

# DIRADICALS

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## ABSTRACT

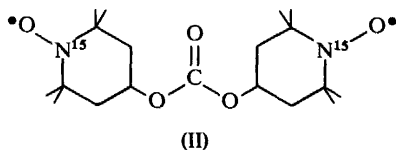
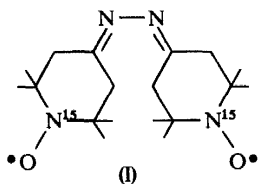
The four states—two diradical states and two zwitterionic states—which arise for a pair of weakly interacting electrons are described in detail for a series of simple systems (twisted ethylene, etc.). Simple rules of thumb are given for the intersystem crossing probability, via spin-orbit coupling, between singlet diradical state and triplet diradical state. Finally it is shown that the knowledge of the relative energies of diradical and zwitterionic singlet states, combined with the chemistry of photochemical reaction intermediates, may lead to a useful classification of photochemical reactions.

## INTRODUCTION: WHAT IS A DIRADICAL?

At the last IUPAC meeting in Saint Moritz, we were a dozen to attend an unscheduled evening discussion on Diradicals. Professor Hammond and I held viewpoints which were at opposite extremes of a wide spectrum of scientific judgements as to what a diradical really *is*. When the products of the meeting finally dissociated to the neighbouring bars and cafés, we had all, I think, learned something from the other person's point of view. Today I would like to summarize what I have learned about radicals and the way in which I understand them. It would be extremely useful, I think, to hear complementary points of view—possibly in a new unscheduled session.

The term 'diradical' is commonly used to describe a system which has two 'unpaired' electrons. This begs the question: how 'unpaired' must the electrons be? A close look shows that the degree of unpairedness which is required is different in different people's minds—and depends essentially on the type of experiment which is being performed.

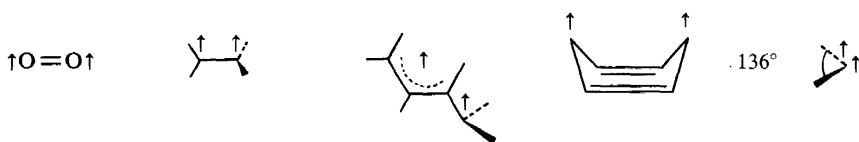
The e.s.r. spectroscopist will distinguish between systems as similar as (I) and (II):



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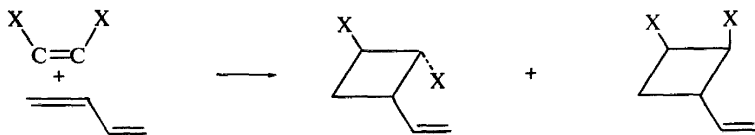
The e.s.r. spectrum of (I) has three lines<sup>1</sup>, with intensities 1:2:1, corresponding to two unpaired electrons *both* interacting with a pair of equivalent nitrogen nuclei of spin  $\frac{1}{2}$ . Since each electron 'sees' both nuclei, the e.s.r. spectroscopist speaks simply of a triplet state for the two electrons, not of a diradical. The e.s.r. spectrum of (II), however, has two extreme lines each surrounded by a pair of smaller ones and resembles the spectrum for two electrons each of which 'sees' only *one* Nitrogen 15 nucleus. Each electron therefore sees only its own nucleus; the electronic exchange is slower than the time for electron spin-nuclear spin hyperfine interaction and the e.s.r. spectroscopist speaks of the system as a diradical.

A second common way of thinking is to consider as diradical any species with parallel spins. Typical examples are oxygen, the ground state of twisted ethylene, the lowest  $\pi \rightarrow \pi^*$  triplet states of dienes and of benzene, and the ground state of methylene. Also, of course triplet diradicals have been in-

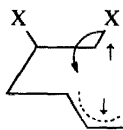


voked in innumerable photochemical reactions<sup>2</sup>. However, again this definition of diradicals is somewhat arbitrary; chemically bifunctional behaviour can be observed in singlet species. Also one can think of triplets—such as the triplet state of planar ethylene—which would not be diradicals in any chemical sense since one electron would be much more reactive than the other.

