

the wave function including polar structures than by the single function I as has been past custom.

Pauling²² has suggested that the so-called "resonance theory" of chemistry should be viewed as essentially empirical in nature and it "should not be identified with the valence-bond method of making approximate quantum-mechanical calculations of molecular wave functions and properties." We feel that the results of this article require that this question be reopened.

(22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Section 6-5.

Although it may be true that many parts of chemistry will remain essentially empirical in nature, the general feeling on the part of most workers that the above identification could not be made in even simple cases may be the result of the inadequacies of the semiempirical approaches rather than due to inherent deficiencies in the model. Certainly, further work is required to settle these questions.

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Localized *ab Initio* Analysis of an Electrocyclic Reaction

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Abstract: The origin of the stereospecificity of a concerted reaction is analyzed through an *ab initio* calculation. The method allows a distinction between the σ , π , and $\sigma\pi$ effects and confirms that the π electronic factors are responsible for the stereospecificity. In a localized approach, the main stereospecific contribution is the π delocalization energy between the π bonds as suggested in a previous demonstration. However, a stereospecific short range repulsion effect also appears, due to the overlap between the π bonds.

Quantum chemistry has brought a major contribution to the understanding of stereospecificity in electrocyclic reactions. The original demonstrations by Woodward and Hoffmann¹ and by Longuet-Higgins and Abrahamson² rely on very simple hypotheses and attribute the origin of the phenomenon to symmetry effects on the π system. Further contributions were mainly numerical, including the σ system, and tried to obtain reaction paths or the heights of reaction barriers.³⁻⁵ In these numerical calculations it is difficult to locate the origin of the stereospecificity and to check the validity of the original theoretical demonstrations.

Both these demonstrations and numerical calculations deal with symmetry delocalized MO's, and symmetry considerations are often supposed to play the major role in the stereospecificity.^{1,2,6} Alternative approaches have been proposed, using localized SCF orbitals.⁷ In a preceding paper, a demonstration of the stereospecificity has been derived, using bond localized MO's and a perturbational development of the energy for the intermediate states.⁸ The origin

of the stereospecificity is attributed there to the π system, through a n th order delocalization contribution involving in a circular mode the n double bonds of the reacting circle. The validity of the hypothesis of this demonstration had been verified on the butadiene-cyclobutene reaction using the PCILO method⁹ in the CNDO parametrization.¹⁰ The present work tries to remove the restrictions of the previous study: namely (i) these calculations were semiempirical and *ab initio* calculations might behave differently, (ii) the perturbation was too strong in the transition state region and the perturbation series does not converge there. A variational procedure distinguishing π and $\sigma\pi$ factors and delocalization and correlation corrections has to be proposed.

I. Hypothesis

The calculation is performed in a minimal basis set of Slater atomic orbitals with optimized exponents ($\zeta_c(2s) = 1.759$, $\zeta_c(2p) = 1.670$, $\zeta_c(1s) = 5.679$, $\zeta_H = 1.227$). The atomic integrals are calculated using the POLYCAL program of Stevens.¹¹ The work is done in a basis of fully localized bond MO's. The nonorthogonal 1s MO's are simply the 1s AO's on the carbon atom. The σ nonorthogonal bond MO's are constructed from two hybrids in the valence shell satisfying the Del Re's criterion of maximum overlap;¹² these

(1) P. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

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

(3) G. Feler, *Theor. Chim. Acta*, **12**, 412 (1968).

(4) (a) D. Hsu, R. J. Buenker, and S. D. Peyerhimhoff, *J. Amer. Chem. Soc.*, **93**, 2117, 5005 (1971); (b) *ibid.*, **94**, 5639 (1972).

(5) J. W. McIver and A. Komornicki, *J. Amer. Chem. Soc.*, **94**, 2625 (1972); M. J. S. Dewar and S. Kirchner, *ibid.*, **93**, 4290, 4291 (1971).

