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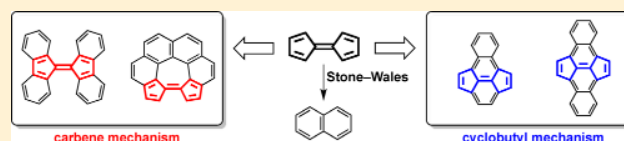
Stone–Wales Rearrangements in Polycyclic Aromatic Hydrocarbons: A Computational Study

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S Supporting Information

ABSTRACT: Mechanisms for Stone–Wales rearrangements (SWRs) in polycyclic unsaturated hydrocarbons containing a pentafulvalene core have been studied using density functional, coupled cluster, and multiconfigurational methods. At the BD(T)/cc-pVDZ/(U)M06-2X/cc-pVDZ level of theory, free energies of activation (at 1000 °C) range from ca. 70 kcal/mol for the model system pentafulvalene → naphthalene (1 → 2) to >110 kcal/mol for the degenerate SWR of pyracyclene (3). Systems studied that do not contain a pyracyclene subunit are predicted to have ΔG^\ddagger less than about 90 kcal/mol and to proceed by a carbene-type mechanism. Substrates containing a pyracyclene subunit should proceed via a cyclobutyl mechanism, and appropriate benzannulation of 3 lowers the activation free energy considerably. Computed ΔG^\ddagger values are consistent with experimental observations reported for known systems. SWRs of two untested substrates, cyclopent[fg]aceanthrylene (18) and dicyclopenta[fg,op]tetracene (21), are predicted to have $\Delta G^\ddagger < 95$ kcal/mol and thus to be accessible via flash vacuum pyrolysis.



INTRODUCTION

Thermal rearrangements in highly unsaturated hydrocarbons play important roles in diverse arenas, ranging from the production and transformations of polycyclic aromatic hydrocarbons (PAHs) in smoke and soot¹ to the rational pyrolytic synthesis of bowl-shaped fullerene fragments.² In extreme cases, such as those with no hydrogens, such processes are central to annealing in fullerenes³ and to the generation of Stone–Wales defects in carbon nanotubes.⁴

Among the menagerie of reactions that may occur in PAHs⁵ and carbon allotropes at high temperatures (e.g., 900–1200 °C, a temperature range accessible by flash vacuum pyrolysis, FVP), one of the most fascinating—and perhaps the most elusive—is the Stone–Wales rearrangement (SWR).⁶ Originally proposed⁶ as a formal way to relate the possible isomers of a given fullerene, the Stone–Wales rearrangement formally refers to pairwise 1,2-shifts of carbon atoms about a C=C double bond, as shown in Scheme 1. The curved arrows in Scheme 1 are not meant to represent a mechanism but only to indicate changes in connectivity.

The reality is that SWRs occur in some systems, do not occur in others, and in some cases, the occurrence of SWR is uncertain (Scheme 2). For example, there is no evidence to support SWRs occurring under FVP conditions in the simplest

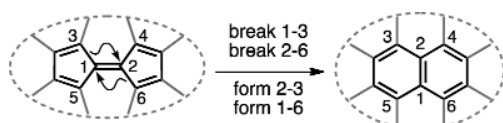
model systems: pentafulvalene (1) to naphthalene (2)⁷ and the automerization of pyracyclene (3 → 3').^{8,9} On the other hand, formal SWR has been observed in the rearrangement of bifluorenylidene (4) to dibenzo[*g,p*]chrysene (5) at 440 °C in a sealed tube.¹⁰ Vollhardt rationalized the isolation of coronene (8) from FVP of angular[4]phenylene by invoking SWRs 6 → 7 and 7 → 8 as the final steps.¹¹

A wide variety of mechanisms (Scheme 3) have been considered for SWRs in different systems, including concerted mechanisms through an acetylenic diradical (path A) or carbene-like transition states (path B) and a stepwise mechanism via a cyclobutyl intermediate (path C). These pathways are illustrated in Scheme 3 for the hypothetical automerization of pyracyclene (3).

