J. Phys. Chem. A **1999,** *103,* 2364−2374

The Singlet-State Photophysics and Photochemistry of Polyenes: Application of the Twin-State Model and of the Phase-Change Theorem

Shmuel Zilberg and Yehuda Haas*

Department of Physical Chemistry and the Farkas Center for Light Induced Processes,
The Hebrew University of Jerusalem, Jerusalem, Israel 91904

Received: September 29, 1998; In Final Form: December 1, 1998

The A(2^1A_g) state of polyenes has been shown by Kohler and co-workers to be of central importance for the understanding of polyene photophysics and photochemistry. The twin-state model is used to provide a physical explanation for the well-known frequency exaltation of the a_g symmetric stretch mode frequency upon excitation of the molecule from the ground X(1^1A_g) state to the A(2^1A_g) state and for the increased stabilization of the planar form. The smaller members of the polyene series, ethylene and butadiene, are nonfluorescent, while higher members are. It is shown that the direct (singlet) photochemistry of all polyenes can be largely accounted for by assuming that these two lowest lying A_g states are connected by a conical intersection. The nature of the products and the stereochemical characteristics of the photoreactions can be rationalized using the phase-change theorem of Longuet-Higgins (Longuet-Higgins, H. C. *Proc. R. Soc. London A* **1975**, *344*, 147). A general procedure for locating the conical intersections and their associated products is suggested.

I. Introduction

Olefins and polyenes play a central role in organic photochemistry and in many biological photoactive systems. Kohler and co-workers[1] discovered the central role of the A(2^1A_g) state in these systems (we shall refer to this state as the A state, for brevity). It is now well-established that initial excitation to the B(1^1B_u) state (termed the B state throughout this paper) is followed by rapid internal conversion to the A state.[2] In the case of ethylene and butadiene, this is followed by nonradiative processes back to the ground X(1^1A_g) state (termed the X state), as deduced from the extremely small quantum yield of fluorescence ($<10^{-6}$).[2] The photochemistry of these smaller members of the series is well-documented, but not yet completely understood. Transition to the ground state was assumed to be important for many years[3] and was substantiated by quantum chemical calculations.[4−6] However, no systematic way of predicting the different products appears to have yet emerged.

For the larger members of the series, fluorescence from the A state was observed. Most studies were carried out at low temperatures using matrix isolation[1] or supersonic jets,[7,8] since a small barrier on the excited-state surface results in rapid deactivation at elevated temperatures. It has been found that in all members of the series, a state-specific frequency exaltation was observed: The totally symmetric a_g C═C stretch mode, whose ground-state frequency is about 1600 cm^{-1},[9] has a frequency of about 1720−1800 cm^{-1} in the A state.[1,7,8b,10−13] A similar phenomenon was observed for the b_{2u} Kekulé mode of benzene and its derivatives[14] upon excitation of the molecule from the ground X(1^1A_{1g}) state to the 1^1B_{2u} state. The analogy between these phenomena was noted, and both were assigned to vibronic interaction.[12,15] Another interpretation is that the A state is a kind of "double triplet", i.e., two triplet excitations coupled to create an overall singlet.[13] We have recently proposed a physical explanation for the aromatic series, made on the basis of the idea that the two states can be considered as twin states since they arise from the in-phase and out-of-phase combinations of two Kekulé structures, respectively.[16] In this paper, we show that a similar mechanism may be applicable to the polyene case. This interpretation is in the spirit of a suggestion by Kohler et al.,[11] that there is a bond reversal on going from the X to the A state.

In another context, the role of the conical intersections in organic photochemistry was recently discussed[17] in view of the phase-change rule formulated by Longuet-Higgins.[18−20] Two electronic states with the same symmetry cannot cross in a diatomic molecule,[21,22] but the crossing can take place in polyatomic systems via conical intersections.[18,23−28] It was shown that the products of a photochemical reaction can be predicted using the concept and that, in many cases, "thermally allowed" products[29] are formed along with "photochemically allowed" ones. The two lowest lying A_g states of polyenes can be connected by conical intersections, as recently shown by extensive quantum chemical calculations. We analyze these systems using the phase-change rule and show that the photochemical properties of the entire series, beginning with ethylene and carried through the larger polyenes, can be systematically accounted for.

The paper is organized as follows: In Section II, a brief summary of the theoretical background is outlined. For more information, more detailed papers should be consulted.[16,17] Section III discusses the nature of the A state as a twin of the ground state, leading to explanation of the frequency exaltation and the fact that for the longer polyenes, in contrast with ethylene and butadiene, the A state has a minimum at the planar conformation. Section IV discusses the photochemistry of the C_2, C_4, and C_6 members of the series and suggests a unified mechanism based on the role of conical intersections and the phase-change rule. Selection rules for the expected products of photochemical reactions are derived. Section V summarizes the present approach with an outlook to the longer members of the series.

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* To whom correspondence should be addressed. Tel.: 972-2-658 5067. Fax: 972-2-561 8033. E-mail: Yehuda@chem.ch.huji.ac.il.

† This paper is dedicated to the memory of Brian Kohler, who lighted up polyenes.

10.1021/jp983893e CCC: $18.00

II. Theoretical Background

All photochemical reactions begin by light absorption that elevates the molecule from the ground state to an electronically excited state. This state is usually at a higher energy than that required for most chemical transformations at the ground state. Since most photochemical reactions (certainly the ones dealt with in this paper) also terminate at the ground state, an essential part of the overall mechanism is the return of the system to the ground state. The geometries at which this process takes place have been termed funnels in the photochemical literature.[30−32] Two main types of funnels have been discussed: those in which the two electronic surfaces touch and those in which the touching is avoided. It has been shown by Teller,[23] and later elaborated by many other workers,[18−20,24] that in polyatomic molecules two different electronic surfaces (defined by the Born−Oppenheimer approximation) can cross, even if they are of the same symmetry. This takes place along two coordinates, defining a conical intersection. Longuet-Higgins[18] has shown that a conical intersection will be present inside a region enclosed by a loop, provided the total-electronic-wave function changes sign (phase) when transported a full circle around the loop. This theorem, which will be referred to as the phase-change rule, was later recognized as a special case of Berry's phase.[33]

To a large extent, experimentalists seem to have refrained from using the conical-intersection model until recently; in the past few years attempts to rationalize the results of ultrafast[34,35] and conventional[36] measurements have begun to emerge. This development is encouraged by recent theoretical and computational studies[4,5,26,27,37−39] demonstrating that, in fact, conical intersections are quite common. These unique loci connecting two potential surfaces account for the rapid internal conversion observed experimentally and for the properties of many photochemical transformations. The actual computation of the structure of conical intersections is difficult, since at the intersection point the Born−Oppenheimer approximation breaks down and standard-quantum-chemical methods are difficult to employ. Nonetheless, thanks mostly to the work of Olivucci, Bernardi, Robb, and their co-workers, the energy and geometry of many conical intersections were computed. Examples of polyenes for which it was computed that conical intersections play a dominant role in their photochemistry include butadiene,[4] hexatriene,[5,6] precalciferol (leading to vitamin D),[40] and C_5H_6-NH_2^+ Schiff base.[41] In these molecules, the excited state that touches the ground state is the 2^1A_g state, which is reached by a rapid nonradiative transition (probably via a conical intersection) from the optically populated 1^1B_u state. Since the products' distribution and stereochemistry is determined at the point at which the system returns to the ground state, it was argued that attention should be focused on the 2^1A_g state.

