MODEL CALCULATIONS OF PHOTOCHEMICAL REACTIVITY

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ABSTRACT

The first part of this paper is a review of the author's recent work on theoretical aspects of organic photochemical reactions. Basic photochemical processes are summarized briefly in terms of Born–Oppenheimer hypersurfaces. The importance of the location of minima, funnels and barriers in the S_1 and T_1 surfaces for determining the outcome of a reaction is pointed out. Various types of minima and funnels through which return to S_0 occurs are listed, discussed in simple MO and VB terms, and used for a simple classification of photochemical reactions, and for a discussion of singlet–triplet differences. Correlation diagrams are used to estimate the location of barriers in S_1 and T_1. This review of previous work is followed by presentation of new results of model calculations for pericyclic reactions, in particular, for photocycloadditions. These illuminate the role of excimers in such processes, point out their relation to the process of triplet–triplet annihilation, and provide new information about the nature of excited electronic states at pericyclic biradicaloid geometries. It is shown that in addition to the well-known tendency to rapidly return to the ground state, the lowest excited singlet state should also exhibit an inclination for cross-bonding in the cyclic array.

INTRODUCTION

One of the numerous challenging aspects of organic photochemistry today is the quest for detailed understanding of the mechanism of the photochemical process proper, i.e. the usually exceedingly fast sequence of events which occur between initial excitation and the appearance of the first ground-state product in thermal equilibrium with the surrounding medium. Direct experimental observations on such a time scale are very difficult. Clearly, this is one of the areas in which quantum theory could contribute really significantly to progress.

This paper will consist of two parts. The first one is a review of the use of potential energy hypersurfaces for qualitative discussion of photochemical processes. Attention will be focused on the role of minima, funnels and barriers in the S_1 and T_1 hypersurfaces, and on the use of simple MO and VB arguments. This review is based on material published by the author in recent years[1-6], which in turn relied heavily on previous work by a number of investigators, of whom only Förster[7], van der Lugt and Oosterhoff[8], Woodward and Hoffmann[9], Longuet-Higgins and Abrahamson[10], and Zimmerman[11] will be mentioned here. A longer list of additional references can be found in a recently published review article[6] which is unfortunately

already somewhat outdated since it was written almost two years ago. Concurrently with our work, papers by other authors on similar topics have appeared, and of these at least the work of Salem and collaborators[12, 13], Devaquet[14], Dougherty[15], Epiotis[16], and Herndon[17] will be mentioned here. Although the views of some of these investigators do not always agree with ours, many of the arguments are similar. Lack of time prevents a more detailed discussion of the contribution of these and other workers in the field and I wish to apologize for this omission (see ref. 6 for a more complete list of references).

The second part of this paper is based on numerical calculations and presents new results obtained in collaboration with Prof. R. D. Poshusta of the Washington State University at Pullman, Wash., and with Dr W. Gerhartz, a NATO postdoctoral fellow at the University of Utah[18]. These results have to do with the role of excimers in photocycloadditions and their relation to triplet–triplet annihilation, with the nature of the electronic states of molecules along pericyclic reaction paths, and with consequences for photochemical reactivity.

A SIMPLE MODEL FOR PHOTOCHEMICAL REACTIONS

1. Photochemical processes in terms of Born–Oppenheimer potential energy hypersurfaces

(a) *Potential energy hypersurfaces*

The physical basis for the discussion will be the Born–Oppenheimer approximation, i.e. the separation of nuclear and electronic motion which underlies the construction of potential energy hypersurfaces governing nuclear motion in various electronic states. The hypersurfaces can be obtained from a calculation or estimated, and are numbered sequentially in the order of increasing energy at any one point in the nuclear configuration space, i.e. $S_0, S_1, S_2 \ldots$ and T_1, T_2, T_3 (singlet and triplet surfaces will be assumed to be non-interacting in light-atom molecules). Each surface (S_0, S_1, T_1, etc.) is common to all species which can be assembled from a given collection of nuclei (e.g. CH_4, $CH_2 + H_2$, $CH_3 + H$, $C + 2H_2$, etc.). Also curves for ionized species can be plotted in the same drawing.

The surfaces touch only relatively rarely, and most of the touchings, even if 'intended', are avoided. Whenever the surfaces do touch, however, troubles with nomenclature arise. An illustration is provided in *Figure 1*, which shows two singlet hypersurfaces of a polyatomic molecule along three mutually perpendicular coordinates in the nuclear configuration space. In part (a), energy is plotted against nuclear geometric parameters a and b, while the value of c is zero, the plot in part (b) involves a and c, while b is zero. The two crossing dashed lines belong to the cross section $b = c = 0$ and show the energies of the two states as a function of a alone. They are thus identical in parts (a) and (b). To give a more concrete representation, one can imagine that for $c=0$ the molecule has higher symmetry than for $c \neq 0$, so that the state touching not avoided in the former case is avoided in the latter.

If one views the 'sheets' as continuing through an intersection and labels them accordingly, as is tempting to do upon inspection of part (a) since this is
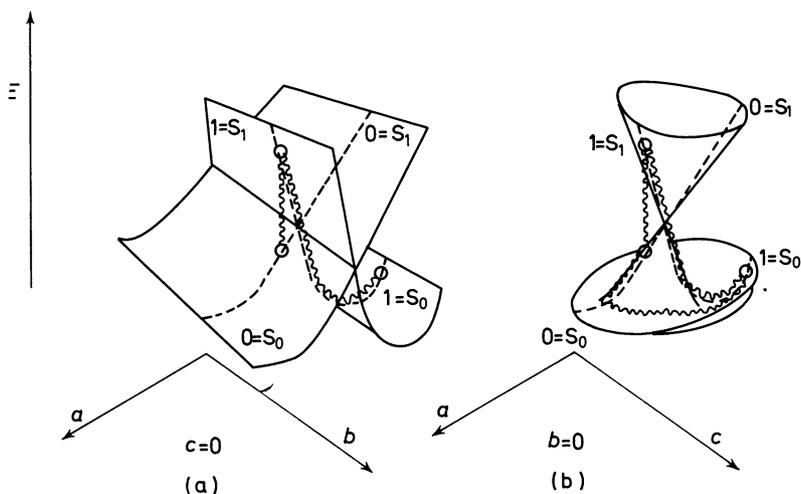
Figure 1. An example of surface touching ('funnel').

the way in which a molecule would actually move across the surfaces (labels 0 and 1), one runs into difficulties. Consider, for instance, a vertical transition from surface 0 to surface 1 followed by travel downhill on surface 1 to the area where it lies below state 0 as shown in *Figure 1*(a). It is now possible to travel back to the starting point while staying on one and the same surface, simply by moving a little along direction *c* first. Thus, we must conclude that 0 and 1 really are the same surface (sheet). Most likely, all singlet states of the molecule will similarly turn out to lie on different 'branches' of one and the same surface, and it will be necessary to label the branches before any useful nomenclature results.

The only instances in which such a definition of what constitutes 'one surface' (labels 0 and 1 in *Figure 1*) appears to be useful are those in which the crossing is avoided at no point in the nuclear configuration space, so that the path shown in *Figure 1*(b) does not exist, or if surfaces never cross or touch, but it is doubtful that such can be the case. Two cases in which we use this nomenclature are states of different symmetries in diatomic molecules, which have $D_{\infty h}$ symmetry at all geometries, and singlet and triplet states of molecules for the usual spin-free Hamiltonian, which appears quite appropriate in light-atom molecules. As a result, we obtained mutually freely penetrating sets of S and T hypersurfaces as already mentioned above.

The above-described difficulties with labelling can be avoided if, at any point in the configuration space, one assigns labels S_0, S_1, $S_2 \ldots$, and T_1 $T_2, \ldots$. strictly in the order of energy, as mentioned earlier and shown in *Figure 1*. Surface touchings then correspond to rather abrupt changes in the slope of a surface, and often to a minimum in the upper state.

(b) *Motion 'on' a hypersurface (strictly speaking, 'above' a hypersurface, or 'governed by' a hypersurface).*

The Born–Oppenheimer approximation only permits molecules to jump

from one surface to another with simultaneous absorption or emission of radiation. In reality, however, terms neglected in the Born–Oppenheimer approximation permit nuclear motion to induce such jumps in a radiationless fashion, in which energy of electronic motion is converted into energy of nuclear motion or vice versa. The total energy of the molecule does not change during the jump, but its nuclear motions become governed by a new surface. The probability of such jumps is small if the energy difference between the surfaces is large and Born–Oppenheimer approximation is good. For instance, lifetime in many minima in S_1 (spectroscopic excited states) is many nanoseconds, i.e. many thousands of vibrational periods. Radiationless jumps generally become more probable as the energy difference decreases, and are very important in the region of avoided surface touchings (their probability is related to the rate of change of the electronic wavefunction during the nuclear motion). For a weakly avoided or altogether unavoided surface touching, for instance for 'downhill' motion in direction a on surface S_1 in *Figure 1*(a), the probability of a jump to S_0 can be up to 100 per cent. Alternatively, one can say that the molecular motion is governed by surface 0 or 1 and the molecule goes through the crossing undisturbed, but this leads to difficulties in nomenclature as pointed out above. We refer to such weakly avoided or unavoided touchings as 'funnels' rather than minima since they effectively provide the upper surface with a 'hole' through which molecules are taken to the lower surface the very first time nuclear motion brings them across the 'touching' line (depending on the details of slopes, the touching need not even lead to a minimum in the upper surface). *Figure 2* represents the situation in a pictorial way.
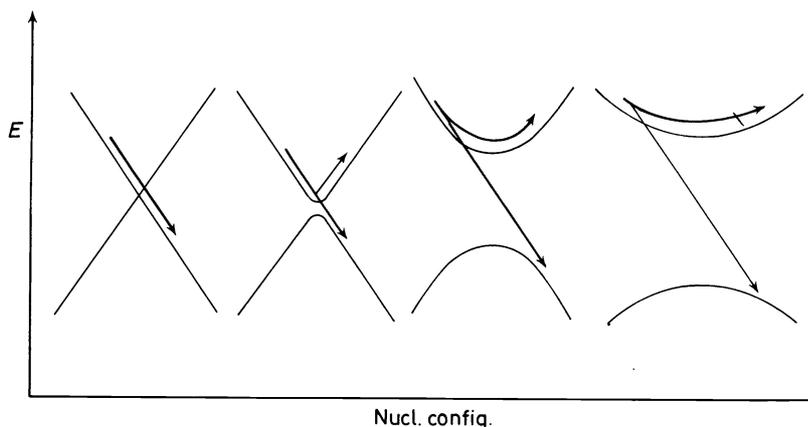
Figure 2. Motion through the region of a crossing (avoided crossing).