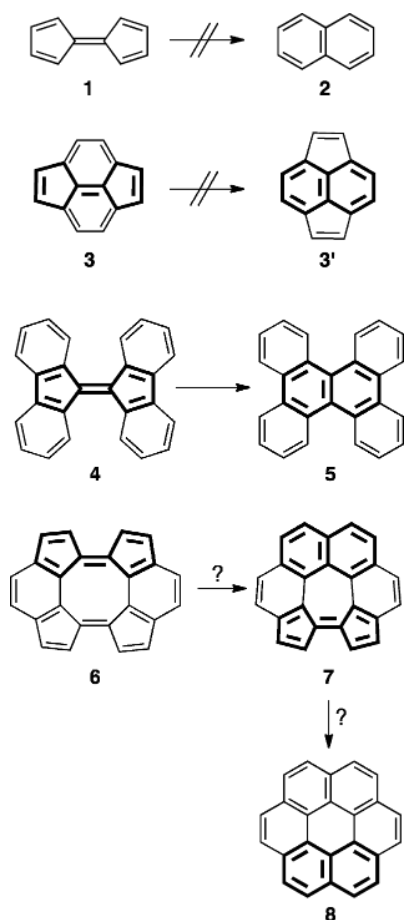
Prior computational studies on these reaction paths in various systems have indicated barriers ranging from 120 to 140 kcal/mol. For example, Scuseria reported calculations on paths similar to A and B for pyracyclene (3 → 3') and C₆₀ (9 → 10, Scheme 4) with BLYP/4s2p1d barriers of >140 kcal/mol.³ Bettinger later computed the barrier for 9 → 10 via both paths A and B to be ca. 130 kcal/mol using a variety of density functional methods.⁴ Using B3LYP, Nimlos computed the *E_a* for SWR in pyracyclene (3 → 3') to be 130 kcal/mol (path B) and 120 kcal/mol (path C).¹²

In contrast to the paths shown in Scheme 3, radical-catalyzed mechanisms (distinct from diradical path A) have also been investigated. For example, following initial H atom addition to pyracyclene, the resulting radical can rearrange and eventually lose H• to form the product. Nimlos found that the radical-

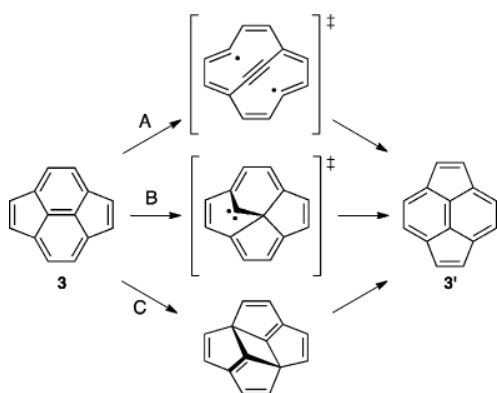
Scheme 1



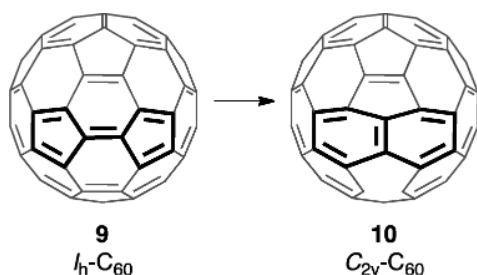
Scheme 2



Scheme 3



Scheme 4



promoted SWR of **3** had a barrier of only 67 kcal/mol. Alder's computational studies on radical-promoted mechanisms for the SWRs in bifluorenylidene (**4**), pyracene (**3**), C_{60} (**9**), and diindenochrysenes indicated barriers for radical-promoted mechanisms much lower than those not promoted by radicals.¹³ For example, from the initial H atom adduct of **4**, the overall B3LYP/6-31G* barrier for SWR was 44 kcal/mol, compared to 65 kcal/mol for the nonradical process.

Here we report a computational study on possible mechanisms for Stone–Wales rearrangement in several polycyclic conjugated hydrocarbons containing a pentafulvalene core to develop generalizations about the relationship between substrate structure, preferred mechanism, barrier height, and feasibility under FVP conditions. We have focused solely on non-radical-promoted pathways because some of the reactions of interest¹¹ have been performed under high-vacuum conditions (10^{-7} Torr), where the contribution of radicals would be minimized. The computed mechanisms and activation free energies for several systems are consistent with whether or not SWR has been observed, and our results for other systems suggest that SWR should be observable.

COMPUTATIONAL METHODS

Geometry optimizations were performed at the (U)M06-2X/cc-pVDZ level of theory.^{14,15} The cc-pVDZ basis set was chosen for geometry optimizations because those geometries gave lower BD(T) absolute energies compared with those obtained with the 6-31G*, AUG-cc-pVDZ, or cc-pVTZ basis sets. Vibrational analyses were carried out at the same level to verify the nature of stationary points. Transition states were confirmed by the presence of exactly one imaginary frequency, and the corresponding reaction paths were verified by intrinsic reaction coordinate calculations. Vibrational analyses were also employed to obtain thermal corrections to the Gibbs free energy for all species, using a temperature of 1273 K—conditions that represent a reasonable approximation to the flash vacuum pyrolysis conditions used for the reactions of interest. Pressure corrections (to 0.0001 atm) led to no change in relative free energies, so the thermal corrections use a pressure of 1.0 atm.