We propose to carry this argument further and to concentrate on the properties of the *ground state* at the vicinity of the conical intersection. Assuming, as the previous workers did, that the system reaches and traverses the conical intersection rapidly, it is the ground-state dynamics that determine the fate of the reaction thereafter. The difference from usual thermal reactions is that phase-inverting reactions are not only possible, but, in fact, essential for a conical intersection to be found. The phase-change rule states that a conical intersection is found somewhere inside a region whenever the phase of the electronic wave function changes sign upon being transported a full loop around that region. In a thermally allowed reaction this phase does not change, while in a photochemically allowed one it does. Therefore, a prerequisite for a conical intersection is that the loop will pass through an odd number of phase-inverting reactant−product transformations (1, 3, ...). There is no restriction on the number of nonphase-inverting transformations in the loop. This property makes it possible to predict, without carrying out any computation, the approximate location of any conical intersection, on the basis of the characteristics of the ground-state potential only.[17]

It was recently proposed that the procedure for doing so involves identification of molecular structures (termed "anchors" in the following) that define the loop and checking whether the electronic wave function changes phase upon being transported around the loop. A phase change at the ground state implies an antiaromatic transition state at the ground state, namely, a "forbidden" reaction. The simplest case is that of the smallest possible loop, which involves three anchors. This can be realized only if either one of the following conditions holds:

(1)The phase changes only once around the loop (Scheme 1a).

(2)The phase changes three times around the loop (Scheme 1b).

Two obvious, convenient anchors are the reactant and the assumed product; the required third structure can be obtained systematically, but is more conveniently found by chemical intuition. Whether or not a conical intersection is obtained can be checked without any computation and without explicitly considering the excited state, by applying the phase-change rule. The definition of the two coordinates leading to the conical intersection was discussed in ref 17. For the sake of completeness, Appendix A provides a brief description of these coordinates.

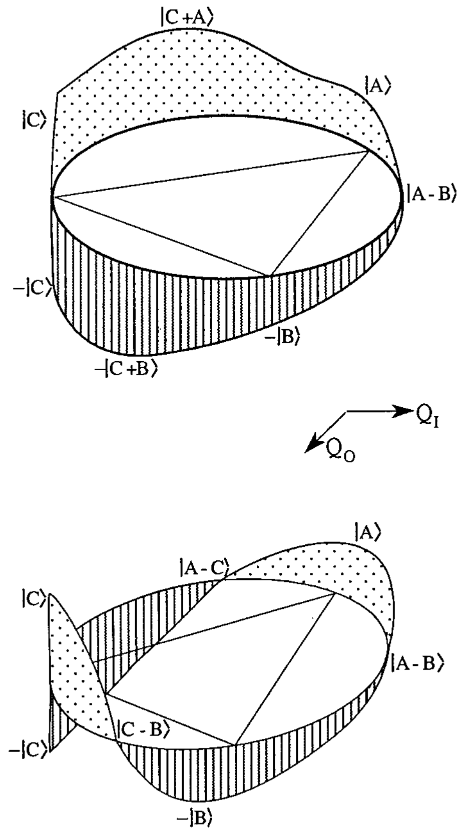
Evidently, in either case each loop may also contain any number of *thermally allowed* products. Likewise, any number of *pairs of thermally forbidden* products may be added to the loops. This shows that whenever a conical intersection is involved in a photochemical reaction a large number of possible products may be formed. However, if the different products are separated on the ground state surface by a high barrier (as is usually the case for chemically distinct species), any given conical intersection is expected to lead only to a small number of products (typically two, in a three-membered loop) directly. It is recognized that the two electronic states may touch in several distinct regions, each leading to different products. In any case, a mechanism involving a conical intersection leads, in principle, to at least two products, one of which *must* be thermally forbidden, while the other may be thermally allowed.

IIa. Downhill from the Conical Intersection—Spin Coupling Schemes and Anchors. After the system reaches the conical intersection, it may roll down the potential gradient into each of the three possible valleys defined by the anchors. This involves new-chemical-bond formation via spin coupling. In ref 17 the symmetric case of the H_3 system ($H_2 + H \rightarrow H + H_2$ reaction), which is a prototype for all 3-electron systems, was discussed. As shown by Longuet-Higgins,[18] the conical intersection in this case has the shape of an equilateral triangle. The phase changes between any two anchors—this is a purely photochemically allowed system.

In the present case, we deal with an even number of electrons. The number of independent spin-coupling schemes is central to the present approach. We shall demonstrate it with the prototypical 4-electron system H_4 and use the results to present the case of butadiene in Section IV.

Scheme 2 shows the three possible independent chemical structures for H_4. Their wave functions are not independent; there are three spin-pairing possibilities—$H_1H_2 + H_3H_4$, $H_1H_3 + H_2H_4$, $H_1H_4 + H_{23}$. Writing out the VB wave function shows that the third may be expressed as a linear combination of the

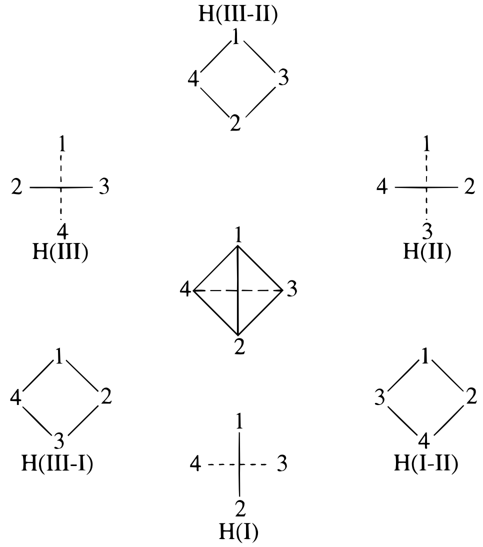
SCHEME 1: Sketch of the Phase Change of the Electronic Wave Function upon Being Transported around a Complete Loop[a]



