Pericyclic Reactions

DOI: 10.1002/anie.200806009

# A Preferred Disrotatory 4*n* Electron Möbius Aromatic Transition State for a Thermal Electrocyclic Reaction**

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Möbius Aromaticity, predicted by Heilbronner in 1964,[1] and computationally discovered unexpectedly only about a decade ago,[2] continues to fascinate many chemists.[3] Zimmerman generalized the concept to include structures that do not possess the Möbius-strip topology and successfully applied the idea to categorize transition states of pericyclic reactions in the Dewar–Zimmerman interpretation of the Woodward–Hoffmann rules for orbital-symmetry controlled reactions.[4,5] According to this rule, thermally activated electrocyclic reactions proceed conrotatory via a $4n$ electron "Möbius" aromatic transition state, and disrotatory via a $4n+2$ electron "Hückel" aromatic transition state structure, while photochemical reactions show an opposite behavior. These concepts have important synthetic applications and might even play a role in biosynthesis.[6] Nicolaou et al., for example, used six and eight π-electron electrocyclic reactions in the biomimetic total synthesis of endiandric acids.[7] Electrocyclase enzymes are even proposed to support six π-electron electrocyclic reactions in vivo.[8]

In 1993, Jiao and Schleyer reported a first computational study on a "Möbius" aromatic transition state for the [1,7]-hydrogen shift in 1,3,5-heptatriene,[9] a reaction that has been proposed to occur in the rearrangement of calciferol to precalciferol.[10] Four years later, Johnson and Daoust suggested that Möbius benzene results from a "forbidden" conrotatory ring opening mode in Dewar benzene.[11] They realized that this reactive mode does not conform with the predictions from the Woodward–Hoffmann rules. However, in a more recent study it was reported that while the conrotatory mode is indeed preferred, Möbius benzene is not involved in the ring opening mode.[12] The "forbidden" disrotatory transition structure for the butadiene–cyclobutene conversion has been found to be a second-order saddle point.[13] High energy "forbidden" transition structures in [1,7]-hydrogen shifts have also been reported.[14]

In 2005, Rzepa proposed a Möbius twisted and Hückel aromatic $4n+2$ electron electrocyclic transition-state structure for the ring opening/ring closure reaction of a (*Z*,*E*,*Z*)-decapentaene.[15] In contrast, Möbius aromatic transition states for electrocyclic reactions and which possess the Möbius strip topology have not been reported to date. Herein we report the first representative of this novel type of pericyclic reaction transition-state structure. Moreover, thermal ring opening in a Möbius twisted dodecahexaene is proposed to proceed preferably disrotatory via an aromatic transition state, rather than via the conrotatory transition structure predicted by the Woodward–Hoffmann rules for rings having the Hückel topology, and that is disfavored energetically by 19.9 kcal mol$^{-1}$ at the coupled-cluster level of theory![16]

Figure 1 shows the four basic types of thermal electrocyclic transition-state structures with their known representatives: the non-twisted Hückel aromatic $C_s$ symmetric and disrotatory transition state for the electrocyclic reaction in 1,3,5-hexatriene, the non-twisted (but bent) Zimmerman-"Möbius" aromatic conrotatory transition state for the ring closure in 1,3,5,7-octatetraene with exactly one orbital phase inversion (because the orbital phases are of opposite sign at the termini of the carbon chain on the same face of the π-system),[17] and finally, Rzepa's novel Hückel aromatic $C_2$ symmetric transition state in Möbius twisted decapentaene (and without an orbital phase inversion).[18,19] The remaining fourth variety—a Möbius aromatic transition state and with the twisted Möbius topology (in the Heilbronner sense, that is, with completely laticyclic overlap) has not been proposed to date and has apparently been overlooked—being a further, rare possibility.[20] Despite its apparent topological connotation, the term "Möbius" been frequently applied for structures that neither posses the Möbius geometry nor the Möbius orbital topology (e.g. in barrelene[4b]) prior to the first report of a Möbius ground state aromatic in 1998 that meets Heilbronner's criteria.[2b]