(c) *The photochemical process*

For discussions of thermal chemistry, one ordinarily needs only the ground-state hypersurface S_0, and looks for low-energy saddle points in the barrier surrounding the minimum corresponding to the initial species. The rate of product formation then depends on the height of the saddle point above the minimum (related to activation energy), the fraction of molecules

which have energy sufficient to pass through the saddle or higher (related to temperature), and the probability that the saddle is reached during the random thermal motion of the initial molecules about their equilibrium nuclear geometry (related to entropy of activation).

The situation is much more complicated in photochemistry. In a simplified but useful picture, the initial excitation can be imagined to bring the molecule essentially vertically from the initial minimum in the S_0 surface to one of the excited S_x or T_x surfaces (Franck–Condon principle). The nuclei then feel a force whose direction and magnitude are given by the gradient of the new hypersurface, and rapidly acquire kinetic energy. The part of nuclear kinetic energy which is in excess of average thermal energy is lost very rapidly, so that one could expect the molecules to rapidly reach thermal equilibrium in one of the minima in the new hypersurface. However, if the initial excitation was not into S_1 or T_1 but into one of the higher states, radiationless jumps are usually fast (excited states are usually close in energy and probably touch relatively frequently). Thus, in 10^{-10}–10^{-12} s after the excitation, one usually ends up with a thermally equilibrated species in one of the minima in S_1 (T_1 if the initial excitation was into T_x or if intersystem crossing is very fast), or, if the molecule has happened to find a funnel in S_1 on its way, with a thermally equilibrated ground state species ('unquenchable photochemistry').

The loss of excess 'heat' from an excited molecule on its way to thermal equilibrium in S_1, T_1 or S_0 can be imagined as a complicated motion of a point on a sloping surface, generally in the direction of the steepest slope, but with interruptions and rebounds due to collisions. Depending on how fast the loss of excess energy is compared with the distance travelled, the point may but need not pass above barriers in S_1, T_1 or S_0 which would have been prohibitively high, at the same temperature of the medium, if the initial excitation had been less energetic. If the 'cool-off' process is approximately vertical, it is considered trivial. If a barrier in $S_1(T_1)$ has been passed while the molecule was still excited, wavelength-dependent ('hot-excited-state') photochemistry can result. If a barrier in S_0 has been passed after return to S_0 but before thermal equilibration, a 'hot-ground-state' reaction results. Clearly, the outcome of a photochemical process is likely to depend on the rate of heat removal by the surrounding medium, and thus on pressure, solvent and temperature.

If an excited intermediate is formed, i.e. thermal equilibrium at a minimum in S_1 or T_1 is reached, it can undergo a variety of processes. In addition to radiative or radiationless transition to S_0, and intersystem crossing between S_1 and T_1, it can absorb light (possibly leading to two-photon photochemistry), or utilize thermal energy to escape from the minimum to reach another one or perhaps a funnel. The latter process of 'escape' can be effectively discussed in terms familiar from thermal reactivity such as activation energy and entropy and provides another source of temperature (and solvent) dependence in photochemistry. Bimolecular phenomena, such as energy transfer, quenching with formation of ground state products, exciplex formation, and bimolecular photochemical reactions leading to ground state products can be discussed effectively in terms of 'supermolecules'. One only needs to postulate that motion along some of the directions in the nuclear configuration space of the composite system is slow (diffusion

controlled). This provides another obvious way in which solvent effects enter photochemistry. A perhaps even more important factor is the direct effect of the solvent on shapes of excited potential energy hypersurfaces due to polarity, hydrogen bonding, etc., or on the shape of S_0, which can affect for instance the ratio of conformers in the starting material. Also temperature and choice of wavelength can favour one or another conformer.

2. Use of simple MO arguments to locate minima and funnels in S_1 hypersurface. Comparison with T_1

(a) *'Spectroscopic' minima*

Minima in S_1 and T_1 frequently occur approximately vertically above minima in S_0. Since such excited states can be studied by light absorption or emission, they are usually referred to as 'spectroscopic' excited states. In many photochemical reactions, these are the first intermediates reached and they often reveal their presence by light emission ('emission from starting material'). Return to S_0 from this minimum, whether radiative or radiationless regenerates the starting material unless a hot ground state reaction follows, and is thus usually of little interest for solution photochemistry. However, the minimum serves an important function in bimolecular photochemical processes as a reservoir of excited molecules waiting for diffusion to bring in a partner and open up new dimensions in the nuclear configuration space, and permit escape to new minima or funnels in S_1 or T_1.

Occasionally, the molecule reaches thermal equilibrium at a spectroscopic minimum in S_1 or T_1 at a geometry significantly different from the starting point ('excited product formation'). These processes are interesting but few are known, except for simple hydrogen transfers.

(b) *'Non-spectroscopic' minima*

In most photochemical reactions, return to S_0 occurs part way between the starting and final geometry and we therefore assume that it occurs from a funnel or a minimum which ground state spectroscopy cannot detect. Emission from such minima might be observable and has been apparently observed in at least one case[19], but can be generally expected to occur at rather long wavelengths and to have relatively long radiative lifetime and low quantum yield, so that its observation will be infrequent. Excited state absorption spectroscopy appears to be the method of choice but work on the picosecond scale will probably be necessary.

Because of these experimental difficulties, a theoretical ability to predict the existence of these 'non-spectroscopic' minima becomes of crucial importance. One general type of nuclear arrangement at which such a minimum in S_1 or T_1 can be expected is the so-called biradicaloid geometry. There may be other such general types, but already this single one accounts for most known types of organic photochemical reactions.

A biradicaloid geometry is one at which the simple MO picture leads one to expect the presence of two approximately non-bonding orbitals for which only two electrons are available in the ground state. At such geometries, the ground state molecule thus effectively has one bond less than at nearby stable geometries, and as a result is rather high in energy. If it is possible to change the geometry so as to bring the two non-bonding orbitals into inter-

action, one previously non-bonding molecular orbital will become bonding, the other antibonding. Since in the S_0 state it is possible to allocate both electrons to the bonding one, the energy goes down, and it should indeed be relatively rare to even have a local minimum in S_0 at a biradicaloid geometry.

In S_1 and T_1, however, biradicaloid geometries should be quite favourable. Geometrical distortions which remove the approximate degeneracy of the two non-bonding orbitals are no longer particularly helpful, since, roughly speaking, only one electron can be placed into the now stabilized bonding orbital and the now antibonding orbital still contains one electron and is usually destabilized even more. Pictorially speaking, excited molecules are happy to have a broken bond—a twisted π-bond, a stretched σ-bond, etc. Of course, one can argue that the bond breaking occurred at the very moment of initial excitation, particularly if it was of bonding→antibonding type, and that the change in nuclear geometry only represents an adaptation to life with one less bond. It must be remembered, however, that the nature of the lowest excited state ($\sigma\sigma^*$, $n\pi^*$, $\pi\pi^*$, etc.) will frequently change as nuclear geometry is changed so that the nature of the initial excitation may be unimportant for description of bonding at the biradicaloid geometry.

(c) *Singlet–triplet differences*

The arguments given above would lead one to believe that minima in S_1 and T_1 should occur at identical biradicaloid geometries. This is, however, incorrect, since the argument was based on inspection of orbital energies alone, while electron repulsion terms also enter the full expression for total energy.

In a simplified picture which considers only the two non-bonding orbitals, a molecule which is at a biradicaloid geometry has four low-lying states, a triplet and three singlets. In all of these states, the two non-bonding orbitals contain a total of two electrons and they differ only in their distribution. We use labels ϕ_1 and ϕ_2 for the non-bonding orbitals in their localized form (e.g. the two carbon 2p orbitals in tetramethylene biradical). In the simple picture, the triplet state and the lowest singlet state are covalent, since the two non-bonding electrons avoid each other, i.e. while one is in ϕ_1, the other is in ϕ_2.

In these states, there is no particular reason to expect an energy lowering if ϕ_1 and ϕ_2 are brought close to each other; rather, energy will increase if ϕ_1 and ϕ_2 remain truly non-bonding, since electron and nuclear repulsion will increase. Thus, 'loose' geometries (formula I) tend to be the best energetically among biradicaloid geometries, and they are usually also favoured by entropy terms.