[a] The three structures (anchors) used to define the coordinates relevant to the system are situated at the vertices of the triangle enclosed in the circle that represents the loop. The top figure illustrates the case in which a single phase change takes place. The total electronic wave function has a positive phase (shown dotted) at the beginning of the trajectory (|C>), at the transition state |C + A> and at |A>. It undergoes a phase inversion at |A − B>, and has a negative phase (shown hashed) at |B> and |C + B>, returning to |C> with a negative phase. The in-phase (phase-preserving) and out-of-phase (phase-inverting) coordinates Q_I and Q_O, respectively, are defined in Appendix A. Q_O, the phase-inverting coordinate, is the reaction coordinate connecting A with B. Q_I, the phase-preserving one, is chosen so that it connects the positive-phase transition state (|A − B>) with the positive-phase |C>. The bottom figure illustrates the case of a system undergoing three phase changes upon being transported around a loop. Again, starting from an initial structure C (with a positive phase), the phase changes between C and B and then between B and A and between A and C. Dotted regions represent a positive phase; negative phase ones are hashed. The coordinates defining the plane are chosen in the same manner as in the single-phase-change case: Q_O, the phase-inverting coordinate is again chosen as the reaction coordinate connecting A with B. The phase-preserving coordinate, Q_I, can be chosen again so that it connects the positive-phase transition state (|A − B>) with the positive phase |C>.

first two. *Nevertheless, this is obviously a separate chemical entity that can be clearly distinguished from the other two.* These three are the anchors, and they are correspondingly designated as H(I), H(II), and H(III). They may be interconverted via the shown phase-inverting symmetric square structure H(I−II), connecting H(I) and H(II), and similarly, by the structures H(II−III) and H(III−I), connecting the other two pairs. By symmetry, the conical intersection lies at the center of the triangle formed by structures H(I), H(II), and H(III). In it, combination schemes are equally probable, so that its form is a perfect tetrahedron. A property that is common to H_4 and all other 4-electron systems is the number of independent pairing schemes involving the entire quartet—it is always two, leading to three possible products. The third may be written as a linear combination of the other two, but is a separate minimum on the ground-state surface. It is connected by a phase-preserving route to the transition state between the other two. Having the form of a perfect tetrahedron, the conical intersection can exist in two enantiomeric structures. However, this distinction is important only when chiral reactions are discussed, which they are not in the present case.

SCHEME 2: H_4 System, Which Is the Parent System for 4-Electron Systems: The Three Possible Distinct Chemical Structures (I, II, and III, Each Forming a Pair of H_2 Molecules) Serve as the Anchors and the Transformation between Them Is Phase Inverting (See Text for Details).



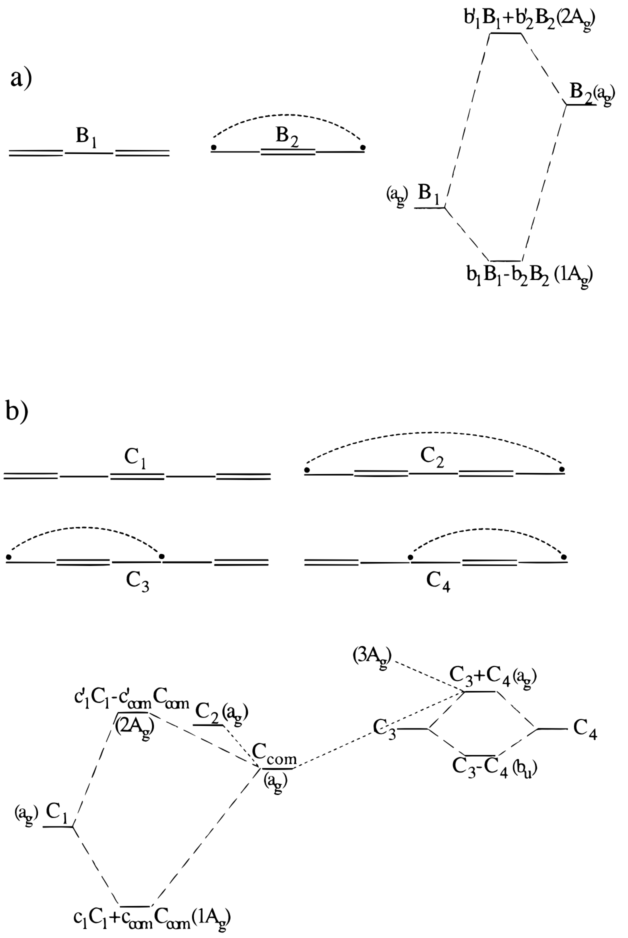
III. The A State as a Twin of the X State

As the A state is a key player in the photochemistry of polyenes, its properties are of great interest. In MO theory it was shown to arise from the combination of several configurations,[42] while in VB it is shown to be a purely covalent state.[43] In this section we outline a simple VB model that shows that the two lowest lying A-type states are actually related to each other, accounting for some of the unique properties of the X−A spectroscopic transition.

The linear polyenes are hydrocarbon molecules composed of alternating single and double CC bonds. In the cyclic polyenes, two VB structures (the Kekulé forms) are the main components of the ground state as well as of the conjugate excited state,[44] which we termed the twin state.[16] The difference between aromatic and antiaromatic molecules was shown to be that in the former the ground state is represented by the in-phase combination of the two, while in the latter by the out-of-phase combination. Therefore, the symmetric form of antiaromatic molecules is necessarily distortive, and the ground-state molecules show bond alternation, in contrast with the case of aromatic molecules.[45]

In cyclic polyenes, the two possible covalent bond alternating structures are equivalent. In linear polyenes this is the case only in the limit of infinite length. Nonetheless, we propose that the properties of the two lowest lying A_g states may be analyzed using a variant of the twin-state model. Only one covalent VB structure can be written for ethylene,[46] while two are possible

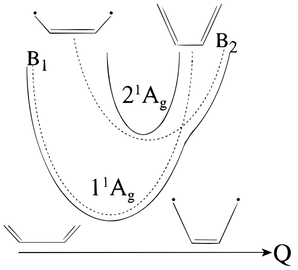
SCHEME 3: (a) Two Bond-Alternating Forms of butadiene and (b) Four Singlet VB Alternating Structures of Hexatriene (the Symmetries Shown in the Figure are for the All-Trans Isomer[a]



[a] The dashed curve connecting atoms 1 and 4 in structure B_2 is a reminder that the two electrons are correlated, forming a singlet biradical. Their out-of-phase combination forms the $X(1^1A_g)$ ground state and their in-phase combination the $A(2^1A_g)$ excited state. In part b the three radical forms are assumed to have the same energy for simplicity. C_3 and C_4 combine to form a low-lying out-of-phase combination (B_2) and a higher energy in-phase combination of A_g symmetry. The latter can interact with C_2, forming C_{com} (also of A_g symmetry), which combines with C_1 to form the spectroscopically observable $X(1^1A_g)$ and $A(2^1A_g)$ states. Note that a covalent excited state of B_u symmetry is predicted by this energy-level scheme.

for butadiene (Scheme 3a). It is obvious that structure B_1 is much more stable than B_2 at ground state geometry; nonetheless, the fact that in butadiene the formally single central bond is much shorter than a usual single CC bond (1.45−1.48 Å vs 1.55 Å[48]), may be attributed to the contribution of B_2. Calculations[13] show that in the A state the outside CC bonds are longer than the central one, as expected if structure B_2 is dominant. Thus, butadiene is the smallest polyene for which the two-state model can be applied. The two low-lying A_g states are formed by in-phase and out-of-phase combinations of the two basic VB structures. As shown elsewhere for the cyclic polyenes,[45] for the even-parity system ($4n$ electrons, $n = 1, 2, ...$), the ground state is an out-of-phase combination and the excited state an in-phase one. These are antiaromatic systems. For the odd-parity systems ($4n + 2$ electrons), the in-phase combination is the ground state. This classification extends to the linear polyene series, as can be seen from the nature of the transition states for cyclization.[49]

