

Bent Bonds and the Antiperiplanar Hypothesis. A Model To Account for Sigmatropic [1,*n*]-Hydrogen Shifts

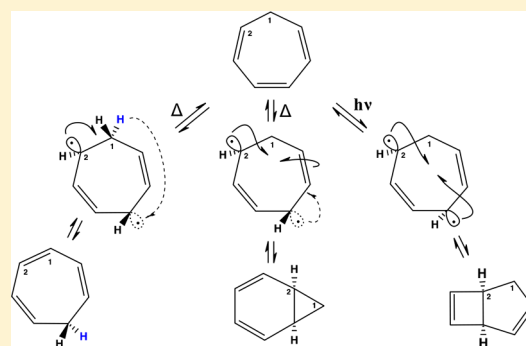
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S Supporting Information

ABSTRACT: The bent bond/antiperiplanar hypothesis (BBAH) is used to propose a mechanism-based orbital model for the facial selectivity of sigmatropic hydrogen shifts under both thermal and photochemical conditions. The BBAH analysis of these concerted rearrangements invokes transient vibrationally excited singlet diradicals in both $4n$ and $4n+2$ polyenes.



INTRODUCTION

In 2011, we reported¹ that the Slater–Pauling bent bond (tau bond, τ bond) model in combination with the antiperiplanar hypothesis (BBAH) is a useful conceptual orbital model to account for the conformation and reactivity of organic molecules containing carbonyl groups and double bonds (Figure 1). This new interpretive model applies concepts of

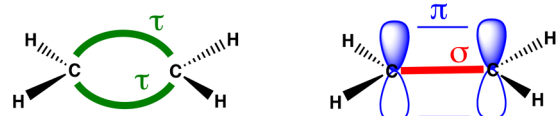


Figure 1. Slater/Pauling tau-bond model (left) versus Hückel sigma/pi model (right) of ethylene.

hyperconjugation² and antiperiplanar electronic delocalization to structures involving τ bonds (Figure 1). A recent essay reinforcing the validity of valence bond theory and the related τ bonds highlights some of the interpretive advantages of the BBAH.³ The BBAH also describes aromaticity, antiaromaticity, and electrocyclic reactions.¹ In addition, this model has been applied to the regio- and diastereoselectivity of Diels–Alder reactions,⁴ the stereocontrolled nucleophilic addition to ketones and aldehydes bearing an α -alkoxy stereocenter,⁵ the glycosylation of pyranosides,⁶ and the chemistry of cyclooctatetraene and its isomers.⁷ As stated in our original reports, the τ bond orbital model confers “tetrahedral character” to olefinic and carbonyl carbons, allowing one to apply stereo-electronic principles associated with saturated systems.^{1,4}

In 2016, we applied the BBAH to the analysis of 28 previously reported [1,3]-sigmatropic alkyl shifts involving various optically active cyclic molecules.⁸ These rearrange-

ments are not all concerted and do not follow the Woodward–Hoffmann (W–H) rules.^{9,10} These rearrangements were adequately rationalized through the analysis of vibrationally excited structures in which pyramidal singlet diradical intermediates can be produced preferentially in staggered conformations. The preference for suprafacial over antarafacial rearrangement pathways as well as the extent of inversion or retention of configuration of the migrating radical intermediates were also well-accounted. In addition, the thermal isomerization of various aromatics and related polycyclic compounds under high temperature was reported in 2018.¹¹ The BBAH suggests that these rearrangements can also be rationalized by invoking vibrationally excited singlet diradical intermediates, which can have pyramidal character. Antiperiplanar delocalization within these diradical intermediates provided a clear rationale for the experimentally observed chemical reactivity of these compounds.

Sigmatropic hydrogen shifts are known to take place thermally and photochemically.¹² It remains to be verified if these reactions can also be rationalized using the orbital model of the BBAH. We now wish to report an analysis of sigmatropic [1,*n*]-hydrogen shifts and related rearrangements based on the BBAH.

