7424 J. Am. Chem. Soc. 1982, 104, 7424–7430

Topological Study of Chemical Reactivity. Diels–Alder Reaction

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Abstract: Quantum chemical approximations have been suggested which permit the study of reaction mechanisms theoretically in terms of a charge flux from space regions where bonds are broken into those in which bonds are formed rather than in terms of changes of nuclear coordinates. Reaction progress on a given molecular site is described by a single angle variable which is called the reaction angle. Reaction mechanisms are explained in terms of stationary points on the energy hypersurface where energy is defined in the space spanned by reaction angles. Two numerical procedures have been suggested for the energy evaluation which are based on approximations of the HMO and PPP type. Both procedures have been applied in order to study the addition of ethylene to butadiene. Calculations suggest a concerted supra-supra mechanism with the activation barrier of 101 (HMO) or 112 (PPP) kJ/mol. The two-step mechanism is forbidden due to Murrell–Laidler rules. Another allowed mechanism is found for the stereoisomerization of cyclohexenes via biradical species. In the first excited singlet state, two minima have been found in supra-supra and supra-antara regions, the latter being lower in energy. These minima can be ascribed to exciplexes. This method is one to two orders of magnitude faster than the "geometrical" method of the comparable level of sophistication and it can be used conveniently for studying medium-sized molecules (30–40 atoms).

One of the most important aims of the theoretical investigation of reaction mechanisms is a quantitative calculation of equilibrium and rate constants. Recently, great progress has been made in this field by utilization of nonempirical quantum chemical methods which, with a sufficiently large basis set and the inclusion of a correlation energy, give results of comparable accuracy to those obtained by experiment. Unfortunately enough, most of the questions raised by chemists cannot be reduced in principle to a calculation of an observable finding. In most cases all structural types of molecules are searched which have or are near prescribed characteristics. It leads to an inverse quantum chemical problem, namely, to find all possible wave functions which are eigenfunctions of prescribed operators and the corresponding eigenvalues of which lie in the prescribed (often extremal) range. Such an inversion problem is generally unsolvable by ready-made quantum chemical methods. Moreover, most of problems in organic chemistry and biochemistry are so complicated that it is impossible to express the general solution in the form of several quantum mechanical operators. For this reason, even at this time classical inductive thinking is exploited which is based on a classification of molecules and their reactions, on an investigation of analogies and contrasts, as well as on the utilization of structure–property or structure–activity relationships.

An exact quantum chemical description is not really necessary for such a study and empirical, semiempirical, and low-level nonempirical methods are largely utilized for these purposes. In almost all cases concerning chemical reactivity the dependence of the potential energy of interacting molecules on coordinates of atomic nuclei is investigated in the Born–Oppenheimer approximation. A classical organic chemistry approach in which a reaction is described in terms of bond breaking/bond formation has only in a few cases been utilized in theoretical calculations.[1] These calculations were in all cases of a rough quality and they were limited to an investigation of the validity of Woodward–Hoffmann rules[2] for selected electrocyclic reactions and cycloadditions.

In preceding papers,[3] quantum chemical approximations were suggested which permit the study of reaction mechanisms theoretically in terms of the charge flux from regions of space where bonds are broken into those in which bonds are formed rather than in terms of changes of nuclear coordinates. In this paper the method will be developed in more detail and the procedure will be applied to the Diels–Alder reaction, which has been carefully studied both theoretically[4–8] and experimentally.[9]

Theoretical Section

The classical structural chemistry concept in its simplest version is consistent with the following set of approximations: (i) the Born–Oppenheimer separation of electronic and nuclear motions is adopted; (ii) a set of basis functions of reactants and products is partitioned into subsets, each of them corresponding to a certain localization center; (iii) all interactions among localization centers are a priori neglected; (iv) basis functions for an intermediate molecular structure in a given reaction stage are expressed as linear combinations of the basis functions of reactants and products.

Approximation ii means that a separate local basis set is chosen for each localization center (atom, σ bond, π-electronic structure, lone pair). Nonempirical calculations have revealed that the use of a local basis set which is formed from localized MO's by truncation of so-called[10] "localization tails" gives an energy error which though small is by no means negligible[11] ($\sim$1.5 eV). When the local basis set is chosen a priori, i.e., when MO expansion coefficients which constitute localization tails being set to zero, and a proper energy optimization is performed, this error decreases[10] to about 0.1–0.3 eV. It should be pointed out that this latter process may not be necessary in the study of reaction mechanisms as only energy differences are being investigated and

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approximate constancy of this error is only required during the reaction course. The good estimation of the rotation barrier in ethane[10] using local basis sets provides some evidence in support of this.

The neglect of all interactions among local basis sets leads to the block structure of the Hartree–Fock matrix and to a simple additivity of bonding energies. In ref 3a it was shown that a simple addition scheme gives higher accuracy in heats of formation than more sophisticated MINDO/3[12] and MNDO[13] treatments. Such a block structure allows us to treat explicitly only those local basis sets which change during a reaction. The effect of the others can be treated as the Hartree field;[10] i.e., they can be included in the core.

Let us now consider the form of the local basis sets. Most conveniently, each of them is expressed as a linear combination of basis functions which can be formally divided into subsets belonging to individual atoms. For example, the local basis set of a σ bond can be expressed as a mixture of s and p STO's centered on atoms with the p's directed along the bond axis.[10] Similarly, π-bond orbitals can be constructed as a proper mixture of p and d-type STO's centered on atoms, the latter being so chosen that an electronic charge maximum is moved into the region between atoms.

Let us denote $|\chi_{ir}\rangle$ a subset of the given local basis set of a reactant which belongs to the atom i. Similarly, we denote $|\chi_{ip}\rangle$ a subset of the corresponding local basis set of a product. If we consider that during the reaction course electrons are flowing from the region where a bond is broken into that where a new bond is formed, a subset of basis functions on an atom i can be expressed as a linear combination of subsets of reactant and product, namely

$$|\chi_i\rangle = a_i|\chi_{ir}\rangle + b_i|\chi_{ip}\rangle \tag{1}$$

When we further assume that the region of space where a bond is broken is well separated from the region where the new bond is formed, basis subsets $|\chi_{ir}\rangle$ and $|\chi_{ip}\rangle$ are strictly orthogonal. In this case a normalization condition brings coefficients a_i and b_i into mutual dependence ($a_i^2 + b_i^2 = 1$). By introducing a trigonometric substitution $a_i = \cos\varphi_i$, $b_i = \sin\varphi_i$, eq 1 can be rewritten as

$$|\chi_i\rangle = \cos\varphi_i|\chi_{ir}\rangle + \sin\varphi_i|\chi_{ip}\rangle \tag{2}$$

