

Symmetry Independent Indicators for the Preferred Rotation in Concerted Electrocyclic Reactions

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Abstract: The preferred mode of rotation for concerted electrocyclic ring opening reactions is predicted from the index T based on the structure of the π system of the reactant. This index describes the energy difference $\Delta E = E^{\text{con}} - E^{\text{dis}}$ as a function of the reaction coordinate for small values of the rotational angle. The smooth, systematic dependence of ΔE on the angle is characteristic for the concerted reactions. As a consequence, the sign of T allows one to predict the relative order of the activation energy for con- and disrotation, respectively; the preferred mode is conrotatory if T is positive and disrotatory if T is negative. In addition, a third class of systems exists, where T is either zero or has a very small value. This is effectively the same class of systems for which the previously introduced bond order rule predicted that: (a) the concerted electrocyclic reaction is nonstereospecific and (b) the product ratio of the two rotations can be shifted by introducing substituents in the π system.

In a previous publication,¹ hereafter referred to as I, we have discussed the electronically controlled electrocyclic reactions from the point of view of the energetics, rather than the symmetry of a one-electron orbital. The qualitative behavior of the energy difference $\Delta E = E^{\text{con}} - E^{\text{dis}}$ as a function of the rotational coordinate follows from the smooth and systematic dependence on the angle of π and σ bonding at the reaction sites as well as the electron interaction terms. The essential properties of ΔE can be summarized as follows. (a) $\Delta E = 0$ for both the reactants and the products, unless steric effects are important; *i.e.*, both modes of rotation lead to the same or electronically equivalent products. (b) For intermediate angles, the energy difference is a smooth, nonoscillatory function. One mode of rotation has an energy consistently below the other for all intermediate angles. Specifically, it has then the lower activation energy and is therefore the kinetically preferred rotation. These general conclusions, which take many-electron effects into account, have been verified by Buenker *et al.*,^{2,3} in *ab initio* calculations on the butadiene-cyclobutene system.

For quantitative theoretical studies of the electrocyclic reaction, extensive *ab initio* configuration interaction calculations (CI) are a necessity, but for many molecules of interest such calculations are still impractical. Fortunately, the prediction of the preferred mode of rotation is a qualitative problem and requires only the knowledge of the relative energy ordering of con- and disrotation. This order is most conveniently obtained from the sign of the energy difference function and, as we have discussed in I, simplified methods are acceptable, provided all electrons that are strongly affected by the rotation are taken explicitly into account and many-electron effects are included, at least in a qualitative way. In this respect, our approach differs from the concept of orbital symmetry conservation in the Woodward-Hoffmann rules.⁴

(1) E. E. Weltin, *J. Amer. Chem. Soc.*, **95**, 7650 (1973).

(2) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *J. Amer. Chem. Soc.*, **93**, 5005 (1971); K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *ibid.*, **94**, 5639 (1972).

(3) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **93**, 217 (1971).

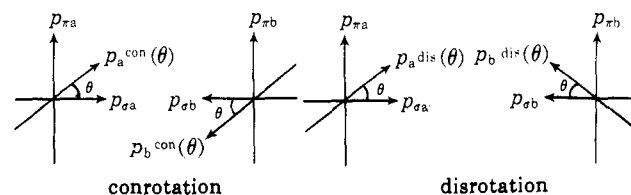
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

The bond order rule discussed in I states: *the electronically controlled electrocyclic reaction proceeds disrotatory if the generalized bond order between the two reacting π centers in the ring open form is positive and conrotatory if this bond order is negative.* The structure of the ring open form is used in this rule which is therefore the natural choice for the discussion of ring closures. Insofar as the over-all behavior of the energy difference function may be inferred from the bond order, it is a valid criterion also for the reverse reaction. However, if one is specifically interested in electrocyclic ring openings one would like to have an indicator of similar quality which is based on the structural properties of the reactants.

Electrocyclic Ring Opening

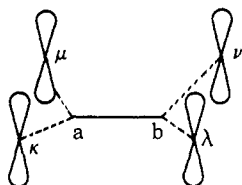
In this paper we consider the electrocyclic ring opening reactions, in which the products have a single connected π system. The reactants may have either a single π system or disconnected π subsystems coplanar with the reacting σ bond. Sterically controlled reactions, in which bulky side groups or constraints due to the carbon skeleton determine the mode of rotation, are excluded from the discussion.

