Pattern of Intrinsic Reaction Coordinates and Separatrices for a Symmetry-Forbidden Reaction

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Z. Naturforsch. **41 a,** 529–531 (1986); received July 29, 1986

The relative distribution of the basins of attraction of the chemical species and of the transition states is derived for the thermal isomerization of cyclobutene to butadiene.

It is shown that the transition states for the symmetry-allowed and symmetry-forbidden pathways are lumomers of one another. Use is made of the structural stability principle of Ariel Fernández and Oktay Sinanoğlu to show that these transition states are respectively the conrotatory and disrotatory Jahn-Teller distortions of the 2-butene diradical.

The results exhibit good agreement with J. A. Berson's conclusions in the sense that even the forbidden pathway is concerted.

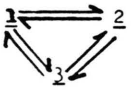
Key words: Directed graph of intrinsic reaction coordinates and separatrices, Jahn-Teller distortion of a diradical as a separatrix, symmetry-forbidden reaction pathway.

1. The Separatrix Passing Through the 2-Butene Diradical

The intrinsic reaction coordinate and separatrix (IRCS) graph contains the topological information on the relative distribution for the basins of attraction of the chemical species and the transition states [1–3].

It represents an equivalence class of cross sections of structurally stable PES's involving two coupled vibrational degrees of freedom. The structural stability principle introduces restrictions in the topology of the gradient field of a standard adiabatic PES: *The steepest descent path from a transition state cannot terminate at another saddle point of index one* (another transition state) *since such a connection violates the transversality condition* [1]. Analogously, this condition imposes restrictions on the topology of the phase portrait in the structurally stable kinetic models for far from equilibrium processes as shown by this author and Sinanoğlu [4, 5].

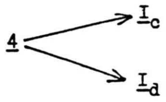
The aim of the present paper is to find the equivalence class of standard adiabatic gradient fields of PES's whose integral lines represent the IRC's and separatrices of the process



Such a class is represented by the IRCS graph since the integral curves joining critical points in the nuclear configuration space determine uniquely the topology of the PES. The diradical **4** has two singly occupied AO's Φ_1 and Φ_2 and it undergoes Jahn-Teller ($J-T$) distortions without activation energy. These distortions lift the orbital degeneracy of the diradical [3, 6]. The diradical is in the singlet state (we are considering a thermal rearrangement); this electronic state is degenerate, therefore the Jahn-Teller theorem applies.

$\mathbf{I}_c$ and $\mathbf{I}_d$ represent respectively the $J-T$ isomers obtained by conrotatory and disrotatory distortion.

The interconvertion of $\mathbf{I}_c$ and $\mathbf{I}_d$ is forbidden since it involves an HOMO-LUMO crossing in the orbital correlation diagram:



Since $\mathbf{I}_c$ and $\mathbf{I}_d$ are configurations with one unstable vibrational degree of freedom, the diradical **4** cannot be a saddle point with index 1 since if it were, there would be a direct saddle-saddle connection in the PES given by $\mathbf{4} \rightarrow \mathbf{I}_c$ and $\mathbf{4} \rightarrow \mathbf{I}_d$. These direct connections are precluded by the structural stability principle [1, 7].

This implies that the diradical **4** is not a transition state for the interconversion $\mathbf{I}_c \rightleftharpoons \mathbf{I}_d$: A transition state cannot be a double or higher order saddle point (see, for example, Murrell an Laidler [8]).

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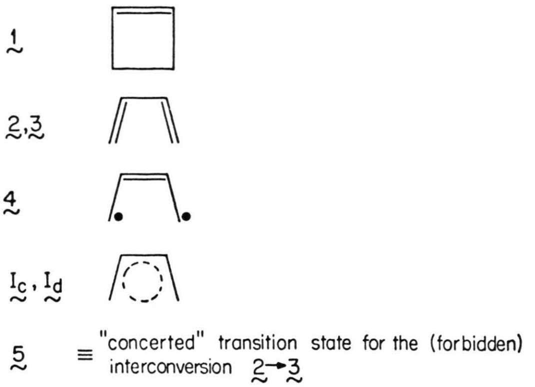

Fig. 1.

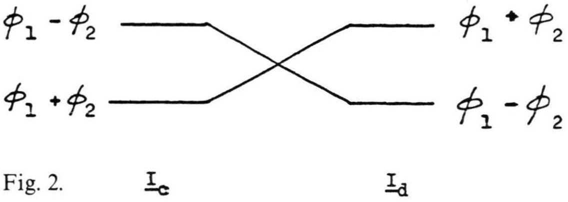

Fig. 2.

But this simply means that the interconvertion $\mathbf{I}_\mathrm{c} \leftrightharpoons \mathbf{I}_\mathrm{d}$ is forbidden.

This is the same conclusion reached by using the frontier orbit correlation.

The union of the stable manifolds of $\mathbf{I}_\mathrm{c}$ and $\mathbf{I}_\mathrm{d}$ separate the basin of attraction of **1** from the basins of **2** and **3**.