SCHEME 4: Potential Energy Diagram of Polyenes, Showing the Construction of the 1^1A_g and 2^1A_g States from the In-Phase and Out-of-Phase Combinations of the Two VB Structures Shown in Scheme 3[a]



[a] For simplicity, the case of butadiene is used as an illustration. B_1 and B_2 are the two bond-alternating forms used to construct the two A_g states. Q is the coordinate that exchanges the two structures; it is basically a C═C bond-length-alternating coordinate of a_g symmetry, whose vector displacement can be seen in Figure 1 of ref 13. The dashed curves show the potential curves of the diabatic B_1 and B_2 states and the solid curves the adiabatic ones obtained by the avoided crossing. The structures shown below these curves depict schematically the nuclear configurations near the equilibrium positions—short double bonds and long single bonds. The structures at the top depict the strained structures obtained by contracting double bonds and stretching single ones. These two structures dominate the excited-state potential curve, resulting in frequency exaltation. See text for further details.

For the larger polyenes, progressively more VB structures may be written, leading to increased stabilization of the twin A state. Thus, for hexatriene four structures may be written (Scheme 3b), making this case analogous to that of anthracene, which is fully discussed in ref 16c.[16c] Scheme 3b shows also how the symmetry-adapted combinations of these four structures can be used to generate the two low-lying states of hexatriene. It is obvious that although each single biradical structure has a higher energy than the fully-spin-paired structure, C_1, their in-phase (A_g symmetry for the all-trans isomer) combination C_{com} can combine with C_1 to form the two twin A_g states. Its relative contribution to the stability of the system is larger than that of the single spin separated structure in butadiene. As the polyene becomes larger, the number of the separated-spin structures increases, and these structures become increasingly more important in determining the properties of the ground state. Calculations[13] support this picture: in the A state, the central and outer bonds are *longer* than the other two, as expected from the model if structures C_2−C_4 are the dominant components of this state.

The A_g excited state of the polyenes may be constructed from the complementary combination (in-phase for even-parity molecules, out-of-phase for odd-parity ones) of the spin-paired structure with the A_g combination of the spin-separated ones. Scheme 4 sketches the energetics of the system, using s-trans butadiene as an example. Q is the bond-alternating coordinate (analogous to the Kekulé mode in the cyclic systems) that transforms one structure to the other. In the all-trans polyenes, this coordinate is of a_g symmetry, and it exchanges the two basic structures forming the twins. Plotted along this coordinate (while keeping all others constant), the two potential surfaces have minima at two different points. They intend to cross at a certain point, but, being of the same symmetry, the crossing is avoided, and two new adiabatic curves arise. Because of the different stabilization energy, the properties of the ground state are primarily derived from the B_1 structure. However, the excited state is formed primarily from the combination of the attractive wing of structure B_1 and the repulsive wing of the biradical structure (B_2). This situation is analogous to that discussed for benzene and other aromatics,[16] except that there the two interacting Kekulé structures were of the same energy. Therefore, in the present case the ground state is dominated by B_1, while in the case of benzene the two Kekulé structures contributed equally. However, as Scheme 4 shows, the excited-state potential surface has a much steeper slope than the ground state, leading to frequency exaltation along the bond-alternating coordinate, Q. The right-hand limb of the potential curve of the excited state is dominated by the strained form of B_1 and the left-hand limb by the strained B_2. Consequently, motion along the Q coordinate, starting from the equilibrium excited A_g structure, takes place in mismatch with the bonding features of the VB structures, since such motion leads to stretching of the double bonds and simultaneous compressing of the single ones. Physically, this situation is manifested in Scheme 4 by the steeper slope of the 2^1A_g potential curve as compared to the shallow slope of the 1^1A_g curve. An analogous situation holds for hexatriene, with C_{com} taking the place of B_2.

This steeper slope is the physical reason for a larger force constant and is manifested by the ubiquitous frequency exaltation of the a_g mode in the excited state of the polyenes relative to the ground state. Since a_g is the *only* coordinate along which the two VB structures interconvert, the mode selectivity is readily accounted for. Furthermore, the 2^1A_g state is the only excited state formed by the out-of-phase combination of the two VB structures, hence the *state* selectivity. The exalted mode was found to be dominant in the two-photon excitation spectrum of benzene and many of its derivatives.[14,50] It is interesting to note that this is also the case for the exalted frequency in jet-cooled *trans,trans*-1,3,5,7-octatetraene (ref 8b, Table 1) and that this frequency is also dominant in the multiphoton ionization spectrum of *cis*-hexatriene (ref 7, Figure 2), probably for the same reason.

Further support for this interpretation of the nature of the two lowest lying A_g states of polyenes may be derived from the well-known fact that, in the planar form, the 2^1A_g state is very high in energy in ethylene, so that it mixes strongly with Rydberg states and is difficult to observe experimentally.[51] This is important for understanding the photochemistry, since the lowest lying excited state in *perpendicular* ethylene is purely covalent[47,52] and correlates with this state. In butadiene, the A state is nonfluorescent, though the energy of its planar form is considerably lower than that of ethylene (by about 1.5 eV), as deduced from experiments (ref 53 and references therein) and from recent computations.[54] Its energy is a little higher than the energy of the B state in the planar molecule (by about 0.2−0.5 eV), but the two cross in the twisted molecule. Thus, it is assumed that initial excitation to the B state populates the A state, which, in turn, couples efficiently with the ground state via a conical intersection. This scenario was indeed verified computationally.[4]

In the larger members of the series, starting with hexatriene, fluorescence is observed under low-temperature conditions.[7,8,10] Even for the first member, hexatriene, the state lies now below all Rydberg states, as low as 4.2 eV for the different isomers.[7,8] This is due to lowering of the energy of this state *in the planar geometry* while the slightly twisted molecule remains at a higher energy, and only twisting, to nearly 90°, leads to strong stabilization. The suggested model explains this specific stabilization of the planar structures: it is only possible for planar molecules to have strong resonance between the different bond-alternating forms.

It has been noted[13] that the C=C stretch frequency in the X state *decreases* monotonically with chain length, while that in the A state *increases*. This result is a natural outcome of the proposed model, in line with the increasingly more important contribution of the "biradical" VB structures as the chain becomes longer. In the limit of infinite length, the case of cyclic polyenes (equal contribution of the two bond-alternating forms) is reached.

Finally, the forbidden nature of the electric-dipole transition between the two A_g states is in line with the model—they arise from different combinations of the same two parent structures. This is an example of a two state system, discussed by Feynmann,[55] who showed that an electric-dipole operator cannot couple the two.

