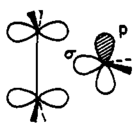

27

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

28

very long CC bond of 1.575 Å.[46] The analogy to ethylene episulfone 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 complexing carbon monoxide fragment has a π^* orbital ideal for participating as the AS orbital.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this work and to T. Norin, T. Kempe, J. M. Howell, and D. T. Clark for valuable comments.

(46) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969); **90**, 1072 (1968).

Bond Order Rule for the Electrocyclic Reaction and the Possibility of Nonsteric 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 $E^{\mathrm{con}} - E^{\mathrm{dis}}$ 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[1–8] since its analysis by Woodward and Hoffmann[9,10] within the framework of "conservation of orbital symmetry." Considered here not only as the ring closure between the termini of a linear polyene, the reaction is the formation of a new σ bond between two centers of a π system. Sterically controlled ring closures, where bulky side groups or constraints due to the carbon skeleton determine the rotational mode, are excluded from the discussion.

In the Woodward–Hoffmann rule for the electrocyclic reaction, henceforth referred to as the W–H rule, the highest occupied orbital is assumed to play a dominant role in the reaction and its symmetry or phase used to predict the preferred rotation.[9,10] The

(1) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 87, 2045 (1965).

(2) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(3) H. E. Zimmerman, *J. Amer. Chem. Soc.*, 88, 1563 (1966); *Accounts Chem. Res.*, **4**, 272 (1971).

(4) C. Trindle and F. S. Collins, *Int. J. Quantum Chem. Symp.*, **4**, 204 (1971); C. Trindle, *J. Amer. Chem. Soc.*, **91**, 4926 (1969); **92**, 3251, 3255 (1970).

(5) W. A. Goddard, *J. Amer. Chem. Soc.*, **94**, 793 (1972); *Int. J. Quantum Chem. Symp.*, **3**, 63 (1969).

(6) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969); W. J. van der Hart, J. J. C. Mulder, and L. J. Oosterhoff, *ibid.*, **94**, 5724 (1972).

(7) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *ibid.*, **93**, 5005 (1971).

(8) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *ibid.*, **93**, 2117 (1971).

(9) R. B. Woodward and R. Hoffmann, *ibid.*, 87, 395, 2046, 2511 (1965).

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

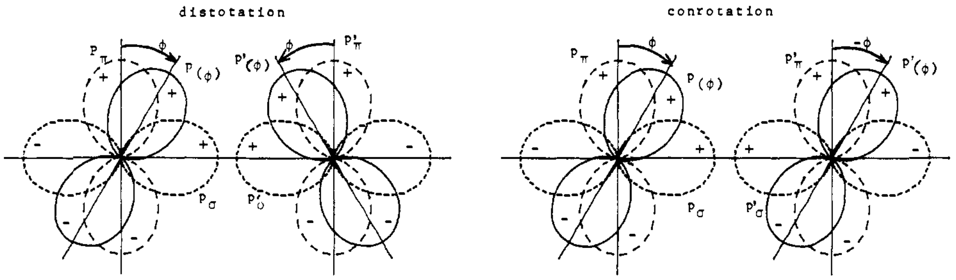

Figure 1. Coordinates for dis- and conrotation.

great strength of the rule is in the ease with which it can be applied. However, in spite of success in a number of cases, the reliance on the highest occupied orbital as a reaction dominating factor is an oversimplification with little theoretical foundation.[11] Counter arguments include the fact that the reaction is controlled by the energetics, *i.e.*, the total energy of the molecular states as a function of the reaction coordinate. In the reaction the size of the π system is reduced by two centers and the number of delocalized electrons is lowered by two. The size reduction has a strong effect on the energies and orbitals of *all* delocalized electrons, as an MO calculation or even a simpler model of electrons in a box clearly demonstrate. Due to this fact and independent of the possible merits of Fukui's frontier electron method[12] in different contexts, the highest occupied orbital cannot exert an exclusive control. Electrocyclic reactions take place in symmetric and nonsymmetric molecules and, as there are no physical forces or energy contributions associated with the concept of symmetry, it is meaningless to talk about "symmetry imposed energy barriers." The noncrossing rule for molecular states generally has the consequence that both rotations lead from a given state of the reactant to the same or an electronically equivalent state of the products. Whenever this requires that different configurations (of the same total symmetry but with different individual orbital symmetries) dominate the state in different ranges of the reaction coordinate, the conservation of orbital symmetries is seen to be of little consequence to the reaction.

