A Stereochemical Analysis of Electrocyclic Reactions of Doublets

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Abstract: The stereochemistry of electrocyclic reactions of spin doublets is explored theoretically and found to be more complex than for singlet molecules. The two most familiar approaches to determining the orbital symmetry/topology based rotatory preference, HOMO and orbital correlation diagrams, are ineffective in the doublet series, the first because it generates demonstrably erroneous predictions and the second because, in general, it generates none. Two alternate approaches, the Zimmerman orbital topology criterion and a quantitatively extended form of the orbital correlation diagram, have been identified as valid on the basis of comparisons with experimental results and INDO reaction path calculations. The orbital symmetry/topology based rotatory selectivity is a damped vibration function of carbon number, with nodes (zero selectivity) at the neutral systems (odd number of carbons) and maximum selectivity at C_4 (conrotation for both cation and anion radicals). The relatively small orbital symmetry/topology effects in the doublet series, especially beyond C_4, present opportunity for additional effects to assert themselves. In particular, molecular symmetry appears to be a second major factor and in fact the generally dominant one where the two are in opposition. Thus, reaction partners having a common C_2 symmetry element geometrically favor conrotation in the doublet series, since the latter rotational mode conserves C_2 symmetry. A symmetric reaction path is therefore available and this generally maintains more efficient cyclic overlap. Disrotation is favored where C_s symmetry is common to reactant and product. Interconversions of planar reaction partners are unaffected by molecular symmetry, since both C_s and C_2 symmetry elements are present. Reaction path calculations for $C_6\cdot^-$ (1,3-cyclohexadiene $\rightleftarrows$ 1,3,5-hexatriene anion radicals) indicate that conrotation is the preferred reaction mode, even though orbital symmetry/topology favors disrotation, because the most stable reaction partners have a common C_2 element. Similar calculations involving planar and C_s hexatriene anion radicals find disrotation favored.

Although the electrocyclic transformation of singlets has been studied extensively, relatively little is known experimentally or theoretically concerning those of the spin doublet subset, including neutral, anion, and cation radicals. Recent experimental determinations of the preferred (conrotatory) stereochemistry in the cyclobutene/1,3-butadiene[1] and benzocyclobutene/*o*-xylylene[2] anion radicals systems have presented an opportunity to probe electrocyclic reaction theory in the challenging domain of doublets. The familiar HOMO mnemonic, e.g., has been found to fail both tests, predicting disrotation in both instances. Orbital correlation diagrams, though correctly foreseeing conrotation in the second reaction, are indecisive in the first, finding both pathways "forbidden". Indeed the scope of orbital correlation diagrams in the doublet domain is severely limited, very few doublets having an "allowed" electrocyclic mode. In effect, orbital symmetry in any of its familiar manifestations is minimally useful for doublets. Nevertheless, viable theoretical criteria have apparently been identified in recent work.[3] These include the familiar Zimmerman orbital topology approach and a quantitatively extended version of orbital correlation diagrams. The intent of the present paper is to apply these latter approaches and also reaction path calculations to the doublet electrocyclic reaction more generally. The stereochemical analysis must, however, proceed beyond the first order, where only orbital symmetry/topology effects are included, since such effects are often rather weak in the doublet series. Specifically, molecular (as opposed to orbital) symmetry effects often appear to exert a strong and even controlling influence on reaction stereochemistry.

Orbital Symmetry/Topology Effects

The selection rules based on HOMO are of earliest vintage.[4] The predictions for several doublet electrocyclic reactions, ranging from the cyclopropyl/allyl radicals ($C_3\cdot$) to the cyclooctatraene anion radicals ($C_8\cdot^-$) interconversions are tested in Table I. As previously noted, the disrotatory prediction for $C_4\cdot^-$ is demonstrably incorrect. Many of the other HOMO predictions in Table I conflict with the otherwise unanimous conclusions of the remaining theoretical approaches (orbital topology, extended orbital correlation diagrams, reaction path calculations), as will be seen.