The use of unrestricted density functional theory (DFT) was necessary due to the presence of RHF-to-UHF instabilities in a few species (primarily carbene intermediates and transition states). $\langle S^2 \rangle$ values for these species were generally in the range of 0.10 to 0.33, with the exception of open-shell singlet carbenes, which had $\langle S^2 \rangle$ values of ca. 1.02 (see Supporting Information). The open-shell singlet carbenes (for $C_{10}H_8$ and $C_{14}H_8$ systems) were also optimized at the CASSCF(n,n)/cc-pVDZ level, where n equals the number of carbons in the system. The CASSCF geometries were not significantly different from the UM06-2X structures and yielded almost identical CASPT2 absolute energies.

Due to the presence of slight diradical character in some species, the Brueckner doubles method, BD(T), with the cc-pVDZ basis set, was employed for single-point energies.¹⁶ Test calculations with larger basis sets did not change the relative energies by more than 2 kcal/mol.

For systems involving open-shell singlet carbenes, single-point energies were computed at the CASPT2/cc-pVDZ level of theory.¹⁷ The active space size was set to the number of π electrons and π/π^* orbitals in the reactant, for example, 10 electrons and 10 orbitals for pentafulvalene (**1**), and 14 electrons and 14 orbitals for pyracene (**3**).

BD(T)/cc-pVDZ and CASPT2/cc-pVDZ relative energies are reported as thermally corrected Gibbs free energies.

Density functional and BD(T) calculations were performed using Gaussian 09.¹⁸ CASSCF and CASPT2 calculations were performed with Molcas 8.0.¹⁹ Structures were viewed with MacMolPlt,²⁰ and vibrational modes and orbitals were visualized with Molden.²¹

RESULTS AND DISCUSSION

C₁₀H₈: Pentafulvalene to Naphthalene. The thermal conversion of pentafulvalene (**1**) to naphthalene (**2**) has not been observed experimentally,²² but this system serves as a useful model for larger ones containing the 10-carbon core. Figure 1 illustrates the three lowest energy pathways we located

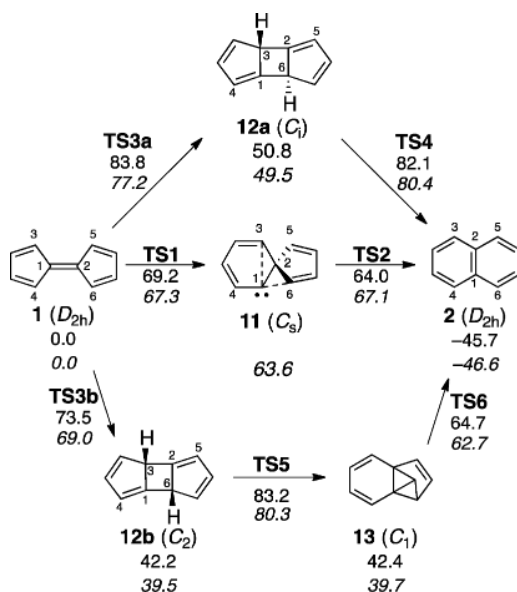


Figure 1. BD(T)/cc-pVDZ//((U)M06-2X/cc-pVDZ (plain text) and CASPT2(10,10)/cc-pVDZ//((U)M06-2X/cc-pVDZ (italics) relative free energies (kcal/mol, 1273 K) for three mechanisms connecting pentafulvalene (**1**) and naphthalene (**2**). All free energies are relative to that of **1**.

for the model Stone–Wales rearrangement of pentafulvalene to naphthalene (**1** → **2**). The (U)M06-2X/cc-pVDZ optimized structures are presented Figure 2. Of these three mechanisms, the carbene pathway has the lowest free energy barrier ($\Delta G^\ddagger = 69$ kcal/mol) by over 10 kcal/mol. It is noteworthy that, using restricted M06-2X, a single transition state similar to **TS1** is found that connects pentafulvalene and naphthalene. However, the situation is more complicated with UDFT. **TS1** has an RHF-to-UHF instability. Reoptimization at the UM06-2X/cc-pVDZ level still yields a similar structure, but intrinsic reaction

coordinate calculations lead downhill to a spirocyclic carbene intermediate **11**. Carbene **11** is an open-shell singlet ($^1A''$ state) in which one of the nonbonding electrons occupies an in-plane orbital on the carbene carbon and the other nonbonding electron occupies an allyl-type π orbital largely localized on the opposite side of the ring. Shifting of the π bonds in the six-membered ring (see Figure 2) leads to closed-shell singlet carbene transition state **TS2** ($^1A'$ state), which connects to naphthalene. The second transition state for this route (**TS2**) is analogous to transition state in the carbene mechanism studied by Nimlos for the SWR of pyracylene¹² (Scheme 3, path B). On going from **TS1** to **11** to **TS2**, the C–C distance across the six-membered ring increases steadily and the angle at the carbene carbon decreases (Figure 2). BD(T) calculations are not possible for **11**, but CASPT2 calculations place **11** ca. 3.5 kcal/mol lower in energy than **TS1** and **TS2** (Figure 1).