IV. The Photochemistry of Polyenes

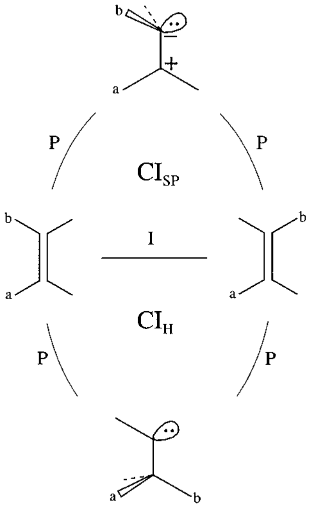
Experimentally, the photochemistry of even the smallest olefin, ethylene, is fairly complex.[3,56,57] This is, in part, a result of the fact that the first valence transition is very high in energy,[42] lying in the same energy range as Rydberg transitions (>6 eV). The large amount of energy makes many reactions possible, including cis/trans isomerization, H-atom transfer, and CH bond fission.

As noted above, no fluorescence is observed from ethylene or its simple aliphatic substituted derivatives. A major decay route from the excited states is by a twist around the CC bond, since in the perpendicular form the excited states have a minimum. The energy of the valence excited states becomes progressively lower in the larger members of the series, making dissociation a negligible channel. Many isomerization reactions are possible, the dominant one appears to be cis/trans. We limit the discussion in the following sections to singlet-state photochemistry only, starting with ethylene and continuing to the larger polyenes. It is shown that all the observed reaction characteristics can be accounted for by assuming that conical intersections are involved. The rich triplet-state photochemistry, not discussed in this paper, was recently summarized by Arai.[58]

We shall discuss the photochemistry of the polyenes, assuming that it is controlled by conical intersections between the A and the X states. By the phase rule, this requires that the total electronic-wave function will change sign upon the molecule being transported around a complete loop. The task is to identify the possible loops, and this is done by considering three anchors. In order for the phase to change, one or all three transformations must be phase-inverting. A simple criterion for phase inversion is whether the transition state is antiaromatic. If it is, then the transformation is phase-inverting, while if it is aromatic the transformation is phase-preserving. Whenever the Hückel-type transition state involves an even number of electron pairs (2, 4, etc.) it is antiaromatic. This is the case for the cis−trans isomerization around a double bond[45,47] and for transformations involving, for instance, all four electrons in butadiene (as in cyclobutene formation[49]). By "freezing out" two electrons (e.g., forming a charge-separated transition state) or by adding two (as in an H-atom transfer), an aromatic transition state is obtained. Conical intersections will be found whenever two such transformations are contained in the same loop with a single phase-inverting one. In this case, in addition to the "photochemically allowed" product[29]), a "thermally allowed" one is necessarily formed. When all transformations are phase inverting, two photochemically allowed products are formed. In large odd-parity ($4n + 2$ electrons) systems, a phase-inverting transition state can be realized by a Möbius type conrotatory ring closure. The search for a conical intersection is performed in an analogous fashion.

IVa. Ethylene. Irradiation into the first absorption band (populating the $B(1^1B_{1u})$ state) leads to cis−trans isomerization as well as H-atom shift. We shall neglect the dissociation

SCHEME 5: Two Loops Leading to a Conical Intersection for the Cis/Trans Isomerization of Ethylene, for Which the Conical Intersection Coordinates Are Easily Visualized[a]

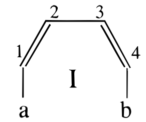


[a] The isomerization coordinate Q_O (mainly the C−C torsional angle) is phase-inverting (labeled I), and is common to both loops. In the lower part, the third anchor is the carbene biradical CH_3CH: that is a derivative of methylene. Its transition to either isomer, along a hydrogen atom migration coordinate, is phase-preserving. This structure leads to H-atom transfer, which was observed in ethylene photochemistry. The conical intersection found inside this loop is CI_H, for hydrogen transfer. The upper part shows that the third anchor can be the pyramidal charge-separated structure shown. Its transition to either isomer is also phase-preserving (labeled P) using a pyramidalization (wagging) coordinate. The resulting structure is polar, and although calculated to have a minimum, was not observed experimentally. The conical intersection inside this loop is CI_{SP} for sudden polarization, the effect considered to be involved in the formation of the polarized structure.[59,60]

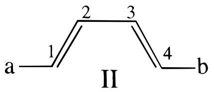
reactions, which require higher energies and are not observed in the larger polyenes. The covalent A state lies at a very high energy in the planar form,[51,54] but is the lowest excited singlet in the perpendicular one. It is very likely that the B and A electronic potential curves cross and that the ground state products are formed after the A and the X surfaces meet at a conical intersection. However, it is also possible that there is a conical intersection between the B and the X surfaces. This system was studied as early as 1985 by Ohmine,[39] who found one conical intersection and suggested the presence of another. In both, the molecule is distorted from the planar form. Scheme 5 shows two predicted conical intersections based on the phase-change rule: the cis−trans isomerization coordinate is phase-inverting. These two possible conical intersections involved in the cis/trans isomerization are predicted by the phase-change rule. Two single-phase-change loops can be formed. In one, the third is the carbene CH_3CH: that is formed by an H-atom transfer from one carbon atom to the other (bottom part of Scheme 5). This structure, in which two electrons occupy an sp^2 orbital, was found by Ohmine[39] to evolve from a conical intersection between the two A states (see also ref 32, p 362−363). The conical intersection in this case is termed CI_H, for H-atom transfer. In this case, starting with the cis isomer, the trans-isomer product is expected to be accompanied by others arising from the biradical.

In the second, the third anchor is the ionic pyramidal structure shown at the top of the sketch. Structures such as this were predicted by MO theory and, since their dipole moment was found to depend strongly on geometry, this phenomenon was termed the sudden-polarization effect.[32,59,60] It leads to reduction of the excited state's energy, which results in a crossing to the ground state. In the ground state, this structure is calculated to be a local minimum, but to our knowledge, has not been observed experimentally. In the context of the phase-change rule, it is seen here to be of key importance in allowing the phase-inverting cis/trans isomerization via a conical intersection. Since the structure is ionic, it may promote the coupling between the ionic B state and the otherwise largely covalent ground state. Note that it is expected[39,59] to be too high in energy to be involved in the *thermal* isomerization. The conical intersection lying inside the triangle formed by this trio is marked as CI_{SP}, for sudden polarization. This conical intersection was suggested in ref 39, but not found computationally. As shown in Figure 5d of ref 39, this third anchor may evolve into two separate methylenes (CH_2), making a computational search very tedious.