Since the work of Bartlett and co-workers<sup>3</sup>, many chemists think of diradicals as bifunctional species in which loss of configuration arises from internal rotation. For instance, a chemical behaviour such as



is ascribed to an intermediate species



in which rotation about the CC single bond is faster than CC bond reclosure. The loss of configuration is thus ascribed to this transient diradical, and the triplet state—in which the rotation is assumed to occur *much* faster than reclosure—serves as reference system of model diradical behaviour. Again this definition suffers from some degree of arbitrariness because you could retain configuration—because of steric reasons or secondary electronic effects—and still have been through two perfectly unpaired electrons. Several

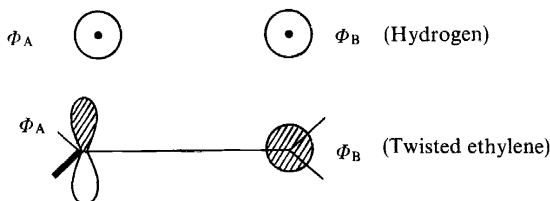
examples of diradicals exhibiting stereospecific behaviour are now known in the isomerizations of  $(-)\text{-}\Delta^3\text{-thujene}$  via (III)<sup>4</sup> and of allene cyclopropane via (IV)<sup>5</sup>:



In both cases the two odd electrons occupy orbitals of different symmetry—with zero overlap. Yet the products are stereospecific.

### WAVEFUNCTIONS FOR DIRADICALS: MIXTURES OF THREE CONFIGURATIONS

To describe a diradical we will consider two electrons which can occupy— independently or simultaneously—two orbitals  $\Phi_A$  and  $\Phi_B$ , localized in different regions of space. A major characteristic is that these orbitals interact



weakly, either via a small overlap or via a small exchange integral (if the overlap vanishes).

The situation where one electron occupies  $\Phi_A$  while the other electron occupies  $\Phi_B$ —which corresponds to the common description of a diradical—is simply described in valence-bond theory by the following two wavefunctions:

$$\begin{aligned} \text{singlet diradical state} &\equiv (2 + 2S_{AB}^2)^{-\frac{1}{2}} [\Phi_A(1)\Phi_B(2) + \Phi_B(1)\Phi_A(2)] \\ \text{triplet diradical state} &\equiv (2 - 2S_{AB}^2)^{-\frac{1}{2}} [\Phi_A(1)\Phi_B(2) - \Phi_B(1)\Phi_A(2)] \end{aligned} \quad (1)$$

These wavefunctions are *covalent* and describe proper diradical states. An essential characteristic of the weak interaction between  $\Phi_A$  and  $\Phi_B$  is that the energies of the two states are nearly equal. Valence-bond theory also tells us that there are two other states with *ionic* character, which have been called charge-resonance states<sup>6</sup> or zwitterionic states<sup>7</sup>:

$$\begin{aligned} \text{singlet zwitterionic state} &\equiv (2 + 2S_{AB}^2)^{-\frac{1}{2}} [\Phi_A(1)\Phi_A(2) + \Phi_B(1)\Phi_B(2)] \\ \text{singlet zwitterionic state} &\equiv (2 - 2S_{AB}^2)^{-\frac{1}{2}} [\Phi_A(1)\Phi_A(2) - \Phi_B(1)\Phi_B(2)] \end{aligned} \quad (2)$$

In these two states the two electrons occupy simultaneously either one or the other orbital. In symmetric molecules neither state has a dipole moment.

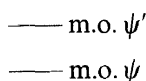
It is essential, when considering a diradical situation, to keep in mind the

coexistence of these four states. In hydrogen or in twisted ethylene the zwitterionic states lie much higher in energy than the covalent diradical states, but this will not always be so (see below).

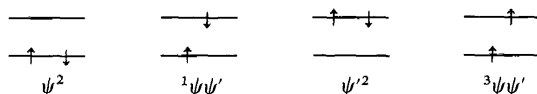
Let us now switch from the valence-bond, localized description of orbitals to the molecular orbital, delocalized description. In twisted ethylene the energy difference between all four states arises solely from the two-electron Coulomb and exchange energies, since  $\Phi_A$  and  $\Phi_B$  have the same one-electron energy. Since only the two-electron energies discriminate between these states, it is clear that a molecular orbital picture relying only on single configurations with given one-electron energies cannot describe diradicals correctly. A correct description will require the *combination of configurations*.