The remaining two mechanisms in Figure 1 both have free energy barriers of 83–84 kcal/mol at the BD(T) level. Both involve a concerted first step to tricyclic stereoisomers **12a** (upper path) and **12b** (lower path); however, while **12a** proceeds directly to naphthalene in the second step, **12b** rearranges to benzvalene derivative **13** before proceeding to naphthalene. Intermediate **12a** (*C_i* symmetry) is analogous to the *C_{2h}*-symmetric cyclobutyl intermediate located by Nimlos¹² for the SW rearrangement of pyracylene (Scheme 3, path C), although again, our computed barrier for this process is much lower. This drop in energy barriers for the model system **1** → **2** compared with pyracylene's barriers is likely due the relative lack of ring strain in the less substituted system.

Thus, in the pentafulvalene model system, numerous pathways for SWR with $\Delta G^\ddagger < 90$ kcal/mol exist on the potential energy surface, with the lowest route having $\Delta G^\ddagger = 69$ kcal/mol. The relatively low computed free energy barrier for this process is undoubtedly influenced by the prediction that the conversion of **1** to **2** is highly exergonic ($\Delta G_{\text{rxn}} \approx -46$ kcal/mol).

C₁₄H₈: Pyracylene and Its Benzo Derivatives. Fusion of additional rings to the core of **1** can prevent some mechanisms and dramatically alter the barriers of others. Pyracylene (**3**) and some of its benzo derivatives illustrate this point. Nimlos et al., using B3LYP, found a cyclobutyl mechanism (analogous to that via **11**) and a carbene mechanism (which they called an sp^3 mechanism, analogous to that via **TS1**, **11**, and **TS2**), with the former having a lower barrier (vide supra) for the SWR of **3** →

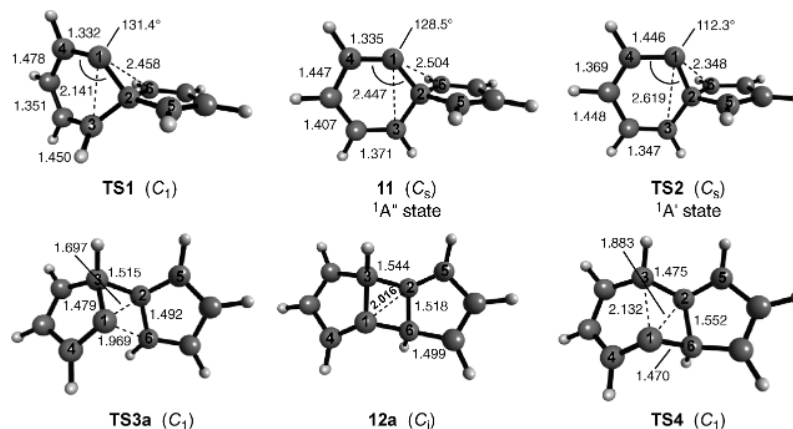


Figure 2. (U)M06-2X/cc-pVDZ optimized structures of stationary points along two mechanisms between pentafulvalene (**1**) and naphthalene (**2**). Distances in Å.

3'.¹² With M06-2X/6-31G*, we located a pathway via the cyclobutyl intermediate **14** ($\Delta G^\ddagger = 112$ kcal/mol, Figure 3).

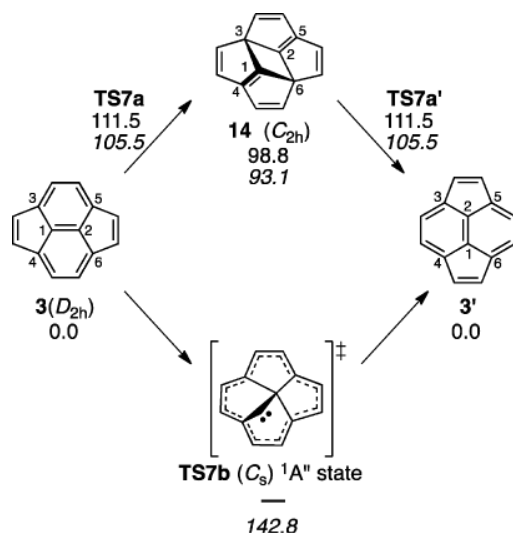


Figure 3. BD(T)/cc-pVDZ//((U)M06-2X/cc-pVDZ (plain) and CASPT2(14,14)/cc-pVDZ//((U)M06-2X/cc-pVDZ (italics) relative free energies (kcal/mol, 1273 K) for the degenerate Stone–Wales rearrangement of pyracylene (**3**).

