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Salem L & Rowland C. The electronic properties of diradicals.

Angew. Chem. Int. Ed. 11:92-111, 1972.

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Four different electronic states that accompany the existence of an organic diradical are described. These states (a singlet "diradical" state, a triplet "diradical" state, and two singlet "zwitterionic" states) are described for different types of diradicals. Rules are given for the spin-orbit-coupling-induced intersystem crossing as a function of the relative orientation of the odd orbitals of the diradical. [The *SCI*® indicates that these papers have been cited in over 475 publications.]

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This work originated when Yves Jean, John Horsley, Jim Wright, Carl Moser, Richard Stevens, and I attempted (in 1969-1970) to elucidate the exact structure of the transition state for the geometrical isomerization of cyclopropane.¹ Bob Nesbet had pointed out to us that to obtain the proper dissociation limit in a reaction such as



(with different radical partners), a 3-by-3 (rather than 2-by-2) configuration interaction calculation is necessary within the singlet manifold. This result led us to the identification of four different states for the diradical product (once the triplet state is included): three singlet states (one diradical $\text{Li}^\uparrow\text{H}$, one zwitterionic $\text{Li}^\bullet \text{H}^\bullet$, and one zwitterionic

$\text{Li}^\bullet \text{H}^\bullet$); plus one triplet state (of diradical type $\text{Li}^\uparrow\text{H}$).

Whereas scientists were relatively familiar with the two "diradical" states proper, many were not aware that two other states accompany them, having ion-pair character. These can even be traced back to Mulliken's 1932 work on twisted ethylene.² Yet I found little enthusiasm in the few colleagues I talked to about this phenomenon. I finally tucked the work away. It would never have appeared had it not been for Roald Hoffmann, who, during a supper chat at a New Orleans meeting, strongly encouraged me to publish the work. Colin Rowland, a postdoc from the UK (now in private industry), and I then worked intensely to complete the investigation; Colin was particularly instrumental in helping me derive the rules for spin-orbit coupling in diradicals. The manuscript was submitted to *Angewandte Chemie* in the fall of 1971 while I was Gast-Dozent in Zurich. Albert Eschenmoser, to whom it was sent for refereeing, accepted it for publication after asking me to make it more palatable to organic chemists.

The success of the paper was a great surprise since, although there was a previous illustrious theoretical paper in the same journal,³ our paper, to the contrary of theirs, contained a good deal of mathematics. Nevertheless, the usefulness of the work on two counts soon became apparent: it allowed me to draw out correlation diagrams for photochemical reactions by using the nature of the product state;⁴ and it allowed William Dauben, Nicolas Turro, and me to write out a classification of photochemical reactions.⁵ Since then chemists have become more and more interested in the predictive power of the rules for spin-orbit coupling in diradicals (since extended by Shaik⁶), and the first experimental verifications have now been published.⁷

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2. Mulliken R S. Quantum theory of the double bond. *Phys. Rev.* 41:751-8, 1932. (Cited 70 times since 1955.)
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