None of the simple, prototype doublet electrocyclic reactions such as those in Table I have an "allowed" mode. Consequently, orbital correlation diagrams per se are not useful in any of these transformations. The benzocyclobutene/*o*-xylylene anion radicals system is, of course, exceptional, and in this case the orbital correlation diagram prediction (conrotation) is correct. It is noteworthy that even the orbital correlation diagram contradicts HOMO in this instance, demonstrating the inequivalence of the two methods.[4] The extended orbital correlation diagram approach makes use of the fact that for a forbidden electrocyclic process the reactant orbitals correlate with an excited state of its reaction partner. Where both reaction modes (disrotation and conrotation) are "forbidden", the preferred mode can be selected on the basis of the relative energies of the two excited states implied by the orbital correlations. In order to avoid the quantitatively more uncertain comparison of σ with π orbital energies, the excited states of the more fully conjugated reaction partner are adopted, i.e., the reactant is assumed to be the cyclic (less extended) partner. In the $C_4\cdot^-$ reaction the disrotatory cleavage of the cyclobutene anion radical intends to produce the 212 butadiene excited state (i.e., the configuration having 2, 1, and 2 electrons in the first three MO's, Figure 1) and the conrotatory cleavage the 2201 excited state. The HMO energies of these two excited states differ by 0.24 β, the 2201 state being the more stable. Thus conrotation, though not "allowed", should be (and is) preferred over disrotation for $C_4\cdot^-$. The results in the doublet series generally are recorded in Table I. The stereochemical results for the C_3^+–C_8 series of singlet reactions are, incidentally, predicted correctly, but are not shown. Figure 2 illustrates the stereochemical selectivity (energy difference between the two excited states in question) as a function of structure. Several interesting trends emerge: (i) the neutral doublets ($C_3\cdot$, $C_5\cdot$, $C_7\cdot$) all exhibit zero selectivity, (ii) the anion and cation radicals of a given system have identical selectivities (true only in the HMO approximation), (iii) the systems having an even number of carbon atoms (charged systems) alternately have con- and disrotatory preferences opposite to those predicted by HOMO for the anion radicals but identical with the HOMO predictions for cation radicals, and (iv) the absolute maximum of selectivity occurs at C_4, coincidentally the only

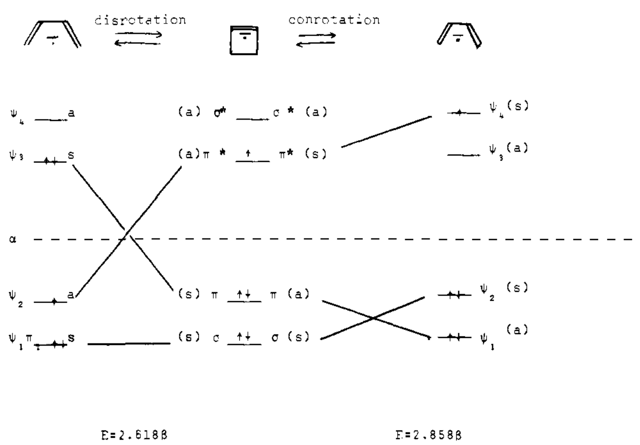


Figure 1. Orbital correlation diagrams for the $C_4\cdot^-$ electrocyclic reaction.

Table I. Stereochemistry of Doublet Electrocyclic Reactions

System	HOMO symmetry	HOMO prediction	Extended orbital correlation diagram prediction	Zimmerman Mobius-Hückel prediction
$C_3\cdot$	A	Con	No preference	No preference
$C_4\cdot^+$	A	Con	Con	Con
$C_4\cdot^-$	S	Dis	Con	Con
$C_5\cdot$	S	Dis	No preference	No preference
$C_6\cdot^+$	S	Dis	Dis	Dis
$C_6\cdot^-$	A	Con	Dis	Dis
$C_7\cdot$	A	Con	No preference	No preference
$C_8\cdot^+$	A	Con	Con	Con
$C_8\cdot^-$	S	Dis	Con	Con

system for which decisive experimental data are available. Succinctly, the plot of selectivity vs. carbon number is a damped vibration with maximum at C_4 and nodes at C_3, C_5, C_7, etc.