The main features of the molecular orbital description of diradicals are as follows<sup>7</sup>:

(1) A pair of diradical states, and the corresponding zwitterionic states, are characterized by *two* degenerate or nearly-degenerate molecular orbitals for the two electrons:



(2) Since there are two odd electrons there are four possible configurations associated with  $\psi$  and  $\psi'$ :



(3) The smaller the separation between the molecular orbitals  $\psi$  and  $\psi'$  the more certain we are that the system has a (triplet, singlet) pair of diradical ground states with wavefunctions (see below) reducing to (1). If the separation between  $\psi$  and  $\psi'$  grows larger, the closed-shell configuration  $\psi^2$  will tend to describe the ground state. Such an increase in energy separation can occur in two ways, as shown in *Figure 1*. There is no quantitative way of defining 'when' the system stops behaving as a diradical; it will depend on the property of interest. A typical molecule in the 'doubtful' region might be 1-norbornene<sup>8</sup>:



(4) The triplet state is always well described by the single configuration  ${}^3\psi\psi'$ .

(5) The diradical singlet state and the zwitterionic states are generally mixtures of *three*, sometimes two, singlet configurations. Only in very rare cases is each state well described by a single configuration. The form of the wavefunction for the singlet diradical state is intimately linked to the geometry of the molecule:

In *homosymmetric* diradicals, where  $\Phi_A$  and  $\Phi_B$  are related by some symmetry element (plane or axis), the molecular orbitals  $\psi$  and  $\psi'$  are proper combinations  $\psi_+$  and  $\psi_-$  of  $\Phi_A$  and  $\Phi_B$ . The lowest singlet then has the form

$$\lambda\psi_+^2 - \sqrt{1 - \lambda^2}\psi_-^2 \quad (1 \geq \lambda \geq 1/\sqrt{2}) \quad (3)$$

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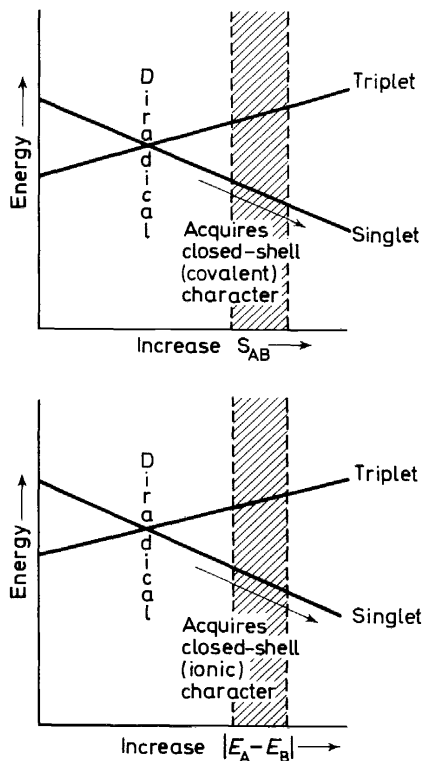


Figure 1. Energies of (triplet, singlet) diradical states as the molecular orbital splitting increases. The author is grateful to Verlag Chemie for kind permission to reproduce this figure.

where  $\lambda$  tends to  $1/\sqrt{2}$  as the overlap between  $\Phi_A$  and  $\Phi_B$  decreases. The other combination of  $\psi_+^2$  and  $\psi_-^2$  yields one of the zwitterionic states, as shown in Figure 2.

In *heterosymmetric* diradicals, such as methylene or oxygen, the orbitals  $\Phi_A$  and  $\Phi_B$  belong to different irreducible representations of the molecular point-group. The diradical state is then described by the single configuration

$${}^1\Phi_A\Phi_B \quad (4)$$

This configuration describes the lowest singlet of edge-to-face trimethylene, for example. However, in some cases the *lowest* singlet state may be a combination of the two ionic configurations and have 'zwitterionic' character. This is illustrated in Figure 3 for methylene<sup>9</sup> and oxygen<sup>10</sup>. The reasons for this inversion of levels are twofold in methylene: lower one-electron energy of the  $\sigma$  orbital, and large positive exchange energy  $K_{AB}$  in the covalent state. The difference in Coulomb energies ( $J_{AA}$  in ionic state,  $J_{AB}$  in covalent state) does not compensate for this. In oxygen, Kearns has shown<sup>10</sup> that the 'ionic' component of the  ${}^1\Delta_g$  state will fall below the covalent component in the presence of an external reagent. It is this ionic component which is responsible for the photochemistry of singlet oxygen.