(6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(7) C. Trindle, *J. Amer. Chem. Soc.*, **91**, 4054 (1969); **92**, 3251, 3255 (1970); *Theor. Chim. Acta*, **18**, 261 (1970).

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(9) (a) S. Diner, J. P. Malrieu, and P. Claverie, *Theor. Chim. Acta*, **13**, 118 (1969); (b) S. Diner, J. P. Malrieu, F. Jordan, and M. Gilbert, *ibid.*, **15**, 100 (1969); (c) F. Jordan, M. Gilbert, J. P. Malrieu, and U. Pincelli, *ibid.*, **15**, 211 (1969).

(10) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(11) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970), and references therein.

(12) G. Del Re, *Theor. Chim. Acta*, **1**, 188 (1963).

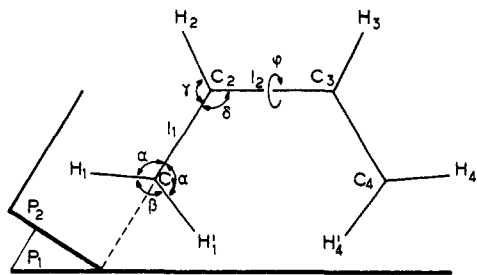


Figure 1. Definition of the geometrical parameters for intermediate conformations. P_1 is the plane $C_1C_2C_3$; P_2 is the plane $H_1C_1C_2$; θ is the angle (P_1, P_2) .

MO's are the same as the semiempirical PCILO MO's. The π localized MO's are defined in section II. These localized MO's are orthogonalized through a five-step procedure; the $1s$ MO's are orthogonalized among themselves through an $S^{-1/2}$ procedure and the bonding valence-shell MO's are orthogonalized to the $1s$ MO's by projecting them into the complementary subspace and then $S^{-1/2}$ orthogonalized among themselves. The virtual antibonding MO's are first projected into the complementary subspace of the occupied MO's, then $S^{-1/2}$ orthogonalized. One may find a justification of this procedure in a previous study.¹³ It represents the starting point of the *ab initio* PCILO method.

The butadiene and cyclobutene geometries are taken from experiment.^{14,15} The intermediate geometries are chosen as follows: assuming a planar structure of carbon skeleton, including H_2 and H_3 in this plane, neglecting the changes of the CH bond lengths, assuming the same valence angle for the hydrogen atoms of the CH_2 groups, and keeping the symmetry of the considered mode along the reaction path, one may consider seven fundamental parameters (five angles and two bond lengths) defined in Figure 1. In this figure, θ is the dihedral angle of the planes $C_1C_2C_3$ and $H_1C_1C_2$. These seven parameters are sufficient to define a symmetrical configuration if the carbon skeleton is kept planar and if the hydrogen atoms H_2 and H_3 are kept respectively in the planes $C_1C_2C_3$ and $C_2C_3C_4$. If one removes the planarity of this skeleton, one must add an angle φ of torsion of the group $H_3C_4H_4$ around the C_2C_3 bond. The seven parameters α , β , γ , δ , l_1 , l_2 , and θ have been changed simultaneously in a linear way according to a parameter v varying from 0 to 100%. If α_0 represents the value of α for the butadiene equilibrium geometry and $\Delta\alpha$ its change when going from butadiene to cyclobutene, for a given value of v , α takes the value $\alpha_v = \alpha_0 + v\Delta\alpha$ and similarly $\beta_v = \beta_0 + v\Delta\beta$, etc. The calculations have been performed for $v = 40, 50, \text{ and } 60\%$, which are likely to be representative of the transition state region. Hsu, *et al.*,⁴ have shown that the actual reaction path is not linear, the methylene groups beginning first to rotate before the breaking of the C-C bond. However, the transition state geometry of this stepwise process corresponds to a partial rotation and a partial lengthening and is rather close to our selected geometries. In their second calcula-

(13) A. Masson, B. Levy, and J. P. Malrieu, *Theor. Chim. Acta*, **18**, 193 (1970).