The other two singlets are 'ionic', i.e. they involve separation of charge between ϕ_1 and ϕ_2 at all times since the two non-bonding electrons travel together and if one is in ϕ_1 (ϕ_2), so is the other. As a result, they are usually of higher energy, particularly if the orbitals ϕ_1 and ϕ_2 are far separated in space. In these states, it is energetically very favourable to acquire a geometry such that ϕ_1 and ϕ_2 overlap in space and thus minimize the electrostatic energy involved in charge separation ('tight' geometries, formula II).

As a result, biradicaloid minima in T_1 tend to occur at loose geometries such as I, distinctly different from the tight geometries such as II at which minima in S_1 can be expected to occur. Return to S_0 from T_1 and from S_1 thus

$$\cdot \; CH_2 \underset{CH_2}{\overset{CH_2}{\diagup}} \underset{CH_2}{\diagdown} \overset{CH_2}{\diagup} \cdot$$

I

$$\begin{matrix} CH_2 & CH_2 \\ | & | \\ CH_2 & CH_2 \end{matrix}$$

II
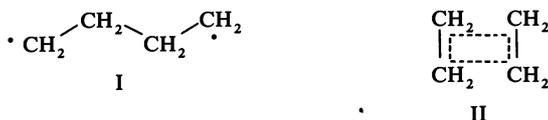
occurs at different points and can be often expected to lead to different products or at least different quantum efficiencies. This argument accounts for the tendency of singlet reactions to proceed in a stereospecific manner (a molecule which restarts life in S_0 at the geometry of II will most likely snap both bonds closed to give a cyclobutane or opened to give two olefins), for the tendency of triplet reactions to proceed in a non-stereospecific manner (steric information may be lost both in T_1 state during sojourn at the minimum at I and thereafter in S_1 state as the two loose ends grope for each other), and for the singlet–triplet differences in other reactions such as hydrogen abstractions and photodissociations. Lack of space prevents a detailed discussion here and the reader is referred to ref. 3. *Figure 3* shows the simple
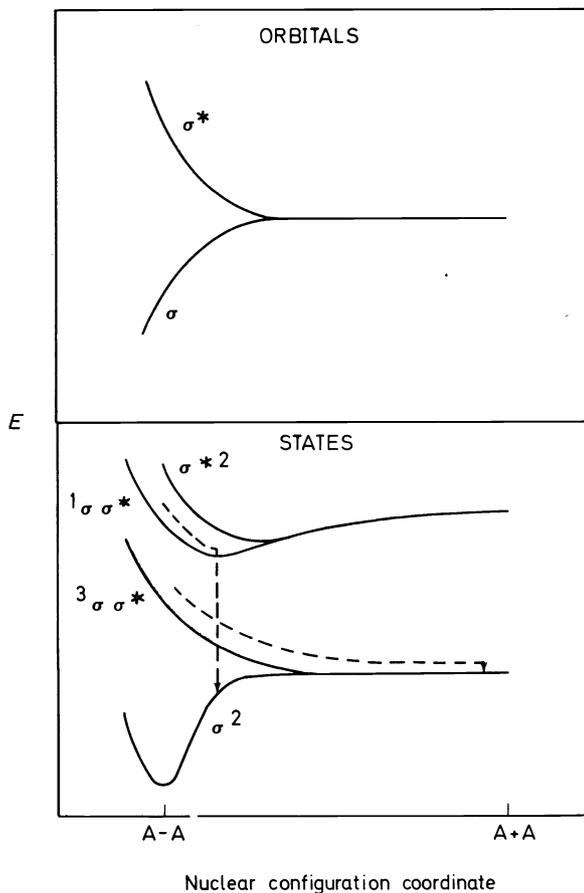
Figure 3. Electronic states of a sigma bond as a function of length

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case of the H_2 molecule for which experimental data are available and serves to illustrate the difference in the location of the minimum in S_1 ($R =$ 1.3 Å) and in T_1 ($R = \infty$).

It should be pointed out here that the first brief mention of the possibility of rationalizing singlet–triplet differences in this manner which the author has been able to find in the literature is due to Kita and Fukui[20]. Finally, it must be mentioned that there are also other obvious reasons for singlet–triplet differences, e.g. in aromatic molecules where configuration inter-action has quite different effects for the two kinds of states.

(d) Kinds of biradicaloid minima. Classification of photochemical reactions

It is difficult to classify photochemical reactions into neat categories other than the generally accepted separation into singlet and triplet reactions. One of the criteria which can be used[21] is the possible occurrence of intermediates in the process, which separates reactions into unquenchable essentially instantaneous ones such as photodissociation and those in which the molecule first equilibrates thermally at one or more minima in S_1 or T_1. Another criterion has already been mentioned and had to do with the rate of loss of heat versus the rate of travel through the nuclear configuration space (change in geometry). It separates reactions into 'ordinary', 'hot-ground-state', and 'hot-excited-state'. Another criterion distinguishes diabatic and adiabatic reactions depending on whether a non-radiative jump between surfaces is involved. Dougherty[15] classifies reactions as type X, in which an excited product is formed, and N and G, in which return to S_0 occurs part way through the reaction path at what approximately corresponds to our loose and tight geometries, respectively.

In practice, one usually only uses classification based on structural simi-larities and talks about Norrish I and II processes, pericyclic reactions, hydro-gen abstractions, and the like. However, such fragmentation can obscure basic similarities between different reaction types, as pointed out recently by Salem[13].

In our work[3], we organize photochemical reactions into groups according to the nature of the minimum (or funnel) in S_1 or T_1 from which return to S_0 occurs. This still sets apart adiabatic reactions as a special category (return from spectroscopic minima in S_1 and T_1), defines a large category of reactions for which the return is from a biradicaloid minimum, and leaves space for possible future introduction of other types of minima. Biradicaloid minima and funnels are then subdivided according to their structure. This subdivision is most easily visualized by imagining that the biradicaloid geometries are reached from geometries stable in S_0 by breaking one or more bonds. For instance, stretching a single bond leads to a 'broken σ-bond' minimum (Figure 3), twisting a double bond to a 'twisted π-bond' minimum (Figure 4), breaking two single bonds at the same atom to a 'carbene minimum', 'nitrene minimum', etc., bending a triple bond to 'bent triple bond' minimum (cis or trans), going halfway along a pericyclic reaction path forbidden in the ground state to a 'pericyclic minimum' (Figure 5) which can be further labelled as 2s + 2s, 4s + 2a, etc., according to the size of the cyclic array of interacting orbitals and also according to the nature of the pericyclic process (electrocyclic, cheletropic, sigmatropic, di-π-methane, etc.). As pointed out
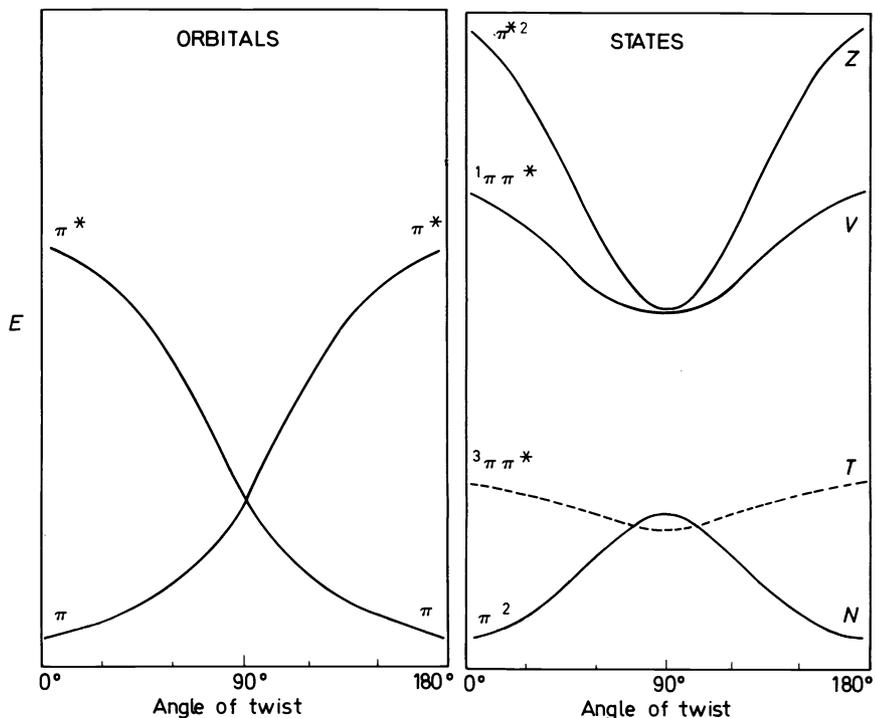
Figure 4. Electronic states of a double bond as a function of twist angle.
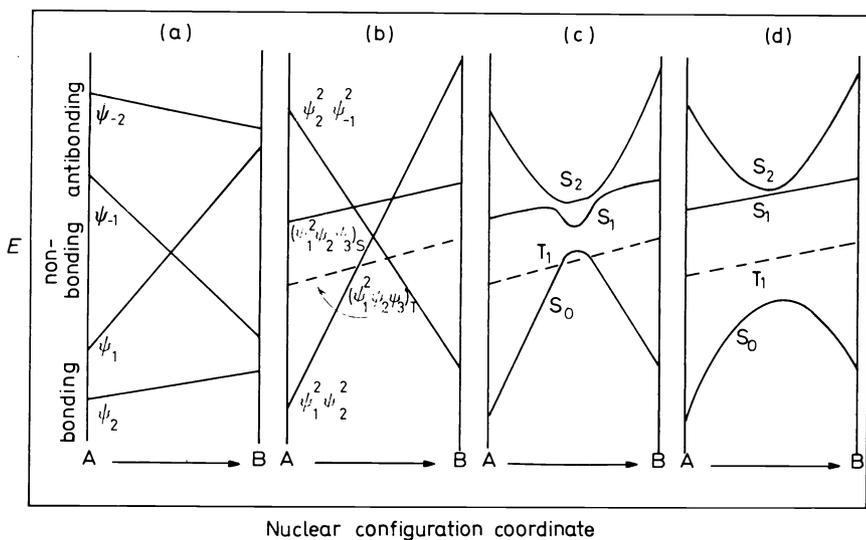
Figure 5. Electronic states along a ground-state-forbidden pericyclic reaction path.

above, pericyclic minima with uninterrupted cyclic arrays of interacting orbitals (tight geometry) are generally encountered in the S_1 surface, in which an interruption of the cyclic interaction by a suitable geometrical change such as II→I would increase energy. In T_1, such an interruption should be favourable and the minima are likely to occur at loose geometries such as I and are actually nothing else but 'broken σ-bond' minima. Because of their relation to pericyclic reactions, we set them apart and refer to them as 'open-chain' biradicaloid minima.

