

WHAT IS A DIRADICAL?

L. Salem

Introduction

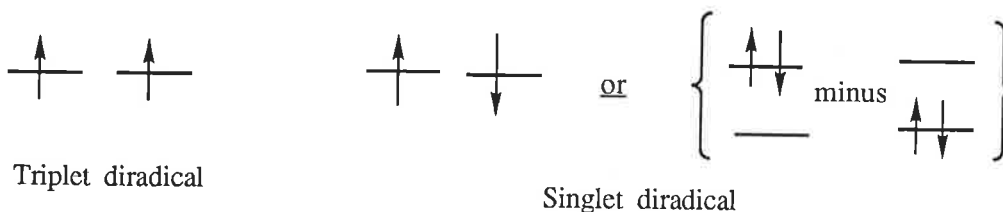
Most organic chemists feel it is better to keep diradicals a vague thing; and call anything more precise a monoradical, etc., (or whatever it really is).

The organic chemist's point of view:

— a diradical reacts like two monoradicals

A more physical point of view:

— two unpaired spins, though these spins may be parallel or antiparallel



The extent to which such situations will prevail relative to the situation in which both electrons are paired in one orbital will depend on the extent to which the degeneracy of the two orbitals holds, i.e., a measure of diradical character would be the extent of orbital degeneracy.

Definition

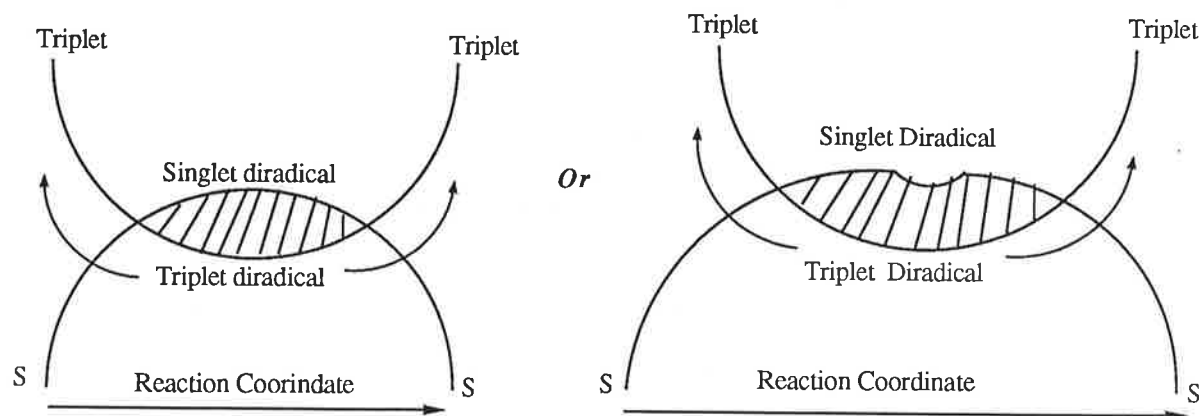
If the orbitals are perfectly degenerate, Hund's rule will hold: the triplet will lie under the singlet. If the degeneracy is not perfect, the triplet will still be the lower state. However, if the orbitals are separated by more than $2K$ (for orthogonal orbitals), the singlet will lie lower.

The limit at which triplet and singlet cross can be considered as the limit of the diradical region. The definition will be somewhat arbitrary, but it does correspond to the physical fact that

— If the triplet is *above* the singlet, the frequency at which the two electrons change place ($2K$) is smaller than the orbital separation (in frequency units) - so the electrons tend to pair up.

— If the triplet is *below* the singlet, the exchange frequency is larger than the orbital separation; so the two electrons can "afford" to be in different orbitals. They can also afford to react independently.

Whence the proposed "definition": A diradical is any triplet or any singlet which can adiabatically decay to the triplet of similar spatial configuration. The definition is related to the potential energy surfaces.