(14) A. Almengen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1967); A. R. H. Cole, G. M. Moroy, and G. A. Osborne, *Spectrochim. Acta*, **23**, 909 (1967).

(15) E. E. Goldish, K. Hedberg, and V. Schomaker, *J. Amer. Chem. Soc.*, **78**, 2714 (1956).

tion, Hsu, *et al.*,^{4b} have shown that a supplementary rotation occurs around the central C_2-C_3 bond (angle φ , Figure 1) without introducing qualitative differences. We also have performed an additional study for $\varphi = 20^\circ$ in the conrotatory mode, and we have verified that the relative influence of the various effects was not affected by this slight rotation. As it is impossible to define a nonplanar disrotatory mode and as we are analyzing the origin of the stereospecificity, the nonplanar calculation has not been reported in full. (See, however, ref 16.) Anyway, one must remember that our purpose is mainly interpretative and that the leading factors of the stereoselectivity are certainly present in the whole transition state region.

II. Perturbative Calculation of the Ground State Energy from a Fully Localized Single Determinant Φ_0 as Zeroth-Order Wave Function

This calculation is the *ab initio* replication of our previous semiempirical study.⁸ For an eventually distorted butadiene molecule, in a localized description, the σ localized MO's, which will not be destroyed during the reaction, may be built through the maximum overlap criterion.¹² On each carbon atom, one gets one π atomic orbital, orthogonal to the σ hybrids on the same center, and these four π AO's are used to build two ethylenic π MO's, π_1 and π_2 , and their antibonding MO's, π_1^* , and π_2^* , as explained in ref 8 (see Figure 2).

The ground state fully localized determinant Φ_0

$$\Phi_0 = \alpha |\sigma_1 \bar{\sigma}_1 \dots \sigma_n \bar{\sigma}_n \pi_1 \bar{\pi}_1 \pi_2 \bar{\pi}_2|$$

may be considered as a zeroth-order description for butadiene slope of the potential surface. But in the course of the reaction, these two π bonding MO's are progressively destroyed, especially during the rotation of the terminal CH_2 groups. For the cyclobutene slope of the potential surface the localized single determinantal description is

$$\Phi_0' = \alpha |\sigma_1 \bar{\sigma}_1 \dots \sigma_n \bar{\sigma}_n \sigma \bar{\sigma} \pi \bar{\pi}|$$

where $\sigma_1 \dots \sigma_n$ are the same as previously, σ is a σ bond between the terminal carbon atoms, and π is a π bond between the central carbon atoms. These simplified descriptions of the molecule, which are rather satisfactory for initial and final products are, of course, very poor for the intermediate region and are simply introduced to visualize the increase of stereospecific effects in the transition state region.

Table I gives the zeroth-order energy $E_0 = \langle \Phi_0 | H | \Phi_0 \rangle$ of the fully localized determinant, and the second-order corrected energy

$$E_2 = E_0 + \sum_I \frac{\langle \Phi_0 | H | \Phi_I \rangle^2}{E_0 - E_I}$$

In this expression the singly excited Φ_I 's give the ΔE_m^2 correction representing polarization and delocalization effects; the doubly excited determinants lead to a correlation correction ΔE_d^2 . According to our demonstra-

(16) The torsion around the C_2-C_3 single bond, found to occur in the transition state region by Hsu, *et al.*,^{4b} does not alter the qualitative aspects of our results. In the conrotatory mode, a dihedral for $\varphi = 20^\circ$ and $v = 50\%$, the butadiene description gives (in au) -154.3104 for E_0 , -154.8991 for E_2 , -0.1654 for ΔE_m^2 , and -0.4395 for ΔE_d^2 , which are very close to the value for the corresponding planar calculation (fourth column of Table I).

