Theoretical Aspects of the Bonding in Some Three-Membered Rings Containing Sulfur

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Abstract: In the series ethylene episulfide, episulfoxide, and episolufone the sulfone stands out by its very long CC bond and short CS and SO bonds. We find that an analysis of the bond length trends in these molecules leads naturally to a bonding picture in which the molecules are described as complexes of an ethylene with S, SO, or SO2. We trace the long CC bond in the episolufone to two factors. First, and invoking no 3d orbitals, when the molecule is viewed as an ethylene-SO2 complex, the S02 provides a low-lying orbital which populates the ethylene σ* level better than in the analogous sulfur case. Second, and directly invoking 3d participation, the SO2 ligand provides 3d orbitals which more efficiently withdraw bonding electron density from the ethylene fragment σ level. Our analysis predicts how to strengthen further the CC bond in episulfides and how to weaken still more the long CC bond in episolufones. The mode of that bond opening should be conrotatory in the episulfide and disrotatory in the episolufone. Finally the ethylene-complex viewpoint is connected to the general theory of substituent effects on cyclopropane bond strengths.

In the heterocyclic series of thiirane (1, ethylene episulfide), thiirane 1-oxide (2, ethylene episulfoxide), and thiirane 1,1-dioxide (3, ethylene episolufone) we are presented by Nature with a regular modification of a three-membered ring by oxygen addition, a progressive change in the coordination of sulfur. The equilibrium structure of the heterocycle responds in a significant and apparently irregular way to the pattern of sulfur coordination. From the several consistent structural studies on these molecules we have chosen the set of microwave spectroscopic structures illustrated below.\(^1\)\(^2\)\(^3\)

The remarkable feature of these structures is the way the episolufone 3 differs from the episulfoxide 2 and the episulfide 1. The geometries of 1 and 2 are "normal," that is both CC and CS distances are in the expected range. In contrast 3 contains a much longer CC bond and much shorter CS and SO bonds than 1 or 2.

In a related heterocycle, the thia diaziridine 1,1-dioxide (4), the MN single bond, analogous to the CC bond in 3, is one of the longest known, 1.67 Å.\(^5\)\(^6\)


To say that 3d orbital participation is responsible for this trend is not very informative. We have previously noted the structural and thermodynamic response of a cyclopropane ring to substituents. Sensing that the bond length anomaly in 3 would be related to these previous studies and that it would yield to us further insight into the electronic structure of three-membered rings, we undertook a detailed analysis of the bond lengths in these molecules.

Calculations and Discussion

We began by asking whether a semiempirical molecular orbital method would reproduce the structural trends. In particular extended Hückel\(^\text{\textsuperscript{a}}\) calculations were carried out on 1, 2, and 3, assuming an identical episulfide substructure in the three molecules. The Mulliken overlap populations for the various bonds should then reflect the tendency of these bonds to stretch or contract from the episulfide model. We did each calculation twice: once without 3d orbitals, a second time with sulfur 3d orbitals sufficiently contracted and at sufficiently low energy to simulate the extreme of 3d participation. The role of 3d orbitals in Si, P, and S bonding is a perpetual problem.\(^\text{10}\) We anticipate that our computational extremes of negligible vs. siz-
able 3d participation will bracket the actual situation. In Figure 1 we show the computed Mulliken overlap populations for 1, 2, and 3.

With or without 3d orbitals the general trend of stronger CS and SO and weaker CC bonds in the episulfone is reproduced. The experimental break between the episulfoxide and episulfone is not apparent if one remains within a series of calculations with or without 3d orbitals. We will return to an analysis of this discontinuity below, but for now let us proceed to trace the source of the trend within one series, specifically those calculations which omit 3d orbitals.

Our standard thirane geometry is shown in 5 below.

