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Quantum control of molecular chirality: Ab initio molecular orbital study and wave packet analysis of l,l′-binaphthyl

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This paper is dedicated to Professor Iwao Yamazaki.

Abstract

The results of a theoretical study on quantum control of an axial chirality change reaction in l,l′-binaphthyl are presented. The chiral change from the **P** form to the **M** form via the third excited electronic state has been considered, the pure enantiomer of the **P**-form being assumed as the initial state. Asymmetric double-well potential energy surfaces of the ground state (S_0) and the third excited electronic state (S_3) and the corresponding transition moment along the reaction coordinate were evaluated using ab initio MO methods. An optimal control theory was applied to the chirality change reaction. The results of the quantum control showed that motions of nuclear wavepackets on both the S_0 and S_3 reaction coordinates were controlled. The mechanism of the quantum control is explained as a sequence of quantum transitions between S_0 and S_3, and the control is performed by irradiating a sequence of a pump-dump pulse.

Keywords: Quantum control; Molecular chirality; Binaphthyl; Wave packet; Isomerization

1. Introduction

Molecular chirality plays important roles in various research areas in chemistry and biochemistry [1,2]. It is well known that chiral molecules are selectively manipulated by photoreactions of racemic mixtures that are equal mixtures of two chiral forms by irradiation of circularly polarized laser light [3]. However, its enantiomer excess is very low. With recent developments in laser science and technology, much interest has been shown in quantum control of chemical reaction dynamics [4–12]. The effectiveness of quantum control originates from the fact that wave functions relevant to reaction dynamics are directly controlled through a coherent interaction between the molecule of interest and laser fields. Electric fields of laser pulses can now be designed using pulse shaper techniques with an adaptive feedback algorithm [13–17].

Theoretical studies on quantum control of molecular chirality have been carried out by several groups [18–34]. In a previous paper [35], we presented results of a theoretical study on quantum control of a chiral exchange reaction of difluorobenzo[c]phenanthrene by using infrared laser pulses. In this paper, we present a scenario for quantum control of an axial chirality control reaction in l,l′-binaphthyl (referred to simply as binaphthyl in the following discussion) using UV lasers; the nuclear wave packet motion on both the ground and electronic excited states is manipulated by using UV laser pulses. UV laser pulses are better than IR laser pulses for quantum control of reaction dynamics especially when a transition state of a chiral exchange reaction has a high-energy barrier in the ground state.

In the present study, we investigated an axial-chirality exchange reaction from the **P** (or **M**) form to the **M** (or **P**) form in binaphthyl. This axial-chirality exchange reaction can also be considered as an isomerization. The ground and excited state potential surfaces and the transition moment functions between them were evaluated by using ab initio molecular orbital (MO) methods. The isomerization does not have a symmetric potential energy surface along a reaction path. The potential energy