The Zimmerman orbital topology approach yields results which are in quantitative accord with those of the extended orbital correlation diagram approach.[5] According to the Zimmerman concept, a conrotatory electrocyclic transition state is analogous to a Möbius annulene, whereas the disrotatory transition state is likened to a Hückel annulene. Since one knows which singlet annulenes ($4n + 2$) are more stable in the Hückel and which ($4n$) in the Möbius topology, an attractively simple and general approach is available for predicting the stereochemical course of singlet electrocyclic reactions. In the case of doublets the topological preferences (if any), though perhaps not well known, are easily found from (for example) the HMO π energies of the appropriate topologues (Table I). For the neutral doublets, the topological preference is nil. In the charged doublets the preference is the same as for the corresponding uncharged singlet, e.g., for the cyclobutadiene anion and cation radicals the Möbius topology is preferred, just as in cyclobutadiene itself; hence conrotation is preferred in the $C_4\cdot^-$ and $C_4\cdot^+$ reactions. In the case of the benzene anion and cation radicals the Hückel topologue is the more stable, as with benzene itself; thus, disrotation is preferred in the $C_6\cdot^-$ and $C_6\cdot^+$ electrocyclic reactions (topologically).

Reaction path calculations (CNDO SCF MO) have been carried out for a few of the doublet reactions under consideration. That for $C_4\cdot^-$ has already been reported and agrees with the more qualitative predictions (conrotation).[1,3] A parallel calculation for $C_4\cdot^+$ also predicts preferred conrotation, again in agreement with the simpler criteria. The calculations for $C_6\cdot^-$ will be discussed in a subsequent section.

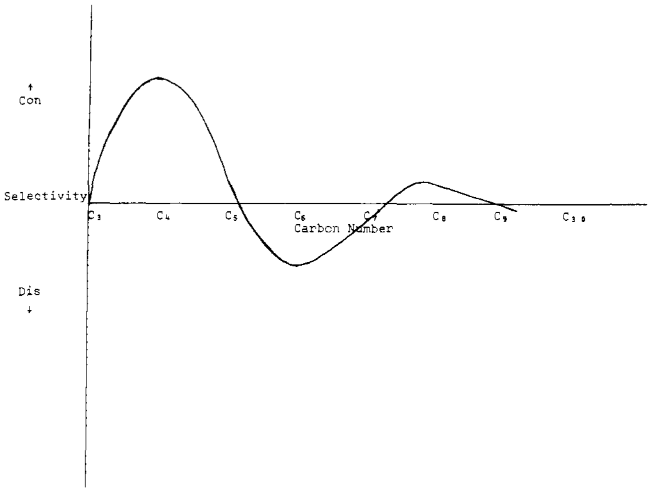


Figure 2. Rotatory stereoselectivity in doublet electrocyclic reactions.

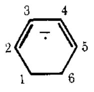
Molecular Symmetry Effects

Orbital correlation diagrams for electrocyclic reactions are conventionally referred to planar reaction partners. They are, therefore, frequently based upon unrealistic molecular geometries. The approach, though imperfect, is useful, since OCD's often cannot be constructed when even one reaction partner has a nonplanar geometry. Nevertheless it should be kept in mind that OCD's on such unrealistic planar systems reveal only an (idealized) orbital symmetry/topology effect. Evidently the consequences of the neglect of real molecular geometry have not been systematically analyzed. In the case of doublet electrocyclic reactions such an investigation is imperative because orbital symmetry/topology effects are relatively weak in this series.

