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Photochemistry by conical intersections: a practical guide for experimentalists

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Abstract

Many photochemical reactions are believed to proceed through conical intersections. The properties of conical intersections leading to the ground state of a given system are discussed using the phase-change rule: the ground-state total electronic wave function changes its sign when the system is transported along a complete loop around a conical intersection. It is shown that this property may be used to find the conical intersections present in the system, to predict possible products and even the energy disposal. An important corollary is that in a photochemical reaction involving a conical intersection, more than one product is necessarily formed. One of the products is always a 'photochemically allowed' one (Woodward–Hoffmann nomenclature), the second may be a thermally allowed one. A method to qualitatively predict the geometry of a conical intersection is presented and compared with previous calculations. For the 1,4-hexadiene system, the method was shown to help in locating computationally a conical intersection that can lead to the formation of benzene and H_2, accounting for the 'helicopter-type' motion observed by Lee and coworkers [J. Chem. Phys. 95 (1991) 297]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Conical intersections; Photochemistry; 1,4-Hexadiene; Phase of electronic wave function

1. Introduction

Conical intersections, introduced over 60 years ago as possible efficient funnels connecting different electronically excited states [2], are now generally believed to be involved in many photochemical reactions. Direct laboratory observation of these sub-surfaces on the potential surfaces of polyatomic molecules is difficult, since they are not stationary 'points'. The system is expected to pass through them very rapidly, as the transition from one electronic state to another at the conical intersection is very rapid. Their presence is surmised from the following data [3–9]:

- very rapid (sub-picosecond) decay of electronically excited states;
- lack of fluorescence;
- rapid formation of products.

In particular, ultrafast experiments, such as reported in [3–7], are readily interpreted in terms of conical intersections.

In recent years, computational evidence for the existence of conical intersections in many polyatomic systems is compelling (see papers by M. Klessinger, M.A. Robb, and by T.J. Martinez in this volume). The existing consensus concerning the ubiquitous existence of conical intersections is due in large part to computational 'experiments'.

In this paper, we present a qualitative analysis of conical intersection based on chemical concepts. We limit the discussion at this point to photochemical reactions leading to ground-state products. This fact means that the system must cross from the electronically excited state to the ground state before, during, or after the final products were formed. We propose that when a conical intersection is involved, the final reaction takes place after the crossing, and the nature of the products depends on the particular conical intersection. The nature of the conical intersection can be predicted based on the properties of the ground electronic surface only. Thus, we propose that the coordinates defining the conical intersection are reaction coordinates connecting the reactant with possible products by elementary chemical reactions.

The analysis is based on the phase-change rule, summarized by Longuet-Higgins [10] and Herzberg [11] as follows: 'a conical intersection necessarily arises within a region enclosed by a loop along which the total electronic wave function changes sign'. A conical intersection is defined as the locus at which two potential curves cross when plotted against two nuclear coordinates. Since a conical intersection in an n-atomic nonlinear molecule is a hypersurface of dimension $3n-8$ and $3n-7$ in a linear one (a rather rare

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situation), several local minima may be found on a given conical intersection when plotted against the other coordinates.

Two coordinates are required to define the basis of a cone and thus for the location of a conical intersection. Several procedures have been suggested to find them ([12–16] and references therein). Our method [17,18] is a chemically oriented one, based on reaction coordinates. A Longuet-Higgins loop can be constructed by using these coordinates, as has been done for instance in the case of the $H_2 + H$ system [10,11]. Suppose we choose the reactant A and a desired product B as two ‘points’ on the potential surface, and the reaction coordinate leading from A to B as one of the coordinates. In order to complete a loop, we need a third ‘point’ C which is chemically distinct from both A and B. The reaction coordinate leading from B to C (or from A to C) may be chosen as the other coordinate. In order to qualify, all reactions must be elementary, i.e. the transition from reactant to product involves only one energy barrier. A Longuet-Higgins loop may now be formed by transporting the system along the trajectory ABCA, and the overall phase change is given by the combination of the phase changes incurred in the individual reactions.