The reaction progress on a given site i is then expressed by a single parameter, φ_i, which hereafter will be called a reaction angle. Evidently $|\chi_i\rangle = |\chi_{ir}\rangle$ for $\varphi_i = 0$ and $|\chi_i\rangle = \pm|\chi_{ip}\rangle$ for $\varphi_i = \pm\pi/2$. Note that if a bond i–j is formed in a disrotatory manner, both $\sin\varphi_i$ and $\sin\varphi_j$ should bear the same sign; i.e., both φ_i and φ_j should lie in the first quadrant. If a bond i–j is formed in a conrotatory manner, $\sin\varphi_i$ and $\sin\varphi_j$ should be of the opposite sign (a Möbius ring[14] is formed) and one of the φ_i, φ_j lies in the first quadrant and the other in the fourth quadrant (e.g., $\varphi_i \in \langle 0, \pi/2\rangle$, $\varphi_j \in \langle 0, -\pi/2\rangle$). This brings about the possibility of distinguishing the stereospecificity of a reaction.

Equation 2 is used to calculate atomic integrals in a given reaction stage from integrals of reactants and products. For example, if a bond is formed between sites i and j we obtain for the one-electron part of a Hamiltonian an expression

$$H_{ij} = \langle\chi_i|h|\chi_j\rangle = \sin\varphi_i \sin\varphi_j \langle\chi_{ip}|h|\chi_{jp}\rangle \tag{3}$$

Equation 3 is a consequence of the fact that in our local basis set only $|\chi_{ip}\rangle$ and $|\chi_{jp}\rangle$ are located in the same part of space and therefore all other terms identically vanish. Similarly, two-center electronic repulsion integrals can be calculated with

$$\gamma_{ij} = \langle\chi_i\chi_j|G|\chi_i\chi_j\rangle = \sin^2\varphi_i \sin^2\varphi_j \langle\chi_{ip}\chi_{jp}|G|\chi_{ip}\chi_{jp}\rangle \tag{4}$$

where again all terms containing any of $|\chi_{ir}\rangle$ or $|\chi_{jr}\rangle$ vanish identically.

Table I. Parameters Used for the Calculation in MJ/mol (For Further Explanation See Text)

	E_C	γ_1	γ_{CC}	R_{CC}^{-1}	H_{C-C}	$H_{C=C}$
TMO-Cl	−0.775	0.557	0.123	0.166	−0.283	−0.232
TMO	−0.775				−0.173	−0.126

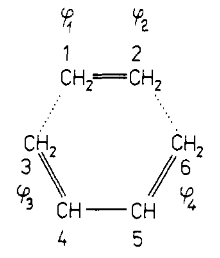

Figure 1. The numbering the carbon atoms and reaction angles in reactants.

Computational Details

In order to make a calculation scheme as simple as possible, we have introduced semiempirical approximations and have suggested two levels of sophistication. The first method is a version of the PPP method,[15] hereafter called TMO–CI method (Topological Molecular Orbitals with Configuration Interaction). In this version the Hartree–Fock total energy is expressed as

$$E = \sum_{\mu} P_{\mu\mu}\left(E_\mu - \frac{1}{2}\gamma_{\mu\mu} + \frac{1}{4}P_{\mu\mu}\gamma_{\mu\mu}\right) + \sum_{\mu<\nu}\left[2P_{\mu\nu}H_{\mu\nu} + \gamma_{\mu\nu}\left(P_{\mu\mu}P_{\nu\nu} - Z_\mu P_{\nu\nu} - Z_\nu P_{\mu\mu} - \frac{1}{2}P_{\mu\nu}^{\ 2}\right) + R_{\mu\nu}^{\ -1}Z_\mu Z_\nu\right] \tag{5}$$

where E_μ is a Mulliken electronegativity, $H_{\mu\nu}$ are resonance integrals, $\gamma_{\mu\nu}$ and $R_{\mu\nu}^{-1}$ are electronic and core–core repulsion integrals, Z_μ is a core charge, and $P_{\mu\nu}$ are elements of the first-order density matrix. Equation 5 is merely eq 2.20 in ref 16 reformulated. In this paper all integrals between nonneighbor atoms were neglected (for discussion of this point see ref 17), and the remaining integrals $\gamma_{\mu\mu}$, $\gamma_{\mu\nu}$, $R_{\mu\nu}^{-1}$, and $H_{\mu\nu}$ were treated as semiempirical parameters. $H_{\mu\nu}$ integrals were estimated from the average bond energies of C—C and C=C bonds; repulsion integrals were calibrated from spectral properties of a set of conjugated hydrocarbons. Details concerning the parametrization will be published elsewhere, and here only a list of parameters is presented in the first row of Table I. In actual calculations the density matrix was calculated using the Hückel orbitals, and total energy was calculated using eq 5 together with correlation energy using all singly excited configurations and those doubly excited where two electrons were promoted from a doubly occupied MO to the virtual one. Such an incomplete CI basis gives the total energy which is not invariant to the unitary transformation of MO's. In actual calculations it leads to discontinuities on the calculated energy hypersurface. This effect was removed using the localized orbitals which were obtained by the Edmiston–Ruedenberg procedure.[18] The use of localized orbitals also enabled a deeper insight into the change of a molecular structure during the reaction. Last but not least, according to our numerical experience it appeared that the independent localization of both sets of occupied and vacant MO's gives the largest correlation energy contribution within the frame of such an incomplete CI. The second method, hereafter called TMO (Topological Molecular Orbitals), is a simplified TMO–CI method where all repulsion integrals are neglected (an analogy of π-electron Hückel theory.[19]

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Table II. Stationary Points on the Ground-State Topological Hypersurfaces Calculated by the TMO-CI Method. E is Energy (MJ mol^{-1}); φ_i Are Reaction Angles (deg); D_i Are the Eigenvalues of the Hessian Matrix (MJ mol^{-1} rad^{-2})

no.	E	φ_1	φ_2	φ_3	φ_4	D_1	D_2	D_3	D_4	note
I	−0.7810	0.0	0.0	0.0	0.0	0.0840	0.0840	0.1472	0.1472	reactants
II	−0.9360	90.0	90.0	90.0	90.0	0.1781	0.1781	0.2358	0.2358	supra-supra product
III	−0.9360	−90.0	90.0	90.0	90.0	0.1781	0.1781	0.2358	0.2358	supra-antara product
IV	−0.6689	42.780	42.780	40.433	40.433	−0.5330	0.4959	0.7055	0.8903	symmetrical saddle point
V	−0.6151	0.01	89.99	0.01	89.99	−0.4306	0.0767	0.1796	0.2605	singlet biradical
VI	−0.5637	0.0	71.043	0.0	72.846	−0.2636	−0.0810	0.1787	0.5249	apex

Only parameters $H_{\mathrm{C=C}}$ and $H_{\mathrm{C-C}}$ were calibrated and average bonding energies were used for calibration. Parameters are presented in the second row in Table I.