In the simple prototype electrocyclic systems the planar versions of the reaction partners have both C_2 and C_s symmetry. The reaction is thus not geometrically biased toward either conrotation (which maintains only a C_2 axis) or disrotation (which maintains C_s symmetry). In such an idealized system the electrocyclic stereochemistry may properly be said to be controlled solely by orbital symmetry/topology. However, electrocyclic and indeed other pericyclic reactions involving either a C_2 or C_s nonplanar reactant and/or product are not similarly free of the bias of molecular geometry. Specifically, it should be noted that a C_2 nonplanar molecule cannot have a rigorously "allowed" disrotatory mode, even though that mode be allowed for the planar version of the same reaction system. The application to a molecule of C_2 symmetry of an operation (electrocyclic disrotation) of inherent C_s symmetry leads to an unsymmetrical reaction path, to which orbital correlation diagrams are inapplicable. Similarly, a reactant of C_s symmetry cannot have an "allowed" conrotatory mode. On the other hand, our original molecule of C_2 symmetry reacting via conrotation utilizes a symmetric path to which orbital correlation diagrams are at least applicable, though the reaction be "forbidden". In the illustrations above, the molecular geometry effect opposes orbital symmetry/topology. In other instances the two effects combine to produce an "allowed" reaction even where realistic geometries are recognized. This occurs for a molecule of C_2 symmetry when conrotation is the orbital symmetry/topology allowed mode and for a C_s molecule when disrotation is allowed. Briefly, then, the following rule can be formulated: C_2 symmetry in a reactant or product is an influence favoring conrotation; C_s symmetry favors disrotation. Though the molecular symmetry effect is also applicable to singlet pericyclic chemistry, it is here applied only to the doublet electrocyclic reaction.

In the $C_3\cdot$, $C_4\cdot^-$, and $C_4\cdot^+$ transformations, fully planar reaction paths are, in fact, realistic. In these cases molecular symmetry is impartial with respect to the selection of a preferred electrocyclic mode. The $C_6\cdot^-$ transformation, however, illustrates the prominent role molecular symmetry can potentially play in electrocyclic reactions.

INDO-SCF-MO calculations indicate the most stable geometry of **1** to be planar. Reaction path calculations have therefore been carried out for the conversion of **1** to the three *all-cis*-1,3,5-hexatriene anion radical local minima **2** (C_2), **3** (C_s), and **4** (planar, C_s and C_2). The conversion **1** $\rightleftarrows$ **2** involves reaction partners which have a common C_2 symetry axis (but not a common C_s symmetry plane). It requires torsions about C_2–C_3 and C_4–C_5 which are conrotatory in relation to each other, i.e., the conversion **1** $\rightleftarrows$ **2** involves a kind of molecular conrotation. Electrocyclic conrotation implies conrotatory twists about C_1–C_2 and C_5–C_6. A reaction path involving a combination of these two deformations conserves C_2 symmetry along its entire course. In contrast, the C_2 torsion involved in **1** $\rightleftarrows$ **2** in conjunction with disrotation conserves no symmetry element. It appears reasonable to assume, and it is born out by the calculation, that such unsymmetric reaction paths are usually intrinsically unfavorable, owing to *spatially* decreased overlap between the electrocyclic reaction termini. Thus, in the reaction **1** $\rightleftarrows$ **2** the conrotatory process maintains C_1–C_6 bonding unusually well in the transition state (**5**), whereas the disrotatory route (**6**) breaks off C_1–C_6 bonding abruptly, before adequate C_1–C_2 and C_5–C_6 π overlap can be established. In this connection, the virtual perpendicularity of the relevant C_1 and C_6 orbitals in the C_2-dis transition state is especially noteworthy. The orbital symmetry/topology effect has already been found to favor disrotation in the $C_6\cdot^-$ reaction. In the specific case of the reaction represented by **1** $\rightleftarrows$ **2**, the orbital symmetry/topology effect and that of molecular symmetry are evidently opposed. Invoking analogous reasoning, the **1** $\rightleftarrows$ **3** reaction should enjoy the concurrence of disrotatory preferences by both effects. In the planar version **1** $\rightleftarrows$ **4** orbital symmetry/topology alone is relevant and a disrotatory outcome is predicted. INDO reaction path calculations indeed predict disrotation in this latter reaction by a margin of 20 kcal/mol. In the **1** $\rightleftarrows$ **3** reaction, again as predicted, disrotation is favored by 20.7 kcal. In the **1** $\rightleftarrows$ **2** reaction, where the two effects are opposed and no qualitative prediction was possible, *conrotation* is favored by 28.8 kcal. In fact, of the three reaction paths considered, the **1** $\rightleftarrows$ **2** conrotation is the one of lowest energy. Evidently molecular symmetry can, and in this system does, dominate the orbital symmetry/topology effect. That the topology at the transition state is indeed the unfavorable Möbius one is further seen by reversing the topology artificially in the calculation. This is done by setting the p_1–p_6 resonance integrals to their negative and recalculating the reaction path. The conrotatory transition state, having been fitted out with the favored Hückel topology and retaining the advantage of molecular symmetry conservation, is now preferred by an even wider margin than before (48.9 kcal).