RESULTS AND DISCUSSION

[1,*n*]-Hydrogen Shifts. Concerted thermal [1,3]-hydrogen shifts could theoretically take place but are not observed, in accord with frontier molecular orbital (FMO) theory. In BBAH formalism, allylic system **1** can be vibrationally excited

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to correspond to singlet diradical **2** in formal bond representation (Figure 2). On the basis of the BBAH,

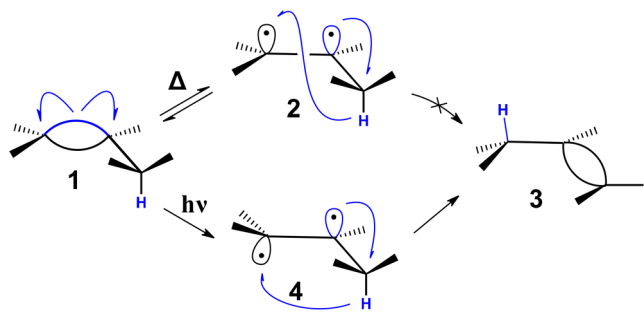


Figure 2. Thermal and photochemical [1,3]-hydrogen shift in allylic system.

migration of a hydrogen radical via the required antiperiplanar participation of the adjacent radical can only occur antarafacially, so the formation of **3** is geometrically not possible. Under photochemical conditions, radical inversion of the same allylic system can produce the corresponding *anti* diradical **4**, which has the proper stereoelectronic alignment to undergo a concerted suprafacial [1,3]-hydrogen shift and formation of **3**. Many cases of such photochemically induced rearrangements are known;¹³ two examples are shown in Figure 3.

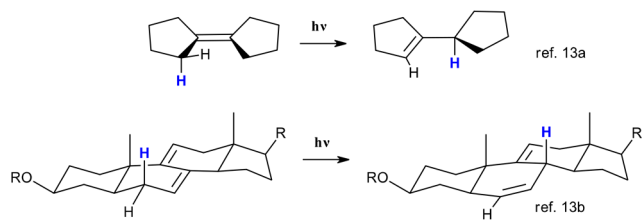


Figure 3. Examples of photochemical [1,3]-hydrogen shifts.

From the principle of antiperiplanar electronic delocalization, the vibrational ground states of polyenes with $4n$ electrons predispose terminal radicals to be *anti* to each other, while those with $4n+2$ electrons display terminal radicals *syn* to each other. Thus, applying the BBAH to *cis*-1,3-butadiene implies that its singlet 1,4-diradical equivalent has its two radicals *anti* to each other under thermal conditions but *syn* to each other under photochemical conditions (Figure 4). This dictates that a thermal closure must proceed in conrotatory fashion whereas the photochemical counterpart

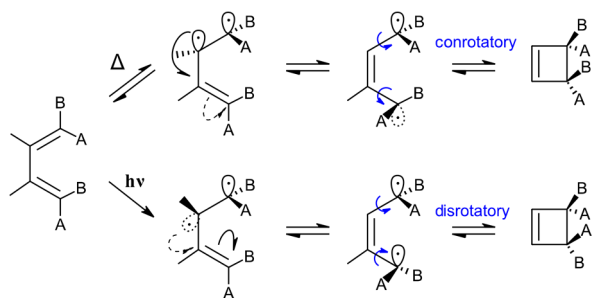


Figure 4. Thermal and photochemical electrocyclicization of 1,3-butadiene.

proceeds in disrotatory fashion, in accord with experimental results and the W–H rules.^{1,4,9}

Concerted [1,5]-hydrogen shifts and other rearrangements in cyclopentadiene (Cp) **5** can be examined next.¹⁴ Under thermal conditions, this cyclic diene can transit to structure **6** and to singlet 1,4-diradical **7**, which has *anti* orientation (Figure 5). The C_2 radical in **7** is antiperiplanar to the α - C_1 –H