Diels–Alder Reaction of Ethylene and Butadiene

The ethylene plus butadiene supermolecule can be treated as the total of local basis sets, namely 6 1s inner electronic pairs, 10 C–H bond orbitals, 4 C–C bond orbitals, and two independent π-electronic structures. The last two local basis sets are those which are changed during a reaction course. Within the topological approximation we have a six-electron problem and the reaction can be investigated in terms of changes of four reaction angles $\varphi_1, ..., \varphi_4$ which describe the reaction progress on reaction sites 1, 2, 3, and 6 (see Figure 1). Nonvanishing atomic integrals at a given reaction stage are defined as

$$\begin{aligned} H_{12} &= H_{\mathrm{C=C}} \cos\varphi_1 \cos\varphi_2 \quad \gamma_{12} = \gamma_{\mathrm{CC}} \cos^2\varphi_1 \cos^2\varphi_2 \\ H_{13} &= H_{\mathrm{C-C}} \sin\varphi_1 \sin\varphi_3 \quad \gamma_{13} = \gamma_{\mathrm{CC}} \sin^2\varphi_1 \sin^2\varphi_3 \\ H_{34} &= H_{\mathrm{C=C}} \cos\varphi_3 \quad \gamma_{34} = \gamma_{\mathrm{CC}} \cos^2\varphi_3 \\ H_{45} &= H_{\mathrm{C=C}} \quad \gamma_{45} = \gamma_{\mathrm{CC}} \\ H_{56} &= H_{\mathrm{C=C}} \cos\varphi_4 \quad \gamma_{56} = \gamma_{\mathrm{CC}} \cos^2\varphi_4 \\ H_{26} &= H_{\mathrm{C-C}} \sin\varphi_2 \sin\varphi_4 \quad \gamma_{26} = \gamma_{\mathrm{CC}} \sin^2\varphi_2 \sin^2\varphi_4 \\ H_{11} &= H_{22} = ... = H_{66} = E_{\mathrm{C}} \\ \gamma_{11} &= \gamma_1(\sin^4\varphi_1 + \cos^4\varphi_1) + 2\gamma_{\mathrm{CC}} \sin^2\varphi_1 \cos^2\varphi_1 \end{aligned} \tag{6}$$

and similarly for $\gamma_{22} ... \gamma_{66}$.

It should be noted that γ_{CC} was chosen to be the same for single and double bonds. The last term in the relationship for γ_{11} is a consequence of the fact that integrals of the type

$$\int \chi_{\mu r}^{+}(1)\chi_{\mu r}(1)(1/r)\chi_{\mu p}^{+}(2)\chi_{\mu p}(2)\, d\tau_1\, d\tau_2 \tag{7}$$

are not vanishing in the given approximation. (For a deeper insight, see ref 3b.) These integrals were set equal to γ_{CC} bicentric ones. Total energy was studied as a function of reaction angles. Such a function is hereafter called "topological hypersurface". Reaction mechanisms are discussed in terms of stationary points on this hypersurface rather than in terms of geometrical arrangement of nuclei in the space.

Analysis of the Energy Hypersurface

The main problem encountered with the pericyclic reactions is whether formation of bonds proceeds in a concerted, synchronous or many-step manner.[20] For this reason, it is convenient to study the corresponding reaction mechanism on multidimensional energy surfaces. In our case, two bonds are formed during the reaction, namely 1–3 and 2–6, when the numbering of carbon atoms shown in Figure 1 is used. Such a reaction can be conveniently treated by considering that the molecular system is under the action of two independent driving forces λ_1 and λ_2. The first one brings together atoms 1 and 3; i.e., it affects reaction angles φ_1 and φ_3. The second one similarly affects reaction angles φ_2 and φ_4 (cf. Figure 1). The action of driving forces can be understood as the existence of two constraints which prohibit the movement along any of the directions of driving forces in a given reaction stage, the energy being fully optimized in any perpendicular direction. In our case the constraints are apparently the following

$$\lambda_1: \quad \varphi_3 \pm \varphi_1 = k_1; \quad k_1 \in \langle 0, \pi\rangle; \quad \varphi_1 \in \langle -\pi/2, \pi/2\rangle; \quad \varphi_3 \in \langle 0, \pi/2\rangle \tag{8}$$

$$\lambda_2: \quad \varphi_2 + \varphi_4 = k_2; \quad k_2 \in \langle 0, \pi\rangle; \quad \varphi_2 \in \langle 0, \pi/2\rangle; \quad \varphi_4 \in \langle 0, \pi/2\rangle \tag{9}$$

where minus signs in eq 8 hold for a conrotatory 1–3 bond formation. Note that the choice of φ_1 as a negative angle is conventional. The alternative choice $\varphi_1 \pm \varphi_3 = k_1$, $\varphi_1 \in \langle 0, \pi/2\rangle$, $\varphi_3 \in \langle -\pi/2, \pi/2\rangle$ does not affect the results. Parameters k_1 and k_2 can be understood to be measures of the formation of bonds 1–3 or 2–6 and the function $E = E(k_1, k_2)$ gives us information about the concertedness of the process. In this paper 91 points on this surface were calculated for equally spaced k_1 and k_2 values. Isoenergetic curves and gradient maps were calculated numerically for these points using a planar third-order cubic interpolation. The Murtagh–Sargent variable metric method[23] was chosen for the energy minimization in the remaining directions of freedom. Stationary points on this surface were found by the Levenberg–Marquardt procedure[22] and they were classified by their rank and signature[23] using the Hessian matrix analysis.

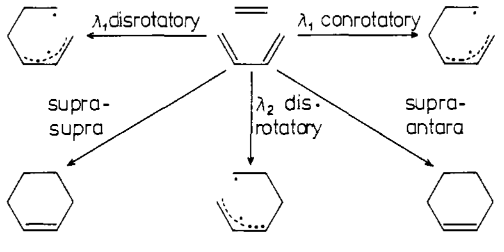

Figure 2. Key diagram for reading the two-dimensional countour diagrams presented in this paper.