Thus, the construction of a Longuet-Higgins loop is intimately connected with the concept of the phase change of the total electronic wave function during a chemical reaction. It has been suggested [19,20] that the total electronic wave function changes continuously during the reaction from that of the reactant (ϕ_R) to that of the product (ϕ_P). The electronic wave function of the transition state may be represented by a linear combination of the electronic wave functions of the reactant and the product. Of the two possible combinations, the in-phase one (Eq. (1)) is phase preserving (p-type), while the out-of-phase one (Eq. (2)) is phase inverting (i-type).[1] Normalization constants are assumed in both equations:

$$\phi_{\mathrm{in}} = \phi_R + \phi_P \quad \text{(phase preserving transition state)} \tag{1}$$

$$\phi_{\mathrm{out}} = \phi_R - \phi_P \quad \text{(phase inverting transition state)} \tag{2}$$

Well-known examples of the former are aromatic transition states, such as found for instance in ‘thermally allowed’ reactions (the Diels–Alder reaction is an example). The latter are found in ‘thermally forbidden’ reactions such as the cyclization of two olefins to a cyclobutane ring, the 1,3-shift of the methyl group in propene, and the isomerization of one rectangular form of cyclobutadiene to another.

The four possible combinations for loops containing three molecules are: p^3, ip^2, pi^2, and i^3. Of these, only i^3 and ip^2 lead to an overall phase inversion. Thus, in the search for conical intersections, we look for triads ABC that will lead to either one of these combinations.

The mechanisms by which a phase change on the ground-state surface can take place have been extensively discussed. One involves the creation of a negative overlap between two adjacent atomic orbitals during the reaction (or an odd number of negative overlaps) [21–23]. A reaction in which this happens is termed Möbius-type. One well-known example of a Möbius reaction is the conrotatory ring closure in pericyclic reactions. We refer to this mechanism as the orbital overlap mechanism. In this case, a new node is

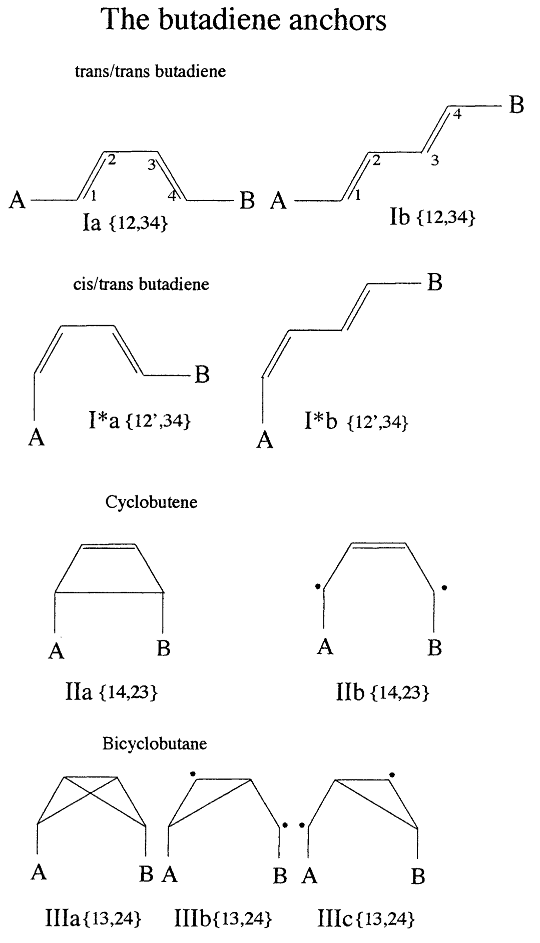

Fig. 1. Examples of anchors used to find conical intersections of the butadiene system: (I) two structures of *trans*/*trans* disubstituted butadiene; the spin pairing of the four π electrons is {12, 34}; (I*) two structures of *cis*/*trans* disubstituted butadiene; the spin pairing of the four π electrons is {12′, 34}; the *cis*/*trans*-isomerization of ethylene is a four-electron process [28]; in the *trans*-isomer, the pairing of the four electrons of the double bond is {12, 1′2′}, while in the *cis*-isomer it is {12′, 1′2}; (II) two structures of cyclobutene (IIa is obtained from Ia by disrotatory closure, see Fig. 3); (III) three structures of bicyclobutane.

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[1] A useful method to recognize a phase-inverting reaction in systems with symmetry higher than C_1 is by the symmetry properties of the electronic wave function of its transition state. If this wave function is invariant with respect to all symmetry operations of the relevant point group, the reaction is phase preserving. The electronic wave function of the transition state transforms as the totally symmetric irreducible representation (irrep) of the group. If the electronic wave function of the transition state is anti-symmetric with respect to even only one symmetry operation, it transforms as one of the non-totally symmetric irreps of the group. This property signifies a phase-inverting reaction.

