Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics 338 (2007) 268–276
Chemical Physics
www.elsevier.com/locate/chemphys

# Stereoselective laser pulse control of an axial chiral molecular model system supporting four stereoisomers

Dominik Kröner *, Bastian Klaumünzer

*Institut für Chemie – Theoretische Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany*

Received 17 January 2007; accepted 13 April 2007
Available online 21 April 2007

Dedicated to Professor Jörn Manz on occasion of his 60th birthday.

## Abstract

We present quantum dynamical simulations on the axial chiral model system 2,2′-difluoro-biphenyl which supports four stereoisomers, i.e. two *diastereomeric* pairs of *enantiomers*, along the torsion around its central C–C bond. A pump-dump control mechanism is developed which consists of *stereo*-selective, i.e. *enantio*- and *diastereo*-selective, ultrashort laser pulses that convert a racemic mixture to one of its diastereomers. For that purpose the enantioselective laser pulse control of previous theoretical investigations is extended for systems that support more than one pair of enantiomers. Still, the polarization of the laser field determines the stereoselectivity of the control mechanism.

*PACS:* 11.30.Rd; 33.15.Hp; 42.50.Ct

*Keywords:* Chiral symmetries; Rotational isomerism; Light interaction with matter

## 1. Introduction

Traditional chemistry offers a variety of ways to synthesize the desired stereoisomer of a species, e.g. by employing chiral catalysts [1–3]. The possibility of producing enantiomeric excess under the influence of electro-magnetic fields was particularly investigated by experimentalists. For example, the difference in the absorption coefficients of two enantiomers for circularly polarized light may be used to induce enantioselectivity in a photochemical reaction [4,5]. Still, the success of asymmetric synthesis by external fields is so far rather limited [6]. Meanwhile, several studies were carried out by theoreticians with the goal to describe molecular chirality by means of quantum mechanics and to be eventually able to control chirality by light [7–10].

Recent simulations based only on the electric dipole electric field interaction have proven that starting from a racemate the selective excitation and even selective transformation of one enantiomer into its mirror image is possible by using linearly polarized light [11–15]. Shapiro and Brumer introduced a coherent control scheme [16] for enhancing the fraction of one desired enantiomer in a racemic mixture of randomly oriented molecules and applied their so-called *laser distillation* method to 1,3-dimethylallene [17,18]. By creating interferences in a 3-level system, Král et al. proposed a *cyclic population transfer* that results in the selective excitation of one enantiomer relative to its mirror image [19]. The selective preparation of a pure enantiomer by a linearly polarized laser pulse sequence was presented by Manz, Fujimura and coworkers for a racemate of pre-oriented axial chiral thiophospinic acid [11,12]. Hoki et al. showed that even if the overall rotation of the molecule is allowed the proposed laser control is still possible if circularly polarized pulses are applied [20]. By using two

---

* Corresponding author. Tel.: +49 331 977 5751; fax: +49 331 977 5058.
*E-mail address:* kroener@uni-potsdam.de (D. Kröner).

0301-0104/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2007.04.010

degrees of freedom of oriented (4-methyl-cyclohexylidene)-fluoromethane we have proven that the enantioselective laser pulse excitation [12,14] can also be applied to the degree of freedom which does not support the direct conversion of one enantiomer into the other [21]. Complete orientation of the axial chiral molecules is not required, but uni-directional alignment, if two perpendicular propagating enantioselective laser pulses are used [22]. Still, the efficiency of our laser control is maximized for oriented molecules. However, orientation of the chiral molecules can be accomplished e.g. by physisorption or chemisorption on a surface. Experimentally, the alignment of chiral molecules on metal surfaces has been studied showing that enantiomers form domains of unique chirality [23,24]. Also lasers can be used to orient molecules [25–28].

While former investigations had as common goal the purification of a racemate by selectively transferring the mixture to the desired enantiomer, the present paper deals with selective conversion of a racemic mixture to a pure diastereomer. This requires a molecule that supports four stereoisomers instead of two. In order to account for all four stereoisomers a new stereoselective laser pulse control was developed. The new control mechanism is derived from our enantioselective laser pulse control [14]. Yet, the extension of the laser pulse control to a system with two pairs of enantiomers is far from being trivial since each stereoisomers has to be excited by a different energy using the same pump pulse. Also here the polarization of the laser field controls the selectivity.

