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PREFACE

The concept biradical means different things to different people. In this Symposium, we have been lucky to receive contributions reflecting a wide range of viewpoints and dealing with a wide variety of biradical structures. The intimate interaction of the two radical centers in some of the reaction intermediates involved in the mechanistic investigations of Baldwin and Chang, Crawford and Chang, Gajewski *et al.*, and Pagni *et al.* stands in stark contrast to the only very loose interaction of the two radical halves of the biradical whose ENDOR is reported by Kurreck *et al.* and of the radical pairs investigated by McBride and Vary and by Turro. The three theoretical contributions to the Symposium differ almost as much. Borden and collaborators make an important point concerning the unsuitability of two otherwise tempting computational procedures for the description of biradicals. Bonačić-Koutecký *et al.* provide a high-quality *ab initio* description of the excited states of a biradical obtained by twisting an olefin, with obvious implications for photochemical *trans–cis* isomerization. Zimmerman reminds us of the close relation between biradicals and "forbidden" pericyclic reactions and places it on a firmer footing.

One of the characteristic properties of biradicals related to the degree of interaction between the two radical centers is the relative energetic proximity of their lowest singlet and triplet states. The interplay of the two states plays a role in many places in the Symposium papers. The S–T splitting is discussed in an enlightening way by McBride and Vary. A new stable ground-state triplet dication with an intriguing potential application is described by Breslow *et al.*, ground state triplets of the non-Kekulé quinodimethane series are examined by Berson *et al.* and Platz *et al.* The most intriguing subject of reactions in which the crossing from the triplet to the singlet surface appears to represent the rate-determining step is addressed by Dowd and Chow, using low-temperature kinetics followed by ESR, and by Scaiano, who bases his arguments on results obtained from flash photolysis.

I believe that a potentially important fine point should be emphasized concerning the least-motion paths of such reactions. At times, we tend to imagine that their course resembles that of the paths of ordinary singlet–singlet reactions in that the motion is approximately the least-motion kind all the way to the product: the least-resistance motion executed by the molecule if it were to proceed from the minimum in the T surface straight to the S–T crossing point continues more or less in the same direction after the crossing to the S surface. We may then invoke tunneling under the barrier along this one-dimensional path.

This picture may be correct at times and totally false at others, in that the motion which would bring the molecule to the lowest energy point on the seam at which the S and T surfaces cross does not need to have anything to do with the direction of motion required for the reaction proper. Indeed, until the crossing to the S surface occurs, the intra-molecular motions are governed by the shape of the T surface. It is only after the crossing to the S surface that the molecule begins to feel the downhill tug of the S surface and finds out that it will be rapidly converted from a biradical to a much more stable ordinary molecule along a "new" path which may well be orthogonal to the initial direction which led to the crossing point. Thus, the initial motion towards the S–T crossing point may be in principle even occur in some part of the molecule quite distant from the reaction center.

I believe that we need to assume that the latter situation is the rule unless proven otherwise. This has two consequences. First, a one-dimensional picture is fundamentally inadequate and a two-dimensional representation of the surface, incorporating both the directions involved, is the minimum required, e.g. for discussions of tunneling. Second, attempts to calculate the activation energy of $T \rightarrow S$ reactions by theoretical methods must not be limited to a search along geometries which lie along the vicinity of the "usual" reaction path, i.e. the more or less "straight" direction from the starting to the product geometry. For instance, it appears quite possible that the planar trimethylenemethane triplet studied by Dowd and Chow reaches the activated complex for conversion to methylenecyclopropane not by a rotation but, say, by a pyramidalization of one or more of its methylene groups. This makes the search for the transition state much harder than is usual in $S \rightarrow S$ reactions.

In conclusion, it seems to me that biradicals are alive and kicking, hard, and will be for a long time to come. It has been a pleasure to read the contributions submitted for this Symposium and I wish to thank the authors and reviewers for their efforts and cooperation.

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