Classification of reactions into singlet and triplet categories is actually also based on the same criterion, namely the nature of the minimum through which return to S_0 occurs (S_1 or T_1), and triplet reactions could be further subdivided according to where the triplet manifold is reached (near the initial geometry, along the reaction path, or near the product geometry).

Most of the above basic categories comprise a large number of reaction types. For instance, return to S_0 via a 'broken σ-bond' minimum accounts for photodissociation reactions of peroxides, nitrites, halogeno compounds, benzylic compounds, ketones (α-cleavage), etc., for intermolecular and intramolecular hydrogen abstractions by excited carbonyls, olefins, nitrogen compounds, etc., for numerous triplet processes such as the stepwise versions of the di-π-methane and oxa-di-π-methane processes (one could argue that some of these should really be classified as 'open-chain' biradicaloid minima), etc. In order to put this type of classification on a firm footing it will be necessary to perform model calculations for various reaction types and such efforts are currently under way in several laboratories (see literature cited in ref. 6. and also ref. 13 and the second part of this report).

However, a classification based on the nature of the minimum or funnel through which return to S_0 occurs still leaves much to be desired since it tells little about the way in which that minimum or funnel was reached. For example, the photochemical sequence[22]

twisted at thick bond · twisted at thick bond
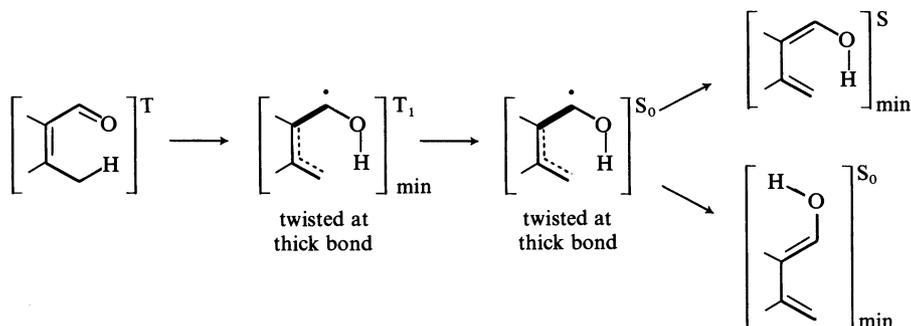
will belong to the 'twisted π-bond' biradicaloid category, along with processes such as *cis–trans* isomerization of olefins or sensitized ring-opening in simple cyclobutenes, and it is useful to subdivide such categories according to the path along which the 'twisted π-bond' minimum was reached.

3. Use of simple MO arguments to locate barriers in S_1 and T_1

(a) *The role of energy barriers*

Finding the location of minima and funnels in S_1 and T_1 and thus identifying the geometries at which S_0 is likely to be reached in the photochemical process represents only a part of the general problem, and the easy part at that. The difficult part is to estimate the probabilities and rates at which the various funnels and minima as well as intermediates along the way are reached, given the starting geometry, excitation wavelength, temperature, solvent, and other reaction variables, and to rationalize the effect of structural modifications in the starting molecule on these probabilities. Although some progress along these lines has been made (see ref. 6 for leading references), the present situation is very unsatisfactory.

It is still relatively easy to calculate which minima cannot be reached at all, given initial excitation conditions, since they are too high in energy themselves, or since they are separated by excessively high energy barriers in S_1 or T_1. Such reaction paths may, however, become accessible if additional energy is imparted to the molecule by use of a more energetic photon, at higher temperatures, or by other means such as absorption of a second photon. We have been engaged in an experimental investigation of pericyclic reactions of this type for some time[23-26].

The existence of barriers in S_1 and T_1 can in principle be established by calculations. Qualitative estimates are often possible using the technique of correlation diagrams, which also provides useful insight into the physical origin of the barriers.

(b) *'Correlation-imposed barriers'*

Sometimes referred to as 'symmetry-imposed barriers', these are the barriers whose existence can be inferred from correlation diagrams. Of course, other types of barriers exist as well and can sometimes be predicted, for instance, those due to steric hindrance.

For our application, correlation between states at the initial geometry and those at the geometry of the funnel or minimum through which return to S_0 occurs must be investigated. Usually, correlation of molecular orbitals is established first, then correlation between configurations (*Figure 5*). Then, an attempt is made to identify states with configurations both at the starting and final geometry. This is sometimes complicated, e.g. for aromatic chromophores, and at least approximate calculations may be required. If the configuration representing the $S_1(T_1)$ state at the starting geometry correlates with one of the low-energy configurations at the final geometry, preferably with the one which represents the S_0 or $S_1(T_1)$ state, no barrier appears in the configuration correlation diagram. If the correlation is with a high-energy configuration at the final geometry, such a barrier appears (*Figure 6*).

Finally, it is necessary to go from the configuration correlation diagram to a state correlation diagram. This will often cause line crossings to be avoided, so that barriers in S_1 diminish (*Figure 6*), and it is unfortunately often difficult to estimate how much, without at least approximate calculations.

Nuclear configuration coordinate
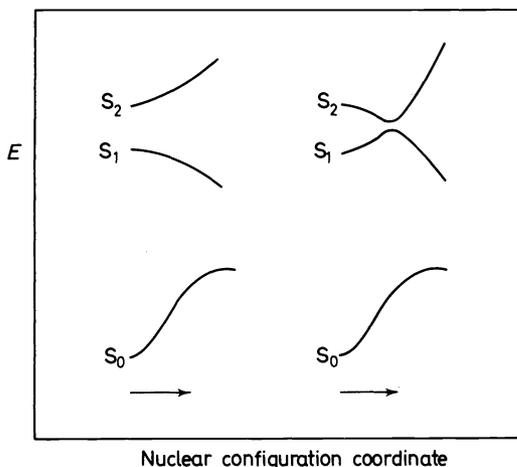
Figure 6. Origin of correlation-imposed barriers in S_1 and T_1 surfaces.

(c) *Correlation diagrams for return through 'spectroscopic' minima*

If the photochemical reaction is one of those which lead to an excited product (return to S_0 from a 'spectroscopic' minimum), construction of the correlation diagram is facilitated since state energies and assignments are often available experimentally both at the starting geometry and at the final geometry in the diagram. Of course, this type of photochemical reaction is rather infrequent.

Examples of this situation are certain pericyclic reactions in the triplet state. We have already mentioned that return to S_0 from T_1 in reactions such as cyclobutene ring opening ordinarily can be expected to occur from a biradicaloid minimum at a loose geometry, off the concerted pericyclic path (in this case, twisted butadiene). However, if the T_1 state of the product is stabilized and that of the loose geometry destabilized by suitable structural features, the minimum at loose geometry may disappear and return to S_0 may occur at the product geometry instead. On this basis it was predicted[3] that ring opening of 'Hemi-Dewar naphthalene' III in the triplet state is likely to lead to triplet naphthalene and this has more recently been confirmed experimentally[27]. Similarly, we believe that the triplet ring opening of various other condensed cyclobutenes studied in our laboratory[23, 25, 26], such as IV, also gives triplet products although in their case no experimental evidence is available at this time (the product molecules are not phosphorescent).

