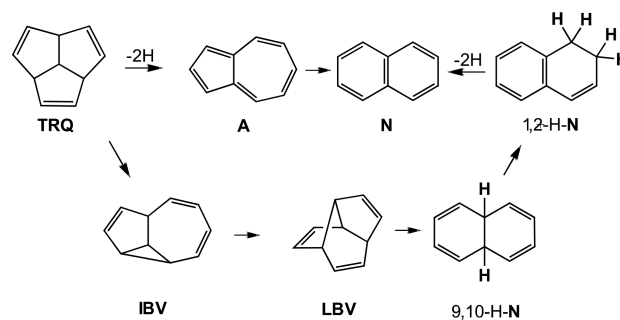


Figure 10. Thermal interconversion of $\text{C}_{10}\text{H}_{10}$ isomers starting from triquinacene.

Other $\text{C}_{10}\text{H}_{10}$ interconversions are known but are not considered here because they can be explained directly by a Diels–Alder–retro-Diels–Alder or Cope rearrangement mechanism.^{16,17} Starting with the $\text{C}_{10}\text{H}_{10}$ isomer triquinacene (**TRQ**), it is converted to C_{10}H_8 azulene (**A**) while losing two hydrogen atoms. We have already described how azulene produces naphthalene at higher temperature. In addition, at temperatures above 650°C , **TRQ** is also transformed into isobulvalene (**IBV**), which produces in situ lumibulvalene

(LBV). At 280 °C, LBV yields 9,10-dihydronaphthalene (9,10-H-N), which can then form 1,2-dihydronaphthalene and finally naphthalene by losing two hydrogen atoms.¹⁷

For the formation of azulene from triquinacene, Scott proposed in 1974¹⁷ that this transformation starts with the loss of two allylic hydrogens to form intermediate **30** which can undergo a 1,5-sigmatropic hydrogen shift in the cyclopentadiene ring to yield **31** (Figure 11). A 1,2-carbon swapping

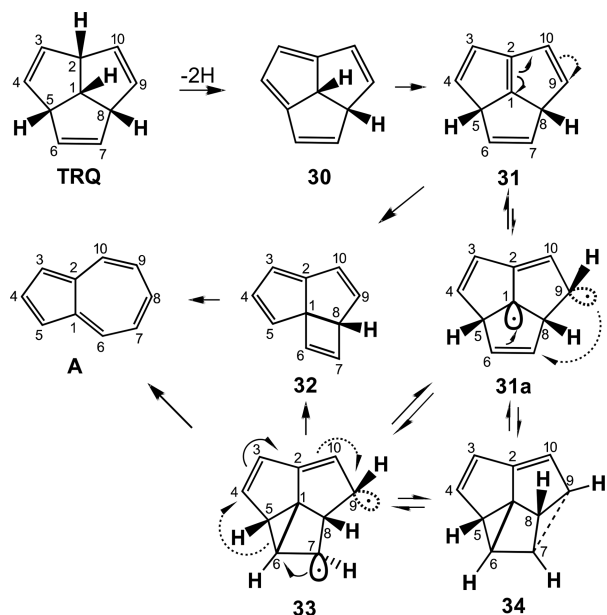


Figure 11. Conversion of triquinacene to azulene.

would then provide the cyclobutene intermediate **32**, which can lead to the formation of azulene (A) through an electrocyclic disrotatory opening of the 4-membered ring. Interestingly, the singlet diradical intermediate **31a** of **31** has necessarily the tertiary radicals at C₁ and C₉ in an *anti* orientation. As a result, **34** can be formed directly. Then, cleavage of **34** at C₇ and C₉ can produce diradical **33**, which can also be obtained directly from **31a**. Finally, **33** can form azulene through cyclobutene intermediate **32**. It is even possible to imagine that **33** (or even **34**) could directly form azulene. For instance, cleavage of the C₅–C₆ and the C₁–C₈ bond in **33** forms directly azulene. We can conclude here that the formation of cyclobutene **32** or azulene would thus occur through diradical **33**, which is formed because of the reactivity of diradical intermediate **31a** as indicated by the BBAH orbital model.