Various methods have been discussed to circumvent such objections. The techniques of Goddard[5] and of Trindle,[4] for example, are concerned with the nodal properties and not the symmetry of the wavefunction. Together with the VB treatments of Oosterhoff, *et al.*,[6] they apply to symmetric and nonsymmetric molecules. The importance of configuration interaction (CI) has been stressed by Longuet-Higgins and Abrahamson[1] and is clearly evident from the recent extensive *ab initio* calculations of Buenker, *et al.*,[7,8] on butadiene. This calculation has suggested: the reaction has a step mechanism where the change from the open molecular geometry to the ring closed form takes place primarily before and after, but only to a very small degree during the rotation. One mode of rotation is found to be energetically preferred over the entire range of the rotational angle. Both conclusions are expected to be quite general.

Unless steric effects are important, the products of both rotational modes have the same energy. The preferred mode is therefore kinetically selected as the rotation with the lower activation energy. Its prediction does not require the knowledge of absolute energies; it is sufficient to study the energy difference between con- and disrotation as a function of the reaction coordinate. *Ab initio* calculations are still impractical for most systems of interest here and fail to give a simple and operationally useful criterion for the prediction of the rotation. In the following section we review the simplified approach that leads to the order criterion. This criterion rivals the W–H rule in simplicity and applies to symmetric and nonsymmetric molecules. Some consequences are discussed and include the prediction of a nonsteric substituent effect on the rotation in a certain class of molecules.

The Difference Function $\Delta E(\phi)$

The preferred mode of rotation follows from the relative order of the state energies of con- and disrotation and therefore from the sign of the difference function

$$\Delta E(\phi) = E(\phi)^{\text{con}} - E(\phi)^{\text{dis}}$$

along the reaction path. The rotational angle (ϕ) in Figure 1 is taken as a convenient reaction coordinate.[13] ΔE is zero for $\phi = 0°$ (reactants) and $\phi = 90°$ (products). For intermediate angles it can be obtained from separate CI calculations on the two rotational modes. It is clear that all factors entering the state energies, *i.e.*, the MO's configurational energies, and configuration mixing coefficients, are smooth systematic functions of ϕ. The same is therefore true for $\Delta E(\phi)$.

If the electrons are grouped in the usual way into core and valance electrons, where the latter group consists of the new σ pair and the π electrons, $\Delta E(\phi)$ can be written as

$$\Delta E(\phi) = \Delta E(\phi)^{\text{core}} + \Delta E(\phi)^{\text{c-v}} + \Delta E(\phi)^{\text{v}}$$

The first two terms, the difference in core energy and in core–valence electron interaction, contain only nonbonded interactions involving the rotating groups. Unless steric effects are important, they are negligible and the electronically controlled electrocyclic reactions are those where $\Delta E(\phi)$ is dominated by $\Delta E(\phi)^{\text{v}}$.

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[11] We agree with the general discussion of *state correlations* in ref 10, which contain, however, no *a priori* justification for a special role of either the highest occupied orbital or of the conservation of one-electron orbital symmetries.

[12] K. Fukui, *Accounts Chem. Res.*, 4, 57 (1971); *J. Phys. Chem.*, **74**, 4161 (1970).

[13] In the light of Buenkers findings of a step mechanism, the discussion is concerned with the rotational step only. If a change in the overall molecular geometry must be considered, it can be parametrized in ϕ.