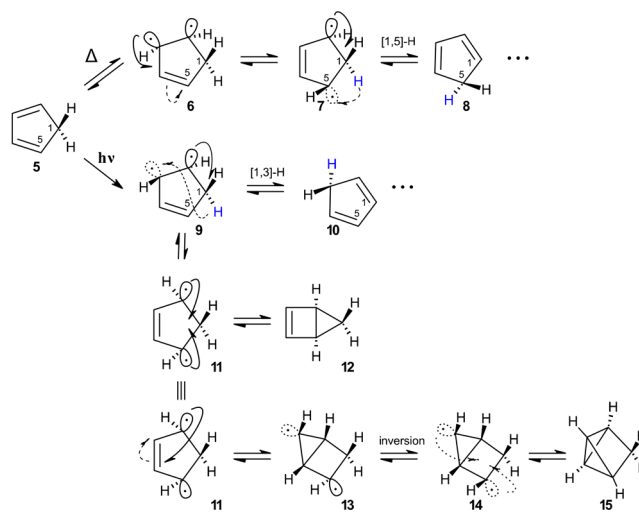


Figure 5. Thermal and photochemical reactions of cyclopentadiene (Cp).

bond, allowing for a concerted suprafacial [1,5]-hydrogen migration to the C_5 radical and formation of isomeric Cp **8**, in agreement with experimental results. Furthermore, the photochemistry of Cp is known to produce two main products, bicyclo[2.1.0]pentene **12** and tricyclo[2.1.0.0^{2,5}]pentane **15**, as well as bond-shifted Cp isomers.^{14b} According to the BBAH, irradiation of **5** can produce *anti* diradical **9**, which can undergo a suprafacial [1,3]-hydrogen shift from the proper stereoelectronic alignment of its C_2 and C_3 radicals to form Cp isomer **10**. Antiperiplanar delocalization of diradical **9** produces *syn* diradical **11**, which has the proper stereoelectronic geometry to produce bicyclopentane product **12**. Alternatively, diradical **11** can form bicyclic diradical **13**, which must undergo radical inversion of its cyclobutyl radical to form **14**, the immediate precursor to tricyclopentane **15**. Recent deuterium-labeling experiments have shown that the bond shifting of Cp under photochemical conditions does indeed proceed by suprafacial [1,3]-hydrogen shift, in accord with the BBAH.^{14b} In principle, diradical **7** does have the proper stereoelectronic alignment to produce tricyclopentane **15** directly, but the photoexcited path via diradical **11** is likely to be more energetically reasonable.

Roth and co-workers¹⁵ showed that heating chiral diene **16** yielded two stereoisomers, one of which is **17** (Figure 6). Diene **16** corresponds to *anti* singlet 1,4-diradical rotamer **18**, which is compatible for suprafacial rearrangement to occur in concerted fashion, producing **17**. The other stereoisomer (not shown) stems from 180° rotation of the C_1 – C_2 bond prior to suprafacial [1,5]-hydrogen shift.

Extending the conjugation by one more $C=C$ segment allows a concerted antarafacial thermal rearrangement to proceed with relative ease. One example is shown in Figure 7, i.e., the [1,7]-deuterium shift from **19** to **21** via the singlet *syn*-1,6-diradical.¹⁶

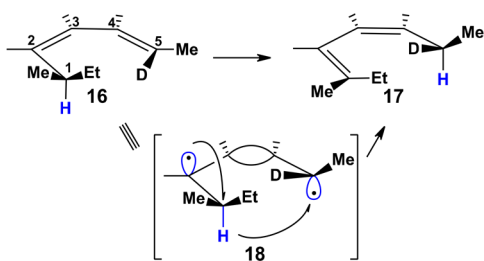


Figure 6. Thermal [1,5]-hydrogen shift in a 1,3-pentadiene system.