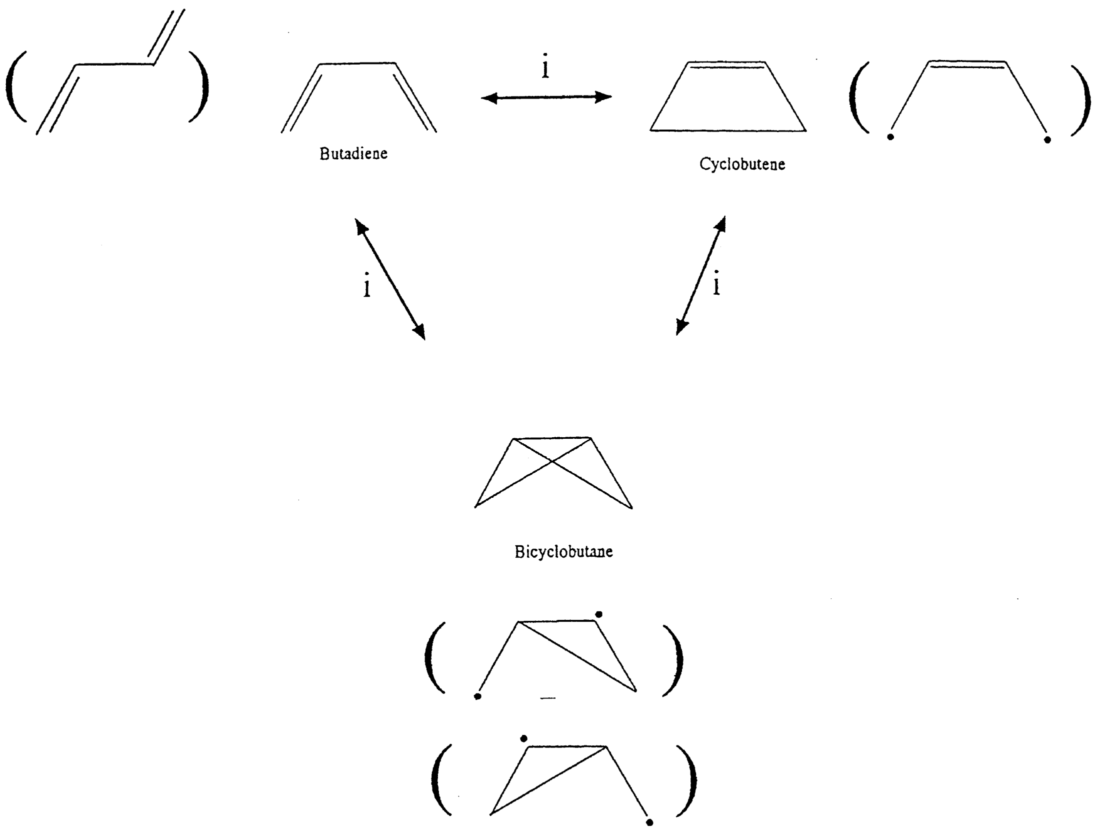

Fig. 2. A Longuet-Higgins loop for the butadiene system. The reactions shown are all Hückel-type and involve the re-pairing of two electron pairs. Therefore, they are all i-type, and the loop is an i^3 one. By the phase-change rule, there is a conical intersection within the loop. Each anchor contains several species.

formed along the reaction coordinate.[2] A reaction in which all overlaps between adjacent atomic orbitals along the reaction coordinate are positive (or such that the number of negative overlaps is even) is termed Hückel-type. Hückel-type reactions are the only ones possible when only s orbitals are involved. In Hückel-type reaction, no new nodes are formed along the reaction coordinate (see footnote 2).

The second mechanism is due to the permutational properties of the electronic wave function and is therefore referred to as the *permutational mechanism* [18,24]. We shall consider mainly Hückel-type systems; for these, it has been shown that if an even number (2, 4, etc.) of electron pairs are exchanged in a reaction, the reaction is phase inverting, while if an odd number of electron pairs (1, 3, etc.) is exchanged, the reaction is phase preserving. The latter case brings to mind Hückel's criterion for aromaticity, therefore the transition state for these reactions is referred to as aromatic transition state. The transition state of the phase-inverting reactions is antiaromatic.

Phase-inverting reactions are rarely observed thermally, since they are normally characterized by high barriers, and other reactions dominate. However, they are important in photochemistry, where the initial energy is high enough to overcome the barrier. Phase-inverting reactions are always involved in conical intersections.

The chemical species, around which the loop is formed, are termed 'anchors' of the loop. They are represented by their Lewis structures, i.e. by spin pairing. In this paper, we deal only with singlet-state reactions, so that all 'points' are spin-paired systems. Spin pairing does not completely define the geometry of the system. Thus, two conformers have the same spin pairing; likewise, a biradical has the same spin pairing as when the two electrons are found in a bond. A discussion of the properties of anchors and their relation to VB resonance hybrids is given in Section 3.1.