The total change in overlap populations on going from episulfide to episulfone can be decomposed into contributions by symmetry type of the orbitals involved. This is done in Table I. (AS means orbital(s) anti-

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>SS</th>
<th>AS</th>
<th>SA</th>
<th>AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C Episulfone</td>
<td>0.684</td>
<td>0.988</td>
<td>-0.296</td>
<td>0.112</td>
<td>-0.120</td>
</tr>
<tr>
<td>Episulfide</td>
<td>0.726</td>
<td>0.973</td>
<td>-0.238</td>
<td>0.110</td>
<td>-0.120</td>
</tr>
<tr>
<td>δ</td>
<td>-0.042</td>
<td>0.015</td>
<td>-0.058</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>C-S Episulfone</td>
<td>0.552</td>
<td>0.304</td>
<td>0.247</td>
<td>0.001</td>
<td>0</td>
</tr>
<tr>
<td>Episulfide</td>
<td>0.537</td>
<td>0.302</td>
<td>0.242</td>
<td>-0.007</td>
<td>0</td>
</tr>
<tr>
<td>δ</td>
<td>0.015</td>
<td>0.002</td>
<td>0.005</td>
<td>0.008</td>
<td>0</td>
</tr>
</tbody>
</table>

symmetric with respect to plane 1 as defined in 5, symmetric with respect to plane 2.)

It is important to note for further reference that the total CC overlap population in either 1 or 3 has a sizable negative component. Manipulation of that antibonding contribution will subsequently allow us to strengthen or weaken that carbon–carbon bond. At this point we observe that the predominant contribution to the weakening of the CC bond in 3 relative to 1 comes from orbitals of AS symmetry. Further inspection of the orbital by orbital breakdown of the overlap population shows that the AS bond weakening can be traced to an interaction of C1p with C2p, that is, there is more such antibonding (as in 6) in the episulfone than in the episulfide.11

We are thus led to an orbital which clearly resembles a π* MO of the ethylene fragment of the heterocycle. An analysis which starts from a totally different point of view can make the decomposition clearer. One of us has developed a method by which the descent of the orbitals of a composite molecule may be traced.12 More precisely, if we have a composite molecule C = A - B with molecular orbitals

$$\Psi_m = \sum_i \psi_i$$

and the molecular orbitals of the fragment molecules A and B, frozen in the geometries they possess in the complex C, are given by

$$a_i = \sum_j c_{i,j} \psi_j$$

$$b_i = \sum_j c_{i,j} \psi_j$$

then we have developed a procedure for expressing the molecular orbitals of the composite molecule or complex C in terms of the orbitals, occupied and empty, of the fragments A and B

$$\Psi_m = \sum_{i=1}^{\text{occupied}} k_{i} \psi_i + \sum_{i=1}^{\text{occupied}} k_{i} \psi_i$$

In our case let A be the distorted ethylene fragment (the C2H4 part of 5) in the geometry it has in episulfide and let B be a sulfur atom or sulfur dioxide molecule. C is episulfide or episulfone. The primary contribution to the AS antibonding is found in the highest occupied orbital of that symmetry type, which happens to be $\psi_s$ in episulfide and $\psi_{s'}$ in episulfone.13 The composition of that orbital is as follows

episulfide $\Psi_s = 0.5414a_1 + 0.6887b_3 + \ldots$

episulfone $\Psi_{s'} = 0.6362a_2 + 0.6075b_{3'} + \ldots$

Here $b_3$ and $b_{3'}$ are specific AS orbitals of the S or SO2 fragments, respectively, and $a_1$ is the unilled $\pi^*$ orbital of the ethylene fragment. All other contributions to $\Psi_s$ or $\Psi_{s'}$ are small. It is clear that the source of the antibonding AS overlap population is the mixing in of a $\pi^*$ ethylene orbital and that the differential in that AS antibonding between episulfide and episulfone can be traced to a greater mixing of $\pi^*$ in the episulfone.

We now can put forward a general and simple picture of bonding in these molecules. It is given by the interaction diagram of Figure 2. A is again an ethylene fragment. B is a fragment viewed as an atom which

(11) CNDO calculations by D. T. Clark, Durham, private communication, also result in a smaller CC partitioned bond overlap in the episulfone. This can be traced, as here, to reduced in-plane $\pi$ bonding.


(13) The primes on $\Psi_s$ and $b'$s are used to distinguish episulfone orbitals from those of episulfide and sulfur dioxide from sulfur.

Figure 1. Computed overlap populations for ethylene episulfide, episulfone, and episulfone: omitting 3d orbitals on sulfur (top), and including them (bottom) with parameters specified in ref 8.
present for interaction with the ethylene only two orbitals, one of SS, the other of AS symmetry. Of course any real B will have other symmetry orbitals, as well as further lower and high-lying orbitals of SS and AS symmetry. But from our analysis these do not contribute much to weakening or strengthening the CC bond of the ethylene fragment. Four electrons enter the two bonding orbitals in this scheme to form the two new bonds. Two of these four electrons can be thought of as coming from the ethylene \( \pi \) level and two from the B fragment.