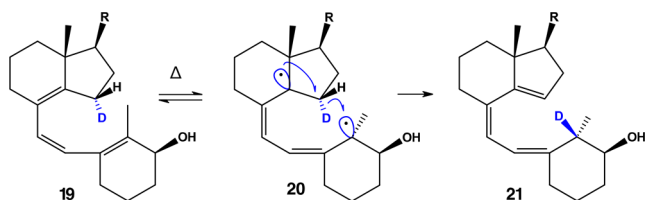


Figure 7. Thermal [1,7]-hydrogen shift is antarafacial.

Another related case is that of methylene cyclohexadiene **22**, which is stable at 350 °C despite the fact that its isomerization to toluene **23** is very exothermic (Figure 8).¹⁷ In principle,

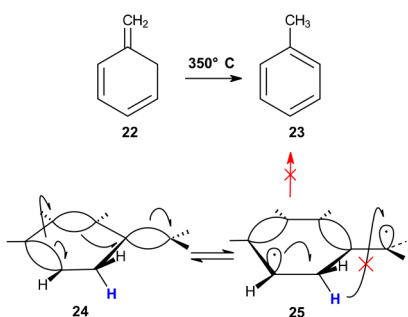


Figure 8. Tautomerization of methylene cyclohexadiene.

toluene can be produced by a [1,7]-hydrogen shift (or [1,3]), but again, this is not allowed by BBAH. As one considers bent bond structures **24** and **25**, both radicals in **25** are *syn* to each other and dictate an improperly aligned antarafacial [1,7]-hydrogen shift, which requires very high energy to take place.

Tropilidene **26** (1,3,5-cycloheptatriene) chemistry has fascinated chemists since the late 19th century.^{18,19} This boat-shaped molecule undergoes low-barrier ring flips ($E_a \approx 6.3$ kcal/mol)²⁰ as well as facile and reversible isomerization to norcoradiene **28** (bicyclo[4.1.0]hepta-2,4-diene), even at low temperature, resulting in up to 2% of **28** at room temperature (Figure 9).²¹ Moreover, tropilidene derivatives undergo “epidermal shifts” where all hydrogen positions can be exchanged thermally via consecutive [1,5]-hydrogen shifts (i.e., **26** to **27**...) as shown by deuteration experiments.^{22,23} In addition, tropilidene produces bicyclo[3.2.0]-hepta-2,6-diene (**29**) under photochemical irradiation.¹⁹

These various observations can be accounted for by BBAH. As shown in Figure 10, the epidermal shift of tropilidene derivatives can be seen as a series of concerted [1,5]-hydrogen shifts. Indeed, tropilidene **26** corresponds to *anti* singlet 1,4-diradical **26a**, which has the proper geometry for stereoelectronically assisted suprafacial migration of a hydrogen radical from C_1 to C_5 to produce tautomer **26b**. In the same

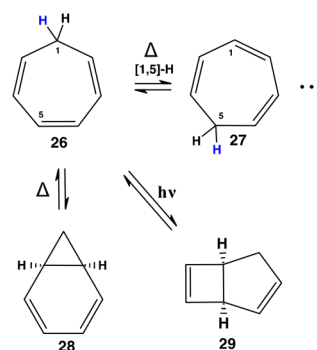


Figure 9. Chemistry of tropilidene.

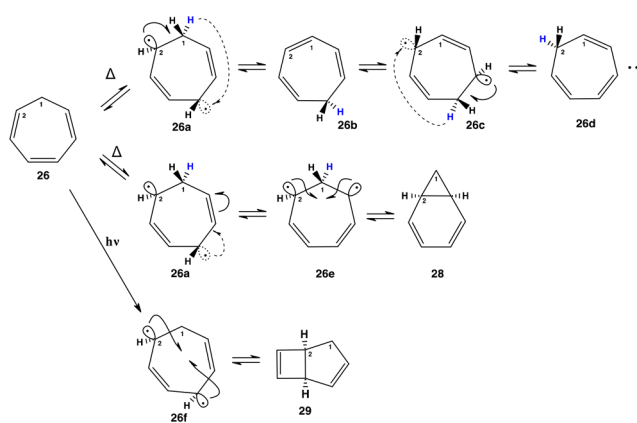


Figure 10. BBAH analysis of tropilidene chemistry.

manner, **26b** can tautomerize to **26d** via *anti* diradical **26c**, etc. Moreover, diradical **26a** can delocalize to generate *syn* diradical **26e**, which has the proper diradical geometry to form norcoradiene **28**. Photochemical excitation of **26** produces the *syn* diradical intermediate **26f**, the stereoelectronic precursor to bicyclic isomer **29**.