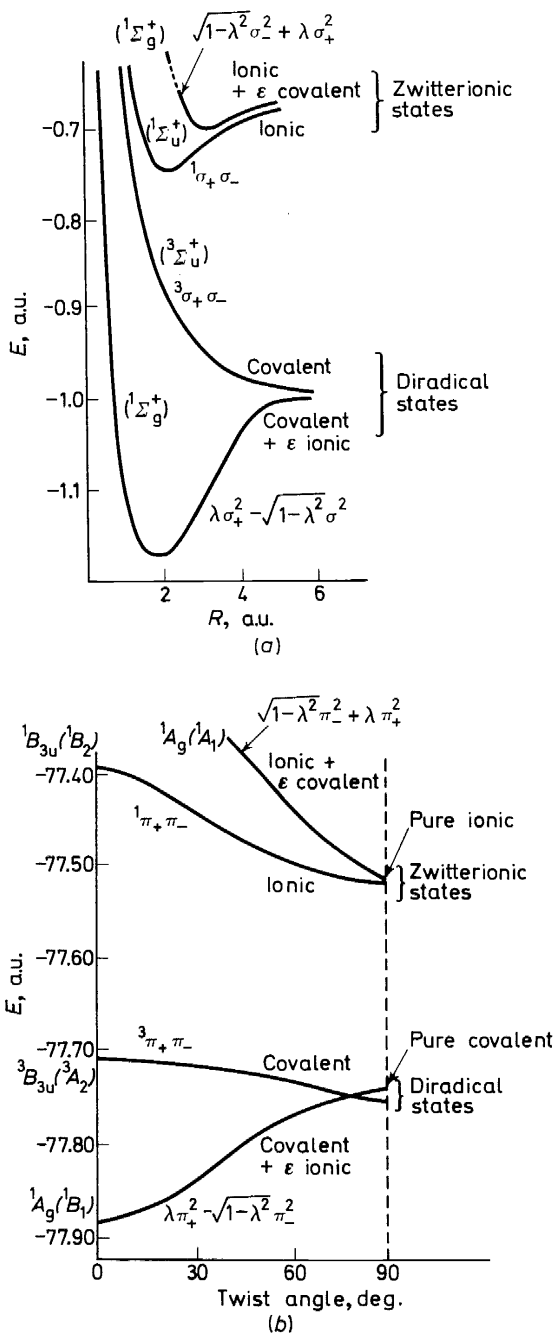


Figure 2. Lowest electronic configurations and states for hydrogen and ethylene. The author is grateful to Verlag Chemie for kind permission to reproduce this figure.

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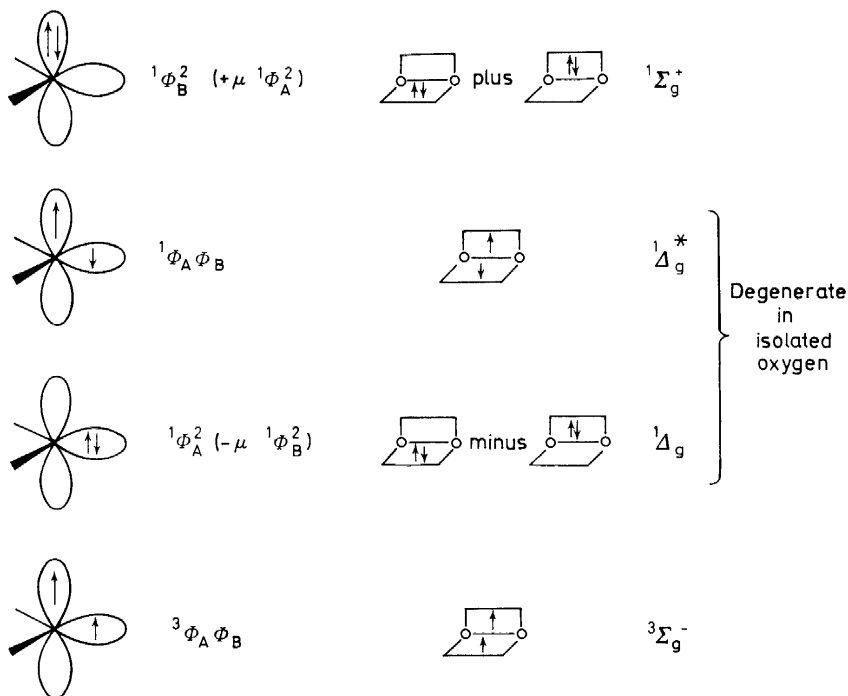
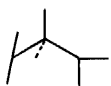


Figure 3. Electronic description of the states, and their ordering, in methylene and oxygen.