In this paper, we show that using the phase-change rule (the requirement of an overall phase change to locate a conical intersection) allows the prediction of all possible conical intersections of a given system. The passage through the conical intersection is very rapid, and the reaction products are formed on the ground potential surface. In contrast with thermal reactions, the system can end up in 'thermally forbidden' products. However, the complete dichotomy between 'thermally allowed' and 'photochemically allowed' reactions, suggested by one-dimensional correlation diagrams [25–27], does not hold in these cases: a 'thermally allowed' product

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[2] In general, in Hückel-type reactions, an even number of new nodes may be formed along the reaction coordinate, and in Möbius-type ones, an odd number.

is formed from a ip^2 conical intersection. On the other hand, an i^3 conical intersection will lead to two 'photochemically allowed' products.

2. Analysis of photochemical reactions using the phase-change rule

We demonstrate the approach by analyzing two photochemical systems for which conical intersections were suggested to be involved. Beginning with the definition of the anchors for these systems, we construct Longuet-Higgins loops, show how different conical intersections may be located, and relate them to observed photochemical results.

2.1. Photochemistry of butadiene

The construction of Longuet-Higgins loops may be introduced by a four-electron system such as butadiene (considering for now only the four π electrons). Photolysis leads mainly to the formation of cyclobutene: the spin pairing changes from $\{12, 34\}$[3] to $\{14, 23\}$ (see Fig. 1). The only third possible spin-pairing scheme is $\{13, 24\}$, which can lead either to a biradical or to bicyclobutane. The latter is a strained molecule; under ambient conditions, it reverts to the more stable butadiene. It has been found to form photochemically in matrix isolation experiments [29].

Fig. 2 displays the Longuet-Higgins loop formed by butadiene, cyclobutene, and bicyclobutane; some other species belonging to these anchors are also shown. Electrons are represented in this simplified version by dots, bonds by lines.

The same system is presented in some more detail in Fig. 3. The p-electrons are represented schematically by the contor of the p-orbital, and the sign of the electronic wave function is shown. If the ring closure of butadiene to cyclobutene is disrotatory, the reaction is phase inverting (the transition state is antiaromatic), while if it is conrotatory, it is phase preserving. Ring closure to bicyclobutane, forming cyclopropane rings, may lead to the formation of a new node (if it is disrotatory) or not (if it is conrotatory). In both cases, the reaction will have the same parity starting from either butadiene or cyclobutene, as can be easily verified. Thus, if the butadiene ↔ cyclobutene ring closure is disrotatory, the loops are either i^3 or ip^2, and conical intersections must exist within them. On the contrary, if the cyclobutene ring closure is conrotatory, the loops are p^3 or a pi^2 ones. No conical intersection can exist within them. The exclusive observation of a disrotatory reaction is in-line with the involvement of a conical intersection in this case. This conical intersection was found computationally, and extensively discussed [30–32].