Homologated Sigmatropic Hydrogen Rearrangements. The BBAH can also be demonstrated to apply to homologated rearrangements. For example, Berson²⁴ performed classic studies on homologated sigmatropic [1,5]-hydrogen shifts, including the thermal rearrangement of vinylcyclopropane **30** in which the cyclopropane ring acts as a nonsymmetric double-bond surrogate (Figure 11). According to the W–H rules, compound **30** can rearrange along two suprafacial pathways, i.e., **30a** to **31** or **30b** to **32**, both of

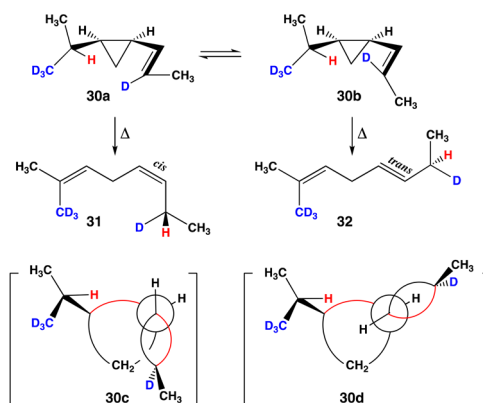


Figure 11. Homodienyl [1,5]-hydrogen shift of vinylcyclopropanes.

which produce the necessary *cis* configuration of the hydrogen-accepting double bond. However, only **31** is observed experimentally. Berson concluded, and as previously formulated by Winstein,²⁵ that “Models indicate that this conformation (i.e., **30a**) is the most favorable for overlap of the developing *p*-orbitals derived from the cyclopropane ring bond with the olefinic group and also the developing *p*-orbital derived from the C–H bond.” However, the exclusive formation of product **31** can also be explained simply by considering reactant conformers in which one of the τ bonds of the accepting olefin is antiperiplanar to the scissile cyclopropyl bond; the migrating hydrogen must also be *syn* to the scissile cyclopropane bond for proper stereoelectronic alignment. The observed product can be inferred from reactant conformer **30c**, which is one of the two low-energy minima (B3LYP/6-31G*). The alternative conformer **30d** is the global minimum but has a much greater distance between the migrating hydrogen and the acceptor olefinic carbon, and would furthermore lead to a product with a *trans* configuration of its hydrogen-accepting double bond, in contrast to the W–H prediction (Supporting Information).

The Winstein group²⁵ first recognized the orbital overlap requirement in the concerted homodienyl 1,5-hydrogen shift. They observed the rearrangement of (*Z*)-bicyclo[6.1.0]non-2-ene **33** into *cis*-*cis*-1,4-cyclononadiene **34**, which was postulated to take place via conformation **33a** (Figure 12).

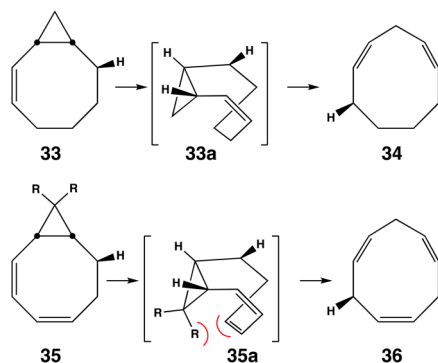


Figure 12. Rearrangement of bicyclo[6.1.0]nonene derivatives.