Based on *ab initio* calculations, Buenker, *et al.*,³ have suggested that the reaction has a step mechanism in which the change of the over-all molecular geometry from the closed to the ring open form takes place primarily before and after and only to a very small degree during the rotation of the side groups and the p orbitals at the reacting centers. To predict the preferred rotation, we are only concerned with the actual rotational step at the intermediate geometry. As in I, the model for the reaction is the simultaneous rotation of p



orbitals (or the p component of hybrid orbitals) at the two centers a and b of the reacting σ bond from p_σ to p_π

orientation.⁵ Up to 4π centers $\mu, \nu, \kappa,$ and λ are bonded



to the reacting centers a and b. The θ dependent resonance integrals are chosen⁶ as

$$H_{a\mu} = H_{a\kappa} = \beta_{\pi} \sin \theta \quad \text{con- and disrotation}$$

$$H_{b\nu} = H_{b\lambda} = \begin{matrix} +\beta_{\pi} \sin \theta & \text{disrotation} \\ -\beta_{\pi} \sin \theta & \text{conrotation} \end{matrix}$$

$$H_{ab} = \beta_{\sigma} \cos^2 \theta$$

β_{π} and β_{σ} negative energies

At $\theta = 0^\circ$ there can be no difference between the rotational modes. If the state of interest is well represented by one dominant configuration, the behavior for *small* angles is essentially determined by the dependence of the dominant configuration on θ in the two rotational modes. That is, the contributions from core electrons (inner shells and σ electrons except for the reacting σ bond), from electron interaction terms, and from CI effects effectively cancel in the energy difference function. (This is not true for intermediate θ , where CI effects assure the smooth behavior of ΔE .)

At $\theta = 0^\circ$ the MO's Ψ_J of the π system

$$E_J \dots \Psi_J = \sum_p C_{pJ} \varphi_p$$

are decoupled from the a-b σ orbitals

$$E_{\sigma} \dots c_a p_{\sigma a} + c_b p_{\sigma b} \quad \text{bonding}$$

$$E_{\sigma}^* \dots c_a^* p_{\sigma a} + c_b^* p_{\sigma b} \quad \text{antibonding}$$

With the zeroth-order wave function constructed from these orbitals, the energy difference function for small angles is given by the second-order perturbation expression⁷

$$\Delta E(\theta) \approx \sum_J b_J \frac{\langle J | h_{(\theta)}^{\text{con}} | \sigma^* \rangle^2 - \langle J | h_{(\theta)}^{\text{dis}} | \sigma^* \rangle^2}{E_J - E_{\sigma^*}} + \sum_J (b_J - 2) \frac{\langle J | h_{(\theta)}^{\text{con}} | \sigma \rangle^2 - \langle J | h_{(\theta)}^{\text{dis}} | \sigma \rangle^2}{E_J - E_{\sigma}}$$

where b_J (2, 1, 0) are the occupation numbers of the π orbitals in the reactant and two electrons occupy the σ orbital. Substituting the θ dependent matrix elements of the perturbation and using the known coefficients $c_{a\sigma} = c_{b\sigma} = (2)^{-1/2}$ and $c_{a\sigma^*} = -c_{b\sigma^*} = (2)^{-1/2}$, one finds

$$\Delta E(\theta) \approx 2 \sin^2 \theta \beta^2 \left\{ \sum_J b_J \frac{(C_{\mu J} + C_{\kappa J})(C_{\nu J} + C_{\lambda J})}{E_J - E_{\sigma^*}} + \sum_J (2 - b_J) \frac{(C_{\mu J} + C_{\kappa J})(C_{\nu J} + C_{\lambda J})}{E_J - E_{\sigma}} \right\}$$

(5) A right- and a left-handed coordinate system is used at a and b, respectively. Note the definition of the rotational angle which differs from the choice in I.

(6) Numerical values of the resonance integrals must be chosen for the geometry of the rotational step and differ from the standard integrals. More sophisticated estimates take rehybridization explicitly into account. While this affects the calculated energy differences, the desired qualitative conclusions are not changed.

(7) E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendungen," Vol. 1, Verlag Chemie, Weinheim, Germany, 1968.