Table I. *Ab Initio* Zeroth and Second-Order Energies (all Energies in au) from Single Determinant Descriptions of the Ground State^a

	Butadiene				Cyclobutene			
	40%		50%		50%		60%	
	Con	Dis	Con	Dis	Con	Dis	Con	Dis
E_0	-154.4785	-154.2885	-154.2485	-154.2077	-154.2105	-154.2016	-154.2553	-154.2609
E_2	-154.9355	-154.8679	-154.8991	-154.8245	-154.9512	-154.8393	-154.8668	-154.8263
ΔE_m^2	-0.0971	-0.1371	-0.1884	-0.1363	-0.1957	-0.1105	-0.1559	-0.1178
ΔE_d^2	-0.3600	-0.4423	-0.4622	-0.4805	-0.5451	-0.5273	-0.4556	-0.4437
$ C_{\pi_1\pi_2^*} $ or $ C_{\sigma\sigma^*} $	0.137	0.180	0.356	0.176	0.449	0	0.262	0
$\epsilon_{\pi_1\pi_2^*}^2$ or $\epsilon_{\sigma\sigma^*}^2$	-0.0079	-0.0098	-0.0355	-0.0080	-0.0433	0	-0.0178	0
$ C_{\pi_1\pi_1^*} $ or $ C_{\sigma\pi^*} $	0.137	0.180	0.356	0.176	0.407	0	0.227	0
$\epsilon_{\pi_1\pi_1^*}^2$ or $\epsilon_{\sigma\pi^*}^2$	-0.0079	-0.0098	-0.0355	-0.0080	-0.0430	0	-0.0171	0

^a All quantities are defined in the text.

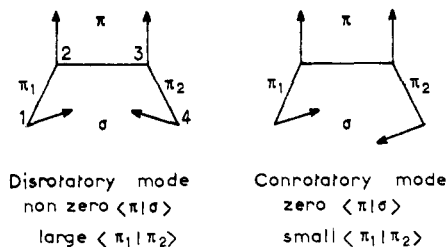


Figure 2. Bond MO's for the two modes. In both modes $\pi_1 = (\chi_1 + \chi_2)/\sqrt{2}$, $\pi = (\chi_2 + \chi_3)/\sqrt{2}$, $\sigma = (\chi_1 + \chi_4)/\sqrt{2}$. According to the dis- or conrotatory mode $\pi_2 = (\chi_3 \pm \chi_4)/\sqrt{2}$.

tion the " $\pi\pi^*$ " excitations in ΔE_m^2 should be responsible for the stereoselectivity, and the corresponding coefficients ($C_{\pi_1\pi_2^*}$ and $C_{\pi_2\pi_1^*}$ or $C_{\pi\sigma^*}$ and $C_{\sigma\pi^*}$) in the first-order wave function and energy corrections ($\epsilon_{\pi_1\pi_2^*}^2$, $\epsilon_{\pi_2\pi_1^*}^2$ or $\epsilon_{\sigma\pi^*}^2$, $\epsilon_{\pi\sigma^*}^2$) have been reported in Table I.

At the zeroth-order level, the conrotatory mode is significantly favored for the cyclobutene representation ($v = 40$ and 50%). The zeroth-order energy only includes electrostatic and short range repulsion effects linked to the overlap.¹⁷ The electrostatic effects are certainly small for this nonpolar molecule. The repulsion effect might come from steric hindrance between the hydrogen atoms of the terminal CH_2 groups or from π electronic factors. To analyze the zeroth-order energy in terms of bond interactions it is necessary to define bond nuclear fields (valence bonds receive one unitary charge on both atoms defining the bond, while inner shells receive two unitary charges on the bearing atoms¹⁸) and to expand the orthogonalization effects in powers of the overlap matrix S . When applied to this problem, the decomposition shows the leading role of the $S_{\pi_1\pi_2}$ overlap, which is larger in the disrotating mode (Figure 2), the repulsion between the CH bonds being far smaller. *The stereospecific zeroth-order contribution in the butadiene representation is a repulsive effect coming from the large overlap between the localized π MO's occurring in the disrotatory mode.* This effect is actually a π electronic effect. In the cyclobutene representation, this overlap effect is less pronounced, the overlap between the π and σ MO's being zero in the conrotatory mode (due to symmetry considerations) and small in the disrotatory mode. This stereospecific effect did not appear in our previous CNDO calculation since the CNDO parametrization only introduces the interbond overlap effects through delocalization.^{9b}

