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Jahn-Teller distortion motions as separatrices in PES

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The topology of the pattern of intrinsic reaction coordinates and separatrices is investigated for 6-electron sigmatropic pericyclic rearrangements.

It is demonstrated that the trajectories of nuclear motion involving HOMO-LUMO crossing are the separatrices of the basins of the chemical species involved. The special case of the Diels-Alder cycloaddition is analyzed.

Key words: Singlet biradical — Jahn-Teller distortion — Separatrix — Structural stability of a dynamical system

1. Introduction

The application of the combinatorial-topological IRCS (intrinsic reaction coordinate and separatrix) graph technique was introduced in previous work [1, 2] for the design of reaction pathways.

The IRCS graph represents the connections of the integral curves of nuclear motion joining critical configuration points of the gradient field of adiabatic PES.

The topology of the full pattern of IRC's and separatrices determines the relative distribution of the basins of attraction of the chemical species.

For each overall reaction, we have several IRCS graphs, each one representing a whole equivalence class of reaction mechanisms (cf. [1] and [2]). The combinatorial rules for building such graphs are subject to the restriction of structural stability in the sense of Adronov and Pontriagin [1-3].

The structural stability restriction holds also in the phase portraits of phenomenological kinetics as studied by Ariel Fernández and Oktay Sinanoğlu [4-6].

2. IRCS graphs for six-electron pericyclic processes

The trajectories connecting singlet biradical configurations to their stabilized Jahn–Teller distortions [7] separate the basins of attraction of the 1,5-hexadienes in their (degenerate) Cope rearrangement [1].

In general, when the single occupied AO's in the singlet biradicals for thermal six-electron rearrangements can interact via hyperconjugation with C–C $p\sigma$ bonding and antibonding orbitals, the integral curves along which HOMO-LUMO crossings occur are the separatrices [1].

Consider as an illustration the 2 + 4 cycloaddition **1** → **2**. The high stereospecificity of the reaction is regarded as persuasive evidence that the concerted transition state alternative holds [8].

Nevertheless, the orientation of addition of monosubstituted diene and monosubstituted dienophile has been taken as evidence for the stepwise process involving a biradical species [9]. The single occupied AO's ϕ_1 and ϕ_2, on C_1 and C_6 respectively, interact in three different ways as shown in Fig. 2:
(i) by hyperconjugation with the C_4–C_5 $p\sigma$MO;
(ii) with the C_2–C_3 π bonding orbital;
(iii) directly with each other.

The Jahn–Teller distortion **4** → **3** leading to the hyperconjugative interaction with the $p\sigma C_4$–C_5 bonding orbital has HOMO $\phi_1+\phi_2$ and LUMO $\phi_1-\phi_2$. The situation is reversed when the distortion leads to the interaction with the antibonding $p\sigma C_4$–C_5 MO; (**4** → **3′**) the HOMO being now $\phi_1-\phi_2$.

The biradicaloids **3** and **3′** are not interconvertible: they are transition states directly connected to the biradicals **4** and **5**, therefore **4** and **5** are not transition states themselves since that would violate the structural stability principle [1] which precludes saddle-saddle direct connections. It can be then concluded that

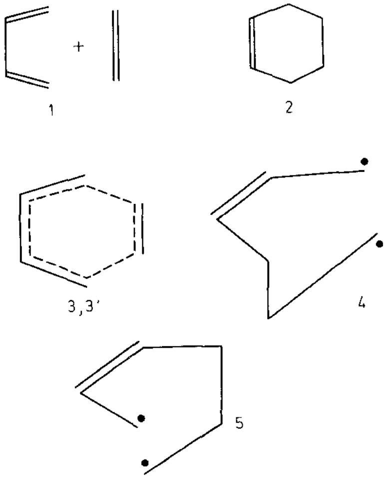

Fig. 1

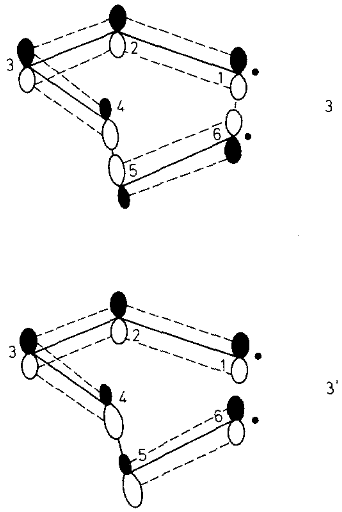

Fig. 2

4 and **5** are critical points with Hessian (force constant) matrix having at least two negative eigenvalues. This conclusion is in agreement with the fact that **3′** and **3′** are lumomers of one another therefore their interconvertion is forbidden [7].