Finally we use $E_J = \alpha + X_J \beta$, $E_{\sigma} = \alpha + b_{\sigma} \beta$, $E_{\sigma^*} = \alpha - b_{\sigma} \beta$, $b_{\sigma} = \beta_{\sigma} / \beta$ and define the term T as

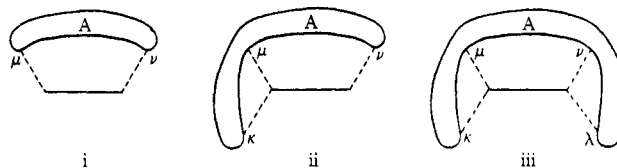
$$T = \sum_J b_J \frac{(C_{\mu J} + C_{\kappa J})(C_{\nu J} + C_{\lambda J})}{X_J + b_{\sigma}} + \sum_J (2 - b_J) \frac{(C_{\mu J} + C_{\kappa J})(C_{\nu J} + C_{\lambda J})}{X_J - b_{\sigma}}$$

This is the desired indicator from which the sign of ΔE and consequently the preferred rotation may be predicted; *the preferred rotation in the concerted electrocyclic reaction is conrotatory if T is positive and disrotatory if T is negative.* In addition, there is the class of systems where T is of indeterminate sign, *i.e.*, has the value zero. As T is at best a semiquantitative index, the molecules where T has a very small absolute value are included in this class. The same arguments as given in I for zero or small bond orders apply; the exact energy difference function may then be dominated by small steric effects. If, however, these reactions are still electronically controlled, we predict the following. *If molecules with zero or a very small value of T undergo the electronically controlled electrocyclic reaction, the products of both rotational modes are formed simultaneously; i.e., there are concerted reactions which are nonstereospecific. Furthermore, the product ratio may be shifted by introducing substituents into the system. The direction and magnitude of the shift depends on both the nature of the substituent and the substitution site.*

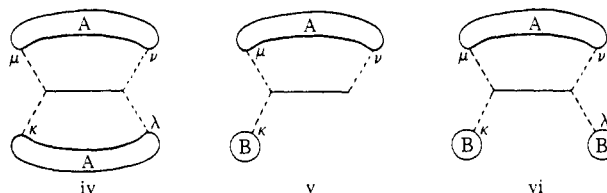
Specialization of the Term T

We consider the cases where the product has a single connected π system. The ring closed reactant belongs then to one of the following types, where A and B represent π systems, (-) is the reacting bond and (...) are σ bonds at $\theta = 0^\circ$ and σ and π bonds at $\theta = 90^\circ$, respectively.

(a) One connected system



(b) Two or three disconnected π subsystems



T for the types i and ii are trivially obtained from the general expression given for iii by dropping the appropriate coefficients $C_{\lambda J}$ or $C_{\mu J}$ and $C_{\kappa J}$, respectively. In types iv to vi with disconnected subsystems, the summation in T runs over all orbitals of the combined MO schemes, with the understanding that for a given J the coefficients of only one subsystem may differ from zero, while those in the other subsystems are set to zero. In type iv this results in a term T which is the sum of two

independent contributions $T = T_A + T_{A'}$ where T_A and $T_{A'}$ are given by the expression for type i for the two fragments separately. The fragments B and B' in types v and vi are connected to one side of the reacting σ bond only and contribute zero to T . While they certainly do have an effect on the absolute activation energies, they affect both con- and disrotation in the same way. On physical grounds this must be the case, as B or B' can "feel" initially the rotation at only one end of the reacting bond which does not determine the rotational mode.

The type ii suggest some interesting possibilities; if the two fragments are chosen to be rotational antagonists then: (a) the observed reaction products may be used to establish the relative "rotation-controlling power" of a π system, (b) the balance of the two contributions may be fine enough that T is very close to zero in which case the products of both rotations are formed and the product ratio can be measurably shifted by substituents in the π systems, and finally (c) two different low-lying excited states favor opposite rotational modes; if A and A' are antagonists in the ground configuration, the combination of the ground configuration of one fragment with the excited configuration of the other fragment in most cases leads to mutual reinforcement of one rotational mode. Depending on which fragment is excited, one or the other rotational mode will be preferred. Special care must be taken in identifying the reacting state and generally a CI calculation will be necessary to properly describe this state and to arrive at reliable predictions. The same caution must be exercised in types v and vi where an excitation of the fragments B and B' has no direct effect on the rotational mode in the region of small angles (but on the total activation energy), while only those states with an appreciable contribution from excited configurations of A may prefer a different rotation from the ground state.

Simplified Expressions for T in Alternant Systems

The expressions for T as discussed above apply to any molecule undergoing the electrocyclic ring opening reaction. For alternant π systems the well-known pairing properties of the orbitals may be used to further simplify the expressions for T . In the following we treat explicitly type iv with the understanding that the other types may be easily obtained as the appropriate sums of such terms.