The second-order effects outlined in the previous study are actually present and mainly due to the single excitations ΔE_m^2 . A more detailed analysis shows that among these single excitations the charge transfer excitations $\pi_1 \rightarrow \pi_2^*$ and $\pi_2 \rightarrow \pi_1^*$ for the butadiene description, $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ for the cyclobutene description, represent almost all the stereospecific effect (cf. lines ϵ^2 of Table I). The " π " charge transfer coefficients for the two modes are the stronger coefficients in the perturbation expansion and their evolution agrees with our previous analysis.¹⁶

These coefficients are very important in the conrotatory mode for $v = 50\%$, and the series may diverge for

(17) See, for instance, J. N. Murrell, M. Randic, and D. R. Williams, *Proc. Roy. Soc., Ser. A*, **284**, 566 (1965).

(18) J. P. Daudey, O. Rojas, and J. P. Malrieu, submitted for publication. An analogous procedure has been proposed by G. F. Musso and V. Magnasco, *Chem. Phys. Lett.*, **23**, 79 (1973).

this conformation. This is the reason why the second-order corrected energy for the cyclobutene description in the transition state region ($v = 50\%$) is lower than the second-order corrected energy of the initial and final conformations. This divergence of the perturbation expansion is of course more pronounced for the cyclobutene description than for the butadiene description because its zeroth-order energy is much worse (line E_0 of Table I). The second-order results are therefore unreliable but this simplified second-order calculation was only made to show the stereospecific increase of charge transfer contributions in the " π " system. This phenomenon has to be proven to persist in a nondivergent procedure.

III. Perturbation of a Multiconfigurational Zeroth-Order Wave Function

The divergence in the simple perturbation procedure comes from the fact that the diagonal Fock energies of the " π " bonding MO's increase, while the corresponding Fock energies for the antibonding " π " MO's decrease when the " π " bonds are destroyed along the reaction. Excitation energies in the π system tend therefore toward zero and near degeneracies begin to occur between the ground state determinant Φ_0 and " π " excited determinants. The new zeroth-order wave function will include, besides Φ_0 , the charge transfer singly excited determinants

$$\begin{pmatrix} \pi_2^* \\ \pi_1 \end{pmatrix} = a_{\pi_2^*} + a_{\pi_1} \Phi_0$$

and

$$\begin{pmatrix} \pi_1^* \\ \pi_2 \end{pmatrix} = a_{\pi_1^*} + a_{\pi_2} \Phi_0$$

(and the β spin analogs) and the doubly excited intra-pair and interpair determinants

$$\begin{pmatrix} \pi_i^* \bar{\pi}_i^* \\ \pi_i \bar{\pi}_i \end{pmatrix} = a_{\pi_i^*} + a_{\pi_i} a_{\bar{\pi}_i^*} + a_{\bar{\pi}_i} \Phi_0 \quad i = 1, 2$$

and

$$\begin{pmatrix} \pi_i^* \pi_j^* \\ \pi_i \pi_j \end{pmatrix} = a_{\pi_i^*} + a_{\pi_j^*} + a_{\pi_i \pi_j} \Phi_0 \quad i \neq j = 1, 2$$

with all possible spin combinations.

Let us call S this subspace of 13 determinants.

This wave function will be used for the "butadiene" slope of the reaction surface. For the cyclobutene slope, we have included, besides Φ_0 , the same type of excitations as for the butadiene slope, changing π_1 into π and π_2 into σ . If one had performed a total CI on the four bonding and antibonding π MO's (including up to the quadruply excited determinants), the butadiene and cyclobutene wave functions would give the same energy for any geometry. As we do not perform the full CI of the π system to build our zeroth-order multiconfigurational wave function, one may simply hope that the two slopes will join together smoothly in the transition state region.