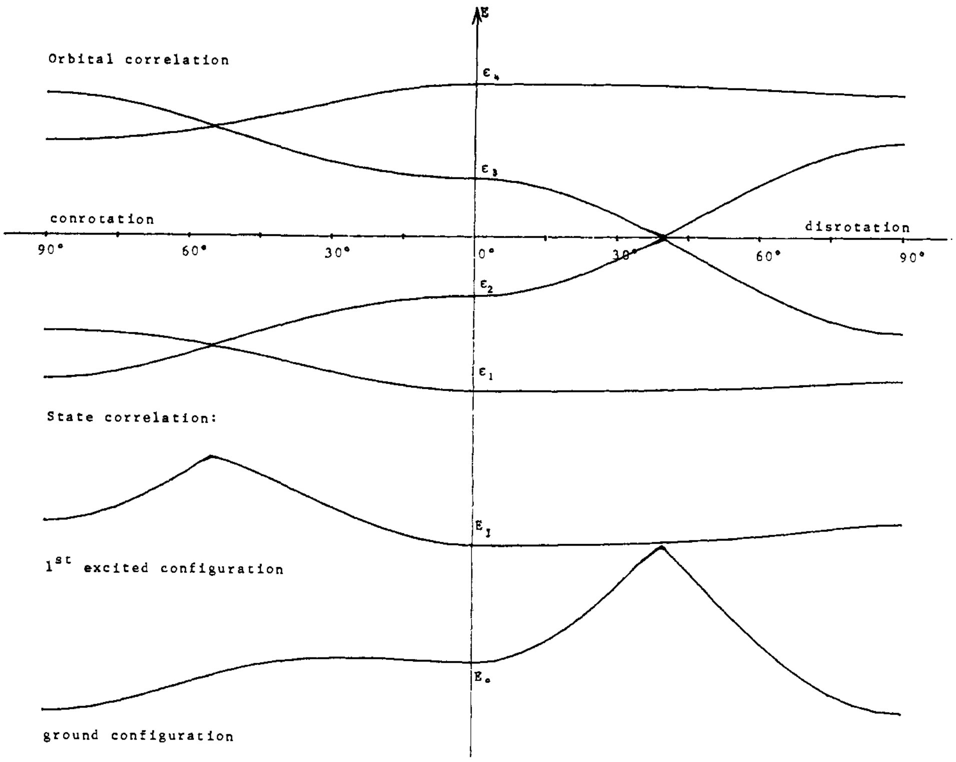

Figure 2. Orbital energies (ϵ_1–ϵ_4) and the resulting one-electron contributions to the ground and first excited configuration (E_0, E_1) as a function of the angular coordinate.

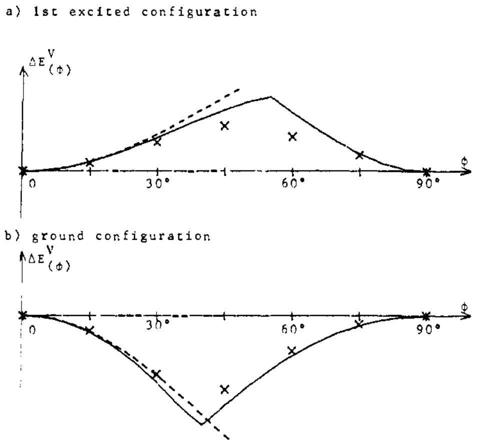

Figure 3. One-electron contribution to the difference function: (—) butadiene (0°)-cyclobutene (90°); (×) nonsymmetric system ($\alpha_2 = \alpha + \beta$); (---) perturbation, eq 3.

A state energy is not expressible as a sum of one-electron orbital energies. Nevertheless, the energy difference between the two rotational isomers is essentially determined by the difference in the one-electron contributions to ΔE^v, provided that the state of interest has in both rotational modes the *same* configuration as a strongly dominant term. For the molecules undergoing the electrocyclic transformation, this is generally true either for small or for large angles ϕ where the ground or the first excited configurations are well separated from the other configurations of the same symmetry. For the intermediate angles, where the lowest lying configurations of the same symmetry in either mode cross or are closely spaced, considerable configuration mixing affects the energy difference.

For quantitative results, explicit CI calculations with all electrons included are no doubt essential. The qualitative behavior and in particular the sign of the function are, however, already apparent from the energy difference between the leading configurations in con- and disrotation, respectively. Once the appropriate dominant configurations are identified, based on many-electron considerations and the noncrossing rule for molecular states, the difference in configurational energies is well approximated by the one-electron contributions from the valence electrons.

In the case of butadiene as an illustrative example, the usual MO treatment[14] leads to the one-electron orbital scheme (ϵ_1 to ϵ_4) and the one-electron contributions to the ground and the first excited configuration (E_0 and E_1) of Figure 2. Figure 3 (solid line) shows the one-electron contributions to the difference function of configurations. For angles close to 0 and to 90° the electron interaction and the CI contributions to the state difference function are negligible. Mixing of configurations in a CI is most effective near the breaks in the curves which are due to a crossing of configurations. The state difference functions are therefore very similar at small and at large angles but have a less pronounced and very smooth extremum at an intermediate angle.[15]

The trends exhibited are significant. The difference function shows no oscillations and is zero or negative in the ground state, and zero or positive in the first excited state. The conrotational mode has, in the ground-state reaction of butadiene, a consistently lower energy and is the kinetically favored mode, at

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(14) The parameters should be chosen for the geometry where the actual rotation takes place and may differ considerably from those of the stable reactants or products. This affects naturally the numerical values but not the qualitative conclusions.

(15) Compare the results of an *ab initio* CI calculation in ref 8, where $\Delta E(\phi)$ for the ground state of butadiene is easily obtained from the lower curves of Figure 4.

whatever angle the actual activation maxima occur. The opposite is true for the excited state where the disrotation is preferred. This result fully agrees with experiment and the prediction of the W–H rule.