The bonding picture we describe is very similar to the inorganic chemist's description of metal–olefin complexes such as Zeise's salt, first presented by Dewar \(^{14}\) and Chatt and Duncanson. \(^{15}\) The original formulation of the Walsh model of bonding in cyclopropane and oxirane \(^{18}\) also contains similar features. We have electron donation from the \( \pi \) orbital of ethylene to an acceptor orbital of B and reverse donation from B into the \( \pi^* \) orbital of the ethylene fragment. Both processes weaken the CC bond from its original ethylenic strength. The stronger the two ethylene–B interactions, the longer the CC bond.

We turn to the detailed analysis of these interactions. Figure 3 shows the calculated energies of the SS and AS orbitals of the ethylene fragment and the primary interacting orbitals of S, SO, and SO\(_2\). In the case of sulfur the SS and AS orbitals are degenerate, being \( 3p_x \) and \( 3p_y \). For sulfur monoxide the S and A orbitals\(^{17}\) are also degenerate. They are the \( \pi^* \) orbitals which are occupied by a total of two electrons in the diatomic. In the particular coordinate axis convention used the A orbital is composed of sulfur and oxygen \( p_z \) orbitals, while the S combination is a mixture of sulfur and oxygen \( p_x \) and \( p_y \). In the case of SO\(_2\) the SS orbital is an \( \alpha_1 \) orbital, \(^{18,19}\) which is a lone pair on sulfur, moderately delocalized to the oxygens. The AS orbital of SO\(_2\) is a \( \alpha_0 \) orbital, primarily localized on S, but with a small antibonding admixture of \( O 2p_z \). Its nodal properties show its descent from the third member of an allylic set of \( \pi \) orbitals that are typical for the triatomics.

If we take the computed energies seriously, we obtain an immediate explanation of the observed bond lengthening as one goes from sulfur to sulfur dioxide. The dominant interaction is donation of electrons into the \( \pi^* \) orbital of the ethylene fragment. The proper symmetry AS orbital of sulfur dioxide is much closer in energy to \( \pi^* \) of ethylene than the corresponding AS orbital of sulfur. Greater interaction means greater bond weakening. \(^{20}\)

Experimental information is available to check the calculations on the level ordering in S, SO, and SO\(_2\). The ionization potential of the sulfur atom is 10.4 eV, \(^{21}\) while that of SO is approximately 10.2–10.3 eV. \(^{22}\) The ionization potential of SO\(_2\) is 12.3 eV. \(^{22a,22}\) The placing of the AS level is difficult but, if we arbitrarily equate its position to the average of the term values for the \( 1B_1 \) and \( 1B \) states of SO\(_2\), \(^{24}\) which arise from the \( \alpha \) to

\( \quad \)


(19) The correlated electron transfer from ethylene \( \pi \) orbitals to an SS orbital is, according to the calculations, a minor effect. It actually opposes the primary bond weakening effect. The SS orbital, despite its lower energy, mixes less with ethylene \( \pi \) than its sulfur counterpart. Apparently this is due to smaller overlap, caused by considerable delocalization to oxygens in the SO\(_2\) SS orbital.

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b excitation, we obtain an energy of approximately 8.9 eV. So the ordering of levels on the right-hand side of Figure 3 appears reasonable.

It is interesting at this point to note that the ionization potential of SO$_2$ is considerably greater in magnitude than that of S or SO. In S ionization is from a 3p level. In SO the highest occupied MO is subject to some extent to the more electronegative oxygen. The balance leaves it not very different in energy from S. In SO$_2$ the highest occupied MO, $a_1$, can be described as a sulfur lone pair, stabilized relative to S and SO by the admixture of 3s.

The careful reader will have noted that the SO$_2$ AS orbital which we speak of as serving as a donor for the ethylene $\pi^*$ is in fact a vacant orbital in the ground state of SO$_2$. This raises an important point. The ethylene—ligand complex picture we use is a construct, a model for interaction of an SO$_2$ fragment and an ethylene. It is not a correlation diagram for the least motion $C_{2v}$ addition of SO$_2$ to ethylene. In fact the necessity to form, in our interaction scheme, the complex from an SO$_2$ with two electrons in AS rather than SS tells us immediately that were we to study a potential energy surface for the least-motion addition of SO$_2$ to ethylene that such a reaction would be a symmetry-forbidden one. This is of course consistent with the general analysis of chelotropic reactions.