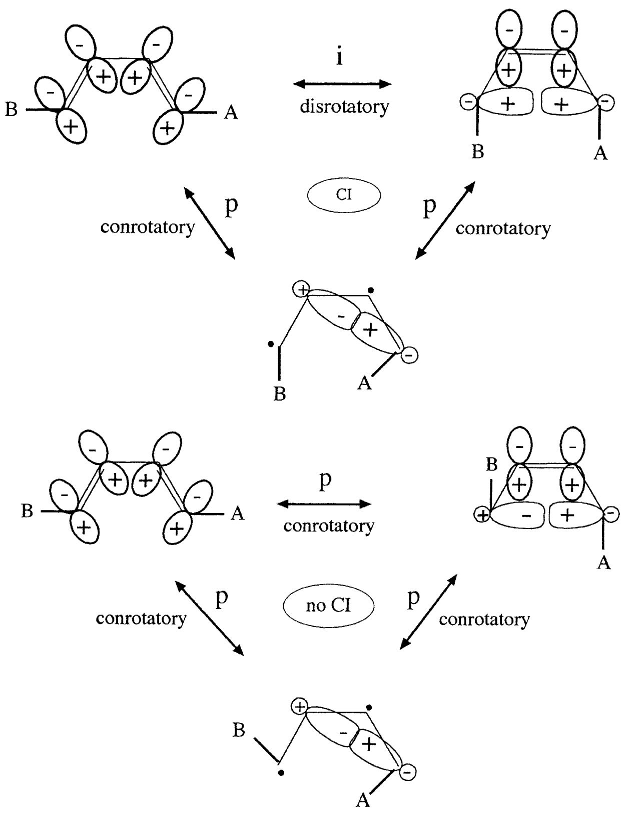

Fig. 3. A more detailed view of the butadiene system. Top: the disrotatory butadiene ↔ cyclobutene closure is phase inverting. The conversion of both to bicyclobutane is either p-type (for conrotatory formation of the cyclopropane rings) or i-type (for disrotatory formation of the cyclopropane rings). A loop constructed of the butadiene, cyclobutene, and bicyclobutane anchors is thus either ip^2 (as shown) or i^3. In either case, it includes a conical intersection (the bicyclobutane anchor is represented by a biradical for clarity). Bottom: a loop for the same system with a conrotatory butadiene ↔ cyclobutene closure which is phase preserving. It is either p^3 (as shown) or pi^2; no conical intersection is enclosed in the loop.

2.2. The 1,4-cyclohexadiene system

Fig. 4 shows some examples of anchors relevant to the 1,4-cyclohexadiene (1,4-CHDN) system. For this larger molecule, there are many more spin-pairing possibilities than for butadiene. In the analysis of photochemical experiments, one uses the minimum number of electrons needed to account for the spin-pairing changes. Structures IV and V are two of the three spin-pairing possibilities of 1,4-CHDN. Structure VIa is one of the six spin-pairing possibilities of 1,3-CHDN. The biradical form (VIb) is less stable than the

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[3] The notation $\{ij, kl\}$ denotes the spin pairing of electrons i with j (i.e. they must have opposite spins) and of electrons k with l. The two paired electrons may reside on the same atom, or on two different atoms. They are numbered by the atoms whose atomic orbitals they occupy. If more than one electron per atom is involved, it is marked by a dash ($'$). Thus, the notation $\{ij, i'j'\}$ represents two pairs of electrons belonging to the same two atoms, as in a double bond. The two electrons residing on the same atom necessarily occupy two different atomic orbitals in this case. We use a short hand notation, in which only electrons changing their spin partners are explicitly included. This notation is based on the idea of Lewis structures.

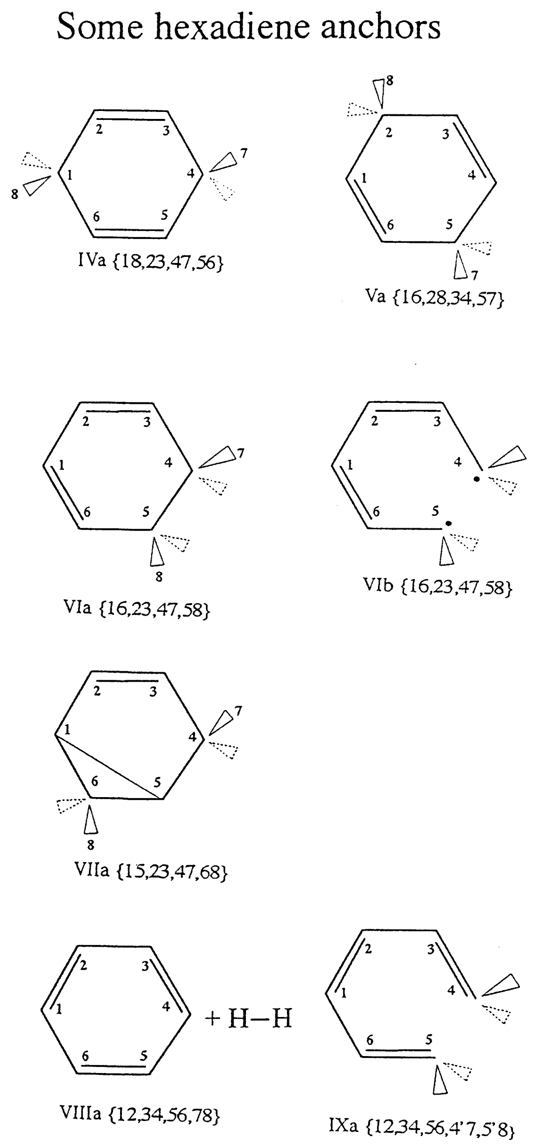

Fig. 4. Examples of anchors used to find conical intersections of the 1,4-cyclohexadiene system: (IV, V) two of the three spin-pairing possibilities of 1,4-CHDN; (VI) one of the six spin-pairing possibilities of 1,3-CHDN isomers (two structures shown); (VII) one of the 12 spin-pairing possibilities of bicyclo-[3,1,0]-hex-2-ene isomers; (VIII) benzene + H_2 (one Kekulé form shown); (IX) hexatriene.

