

# WHAT IS A DIRADICAL?

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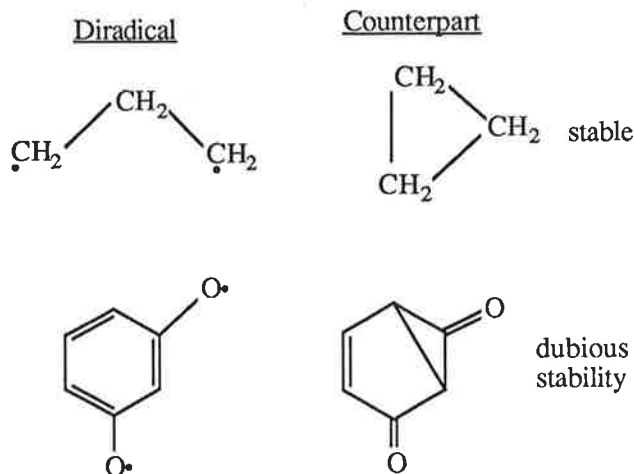
## Preface

These notes are written to both clarify and share some of my thoughts on this matter which has been a subject of discussion at nearly every meeting that I have attended during the past few years. I have chosen to refer to the notes by Lionel Salem out of laziness, not because I am in particular disagreement with his position. I probably agree with him about as completely as with anyone in the field. However, he does raise implicitly, many questions about which I have severe misgivings.

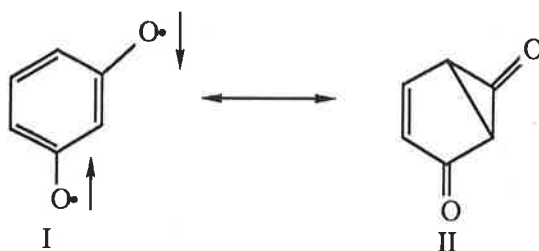
## Introduction (A Naive Position)

I find that it is most important to keep in mind the real origins of the words which we use. A word which had a perfectly clear meaning in the mind of the man who first used it, may become meaningless, or worse; when it is extended to cover concepts in addition to the original ones. There surely comes a time when a word becomes useless because its use must be accompanied by long and turgid exposition. When this becomes the case, it is better to drop the catchword and just say what one has in mind. For many purposes, the terms "diradical" and "zwitterion" seem to have reached this stage.

For my own part, I would be quite willing to use the term "diradical" *to speak roughly about a species which has bifunctional reactivity of a high order*. We have to put in the concept of high reactivity, or else we will find ourselves calling ethylene a diradical, a move that would not rest well with most chemists. Since "high" is a qualitative concept we know that cases will arise in which there will be argument as to whether or not the reactivity is high enough to fit the description. When this problem arises, I will quit using the term "diradical" and talk directly about reactivity. We also need some minimum description in structural as well as dynamic terms. The simplest operational terms relate the biradical to other species for which one could formulate a conventional, electron-paired, valence bond or molecular orbital structure. Note that we can't specify anything about thermodynamic relationships. In some cases the paired structure will represent a known stable species and in other cases not.



In the second case above we can anticipate that the nitpickers will turn out in joyous droves. If we start saying a lot of extra things about our biradical, such as that it is in a singlet state, we must recognize that the two formulae belong to a canonical set of valence bond structures.



Since formula II would represent a species which would look to most chemists like a reactive, bifunctional molecule, we aren't in real trouble. However, we may want to admit that the atomic skeleton shown may actually have two (or more) distinguishable nuclear configurations, all of high energy content compared to the isomeric *p*-benzoquinone. When such considerations become important, I will refuse to discuss the question of which configuration is a biradical and which a molecule. Instead, I will talk about configuration A and configuration B and their properties. By the time we know that much about the system we will have enough really interesting things to discuss so that we will not need the diradical controversy to keep discussion alive.

To me, then, the term "diradical" only has value *as a rather vague and nondescriptive word*. When we need to introduce other ideas, such as electron correlation into the discussion to say what we want to say, we might as well say those things and forget the biradical nomenclature. Under these circumstances I can set up a rough hierarchy of cases in which I would want to use the term with varying frequency.