The n centers of the π system may be separated into two sets (* and 0) with n^* and n^0 members, respectively, such that no two members of the same set are bound. If K is the paired orbital of J then

$$X_K = -X_J \text{ and } C_{K\mu}C_{K\nu} = \pm C_{J\mu}C_{J\nu}$$

with the + sign if μ and ν belong to the same set (** or 00) and the - sign if they belong to different sets (*0). The minimum number of nonbonding, *i.e.*, $X_{nb} = 0$, levels is given by $|n^* - n^0|$. One obtains

(1) n even and no nonbonding level

(a) ground configuration

$$T_g^{*0} = 4 \sum_{J=1}^{n/2} \frac{C_{\mu J} C_{\nu J}}{X_J + b_\sigma}$$

$$T_g^{**} = T_g^{00} = 0$$

(b) first excited configuration

$$T_i^{*0} = 4 \sum_{J=1}^{(n/2)-1} \frac{C_{\mu J} C_{\nu J}}{X_J + b_\sigma} + 2C_{\mu n/2} C_{\nu n/2} \times \left(\frac{1}{X_{n/2} + b_\sigma} + \frac{1}{X_{n/2} - b_\sigma} \right) = T_g^{*0} - 4C_{\mu n/2} C_{\nu n/2} \frac{X_{n/2}}{X_{n/2}^2 - b_\sigma^2}$$

$$T_i^{**} = T_i^{00} = 0$$

(2) n odd with one nonbonding level $X_{(n+1)/2} = X_{nb} = 0, n^* = n^0 + 1$

(a) neutral radical, ground configuration

$$T_g^{*0} = 4 \sum_{J=1}^{(n-1)/2} \frac{C_{\mu J} C_{\nu J}}{X_J + b_\sigma}$$

$$T_g^{**} = T_g^{00} = 0$$

(b) positive ion, ground configuration

$$T_g^{*0} = 4 \sum_{J=1}^{(n-1)/2} \frac{C_{\mu J} C_{\nu J}}{X_J + b_\sigma}$$

$$T_g^{**} = -2 \frac{C_{\mu nb} C_{\nu nb}}{b_\sigma} \quad T_g^{00} = 0$$

(c) negative ion, ground configuration

$$T_g^{*0} = 4 \sum_{J=1}^{(n-1)/2} \frac{C_{\mu J} C_{\nu J}}{X_J + b_\sigma}$$

$$T_g^{**} = +2 \frac{C_{\mu nb} C_{\nu nb}}{b_\sigma} \quad T_g^{00} = 0$$

(d) positive ion, first excited configuration

$$T_i^{*0} = T_g^{*0} + 2C_{\mu(n-1)/2} C_{\nu(n-1)/2} \frac{b_\sigma}{X_{(n-1)/2}^2 - b_\sigma^2}$$

$$T_i^{**} \text{ or } T_i^{00} = 2C_{\mu(n-1)/2} C_{\nu(n-1)/2} \frac{b_\sigma}{X_{(n-1)/2}^2 - b_\sigma^2}$$

(e) negative ion, first excited configuration

$$T_i^{*0} = T_g^{*0} + 2C_{\mu(n-1)/2} C_{\nu(n-1)/2} \frac{b_\sigma}{X_{(n-1)/2}^2 - b_\sigma^2}$$

$$T_i^{**} \text{ or } T_i^{00} = -2C_{\mu(n-1)/2} C_{\nu(n-1)/2} \frac{b_\sigma}{X_{(n-1)/2}^2 - b_\sigma^2}$$

Consistent with the assumption that the low-lying excited configurations of interest are excitations of the π system, the doubly occupied bonding σ orbital is of lower energy than the highest occupied π orbital. This and the known closed expressions for MO's of linear systems⁷ allow one to derive the sign of T of end to end ring closed polyenes of any given length. If n , the number of π centers in the ring closed reactant, is even, one can easily verify that T_g is negative if $n/2$ is even and positive if $n/2$ is odd. The reverse sign is found in the first excited configuration. This leads to

ring closed no. of centers	ring open no. of centers	ground	excited
4, 8, 12, ...	6, 10, 14, ...	dis	con
2, 6, 10, ...	4, 8, 12, ...	con	dis

For odd n , T_g is zero for the ground configuration of the neutral radical. Positive and negative ions are in-

cluded, if the previous table is given in terms of n_e , the number of π electrons (k integer).

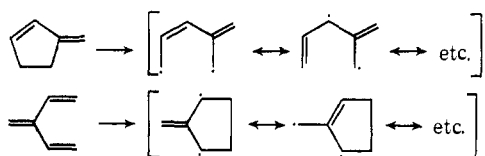
ring closed n_e	ring open n_e	ground	excited
$4k$	$4k + 2$	dis	con
$4k - 2$	$4k$	con	dis

These results are in full agreement with the conclusions from the bond order rule¹ and with the predictions of the Woodward-Hoffmann rules.⁴

Special Class with Zero or Very Small T

Even in the framework of a qualitative treatment, which uses only the sign of T as an indicator for the preferred rotation, the cases $T = 0$ play a special role, as zero is of indeterminate sign. We include in this class also the systems where T has a small value.