It should be noted that in a chemical laboratory a racemate is usually purified in a chiral environment, i.e. by conversion of both enantiomers into two different diastereomers, e.g. by reaction with a chiral substance. The two produced diastereomers can be separated because of their different physical and chemical properties. After removing the chiral auxiliary both enantiomers are obtained isolated. In this work, by contrast, both enantiomers of the racemic mixture are selectively transformed into the same diastereomer. Once the pure diastereomer is isolated it can further be converted to any other desired stereoisomer. Therefore, our approach is no purification in terms of a separation of both enantiomers, but rather a selective change of chirality of the molecules.

The rest of the paper is organized as follows: The molecular model system, theory and methods are explained in Section 2. The concept and the results of the stereoselective laser control are presented in Section 3. Section 4 summarizes.

## 2. Theory and model system

Our investigations are based on the axial chiral 2,2′-difluoro-biphenyl. The chiral axis runs along the central C–C bond connecting both benzene rings. Four stable chiral conformers, so-called atropisomers, can be distinguished at very low temperature ($T < 30$ K). They form two pairs of enantiomers ($aS_c$)-/($aR_c$)- and ($aS_t$)-/($aR_t$)-2,2′-difluoro-biphenyl, as sketched in Fig. 1. The subindex c and t stand for cis and trans. Here we use cis for isomers with both F-substituents being close to each other, i.e. they are on the same side of an imaginary plane along the central C–C bond and perpendicular to the paper plane. Trans denotes isomers with both F-atoms being on opposite sides of this plane. Conformers that are not mirror images of each other are diastereomers, e.g. $aS_c$ and $aR_t$.

The molecule is assumed to be oriented with its $C_1$–$C_1'$ bond along the $z$-axis, as depicted in Fig. 2a. The degree of internal rotation (torsion) is measured by the dihedral $\theta$ between $C_2$, $C_1$, $C_1'$ and $C_2'$, cf. Fig. 2a.

In passing we note, that the overall rotation of the molecule is neglected in this approach even though both phenyl rings have the same mass. We assume that the lower ring in Fig. 1 is fixed to a much heavier object like a solid surface by linking substituents in $C_3$ and $C_5$ position. For enantioselective laser control including overall rotation of an axial chiral molecular model system the reader is referred to Ref. [20].

The geometry of the molecule was optimized with density functional theory (DFT) using the hybrid functional B3LYP with a 6-311+G(d) basis set, as implemented in GAUSSIAN03 package [29]. The minimum energy geometry was found for $\theta = 57°$ and $\theta = 303°$ corresponding to the cis enantiomers $aS_c$ and $aR_c$, respectively. A second pair of energetically higher minima was found for $\theta = 130°$ and $\theta = 230°$ corresponding to the trans pair of enantiomers $aS_t$/$aR_t$. The calculated geometrical parameter are in good agreement with those obtained from DFT by Adam et al. [30].

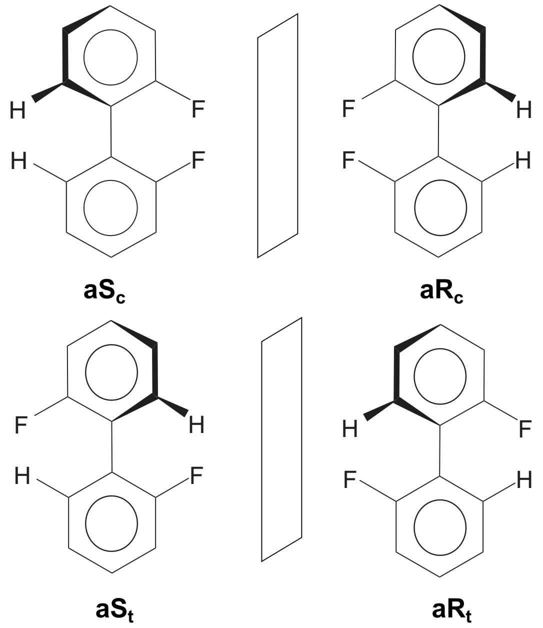

Fig. 1. The four chiral stereoisomers (atropisomers) of 2,2′-difluoro-biphenyl consisting of 2 diastereomeric (c = cis and t = trans) pairs of enantiomers ($aS_c$/$aR_c$ and $aS_t$/$aR_t$). Conformers that are enantiomers are shown as mirror images of each other with a mirror plane in between.