In such a case the correlation diagram is identical with the ordinary Woodward–Hoffmann correlation diagram, and a 'ground state allowed' reaction path will generally exhibit a barrier in T_1 (Woodward–Hoffmann rules are applicable). Along 'ground state forbidden' paths there may but need not be a barrier in T_1. Along such paths one originally bonding orbital, say ψ_1, becomes antibonding, and one originally antibonding orbital, ψ_2, becomes bonding as one goes from the starting to the final geometry. *Figure 7* shows that the only singly excited configuration at the initial geometry which
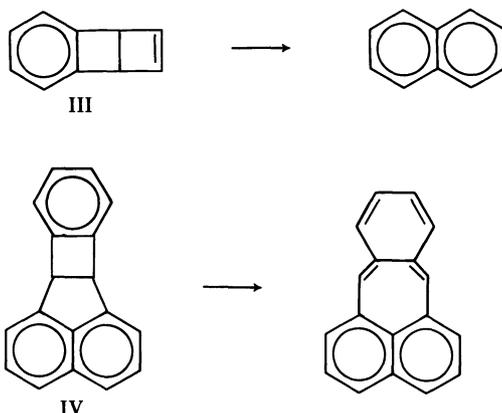
ORBITAL ENERGIES
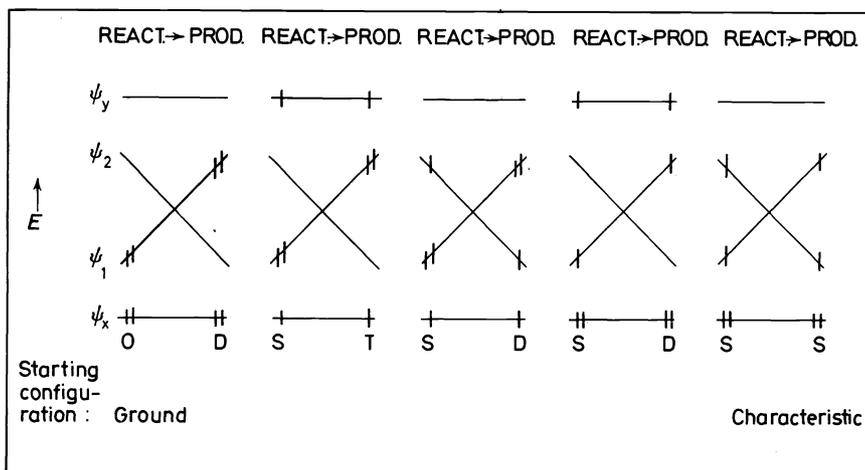
Figure 7. Correlation diagram for various types of configurations along a ground-state-forbidden reaction path. O: ground configuration, S: singly excited, D: doubly excited, T: triply excited.

correlates with a singly excited configuration at the final geometry is $\psi_1 \rightarrow \psi_2$, (the 'characteristic configuration'). If this represents the T_1 state of the starting molecule and a low–lying state of the final molecule, no correlation–imposed barrier is expected; if these conditions are not fulfilled, a barrier must be expected in spite of the fact that the path is 'ground state forbidden'. This can occur, first, if ψ_1 is not the highest occupied molecular orbital (HOMO) at the starting geometry (or if ψ_2 is not the lowest free molecular orbital, LFMO), and we refer to this case as 'abnormal orbital crossover', and second, even if ψ_1 is HOMO and ψ_2 is LFMO ('normal crossover'), but if for some reason such as strong configuration interaction the T_1 state is represented by a configuration other than HOMO$\rightarrow$LFMO. We believe that

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'abnormal orbital crossovers' and associated barriers are responsible for the peculiar behaviour of condensed cyclobutenes such as IV which we have been studying experimentally (two-photon photochemistry)[23, 25, 26]. The first mention of a barrier of this origin which we have been able to find in the literature is due to Chu and Kearns[28]. The existence of these barriers does not follow from the various ordinary versions of Woodward–Hoffmann rules.

It is possible to estimate whether the orbital crossover will be 'normal' or 'abnormal' from simple inspection of Hückel molecular orbital coefficients of the chromophores involved[4], but a detailed description of this procedure is outside the framework of this review. This extremely simplified approach has allowed us to make predictions of which some have been verified[4, 5, 25, 29], but suffers from the vague nature of a requirement of 'large' coefficients at certain atoms since too little is presently known about just what is 'large enough'[4, 5, 26].

(d) Correlation diagrams for return through 'biradicaloid' minima

In the much more common case of reactions which involve return to S_0 via a biradicaloid minimum, the situation is often complicated by the fact that experimental information is available only at the start of the correlation diagram and a reasonable guess needs to be made for state energies at the final geometry. Again, even approximate calculations can be of considerable help.

In the molecular orbital correlation diagram, one of the orbitals which are bonding at the starting geometry (ψ_1) and one of those which are antibonding at the starting geometry (ψ_2) become approximately non-bonding at the final biradicaloid geometry. As before, no 'correlation imposed' barrier is to be expected if $S_1(T_1)$ at the starting geometry is represented by the 'characteristic configuration' $\psi_1 \rightarrow \psi_2$, and if this configuration represents one of the low-lying states at the final geometry. Otherwise, a barrier will be present in the configuration correlation diagram, and if effects of configuration interaction are not overwhelming, also in the $S_1(T_1)$ surface in the state correlation diagram. Of course, an uphill slope will at any rate be present in S_0 as follows from the very definition of a biradicaloid geometry.

'Ground state forbidden' pericyclic reactions in the singlet state represent perhaps the simplest case for which such correlation diagrams can be constructed. Ordinarily, the diagram extends from the starting geometry via the pericyclic biradicaloid minimum all the way to product geometry (Figures 5, 7) and is of course identical with standard Woodward–Hoffmann correlation diagrams[9, 10]. Even the existence of the pericyclic biradicaloid minimum itself follows from the orbital crossing in such an extended diagram (Figure 5)[8, 11].

Again, there are two main factors which can prevent the $\psi_1 \rightarrow \psi_2$ configuration from corresponding to S_1 at the starting geometry. First, the orbital crossover may be 'abnormal', so that ψ_1 is not HOMO and/or ψ_2 is not LFMO, and this can be predicted in simple ways as already discussed. Alternatively, configuration interaction or other factors may cause the state corresponding to HOMO→LFMO excitation to be only second or even higher in energy, for instance, in various aromatic chromophores. We believe that both cases have been encountered in our studies of electrocyclic

. and cycloreversion reactions of condensed cyclobutenes[23−26], as well as in other instances.

For other reaction types, construction of molecular orbital correlation diagrams is more difficult, particularly if molecular symmetry is low (biradicaloid minima at loose geometries). Individual types of biradicaloid minimum have their associated characteristic configurations. For instance, the configuration resulting from $\sigma\sigma^*$ excitation in a single bond is characteristic for the minimum reached by stretching that bond (*Figure 3*). This is often not identical with the configuration representing S_1 and T_1 at the starting geometry, which is more likely of $\pi\pi^*$ or $n\pi^*$ nature, so that barriers result, and emission from the starting material can be often observed.

A MODEL CALCULATION FOR PERICYCLIC PROCESSES

1. General

Although the above described model for photochemical processes is partly based on approximate numerical calculations, and partly on general arguments which appear to rest on fairly firm grounds, its intuitive and qualitative nature is obvious. Indeed, it is best thought of as a small step towards providing a way of thinking about organic photochemical processes, organizing and classifying them in terms of simple concepts, and suggesting directions for further work.

Two such lines of further work appear most important at present. First, one needs to obtain at least semiquantitatively reliable hypersurfaces for representative cases of important classes of photochemical reactions and a safer understanding of the nature of the electronic states and general principles involved; second, one needs to develop methods for estimating relative probabilities with which various processes on these hypersurfaces occur, i.e. a feeling for the molecular dynamics, including surface-jumping probabilities.

Here we shall only consider the first of these topics. There are basically two ways how one can approach the problem, and both seem well worth pursuing. One can make necessarily highly approximate calculations on fairly faithful and thus rather complicated models of suitably selected representative photochemical reactions (several references to such studies are given in ref. 6 and a nice recent example is ref. 13). Alternatively, one can perform fairly accurate calculations on very simple models, which might turn out to be easier to interpret in qualitative terms transferable to a whole class of more complicated systems.

We shall discuss the results of a study of the latter type, in which we attempt to obtain further qualitative insight into the nature of photochemical pericyclic processes occurring in the singlet state along 'ground state forbidden' paths. Our starting point is the now classical work of van der Lugt and Oosterhoff on the butadiene–cyclobutene interconversion[8], which provides good reason to believe that the reactions proceed through a minimum or funnel at a pericyclic biradicaloid geometry [*Figure 5*(c)]. Woodward–Hoffmann rules indicate that the miminum can be reached from the starting geometry without encountering a barrier in S_1 (unless the orbital crossing is

of the 'abnormal' type or configuration interaction unfavourable, as discussed above).

We are now interested in answers to questions such as the following:

(a) How different will the results be for pericyclic reactions other than electrocyclic, say for photocyloadditions?

(b) What role if any do excimers and exciplexes play in photocycloadditions? What is their place on the correlation diagram and what is their relation to the pericyclic biradicaloid minimum?

(c) Triplet–triplet annihilation produces excited singlet molecules. What is the place of the singlet state arising by triplet–triplet coupling on the correlation diagram? Could it have anything to do with the photochemical process? Such a state has been consistently predicted to lie at quite low energy in calculation of spectra of p-cyclophanes and their simple models[30], as well as in a recent study of dioxetane decomposition[31].

(d) What is the nature of electronic states at the pericyclic biradicaloid geometry? Simple VB theory using covalent structures only leads one to expect two low-lying covalent singlet states[8]. On the other hand, simple MO theory with first-order configuration interaction predicts one covalent and two ionic states[3, 12]. How will this be reconciled in the full CI description?

(e) What is the order of the three low-lying states at the pericyclic biradicaloid geometry? 'Singly excited' below 'doubled excited', as in *Figure 5*(d)? Or the opposite, as in *Figure 5*(c)? The latter is needed for the original van der Lugt–Oosterhoff mechanism, and is predicted by their calculation as well as from a simple VB picture[8]. The former is predicted by the simple MO picture (and by a more recent CNDO/2 calculation[32]). It places a minimum in S_2 rather than S_1. At first sight, one might then expect excited product formation rather than return to S_0 at the biradicaloid geometry, but this is almost never observed. Does this mean that the surface arrangement shown in *Figure 5*(d) still efficiently causes $S_1 \rightarrow S_0$ jumps at the geometry of the minimum in S_2? Or is the ordering in *Figure 5*(c) correct? Why are the results so sensitive to the method of estimate or calculation? Could one predict when excited products will actually be formed?