The present example also shows a feature common to all even alternant systems, where the new σ bond does not introduce an odd-membered ring. The pairing properties of the orbitals in alternant systems are well known. They require that paired orbitals and in particular the highest bonding and the lowest antibonding change in exactly opposite ways as a function of the rotational coordinate. In the first excited configuration these two orbitals are singly occupied and their contributions to the state energy as a function of ϕ cancel. It is an ironic coincidence that the only two orbitals explicitly considered in the W–H rule have in the first approximation very little effect on the energetics of the first excited state of these systems. To show furthermore explicitly that the energy ordering is not in any way based on symmetry, the calculations have been repeated with a Coulomb integral at center 2, strongly different from the others. No symmetry element is present for intermediate angles. The results are entirely according to the expectations. The orbital correlation has no crossings and orbital and configurational energies are shifted by an appreciable amount. The difference function, however, is only slighly changed (see × in Figure 3). Identical predictions hold in this case for the symmetric and the unsymmetric molecules.

Bond Order Criterion for the Rotation

In order to be useful to organic chemists, a criterion for the prediction of the rotation in the electrocyclic transformation must be easy to obtain, simple to apply, and should predict and offer some insight into general new effects. The W–H rules admirably satisfy this requirement. The same cannot be said of the difference functions $\Delta E(\phi)$, as they require multiple MO calculations on each molecule of interest.

The bond order criterion we propose as a replacement and generalization of the W–H rule takes advantage of the following facts, generally valid for molecules undergoing the electrocyclic reaction.

(a) The ground or first excited configurations are nondegenerate, *i.e.*, the corresponding states are well represented by the leading configurations only. Clearly, for small angles ϕ, this leading configuration in a given state is the same for both rotational modes.

(b) The difference $\Delta E(\phi)$ is a smooth systematic function of ϕ. The energy ordering observed for small angles persists through intermediate angles and in particular at the activation maxima.

(c) The difference in the resonance integral[14] $\beta\sigma(\phi)^{\text{con}} - \beta\sigma(\phi)^{\text{dis}}$ for the new σ bond is zero or a positive energy term.[16]

For small angles, the difference function is essentially given by the one-electron contributions and is well approximated by the first-order perturbation expression[17]

$$\Delta E(\phi) \cong \sum_{\chi,\lambda} p_{\chi\lambda}(H_{\chi\lambda}(\phi)^{\text{con}} - H_{\chi\lambda}(\phi)^{\text{dis}}) \tag{1}$$

where

$$p_{\chi\lambda} = \sum_j b_j c_{j\chi} c_{j\lambda} \tag{2}$$

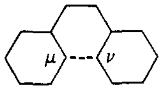
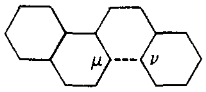
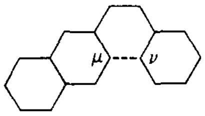
is the generalized bond order of the reactant in the configuration characterized by the occupation numbers b_j. All matrix elements $H_{\chi\lambda}$ which either do not depend on ϕ or depend only on the absolute value of the angle drop out. In a Hückel approximation with only nearest neighbor interactions eq 1 reduces to the single term

$$\Delta E(\phi) \cong 2p_{\mu\nu}(\beta\sigma(\phi)^{\text{con}} - \beta\sigma(\phi)^{\text{dis}}) \tag{3}$$

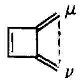
the generalized bond order between the two reaction centers μ and ν multiplied by a positive energy term. For butadiene the result of this expression is given in Figure 3 (dotted lines). From remark (b) and this expression it follows that the sign of the bond order is an indicator for the ordering of the activation energy for the two rotational modes. We arrive thus at the general bond order rule: *the electronically controlled electrocyclic reaction proceeds disrotatory if the generalized bond order between the two reacting centers is positive and conrotatory if this bond order is negative in the reactant.*

For many molecules of interest the orbitals and generalized bond orders of the ground state are directly available from tables.[18] It is then a trivial task to calculate the necessary bond orders for the first excited state. For butadiene one finds: ground state $p_{14} = -0.447$. . . .conrotation; 1st excited state $p_{14} = +0.276$ . . . .disrotation. From the closed form of the MO coefficients for linear polyenes C_nH_{n+2} the bond orders p_{1n} can be calculated for general n (see Appendix 1). Their signs are collected in Table I. This table agrees with the predictions of Woodward and Hoffmann who cite some experimental support.