In diradicals without any symmetry ('non-symmetric'), then, the singlet ground state is a mixture of all three configurations  $\psi^2$ ,  $\psi'^2$  and  $^1\psi\psi'$ . A typical example is trimethylene in which one terminal group is in the carbon

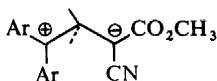


plane and the other rotated at some arbitrary angle. Figure 4 shows the behaviour of the three configurations and that of the states throughout the rotation. Although the energies of the former vary widely, the latter have a nearly constant energy. It can be verified that the complicated mixture which describes the ground singlet at  $50^\circ$ ,

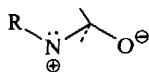
$$S_0 = -0.60(^1\psi\psi') + 0.58(\psi^2) - 0.55(\psi'^2) \quad (5)$$

is identical with a perfectly covalent wavefunction of type (1).

Finally, it may be asked what happens if the lack of symmetry is due to substituents at A and B which make one atom more electronegative than the other:



or to heteroatoms



Now the local energy of atom B is lowered relative to A. So the proper ionic wavefunctions are no longer the two singlets given in (1), but rather:

- $\Phi_B(1)\Phi_B(2)$  with very low energy
  - $\Phi_A(1)\Phi_A(2)$  with very high energy
- (6)

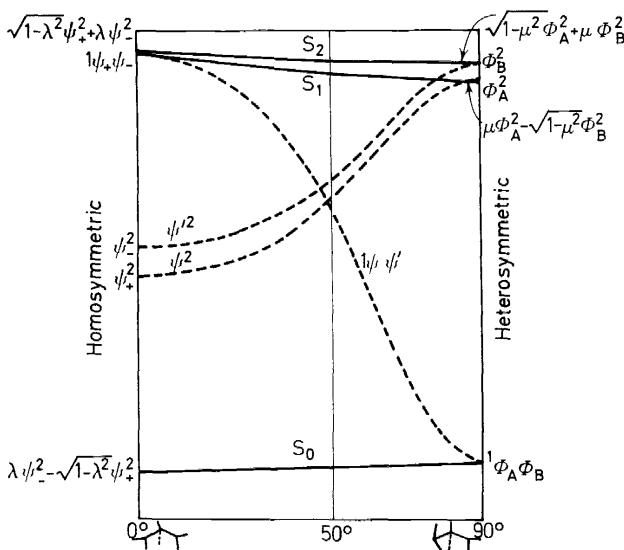


Figure 4. Singlet configurations and singlet states for internal rotation in the trimethylene diradical. The author is grateful to Verlag Chemie for kind permission to reproduce this figure.

with possibly some residual admixture. The low energy function will now describe the ground state of the molecule, which is a *zwitterion*; whence the term *zwitterionic* wavefunctions for the corresponding components in a diradical.

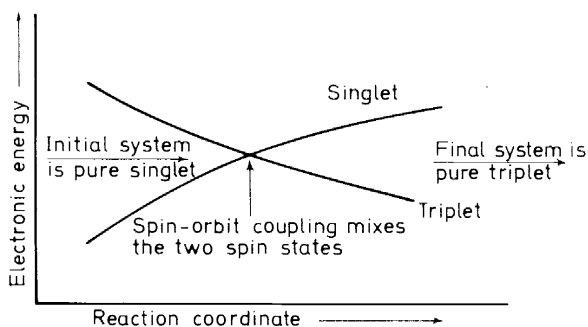
To conclude, we notice that in the same manner a diradical has two high-energy *zwitterionic* states, similarly a *zwitterion* has a high-energy diradical state.