It should be noted that, for example, the conrotatory so-called "Möbius" transition state for the ring closure in butadiene neither possess the Möbius topology (i.e. where the passage along one side of the π system invariably leads to the opposite side) nor does it possess the purely laticyclic overlap originally anticipated by Heilbronner. The delocalization pathway in the similarly bent transition structure for the ring closure in 1,3,5,7-octatetraene (schematically depicted in Figure 1) necessarily passes through a p-orbital node in the basis orbital picture while the genuine Möbius transition structures allow the two faces of the π-system to be connected without passage through such an orbital node. The realization of this fact a little more than a decade ago, led to the proposal of the long hypothetical Möbius aromatic $4n$ electron annulenes and the discovery of their basic design principles,[2a] a finding that has attracted considerable atten-

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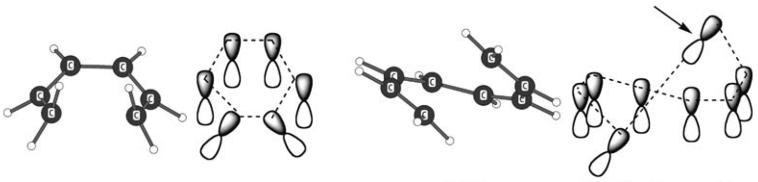
[**] The authors gratefully acknowledge generous financial support from the Deutsche Forschungsgemeinschaft.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806009.



a) Hückel aromatic, disrotatory, $4n + 2$ electrons, zero phase inversions

b) Zimmerman-"Möbius" aromatic, conrotatory, $4n$ electrons, one phase inversion

c) Rzepa's Hückel aromatic, conrotatory, $4n + 2$ electrons, zero phase inversions

d) Unknown Heilbronner-Möbius aromatic, disrotatory, $4n$ electrons, one phase inversion

***Figure 1.*** B3LYP/6-31G* optimized geometries of the three known types of transition structures for the polyene–cycloalkene conversions: a) 1,3,5-hexatriene, b) 1,3,5,7-octatetraene, c) a conformation of (*Z*,*E*,*Z*)-decapentaene. In (a) and (b) the delocalization pathway is schematically depicted, the arrow in (b)—one of several equivalent representations in the $C_{2p}$ basis orbital picture—marks the position of the passage through an orbital node. In (c) the p-orbital axis vector is rotated (by 180°)—as well as translated—moving along the carbon chain from one terminus to the other. Longicyclic and laticyclic overlap types are combined in (b) and (c). Examples for the fourth possible type of pericyclic transition structure (d), and with fully laticyclic overlap, have not been reported to date.

tion among chemists,[21] physicists,[22] and also stimulated experimental corroborations of the concept of Möbius aromaticity.[23]

The concerted twelve-electron ring closure of **1** proceeds via an aromatic transition state **2**, and towards the cyclic minimum structure **3** (Figure 2). The activation barrier for the ring-closure reaction is however sizable and computed to be 35.7 kcal mol$^{-1}$ at the CCSD(T)/6-31G//B3LYP/6-31G* level of theory (Table 1) and with the GAUSSIAN 03 quantum chemistry package.[24] The NICS[25] value of **2** is −12.8 at the B3LYP/6-31G* level (cf. benzene −9.6 at the same level of theory) and the variation of the C−C bond lengths is with 0.02 Å remarkably small.[26] Ring closure, rather than ring opening is preferred on this "asymmetric" potential energy surface (PES; Table 1). It can be clearly seen (Figure 2) that the structure of **2** does have the Möbius topology and that the mode of bond formation/breaking is disrotatory. In the basis orbital picture the conceived translational shift is of one terminal p-orbital along the annulene backbone accompanied by a rotation around the carbon chain of 180°. Note that for example, in the four-electron conrotatory transition state for ring closure in butadiene or the eight-electron conrotatory transition structure for the ring closure in 1,3,5,7-octatetraene which both conform to the Woodward–Hoffmann rules, there is only a translation, rather than a combination of translation and rotation of a p-orbital orientation vector when passing along the carbon chain from one terminus to the other.

Our result suggests that the "forbiddenness" of a certain reactive mode in pericyclic reactions should be evaluated additionally in the context of the topology (i.e. geometric properties) of the (Hückel or Möbius) transition structure and it does not depend on the electron count (e.g. $4n$ or $4n+2$ electrons) and the wave-function boundary conditions (i.e. the presence or absence of a "phase inversion") alone.[27]

Concerted pericyclic reactions which involve 12 π electrons should be very rare. In contrast, many experimental or computationally proposed examples for electrocyclic reactions with 10 or 8 π electrons are known and it appears desirable to find Möbius aromatic transition structures for electrocyclic reactions involving a smaller number of electrons and/or short carbon chain lengths.