The geometries of **14** and the associated transition state TS7a (Figure 4) show a much shorter C1–C2 distance in **14** (1.77 Å) compared to that in **12a** (2.02 Å), and in TS7a (1.60 Å) compared to that in TS3a (1.70 Å), due to compression by the additional fused rings.

Early attempts to locate a closed-shell carbene-like transition state or intermediate failed (guess structures collapsed to **14**),

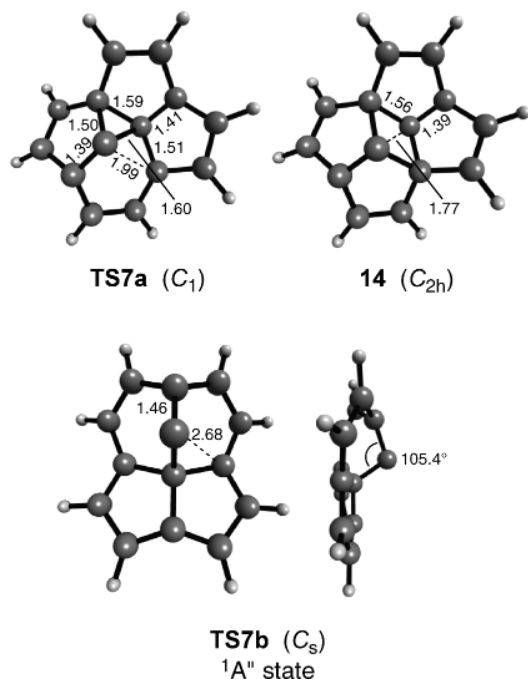


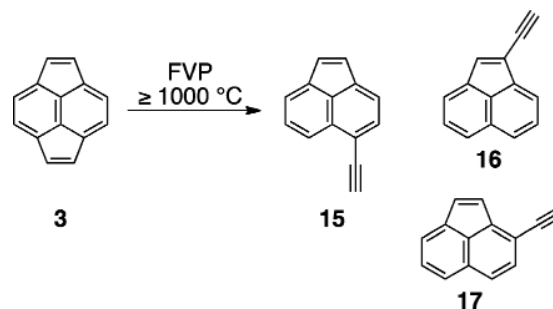
Figure 4. (U)M06-2X/cc-pVDZ optimized structures of the transition states and a cyclobutyl intermediate for two mechanisms of the Stone–Wales rearrangement of pyracylene (**3**). Distances in Å.

but forcing the wave function into a $1A''$ state revealed an open-shell singlet transition state TS7b, analogous to **11** in the $C_{10}H_8$ system. Nevertheless, at the CASPT2 level, transition state TS7b is computed to be 143 kcal/mol higher than **3**.

Further, in the SWR of **3**, no C_2 -symmetric intermediate analogous to **12b** could be located. Due to the five-membered rings that bridge C4 and C6 and C3 and C5 in **14**, only a cyclobutyl intermediate with an inversion center is feasible. This has implications for larger systems containing the pyracylene subunit (vide infra).

In general, 100 kcal/mol represents an approximate boundary between feasible and unfeasible reactions under FVP conditions.²³ Thus, the computed barrier of >110 kcal/mol for **3** → **3'** is consistent with the fact that SWR in pyracylene (e.g., with isotopic labels) has not been observed.⁹ Instead, at high temperatures (≥ 1000 °C), **3** produces a mixture of ethynylacenaphthylenes **15**–**17** by cleavage of a bond in the cyclopentyl ring (Scheme 5).⁸

Scheme 5



The >100 kcal/mol barrier for **3** → **3'** might suggest that any systems containing a pyracylene subunit should have similarly high barriers to SWRs, but this is not so. Benzannulation of the pyracylene core can in some cases lower the activation energy enough to make SWR feasible. As shown in Figure 5, the benzannulated derivatives studied here react only via the cyclobutyl mechanism. The BD(T) computed free energy barriers for SWR of cyclopent[fg]aceanthrylene (**18**) to acefluoranthene (**20**) and of dicyclopenta[fg,op]tetracene (**21**) to indeno[1,2,3-cd]fluoranthene (**23**) are 87 and 94 kcal/mol, respectively. In contrast, the computed ΔG^\ddagger for the degenerate SWR of indeno[1,2,3-fg]aceanthrylene (**24**) is 107 kcal/mol.²⁶ These results can be explained at least partly by noting that the number of Clar sextets²⁷ increases in both **18** → **20** and **21** → **23** but not in **24** → **24'**. The increase in Clar sextets also contributes to the highly exergonic nature of **18** → **20** and **21** → **23**.²⁸