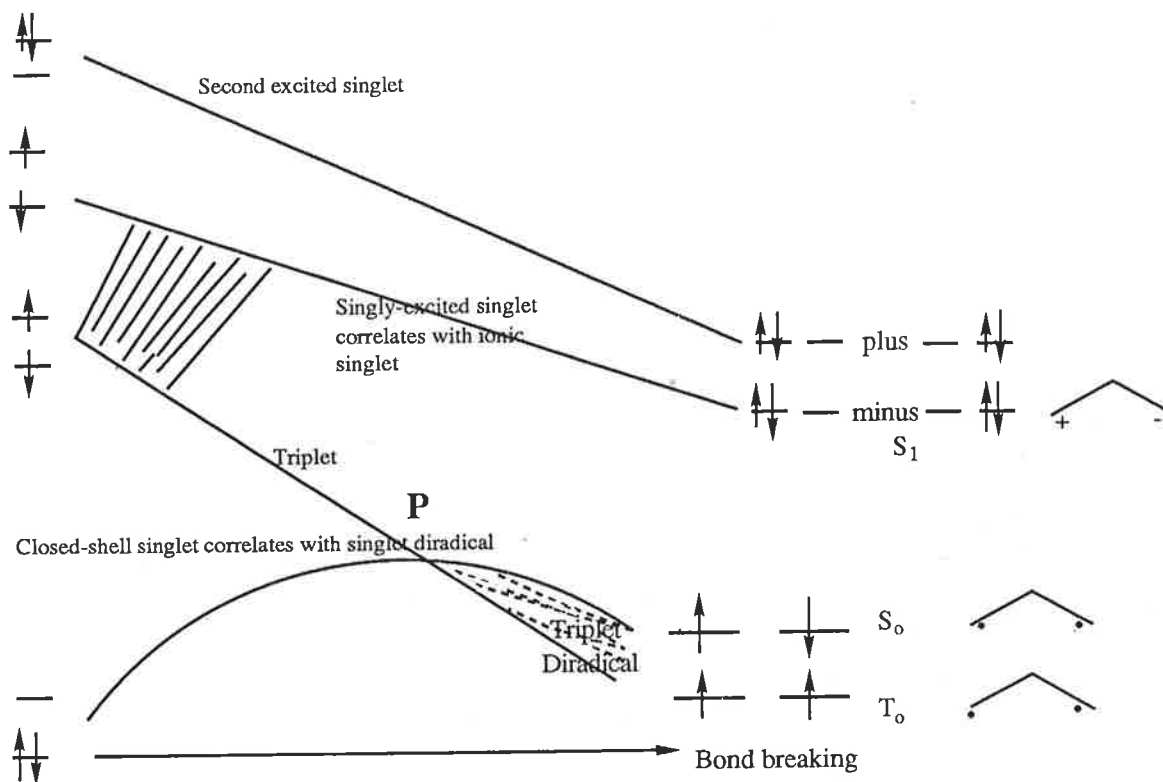
Experimental Test

The previous definition may be too "restrictive" and "binding", but it seems to be a working definition.

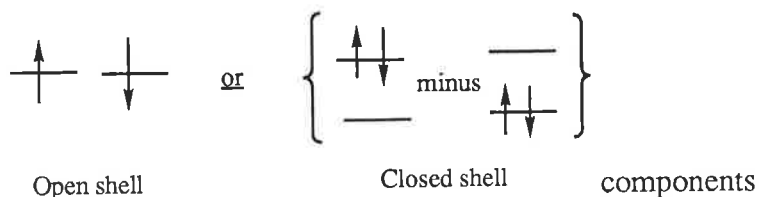
An experimental "test" would be the study of the e.s.r. signal given by the system in the shaded region. If we assume that singlet-triplet mixing (*via* intersystem crossing, etc.) ensures thermal equilibrium between molecules in the two states, the e.s.r. signal will *decrease* with temperature since the singlet lies above the triplet.

Overall behavior of the wave function as a bond is broken in the formation of a diradical.

The interesting case is that in which the odd electrons are relatively close in space (1, 2; 1, 3; 1, 4).



Near point P, the singlet wave function will actually be a *mixture* of



In the diradical region the open-shell component will have the largest weight. These functions will be:

Triplet $\phi_A(1)\phi_B(2) - \phi_B(1)\phi_A(2)$ *strictly*

Singlet $\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)$ *plus small contamination by ionic terms.*

where ϕ_A and ϕ_B are localized orbitals.