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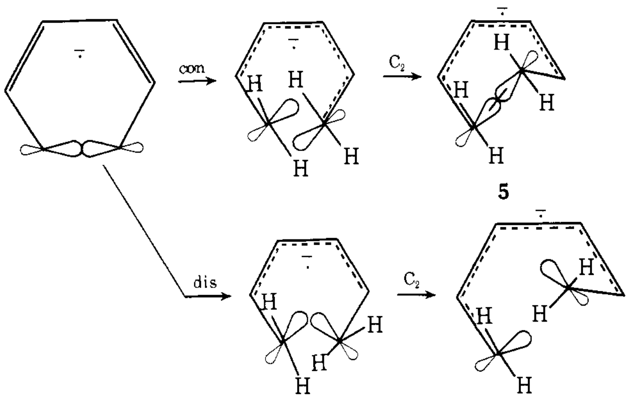

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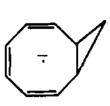
The molecular symmetry criterion is not regarded as fundamental but rather as a convenient means of selecting those transition states which are mor efficiently cyclically conjugated, just as orbital symmetry criteria predict the favored topology. Obviously, an efficiently conjugated Möbius system (such as the conrotatory transition state for **1** $\rightleftarrows$ **2**) need not be of higher energy than a highly twisted and therefore poorly conjugated, Hückel system, even though the latter type system be favored in a comparison of the fully conjugated (planar) forms. An important class of exceptions can be expected in singlet electrocyclic (and other pericyclic) reactions involving C_3^-, C_4, and C_5^+ "antiaromatic" systems. In such systems cyclic conjugation is *destabilizing,* and molecular symmetry is preferentially lost. The unsymmetric (or lag rotatory) mechanism for "forbidden" electrocyclic reactions was proposed initially from this laboratory,[6] subsequently receiving confirmation via MINDO/3 calculations. Finally, the greater terminal (H/H and C/H) steric repulsions in the disrotatory than in the conrotatory version of **1** $\rightleftarrows$ **2** can be shown to contribute to, but not to be the major factor in, favoring the latter. Thus, nullifying these interactions in the INDO calculations still leaves the conrotatory path strongly preferred.

The foregoing calculations and conclusions regarding the $C_6\cdot^-$ reaction have not yet been decisively checked by experiment. However, kinetic data[7] on the cleavage of the *cis*- and *trans*-9,10-dihydro-9,10-diphenylphenanthrene anion radicals is more comfortably accounted for in terms of preferred conrotation. The pertinent observation is that the less stable cis isomer cleaves at a rate essentially equal to that of the trans isomer. Conventionally, this kind of observation has been rationalized in terms of conrotation, though normally the cis isomer cleaves appreciably more slowly than the trans.

Calculations on the corresponding $C_6\cdot^+$ reaction are not yet available, but a tentative prediction, based on the foregoing discussion, seems justified. The orbital topology effect, being of the same nature as for the anion radical, favors disrotation, as shown earlier. In contrast to the anion radical reaction, however, molecular symmetry appears likely to play no role in the cation radical case. This surmise is based upon the general rule that cation radicals are far more susceptible to conjugative stabilization than anion radicals; therefore, the planar structure analogous to **3** is likely to be the most stable all cis minimum. As was pointed out previously, molecular symmetry exerts no bias in electrocyclic transformations between planar reaction partners. Thus, despite similar topological preferences, corresponding anion and cation radicals need not and probably only rarely will have the same rotatory penchant.