Results and Discussion

As stated above, the topological hypersurface was analyzed with regard to two driving forces which act on the disrotatory or conrotatory formation of the 1–3 bond and the disrotatory formation of the 2–6 bond. Both supra-supra and supra-antara mechanisms can be merged in a combined diagram which is schematically drawn in Figure 2. A TMO–CI topological energy surface for the electronic ground state is presented in Figure 3. Stationary points found on this surface were fully optimized and their energy characteristics are given[24] in Table II. Standard chemical structures which correspond to these stationary points are presented in Figure 4. Only three local energy minima, I, II, and III, can be found on this surface, namely reactants and products. Both supra-supra and supra-antara (nonsymmetrical) concerted mechanisms proceed through saddle points that for the supra-supra approach having a substantially lower energy which is in complete accord with the Woodward–Hoffmann rules.[2]

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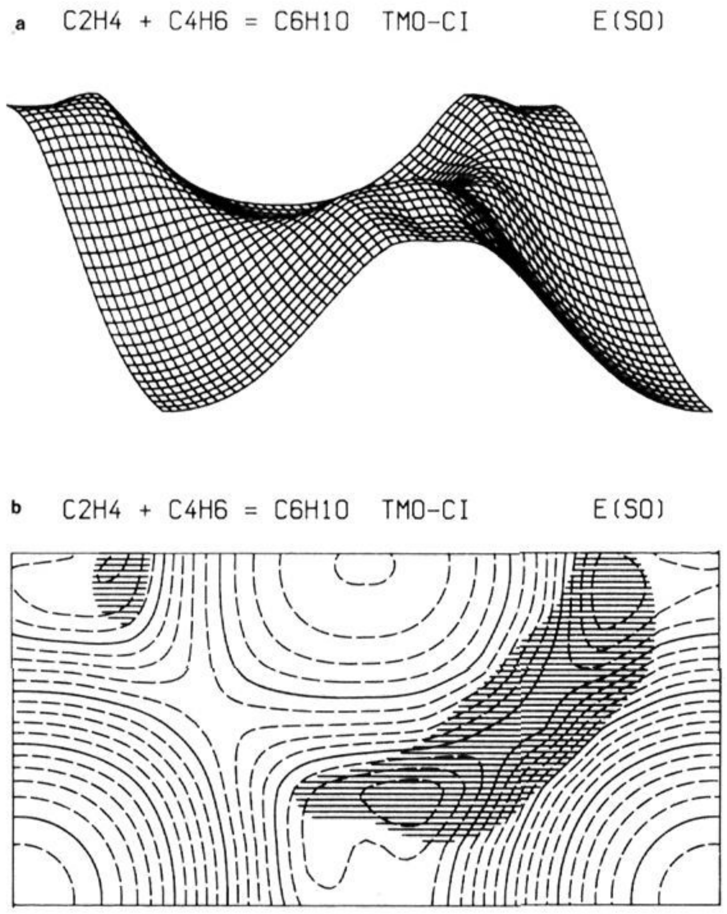

Figure 3. Three-dimensional drawing and a countour diagram of the topological surface in the ground state calculated by the TMO–CI method. Areas where the lowest excitation energy is less than 0.25 MJ/mol are covered by horizontal lines. For further explanation, see Figure 2.

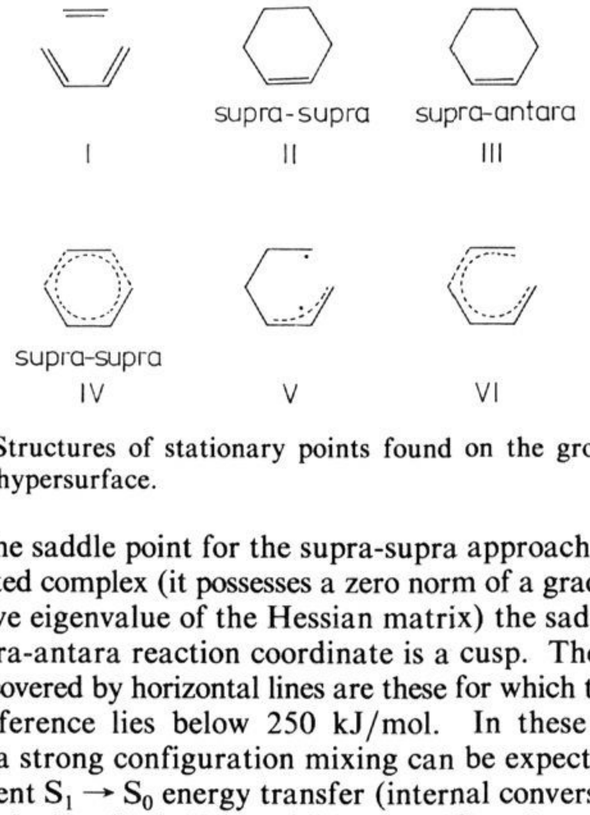

Figure 4. Structures of stationary points found on the ground-state topological hypersurface.

Whereas the saddle point for the supra-supra approach, IV, is a true activated complex (it possesses a zero norm of a gradient and one negative eigenvalue of the Hessian matrix) the saddle point on the supra-antara reaction coordinate is a cusp. The regions which are covered by horizontal lines are these for which the S_1–S_0 energy difference lies below 250 kJ/mol. In these regions, therefore, a strong configuration mixing can be expected and a most efficient $S_1 \rightarrow S_0$ energy transfer (internal conversion) can occur. Singlet biradicals V are additional saddle points; however, a reaction coordinate which links reactant and such a biradical passes through a stationary point with two negative eigenvalues of the Hessian matrix (structure VI). The two-step Diels–Alder reaction is thus forbidden due to a violation of Murrell–Laidler rules.[25] However, this biradial is accessible from either products II or III. This is a possible mechanism for cases where the decreased stereoselectivity of the Diels–Alder reaction is observed.[26] Apparently this barrier can be lowered by the proper substitution.

Before further discussion, the nature of the stationary points found should be discussed in more detail. With ordinary "geometrical" methods the energy hypersurface is a scalar field in the Euclidian vector space which is spanned by coordinates of nuclei. Stationary points are such geometrical arrangements where the energy is not changed by any infinitesimal displacement of atoms. It should be remembered that such a treatment is valid only in the frame of the Born–Oppenheimer approximation. When this approximation is abandoned such a treatment is no longer possible. This classical concept was recently criticized by Wooley,[27] who pointed out that a term "molecule" is only a consequence of an above-mentioned approximation and its justification does not come from basic quantum mechanical postulates. Bader et al.[28] suggested an alternative definition of a "molecule"which is based on topological properties of the quantum mechanical charge distribution. Such a definition is free of approximative thinking.