The above discussion has analyzed the CC bonding. From Figure 1 it can be seen that in the absence of 3d orbitals the CS bonding differential between 1 and 3 is small. The symmetry breakdown of Table I does not show any dominant term in that differential. We are able to analyze each contribution, but the effort is not worth reproducing. As will be shown below, the primary effect in strengthening CS bonding in the episulfone is likely to be the participation of the 3d orbitals.

The Role of 3d Orbitals. Figure 1 shows that inclusion of 3d orbitals with orbital parameters allowing great interaction has a definite effect on the various overlap populations. The effect is approximately constant as one goes from episulfide to episulfone: the CC bond is slightly weakened, the CS bond significantly strengthened, and the SO bond dramatically so.

It is clear that the two most important factors required to bring out or enhance the participation of vacant 3d orbitals are (1) substitution of the central atom by more electronegative ligands, to lower the energy and contract the shape of the 3d orbitals, and (2) the presence on the ligands of donor orbitals to take advantage of the acceptor properties of the 3d orbitals. The oxygen lone pairs in episulfone or episulfoxide are such donors. Given our accessible placement of the 3d orbitals, the effect on the SO overlap population is nothing but 3d–2p $\pi$ bonding. It shows up in the calculation not only in the large SO overlap population but in significant population of the formally vacant 3d orbitals on sulfur.

The increase in the CS overlap populations can be analyzed by a symmetry orbital breakdown analogous to Table I. The change in the CS bond can be traced to SS and AS orbitals. Examination of the wave functions shows that the increased overlap population is primarily due to the complex bonding orbitals (bottom of Figure 2) and the fact that in these $d_{x^2}$ (SS) and $d_{z^2}$ (AS) mix in just such a way as to make a better hybrid for CS overlap.

A similar symmetry analysis shows that the decrease in the CC overlap population on inclusion of 3d orbitals is dominated by the SS orbitals. Electron density is withdrawn from both the $\sigma$ ($p_z-p_z$) and $\pi$ ($p_y-p_y$) bonds of the ethylene fragment and deposited in the $d_{z^2}$ and $d_{x^2-y^2}$ sulfur orbitals. The net transfer of electrons shows up in the charges on the carbons and hydrogens.

At this point we should mention the interesting $ab$ initio calculations of Van Wazer and Absar on H$_2$S, H$_2$SO, and H$_2$SO$_2$. The overlap populations obtained by these authors are shown below. We have included the nonbonded H–H overlap populations since these form a parallel to our bonded CC populations.

The following points are to be noted. (1) The $ab$ initio calculations show the increasing importance of 3d orbitals, just like the semiempirical calculations, as one increases the number of oxygens bonded to sulfur. This is to be seen most directly in the SO and SC overlap populations and also in the energetics of the molecules, not shown here but detailed in the original work. (2) The trend in nonbonded H–H overlap populations in the $ab$ initio calculations parallels the trend calculated semiempirically (Figure 1) for the CC bonds (weaker bonding in the episulfone). (3) The SH bond strengths, when calculated with 3d orbitals, do not agree with the trend of the extended Hückel calculations.


Conclusions Regarding Bond Strengths

With or without 3d orbitals we believe we understand the overlap population trends exhibited in Figure 1. Since 3d orbitals are likely to come more into play with increasing electronegativity of the ligands on sulfur, we see the general effects of 3d participation, exhibited by the second row of Figure 1 and analyzed in the preceding section, as becoming more prominent when we proceed from episulfide to episulfone.

To summarize our analysis, we believe that the long CC bond in episulfone is due to two factors. First, and invoking no 3d orbitals, when the episulfone is viewed as an ethylene-SO₂ complex, the SO₂ provides a low-lying orbital which populates the ethylene π* level better than in the analogous sulfur case. Second, and now directly invoking anticipated 3d participation, the SO₂ ligand provides 3d orbitals which by mixing with available 3s and 3p orbitals allow a more efficient depletion of bonding electron density from the ethylene fragment π level. The CS bond strengthening should also be due to 3d mixing providing better overlap for bonding. The SO bond length decrease we attribute to 3d-2p π bonding.