closed form, but may have a local minimum. VIIa is one of the 12 spin-pairing possibilities of bicyclo-[3,1,0]-hex-2-ene (BCH) isomers.[4]

VIIIa is an anchor consisting of two molecules, benzene and H_2. Only one Kekulé form of benzene is shown; it turns out that for the analysis leading to a conical intersection, either form can be used. The transition from IV involves

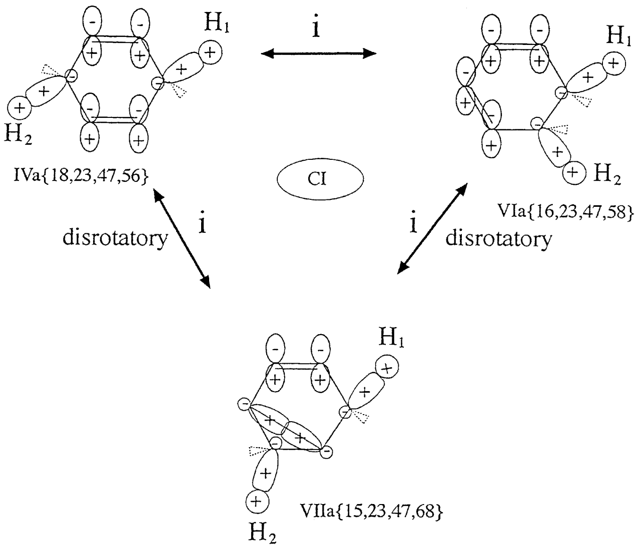

Fig. 5. A loop for the hexadiene system. The reaction converting 1,4-CHDN to 1,3-CHDN involves re-pairing of the p-electrons from {56} to {61} and the suprafacial motion of a hydrogen atom (H_2) from carbon atom number 1 to 5. Two electron pairs are re-paired in this Hückel-type reaction, making it a phase-inverting reaction. Likewise, the disrotatory ring closure of either CHDN to form the cyclopropane ring in BCH and the relocation of atom H_2 to carbon atom number 6 is a Hückel-type two-electron pair system, and thus also phase inverting. The loop is an i^3 one and contains a conical intersection.

in this case, the re-pairing of only three electron pairs.[5] Finally, structure (IXa) represents an open-chain molecule, hexatriene (IX). The formation of this molecule requires the breaking of a sigma C–C bond — we shall not discuss this product further in this report. In the discussion of the transformation of IV to any of the anchors represented by structures V through VIII, it is sufficient to consider the four electron pairs shown in the curled parentheses.

The major photo-products formed from 1,4-CHDN (IV) are [33] 1,3-CHDN (VI), BCH (VII), benzene, and hexatriene. Although not explicitly reported, it is likely that isomerization to other 1,4-CHDNs (such as Va) takes place. The simultaneous formation of VI and VII is readily understood if a conical intersection is involved, as shown in the Longuet-Higgins loop of Fig. 5. This i^3-type loop contains a conical intersection. Others may be formed using various anchors of the IV, VI, and VII type. Some were reported [34] as further discussed in Section 4.

None of these conical intersections is expected to lead to the formation of benzene and H_2 from 1,4-CHDN. Since the H_2 elimination reaction is phase preserving, it has been assumed to take place on the ground-state surface, following

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[4] The enumeration of the possible spin-pairing structures does not consider the fact that in these molecules, there are two tetrahedral carbon atoms which are potential chiral centers. Each enantiomer is a separate anchor, so that the total number of anchors in this system is much larger.

[5] In order to establish the number of electron-pairs re-pairing, it is sufficient to consider one Kekulé structure. The conversion of 1,4-cyclohexadiene to a Kekulé structure leaves one double bond intact, (in the example of Fig. 4, electrons 5 and 6). Thus, only three pairs are exchanged. This result holds for any of the three 1,4-CHDN structures and for any of the two Kekulé structures.

