

# Photoisomerization by Hula-Twist: A Fundamental Supramolecular Photochemical Reaction

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### ABSTRACT

The volume-conserving hula-twist *cis/trans* isomerization process has been incorporated in a general scheme for photoisomerization of polyenes, applicable to small organic molecules as well as to protein-bound polyene chromophores. The main theme is that in contrast to the conventional one-bond-flip mechanism, which requires a large conformational change, the hula-twist process is a concerted, volume-conserving process that is much easier to do. In our examples of photoisomerization obtained under confined conditions have been critically reviewed, the applicability of HT has been examined, and new systems unambiguously testing this volume-conserving process are proposed.

followed, perhaps could have contributed to the general impression that we now know everything about the photoisomerization reaction.

### II. Photochemical *Cis/Trans* Isomerization—A Not-Full-Understanding Perspective

However, a careful examination of the literature reveals scattered results that are not accounted for by the existing knowledge on photoisomerization. For example, Liu and Hammond recently advanced a general mechanistic scheme for all photoisomerization reactions<sup>13</sup> incorporating the volume-conserving hula-twist process<sup>14</sup> 15 years ago,<sup>14</sup> which is repeated in the abbreviated form of "W"-to-"U" conversion.



Before we present this generalized scheme, the unexplained facts on photoisomerization will be summarized.

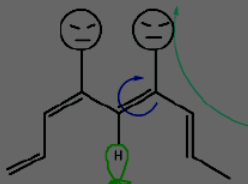
**Systems Undergoing Non-NEER (Seemingly) Behavior:** The concept of NEER (non-equilibrating energy relaxation) was reached after an incisive analysis of products

# Ultrafast Reactions of Polyene Chromophores. From Hula-Twist to a Photo-Trigger of Rhodopsin

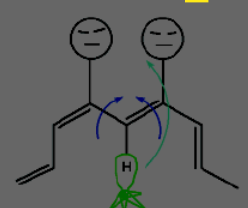
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Scheme 1  
Conventional One-Bond-Flip Process



The Hula-Twist Process



Difficult to do and an unhappy ending

Easier to do and a happy ending



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