



Nonadiabatic dynamics and photoisomerization of biomimetic photoswitches



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ABSTRACT

N-alkylated indanylidene pyrroline Schiff bases (NAIPs) are of great interest because their photoisomerization mimics the primary photoreactions of the retinal chromophore in rhodopsin. The nonadiabatic dynamics of two NAIP models (OMe-NAIP and dMe-OMe-NAIP) are investigated by trajectory surface-hopping method at the semi-empirical OM2/MRCI level. Both molecules show ultrafast isomerization governed by nonadiabatic dynamics via the S_0/S_1 conical intersections (CIs). Two CIs, CI_α and CI_β , play important roles in the $E \rightarrow Z$ and $Z \rightarrow E$ isomerization dynamics, respectively, and are mainly distinguished by different twisting statuses of the central $C1'-C4$ double bond. Although both compounds show ultrafast nonadiabatic dynamics, the S_1 lifetime of dMe-OMe-NAIP is much longer than that of OMe-NAIP. By removing the methyl group, dMe-OMe-NAIP allows less twist at the $C1'-C4$ double bond than OMe-NAIP. This result in the slower excited-state decay of dMe-OMe-NAIP, providing solid evidence to support a similar hypothesis proposed in a previous study.

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1. Introduction

Molecular switches have been intensively studied for several years [1,2] because their physical, chemical and biological properties can be controlled by external stimulation, e.g., pH, light, temperature, electric fields. Photoinduced molecular switches are compounds that experience geometry transformation upon light excitation; these play important roles in sensors [3,4], self-assembly [5,6] and photoinduced biological processes [7–9]. Recently, photoswitches based on the E/Z isomerization have become of great interest. These compounds normally contain C–C, C–N and N–N double bonds and the resulting two configurations (E and Z) can be converted to each other after photoabsorption [10–15]. Several families of E/Z photoswitches have been constructed in recent years, including azobenzenes [16–21], chiral diarylidene [22–25] and protonated Schiff bases (PSB, mimicking the retinal chromophore of rhodopsins) [26–30]. Due

to their photo-controlled properties, these photoswitches have potential applications in several fields [31–34].

One particularly interesting group of photoswitches is based on N-alkylated indanylidene pyrroline Schiff bases (NAIPs) and their derivatives. They serve as simplified biomimetic models to investigate the photoisomerization mechanism of retinal chromophores in rhodopsin [35–41]. In addition, the functionalization of NAIP-based compounds helps us to develop novel biomimetic photoswitches for future applications [42–46]. Consequently, a good understanding of the photoinduced E/Z isomerization of NAIP-based compounds is critical.

Both time-resolved spectroscopies and quantum-chemical calculations suggest that the photoinduced E/Z isomerization of NAIP-based switches is governed by an ultrafast nonadiabatic process via the S_0/S_1 conical intersections (CIs) [42–46]. After photoexcitation, the NAIP-family molecules move in the excited state, access the S_0/S_1 CIs by twisting the central C–C double bond, then jump back to the ground state [42–46]. A joint experimental–theoretical study was performed to understand the E/Z isomerization of OMe-NAIP (Scheme 1), a NAIP derivative with an $-OCH_3$ group attached to the six-membered ring [44]. The experimental observations suggested that the excited-state lifetime is approximately 300 fs, which is consistent with the value (~ 200 fs) obtained by the theoretical simulation using trajectory calculations on the basis

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of the reduced dimensional potential-energy model constructed in the combined CASSCF/CASPT2/AMBER approach [44]. Subsequently, the excited-state dynamics of another NAIP derivative was explored by theoretical simulation using a few typical trajectories at the scaled CASSCF/AMBER level [43] which suggested that the nonadiabatic decay takes place ~ 300 fs. These theoretical studies employed very accurate high-level electronic-structure methods and even considered the QM/MM approach to account for solvent effects, all of which requires huge computational costs.

Recently, a new biomimetic photoswitch, dMe-OMe-NAIP (Scheme 1), was constructed by removing the methyl group from the pyrrolinium in the structure of OMe-NAIP [47]. Time-resolved spectroscopy studies indicate that the lifetime of dMe-OMe-NAIP is above 500 fs, much longer than that of OMe-NAIP. This strongly suggests that the removal of the methyl group has a dramatic influence on the E/Z isomerization of NAIP derivatives. Simple ground-state geometry calculations indicate a possible explanation of this effect: the removal of the methyl group reduces the central double-bond twisting angle and the resulting more planar geometry may be responsible for the slower isomerization dynamics of dMe-OMe-NAIP [47].