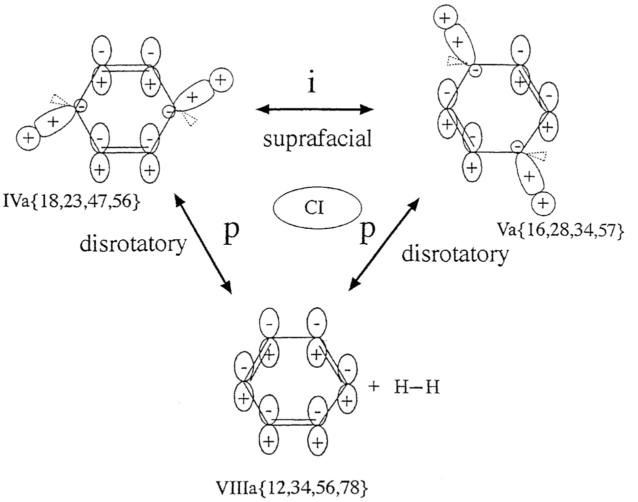

Fig. 6. A loop for the hexadiene system leading to the helicopter-type motion. The reaction converting 1,4-CHDN (IVa) to 1,4-CHDN (IVb) involves the relocation of two double bonds and the suprafacial motion of two hydrogen atoms. Four electron pairs are re-paired in this Hückel-type reaction, making it a phase-inverting reaction. The reaction of either CHDN to form the benzene ring and H_2 is a Hückel-type three-electron pair system, and thus phase preserving. The loop is an ip^2 one and contains a conical intersection.

IVR. However, such a mechanism is not compatible with the helicopter-type motion observed in the collision-free environment [1]. We therefore suggest that under those conditions, another conical intersection becomes operative. The loop in which this conical intersection may be found is shown in Fig. 6. As seen from the nature of the loop, a rotational motion of the H_2 fragment with respect to the C_6H_6 frame must take place. This ip^2 loop encloses a conical intersection that is expected to lie at a higher energy than the other two. Under collisional conditions, rapid vibrational relaxation tends to favor low-lying conical intersections. However, in the absence of collisions, this conical intersection may be operative. The existence of the conical intersection was confirmed computationally [36]. Its structure was found to be similar to that of the phase-inverting transition state between IVa and Va.

3. Discussion

The chemically motivated method for finding conical intersections, presented here, is based on the concept of electron pairs being a key element of chemical bonding. This idea was introduced by G.N. Lewis in 1916 [37], and eventually found support by the discovery of electron spin. Our method is based on using Lewis structures to represent molecules, and on the idea that the phase of the electronic wave function may change during a chemical reaction. Phase-inverting reactions are required for a Longuet-Higgins loop to enclose a conical intersections, and are thus connected with photochemical transformations involving passage through conical intersections. It has been shown by many authors [3] that a large number of photochemical reactions can be understood, if a conical intersection is assumed as a funnel to the ground state. Bernardi et al. [38] developed a computational method to locate the minimum of conical intersections, and their work established unequivocally the ubiquitous nature of these structures.

Our method extends previous work in providing a systematic way for locating all possible conical intersections as well as a classification. We distinguish between i^3 and ip^2 loops: the conical intersections located within these two loops have different properties. The i^3 loop leads to two ‘photochemically allowed’ (Woodward–Hoffmann nomenclature) products. The ip^2-type loop leads to one photochemically allowed product and also to a thermally allowed one.

3.1. *Anchors and resonance hybrids*

Anchors were introduced in order to classify different spin-pairing schemes. Each anchor represents a domain in the phase space of the system rather than a single point. Their relationship to other terms used in relation to the representation of molecules is now briefly discussed.

In VB theory, the ‘real’ structure of a molecule in its ground state is defined in terms of resonance structures. Each resonance structure has a different spin-pairing arrangement, and thus belongs to a different anchor. In that sense, a combination of structures should be useful for each anchor. This may be done, provided the correct sign for the electronic wave function of each structure is used. Thus, benzene may be represented by the in-phase combination of the two Kekulé structures, while butadiene would be represented by an out-of-phase [39] combination of structures Ia and IIb (with A and B taken to be H atoms). The relative contribution of each resonance hybrid to the equilibrium structure varies: in many cases, one VB structure dominates and may be used alone. In benzene, the two Kekulé forms contribute equally, and together provide a correct representation of the ground state. The contribution of other possible VB structures, such as Dewar benzene and the 170 possible ionic structures, is negligible [40,41].

In the case of butadiene, one VB structure dominates the properties of the ground state. The disrotatory ring closure of butadiene to cyclobutene involves an i-type transition state. In VB, the electronic wave function of the ground state may be written as the combination

$$\Psi(\text{butadiene}) = a\Psi(\text{I}) - b\Psi(\text{II}) \tag{3}$$

where $a \gg b$ and Ψ(I) and Ψ(II) represent the wave functions of I and II, respectively. Other VB structures are of minor importance [42]. The wave function of cyclobutene is represented by

$$\Psi(\text{cyclobutene}) = a'\Psi(\text{I}) - b'\Psi(II) \tag{4}$$

The transition state for the ring closure is phase inverting (ensured by the minus sign) in Eqs. (3) and (4). It is evident that either anchor could be used to construct the Longuet-Higgins loop, the natural choice being the dominant structure.