(f) If the van der Lugt–Oosterhoff mechanism and their assertion that the 'singly excited' ionic state is only accidentally present and irrelevant for the reaction are correct, why do arguments[14, 17] using perturbation theory on the initially reached state, i.e. the 'singly excited' state work? Why is the slope of this state at the initial geometry important? Or is the agreement only accidental?

(g) Also, if *Figure 5*(c) is correct and the minimum is in S_1, are there probable processes other than return to S_0 which a molecule in this minimum might undergo?

2. Method

We have started with the 2s + 2s pericyclic process as representative of the 'ground state forbidden' pericyclic paths. The only general feature which is common to all such processes is the involvement of four orbitals with four electrons, interacting in a cyclic array in the bond-switching process. The simplest model for such a process would appear to be an interaction of four hydrogen atoms. We have therefore started an investigation of the six-

dimensional hypersurfaces for the low-lying states of H_4. These are of considerable interest in themselves for a study of bimolecular photochemistry of molecular hydrogen, of vibrational and rotational energy transfer, the possibly chemiluminiscent $H_3^+ + H^-$ ion recombination reaction, of a possibly observable molecular hydrogen excimer, etc., but here we shall only discuss their significance as a model for pericyclic reactions. Since we concentrate on photocycloadditions, we shall in particular discuss the results for that part of the six-dimensional nuclear configuration space which corresponds to an approach of two H_2 molecules, one of which is excited. To provide a concrete model, we can imagine that we are modelling a face-to-face approach of two olefins to form a cyclobutane.

The choice of the method of calculation was guided by the desire to provide good interpretability in simple and intuitive physical terms with the minimum sacrifice of accuracy. This condition suggested the use of a minimum basis set, i.e. four 1s orbitals, in order to provide simple transferability of the results to other four-centre reaction systems. Most of our calculations were performed with such a basis set, but because of its well-known shortcomings we have considered it necessary to repeat the calculations with a 1s2s basis set at representative geometries. We found that all essential results, and in particular the nature and order of the excited states, remained unchanged. This is also true when we compare our results with data for a few selected geometries which already exist in the literature, including some obtained with a 1s1s′ basis set[33].

In order to compensate at least partially for the limited basis set, we have optimized all other aspects of the calculation: orbital exponents were optimized separately for each state and each geometry, full CI was used, and at many geometries we have investigated the effect of allowing the orbitals to become polarized by floating the centres of each member of a contraction[34] (the orbitals were contractions[35] of four Gaussian type orbitals). The calculations were performed in the VB formalism using a programme which had previously proved valuable[36] for molecules of type H_n^+.

Qualitatively similar results were obtained with the extended Hückel method combined with a full configuration interaction procedure in which the Mulliken approximation is used for multicentre integrals, using a programme developed by Harris[37]. The absolute values of energies and the scale of internuclear energies did not agree well with the *ab initio* results, but the ordering and shapes of the surfaces are so similar in the two methods that it is almost impossible to tell them apart without looking at the scales on the axes. This encouraged us to use the cheap Hückel method for calculations on more realistic models for organic photocycloadditions, and these are currently in progress.

3. Results

Since we wish to extrapolate from the H_4 case to cycloaddition in general, and possibly to pericyclic reactions in general, only the very basic features of the results of our calculations are of interest here, such as the nature of the excited states, and general shape and ordering of the hypersurfaces. The fact that the same basic features are obtained from the *ab initio* work and from the very simple semiempirical calculation makes us believe that they could

also be abstracted from any other reasonable calculation on a four-orbital four-electron model.

The particular subspace of the total six-dimension nuclear configuration space of H_4 which is of greatest interest for modelling a concerted cyclo-addition path is three-dimensional. In this subspace, H_4 is planar and has a trapezoidal, rectangular or square geometry. The three dimensions can be taken to be, for instance, the distance R between the centres of the two approaching H_2 molecules, and their respective lengths R_1 and R_2. The hyper-surfaces of the lowest three singlet states have been mapped quite thoroughly in this subspace. Displacements in the remaining three dimensions have so far been examined only in a sporadic fashion; some of these results will also be mentioned in more detail below.

Three-dimensional contour diagrams for the lowest three singlet surfaces in the R, R_1, R_2 subspace are shown schematically in *Figure 8*. The purely repulsive predominantly covalent ground state G contains the well-known hypothetical rectangular path for the exchange $(H_2 + D_2 \rightarrow 2HD)$ reaction of two ground state $(X^1\Sigma_g^+)$ molecules proceeding through a square transition state and provides nothing new.
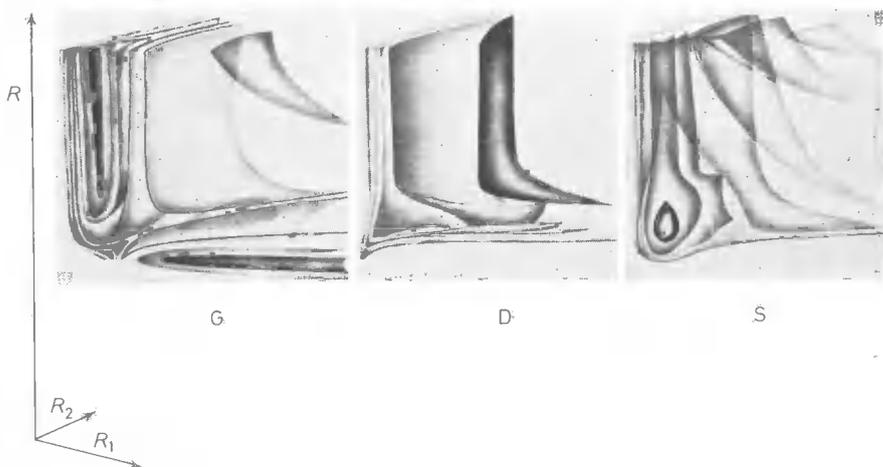
Figure 8. A schematic representation of three-dimensional contour maps for the lowest three singlet surfaces of H_4 in the R, R_1, R_2 subspace (trapezoidal geometries). Darkest surface in each drawing corresponds to lowest energy. The vertical cutting plane in front corresponds to $R_1 = R_2$ (rectangular geometries). The vertical R axis lies in the plane of the paper, R_1 and R_2 are horizontal and run out of the plane of the paper towards and away from the viewer, respectively. The scale on the R axis is half the scale on the others. In most areas, the surfaces are spaced 0.05 Hartree apart. A more complete representation will be shown elsewhere (W. Gerhartz, J. Michl and R. D. Poshusta, to be published).

The higher lying purely attractive 'excimer' state S corresponding to the trapezoidal approach of a singlet $\sigma \rightarrow \sigma^*$ excited H_2 molecule $(B^1\Sigma_u^+)$ to a ground state molecule $(X^1\Sigma_g^+)$ contains a minimum not far from the square ground state transition complex geometry, namely at a trapezoid with

parallel sides of 1.6Å and 0.95Å lying 1.35Å apart. Similarly as the $B^1\Sigma_u^+$ state of H_2, which can be well represented as $H^+H^- \leftrightarrow H^-H^+$, the excimer state is an 'ionic' state. 'Charge resonance' and 'exciton resonance' contributions are clearly apparent in the wavefunction. In MO language, this is a singly excited state. Its absolute energy minimum actually lies outside the R, R_1, R_2 subspace, at a planar kite geometry, but the energy decreases on going from the best square (1.25 × 1.25 Å) to the best trapezoid (4 kcal/mol) and the best kite (11 kcal/mol) are so small that no attempt will be made to extrapolate to organic molecules. However, the bound nature of the excimer (~ 25 kcal/mol), absence of avoided crossings along the trapezoidal path for its formation, the consequently expected adiabatic reversible formation, and the nature of the wavefunction are in good correspondence with the present understanding of excimers of organic molecules.

The S state only forms the S_1 surface if the internuclear distances are very small. Elsewhere, it corresponds to the S_2 surface. At its minimum geometry (kite) it is about 20 kcal/mol above S_1, and 120 kcal/mol above S_0. Thus, throughout most of the R, R_1, R_2 subspace, the S_1 surface is formed by a purely repulsive state, D, originating in overall singlet coupling of two triplet $\sigma \rightarrow \sigma^*$ excited H_2 molecules ($b^3\Sigma_u^+$). The shape of the D surface in the R, R_1, R_2 subspace indicates that each of the triplet H_2 molecules is trying to fall apart, and in addition, the two triplet H_2s repel each other. The path of least ascent for bringing the four H atoms together in this state proceeds along square geometries. About 50 kcal/mol are needed to reach the 1.25 × 1.25 Å square. Thereafter energy rises rapidly and the D state crosses the S state near a 0.75 × 0·75 Å square. The reason why the square geometries are low in energy is easily found in the nature of the wavefunction. The local minimum is due to an avoided touching between the G and D states along the line of square geometries. The course of the energies of G, D, and S states along the line of square geometries is given in *Figure 9*, which shows that the crossing is avoided less as the size of the square increases. The origin of the avoided touching is simple: in VB terms, it corresponds to the avoided crossing of zero-order surfaces corresponding to the two 'Kekulé' structures (in the G state, neighbouring atoms are coupled into local singlets, in the D state, into local triplets); in MO terms, it originates in an orbital crossover familiar from Woodward–Hoffmann rules.