The zeroth-order wave function Ψ_0 of the ground state for a given geometry is obtained as an eigenvector of the CI matrix restricted to the subspace S . If P_s is the projector on the subspace S

$$P_s H P_s \Psi_0 = E_1 \Psi_0$$

$$E_1 = \langle \Psi_0 | H | \Psi_0 \rangle$$

E_1 will be called the first-order energy. It includes, therefore, the total (σ and π) short range repulsion, the π delocalization, and purely π correlation energies. E_0 and E_1 are upper bounds to the energy.

The Ψ_0 wave function is perturbed under the influence of the other determinants of the CI, up to the second order in energy. Due to the diagonalization of S , the other components of S are orthogonal to Ψ_0 ($\langle \Psi_i | \Psi_0 \rangle = 0$). Therefore, they do not interact with Ψ_0 and are not involved in the second-order energy

$$\Delta E_2 = \sum_{I \in S} \frac{\langle \Psi_0 | H | \Phi_I \rangle^2}{E_0' - E_1}$$

The choice of E_0' and of the unperturbed Hamiltonian H_0 are discussed elsewhere.¹⁹ This second-order correction includes some π correlation effects due to the purely π triply and quadruply excited configurations, which interact with Ψ_0 through its singly and doubly excited components. But most of the second-order correction represents the purely σ and $\sigma\pi$ delocalization and correlation corrections. The second-order corrected energy $E_2 = E_1 + \Delta E_2$ is not an upper bound to the energy, and the perturbation may diverge if the σ or $\sigma\pi$ effects are too strong.

All the theoretical explanations of the stereoselectivity attribute its origin to " π " electronic factors, " π " meaning the electrons of the bonds which are destroyed in the course of the reaction. The correlation diagrams only consider the corresponding MO's, and the same feature was explicitly supposed in our localized demonstration. The analysis of E_0 allowed us to see the role of the short range repulsion. When going from E_0 to E_1 one gets the role of the other π electronic factors and when going from E_1 to E_2 one gets the role of the σ and $\sigma\pi$ electronic factors.

In the previous second-order calculation the excitations from the 1s levels had been isolated and shown to give a small and almost invariant contribution (0.0127 au). They have been frozen in the present calculations. For a purpose of economy the conformations $v = 40$ and 60% have not been calculated.

Table II gives the corrections due to the π CI (Δ IC) and the second-order influence of the other configurations (ΔE_2). This perturbation takes into account more than 215,000 singly, doubly, triply, and quadruply excited determinants; and the energy obtained is lower than that of other *ab initio* calculations despite the crudeness of the initial Φ_0 description. The enthalpy of the reaction is 14.7 kcal/mol after the second-order correction.

As concerns the intermediate region, the two descriptions, which were strongly different for the single determinant wave function energy E_0 , have almost the same energy ($|E_2^{\text{but}} - E_2^{\text{cyclob}}| \leq 0.009$ au). The divergence which appeared in the ordinary second-order calculation has been removed and was mainly due to the strong " π " interactions. The energies for the intermediate region are now reliable. Keeping for $v = 50\%$ the description which gives the lowest E_0 value, the second-order calculated barrier from the butadiene geometry is 44.5 kcal/mol for the conrotatory mode and 89.1 for the disrotatory mode.

(19) B. Huron, J. P. Malrieu, and P. Rancurel, *J. Chem. Phys.*, **58**, 5745 (1973).

Table II. *Ab Initio* Zeroth, First- and Second-Order Energies (in au) for Multiconfigurational Descriptions of the Ground State^a

	Butadiene			Cyclobutene			
	0%	Con	50% Dis	Con	50% Dis	Dis	100%
E_0	-154.4785	-154.2485	-154.2077	-154.2100	-154.2010	-154.4490	
ΔIC	-0.0882	-0.1604	-0.1292	-0.1893	-0.1445	-0.0563	
$E_1 = E_0 + \Delta IC$	-154.5667	-154.1089	-154.3369	-154.3993	-154.3455	-154.5053	
ΔE_2	-0.3356	-0.4225	-0.4325	-0.4239	-0.4148	-0.3735	
$E_2 = E_1 + \Delta E_2$	-154.9023	-154.8314	-154.7694	-154.8232	-154.7603	-154.8760	
$M, \%$	2.04	12.64	2.11	11.59	0	0	
$D, \%$	9.19	18.05	17.92	21.24	22.18	6.28	

^a All quantities are defined in the text except M and D , which represent (in per cent) the weight of the singly (M) and doubly (D) excited configurations in Ψ_0 .