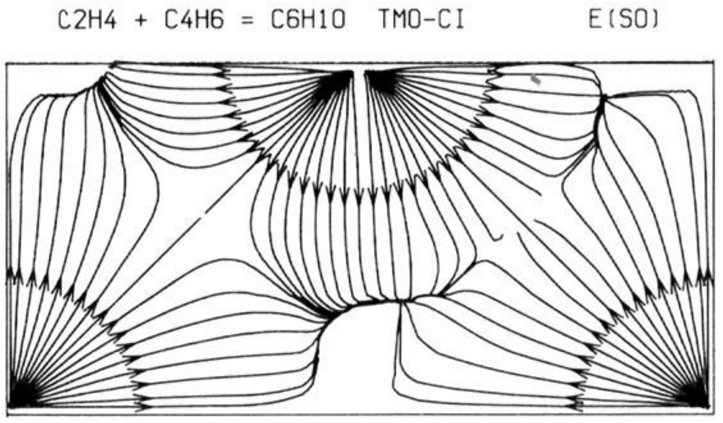

Figure 5. Force field diagram of the ground-state topological surface. Arrows show the direction in which energy is increasing. For further explanation, see Figure 2.

Stationary points on our topological energy hypersurface represent such charge distributions for which energy is not changed by an infinitesimal electron flux from one region of space to another. (Remember that reaction angles introduced in this paper affect primarily changes in the density matrix.) It follows that such an analysis is in accord with Bader's definition and it can be performed, at least in principle, even out of the frame of the Born–Oppenheimer approximation.

The force field or Collard–Hall[29] diagram of the surface shown in Figure 3 is presented in Figure 5. Arrows show directions of an energy increase. It is seen that there exist three catchment regions[30] with such a characteristic that all trajectories start and terminate only in a given region. The localization procedure due to Edmiston–Ruedenberg[18] showed that all structures which belong to a given region have very similarly shaped molecular orbitals. On the left hand boundary between regions (a ridge) in which reactants and supra-supra product lie (cf. Figure 5), the infinite number of structures satisfy the Edmiston–Ruedenberg localization criterion. On crossing on the ridge on either of the two slopes only a single localization structure is obtained. On the right hand boundary between the reactant and supra-antara product, no structure can be found which satisfies the Edmiston–Ruedenberg criterion and the structre of a reactant does not correlate with that of a product. As an illustration, expansion coefficients of doubly occupied molecular orbitals are presented in Table III for reactants, products, and several structures near the mentioned boundaries.

A topological energy surface for the vertical S_1 state is shown in Figure 6. This surface is constructed from energies of the first excited singlet state which were drawn from a CI matrix of ground-state optimized structures. Both reactants and products are maxima on this surface and two minima can be found which correspond to exciplexes in supra-supra and supra-antara regions. The saddle point between them is an activated complex for their mutual interconversion. It should be pointed out that both ste-

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Table III. MO Expansion Coefficients of the Selected Points on the Topological Hypersurfaces. φ Is a Vector of Reaction Angles in Degrees which Define a Given Point; ψ_i Is a Vector of the *i*th MO Expansion Coefficients; E Is Bonding Energy in MJ mol^{-1}, g Is a Norm of Gradient in MJ mol^{-1} rad^{-1}. For Numbering of Atoms and Reaction Angles See Figure 4

φ:	90.0	90.0	90.0	90.0		
ψ_1:	0.0	0.7071	0.0	0.0	0.0	0.7071
ψ_2:	0.7071	0.0	0.7071	0.0	0.0	0.0
ψ_3:	0.0	0.0	0.0	0.7071	0.7071	0.0
$E = -0.9360$; $g = 0.0$						
φ:	43.23	43.23	40.89	40.89		
ψ_1:	0.2510	0.6465	−0.1911	−0.1746	0.2133	0.6376
ψ_2:	0.6444	0.2463	0.6397	0.2169	−0.1735	−0.1943
ψ_3:	−0.1476	−0.1461	0.2330	0.6500	0.6515	0.2361
$E = -0.6701$; $g = 0.1143$						
φ:	42.73	42.73	40.39	40.39		
ψ_1:	0.6528	0.6503	0.2491	−0.1200	−0.1225	0.2439
ψ_2:	0.1939	−0.1924	0.6294	0.6503	0.2586	−0.1988
ψ_3:	−0.1906	0.2001	−0.2045	0.2504	0.6466	0.6332
$E = -0.6690$; $g = 0.0013$						
φ:	0.0	0.0	0.0	0.0		
ψ_1:	0.7071	0.7071	0.0	0.0	0.0	0.0
ψ_2:	0.0	0.0	0.6882	0.6882	0.1625	−0.1625
ψ_3:	0.0	0.0	−0.1625	0.1625	0.6882	0.6882
$E = -0.7810$; $g = 0.0$						
φ:	−45.26	45.26	38.74	38.74		
ψ_1:	0.6997	0.6997	−0.0719	0.0723	−0.0723	0.0719
ψ_2:	−0.0526	0.0874	0.6812	0.6830	0.1684	−0.1755
ψ_3:	−0.0874	0.0525	−0.1755	0.1684	0.6830	0.6812
$E = -0.5541$; $g = 0.3710$						
φ:	−43.76	43.76	42.24	42.24		
ψ_1:	0.0639	0.6935	0.0828	−0.1185	0.1102	0.6942
ψ_2:	0.6936	0.0640	−0.6942	−0.1102	0.1185	−0.0827
ψ_3:	0.1220	−0.1220	0.1063	0.6883	0.6883	0.1062
$E = -0.5660$; $g = 0.4622$						
φ:	−90.0	90.0	90.0	90.0		
ψ_1:	0.0	0.7071	0.0	0.0	0.0	0.7071
ψ_2:	0.7071	0.0	−0.7071	0.0	0.0	0.0
ψ_3:	0.0	0.0	0.0	0.7071	0.7071	0.0
$E = -0.9360$; $g = 0.0$						