Separatrix $= M^s(\mathbf{I}_\mathrm{c}) \cup M^s(\mathbf{I}_\mathrm{d}) = (J-T$ distortion trajectory $\mathbf{4} \to \mathbf{I}_\mathrm{c}) \cup (\partial\mathcal{D} \to \mathbf{I}_\mathrm{c}) \cup (J-T$ distortion trajectory $\mathbf{4} \to \mathbf{I}_\mathrm{d}) \cup (\partial\mathcal{D} \to \mathbf{I}_\mathrm{d})$, where $\mathcal{D}$ is a region invariant under the gradient field of the PES.

2. The IRCS Graph

It follows from the discussion of the previous section that the IRCS graph of the gradient field for a structurally stable PES is subject to the following restrictions:

1) There are three minima in the domain $\mathcal{D}$: **1**, **2**, **3** represented in the graph by three sink vertices.

2) The separatrix between the basins of **1** and **2** is represented by the union of the two directed edges $\mathbf{4} \to \mathbf{I}_\mathrm{c}$ and $\partial\mathcal{D} \to \mathbf{I}_\mathrm{c}$. The separatrix between the basins of **1** and **3**, by the union of the two directed edges $\mathbf{4} \to \mathbf{I}_\mathrm{d}$ and $\partial\mathcal{D} \to \mathbf{I}_\mathrm{d}$.

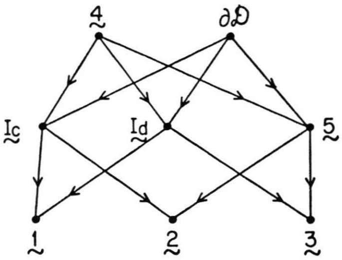

Fig. 3.

3) A transition state **5**, corresponding to the symmetry-forbidden interconversion $\mathbf{2} \leftrightharpoons \mathbf{3}$ is represented by a saddle vertex **5**.

4) The separatrix between the basins of **2** and **3** is $M^s(\mathbf{5})$ and it is represented by the directed edges $\mathbf{4} \to \mathbf{5}$ and $\partial\mathcal{D} \to \mathbf{5}$. The only IRCS graph satisfying these restrictions is displayed in Figure 3.

3. Closed Shell Electronic Correlation Along the IRC's

The structural stability proof that the lumomers [8] $\mathbf{I}_\mathrm{c}$ and $\mathbf{I}_\mathrm{d}$ are not interconvertible is the rigorous proof. The argument based on the frontier orbital diagram is not since a single Slater determinantal wave function is a poor approximation for the electronic wave function $\Psi_{\mathrm{I_d}}$ of $\mathbf{I}_\mathrm{d}$. $\Psi_{\mathrm{I_d}}$ requires configuration interaction.

The closed shell electron correlation diagram for the conversion $\mathbf{1} \leftrightharpoons \mathbf{3}$ (the disrotatory opening), exhibits crossing of electronic states of the same symmetry [9].

These states are $(\sigma^2\pi^2 - \chi_1^2\chi_3^2)$ and $(\sigma^2\pi^{*2} - \chi_1^2\chi_2^2)$ $\sigma^2\pi^2$ and $\chi_1^2\chi_2^2$ are the ground states of cyclobutene and of butadiene respectively and $\sigma^2\pi^{*2}$ and $\chi_1^2\chi_3^2$ their respective first doubly excited states. Therefore an approximation to $\Psi_{\mathrm{I_d}}$ should take the form $\Psi_{\mathrm{I_d}} = c_1|\sigma^2\pi^2\rangle + c_2|\sigma^2\pi^{*2}\rangle$. The correlation along the IRC $\mathbf{1} - \mathbf{I}_\mathrm{c} - \mathbf{2}$ is $\sigma^2\pi^2 - \chi_1^2\chi_2^2$. Along the IRC $\mathbf{1} - \mathbf{I}_\mathrm{d} - \mathbf{3}$: $\sigma^2\pi^2 - \Psi_{\mathrm{I_c}} - \chi_1^2\chi_2^2$. And, along the separatix $\mathbf{I}_\mathrm{c} - \mathbf{4} - \mathbf{I}_\mathrm{d}$: $\Psi_{\mathrm{I_c}} - \Psi_{\mathrm{I_d}}$ (certainly not in correspondence with the HOMO-LUMO crossing in Figure 2).

4. Conclusion

The symmetry-forbidden interconversion $\mathbf{1} \rightleftharpoons \mathbf{3}$ is equivalent to the virtual process $\mathbf{1} \rightleftharpoons \mathbf{I}_\mathrm{c} \leftrightharpoons \mathbf{I}_\mathrm{d} \leftrightharpoons \mathbf{3}$. Only the portion of the path $\mathbf{I}_\mathrm{c} \leftrightharpoons \mathbf{I}_\mathrm{d}$ is forbidden.

The structural stability proof of the forbiddness of the interconvertion of **1** and **3** is an alternative and rigorous proof agreeing with the conclusion derived by inspecting the electronic state correlation diagram (c.f. [9]).

The "concertedness" of the forbidden pathway should be interpreted as follows: It is proven in this paper that the symmetry-forbidden disrotatory conversion **1** $\rightleftharpoons$ **3** involves a transition state which is the Jahn-Teller distortion of the 2-butene diradical **4**. This result agrees with the conclusions presented by J. A. Berson (c.f. [10]) in the sense that the forbidden pathway does not proceed stereorandomly via a diradical intermediate.

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