One of the conceivable approaches to achieve this goal involves Möbius $4n+2$ electron triplet aromaticity,[2a,28] first described in 1999,[2a] a conceptual combination of Hückel $4n$ electron triplet aromaticity[29] and Möbius $4n$ electron aromaticity on the singlet potential surface: a $4n+2$ electron cyclically conjugated and Möbius twisted compound is aromatic in the electronic triplet state.[2a] Consequently, the dicationic transition structure **4** with 10 π electrons and on the triplet potential surface is also aromatic (NICS = −12.1). The activation barrier to ring opening in **5** via T.S. **4** to give an open-chain dodecahexaene triplet dication is 18.6 kcal mol$^{-1}$ at the B3LYP/6-31G* level and 20.5 kcal mol$^{-1}$ at the CCSD(T)/6-31G//B3LYP/6-31G* level with ZPE corrections (Table 1).

We wondered whether the length of the carbon chain in these Möbius aromatic transition-state structures can be further reduced to comprise only ten carbon atoms. Indeed, ring closure in acyclic decapentaene dication **6**, with 8 π electrons, proceeds via Möbius aromatic T.S. **7** (with a NICS = −13.8) with an activation barrier of 23.9 kcal mol$^{-1}$ at the CCSD(T)/6-31G* level on the singlet potential surface towards the cyclic dication **8**, albeit a mere 0.2 kcal mol$^{-1}$ higher in energy than **6** (0.6 kcal mol$^{-1}$ at the B3LYP/6-31G* level of theory)—that is, in this case the reaction proceeds in the direction of ring opening, rather than ring closure. All these transition-state structures have the disrotatory modes of torque-selectivity in common, which has also been verified by analysis of the atomic displacement vectors. These results also demonstrate that there is nothing wrong with the validity of the Hückel–Möbius concept for these nonplanar structures with unavoidable σ–π-mixing: the $4n$ and $4n+2$ electron-count rules hold exactly, because they have nothing to do with the topological representation of a structure.[21b,q] The surprisingly large (that is, less negative) NICS value of −4.6 for **8** (Table 1) could be due to the deshielding influence of the positive charge. With some justification the practical relevance of the dicationic structures might be questioned. However, we see these species also as a proof of principle for the general applicability of our idea.

The Woodward–Hoffmann rules predict a preferred conrotatory mode for the conversion of $4n$ electron polyenes into cyclic alkenes.[5] The corresponding transition structure **9**, conforming to these rules, however, although "Möbius" aromatic (in the Zimmerman sense, albeit to a lesser extent than **2**—judged from geometric and magnetic criteria), is a remarkable 20.5 kcal mol$^{-1}$ higher in energy (including ZPE