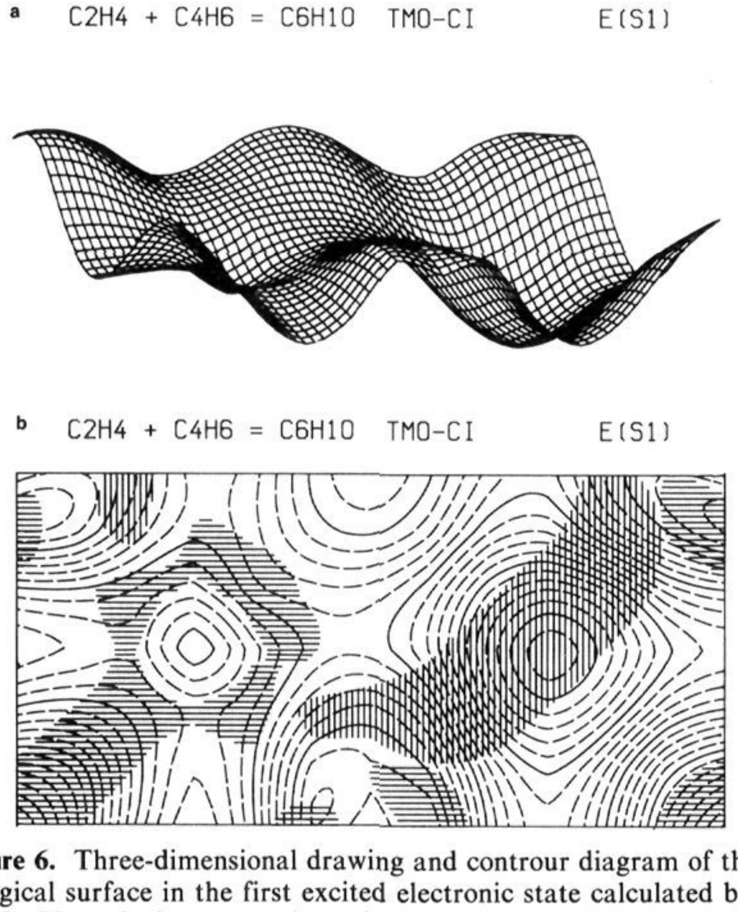

Figure 6. Three-dimensional drawing and contour diagram of the topological surface in the first excited electronic state calculated by the TMO–CI method. Areas where the S_2–S_1 energy differences are less than 0.1 MJ/mol are covered by horizontal lines; areas where the S_1–S_0 excitation energy is less than 0.25 MJ/mol, by vertical lines. For further explanation, see Figure 2.

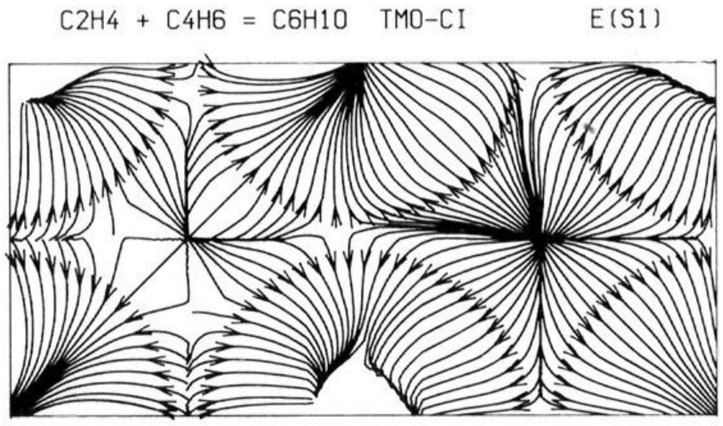

Figure 7. Force-field diagram of the first excited-state topological surfaces. *Arrows show the direction in which energy is increasing.* For further explanation, see Figure 2.

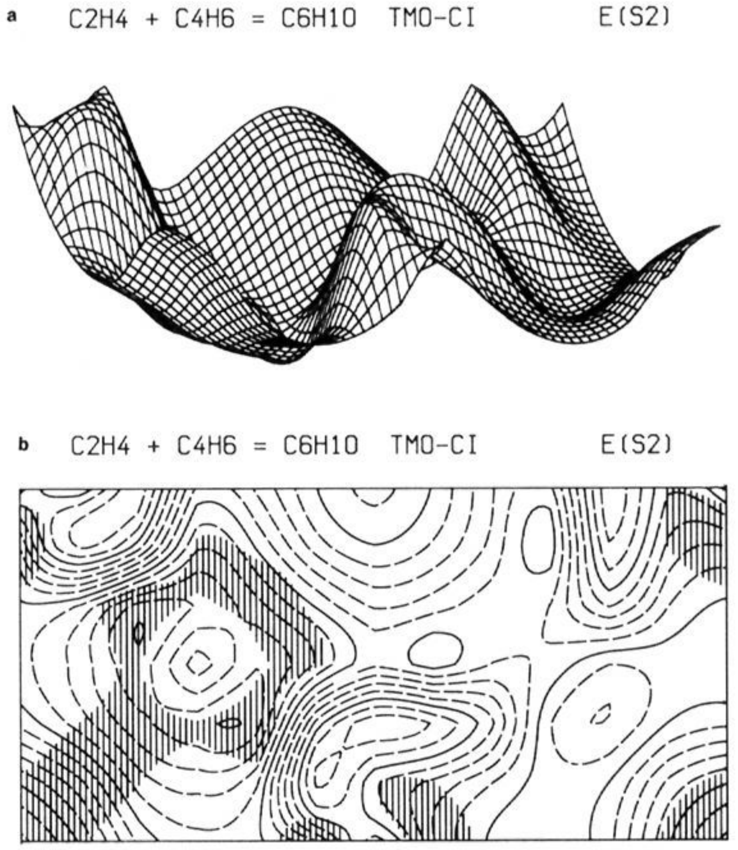

Figure 8. Three-dimensional drawing and a contour diagram of the topological surface in the second excited electronic state calculated by the TMO–CI method. Areas where the S_2–S_1 energy differences are less than 0.1 MJ/mol are covered by vertical lines. For further explanation, see Figure 2.

reoisomers are stable. The Woodward–Hoffmann rules can be interpreted in such a way that the supra-antara exciplex is more stable that the supra-supra one and that the internal conversion from the former is more feasible due to a lower value of the S_1–S_0 difference (such a region is covered by vertical lines in the contour diagram 6b). Let us note that both minima lie well above descent paths toward products on the S_0 surface. This gives us a tentative explanation of why the photochemical retro-Diels–Alder reaction is not known.

The force field diagram of the S_1 state is presented in Figure 7. This diagram is more complicated than that of the S_0 state and it can be separated into six distinct catchment regions. A topological surface for the S_2 state is presented in Figure 8. The rather complicated shape is a result of numerous avoided crossings. The internal conversion to the S_1 state is most effective in the supra-supra region (cf. vertical lines in Figure 8b).

