

Pattern of separatrices and intrinsic reaction coordinates for degenerate thermal rearrangements

Ariel Fernández

Department of Chemistry, Yale University, New Haven, CT 06511, USA and Chemical Physics Dept., The Weizmann Institute of Science, 76100-Rehovot-ISRAEL

A structurally stable model of the standard adiabatic gradient field of the potential energy surface for certain pericyclic reactions is derived.

These reactions are not subjected to the principles of orbital isomerism or to the Woodward–Hoffmann rules.

Use is made of a principle established by Ariel Fernández and Oktay Sinanoğlu which precludes direct meta-IRC connections between transition states.

It is shown that Jahn–Teller isomers of the singlet biradicals involved in the process are not interconvertible since the biradical configuration is not a transition state but a critical point with Hessian matrix with two negative eigenvalues.

The topological features of the PES obtained by combinatorial methods are in full agreement with earlier results obtained from MINDO calculations.

Key words: Direct graph representing a planar dynamical system—degenerate Cope rearrangement—structural stability of a PES—biradicaloid intermediate

1. Separatrices passing through singlet biradical configurations

An IRCS graph [1, 2] represents the full set of integral curves that join critical points in a representative of an equivalence class of gradient fields of adiabatic potential energy surfaces. It contains the mechanistic information on the chemical process given by the pattern of intrinsic reaction coordinates (IRC's, [3]) and the relative distribution of the basins of attraction of the chemical species [4]. Ariel Fernández and Oktay Sinanoğlu have proven in previous work that the boundaries of these basins are given by the meta-IRC's [3] joining transition

states to nuclear configurations with two unstable degrees of freedom. These integral curves are called separatrices [4].

The combinatorial rules for building the IRCS of a given overall reaction narrow down to an adequate coupling of a pattern of IRC's to a pattern of separatrices.

An example of separatrix is the meta-IRC joining one singlet biradical configuration (like the boat conformer **5** or the chair conformer **6**; see Fig. 1) with a transition state configuration obtained by a Jahn-Teller distortion of the biradical which lifts its orbital degeneracy ([1], [5]) and stabilizes one particular linear combination of the single occupied atomic orbitals.

The two Jahn-Teller (J-T) isomers are transition states (the Hessian matrix H has only one negative eigenvalue) and the biradical (**5** or **6**) decays to them without activation energy. This decay corresponds to a Jahn-Teller distortion which is represented in the IRCS graph by a meta-IRC edge joining a saddle point vertex (one of the J-T isomers) with the critical biradical configuration vertex.

Since the PES is structurally stable in the sense of Adronov and Pontriagin [1], [6], there are no critical points which have H with a zero eigenvalue and, also, direct saddle-saddle connections are forbidden.

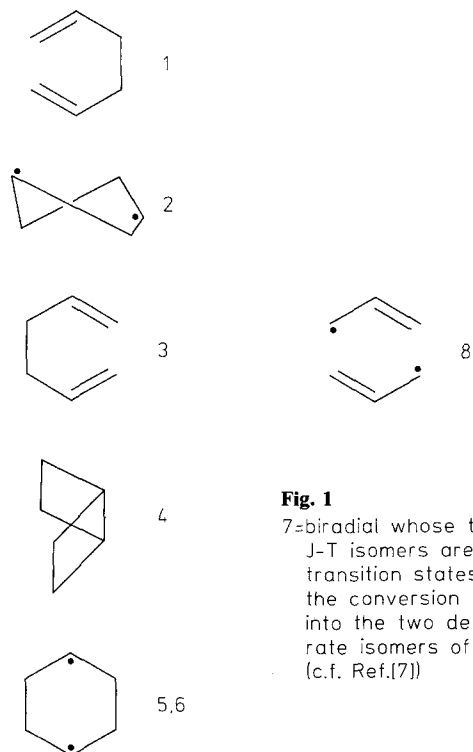


Fig. 1
7-biradical whose two J-T isomers are the transition states of the conversion of **2** into the two degenerate isomers of **4** (c.f. Ref.[7])

Therefore, it can be stated that **5** or **6** cannot be classical transition states for if they were, their respective Jahn–Teller distortions would be direct saddle saddle connections in the PES.

Hence, **5** and **6** are critical configurations for which H has two negative eigenvalues. Also, the interconversion of the J–T isomers is then forbidden since the meta-IRC joining them passes through a critical configuration which, in addition to the promoting vibrational mode, presents another unstable degree of freedom.

Other illustrations of this principle can be found in an early work (cf. [2]).

The conclusion thus derived from the principle of forbidden direct meta-IRC connections of transition states thoroughly agrees with the HOMO-LUMO non-crossing rule which precludes the interconversion of lumomers, [7].

2. IRCS graph for a degenerate Cope rearrangement

It was first suggested by Doering and co-workers [8] that the Cope rearrangement $3 \rightleftharpoons 1 \rightleftharpoons 4 \rightleftharpoons 3$ involves a biradicaloid [7] intermediate analogous to the chair and boat conformers of the 1,4-cyclohexylene biradical.