Also the shape of the G, D and S curves along the square geometries is easily understood. In the limit of infinite square, the two covalent 'Kekulé' structures have equal energies and their interaction vanishes (no overlap), so that G and D are both purely covalent and have equal energies, while the ionic state S is much higher in energy (no stabilization by charge or exciton resonance). In the limit of very small squares, the interaction between the two covalent 'Kekulé' structures is very strong so that G and D split considerably and D acquires a large degree of ionic character, while S is relatively much less unfavourable than before since charge separation which it involves is only over very small distances, and since exciton and charge resonance are effective. As the size of the square goes to zero, nuclear repulsion of course takes over and energies of all states rise very steeply.

Figure 9 may be characterized briefly by saying that the simple VB description of the low-lying electronic states of the square biradicaloid species is
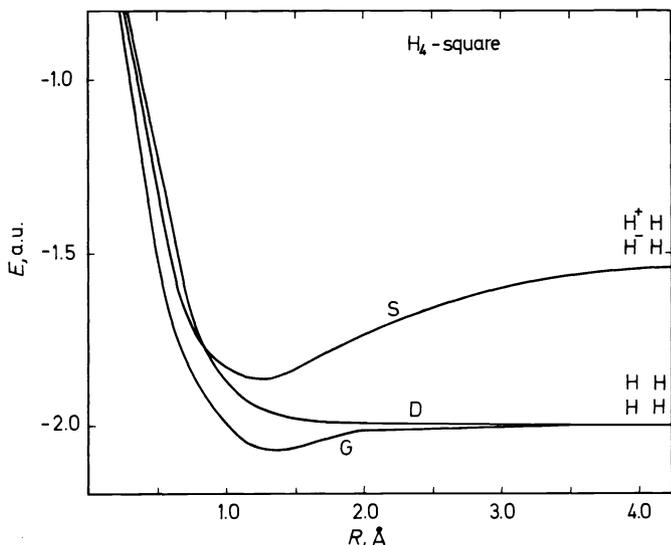
Figure 9. The lowest three singlet states of H_4 at square geometries.

correct for large squares (two covalent low-lying states[8]) while the simple MO description with first-order CI[3, 12] is essentially correct for small squares (a covalent ground state and two ionic low-lying excited states, the lower of which is of singly excited nature). Analogy to the VB–MO description of the dissociation of a diatomic molecule is striking.

At the region of greatest interest, i.e. 1.25×1.25Å square, neither description is good by itself. The D state lies below the S state, contrary to what the simple MO picture with first-order CI predicts, but not far below, and has considerable ionic character, not obvious from the simplest VB picture. Either picture can be brought to perfection by extending it into full CI. In MO terms, this indicates the necessity of strongly increased (second-order) configuration interaction as the size of the square increases, and indeed, already in the 1.25×1.25Å region. No such effect is needed for the S state whose purely ionic nature does not change significantly along the correlation diagram in *Figure 9*. It has been noted even in other biradicaloid systems that the D state generally involves heavy configuration mixing while the S state does not[38], and the T–T nature of the D state undoubtedly again is to blame. The T–T nature of the lowest excited gerade state of butadiene ('doubly excited state') has been recognized by others[39].

Leaving now the R, R_1, R_2 subspace, we note first that the D state also strongly slopes downhill from the 1.25×1.25Å square geometry along a path which distorts the square into a rhomb (b_{2g} mode). Following the downhill path, one arrives at one ground state H_2 molecule in which two originally diagonally opposed hydrogen atoms are now bonded, and two hydrogen atoms, coupled into a 'local' singlet. Along this path, the D state thus becomes S_0 (it crosses the G state which rises in energy).

The logical next step thus is an investigation of a path in which both diagonal bonds are allowed to develop by an out-of-plane distortion of the

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square which can be best imagined as pulling the two diagonals apart. *Figure 10* shows the state correlation along this path in a schematic fashion. In the infinite separation limit, the length of the diagonals is adjusted so as to minimize the energy, so that in this limit D corresponds to two ground state
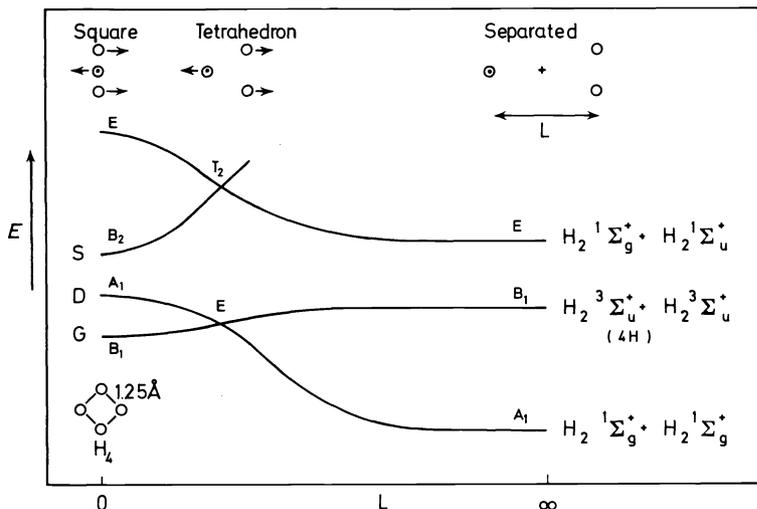
Figure 10. The lowest singlet states of H_4 along the 'perpendicular' path of approach (schematic). On top, side view of the molecule.

H_2 molecules ($X^1\Sigma_g^+$), G to four H atoms (two infinitely long $\sigma \rightarrow \sigma^*$ triplet H_2 molecules ($b^3\Sigma_u^+$) infinitely far apart, coupled into an overall singlet). Upon lowering the symmetry, state crossings are avoided, and we note that G and D really are one and the same surface in the sense of our initial discussion (*Figure 1*). However, S_0, S_1 and S_2 are still well defined using our convention.

This behaviour of the D state is easily understood in qualitative VB terms: if neighbouring atoms in a square are coupled into local triplets, diagonally opposed atoms are coupled into local singlets. The D state can therefore be thought of not only as two triplet H_2 molecules brought together side by side, but also as two ground state singlet H_2 molecules placed across each other. Similarly, the G state can be thought of as two ground state singlet H_2 molecules side by side as is usual, but also as two triplet H_2 molecules placed across each other. We are now attempting to find out whether these considerations might provide a clue to the presently mysterious mechanism of the $H_2 + D_2$ exchange reaction in the ground state.

Figure 10 again clearly sets apart the ionic S state from the G and D states and indicates why D should have a partly covalent nature. It also indicates that the perpendicular approach excimer formation from $H_2(X^1\Sigma_g^+)$ + $H_2(B^1\Sigma_u^+)$ is unfavourable compared with the trapezoidal approach shown in *Figure 8*. We have also performed a few calculations including distortions in the remaining two dimensions, such as T-shaped approach, but have so far not discovered any path more favourable than the trapezoidal approach

although we can be certain that some distortions toward kitelike shapes will be favourable at the final stages of the approach, since the minimum itself is at kite geometry.

The results obtained so far suggest the following possible outcomes of a reaction of ground state $H_2(X^1\Sigma_g^+)$ with singlet $\sigma \rightarrow \sigma^*$ excited $D_2(B^1\Sigma_u^+)$ under conditions of efficient removal of vibrational energy (such conditions are common in the organic photochemical processes we are trying to model, but not necessarily in the photochemistry of H_2 itself, about which little seems to be known at present). First, adiabatic reversible formation of an excimer (S state). Second, radiative or radiationless transition into the G or D state. Third, if G state is reached, it is reached near the square transition complex geometry, and formation of ground state $H_2 + D_2$ or HD + HD along the familiar rectangular path follows. If D state is reached instead, four H atoms may be formed (*Figure* 9), ground-state HD, H and D may be formed (distortion into a rhomb), or 2HD may result from cross-bonding (*Figure* 10). Finally, because of the avoided crossing between G and D states, radiationless transition from D to G induced by nuclear motion along the b_{1g} mode may be quite probable. Again, $H_2 + D_2$ or HD + HD would result. Additional results also suggest the existence of a quite fascinating reversible adiabatic fragmentation path for the excimer, namely formation of H_3^+ and H^-, but a more detailed discussion lies outside the present framework.

If a Woodward–Hoffmann type of diagram were now to be drawn for the photochemical $H_2 + D_2$, 2s + 2s pericyclic process on the basis of our results, it would look much like *Figure* 5(c), except that it would be symmetrical and contain a minimum in the singly excited state S just above the one in the doubly excited state D.

We can now finally proceed to an attempt to extrapolate the basic features of our results to organic pericyclic processes. A photocycloaddition reaction of two olefin molecules will differ in several important respects from the H_4 case, even if we make the assumption that the four π-electrons are the only ones which need to be considered explicitly. First, the orbitals involved will be p, not s. Our results are thus limited to processes which do not involve the use of both lobes of a p orbital, for instance, 2s + 2s. Second, additional sigma bonds are present, and these will prevent fragmentations such as $H_2 + H_2^* \rightarrow 4H$. Also, the bonds destroyed in the reaction are of π type and the ones formed are of σ type, so that the high symmetry of the H_4 case is lost. Finally, H_4 is non-polar, so that comparison will be best made with equally non-polar hydrocarbons.

In spite of these differences, we believe that the basic similarity (identical topology) is sufficient to permit generalizations to be made as long as these are limited to qualitative insight into the nature of bonding or antibonding in various electronic states. Clearly, quantitative results such as absolute energies and details of shapes of the surfaces cannot be transferred to other isoconjugate systems, while generalized qualitative notions which have been abstracted from the wavefunctions can. This is the reason for which the previous discussion has emphasized questions such as 'which feature of the wavefunction makes the energy go strongly downhill in a certain direction?'.