### SOME SIMPLE RULES OF THUMB FOR INTERSYSTEM CROSSING IN DIRADICALS

It is well known that singlet and triplet states are not proper stationary states of a system when certain intramolecular magnetic interactions are allowed for. In the presence of these interactions there are matrix elements of the total Hamiltonian between singlet and triplet, and the proper states are mixtures of the 'pure' spin triplet and singlet states. Time-dependent perturbation theory shows that a system prepared in one of the pure states—as would be a singlet diradical by bond rupture—can evolve by an appropriate interaction,



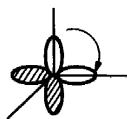
into an oscillatory *mixture* of the two (singlet and triplet) states. If the triplet component can be stabilized further energetically, the entire system can end up in the triplet state<sup>11</sup>. This process is known as intersystem crossing and is illustrated in *Figure 5*.



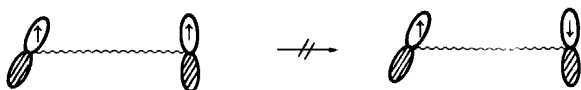
*Figure 5*. Intersystem crossing. The author is grateful to Verlag Chemie for kind permission to reproduce this figure.

Spin-orbit coupling is the most common mechanism by which intersystem crossing can occur. Spin-orbit coupling is the process whereby the magnetic field created by the orbital motion of the electron and its associated angular momentum can interact with the magnetic moment associated with the spin angular momentum. The effect is particularly important in heavy atoms because orbital motion of the electron around the nucleus is equivalent, when we are concerned with what is happening at the position of the electron, to a motion of the nucleus 'around' the electron<sup>12</sup>; whence the effect of large nuclear charges. The net result of this interaction is that the magnetic moment of spin can be *reversed*.

Now since the spin is flipped over, there can be a 'transition' between singlet and triplet states, for instance. And it is not the permanent angular momentum in one of these states which creates the spin flip, but precisely the *angular momentum change* accompanying the transition itself. In other words the spin flip and the momentum change which creates it occur simultaneously. One can show that the ideal situation to create such an angular momentum change is the electronic transition between a *p* orbital along one axis and a *p* orbital along an orthogonal axis. The angular momentum is created around the third axis:

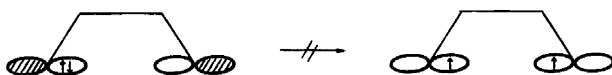


What are the consequences of this pre-requisite in diradicals? Clearly the first condition for a large singlet-triplet mixing (or matrix element) is that the electronic 'transition' carry one electron from some atomic orbital to a *different* one. Now, since the triplet is purely covalent, this requires that the singlet be not also purely covalent:

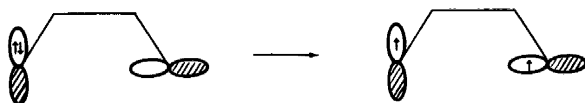


In the above process there is spin flipping without any simultaneous creation of orbital angular momentum. Thus the *more ionic the character* in the singlets, the better the intersystem crossing. (However, too much ionic character will be detrimental to the near-degeneracy of the triplet and singlet electronic states, the latter falling rapidly.) A typically poor case would be ethylene twisted at  $90^\circ$ .

A second condition is that the axes of the 'initial' and 'final' orbitals for the spin-flipping electron be as nearly orthogonal as possible. For instance,



whereas the transition would give zero spin-orbit coupling matrix element—implying that rebonding in a face-to-face triplet may require a distortion<sup>13</sup>—the transition



should lead to a non-zero matrix element. For this factor,  $90^\circ$ -twisted ethylene is a favourable case.

Thus intersystem crossing via spin-orbit coupling is controlled both by an 'ionic' factor and by an 'orientational' factor. A molecule where both factors have optimum values is methylene, where the lower singlet has strong ionic character and where the orthogonality of the  $\sigma$  and  $\pi$  orbitals ensures the creation of angular momentum around the axis which is perpendicular to both orbital directions (Figure 6). The matrix element of interaction between

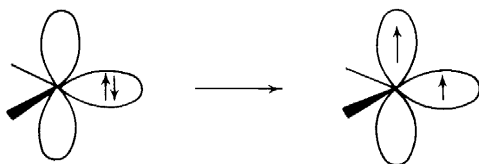
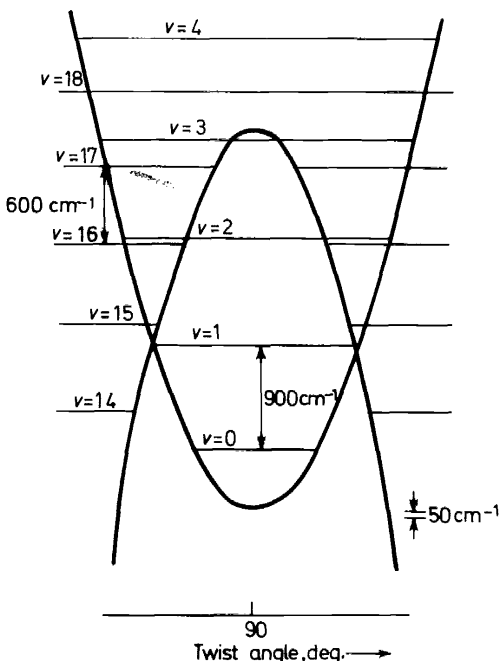