The unsatisfactory aspect of this analysis is that while we understand the general trend from episulfide to episulfone we cannot pretend to have rationalized why the change through the episulfoxide is not gradual but discontinuous. Clearly there should be more 3d participation in episulfone than in episulfoxide, but why should the latter structure so much resemble the episulfide one? We have no answer to this question, but we would welcome further structural (and chemical) studies of the ethylene episulfoxides to confirm the structural evidence at hand.²⁸

We now turn to a discussion of some of the other available evidence on the strength of CC bonds in episulfides and episulfoxides, accompanied by some predictions our model allows us to make.

Experimental Evidence and Some Predictions

cis-2,3-Divinylthiirane 1,1-dioxide, 9, is a presumed intermediate in the reaction of vinylidiazomethane with sulfur dioxide, rearranges to 4,5-dihydrothiepin 1,1-dioxide considerably faster³⁰ than the related thirane 10.³⁰ This is consistent with a weakened CC bond in 9.

Carbon–carbon bond cleavage has also been suggested to follow the formation of the hypothetical episulfone intermediates 11,³¹ 12,³² and 13.³³ It also occurs in the thermal rearrangement of tetraphenyl ethylene episulfoxide.³⁴

(28) It should be noted that if the SH overlap populations in the calculations of Van Wazer and Absar (ref 27) can be taken as modeling the SC bonds in episulfide through episulfone, then the ab initio calculations do rationalize the observed discontinuity.


(38) H. L. Ammon, private communication.

Thiepin 1,1-dioxide, 14, has been synthesized.³³ There are some interesting structural features in this molecule,³⁵ including CS and SO bond lengths similar to those in episulfone. The structure is similar to that of cycloheptatriene. No evidence for another, norcaradiene type, isomer, 15, has ever been obtained, and it could simply be that because of the weakened episulfone bond in 15 the potential energy surface which interconnects 14 and 15 has but a single minimum, the structure 14.

Derivatives of thirene 1-oxide, 16, and thirene 1,1-
dioxide, 17, are known.³³,³⁷ Structural studies on these molecules are in progress,³⁸ but the final details are not yet available.

Given the observed short CC bond in the episulfide 1 and the much longer CC bond in the episulfone 3, it becomes of interest to speculate on how one could strengthen CC bonding still further in 1 and weaken it more in 3. In the former case the interest is only structural, but in the latter case there may be consequences of synthetic value as well. Normally CS bonds are weaker than CC, so that the latter bond cleavage is not observed. But if the CC bond can be weakened further, then some new possibilities for reaction may occur.

The ethylene complex model makes the prediction of such effects feasible. Let us consider episulfides and episulfoxones substituted on the ethylene fragment as in 18. The effect of these substituents is to perturb the π* orbital of the ethylene fragment. π donors such as –OR, –NR₂, and –X will raise the energy of the π* level and π acceptors such as –CN, –COR, –NO₂, and –NO will lower it. A lower energy π* level implies greater interaction with the AS level of S or SO₂, a weaker CC
bond. A higher energy \( \pi^* \) level would lead to less interaction, a stronger CC bond. These qualitative ideas were checked by detailed calculations with \( R = \text{CN} \) and \( \text{OH} \). Thus an episulfide with a still shorter CC bond would be the hypothetical 19, and an episulfone with a still weaker CC bond might be 20. The substituents are not specific for the effect, only examples of typical \( \pi \) donors or acceptors. Neither is the full ethylene fragment substitution required (the effect should show up on partial substitution as well).

Given the theoretical conclusions on the effect of acceptors on the CC bond strength in episulfones, we find surprising the remarkable thermal stability attributed to 21.39 The structural assignment of 21 has indeed been recently questioned.40

\[
\begin{array}{c}
\text{Ph} \quad \text{SO}_2 \quad \text{Ph} \\
\text{PhOC} \quad \text{COPh}
\end{array}
\]

**The Mode of Opening of the CC Bond**

We next pose the question whether 1, 2, or 3 will open in a conrotatory or a disrotatory manner.25 The method of analysis29,35 focuses on the diradical orbitals of the ring-opened form, 22 and 23, and the interaction of these with the orbitals made available by the central atom, \( X \). If \( X \) acts in such a manner as to have \( S \) occupied by the two available electrons, the electrocyclic opening will be disrotatory. If \( A \) is occupied, the opening will be conrotatory.