At the E_1 level, including only the “ π ” interactions, the barriers were respectively 99.0 and 138.9 kcal/mol. The interaction with the σ system has considerably lowered the activation energy in the same way as in the semiempirical calculations.

The σ system has therefore a quantitative role, but one may notice that the energy difference between the two barriers, *i.e.*, the stereospecificity, is already given by the “ π ” CI (39.8 kcal/mol for E_1 , 44.5 kcal/mol for E_2), which corroborates the attribution of the stereospecificity to the “ π ” electronic factors. The leading role of the “ π ” charge transfer single excitations is illustrated by the analysis of the coefficients of the CI wave function (Table II, lines 6 and 7).

The second-order results are in rather good agreement with experiment. The calculated enthalpy of the reaction is 15 kcal/mol, while it was estimated to be 20 kcal/mol by Dauben,²⁰ 15 kcal/mol by Srinivisan,²¹ and 8.8–8.9 kcal/mol in ref 5, using experimental measurements by Wiberg,²² in good agreement with the 7.8 kcal/mol calculated by Hsu, *et al.*⁴ As concerns the activation energy, the calculated altitude of the point $v = 50\%$ is 42–48 kcal/mol in the conrotatory mode in reasonable agreement with the experimental evaluations (30 kcal/mol²³ or 40 kcal/mol²⁴) and with the theoretical results (48 kcal/mol of Hsu, *et al.*⁴). But no systematic research of the saddle point was done, and these numbers are simply quoted to show the likeliness of the analysis.

(20) W. G. Dauben, “Reactivity of the Photoexcited Organic Molecules,” Interscience, New York, N. Y., 1967, p 171.

(21) R. Srinivisan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962).

(22) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

(23) H. M. Frey, B. M. Pope, and R. F. Skinner, *Trans. Faraday Soc.*, **63**, 1166 (1967).

(24) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

Conclusion

A method has been proposed here to analyze the origin of the stereospecificity of a concerted reaction through an *ab initio* calculation and to confirm both the delocalized^{1,2} and localized⁸ demonstrations of the Woodward–Hoffmann rules.²⁵ A zeroth-order fully localized determinant was built in which the σ localized MO's are kept almost invariant in the reaction, as supposed in ref 1, 2, and 8. The “ π ” system of the bonds which are broken in the course of the reaction was first localized. A stereospecificity already appears at this stage through the stereospecific overlap between the localized π bonds, creating a π short range repulsion energy. This factor had never been suggested before and will be analyzed with more details in a further publication. Then one takes into account the π delocalization and correlation effects through a π CI, the σ system being frozen. The main stereospecific factors appear at this level, essentially through π delocalization effects, as revealed by the perturbation development and the weight of the various excited determinants in the eigenvector of the π CI matrix. Then this π delocalized and correlated wave function is perturbed to the second order through its interaction with the σ system, showing that the σ system plays a significant role on the height of the barrier, but not on the stereospecificity (*i.e.*, the energy difference between the two modes). This work has not been done to explore the potential surface and the most probable pathways, but it shows that one may analyze the *ab initio* results and it confirms the validity of the simple preliminary demonstrations.

(25) The method has been applied in a semiempirical framework to 400 points of the potential surface, confirming that the stereospecific factors are the same for all intermediate conformations. The results are not reported here because the CNDO parametrization gives a cyclobutene final state lower than the butadiene initial state by 120 kcal/mol preventing any reliability in the quantitative results.