Topological surfaces for S_0 and S_1 states calculated by the simple TMO method are presented in Figures 9 and 10. The S_0 surface does not differ substantially from that calculated by the TMO–CI method. Perhaps the most striking difference is the existence of a maximum on the concerted supra-antara reaction path and it is not a stationary point but rather a cusp similar to that in the preceding calculation. However, the S_1 surface is quite different from that calculated by the TMO–CI method and it does not reflect the Woodward–Hoffmann rules at all. It can be concluded that the electron repulsion integrals and the electron

Table IV. Stationary Points on the Ground-State Topological Hypersurface Calculated by the TMO Method. E Is Energy (MJ mol^{-1}); φ_i Are Reaction Angles (deg); D_i Are the Eigenvalues of the Hessian Matrix (MJ mol^{-1} rad^{-2})

no.	E	φ_1	φ_2	φ_3	φ_4	D_1	D_2	D_3	D_4	note
I	−0.8155	0.0	0.0	0.0	0.0	0.2254	0.2254	0.2520	0.2520	reactants
II	−0.9440	90.0	90.0	90.0	90.0	0.2398	0.2398	0.3460	0.3460	supra-supra product
III	−0.9440	−90.0	90.0	90.0	90.0	0.2398	0.2398	0.3460	0.3460	supra-antara product
IV	−0.7148	39.202	39.202	36.087	36.087	−0.3822	0.0424	0.2821	0.3692	symmetrical saddle point
V	−0.7024	0.0	90.0	0.0	90.0	−0.1713	−0.0109	0.2528	0.3495	diradical (apex)
VI	−0.6984	0.0	66.051	0.0	68.991	−0.0987	−0.0939	0.3205	0.3387	apex

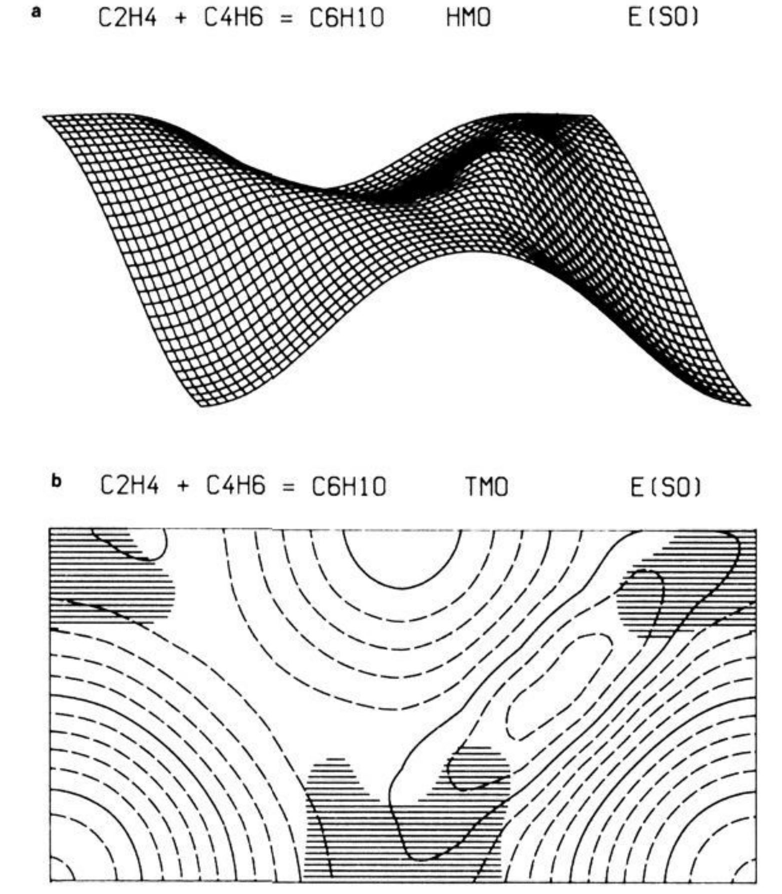

Figure 9. Diagrams similar to those in Figure 3 but calculated by the TMO method.

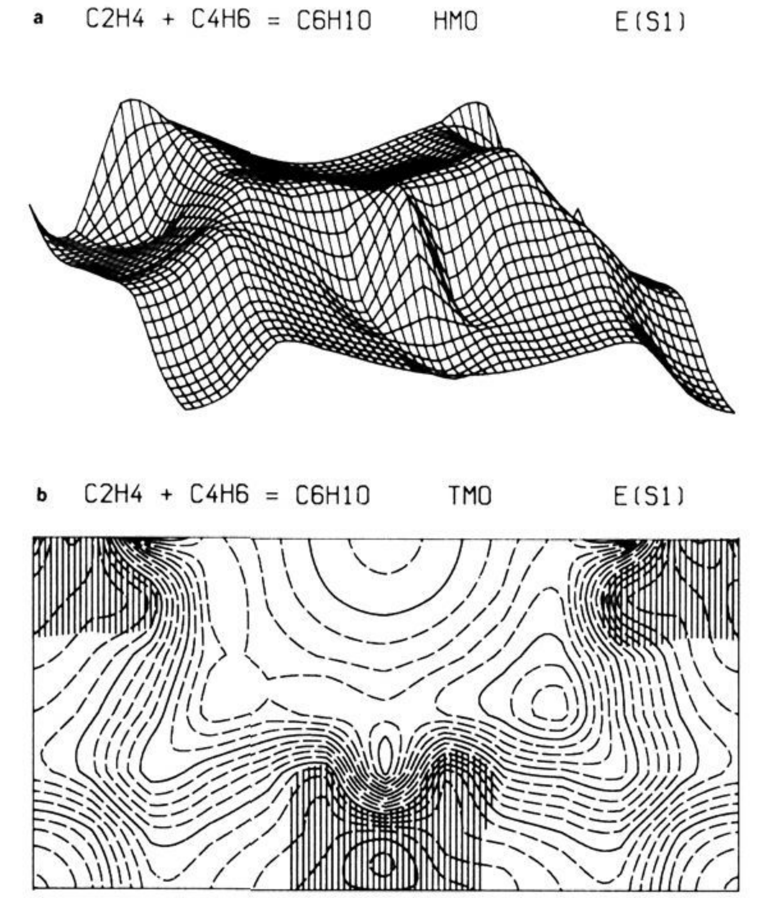

Figure 10. Diagrams similar to those in Figure 6 but calculated by the TMO method.

Table V. Heats of Reaction ΔH_0^{298} and Heats of Activation for Forward and Backward Diels–Alder Reactions of Ethylene and Butadiene (kJ/mol)

method	ref	$\Delta E^{\ddagger}$ (forward)	$\Delta E^{\ddagger}$ (backward)	ΔH_0^{298}	note
experimental	33a–d	115	259, 276	−170	
CNDO/2	4		active complex the most stable species		
MINDO/3	6a	173	429	−256	two-step
MINDO/3 + 3CI	6b	103	346	−244	two-step
STO-3G	8	169	607	-439^a	
7s3p	8	87	464	-377^a	
4-31G + 3CI	7	178	334	-156^a	
this work, TMO		101	229	−129	
this work, TMO–CI		112	267	−155	

[a] This value should be compared with a corrected experimental value, −135 kJ/mol (cf. ref 7).