From a theoretical point of view, it is essential to simulate the reaction dynamics to provide direct evidence of the influence of removing the methyl group on the E/Z isomerization. One possibility of examining such phenomena is to run nonadiabatic dynamics simulations of both NAIP derivatives (dMe-OMe-NAIP and OMe-NAIP) with on-the-fly surface-hopping methods. By employing a large number of trajectories and including all nuclear degrees of freedom (full dimensionality), more details on the nonadiabatic dynamics of dMe-OMe-NAIP and OMe-NAIP are derived. When the high-level electronic structure methods (such as CASSCF) were employed, the dynamics study is only possible for the small simplified model systems [42]. Here, we wish to simulate the E/Z isomerization dynamics of realistic systems, dMe-OMe-NAIP and OMe-NAIP, with on-the-fly surface-hopping and the Tully-fewest switches algorithm [48–50]. Because we need enough trajectories to achieve a statistically meaningful conclusion, the semi-empirical OM2/MRCI method was employed to speed up the calculations. As discussed in many previous studies, the OM2/MRCI method provides a reasonable compromise between computational cost and accuracy in the nonadiabatic dynamics simulations of many photochemical and photochemical processes [21,51–63], particular for

middle-sized molecular systems. Certainly, the performance of the OM2/MRCI method should be examined by the benchmark calculations with high-level ab initio method for validation purpose.

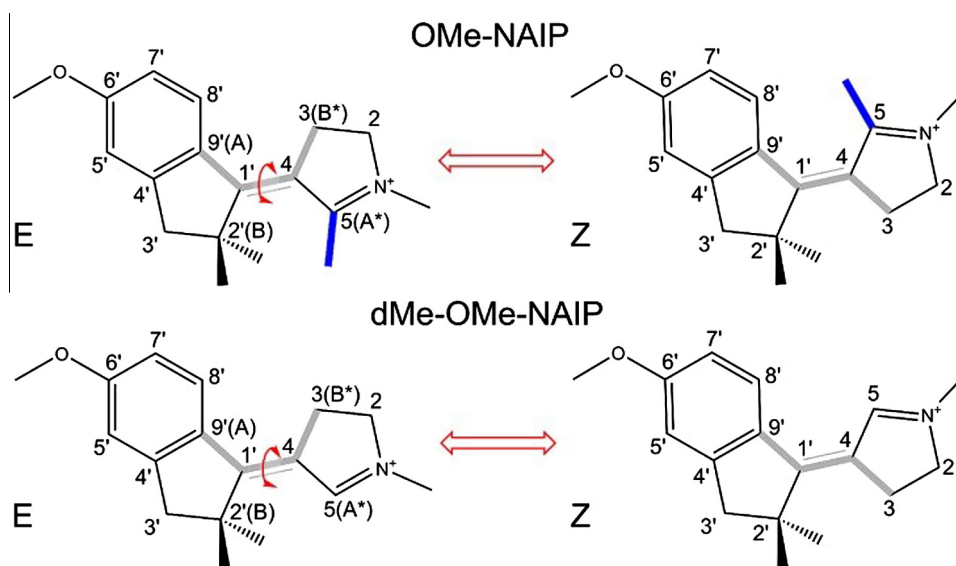
This article is organized as follows: first, the computational details are described, including the molecular models, the OM2/MRCI method and the surface-hopping method. To test the accuracy of the OM2/MRCI method, high-level calculations were also applied for validation. Second, the results for OMe-NAIP and dMe-OMe-NAIP, including PESs and nonadiabatic dynamics, are presented. Third, the discussion section is given. Finally, we summarize the whole work.

2. Computational details

2.1. Molecular models

The current work focuses on the photoinduced E \rightarrow Z and Z \rightarrow E isomerization processes of two NAIP switches, namely OMe-NAIP and dMe-OMe-NAIP (Scheme 1). Both have two isomers: E-OMe-NAIP and Z-OMe-NAIP for OMe-NAIP and E-dMe-OMe-NAIP and Z-dMe-OMe-NAIP for dMe-OMe-NAIP. Their chemical structures and atomic labeling are shown in Scheme 1 and all key geometry parameters are listed in Table 1. In this table, the central double bond (C1'–C4) length is defined by r_a . The dihedral angle C9'–C1'–C4–C3 (τ_a) describes the twisting motion around the C1'–C4 double bond. The dihedral angles C9'–C2'–C4–C1' (τ_b) and C3–C1'–C5–C4 (τ_c) describe the pyramidalizations at the C1' and C4 atoms, respectively. The five-membered ring distortion is described by the dihedral angle C4–C3–C2–C5 (τ_d). The five-membered ring moiety and the double-ring panel are defined as the “rotator” and “base”, respectively. For convenience, the switch process always refers to the twisting motion of the rotator with respect to the base.

In our two simulated molecules, OMe-NAIP and dMe-OMe-NAIP, the rotator is connected to the base by the C1'–C4 double bond (Scheme 1). Because the rotation of the five-membered ring with respect to the base may be clockwise or counter-clockwise, two different configurations exist for the same E (or Z) isomers (Scheme 2). In fact, these two configurations with different orientations are explained by the P/M chirality [64]. According to the different substituents along the rotation axis (C1'–C4 double bond) (Scheme 1), the P and M chirality can be defined as follows: first,



Scheme 1. The E \rightarrow Z and Z \rightarrow E isomerization of OMe-NAIP (top) with the methyl group and dMe-OMe-NAIP (bottom) without the methyl group.

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