We then expect the following for the lowest three singlet states along the concerted olefin cycloaddition path, which we shall again label G, D, S.

Because of the difference beween σ and π interactions, the avoided crossing of G with D will occur before the square geometry (cyclobutane) is reached. Also, the excimer minimum in the S state will be reached while the olefins are still relatively far apart. The D state can no longer dissociate into four separate atoms—that is prevented by the σ half of the double bond in the olefin. The other downhill path which involves cross-bonding may still be accessible but suffer from steric strain. If this is excessive, there will be a local minimum in the D state at the geometry of avoided touching with the G state. However, it will no longer be right below the minimum in the S state—that is more likely to occur at larger separations between the olefins. Most of these features can be reproduced qualitatively very simply, by adding Morse potentials to the H_4 surfaces so as to simulate the sigma components of the double bonds in the two olefins. This gives surfaces and curves such as those shown in *Figure 11*, which clearly bears strong resemblance to *Figure 5(c)*.
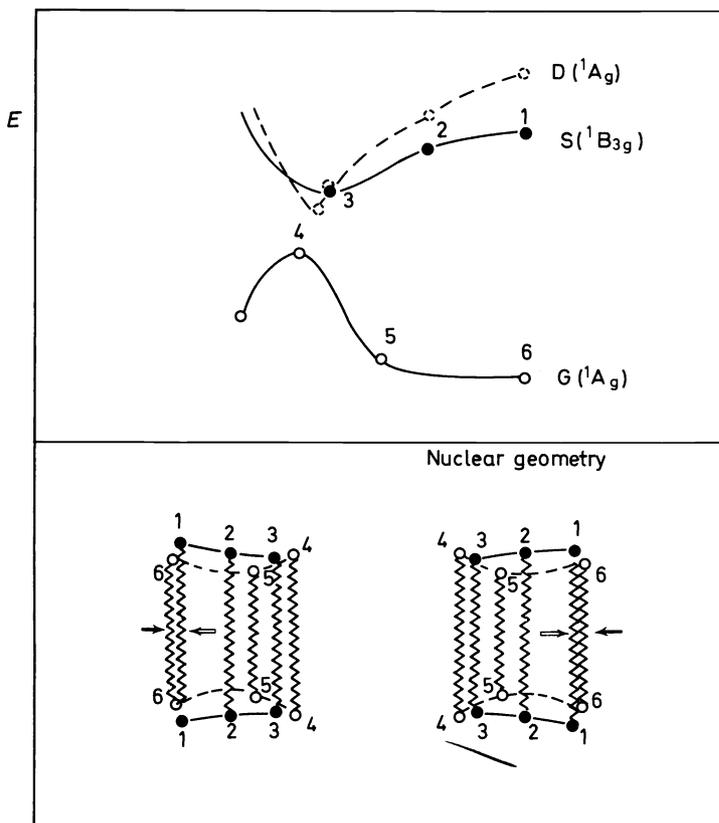
Figure 11. The lowest three singlet states of H_4 along the concerted cycloaddition path with Morse potentials added (schematic).

If the minima in S (excimer) and D (avoided touching, pericyclic biradicaloid minimum) occur at sufficiently different geometries, both can lie in the

S_1 surface, separated by a barrier. We hypothesize that the overall photo-chemical process is as follows: first, rapid, reversible, and adiabatic forma-tion of an excimer (minimum in S). If several orientations are possible (e.g. head-to tail and head-to-head), the most stable one will be preferred. Some of the excimer molecules may emit, causing return to starting olefins. The next step is thermally activated transfer over a barrier in S_1 into the pericyclic minimum (minimum in D), followed either by rapid radiationless vertical deactivation to the S_0 surface ('hump' in G) or, structure permitting, motion to the 'cross-bonding' funnel in S_1 (*Figure 10*) and formation of cross-bonded product. After vertical deactivation to G, formation of a cyclobutane or re-version to the two olefins could occur. *Figure 12* summarizes the situation and shows that other relative arrangements of the D and S surfaces can be imagined, such that the S_1 state has only one minimum. Then, only excimer emission or only return through the pericyclic minimum should be observed. Even if S_1 contains two minima, the barrier between them may be prohibitive at a given temperature.

Nuclear configuration
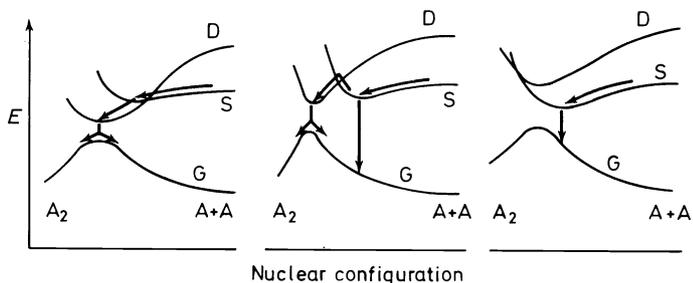
Figure 12. Various possible arrangements of the G. D and S surfaces along a cycloaddition path.

In this picture, the S state plays an important role—it provides a reservoir of excimers at a particular orientation, say, head-to-head, ready to reach the pericyclic minimum and proceed to products. In this way, estimates of the initial slope of the S surface are directly relevant for product structure.

Although our results are for a 4-electron system, their gross features can probably be also extrapolated to other 4N-electron cases, such as 4s + 4s photocycloadditions. Similarly, we believe that a similar picture holds for mixed dimerizations and for olefins with slightly polar substituents.

The above outlined reaction scheme appears to account for various features of the experimental results such as the intermediacy of excimers on the way to products[40, 41], the activation energy needed to proceed from the excimer to products[41], the applicability of arguments based on slope of the S surface to prediction of the reaction outcome[16, 17], including e.g. substituent effects, preference for syn-dimer formation from acenaphthylene, coumarins, etc. and lack of singlet cycloadditions of acenaphthylene to olefins without a low-lying empty orbital (unfavourable interaction diagram). The scheme is even in accord with the recent observation[42] of weak excimer emission resulting from irradiation of a substituted anthracene dimer if one assumes that travel across the barrier separating the S and D minima is possible in

both directions. Of course, the scheme cannot be considered confirmed until the presence of the postulated pericyclic minimum in S_1 is actually proved experimentally. Cross-bonding has also been occasionally observed[43].

It is tempting to speculate that minima in the S state analogous to the excimer minimum occur also in other types of pericyclic reactions, and that they serve a similar role of a reservoir. Since the S state is usually the one reached by the initial excitation (usually also the lowest singlet), an investigation of its initial slope[14] would indicate where the minimum in S lies and would thus correctly predict the reaction product if the minimum in S indeed serves as a channel leading molecules to the pericyclic minimum in the D state.

It is also interesting to speculate about the likelihood of excited product formation in pericyclic photochemical processes. Two main possibilities would seem to exist: either, the thermally activated travel from the pericyclic minimum in D to the excimer minimum in S would have to be able to compete with other processes which deplete the population of the former (and this may have been observed in a substituted anthracene as mentioned above[42]), or the S state would have to lie below the D state in the region of biradicaloid geometries as in *Figure 5*(d) (the latter possibility may have been realized in the electrocyclic opening of Dewar aromatics[27, 44]).

4. Summary

Our results can be summarized by suggesting answers to the questions (a)–(g) raised above.

(a) General qualitative features of the theoretical description seem to be common to various types of pericyclic reactions, at least to electrocyclic reactions and photocycloadditions.

(b) Excimers and exciplexes serve as reservoirs of molecules to be fed to the pericyclic reaction minimum. The excimer minimum lies on the singly excited surface in the ordinary correlation diagram and is distinct from the pericyclic minimum, which lies on the 'doubly excited' surface.

(c) The singlet state produced in triplet–triplet annihilation is identical with the 'doubly excited' state of the usual correlation diagrams. Ordinarily, internal conversion to a lower singlet state occurs while the two triplet molecules are still quite far apart. If this could be prevented, T–T annihilation would lead directly to the pericyclic minimum and might thus give a photo-cycloaddition product.

(d) At the pericyclic biradicaloid geometry, the ground state (G) is covalent, the excimer state (S) is ionic, the 'doubly excited' state (D) is of mixed nature, as can be most simply seen from a suitable correlation diagram.

(e) At the pericyclic biradicaloid geometry, there are good reasons to expect the 'doubly excited' state D to lie somewhat below the singly excited state as in *Figure 5*(c) (it contains less of the high-energy ionic structures). A calculation hoping to establish the order for any particular molecule should take care to properly recognize the 'mixed' nature of the D state. It should include extensive CI if it is of MO–CI type, in order to properly describe the triplet–triplet nature of the state, and it should include ionic structures if it is of the VB type. Further, enough flexibility in the atomic orbitals used should

be provided to allow adjustment of their size to the ionic character of each state separately.

As for excited product formation, the safest approach would be to search for cases in which the state ordering is reversed by suitable structural features.

(f) The singly excited state is an integral part of the photocycloaddition reaction scheme, since it leads the molecules to the excimer minimum. Arguments concerning its initial slope, stability of the excimer, etc. are germane to the problem, although return to the ground state which yields products occurs from the D state and not the S state.

(g) The D state can be viewed as originating from two triplet molecules side by side, but also as two singlet molecules crossed. One might therefore also expect a tendency for return to the ground state via cross-bonding.

ACKNOWLEDGEMENT

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[37] We are indebted to Prof. F. E. Harris (Departments of Physics and Chemistry, University of Utah), for providing us with the programme.

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