The bond order rule can be applied with equal ease to symmetric and nonsymmetric molecules. For example

	$p_{\mu\nu}$	
	Ground state	Excited state
	+0.089	−0.061
	+0.105	−0.046
	+0.068	+0.040

This last example is of interest, because it shows a molecule where the bond order has the same sign in the ground and the excited state. The bond order rule consequently predicts the same mode of rotation in both states. This is a direct contradiction to the W–H rule based on the relative phase of the highest occupied orbital which predicts opposite rotations. Another example of the same contradiction is

	$p_{\mu\nu}$	
	Ground	Excited
	−0.086	−0.436

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(16) If only a rotation of p orbitals (see Figure 1) is considered, one finds $\beta\sigma(\phi)^{\text{con}} = -\sin^2\phi\beta\sigma$ and $\beta\sigma(\phi)^{\text{dis}} = \sin^2\phi\beta\sigma$ where $\beta\sigma$ is a negative quantity. If rehybridization and/or a change in the distance of the reacting centers are included, more complicated expressions result but the statement (c) remains valid.

(17) E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendungen," Vol. I, Verlag Chemie, Weinheim/Bergstr., Germany, 1968.

(18) E. Heilbronner and P. Straub, "Hückel Molecular Orbitals," Springer-Verlag New York, New York, N. Y., 1966; ref 17, Vol. III.

Table I. Signs of Bond Orders p_{1n} for Linear Polyenes C_nH_{n+2}[a]

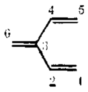
	n	Ground state	Excited state
n even	2,6,10···4k − 2	+	−
	4,8,12···4k	−	+
n odd	3,7,11···4k − 1	+	−
+ ion	5,9,13···4k + 1	−	+
n odd	3,7,11···4k − 1	−	+
− ion	5,9,13···4k + 1	+	−

[a] + implies disrotation, − implies conrotation.

New Predictions for Rotations Based on the Bond Order Rule

The bond order rule differs in its physical basis completely from the symmetry or phase considerations of only one, the highest occupied orbital of the W-H rule. Both rules are equally easy to apply. The bond order criterion is based on energy differences between the two rotational modes and is very general except in cases where steric effects override the electronic control. Except for the large class of molecules discussed below and examples similar to those given at the end of the preceding section, the predictions of both rules are found to coincide in many systems. In fact, all experimental support cited by Woodward and Hoffmann[10] for their rule supports equally well the bond order rule.

One of the most interesting aspects of the present analysis of the electrocyclic reaction is the new prediction that a class of molecules exists in which the direction of rotation can be controlled by the nature and position of substituents on the π system, not in the direct vicinity of the reacting centers. In the discussion in the preceding section, we have not mentioned the frequent occurrence of generalized bond orders which are either exactly zero or of very small absolute value. If such a bond order is found between the reacting centers, the contribution of the valence electrons to the difference in activation energy between con- and disrotation is negligible. If the core contribution is also negligible or if core and valence contributions to the difference in activation energy cancel, one concludes: *there are concerted electrocyclic reactions which are nonstereospecific; i.e., the products of both rotational modes are formed in a measurable ratio in the reaction. The most likely candidates are molecules with zero or very small bond orders between the reacting centers.* A whole class of molecules with zero bond orders are alternant π systems where the new σ bond formed in the electrocyclic reaction introduces an odd-membered ring. Examples are the cross-conjugated triene



in the 1,5 but not the 1,6 or 5,6 ring closure or the k to $k + 2i$ ring closures in a neutral linear polyene. One finds in general zero bond orders in alternant systems between two centers separated by an odd number of centers in the following cases: (a) ground and first excited state of even-membered, neutral molecules; (b) ground state of odd-membered radicals; (c) ground state of odd-membered anion and cation, if the MO coefficients at the two centers in the nonbonding level are zero.[19]

If the energy difference $\Delta E(\phi)$ is zero throughout the range of ϕ, the products of the two rotations are formed in a ratio 1:1. The product ratio, however, is extremely sensitive to even small differences in activation energy for con- and disrotation. Therefore, if we introduce into the system a small perturbation that affects the energy of the two rotational modes differently, the product ratio will be shifted in a measurable way.