As is apparent from the previous section, a sufficient criterion for $T = 0$ is that the reactant and the products have alternant π systems and the π centers μ and ν (and κ and λ where appropriate) all belong to the *same* set either * or 0. The structural criterion therefore is that the ring containing the reacting σ bond is the only *odd* ring in the system. In the product ($\theta = 90^\circ$), which is also alternant, both centers a and b belong to the opposite set. It is highly gratifying to see that this is exactly the same criterion as the sufficient condition for zero bond orders. Molecules satisfying this condition are the most likely systems in which the predicted substituent effect on the rotation may be observed experimentally. To an experimentalist interested in such systems, it is only fair to point out a further peculiarity of these cases. We have mentioned already that in the Hückel MO model the absolute value of the difference $|n^* - n^0|$ equals the minimum number of nonbonding ($X_{nb} = 0$) energy levels. In the electrocyclic reaction of these systems (either ring opening or closure) the number of centers in one of the sets is changed by two. If n is odd, both reactants and products have at least one nonbonding level each. For even n , a reactant with no nonbonding level leads to a product that must have at least two nonbonding levels and is formally drawn as a biradical, for example



The odd ring is a sufficient but not necessary structural criterion for a very small T . The present discussion shows another class of molecules which may show the substituent effect that is not immediately apparent in the bond order rule. These are type iv, more specifically certain states of these systems, where A and A' are chosen such that their contributions to T cancel as closely as possible. Interestingly, the simplest examples of this type are A and A' even polyenes in the ground configuration and differing by 2 (generally $2 + 4k$) centers, open to a ring of $4m$ centers which have, in a planar configuration, also two nonbonding levels.

Conclusion

The numerical value of T clearly depends on the

choice of the positive parameter b_σ , the ratio of a σ to a π resonance integral for the geometry of the rotational step. It is, however, very easy to verify that the sign of T in the ground configuration of end-to-end ring closed polyenes is *independent* on the magnitude of b_σ . For the first excited configuration of these molecules, the choice of b_σ is no longer entirely arbitrary, but a *sufficient* condition for the signs given in an earlier section and leading to the predictions summarized in the tables is the requirement that the bonding σ orbital has a lower energy than the highest bonding π MO. This is of course equivalent to the assumption that the π system is excited while the σ electrons occupy the bonding σ MO. In passing we note that the opposite assumption, excitation of the reacting σ bond with the π system in the ground configuration, leads to an expression for the ΔE different from the T criterion but with exactly the same prediction of the preferred rotation!

The T criterion is based on the structure of the ring closed molecule and takes explicitly into account all electrons that are strongly affected by the rotation. It is not restricted to symmetric molecules and does not require any assumption of a special role played by a single one-electron MO. It is the natural choice of an indicator of the preferred rotation in the electrocyclic ring openings, in the same way as the bond order criterion is the natural choice for the reverse reaction. As both criteria refer to the same energy difference function, they both apply equally well to the forward and the reverse reaction. It is then a matter of convenience which criterion is preferred.

It is by no means obvious why the two criteria should necessarily predict the same mode of rotation. It is a fact that identical predictions are obtained for linear polyenes of any length in the end-to-end ring closure, and the structural criterion of the reacting σ bond being part of an odd ring leads to zero T and zero bond order. In addition we have checked a number of other cases and have yet to find any conflicting predictions.⁸ Of course the structures of reactants and products are not independent from each other. Nevertheless, the wide agreement is somewhat surprising, especially in view of the fact that ΔE is dominated in different ranges of the rotational coordinate by entirely different effects. At small θ the energy difference is essentially given by the differences in weak π bonding, while the loss of σ bonding is the same for both modes. At the other end, $\theta \sim 90^\circ$, the opposite is true; the difference is due to weak σ bonding, while the loss of π bonding affects both rotations in the same way. For intermediate angles, ΔE is dominated by entirely different effects, the many-electron configuration interactions. It is typical for concerted reactions that all factors entered in the CI are smooth continuous functions of the rotational coordinate. This assures the smooth, nonoscillatory connection between the two extremes of θ . It also shows very clearly that the highest occupied orbital alone and in particular its symmetry is not the reaction-controlling factor.

(8) We cannot exclude the possibility that among larger π systems situations may be found where the bond order and T both have very small values and the sign of T depends critically on the choice of b_σ . These molecules are included in the class of zero or small T .