Figure 6. Spin-orbit coupling in methylene.

singlet and triplet is  $\sim 38 \text{ cm}^{-1}$ . But even in this extremely favourable case we know that the intersystem crossing is not very fast, since singlet methylene and triplet methylene have distinct chemistries<sup>14</sup>.

The reason for this low efficiency is that, of course, a large electronic matrix element in itself does not suffice to ensure a large singlet-triplet mixing. One of the major pre-requisites for a perturbation to create a large mixing is that it be at least as large, if not larger, than the separation between the energy levels of the states it is mixing together. For perturbations of the order of  $1 \text{ cm}^{-1}$ , it is useless to enquire about the closeness of the electronic levels.

one must enquire about the fit of *vibronic* levels. Since vibrational spacings are of the order of  $500\text{ cm}^{-1}$  to  $1000\text{ cm}^{-1}$ , such a perfect fit is unlikely to occur, as shown in *Figure 7* for  $90^\circ$ -twisted ethylene.



*Figure 7.* Estimated vibrational spacings in twisted ethylene. The author is grateful to Verlag Chemie for kind permission to reproduce this figure.

What is needed is that one of the two electronic states shall provide a dense manifold of vibronic levels, for instance if the diradical has large sidechains which can play the role of a collisional solvent. It is possible that the flat nature of the potential surface for singlet diradical transition states can also create a dense manifold of oscillating vibrational wavefunctions. Intersystem crossing to the triplet diradical (with well-separated discrete vibrational levels) might then be comparable to that in aromatics and occur in  $10^{-8}$  to  $10^{-6}$  second.

Dr Devaquet at the University of Western Ontario is presently investigating the detailed time-dependent behaviour of the (singlet-triplet) system in twisted ethylene.

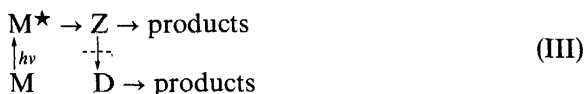
### RELEVANCE TO PHOTOCHEMISTRY: TOWARDS A CLASSIFICATION OF PHOTOCHEMICAL REACTIONS

The insight which we have gained into the nature of the four different electronic states of a species with two weakly coupled electrons allows us to envisage a possible classification of photochemical reactions. The mechanistic or kinetic schemes generally used to interpret photochemical reactions almost always involve intermediate-type species. *It is now possible to specify, by*

considering the chemical nature of these species and our theoretical knowledge of potential surfaces, to which—excited or ground—surface the species belongs and the nature of the corresponding species on the neighbouring surfaces.

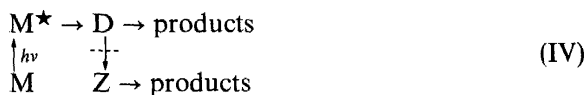
For example, for singlet reactions involving bond cleavage in a molecule M, we can distinguish between:

(a) those reactions for which the cleavage is heterolytic (or liable to lead to heterolytic character) in the excited state and homolytic in the ground state:



In (III), Z indicates a zwitterionic state, D a diradical state. The dotted line indicates the passage from the excited surface to the ground surface.

(b) those reactions for which the cleavage is homolytic in the excited state and heterolytic in the ground state (or liable to lead to heterolytic character):



It is clear that a sub-classification will arise depending on whether the products are created in the excited state or in (vibrationally excited) ground state. Also the probability of intersystem crossing to triplet, and of reactions in that state, should be larger in type III than in type IV reactions.

We are presently attempting to establish such a classification, in collaboration with Professors Dauben and Turro.

## ACKNOWLEDGEMENT

Many aspects of the theory of diradicals were developed in close collaboration with Dr Colin Rowland<sup>7</sup>.

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