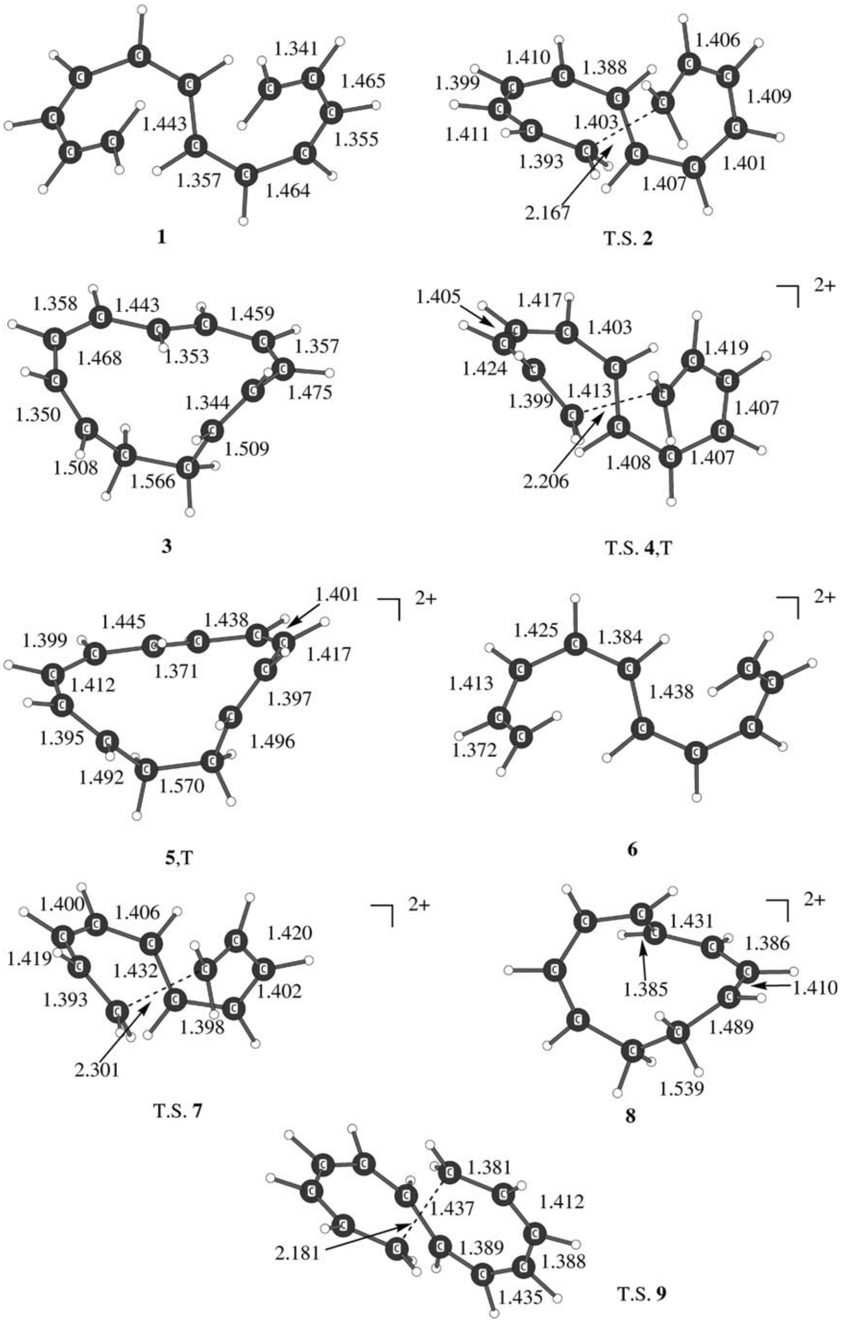


***Figure 2.*** B3LYP/6-31G* optimized geometries of the species **1**–**9** discussed in the text. Bond lengths are given in Å. T.S. = transition state. Unless indicated all structures are on a singlet potential energy surface; T = triplet.

corrections) than T.S. **2** at the coupled-cluster level of theory (Table 1). One objection could be that while both T.S. **9** and T.S. **2** coexist on the same PES, there is no direct competition between them as these structures pertain to different pairs of minimum structures. However, the energy difference between the open-chain minima that could undergo ring closure via either transition structure **9** or **2** is small: 6.0 kcal mol$^{-1}$ at the DFT level (with **1** being energetically preferred). These minima could facially interconvert through rotation around C–C bonds. Moreover, the activation barrier for reaching the "allowed" conrotatory T.S. **9** from its pertaining open-chain minimum is 36.9 kcal mol$^{-1}$ at the B3LYP/6-31G* level—about the same size as the barrier to reach **2** from **1** (Table 1). Ring closure is also preferred in this case (by 14.8 kcal mol$^{-1}$ at the DFT level). Thus, regardless of the initial polyene conformation, the disrotatory ring closure, "forbidden" for Hückel topology 4*n* electron compounds, is in this case always preferred.

This situation does not mean that a "forbidden" pathway has become allowed, but rather that the change from Hückel to Möbius topology reverses the rule for the stereoselectivity of the reaction and via a different, allowed pathway. Both Möbius and Hückel transition structures considered herein are favored by aromatic stabilization and are, hence, "allowed" rather than "forbidden". The latter should instead involve antiaromatic transition structures and which could possibly not be described by a single Slater determinant approach (owing to their potentially diradicaloid open-shell nature). Such forbidden transition structures are not considered herein.