Different structures representing the same anchor (such as Ia and Ib) may have separate minima. The barrier is due to nuclear repulsion, and is usually quite small. A certain conformer may be preferred under certain conditions due for instance to steric effects. Two structures that differ only in the distance between the two atoms carrying the spin-paired electrons (such as IIa and IIb) are often not separated by a barrier, and only one of them will be formed at the end of the reaction. The structure of conical intersections is often such that the two atoms are further apart than in the stable molecule, as expected for a biradical. This may be the origin of photochemical mechanisms assuming the existence of biradicals as intermediates; yet these assumed intermediates were rarely observed directly [3]. Recent femtosecond experiments [43] may be interpreted as indicating the formation of biradicals in photo-excited systems.

4. Comparison with previous work

Efficient computational methods were developed recently by which conical intersections may be found and characterized [12–16]. Two coordinates, x_1 and x_2, are followed on the excited-state potential surface. The coordinates are defined as the gradient difference vector and the nonadiabatic coupling vector [12]. They lead from the Franck–Condon region to the lowest energy point in which the two electronic surfaces degenerate.

Our method uses ground-state properties only to locate approximately the conical intersection. Computation can be implemented by considering two coordinates: one that connects one of the products with the reactant, and the other that connects the transition state between them and a second product represented by the third anchor. The method can detect all possible conical intersections, regardless of the gradient on the excited-state surface. Quantitative calculations using this procedure were performed for the 1,4-CHDN to benzene conversion; a high-lying conical intersection compatible with the helicopter motion was found [36].

The phase-change rule may also be used to find which pairs of product cannot be formed from the same conical intersection. As shown in Fig. 7, the loop formed with 1,4-CHDN, benzene + H_2, and 1,3-CHDN as anchors is a pi^2 one, and thus does not contain a conical intersection.

The qualitative predictions of the phase-change rule method were found to agree with numerical studies. For instance, the conical intersection enclosed in the loop shown in Figs. 2 and 3 is the one computed in [30,31] and the disrotatory reaction mode in [31] the favored one.

The loop shown in Fig. 5 involves the re-pairing of four electrons, and encloses the H/allyl conical intersection found by Wilsey and Houk [34]. From its construction, it is clear that an active space of (4, 4) suffices in this case to pick up the main features of the conical intersection. By symmetry, other loops formed by different combinations of structural isomers of cyclohexadiene exist. They also enclose conical intersections that lead to 1,2- or 1,3-hydrogen shift reactions.

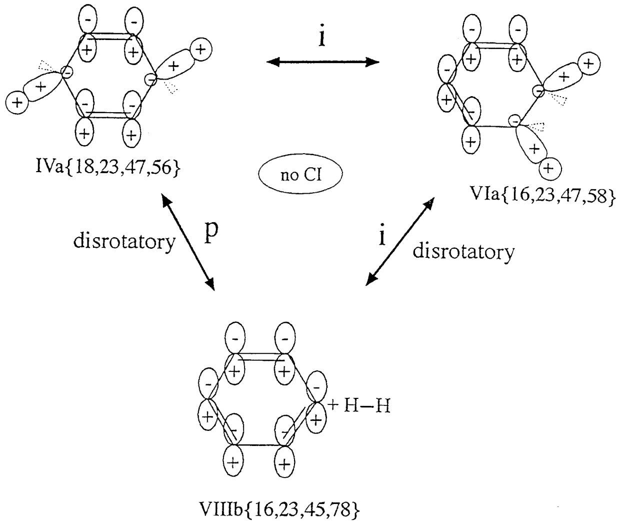

Fig. 7. A loop for the hexadiene system that does not contain a conical intersection. The reaction converting 1,4-CHDN (IVa) to BCH (VII) cannot proceed through a conical intersection, if the third anchor is 1,3-CHDN (VIa). The loop is an pi^2 one.

The alkyl/allyl one discussed by several authors [34,35] can also be found using the phase-change rule. Since a C–C bond is broken in this case, it is necessary to consider electron pairs within a sigma bond, which is beyond the scope of this paper. The construction of loops may help in determining the minimum active space required in the computation of conical intersections.

5. Summary

The phase-change rule provides a chemically oriented method for locating conical intersections. The method can be used systematically to obtain all possible conical intersections of a given system. Two products are expected for any reaction proceeding via a conical intersection, the phase-change rule providing a means to establish which pairs of products are possible. The method can be used to simplify the computational search for a conical intersection, as demonstrated for the photochemistry of 1,4-hexadiene [36].

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