Table VI. Time Needed for a Single Energy Calculation (Minutes of CPU Time on an IBM 370, Model 148)

topology, TMO (+ gradient)	0.03
topology, TMO–CI (+ gradient)	0.27
EHT	1.2
CNDO/2, MINDO/3	2.1^a
MNDO-type	3.1^a
STO-3G	84^a
4-31G	1020^a

[a] Interpolated value using estimates from ref 13.

correlation play a substantial role in the topological description of excited-state energy surfaces.

Let us now turn our attention to the numerical results and compare stationary point characteristics calculated by the TMO–CI method[31] (Table II) with those calculated by the TMO method (Table III). Using the Bader terminology,[23] stationary points which correspond to structures I, II, and III are of the (4,4) type, the saddle points for the supra-supra reaction and biradicals are of (4,2) type and structure VI is of (4,0) type (cf. Figure 4 and Table IV). It should be pointed out that there is a small difference in energy between results obtained by the TMO method and those calculated by the much more complicated TMO–CI method. Results prefer the concerted supra-supra mechanism which is in accord both with ab initio calculations[7,8] and experiment.[9] They are, however, in disagreement with results based on semiempirical MINDO/3 calculations.[6] The singlet biradical lies 54 kJ/mol above the concerted saddle point and the triplet is in additional 19 kJ/mol higher. Ab initio results[7] based on 4-31G level with 3 × 3 CI suggest that the biradical lies below the energy of a symmetric transition state but it was not the highest point on the lowest two-step energy path. This conclusion is not supported by experimental findings because in this case the first concerted step I–IV–II would be followed by a rapid stereoisomerization II–V–III with a lack of a reaction stereospecifity. Nevertheless, the rather high energy of a biradical obtained by the TMO–CI procedure will be reduced to some extent by considering a more advanced topological model in which the radical stabilization due to hyperconjugation with the neighbor CH_2 group is explicitly considered. The topological study of this secondary

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(31) Stationary points which lie on boundaries of catchment regions were shifted by a small amount (0.02°) because only a single localized structure for both occupied and virtual orbitals gives us the satisfactory energy contribution when using the incomplete CI treatment.

effect as well as a perturbation study of substitution effects is now in progress in our laboratory.

General Remarks

In Table V the energies calculated by various semiempirical or nonempirical methods are compared with experimental data. The estimates of computing time for a single energy calculation calculated by an IBM 370/148 computer are presented in Table VI. It is seen that this method is rapid enough to enable such advanced techniques as full energy minimization and analysis of the Hessian matrix for medium-sized molecules (10–40 atoms) and it seems to be of sufficient accuracy for mechanistic studies.

Nonempirical calculations are consistent with the thinking of physicists, the goal being the evaluation of observables as exactly as possible. Topological calculations are consistent with the thinking of chemists; they can give a deeper insight into how individual functional groups participate in a given reaction and which substitutents, catalysts, or solvents have a favorable effect on the reaction rate. This point of view will be pursued in subsequent papers. It should be noted that at least in principle this method can be extended by removal of all semiempirical approximations and by the inclusion of nonneighbor interactions. This promises better results but with the necessary loss of simplicity and performance. Construction of topological energy hypersurfaces and a subsequent ab initio study of pertinent structures suggested by the topological treatment seems to be a promising way. The possible incorporation of the topological procedure into programs for searching chemical syntheses[32a,b] and heuristic investigations in the structure-reactivity projects[32c] should also be considered.

Acknowledgment. The basis of this topological treatment originated in numerous enlightening discussions with Dr. J. Kopecký from the Institute of Hygiene and Epidemiology, Prague. The author is very grateful to Dr. R. Zahradník and Dr. P. Čársky from our Institute as well as to Professor B. A. Hess from Vanderbilt University, Nashville, TN, for stimulating discussions and assistance.

Registry No. Ethylene, 74-85-1; butadiene, 106-99-0.

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Absolute Configuration of 1,2-Disubstituted *trans*-Cyclodecenes Based on Chemical Correlation with (+)-Dimethyl (2*R*)-2-Butyl-2-methyloctanedioate

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Abstract: The absolute configuration of (−)-*trans*-1,2-dimethylcyclodecene (**4**) has been determined to be *R* through chemical correlation with (+)-dimethyl (2*R*)-2-butyl-2-methyloctanedioate (**13**). Diester **13** was prepared from (+)-(4a*S*)-4a-methyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-one (**12**) through a sequence involving Eschenmoser fragmentation of the related epoxy ketone, hydrogenation of the resulting acetylenic side chain, oxidative cleavage of the derived cyclohexanone trimethylsilyl enol ether, and two-carbon malonic ester homologation of the hydroxy ester thus produced. The enantiomer of enone (+)-**12** and closely related congeners have been well studied by optical rotatory dispersion, and a precursor of enone (+)-**12** has been converted to a natural steroid, thereby establishing the absolute configuration.

Thirty years ago, Blomquist noted that *trans*-cyclononene (**2**) is "asymmetric" and "should exist in two enantiomorphic modifications".[1] Ten years later, Cope et al. resolved *trans*-cyclooctene using a chiral amine–platinum(II) complex.[2] They subsequently applied their resolution methodology to *trans*-cyclononene and found that the separable diastereomeric complexes gave optically active product only if the liberated alkene was immediately cooled to −78 °C.[3] Racemization took place at room temperature with a half-life of less than 20 s. Analogous treatment of the resolved *trans*-cyclodecene–platinum(II)–amine complex led only to racemic alkene, even at low temperature. These findings indicate that racemization of *trans*-cycloalkenes via rotation of the bridging methylene chain about the double bond has an energy barrier that decreases with increasing ring size (Figure 1).

Roberts and Binsch[4] estimated a rotational barrier of 11 kcal/mol for *trans*-cyclodecene (**3**) through variable-temperature ^{1}H NMR analysis. Using these results and Cope's racemization kinetic studies, they calculated half-lives for *trans*-cyclooctene, *trans*-cyclononene, and *trans*-cyclodecene of 10^5 years, 10 s, and 10^{-4} s, respectively, at room temperature.

Attemps at the isolation of other optically active *trans*-cycloalkenes have generally not been successful. Cope[5] prepared (+)-*cis,trans*-1,5-cyclooctadiene from resolved (*cis*-4-cyclooctenyl)dimethylamine, and Hill[6] obtained both (+)- and (−)-*trans,trans*-2-isopropylidene-5,9-dimethylcyclodecadienone(germacrone) from the resolved alcohols.

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