Journal of Photochemistry and Photobiology A: Chemistry 237 (2012) 53–63

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Invited feature article

# Hula-twist cis–trans isomerization: The role of internal forces and the origin of regioselectivity

Werner Fuß*

*Max-Planck-Institut für Quantenoptik, D-85748 Garching, Germany*

ARTICLE INFO

*Article history:*
Received 29 November 2011
Received in revised form 23 January 2012
Accepted 28 January 2012
Available online 9 April 2012

*Keywords:*
Polyenes
Double-bond isomerization
Potentials
Conical intersections
Branching
Momentum effects

ABSTRACT

In photochemical Hula-twist isomerization of conjugated polyenes, a double bond and an adjacent single bond twist concertedly by 180°. It is here considered to be driven by passing through the last conical intersection (CI), between potentials of the dark covalent $S_1$ (2A) and the ground $S_0$ (1A) states. If several such CIs are available, that is, if isomerization of different bonds is possible, regioselectivity can be caused by a sterically induced pre-twist in $S_0$, so that the pre-twisted group isomerizes: this deformation is amplified in the Franck–Condon region of the spectroscopic (1B) state; on entering the 2A surface with this geometry, the nearest $S_1/S_0$ CI will be chosen, if the reaction is ultrafast. If the reaction is slower, that is, if there is a barrier before each CI, a local pre-twist reduces one of them and thus also selects the site of isomerization. Another pre-twist can be caused in the initially excited (ionic) 1B state by electrostatic effects, thus also giving rise to regioselectivity. The explanations only consider potentials of the molecule, in the majority of cases with no external forces. Also other observations are summarized that support the idea that Hula twist can work without influence of the environment. A variant of Hula twist is also proposed and used, in which the torsion of the two adjacent bonds is not disrotatory as usual but conrotatory.

## 1. Introduction

Hula-twist (HT) isomerization is a mechanism for photochemical cis–trans interconversion of polyenes, in which only one CH group rotates by 180°, whereas the groups attached to it reorient in the original plane. An alternative description says that these two groups (or the CC double bond and an adjacent single bond) rotate in disrotatory direction versus the CH group (Scheme 1). Originally postulated in 1985 by Liu et al. for cases, where volume saving seems important [1,2], it was experimentally identified only in 1998 [3] in photoisomerization of previtamin D. In the mean time Liu et al. have found plenty of additional examples, which they have repeatedly reviewed [4–8]. As nearly all examples were carried out in a matrix or under other conditions of mobility limitation, Liu ascribes this mechanism to a medium effect, pointing to the minimal volume need of Hula twist as compared to one-bond flip (OBF). On the other hand, quantum chemistry points to the slope through an $S_1/S_0$ conical intersection (CI) (i.e., the crossing between the potentials of the dark covalent 2A state with that of the ground state), which could drive the molecule towards HT also without interaction with a medium, as is pointed out in [3,9,10].

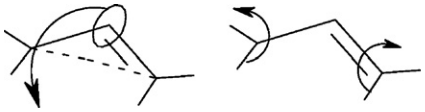
Part of the present work (Section 2) is devoted to summarize the evidence that HT is due to internal driving forces and is the standard path for cis–trans isomerization of nonpolar polyenes. The evidence is based primarily on experimental observations and their comparison with quantum chemical calculations; the latter alone have not yet given a clear-cut decision whether and when HT is preferred over OBF. Sections 3–5 then give explanations, again based on internal forces (pre-twist for steric or electrostatic reasons), for regioselectivities observed in the literature, that were not (or only partially) explained before.

It should be noted here (see, e.g. [11]) that normally (with possible exceptions in polar solvents) in all conjugated polyenes (but not in strongly polar double-bond systems such as protonated Schiff bases of unsaturated aldehydes) a two-electron excited totally symmetric (2A: $2A_g$ in $C_{2h}$ and $2A_1$ in $C_{2v}$) "dark" state at suitable geometry reaches to below the HOMO → LUMO excited (1B: $1B_u$ in $C_{2h}$ and $1B_2$ in $C_{2v}$) "spectroscopic" state. The latter is optically strongly coupled with the ground state and is usually first populated. It is depleted in all polyenes within 50–250 fs around the 1B/2A CI (survey in [11]) to the dark state, that has only a very weak optical transition probability to the ground state. From there, the population can flow (with time constants that vary by orders of magnitudes [11]) through the 2A/1A CI to the ground state. This is the $S_1/S_0$ CI mentioned above that is also responsible for the photochemical transformation. Valence bond theory describes the 1B

---

* Tel.: +49 89 3201807.
*E-mail address:* w.fuss@mpq.mpg.de

1010-6030/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochem.2012.01.019



**Scheme 1.** Two alternative ways to describe Hula twist isomerization (i.e., its disrotatory variant, see below) of a conjugated polyene. The broken line not only indicates the rotation axis but also a partial bond formed in the CI. HT and OBF differ in the conformer produced; if the molecules are sufficiently asymmetric to distinguish the conformers (and if the experiment can identify them before rotamerization, e.g. by sufficient time resolution or by freezing the conformer isomerization), there is no ambiguity in the decision, which pathway has been taken.

state as ionic (superposition of zwitterionic structures) and the 2A state as covalent. The former is sensitive to electrostatic effects and its energy may be lowered by (polar or polarizable) solvents [12], whereas the latter is much less so. However, with strong distortion of the molecule, the two states can mix, so that the covalent state can borrow ionic character at such a geometry (see, e.g. [13]). For convenience, the notation 1B and 2A is here kept even when mixing plays a role.