In the case of \( X = S \) or \( \text{SO} \) the dominant feature of \( S \) is a lone pair, symmetric with respect to the vertical mirror plane. Interaction with this lone pair destabilizes the symmetric diradical combination 22. A is occupied and the breaking of the CC bond is expected to proceed in a conrotatory way. It is difficult to predict the effect of 3d orbitals on this conclusion since the set of 3d orbitals includes orbitals which can interact both with 22 and 23. We examined a potential surface for both conrotatory and disrotatory opening modes and found a clear preference for the former whether 3d orbitals were included or not. The conrotatory nature of the reverse process, the closure of a thio carbonyl ylide to a thiirane, has been elegantly demonstrated.41

The \( X = \text{SO}_2 \) case is less clear-cut. Our recent concern with the role of polar bonds in hyperconjugation39 has been recently questioned.40

\[
\begin{array}{c}
S \\
22
\end{array}
\]

\[
\begin{array}{c}
A \\
23
\end{array}
\]

**The Ethylene-Complex Viewpoint Applied to Substituted Cyclopropanes**

In some previous work2 we have analyzed the response of the cyclopropane ring to substitution by \( \pi \) donors and acceptors. The significant result, now supported by ample structural, kinetic, and thermodynamic evidence, is that \( \pi \) acceptors should strengthen or shorten the CC bond opposite to the site of substitution (25), while \( \pi \) donors should weaken or lengthen the same bond (26). The theoretical argument we gave for this effect was based on the specific bonding properties of the donor or acceptor Walsh orbitals of cyclopropane. We now can provide an equivalent derivation based on a decomposition of cyclopropane into methylene and ethylene. The general interaction diagram of Figure 2 applies; the role of the SS orbital is played by the \( \sigma \) orbital of methylene,40 the \( \pi \) orbital is the AS partner. This is shown below.

\[
\begin{array}{c}
\text{strong} \\
\pi\text{-Acceptor}
\end{array}
\]

\[
\begin{array}{c}
\text{weak} \\
\pi\text{-Donor}
\end{array}
\]

(25)

(26)


The magnitude of the AS type interaction between carbene fragment p and ethylene fragment π* is obviously sensitive to the position of the carbene p level. The higher the energy of that orbital, the more interaction there will be and the weaker the ethylene CC bond. The carbene p level is influenced in an obvious way by substituents at the carbene. If the substituents have high-lying occupied levels (π donors), they destabilize the p level. If the substituents have low-lying unoccupied levels (π acceptors), then they will stabilize the p level. The conclusion summarized in structures 25 and 26 follows. There is a secondary conclusion we can draw from the fact that interaction of carbene p with either donors or acceptors delocalizes the p orbital and thus reduces its overlap with ethylene π*. This is that the effect of π acceptors will be differentially greater than that of π donors. Delocalization decreases the overlap of the modified p orbital with π* and this has the consequence of a stronger CC bond.

This effect counteracts the bond weakening by π donors and reinforces the bond strengthening by π acceptors. It should be noted that cyclopropanone, 28, has a very long CC bond of 1.575 Å. The analogy to ethylene epoxide is obvious. From the viewpoint of the present section the p type oxygen lone pair of the CO fragment is an excellent donor, held in an ideal conformation for interaction with the cyclopropane ring. From the viewpoint of the ethylene complex the modifying carbon monoxide fragment has a π* orbital ideal for participating as the AS orbital.

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Bond Order Rule for the Electrocyclic Reaction and the Possibility of Nonstereic Substituent Effects on the Rotation

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Abstract: The energetics of concerted electrocyclic reactions are reviewed in qualitative terms. Instead of absolute energies, the difference function $E_{on} - E_{dis}$ is used to find the rotation with the lower activation energy and therefore the kinetically preferred mode. The general trends of this function are shown to lead to the bond order criterion: the preferred mode is disrotatory if the bond order between the reacting centers is positive, conrotatory if the bond order is negative. This rule applies to symmetric and nonsymmetric molecules. An important consequence is the theoretical prediction of a new class of electrocyclic reactions: the concerted ring closure in the class of systems with zero or very small bond orders between the reacting centers is nonstereospecific and the product ratio can be shifted by introducing substituents. The direction of the shift is determined by both the position and the nature of the substituents.

The electrocyclic transformation as an example of a concerted reaction has received considerable attention since its analysis by Woodward and Hoff-