In view of the predicted prominent role of the molecular symmetry effect in the $C_6\cdot^-$ reaction and of the fact that, excluding $C_4\cdot^-$, $C_4\cdot^+$, this system should have the highest orbital symmetry/topology based selectivity of the doublet systems under consideration, it would appear reasonable to project an important and quite possibly dominant role for the molecular symmetry effect in doublet electrocyclic chemistry generally. Indeed an example of the $C_8\cdot^-$ reaction studied by the Winstein group appears again to reflect molecular symmetry control. The pertinent observation is that the *cis*-bicyclo-

[6.1.0]nontriene anion radical (**7**) undergoes cleavage more rapidly than the less stable trans anion radical (**8**).[8] The product, observed by ESR spectroscopy for the cleavage of the cis isomer only, is the cyclononatetraene **9**, of C_s symmetry. One may note immediately that the faster reaction (**7** $\rightleftarrows$ **9**) involves reaction partners of the same (C_s) symmetry. The slower reaction connects partners of differing symmetry (**9** has C_2 symmetry). This is true despite the fact that the faster reaction (**7** $\rightleftarrows$ **9**) is disrotatory, i.e., not the orbital symmetry/topology favored route, whereas the slower one is conrotatory, the mode favored by orbital symmetry/topology. Again, molecular symmetry appears dominant. It appears noteworthy that **8** does have a molecular symmetry allowed path, one leading to the planar cyclononatetraene **10**. The angle strain inherent in this latter structure may, via product development control, be responsible for the apparent slowness of the reaction **8** $\rightleftarrows$ **10**.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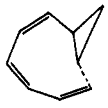
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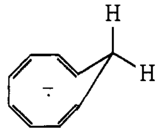

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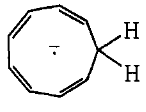

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Of course the prototype $\mathrm{C}_8\cdot^-$ reaction need not have the same stereochemical preference as in the preceding bicyclic example. The topology effect, of course, still exerts a weak conrotatory preference. The crucial question, from the point of view of the present theory, is the symmetry of the most stable *all-cis*-octatetraene anion radical. Pending further calculations, it appears likely that a geometry of C_2 symmetry will be favored, as with $\mathrm{C}_6\cdot^-$. In this circumstance both effects would agree on conrotation. Though the immediately preceding discussion is still somewhat speculative, it is intended to further illustrate the application of the theory. Thus, in nonrigid systems, where preferred geometries may not be known, a more certain prediction would involve a calculation of the optimum all-cis geometry for the more extended (doublet) reaction partner. This is still quite feasible for systems as large as C_8, whereas a full reaction path calculation would be extremely expensive.

In conclusion, the description of cyclic conjugation in terms of topology alone is incomplete and appears seriously inadequate in doublet chemistry. The efficiency of the cyclic conjugation, irrespective of its topological type, is another important factor, apparently the dominant one in most doublet reactions. Molecular symmetry provides a convenient means of categorizing electrocyclic transition states as symmetric or *un*symmetric and therefore as relatively efficiently or inefficiently cyclically conjugated. In effect, it can be regarded as a means of selecting those transition states which best conform to the principle of maximum continuous overlap.

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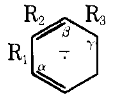
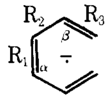
Appendix

The geometrical parameters and procedures used in the $\mathrm{C}_6\cdot^-$ reaction path calculations were as follows. For the cyclohexadiene anion radical: $R_1 = 1.40$, $R_2 = 1.39$ Å, $\theta = 0°$ (where θ is the diene dihedral angle, i.e., a planar conjugated system was assumed) are optimization results for the 1,3-butadiene anion radical; $R_3 = 1.525$ is an experimental value for 1,3-cyclohexadiene; $\alpha = 120°$, $\beta = 125.6°$, and $\gamma = 114.4°$; R(C–H) = 1.09 Å and ϕ(H–C–H) = 109.5°; pyramidalization at unsaturated carbon was not investigated; all C–H bonds were assumed to be on the bisector of the relevant C–C–C angle. For the 1,3,5-hexatriene anion radical: $R_1 = 1.4186$, $R_2 = 1.4305$, $R_3 = 1.375$, $\alpha = 122.1°$, $\beta = 125.9°$, R(C–H) = 1.09, and ϕ(H–C–H) = 120°. The optimized angle for C_2 twisting about bond R_2 is 25°/bond; for C_s twisting about the same bond both twists are 60°. A reaction path linear in all varying parameter was assumed.





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