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Regular Article

Excited-State Decay Paths of Ortho-Terphenyl: Electronic Structure Calculations and Nonadiabatic Dynamics Simulations

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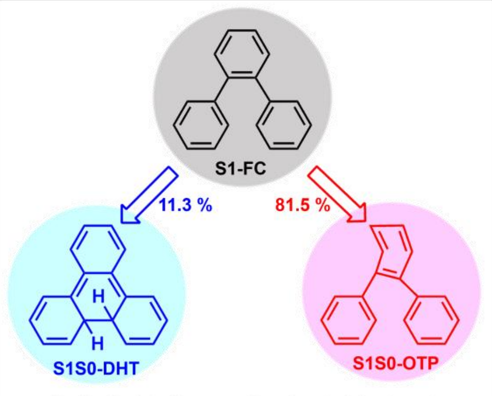

Excited-state decay paths of *ortho*-Terphenyl

Abstract: Photoexcitation of *ortho*-terphenyl (OTP) to cyclize into *4a,4b*-dihydrotripheneylene (DHT) is regarded as the first step in the synthesis of triphenylene. Surprisingly, the nonadiabatic cyclization mechanisms of this textbook reaction have not been examined explicitly until now. Herein we focus on the photoinduced dynamics of OTP by using static electronic structure calculations (MS-CASPT2//CASSCF) and trajectory-based surface-hopping dynamics simulations (OM2/MRCI). In terms of the calculated results, we shed light on two distinct relaxation pathways from the S_1 state and also the mechanism of photocyclization. The pyramidalization of central benzene ring and the subsequent $S_1 \rightarrow S_0$ transition via the S1S0-OTP intersection region is the predominant route (PATH I, ~ 81.5%); while the relaxation from the S_1 state to the S_0 state through the S1S0-DHT intersection region is the minor pathway and can be determined to be the key step for the formation of DHT conformer in the ground state (PATH II, ~ 11.3%). In the simulated period of 3.0 ps, the final recovery yield of S_0 OTP conformer is predicted to be 92.8% due to thermally activated ring reopening of DHT conformer; that is, the intermediate DHT is not so stable in the ground state. In addition, two relaxation time constants (538.7 fs and 5.1 ps) are predicted for the S_1 dynamics of OTP with the faster process assigned to the nonreactive deactivation (PATH I) and the slower one assigned to the ring closure reaction (PATH II), which are well consistent with the experimental values of 700 fs and 3.0 ps in the solutions of tetrahydrofuran (THF). Finally, the present work can provide important photocyclization mechanistic insights for OTP system and also the similar *ortho*-arenes.

Key words: ortho-terphenyl, excited-state decay, nonadiabatic dynamics, photo-cyclization.

1. Introduction

Nonadiabatic transitions between different electronic states are very important in the photo-induced chemical, biological, and material systems, involving deactivation of excited states, photo-dissociation of small molecules, photo-isomerization of large biological systems, and nonadiabatic recombination of charge carriers of photovoltaic materials, and so on [1-9]. Since the first observation of photo-induced carbon-carbon bond formation in stilbenes and related systems in the first mid-20th century, much attention has been attracted to investigate the photochemical cyclization behaviors [10-15]. Photocyclization reactions have been applied to various fields, such as light-assisted synthesis of ployaromatic compounds and design of molecular photo-switches [14-25]. For instance, photocyclization reaction has been used to synthesize pharmaceuticals (e.g., antibiotics and antitumor agents) [23-25] and large polycyclic aromatic hydrocarbon materials (e.g., graphite ribbons) [20,21]. Besides, photocyclization has also been utilized to design molecular photo-switches for the applications in memory storage and chemical sensitization [19,22].

In addition to the above fundamental applications, experimental and computational scientists have also been dedicated to studying the underlying mechanisms of photocyclization reactions, especially, for identifying the relationships of molecular structures – potential energy surfaces – nonadiabatic chemical dynamics [26-38]. In the present work, we will concentrate on the nonadiabatic photocyclization reaction of an ideal system *ortho-*