<u>System</u>	<u>Frequency of use of term "diradical"</u>
<p>(Twisted and skewed form of ethylene)</p>	(almost ?) <span style="border: 1px solid black; border-radius: 50%; padding: 2px;">never</span>
	occasionally
	nearly always

I have no qualms at all about calling a species a biradical in one conversation and then turning around and eschewing the term in the next discussion of the subject. This is not different from referring to R. Nixon as a politician in one context and then on another occasion describing him in terms not clearly appropriate for all politicians.

### The Salem Notes

1. I object to the terms "organic chemists' view" and "a more physical view". The two views are roughly dynamic and structural in origin. Certainly we do not want to engage in discussions as to whether or not dynamics is more or less physical than structure. Note that a very different set of words would be used if we chose to treat the problem as Goddard, and few others might, by using occupied, nonorthogonal orbitals. If carried out properly the method would generate singlets, triplets, energies as a function of internuclear distance

and so on, just as does the model used by Salem and most of the rest of us. If carried to the grim end, both methods should give all the same results. However, the description of details at intermediate stages would generate a different set of words and "physical concepts".

I am not disapproving of the MO method, but only pointing out that the form of the physical description is created by the choice of method. This is too seldom made clear, with consequent polemical controversy of non-existent "phenomena".

2. Granting the premises implicit in the method, the definition is OK. However, perfect degeneracy becomes a rather meaningless criterion in some cases. If we consider a pair of methyl "radicals" and a pair consisting of one methyl and one ethyl the orbitals are perfectly degenerate in one case and not in the other. However, the splitting of levels will be a trivial matter in comparing the systems if the paired partners happen to be separated by a few kilometers in each case.

3. The "proposed definition" (p. 27) turns me off on almost any grounds that I can think.

a. Enormously precise knowledge of the potential surfaces will be necessary to make a definitive identification of the "diradical". In cases where this information is available, description of the system will be given in such a way as to include the information so that use of the general term will be pointless. Look at the example of *diatomic molecules*. As far as I know, no one really worries about whether or not the states should be called "diradicals"; too much is known about the states to waste the word in describing them.

b. The concept of adiabatic decay will, I think, begin to suffer seriously in just the cases portrayed (p. 27).

c. In the cases of most interest, the ESR experiment will become impossible, because of the short lifetime of the ensembler, or difficult to interpret.

4. Remember, again, that the discussion refers to the behavior of a particular brand of wave function. The operation described is exactly the one that I have put in different terms in these notes. For some purposes I would be willing to describe Salem's final states as a biradical manifold containing both singlet and triplet components. I might use the term in a discussion where no one cares whether things are singlet or triplet, or where I have no notion of what spin state is involved, or when I believe that interconversion of the states is faster than any dynamic test that I may have to monitor behavior of the system.

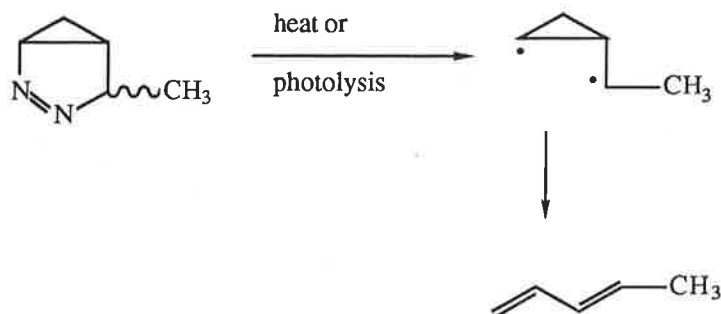
The latter case is essentially equivalent to saying that, under some circumstances, I will think of the system as describable in terms of a zero order Hamiltonian in which a spin mixing term is included, so that the eigenfunctions *are always mixtures of singlet and triplet*. In short, spin will not really be a useful quantum number for description of the system.

On the whole, I expect that this is a case in which I will usually spurn the term biradical and talk about "the acyclic species" which may be either singlets or triplets. Incidentally, if any other change in geometry besides the simple stretching of one bond occurs, I don't see how one can keep *the closed shell singlet configuration from mixing with the open shell singlet configuration*. In a rough sense this is analogous to vibronic mixing of electronic transitions. This is, presumably, Salem's "small contamination from ionic terms". I am, however, much concerned that the role of nuclear geometry in this mixing be recognized.