The desired perturbations are introduced by substituting a heteroatom in the π system or attaching substituents in positions which do not sterically affect the rotations. For the theoretical analysis, substituents which change neither the size of the π system nor the number of the π electrons are characterized by the changes $\delta\alpha$ and $\delta\beta$ of the appropriate Coulomb and resonance integrals.[20] The electronic effect of the substituents on the energy and the bond order $p_{\mu\nu}$ can be studied by perturbation theory,[16] using the polarizabilities. The expression derived for the change $\delta\Delta E^{\mathrm{v}}$ of the energy difference between con- and disrotation is again very simple, because the changes $\delta\alpha_\zeta$ and $\delta\beta_{\zeta\sigma}$ do not depend on the direction of the rotation: (1) Coulomb integral

$$\delta\Delta E(\phi)^{\mathrm{v}} = 2\pi_{\mu\nu,\zeta}\delta\alpha_\zeta(\beta\sigma(\phi)^{\mathrm{con}} - \beta\sigma(\phi)^{\mathrm{dis}})$$

$$\delta p_{\mu\nu} = \pi_{\mu\nu,\zeta}\delta\alpha_\zeta$$

(2) resonance integral

$$\delta\Delta E(\phi)^{\mathrm{v}} = 2\pi_{\mu\nu,\zeta\sigma}\delta\beta_{\zeta\sigma}(\beta\sigma(\phi)^{\mathrm{con}} - \beta\sigma(\phi)^{\mathrm{dis}})$$

$$\delta p_{\mu\nu} = \pi_{\mu\nu,\zeta\sigma}\delta\beta_{\zeta\sigma}$$

where $\pi_{\mu\nu,\zeta}$ and $\pi_{\mu\nu,\zeta\sigma}$ are the bond–atom and bond–bond polarizabilities, respectively, of the unsubstituted reactant. These changes are simply additive, if the substitution affects more than one center or bond.

The sign and magnitude of $\delta\alpha$ and $\delta\beta$ depend on the type of substituents and the polarizabilities on the unsubstituted π system only. The sign of $\delta\Delta E(\phi)^{\mathrm{v}}$, on the other hand, is controlled by the product of these quantities. As a consequence, a substituent with a positive $\delta\alpha$, for example, in a position ζ with a positive bond–atom polarizability favors disrotation; the same substituent in a position with a negative polarizability favors the conrotation. Similarly, two substituents with different signs of the integral changes affect the rotation in opposite ways if introduced in the same position.

It should be stressed that this electronic substituent effect is general to any molecule.[21] As a second-order perturbation in energy, it is small and can probably not be detected in the cases where the "rotation controlling" bond order has an appreciable value but we predict: *if, in a molecule with zero or very small bond order between the reacting centers, the products of both rotations are formed in measurable quantities, the product ratio can be shifted by introducing substituents into the π system. The direction of the shift can be predicted from the nature of the substituent and*

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(19) The centers in alternant systems can be separated into two sets such that no two members of the same set are directly bound. Case (c) is met if the two reacting atoms belong to the set with the smaller number of centers.

(20) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(21) Compare Figure 3, nonsymmetric butadiene.

the polarizabilities between substitution and reaction sites.

This electronic, rather than steric, substituent effect, we predict, is not only of interest to the problem of the electrocyclic reaction but also opens a novel way for the direct study of second-order substituent effects on π-electron systems.

Conclusions

The smooth systematic trends of the energy difference functions are assured by the smooth change of σ and π bonding with the rotational coordinate and as a direct consequence, the systematic behavior of the many electron CI effects. This fact is the basis for the bond order rule, which takes into account explicitly all electrons that are strongly affected by the rotation. The qualitative conclusions from the bond order, *i.e.*, the prediction of the preferred mode of rotation, are therefore reliable, at least in all cases where the bond order has an appreciable value. A special class of electrocyclic reactions, those with zero or very small bond orders, is recognized. This new class differs from the usual concerted reactions by the fact that the reactions are not stereospecific.

In its physical basis, the bond order criterion differs completely from the W–H rule, as there is no cause–effect relationship between symmetry and energetics. There exists, however, a high statistical correlation between the predictions based on the two rules. This is not too surprising, because the energy on one hand and the coefficients and the symmetry or phase of MO's on the other hand are direct consequences of the topological structure of the π system.

With the theoretical prediction of a new electronic substituent effect on the rotation in a large class of molecules, we hope to stimulate experimental work. A single conclusive demonstration of the effect in a symmetric molecule would permanently lay to rest any notion of orbital symmetry control of electrocyclic reactions. More important, however, are new methods of probing into the effects of substituents on the electronic structure of π systems, which may be based on this prediction.