The isomerization of TRQ to IBV is believed to occur by cleaving the C₁–C₈ bond producing diradical **35** with an inversion at C₈ (Figure 12) which is properly oriented to lead to IBV directly as shown. Then, IBV can suffer another cyclopropane bond cleavage with inversion at C₅ and C₆, producing a new allyl diradical **36** properly aligned to form the C₃–C₈ bond to yield LBV. It is also possible that IBV is converted to LBV through a Cope rearrangement by cleavage the C₅–C₆ bond while forming a bond between C₃ and C₈ in a concerted manner. In addition, using deuterium labeling, it has been shown that LBV can isomerize to *ent*-LBV. This can occur by the cleavage of the C₁–C₂ bond with inversion at C₂. The resulting diradical **37** can form a new bond between C₁ and C₉, providing *ent*-LBV.¹⁸

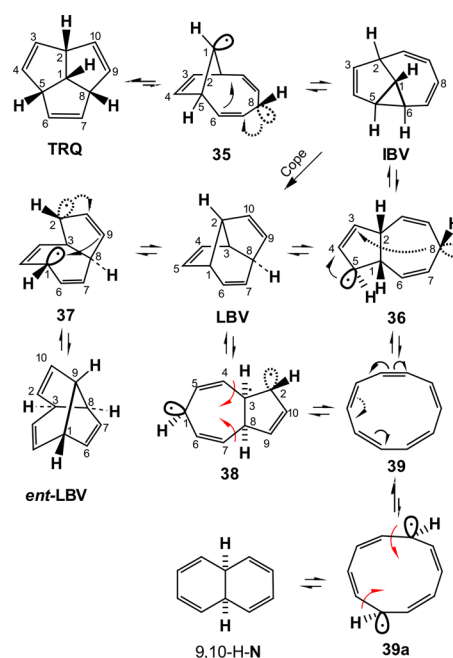


Figure 12. Triquinacene to 9,10-dihydronaphthalene.

In addition, if LBV undergoes a cleavage between C₁ and C₂ but with inversion at C₂ (or that of C₃ and C₈) it leads to diradical **38**, which can undergo an electrocyclic disrotatory opening to produce the *all-cis* cyclodecapentaene **39**. Now, the singlet diradical intermediate **39a** of **39** has the two radicals *syn* and can thus only undergo a disrotatory electrocyclozation to *cis* 9,10-dihydronaphthalene (9,10-H-N). Diradical **36** has the same diradical relative orientation as **38**; it can also produce **39** directly.

The isomeric *cis,cis,cis,cis,trans*-cyclodecapentaene (**40**) having one olefin *trans* oriented gives *trans*-9,10-dihydronaphthalene (**41**) (Figure 13).¹⁹ This result is simply explained because the singlet diradical intermediate **40a** allows a disrotatory electrocyclozation, which yields **41**.



Figure 13. Conversion of *cis,cis,cis,cis,trans*-cyclodecapentaene **40** into *trans* 9,10-dihydronaphthalene (**41**) through singlet diradical intermediate **40a**.

Scott has studied the thermal isomerization of several polyarenes, all of which undergo 1,2-swapping of hydrogen and carbon atoms and highly specific skeletal rearrangements. His outstanding synthetic work in this area has led him to prepare several so-called geodesic polyarenes and to realize the first site-specific synthesis of C-60 fullerene.¹ In addition, he has discovered the necessary basic knowledge toward the synthesis of uniform carbon nanotubes. It is not the purpose of this paper to review in detail his work while considering the implication of the BBAH orbital model, but examples are illustrated in the Supporting Information.

In conclusion, this paper shows that the BBAH orbital model is highly useful. First, it indicates that high energy singlet

diradical intermediates of organic compounds may have a pyramidal character. Second, as a result of the antiperiplanar hypothesis, these pyramidal diradical intermediates through the resulting electronic delocalization serve as a guide to rationalize the ensuing chemical reactivity which is observed experimentally by thermal isomerization under high temperature of various aromatic and related polycyclic compounds.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00095.

Skeletal isomerization of acenaphthylene, conversion of phenanthrene to pyracylene and formation of corannulene are analyzed by the BBA hypothesis (PDF)

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Notes

The authors declare no competing financial interest.

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(11) We thank Professor L. T. Scott for clarification of this point.

(12) The homolytic cleavage of a bond to a diradical with retention of configuration normally favors the reclosure because singlet diradicals have little or no inherent enthalpy barrier to bond formation as shown in the case of our previous work on sigmatropic alkyl shift.^{10c} In the case of a bicyclobutane which is highly strained, the reclosure of a *syn* diradical can be a higher energy process.

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(15) Scott's high-level calculations have indicated that the energy required to reach carbene **13** is greater than that required for two alternative pathways, a direct cleavage of benzvalene or a 1,2-hydrogen shift.^{7a} Calculations should provide a way to distinguish among multiple pathways that emerge from the BBAH orbital model.

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