5. Consider the case of twisted ethylene. Assume the potential functions shown on p. 29 of the Salem notes. Let's put a triplet molecule in the potential well, but let's also give it one or two quanta of vibrational energy in the twisting mode. We now face the ugly fact that, according to Salem, the thing will be biradical during some phase of the vibration and not during others. I am less than enthusiastic about dealing with this situation.

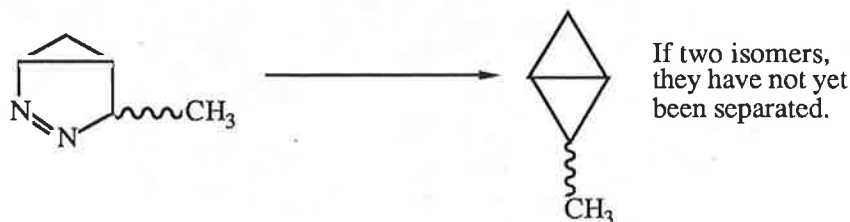
There is a further problem which illustrates my concern about the concept of adiabaticity. Let's consider the T molecule in a vibrational state such that the amplitudes of vibration carry the system outside of the region between  $87^\circ$  and  $93^\circ$ . Can the system start a vibrational cycle as a triplet and then become singlet before the cycle is completed? I think so. Given the shallow potential function we would expect the torsional matrix to be of low frequency. We know that some singlet to triplet processes are very fast. Hochstrasser assures us that the  $S_1 \rightarrow T_1$  transition in benzophenone crystals is at least as fast as  $3 \times 10^{-11}$ . Since there is a bigger energy gap in benzophenone than we can imagine to exist between the  $90^\circ$  singlet and triplet of ethylene, I can well imagine that the electronic matrix element between the states might be higher in the ethylene case, although I know that this does not have to be the case. If we can conceive that the T to S transition times are at least as short as vibration times, what is the proper quantum number to use in defining adiabaticity? Why spin rather than vibration?

6. I pose a problem based upon experimental observations. Using the biradical terminology, on of my student (David F. Eaton), formulated the following interesting path into some kind of excited form of the piperylenes.



Photolysis of the pyrazoline proceeds much as anticipated. The products are principally piperylenes and there is a rather high degree of stereospecificity in the ring opening. One stereoisomer gives principally *trans*-piperylene and the other gives mostly the *cis* isomer. Eaton is not yet sure of his assignments of the configurations of the pyrazolines, so I will not comment further on the steric course of reaction.

Decomposition using benzophenone as a sensitizer takes a different course. Virtually the only reaction products are bicyclobutanes.



This result can be read out of the Salem potential surfaces, if one assumes that spin changes are as fast as vibrational relaxation of the triplet difunctional thing formed by blow up of the excited triplet of the pyrazoline. Note that this result is going to be unwelcome when expressed in terms of the biradical language. We would say that the singlet biradical produced by direct photolysis cannot close to bicyclobutane but that the triplet biradical formed in the sensitized reaction does so preferentially.

How do we describe the results so as to confound the public? I can see two approaches:

1. The bifunctional singlet, when relaxed would lie above the maximum in Salem's curve for the ground singlet of cyclopropane. The system refuses to undergo the relaxation from one singlet to the other.
2. Vibrational quantization is more important than spin quantization. The biradical formed from singlet pyrazoline opens to piperylene because it is hotter than the biradical formed from the triplet.

The spin system approach gives the right answer - if we are willing to freely mix spin states at the crossing point of Salem's curves. On the other hand, if we mix the singlet and triplet systems freely at all times (on the vibrational time scale), we can get a believable answer from energetics alone and might even improve it by correlating vibrational modes in the biradical with those in piperylene and the bicyclobutane.

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Retyped with permission from handwritten notes of G. S. Hammond, 1970-71. At the time the notes were written G. S. Hammond was a Professor of Chemistry at California Institute of Technology, Pasadena, California. Please see the writeup in pages 11-14 for further details.