We think that it would be desirable and also possible to locate further examples of such Möbius (or Hückel) aromatic transition structures that constitute an extension to the Woodward–Hoffmann rules. Further promising lines of research might be suggested by the work of Hoffmann and Tantillo, who pointed out the similarities between transition structures for sigmatropic shifts and those for electrocyclic reactions.[30] In a rather different approach, truly "forbidden" pathways could also be preferred in certain concerted cycloreversion reactions in 4*n* electron systems in which the "expected" allowed pathways are strongly disfavored by strain energy.[31] In the case described herein, however, the preference of the disrotatory pathway does not need such enforcement because the reactions are allowed, not forbidden.

A conceivable first application could be an unprecedented synthetic approach to the preparation of (still unknown, but computationally proposed)[2a,21c] Möbius[12]annulenes by a Bergman-type cyclization, originating from an enediyne.[32] The feasibility of such a mechanism has, however, still to be demonstrated both theoretically and experimentally.

While the stabilization through Möbius aromaticity in ground-state neutral systems appears to be rather weak,[21c–f,q] charge delocalization might enhance the effect and species **4** and **7** might profit from this.[2a,21i] In contrast, neutral T.S. **2** appears to be already strongly favored with respect to transition structure **9** (Table 1). Also Rzepa noted that the

***Table 1:*** Relative energies for neutral and charged $C_{12}H_{14}$ species and for $C_{10}H_{12}$.[a]

| Species (NIMAG) | Multiplicity of PES [Singlet=S, Triplet=T], Charge | Torque-selectivity,[b] Point group | Rel.[c] Energy [kcal $mol^{-1}$] | $\Delta R_{cc}$ [Å] | NICS[d] |
|---|---|---|---|---|---|
| **1 (0)** | S,0 | –, $C_2$ | 0.0 | – | – |
| **2 (1)** | S,0 | dis, $C_1$ | 36.2[e] | 0.02 | −12.8 |
| **3 (0)** | S,0 | –, $C_1$ | −13.1 | – | −2.1 |
| **4 (1)** | T, +2 | dis, $C_1$ | 18.6 | 0.02 | −12.1 |
| **5 (0)** | T, +2 | –, $C_1$ | 0.0 | – | −2.9 |
| **6 (0)** | S, +2 | –, $C_2$ | 0.0 | – | – |
| **7 (1)** | S, +2 | dis, $C_1$ | 23.9 | 0.04 | −13.8 |
| **8 (0)** | S, +2 | –, $C_2$ | 0.2 | – | −4.6 |
| **9 (1)** | S,0 | con, $C_2$ | 56.7[f,g] | 0.06 | −9.9 |

[a] Relative energies at the CCSD(T)/6-31G level (for neutral and charged $C_{12}H_{14}$ species) and CCSD(T)/6-31G* level of theory (for $C_{10}H_{12}$) and including ZPE corrections at B3LYP/6-31G*, range of CC bond lengths ($\Delta R_{cc}$) and NICS aromaticity indices for transition structures (with NIMAG = 1) and minima (NIMAG = 0). [b] "Conrotatory" (con) or "disrotatory" (dis) stereoselectivity of the polyene-cycloalkene conversion. [c] With respect to the respective reference structure on the same potential energy surface. [d] Calculated for the center of mass. [e] 35.7 kcal $mol^{-1}$ without ZPE corrections. [f] With respect to **1**. [g] 55.5 kcal $mol^{-1}$ without ZPE corrections.

Möbius twisted Hückel T.S. reported by him was slightly lower in energy by 2.6 kcal $mol^{-1}$ (at the B3LYP/6-31G* level) than the "expected" (disrotatory) transition structure pertaining to the (*Z*,*Z*,*Z*)-conformation of decapentaene, indicating that the "twist" might give such transition-state structures an edge over the "classical" textbook forms.

Concluding, we have shown that genuine Möbius orbital topology, which had not been taken into account in the formulation of the Dewar–Zimmerman interpretation and of the Woodward–Hoffmann rules, leads to new results which may reverse the predictions of torque-selectivity and "forbiddenness" of reactive modes from these rules.[33] Further potential applications might also be envisaged in photochemistry, where polyenes such as dodecahexaene **1**, are studied as model compounds for the carotenoids as examples of light-harvesting molecules.[34]

Received: December 9, 2008
Revised: January 25, 2009

**Keywords:** aromaticity · density functional calculations · möbius aromaticity · pericyclic reactions · transition states

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