The reactions of isomers **21** and **24** are compared on a single free energy diagram in Figure 6. The two intermediates **22** and **25** differ by only 2.2 kcal/mol. However, destabilization of **21** relative to **24** by almost 20 kcal/mol and stabilization of **23** relative to **24** by ca. 10 kcal/mol are the primary factors leading to the lower barrier for SWR of **21**. As the reactions **18** → **20** and **21** → **23** have not been reported, our results allow the prediction that the SWR of pyracylene derivatives **18** and **21** should be observable under flash vacuum pyrolysis conditions.

C₂₆H₁₆: Bifluorenylidene to Dibenzochrysene. Pyrolysis of bifluorenylidene (**4**) yields dibenzo[*g,p*]chrysene (**5**) at temperatures as low as 440 °C under sealed-tube conditions.¹⁰ This reaction allows assessment of the effect of benzannulation

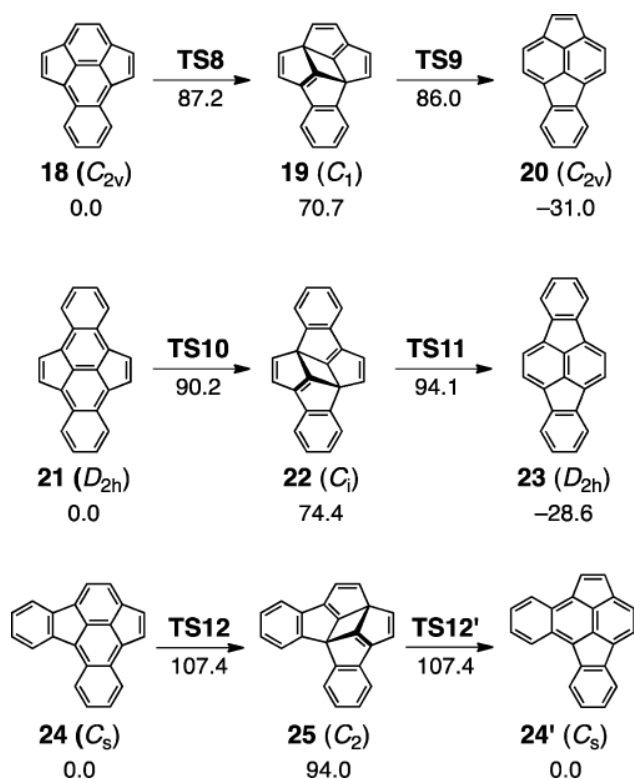


Figure 5. BD(T)/cc-pVDZ//M06-2X/cc-pVDZ relative free energies (kcal/mol, 1273 K) for the Stone–Wales rearrangement of benzannelated pyracylene derivatives. Free energies are given relative to the starting material in each case.

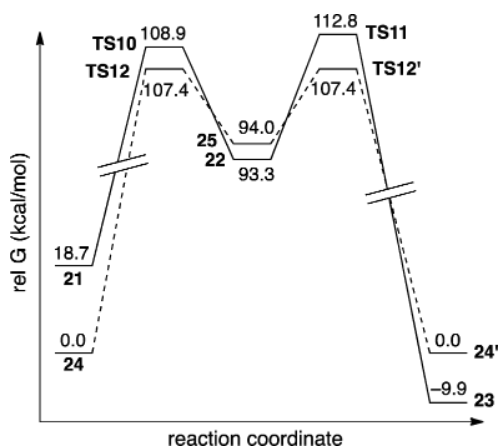


Figure 6. Comparison of pathways for $C_{22}H_{12}$ systems $21 \rightarrow 23$ (solid lines) and $24 \rightarrow 24'$ (dashed lines). BD(T)/cc-pVDZ//M06-2X/cc-pVDZ relative free energies (1273 K) in kcal/mol.

of the cyclopentadienyl rings. Alder reported DFT results on nonradical and radical-promoted mechanisms for $4 \rightarrow 5$.¹³ However, if the reaction were carried out under high-vacuum FVP conditions (e.g., 10^{-7} Torr), it is not clear if radicals would be generated in sufficient concentrations to promote the reaction, and alternative computed mechanisms seem warranted.