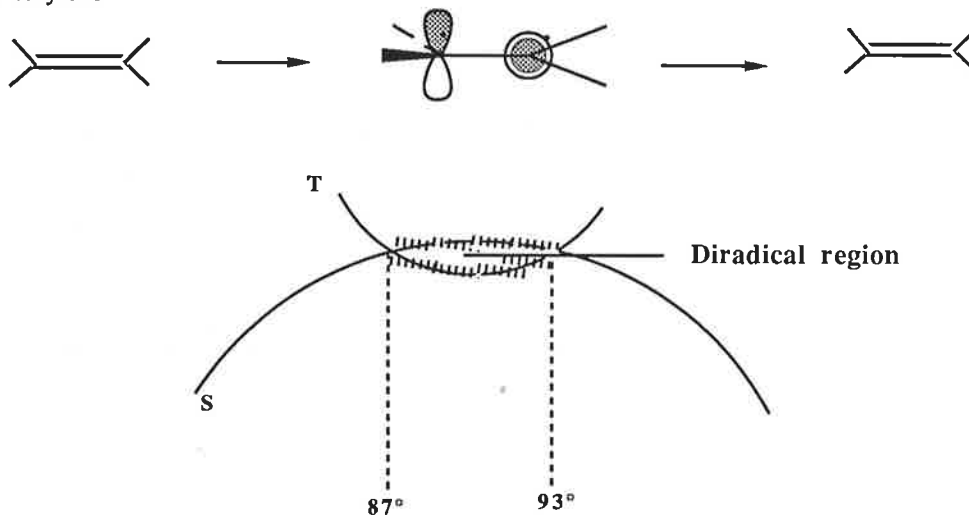
Examples

1) H_2



With our definition, H_2 is never a diradical in its ground state: the singlet is always below the triplet. At infinity we have two monoradicals or a "double radical".

2) Twisted ethylene



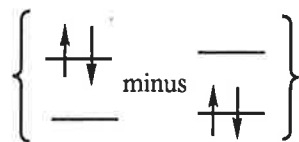
We have a diradical between 87° and 93°.

3) Trimethylene, tetramethylene

It has been found that there is a significant region along the reaction coordinate where lowest triplet lies under ground singlet. There again, it is legitimate to speak of a diradical.

4) Methylene (the one-center exception)

Here the two odd electrons are on the same center. This is the only case where the