Appendix 1

The closed form expression for the MO coefficients of a linear polyene with n centers is

$$c_{j\mu} = \left(\frac{2}{n+1}\right)^{1/2} \sin \frac{j\mu}{n+1}\pi$$

The bond order $p_{\mu\nu}$ is

$$p_{\mu\nu} = \frac{2}{n+1}\sum_j b_j \sin\frac{j\mu}{n+1}\pi \sin\frac{j\nu}{n+1}\pi =$$

$$\frac{2}{n+1}\sum_j b_j\left(\sin^2\frac{(\mu+\nu)}{n+1}\frac{\pi}{2}j - \sin^2\frac{(\nu-\mu)}{n+1}\frac{\pi}{2}j\right)$$

For the end to end bond order p_{1n} one finds after some algebra:

(a) n even, ground state

$$p_{1n} = \frac{\sin (n-1)\frac{\pi}{2}}{n+1}\left(\frac{1}{\sin\frac{(n-1)}{(n+1)}\frac{\pi}{2}} + 1\right)$$

positive for $n = 2,6,10\cdots 4k - 2$ and negative for $n = 4,8,12\cdots 4k$.

(b) n even, first excited state

$$p_{1n} = \frac{\sin (n-1)\frac{\pi}{2}}{n+1}\left(\frac{\cos\frac{(n-1)}{(n+1)}\pi}{\sin\frac{(n-1)}{(n+1)}\frac{\pi}{2}} - 1\right)$$

zero for $n = 2$, negative for $n = 6,10,14\cdots 4k + 2$, and positive for $n = 4,8,12\cdots 4k$.

For odd n, p_{1n} of the radical in the ground state is zero. The negative and positive ion behaves in exactly the opposite way.

(c) n odd, ground state

$$+\ \text{ion}\ p_{1n} = -\frac{2}{n+1}\sin\frac{n\pi}{2}$$

positive for $n = 3,7,11\cdots 4k - 1$ and negative for $n = 5,9,13\cdots 4k + 1$; and

$$-\ \text{ion}\ p_{1n} = +\frac{2}{n+1}\sin\frac{n\pi}{2}$$

negative for $n = 3,7,11\cdots 4k - 1$, positive for $n = 5,9,13\cdots 4k + 1$.

(d) n odd, first excited state

$$+\ \text{ion}\ p_{1n} = -\frac{\cos (n-1)\frac{\pi}{2}}{n+1}\left(\cos\frac{(n-1)}{(n+1)}\pi - 1\right)$$

negative for $n = 3,7,11\cdots 4k - 1$ and positive for $n = 5,9,13\cdots 4k + 1$; and

$$-\ \text{ion}\ p_{1n} = +\frac{\cos (n-1)\frac{\pi}{2}}{n+1}\left(\cos\frac{(n-1)}{(n+1)}\pi - 1\right)$$

positive for $n = 3,7,11\cdots 4k - 1$ and negative for $n = 5,9,13\cdots 4k + 1$.

For $n > 2$ these results are summarized in terms of n_e, the number of π electrons.

	Ground state	First excited state
conrotation	$n_e = 4k$	$n_e = 4k - 2$
disrotation	$n_e = 4k - 2$	$n_e = 4k$

Appendix 2

For a molecule with a large value of the bond order, specifically for the ground state of butadiene, we have allowed for the independent variation of the rotational angles ϕ and ϕ' at the reacting centers instead of the fixed choices $\phi' = \phi$ for disrotation and $\phi' = -\phi$ for conrotation. The energy surface $E_0^V(\phi,\phi')$ for $0 \leq \phi \leq 90°$ and $-90 \leq \phi' \leq +90°$ is represented in Figure 4. The same surface is repeated periodically for angles outside this range. The two dotted lines ($\phi' = -\phi$ and $\phi' = +\phi$) represent the con- and disrotational reaction paths.

For a given ϕ, the energy as a function of ϕ' has only one mininum which is found close to, but not exactly at $\phi' = -\phi$, except for the reactant and product where the minimum occurs at $\phi' = \phi = 0°$ and $\phi = |\phi'| = 90°$. The minimum energy path differs slightly from the conrotatory path. The difference depends on the relative strength of σ and π bonds, *i.e.*, in our model on the ratio of the resonance integrals.