In order to build the IRCS graph, one first considers an invariant region $\mathscr{D}$ (Fig. 3a) such that the gradient field points inwards along $\partial\mathscr{D}$.

$\mathscr{D}$ contains no critical points other than **1**, **2**, **3**, **3′** and **4** since the following version of the Euler–Poincaré relation holds (cf. Ref. 1):

$$\#\,\text{biradicals} - \#\,(\text{biradicaloids-transition states}) + \#\,\text{chemical species} = 2.$$

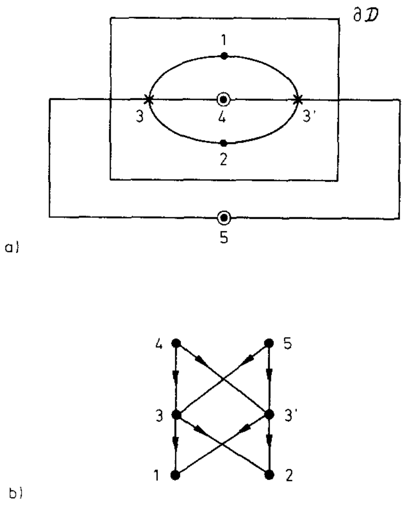

Fig. 3

Hence the IRCS graph is subject to the following restrictions:
(i) there are only two source vertices corresponding to the two biradicals **4** and **5**;
(ii) there are two saddle vertices corresponding to the two Jahn–Teller distortions of the biradicals;
(iii) when the Jahn–Teller distortion **4**→**3** is pursued further, it produces species **5** since it leads to the breaking of the σ-bond C_4–C_5 which was interacting via hyperconjugation and the enhancement of the direct interaction of the AO's ϕ_1 and ϕ_2 leading to the formation of the σ-bond C_1–C_6. Moreover, it can be shown analogously that the separatrix is the closed integral curve **4**→**3**→**5**→**3′**→**4**.

The only IRCS graph satisfying these restrictions is depicted in Fig. 3b.

3. Conclusion

The classical transition state configurations were rigorously characterized in the work of Murrell, McIver and their coworkers by means of the Hessian (force constant) matrix: At such configurations the matrix has a single negative eigenvalue corresponding to the promoting mode and there is no vanishing eigenvalue [11–15].

Since in structurally stable models no critical configuration with a metastable mode can occur (there are no vanishing eigenvalues in the Hessian matrix at critical points), only transition states in the sense of Murrell and Laidler can be involved in the case we are considering in the present work. That is, we regard transition states as saddles of index one. Direct saddle-saddle connections are precluded by the structural stability principle.

Since the biradicals **4** and **5** decay without activation energy to the biradicaloids **3** and **3′** via Jahn–Teller distortions, it follows that the configurations **4** and **5** cannot be themselves transition states as **3** and **3′** are. Otherwise, there would be a meta-IRC connecting two saddles without passing through any other critical point in between.

The closed meta-IRC **4**→**3**→**5**→**3′**→**4** is a separatrix which determines two regions, the one interior to it being the basin of attraction of the Diels–Alder adduct **2** and the one exterior being the basin of attraction of the species **1**. The two IRC's joining **1** and **2** pass through the biradicaloids **3** and **3′**.

It should be emphasized that the definition of Murrell and Laidler [11] not only satisfies the structural stability restrictions but it is regarding transition states in this sense that one can rule out the biradical pathway and elucidate the nature of the interconvertion **1**→**2**. Our results ruling out the biradicals as the transition states in the process are in perfect agreement with the conclusion of Murrell [12] concerning the application of the Jahn–Teller theorem to transition states: If at the biradical configuration there are two modes with negative curvature (the Jahn–Teller distortion mode and the promoting mode), there must be [11, 12] a lower energy path for the reaction than the one passing through the biradical configuration.

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