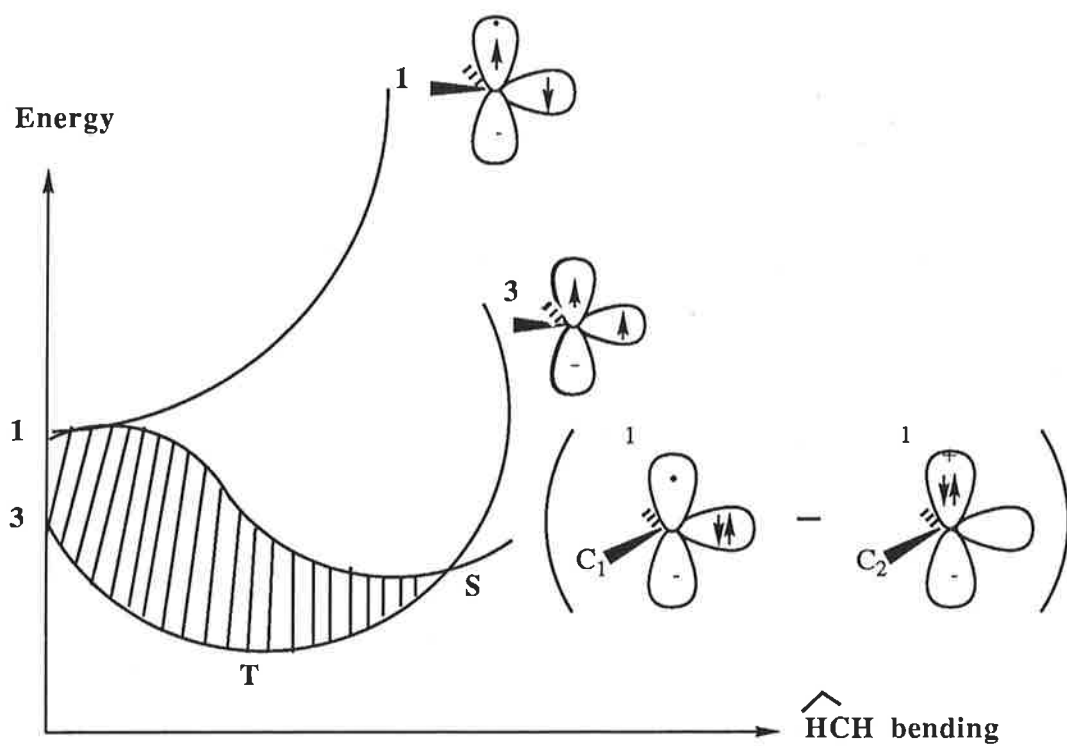


Closed shell

$$\text{i.e. } \phi_A(1)\phi_A(2) - \phi_B(1)\phi_B(2)$$

situation can occur with low energy: the high cost of the ionic terms in the wave function is offset by the large exchange integral. Also the self-repulsion J_{aa} of two electrons in one orbital is hardly more energetic than the mutual repulsion J_{ab} which would occur if they were in different orbitals.

The states in methylene are thus:



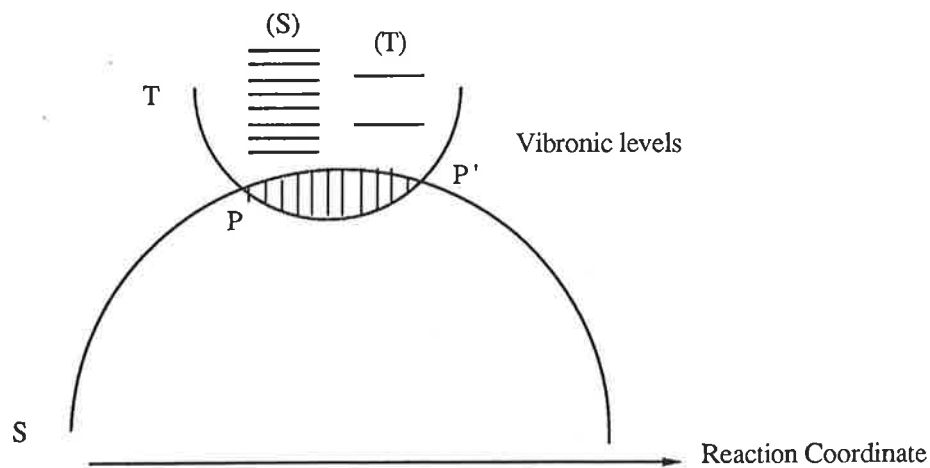
JACS 92, 4984 (1970)

Although the ground state triplet does *not* correspond to the same spatial configuration as the ground singlet, it is tempting to consider the shaded region as a diradical region for singlet methylene.

Singlet carbenes are probably generated with sufficiently excess vibrational energy to react in this region.

Singlet-Triplet Mixing by Spin-Orbit Coupling in Diradicals.

The passage from the dense singlet vibronic manifold to the discrete triplet vibronic manifold is particularly interesting in the diradical region of a reaction path.



Note that we have the reverse of the familiar radiationless decay process, and that the crossing is entropy-unfavored. Note however, that the spin-orbit coupling will generally be *small*, because the triplet and singlet have precisely the *same* orbital configuration (efficient coupling on any atom requires the singlet "atomic" orbital and "triplet" atomic orbital to have different directions: a magnetic field is created by the orbital transitions, and the electron spin fails with torque).

An exception of course is the one-center methylene case, where the triplet does have a different configuration from the singlet, and where spin-orbit coupling is efficient (10^{-12} seconds, Basch and Chang).

The probably most efficient manner in which coupling between

	Triplet	$\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)$
and	Singlet	$\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)$

can occur in the two-center case is *via* configuration interaction of the singlet with the excited

Ionic Singlet	$\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)$
---------------	-------------------------------------------

(which has a large matrix element of mixing with the triplet).

Nuclear Spin Polarization via Hyperfine Interaction

Should occur in the singlet-triplet cross-over regions (even if the odd electrons are physically close in space).

Acknowledgements

Pople, El-Sayed, Rowland, Hoffmann, S. Rice, Osterhoff.

Reprinted with permission from handwritten notes of L. Salem. (1970-71). L. Salem whose mother tongue is English is a Professor of Chemistry in the CNRS, Orsay, France. He has held several unique positions—Advisor in the cabinet of the French Universities Minister, Member of International advisory panel created by the World Bank and the National Academy of Sciences, Investment Advisor of the Paribas Bank in Paris and Advisor to the General Director of the CNRS.