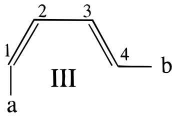
IVb. Butadiene. In the photochemistry of butadiene, all the ethylene type reactions are possible, if the other two π electrons are somehow "frozen" and do not participate in the reaction. However, novel possibilities arise, due to the presence of four electrons. The parent structure of such a system is H_4 (section IIa), which was extensively investigated theoretically.[61,62] In Scheme 2 the three independent reaction channels leading to two H_2 molecules were depicted, along with the phase-inverting transition states connecting them. The photochemistry of butadiene is expected to follow a similar pattern, though the situation is more complicated (and the photochemistry much richer), since here p electrons are involved rather than s electrons as in H_4. As p-type orbitals can be rotated, many structural isomers can be formed (structures I, II, III, and IV), and the electrocylic-ring-closure reaction to form cyclobutene can be either phase-inverting or -preserving depending on whether the motion is conrotatory or disrotatory, respectively. Table 1 shows the different possibilities for the four possible isomers I, II, III, and IV. In a similar way Table 2 summarizes how the phase changes upon interconversion among the isomers. Inspection of the two tables shows that, for any loop containing three of the possible isomers (open chain and cyclobutene ones), *the phase either does not change or changes twice.* Thus, there cannot be a



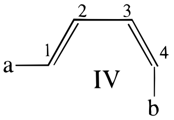
I



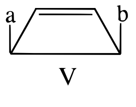
II



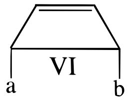
III



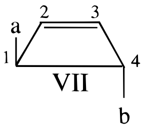
IV



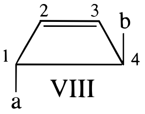
V



VI



VII



VIII

TABLE 1: Phase Change Upon Cyclization of Different S-Cis Cyclobutadiene Isomers

reactant	product V	 VI	 VII	 VIII
I	i[a]	i	p	p
II	i	i	p	p
III	p[a]	p	i	i
IV	p	p	i	i

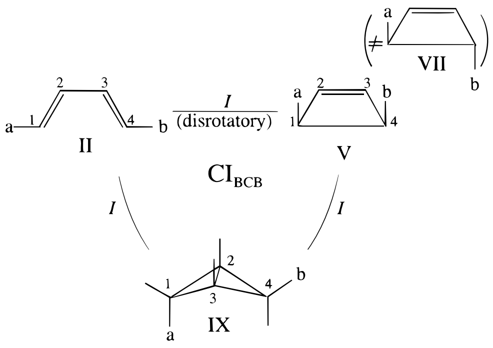
[a] p stands for phase-preserving reaction, i for phase-inverting.

TABLE 2: Phase Change Upon Interconversion Reactions between Different S-Cis Butadiene Isomers

reactant	product I	 II	 III	 IV
I	–	p	i[a]	i
II	p[a]	–	i	i
III	i	i	–	p
IV	i	i	p	–

[a] p stands for phase-preserving reaction, i for phase-inverting.

SCHEME 6: Location of a Conical Intersection in the Butadiene–Cyclobutene Isomerization Reaction[a]

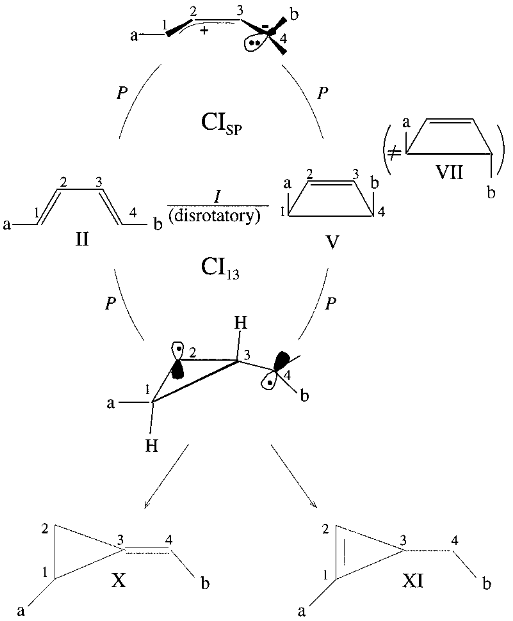


[a] This scheme is analogous to that used in Scheme 2 and shows the only way in which all four electrons are spin-paired to form covalent bonds. The third anchor is the bicyclobutane structure IX; the conical intersection is therefore labeled CI_{BCB}. It can be seen that the phase of the electronic wave function is inverted between any two anchors. Note the selective nature of the reaction—as seen from Table 1, cyclobutene V is one of the allowed isomers that can be formed via a disrotatory ring-closure coordinate; Isomer VII (formed by a conrotatory phase-preserving coordinate) is a forbidden isomer.

conical intersection inside any of these loops; in other words, *photochemical transformations between just these species cannot occur via a conical intersection, regardless of the nature of the excited state.*

The situation is quite different when three anchors are used, such that the phase changes for any transformation between them. An example, using the II isomer, is shown in Scheme 6, which is completely analogous to Scheme 2. It shows the only three spin-pairing schemes: in the linear butadiene II, the pairing connects atom 1 with 2, and 3 with 4. In the cyclobutene, atoms 1 and 4 are paired and also atoms 2 and 3. The third possibility connects 1 with 3 and 2 with 4. This leads to bicyclobutane, which was indeed observed in some photochemical reaction schemes.[56] Since the total phase of the electronic wave function changes sign upon being transported around a complete loop between these three structures, a conical intersection must be present inside the loop. Irradiation of butadiene is thus expected to lead to both products. It may be added that a given spin-pairing scheme can lead to different conformers, which may be revealed in low-temperature experiments (such as matrix isolation[53]). For instance, s-cis/s-trans isomerization of butadiene is possible. However, in the present context, both conformational isomers are connected to the same anchor.

SCHEME 7: Two Other Loops Leading to Conical Intersections in the Butadiene Cyclization Reaction[a]

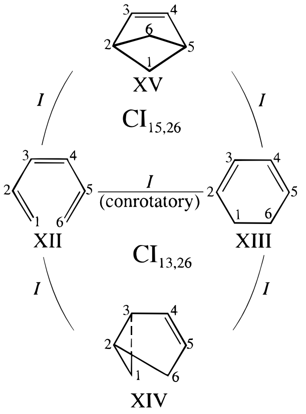


[a] Here the third anchor uses only two electrons to form a covalent bond. Therefore, the reaction connecting it with the butadiene on one hand and with the cyclobutene on the other is phase-preserving. The upper loop uses an ionic structure as the third anchor, analogous to ethylene (see Scheme 4). The lower loop uses the shown cyclopropyl biradical, which may lead to either methylene cyclopropane (IX) or methyl cyclopropene (X). The conical intersection found within this loop is labeled CI_{13}. The phase-preserving reaction coordinate in this case is the CCC bending angle.