Of higher significance is the fact that the disrotatory

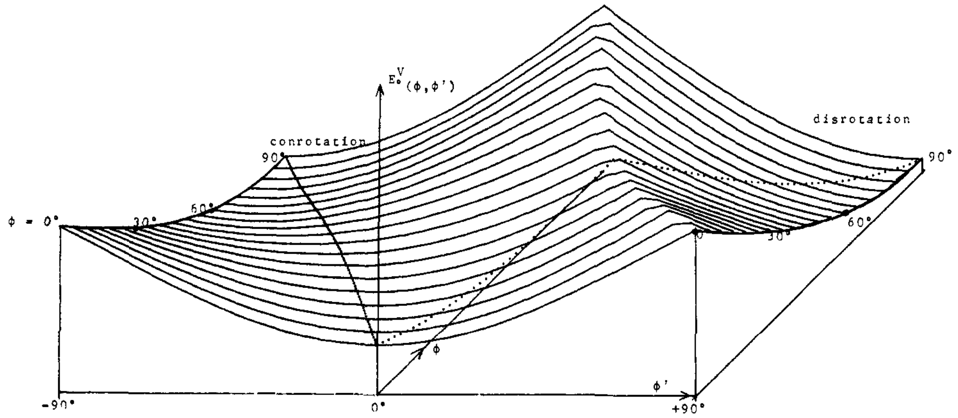

Figure 4. Energy surface (one-electron contributions) of the butadiene–cyclobutene ground configuration as a function of independent rotational angles ϕ and ϕ'. Dotted lines: $\phi = -\phi'$ conrotation, $\phi = +\phi'$ disrotation. (Note: $\phi' = +90°$ is electronically equivalent to $\phi' = -90°$ and the surface repeats periodically for angles outside the given range.)

path in this molecular state lies on a smooth energy slope, with no intervening energy maximum between the two paths. (This is true on either side of the peak value!) This in effect represents a highly unstable situation with strong restoring forces (negative derivatives of the energy with respect to the coordinates) directed toward $\phi' = -\phi$. Within this simplified model a synchronized disrotational motion appears therefore extremely improbable, not only on the grounds of a higher activation energy.

The energy difference between con- and disrotation is primarily controlled by the energy of the new σ bond. We expect therefore the same type of qualitative behavior in all reacting states with an appreciable value of the bond order: the energy minimum path is close to the predicted preferred rotation; the opposite rotation is energy wise unstable. The model supports the view of the concerted electrocyclic reaction as simultaneous rotations of the two reacting centers; along the minimum energy path, the rotations are, however, not in perfect synchronization. A twofold axis or a symmetry is then *not* retained during the reaction.

This observation detracts in no way from any previous conclusions as con- and disrotation refer to convenient, but not necessarily physically realized reference paths. It points, however, again to the fact that the bond order criterion is by its very nature a qualitative criterion for the prediction of rotations in electronically controlled electrocyclic reactions.

Cholesteric Liquid Crystal Induced Circular Dichroism (LCICD). V.[1] Some Mechanistic Aspects of LCICD

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Abstract: The influence of cholesteric liquid crystalline mesophase pitch (degree of helicity), temperature, texture, solute concentration, and cholesteric matrix on the intensity and sign of the cholesteric liquid crystal induced circular dichroism (LCICD) in pyrene was investigated. The spectroscopic information (polarizations of electronic transitions, detection of hidden transitions) provided by the LCICD spectra is also discussed. The LCICD intensity is dependent on pitch of the cholesteric mesophase, temperature, and texture. The sign of the LCICD is dependent on the position of λ_0 of the cholesteric pitch band relative to the wavelength of absorption, cholesteric matrix properties, as well as the chirality of the mesophase. The molecular ellipticity, $[\theta]$ (deg cm^2/dmol), for pyrene in a single cholesteric matrix is independent of solute concentration over a range in which the concentration was altered by two orders of magnitude. The concentration independence of $[\theta]$ indicates the lack of a mechanism change over the concentration range studied and that solute–solute interactions do not play an important role in the origin of LCICD for dilute solutions of solutes in cholesteric mesophases. Rotational strengths for pyrene in 70:30 (wt %) cholesteryl nonanoate–cholesteryl chloride are in the range of 1.0–3.0 $\times$ 10^{-38} cgs depending on the pitch of the cholesteric mesophase.

In the past decade or so there have been several reports of induced optical activity and circular dichroism (CD) in chirally perturbed achiral molecules. Certain achiral molecules display extrinsic CD while complexed to polypeptides in an α-helical confor-

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[1] F. D. Saeva, *Mol. Cryst. Liquid Cryst.*, **18**, 375 (1972), and ref 2–4 are considered the first four in this series.

[2] F. D. Saeva and J. J. Wysocki, *J. Amer. Chem. Soc.*, **93**, 5928 (1971).

[3] F. D. Saeva, *J. Amer. Chem. Soc.*, **94**, 5135 (1972).

[4] F. D. Saeva, *Mol. Cryst. Liquid Cryst.*, in press.

[5] Rochester Institute of Technology Co-op.