Regioselectivity in Hula-twist isomerization was reported by Liu's group in substituted diphenylbutadienes, in cinnamic esters [14,15] and in naphthyl-phenyl-ethenes [16]. In all these cases, rotation of the CH group closer to the phenyl ring (HT-1) is preferred over that in β position to it (HT-2). Whereas electronic or mass effects were tentatively assumed in [14] for explanation, I invoke the sterically induced pre-twist of the phenyl group (Section 3).

A different kind of regioselectivity, caused by electrostatic effects, was found by the groups of Squillacote, Liu and Singh [17–21] and discussed in terms of a zwitterionic state, an allyl-cation methylene-anion intermediate. Further such examples are discussed on pp. 208–211 of the review [22]. This either means that the (ionic) spectroscopic state (1B) takes over the control, or that the dark state (2A) is not purely covalent but can assume some ionic character. The latter property in fact resulted from the recent quantum chemical calculation of butadiene excited states [13]. On the other hand, this calculation favored OBF over HT, which seems in conflict with the mentioned experimental results, as discussed in Section 2. It is here suggested (Section 4) that in the case of ultrafast reactions, zwitterionic polarization in the 1B state can cause (pre-)distortion that in turn guides the molecule on the 2A surface to the (HT-type) conical intersection that is connected with the observed regioselectivity. Section 5 then argues that in slower reactions the effect of pre-twist still exists, but electrostatic effects are not easy to foresee.

The decision, into which CI (i.e., into which part of the intersection space) the molecule enters, depends on fine differences of slopes or/and barriers, which are still hard to reliably find out by quantum chemical calculations alone. Section 2 therefore recalls and compiles also experimental evidence. Little noticed theoretical results and some plausibility considerations (such as a correlation diagram) suggest also the existence of another form of HT, with conrotatory (instead of the usual disrotatory) motion of molecular moieties, that is then invoked in Sections 3–5 to explain the pre-twist induced regioselective HT.

## 2. Hula-twist versus one-bond flip in nonpolar polyenes

The traditional view of photochemical cis–trans isomerization of singlet-excited olefins is that of a one-bond flip (OBF) mechanism, in which one double bond rotates by 180°. This is established for mono-olefins, where the $\pi\pi^*$ excited state and the doubly excited dark state have a deep minimum at a twist angle of 90° (ignoring other coordinates such as pyramidalization of one carbon that can further lower the energy but do not leave permanent signatures in the products) (see, e.g. [23]). Also in butadiene there is a driving force – although weaker – towards twist in both the 1B and 2A state [13] (although on the 2A surface probably not in OBF direction, see below), and in trienes it is probably further attenuated. Longer polyenes such as octatetraene are planar in their $S_1$ minimum, as known from spectroscopic evidence [12,24]. In spite of such systematic variations, it is popular to assume OBF for all conjugated systems (e.g., in the recent edition of a photochemistry textbook [25]). Evidence that the simple OBF mechanism cannot be the only one or not even the predominant one, came independently from (a) computation of photochemical reaction paths and (b) the conformation of the primary products of the photoinduced cis–trans isomerization of certain polyenes.

### 2.1. Computational results

In a series of quantum chemical calculations, the groups of Olivucci, Robb and Garavelli found that in conjugated hydrocarbons (polyenes of different length, styrenes and stilbenes) the minimum energy CI between the lowest singlet excited (2A) and the ground state (1A) involve concerted twisting about a double bond and an adjacent single bond [26–35], that is a motion as in HT; a review emphasizing conformational aspects [36] and another one focusing on the discussion of Hula twist [10] is available. Due to the common geometrical structure, a triangle that was interpreted as a three-electron three-center bond, the CI was initially called kink-type [33] and later also HT-type [10]. The twist angle of the two bonds is less than 90° (about 60°), and it was pointed out in [10] that on relaxing from the CI on the lower cone the molecule can either complete the HT to 180°or turn one of the two bonds back (resulting in "attempted (aborted) HT" leading either to an OBF product or another rotamer) or revert both twists (resulting in internal conversion): as there are no deep valleys on the lower cone [10], it exhibits practically no directional force, and the actual path will be sensitive to momentum effects or influence of an environment. Momentum can be accumulated from the entrance cone to the CI, and the environment can change the slope in specific directions.

The calculations were done by CASSCF (complete active space self-consistent field) with all π electrons and all π orbitals as active space. In a recent work [13], Levine and Martínez pointed out that this method does not take electron correlation into account in a balanced way for both the dark (2A) and the spectroscopic (1B) states. They therefore reduced the active space in butadiene to three π orbitals (CASSCF(4/3)), which is better in this respect. In fact, the results compared well with those of CASSCF(4/4) with PT2 correction for correlation. According to these calculations [13], which also followed the dynamics of the molecule, butadiene twists a terminal $CH_2$ group already on the 1B state by 90° and with this structure reaches on the 2A surface an OBF-type CI, where it passes to $S_0$. This twist also imparts some zwitterionic character to the dark state by mixing the two states. An HT-type CI was also found (called there "transoid CI") but located at higher energy. For systems polar enough that the (ionic) 1B-like state is below the (covalent) 2A-like state, also the Olivucci group found that an OBF-type CI is more easily accessible than an HT-type [10], and both types compete in intermediate cases [10]. Hence zwitterionic electronic structures seem to favor OBF type distortions, whereas covalent states initiate motion towards HT-type isomerization.

However, there is also a recent calculation on previtamin D (a steroid triene) on the basis of time-dependent density-functional theory that favors an HT pathway from the spectroscopic state [37]. Furthermore, an accessible HT-type CI (though not at lowest energy) was also found by CASSCF for a protonated Schiff base of pentadienal [38]. It is interesting that HT-type $S_1/S_0$ CIs were recently also found for different systems: symmetric monomethine cyanines [39], using a minimalistic model with