Another possible way of achieving ring closure is by coupling it to a phase-preserving anchor. This is possible by freezing out two of the electrons, as shown in Scheme 7. One way of doing this is by moving an electron from carbon 2 to 3, forming a pyramidal dipolar structure (top part of Scheme 7). This situation is analogous to that encountered for ethylene, i.e., the conical intersection is of the sudden-polarization type. The other is by forming a cyclopropyl biradical (lower part). This is done by bending the $C_1C_2C_3$ angle and rotating the p orbitals of atoms 2 and 4 90° out-of-plane, removing them from the spin-pairing scheme. Two types of cyclopropyl biradicals can be formed, depending on whether the two p electrons are rotated in a disrotatory or conrotatory manner. The former will lead to a phase-preserving anchor, the latter to a phase-inverting one. These two cases will result in two separate conical intersections, whose energies may be very similar. Ito and Ohmine recently reported this conical intersection in a computational study of s-trans butadiene.[63]

It is concluded that several conical intersections may be found for certain reactant–product pairs, which, in turn, can be identified using Tables 1 and 2. For instance, structure II may cyclize to V or VI, but not to VII or VIII, as shown in Schemes 6 and 7. In a similar way, isomer I may convert to either III or IV, but not to II. In each of these cases, a second product that can be traced to either the cyclopropyl biradical or bicyclobutane is also formed. Although the relative yield of the products cannot be estimated from this analysis, these *selection rules* are strict as long as conical intersections are involved, and they can predict which pairs of products are possible. The ionic form does not lead to observed products, so that if a conical intersection of

SCHEME 8: Two Examples of Three-Phase-Change Loops in the photochemistry of *cis*-Hexatriene[a]



[a] The conrotatory ring closure to hexadiene is phase-inverting. The other two anchors involve spin pairing of four resonating electrons and are therefore also phase-inverting (see text).

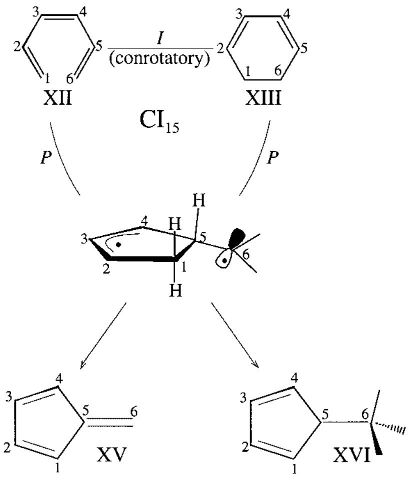
the CI_{SP} type is active, the system will appear to yield a single product isomer (apart from conformational isomerization).

This result may generalized as follows: Reactions in which all four π electrons participate cannot result in cyclization or cis/trans isomerization *only*. These photochemical transformations involving a 4-electron system must be accompanied by an additional, fairly strained transformation in which there is a cyclopropyl ring or a bicyclobutane product.

IVc. Longer Polyenes. As the chain becomes longer, the number of possible reactions increases dramatically. The systematic analysis becomes tedious even for the hexatrienes, and we shall confine the discussion only to highlight a *few* of the possible reactions in this system. Larger polyenes will be taken up in a separate paper. Thanks mainly to Kohler's contributions, it is well-known that, in contrast with ethylene and butadiene, the A state of longer polyenes has a minimum in the planar form.[1] It is shallow in hexatriene,[64] so that at room temperature the lifetime of this excited state is very short, and the system is photochemically active. Any ethylene or butadiene type reactions are obviously possible, and in addition, other reactions such as 1,5 H-atom migration or 1,5 and 1,6 cyclizations can take place. Experimentally, the dominant reactions are cis/trans isomerizations around one of the double bonds. An analysis similar to that carried out for the butadienes shows that no three isomers can be connected via an odd-phase-change loop, so that in any reaction that interconverts two geometric open-chain isomers, a third species is necessarily involved, which is connected to the reactant and product by a phase-preserving transition state.

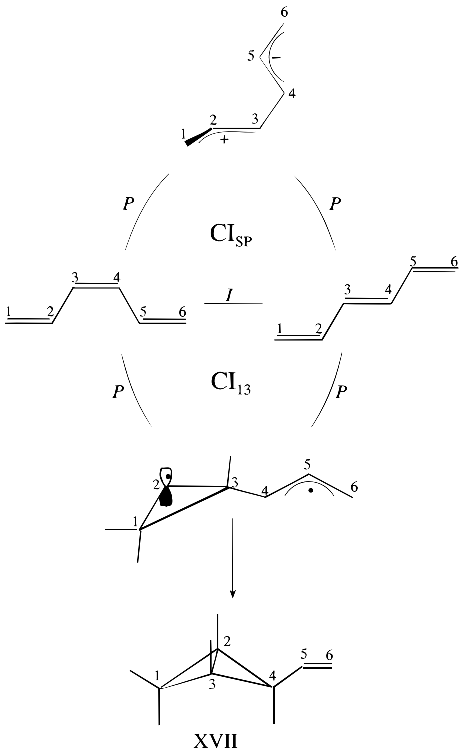
While in butadiene only three spin-pairing, phase-inverting schemes involving four electrons are possible; for each hexatriene, nine such different schemes can be constructed. Scheme 8 illustrates two of them, connected with the conrotatory (phase-inverting) cyclization of *cis*-hexatriene (cHT) to cyclohexadiene (HD). The bicyclic structure XIV is obtained by coupling the p electrons of carbon atom 1 with carbon 3, and those of carbon 2 with carbon 6. It is transformed to both cHT and HD by phase-inverting transition states, so that a three-phase-change conical-intersection structure (labeled $CI_{13,26}$) is found inside the loop. In an analogous way, the conical intersection structure $CI_{15,26}$ is formed, using the bicyclic XV anchor.

SCHEME 9: Single-Phase-Change Loop in the Photochemistry of *cis*-Hexatriene[a]



[a] The anchor shown is a 1,5H-atom-transfer one. It is analogous to the CI_{13} anchor shown in Scheme 7 for butadiene and leads to the cyclopentadiene derivatives shown.

SCHEME 10: Two Single-Phase-Change Conical Intersections That Lead from tct-Hexatriene to All-Trans Hexatriene, by Isomerization around the Central Double Bond[a]



[a] The two anchors are a charge-separated dipole (top part) and a 1,3 cyclopropyl biradical, which may lead to the bicyclobutane derivative shown.

Scheme 9 depicts a single-phase change conical intersection that can lead from cHT to HD. It is completely analogous to the biradical-based conical intersection (CI_{13} discussed for butadiene (Scheme 7, bottom), having an H-atom-transferred anchor. The anchor, which is a methyl cyclopenten diradical (MCPD), may produce 5-methylene pentadiene (XV) or 5-methyl-penta-[1,2],[3,4]-ene (XVI). Both are thermally allowed products of HD or cHT isomerization.

Scheme 10 shows two single-phase-change conical intersections that lead from tctHT to all-trans HT, by isomerization around the central double bond. The two anchors are again a charge-separated dipole (top part) and a 1,3-cyclopropyl biradical. The first is not expected to show up in the final products, while the latter will lead to a bicyclobutane derivative.

These three examples indicate the potential complexity inherent in large polyene photochemistry. However, rather few products are usually observed. This must be due to energetic and dynamic constraints. For instance, as the energy of the A state is lowered (with the chain lengthening) the energy of some of the possible anchor structures is high enough for them to be discarded. Guided by the phase-change rule, quantum chemical calculations may be used to select the more efficient pathways.