This analysis was further supported by the observation that diene analogue **35** ($R = H$) rearranged easily to **36** (via conformation **35a**) but that the disubstituted analogues ($R = \text{alkyl}$) were unreactive because they could not adopt the requisite saddle conformation **35a** due to severe transannular repulsion. Reactive conformations **33a** and **35a** are compatible with the BBAH in which the bond of the migrating hydrogen is *syn* to the scissile cyclopropane bond, and the latter is at a relatively small dihedral angle from the acceptor double bond for a concerted process, as illustrated in **30c**.

Overall, the BBAH correctly predicts the feasibility and stereochemistry of [1,*n*]-hydrogen shifts under both thermal and photochemical conditions. As shown in Figure 13, the predicted outcomes are the same as those predicted by FMO analysis or generalized orbital symmetry rules. Photoexcitation corresponds to a single radical inversion in BBAH formalism, which switches the stereochemical outcome of the ensuing reactions.²⁶

CONCLUSION

The bent bond/antiperiplanar hypothesis (BBAH) has been extended to the analysis of sigmatropic hydrogen shifts. Key to

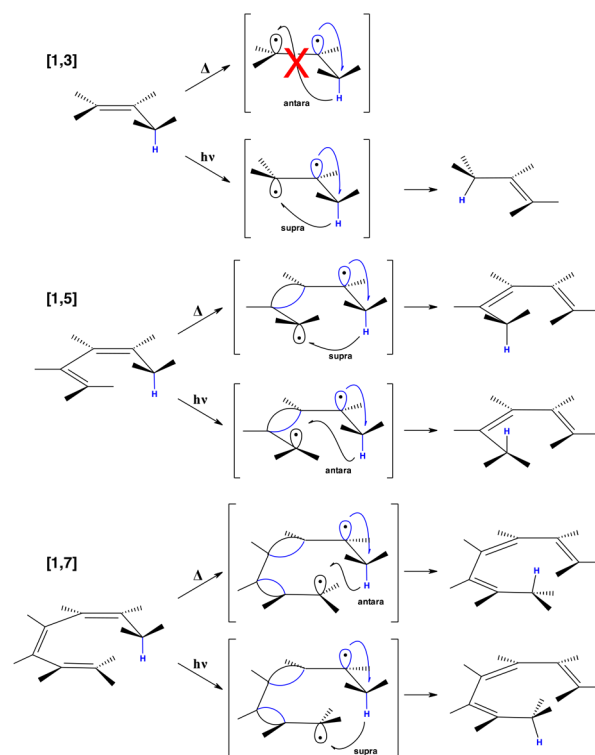


Figure 13. Thermal versus photochemical hydrogen shifts.

this model is the notion of *antiperiplanar electronic delocalization* involving τ bonds in polyene systems. By applying the BBAH to singlet diradical representations of polyenes, the feasibility and stereochemistry of hydrogen sigmatropic shifts can be readily rationalized. Byproducts and side reactions can also be correctly anticipated. Rearrangements under photochemical conditions are also readily interpreted using the BBAH by invoking single radical inversions. Although only a handful of experimental examples from the literature are presented here, an overwhelming number of other cases in the literature are consistent with our analysis.¹² Detailed computational investigations on both conformational and reactivity aspects of the BBAH are underway and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01472.

Geometry optimized structures of conformers **30c** and **30d** (PDF)

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Notes

The authors declare no competing financial interest.

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- (29) In summary, sigmatropic [1.5] and [1.7] hydrogen shifts are known to occur thermally in a concerted stereocontrolled suprafacial and antarafacial fashion, respectively. These results are explained through the BBAH orbital model, which invokes antiperiplanar electronic delocalization on τ bonds and implies that vibrationally excited polyenes can have some pyramidal singlet diradical character

(or the equivalent diradical resonance structure). On the other hand, sigmatropic [1.3] hydrogen shifts do not occur thermally; the BBAH orbital model explains this behavior as the bonds involved are not properly oriented for a concerted process. This further indicates that real diradical intermediates are not involved.