The existence of such a stable species can be elucidated by combinatorial-topological rules as shown below.

In order to count the number of critical configurations in the APES we first isolate a region \mathcal{D} in the configuration space so that the gradient field points inwards along its boundary $\partial\mathcal{D}$.

All the separatrices passing through the biradicals **5**, **6**, **7** join their respective Jahn–Teller isomers to the bond-breaking limit represented by the biradical **8**.

The biradical configuration **8** is excluded from the region \mathcal{D} so that the standard adiabatic gradient field points inwards.

If M represents the number of nuclear configurations with two unstable vibrational modes; S , the number of saddle point-transition states and C , the number of chemical species, we have (cf. [1]):

$$M - S + C = 2$$

or: number of biradicals – number of Jahn–Teller isomers + $C = 2$.

Only the biradicals **5**, **6**, **7** have associated Jahn–Teller isomers, hence $4 - 6 + C = 2$.

*This means that the PES presents four minima within \mathcal{D} therefore there exists one and only one stable intermediate besides the stable species **1**, **3** and **4**.*

This conclusion is in agreement with MINDO calculations of Dewar et al. [7], [9] who found a stable intermediate **2** such that all the transition states decay without activation energy to it.

Therefore the construction of the IRCS graph is subject to the following restrictions;

- a) There are four source vertices corresponding to the four biradical configurations.
- b) There are six saddle vertices corresponding to the six J-T isomers-transition states.
- c) There are four sink vertices corresponding to the three species **1**, **3** and **4** and the stable intermediate **2**.
- d) The bond-breaking limit configuration vertex representing the biradical **8** presents six outgoing edges, each directed to a different saddle point vertex.
- e) The sink vertex for the stable intermediate **2** presents six incoming edges corresponding to the six IRC's representing the decaying without activation of the six transition states to the intermediate.
- f) All the other sinks or sources present two edges respectively incoming or outgoing. They correspond to two IRC's or to two separatrices.

There is only one IRCS graph which satisfies the restrictions a)-f) and it is represented in Fig. 2.

The basins of attraction of the stable species **1**, **2**, **3** and **4** are limited by the boundary $\partial\mathcal{D}$ and by the three separatrices **8-5-8**, **8-6-8**, **8-7-8**.

Supporting the view of Dewar and co-workers [7, 9], the basin of the stable intermediate **2** is surrounded by a "crater of biradicaloid species" given by the portion of the three separatrices lying within the preserved region \mathcal{D} .

The only "routes of access" to the species **2** from the basins of **1**, **3** and **4** are the six IRC integral curves which enter the region delimited by the three separatrices (cf. Fig. 3).

In an early paper [1] A. Fernández and O. Sinanoğlu have shown how the "concerted" transition state becomes a J-T isomer of the biradical configurations **5** and **8**. This view agrees with the results presented in the present paper where

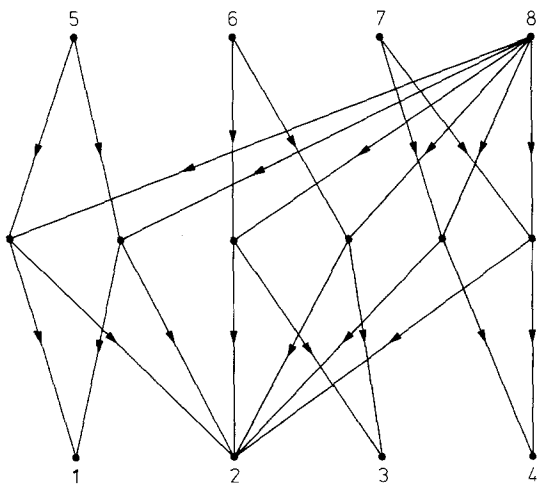


Fig. 2

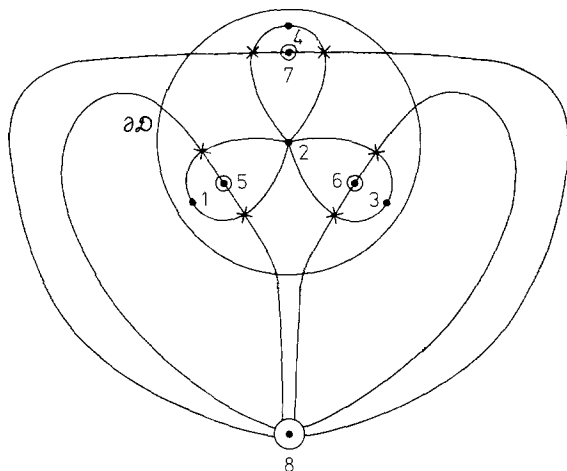


Fig. 3

a higher resolution of the PES exhibits the “Eyring lake” depression **2**. (also cf. Sect. 4 paper [1]).

In the early picture presented in Ref. [1], the high stereospecificity of the reaction makes the “concerted” transition state to be preferred over the other J-T isomers of the biradicals **5** and **8**.

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