Similar to the model system $1 \rightarrow 2$, the lowest pathway for $4 \rightarrow 5$ is a carbene mechanism (Figure 7), with a comparable free energy barrier of 70.9 kcal/mol, which is similar to Alder's computed barrier of 65 kcal/mol.¹³ However, in contrast to 1

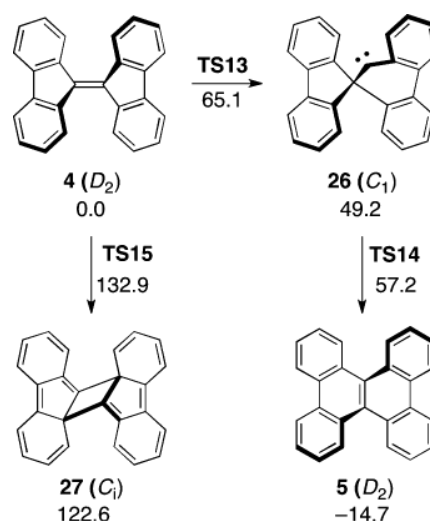
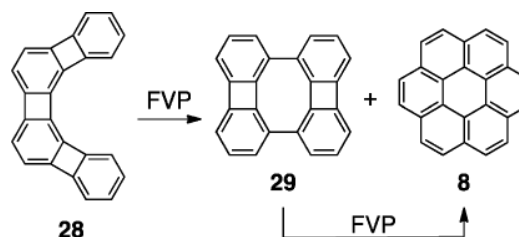


Figure 7. BD(T)/cc-pVDZ//M06-2X/cc-pVDZ relative free energies (kcal/mol, 1273 K) for the Stone–Wales rearrangement of bifluorenylidene (**4**).

$\rightarrow 2$, the carbene is predicted to be an intermediate rather than a transition state, presumably due to benzylic stabilization of the carbene in **26**.²⁹ In addition, the fusion of benzenes to the core system renders the reaction pathway via cyclobutyl intermediate **27** uncompetitive ($\Delta G^\ddagger \geq 133$ kcal/mol, Figure 7), due to disruption of aromaticity in all four benzenes. Thus, benzannulation as in **4** lowers the barrier to the carbene mechanism and dramatically hinders the cyclobutyl mechanism.³⁰

$C_{24}H_{12}$: Precursors to Coronene. FVP of angular[4]-phenylene (**28**) produces coronene (**8**) as well as some biphenylene dimer **29**.¹¹ FVP of **29** also yields coronene (Scheme 6).¹¹ The part of the mechanism proposed by

Scheme 6



Vollhardt that includes SWRs in the final steps for the formation of coronene is shown in Figure 8, along with our computed relative free energies.

The lowest overall free energy barrier we located for $6 \rightarrow 8$ is 84 kcal/mol. While the first SWR ($6 \rightarrow 7$) occurs via a carbene intermediate (**30**) that lies in a shallow well, the second SWR ($7 \rightarrow 8$) occurs in one step via a carbene-like transition state.³⁰ Efforts to locate cyclobutyl intermediates were unsuccessful and resulted in structures optimizing to **6**, **7**, or **8**. The bridge between the two ends of the cyclopentenyl subunit in both **6** and **7** apparently renders such intermediates untenable. These computed results indicate that SWRs of **6** and **7** are feasible under FVP conditions, and the mechanism proposed by Vollhardt et al. for production of coronene from **6** is reasonable.

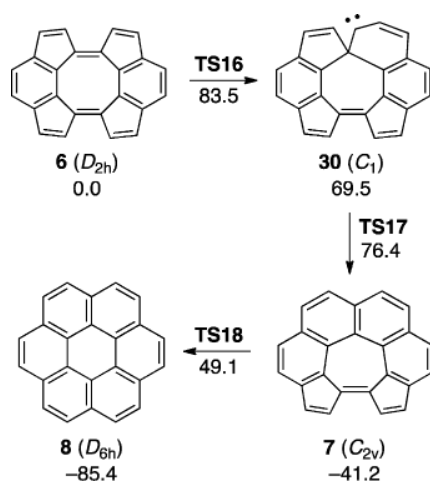


Figure 8. BD(T)/cc-pVDZ//((U)M06-2X/cc-pVDZ relative free energies (kcal/mol, 1273 K) for the Stone–Wales rearrangements leading from **6** to coronene (**8**).

Patterns of Reactivity. The computed results reveal a few trends in preferred mechanism, activation free energy, and feasibility, with respect to structure. Here we consider a reaction “feasible” if the free energy of activation is less than 100 kcal/mol.²³ Our reference point is unsubstituted pentafulvalene (**1**) with a barrier of 70 kcal/mol. Substrate **1** can react via either a carbene or a cyclobutyl mechanism, but the former is preferred. The effects of different modes of benzannulation of **1** are summarized in Figure 9. Benzannulation of the “flanks” of **1** favors the carbene mechanism and preserves the feasibility of Stone–Wales rearrangement, as shown for **4**, **6**, and **7**. Additional ring fusions increase the strain and the barrier but not prohibitively so. In contrast, benzannulation of the bay regions of **1** favors the cyclobutyl mechanism and leads to significantly higher barriers. For pyracylene (**3**), the reaction becomes infeasible, but extended benzannulation as in **18** and **21** brings the activation free energy back down below 100 kcal/mol. Accounting for changes in the number of Clar aromatic sextets²⁷ during the course of reaction explains the trend from **1** to **3** and then from **3** to **18** and **21**.