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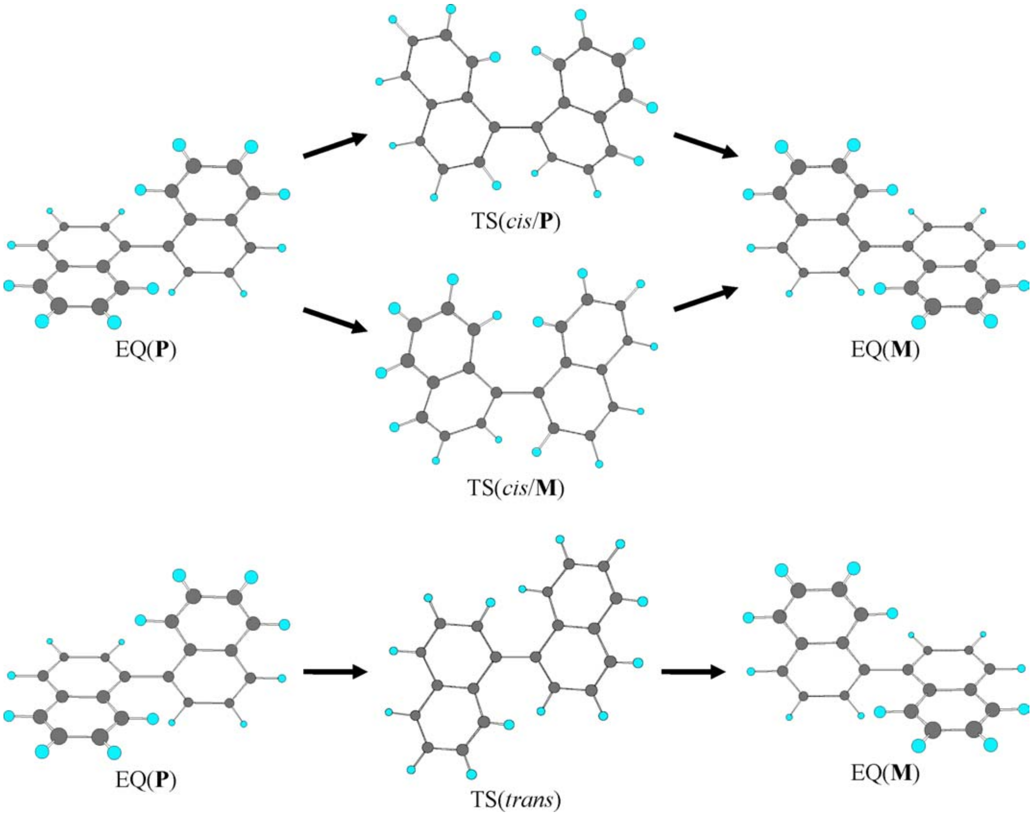

Fig. 1. Stationary structures along the isomerization of binaphthyl via TS(*cis*) (top part) and TS(*trans*) (bottom part).

surfaces also have several wells along the reaction path. An optimal quantum control theory was applied to molecular-chilarity exchange reaction that proceeds on such relatively complicated potential surfaces. The results showed that the motion of nuclear wave packets can be controlled by consecutive electronic transitions, and the transitions are induced by using a pump-dump pulse sequence.

In Section 2, we present results of ab initio MO studies on binaphthyl. In Section 3, we present results of optimal control of the axial-chirality exchange reaction and wave packet analysis.

2. Ab initio molecular orbital studies

Stationary structures on the potential energy surface of the ground state in binaphthyl were optimized using the RHF/6-31G(d,p) method [36]. The equilibrium structures, EQ(**P**) and EQ(**M**), are illustrated in Fig. 1. The reaction path is defined by the intrinsic reaction coordinate (IRC) at this computational level of theory. The total energies of the low-lying electronic states along the IRC were calculated on the basis of the more reliable MCSCF + FOCI level of theory, where the MCSCF active space includes four occupied and four vacant orbitals close in energy to the HOMO and LUMO. The total energies are plotted against the dihedral angle $C_2 - C_1 - C_1' - C_2'$ at each point along the IRC in Fig. 2 (see Scheme 1). The transition moments among these states were also computed at this level of theory. Table 1 shows the relative energies of the stationary structures along the IRC. The stationary structures and their relative energies are in good agreement with the results reported by other groups [37].

The top part of Fig. 1 illustrates the isomerization paths via the *cis* configuration: the transition state TS(*cis*) has C_2 symmetry and has an optical isomer. They are referred to have as TS(*cis*/**P**) and TS(*cis*/**M**). Accordingly, two paths must exist for the isomerization: (1) EQ(**P**), for example, climbs up the relatively gentle slope of the potential energy curve in the ground state and goes through TS(*cis*/**P**) to reach EQ(**M**) and (2) EQ(**P**) climbs up the very steep slope and goes through TS(*cis*/**M**) to reach EQ(**M**). This fact indicates that there are at least two important vibrational motions, rotation around the inter-ring C–C bond and C–H bending motions near the inter-ring C–C bond. The selection of the isomerization paths depends on which motion is promoted at the initial stage of reaction. According to the results of our previous investigation [35], it is much easier to control the reaction by an optimal laser field when the steeper motion is promoted first.

Table 1
Relative energies (kcal/mol) of stationary structures

	EQ	TS(*cis*)	TS(*trans*)
Symmetry	C_2	C_2	C_1
RHF	0	39.8	30.2
MCSCF	0	38.5	29.5
MCSCF + FOCI	0	38.6	29.4