V. Discussion

This paper provides a unified physical interpretation for various experimental and computational results concerning the photophysics and photochemistry of polyenes. Beginning with ethylene and proceeding to butadiene and hexatriene, we showed how the lengthening of the conjugated-double-bond frame affects the photophysical properties. The extension to even longer members is obvious and will be treated in detail in a separate paper. The VB based model, which treats the A and X states as twin states, provides a simple physical explanation for both the specific frequency exaltation of the a_g symmetric stretch in the A state and the appearance of a minimum in the A-state potential surface at the planar form, even though the driving force for isomerization around the double bond is quite strong in these systems. The resonance stabilization due to the other biradical structures is expected to be strong only at (or near) the planar structure. The number of these structures increases as the chain length increases, so that the minimum is expected to be more pronounced for them, leading to higher fluorescence yields even at elevated temperatures and to higher photochemical stability. On the other hand, the increased contribution of the bond-order-reversed form, which has a biradical nature, to the *ground* state is in line with the increased tendency of these longer chain molecules to polymerize, as suggested by Kohler and co-workers in 1988.[11]

Thanks to the detailed computational investigations, mainly of Olivucci, Bernardi, Robb, and their co-workers,[37] the involvement of conical intersections in many photochemical reactions appears to be well-established. These unique loci on the potential surface are the main funnels[31,32] by which the system transforms from the electronically excited state to the ground state. It follows that the understanding of photochemical reaction mechanisms involves two main parts:

(1) Motion of the system on the excited state(s) surface(s) from the Franck–Condon region to the conical intersection(s) with the ground state.

(2) Motion on the ground state from the conical intersection to the allowed potential minima (products or back to the reactant).

The large number of different products often observed in photochemical reactions may be traced to two main sources—the presence of several conical intersections and the fact that from each conical intersection several products may be formed (two valence isomers and any number of conformational isomers).

The main result of this paper is that *analysis of the properties of the ground-state potential surface by itself* provides valuable information on the possible products and their stereochemistry. It was shown that, regardless of the nature of the excited state, two different products are always formed, in principle, from any conical intersection. Moreover, in general, two different product pairs will implicate two different conical intersections, though one of them may be formed from both. The phase-change rule results in *selection rules* that state which pairs of products are possible and which are forbidden. This was demonstrated, for instance, for the butadiene–cyclobutene reaction; it was shown that a third product (such as forming a cyclopropane ring) *must accompany the four-membered-ring cyclization.* The actual *relative* yields are determined by the details of the potential surface and cannot be predicted on the basis of the above general considerations.

The cyclohexadiene/hexatriene (cHD/HT) photochemical conversion was recently studied in detail by Celani et al.[6] In this work the conical intersection was identified, and it was established that the six π electrons which are essentially uncoupled in the conical-intersection region may recouple in three different ways. Two lead to the hexadiene and the hexatriene (the cZc isomer) and one to another product, methyl cyclopenten diradical (MCPD). Our model predicts that such a conical intersection must be present, since the cHD–HT reaction is phase-inverting, and the reactions of both to form MCPD are phase-preserving (Scheme 9). The potential surface calculated in ref 6 predicts that MCPD will be a minor product, for dynamic reasons.

At the conical-intersection point the fate of the reaction is not determined: several products (including the reactant) may be formed eventually. We thus interpret the picosecond appearance time of the resonance Raman signature of the product,[65] as a result of vibrational relaxation *on the ground-state surface.* In that sense, we disagree with the statement that the formation of the products must occur within the lifetime of the excited state.

VI. Summary

Kohler's seminal work changed the field of polyene photophysics and photochemistry. The central role of the electric-dipole-forbidden state, A, is becoming more and more apparent with the evolution of novel experimental and theoretical methods. In this paper we showed that the two lowest A states may be considered as twins, which accounts in a straightforward way for the frequency exaltation of the a_g C=C symmetric-stretch frequency in the A state and for the fact that the planar form has a local minimum. The two states can be connected by conical intersections, which determine the course of many photochemical reactions. The phase-change rule is used to locate possible conical intersections and to predict the product distribution and their stereochemical properties. Three molecular structures are essential in order to determine the location of a conical intersection, so that electronic excitation will result, in general, in *two* different products. The rule can be used to reject structures that cannot lead to a conical intersection and to predict which pairs of products arise from a given conical intersection. This analysis, based on the ground-state potential surface only, was applied to the photochemistry of ethylene, butadiene, and (partly) hexatriene. It is easily extendable to larger systems, although their size makes it more tedious.

Acknowledgment. We thank Dr. W. Fuss and Prof. I. Ohmine for stimulating discussions on the photochemistry of polyenes. This work is supported by the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities. The Farkas Center for Light Induced Processes is supported by the Minerva Gesellschaft mbH, Munich.

Appendix A. The Conical Intersection Coordinates

With the aid of three anchors, we can define the two coordinates forming the conical intersection. Let the position vectors of the three molecular structures A, B, and C be $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{r}_C$, respectively (each of which is determined by the coordinates of the atoms forming the molecules). The wave functions of these structures are denoted as $\pm|A>$, $\pm|B>$, and $\pm|C>$, where the plus and minus signs indicate a positive or negative phase, respectively, of the total electronic wave function. The adiabatic transformation of one structure to another can take place either with or without a phase change. As an example, let the phase change between A and B and remain put between A and C and between B and C (Scheme 1, upper panel). By its assumed continuity, the wave function $|A,B>$ anywhere between A and B may be written as the out-of-phase combination

$$|A,B> = a(R)|A(R)> - b(R)|B(R)> \qquad (A1)$$

i.e., it is parametrically dependent on the nuclear coordinates $R = \{\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_C\}$. This form ensures the phase change. The structure at which the node is located will be denoted by A−B, with the associated wave function being $|A-B>$.

In a similar fashion, the wave function $|B,C>$ anywhere between B and C may be written as the in-phase combination

$$|B,C> = b'(R)|B(R)> + c(R)|C(R)> \qquad (A2a)$$

and also

$$|C,A> = c'(R)|C(R)> + a'(R)|A(R)> \qquad (A2b)$$

For this system, a convenient choice of two coordinates for describing motion on this surface is as follows. The first is the phase-preserving coordinate Q_I (for in-phase), connecting C with A−B, defined by

$$Q_I = 2\mathbf{r}_C - \mathbf{r}_A - \mathbf{r}_B \qquad (A3)$$

and the other is Q_O (for out-of-phase), the coordinate connecting A with B, which is a phase-inverting mode

$$Q_O = \mathbf{r}_A - \mathbf{r}_B \qquad (A4)$$

Since at least one phase change must take place between the anchors, it is possible to choose as a phase-inverting coordinate the reaction coordinate that connects these two anchors. In Scheme 1 this is the coordinate connecting A and B for both the one- and three-phase-change cases. The phase-preserving coordinate, Q_I, can likewise be chosen as the one connecting the transition state between A and B and the third anchor C, in both cases.

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