All of the starting systems considered here are planar or nearly so. For those containing a pyracylene core, the preferred cyclobutyl mechanism depends on the ability to form the locally C_2 -symmetric intermediate. For fullerenes and bowl-shaped fullerene fragments, such an inversion-center-based substructure may be untenable due to strain, rendering the cyclobutyl mechanism either extremely difficult or nonexistent.

Finally, it should be noted that, while our results pertain to non-radical-promoted mechanisms, the reactivity trends might apply equally to radical-promoted mechanisms. Previous calculations on both types of mechanisms (e.g., for **3** and **4**) show that a lower barrier for non-radical-promoted SWR corresponds to a lower barrier for radical-promoted SWR.^{12,13} The same generalization may hold true for the systems considered here.

CONCLUSIONS

For the conjugated hydrocarbons considered, depending on the structure of the substrate, Stone–Wales rearrangement can occur by one of two general mechanisms—a carbene mechanism involving a carbene-like transition state or

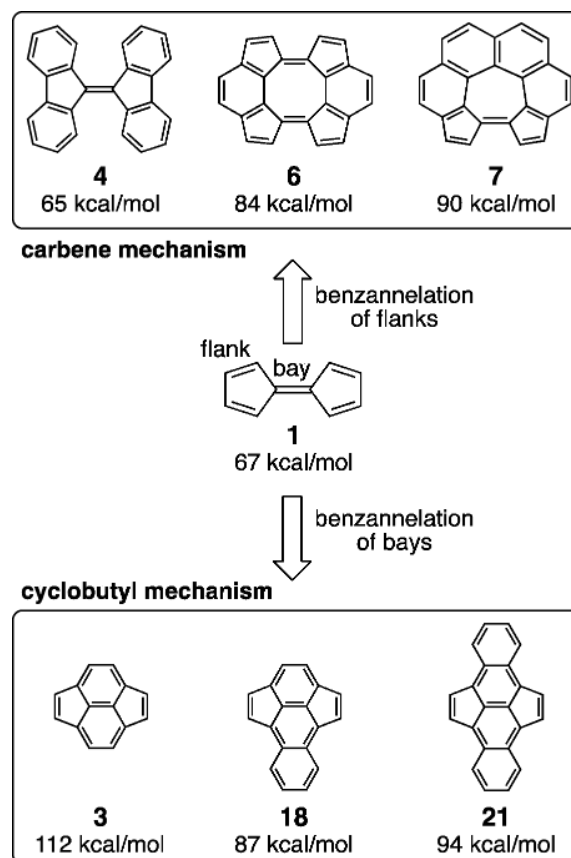


Figure 9. Effect of benzannulation of pentafulvalene (**1**) on free energy of activation and preferred mechanism of Stone–Wales rearrangements. The overall ΔG^\ddagger for each starting material is given at the BD(T)/cc-pVDZ//((U)M06-2X/cc-pVDZ level of theory for conditions of 1273 K.

intermediate or a cyclobutyl mechanism via an intermediate containing a C_2 -symmetric four-membered ring. The free energies of activation computed at the BD(T)/cc-pVDZ//((U)M06-2X/cc-pVDZ level range from ca. 70 to 112 kcal/mol and are consistent with previous experimental observations of whether or not SWR occurs in each system under pyrolytic conditions. Building up from a pentafulvalene (**1**) core, benzannulation on the bay regions of **1** leads to preference for the cyclobutyl mechanism and can render SWR infeasible (as for pyracylene). Benzo fusion on the flanks of **1**, however, causes the carbene mechanism to dominate, with computed barriers below 95 kcal/mol. In Vollhardt’s pyrolytic conversion of angular [4]phenylene (**28**) to coronene (**8**), the proposal of sequential SWRs as the final two mechanistic steps is supported by our computed barriers. Our results also allow the prediction that two pyracylene derivatives with extended benzannulation (**18** and **21**) should undergo SWR under flash vacuum pyrolysis conditions.

ASSOCIATED CONTENT

Supporting Information

Absolute energies, zero-point energies, $\langle S^2 \rangle$ values, thermal corrections, and optimized Cartesian coordinates for all stationary points and complete citation for Gaussian 09. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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