Theoretical Investigation of the Dynamics of the Binaphthol Isomerization

O <u>Riadh Sahnoun</u>,^a Shiro Koseki^b, and Yuichi Fujimura^a

^a Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

^b Department of Material Science, College of Integrated Arts and Sciences, Osaka Prefecture University, Osaka 599-8531, Japan.

email: sahnoun@mcl.chem.tohoku.ac.jp, fujimura@mcl.chem.tohoku.ac.jp, shiro@ms.cias.osakafu-u.ac.jp internet: http://www.mcl.chem.tohoku.ac.jp/, http://chem.cias.osakafu-u.ac.jp/~shiro/

Introduction: A tremendous interest has been addressed to the axially chiral C₂-symmetrical 1,1'-bi-2-naphthol (BINOL). It has been shown in the literature that this compound is a reliable source of a variety of binaphthyl compounds. It is widely used in chiral recognition [1] and many other chemical and industrial processes [2]. It has been also used as chiral host for optical resolution and chiral shift reagent for the determination of the optical purity and absolute configuration of a wide range of chiral compounds [2]. As a useful core unit for the preparation of a wide range of molecular structures, a detailed knowledge about its conformation is essential for the design of new chiral compounds. Of a central importance for the synthetic chemists is the rotational barrier of the chiral axis C-1-C-1'. Chow and coworkers have reported recently that the high rotational barrier can be attributed to the presence of substituents, when compared to binaphthyl (whithout substituents) [3]. BINOL would be the most appropriate candidate owing to its geometric structure and wide applicability. In this regard, theoretical investigations of the mechanism of BINOL isomerization can be of importance in the understanding of the "unusual" high rotational barrier. To this end, we have carried out a B3LYP investigation of the fully isomeriztaion potential energy surface (PES).

Computational details: All calculations have been carried



out using the Gaussian 98 suites of program. Throughout this work we adopted density functional theory as method of calculation. Geometry optimizations were carried out at the B3LYP level of theory, which consists of a hybrid Becke+Hartree–Fock exchange and Lee–Yang–Parr correlation functional with nonlocal corrections. The 6-31+G(d,p) basis set implemented in Gaussian 98 has been used for C, O and H atoms. All structures were optimized

without any symmetry restrictions. Local minima and transitions state structures have been identified by the number of imaginary frequencies calculated from analytical Hessian matrix. The intrinsic reaction coordinates (IRC) connecting reactants and products on the potential energy surface (PES) have been carried out for each transition state structure.

Results: The geometric structures of the three isomers of 1,1'-bi-2-naphthol and their respective enantiomers are presented in Fig. 1. All optimized geometry parameters were found to be nearly identical for all the compounds considered. This was reflected on their relative stabilities where relative energies of **I2** and **I3** deviate only by 0.17 and 0.31 eV, respectively, with respect to **I1**. Examination of a possible reaction path that connects the different

isomers/enantiomers considered in this work has been followed by the possible rotation around the C-1–C-1'single bond that connects napththols. the two The calculations show that rotational barrier of the interconversion between all isomers is, as expected, relatively high. Ila can be interconverted to I2b by 2.1 eV, whereas I2b needs 1.9 eV to achieve its interconversion to I3a. The energy diagram of the



Figure 2. Energy diagram of the isomerization/ enantiomeristaion process of 1,1'-bi-2-naphthol.

mechanism of the interconversion is depicted in Fig. 2. As can be deduced from Fig. 2, the rotation around C-1–C-1' bond for **I1a** and **I3a** can lead to their respective enantiomers. Over all, the mechanism of enantiomerization is more energetic. The rate determining step of the whole PES was the enantiomerization of **I1**. As far as the control of the dynamics by a laser field of the most stable structure, namely **I1**, is concerned, examination of the excited state enantiomerization is needed. The calculations are now in progress.

Conclusion: The PES of the isomerization/enantimerisation of the 1,1'-bi-2-naphthol has been achieved. A highly rotational barrier across the interconversion mechanism has been found, in agreement with the experimental observations. As a chiral compound, 1,1'-bi-2-naphthol is a promising and challenging system for quantum dynamics control in the aim to understand the chemical aspects of its binaphthol congeners involved in different processes.

References:

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