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DFT Study on the Structure and Racemization Mechanism of 1,1'-Binaphthalene-8,8'-diol

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Density functional theory (DFT) was applied to study the ground state geometries and isomerization processes of 1,1'-binaphthalene-8,8'-diol. Three isomers, denoted as ISO1, ISO2, and ISO3, were found, distinguished by different orientations of the OH groups, and each OH-orientational isomer has R- and S-enantiomer. The conformational stabilities of these isomers were investigated by tracking the energy change with respect to the ring-to-ring torsion. The inter-conversions between the three OH-orientational S-isomers were found to have quite low barriers owing to the nearly free rotation of OH groups around the O−C single bonds. The S-R enantiomerization of ISO1 and ISO2 can take place through the ring-ring torsion around the C1−C1′ single bond, either in the anti-rotation manner or in the syn-rotation manner. The barriers of the anti routes are lower than those of the corresponding syn routes by 87.95 and 75.04 kJ/mol. For the S-R enantiomerization of ISO3, only the anti route was found. The barriers for the anti route enantiomerizations of ISO1, ISO2, and ISO3 are 119.61, 120.43, and 121.59 kJ/mol, respectively. A parallel reaction mechanism via three anti enantiomerization routes was proposed for the racemization of 1,1'-binaphthalene-8,8'-diol.

Key words: Density functional theory (DFT), 1,1'-Binaphthalene-8,8'-diol, Racemization

I. INTRODUCTION

The 1,1'-binaphthyls have attracted increasing interest due to their well-recognized chiral structures. This special class of compounds has been extensively utilized as chiral inducers for asymmetric organic synthesis and asymmetric catalytic reactions [1,2]. Among various derivatives of 1,1'-binaphthyl, the optically active 1,1'-binaphthalene-2,2'-diol (refered to as 2,2'-BINOL) has been widely used as a chiral auxiliary in enantioselective reactions and has demonstrated outstanding performance in chiral recognition [3-8]. Furthermore, since the hydroxyl groups can be easily modified with various functional groups, 2,2'-BINOL often serves as the starting materials to synthesize other sophisticated chiral compounds. For these reasons, 2,2'-BINOL has attracted considerable theoretical interest. Recently, density functional theory (DFT) calculations of 2,2'-BINOL have been carried out to study its structural and spectroscopic properties [9-13]. The computational results were used to explain the measured vibrational circular dichroism (VCD) and resonance Raman (RR) spectra [9-11]. The DFT calculations have also been utilized to investigate the isomerization/racemization mechanisms of 2,2'-BINOL [12,13]. Various pathways for its racemization have been proposed based on the DFT calculations.

The 1,1'-binaphthalene-8,8'-diol (denoted as 8,8'-BINOL hereafter) is an isomeric compound of 2,2'-BINOL in which the two hydroxyl groups are attached on the C8 and C8′ atoms of the 1,1'-binaphthyl [14-21]. The 8,8'-BINOL has been found to be a superior chiral auxiliary to 2,2'-BINOL in the highly enantioselective synthesis of optically active ketones [14]. Optically active 8,8'-BINOL was also used as a chiral auxiliary for the enantioselective protonation of enolates [15], asymmetric Diels-Alder cycloaddition [16], asymmetric Michael addition [17], and the synthesis of new chiral monodentate ligand [18]. Other uses of 8,8'-BINOL include the chiral recognition of amino acid derivatives [19] and the determination of absolute configuration of carboxylic acids [20]. It has been well documented that the 8,8'-substituted 1,1'-binaphthyls are stable at room temperature but tend to atropisomerization at elevated temperature [22]. Thus, a detailed knowledge about the structure and the racemization mechanism of 8,8'-BINOL is of great academic importance in view of its versatile roles in the asymmetric synthesis and chiral recognition. However, to our knowledge, there has been no computational work reported for 8,8'-BINOL yet.

In this paper, we report a theoretical study on the ground state structures and the mechanism of the isomerization/enantiomerization processes of 8,8'-BINOL by DFT calculations.

II. COMPUTATIONAL DETAILS

Geometry optimizations and energy calculations for the ground-state structures and the transition states were carried out with the DFT methods using Becker's

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three-parameter hybrid functional (referred as B3LYP) [23,24] and the standard 6-31G(d) basis sets. Initial optimizations were done without any symmetry constraint in order to avoid overlooking possible steady structures. For cases where the initially optimized structures turned out to be symmetric, the obtained structures were re-optimized with an appropriate symmetry constraint. Frequency calculations at the optimized structures were performed using the same methods as in the geometry optimization to estimate the zero-point energy corrections and to identify whether the obtained structures are the stable structures (without imaginary frequency) or the transition states (with sole imaginary frequency). Connection of the transition state with the reactant and product was tracked by inspecting the atomic displacements of the imaginary frequency and examined by the intrinsic reaction coordinate (IRC) technique. All calculations were performed with the Gaussian03 program suite [25] on a P4-3.0G computer.

III. RESULTS AND DISCUSSION

A. The ground-state structures and torsional stabilities of 8,8'-BINOL isomers

1. Ground-state structures

Due to the different orientations of the two hydroxyl groups and the enantiomorphous varieties, 1,1'-binaphthalene-8,8'-diol has six isomeric conformations, denoted as ISO1(S), ISO2(S), ISO3(S), ISO1(R), ISO2(R), and ISO3(R); where ISO1(S)/ISO1(R), ISO2(S)/ISO2(R), and ISO3(S)/ISO3(R) are enantiomorphous pairs. In ISO1 both the hydroxyl hydrogen atoms orient towards the C1−C1′ bond, whereas they orient away from the C1−C1′ bond in ISO3. For ISO2, one hydroxyl hydrogen atom orients towards the C1−C1′ bond, and the other away from the C1−C1′ bond. Both ISO1 and ISO3 are symmetric (C2 point group) whereas ISO2 is non-symmetric (C1 point group). Figure 1 displays the optimized structures of these six isomers.

Our calculation demonstrated that the energy of ISO1 is the lowest among the three OH-orientational isomers. The energies of ISO2 and ISO3 are higher than that of ISO1 by 11.97 and 22.05 kJ/mol, respectively. The slight lower energy of ISO1 compared with ISO2 and ISO3 seems to be due to the relief of weak repulsion between the OH (O′H′) hydrogen and the hydrogen atom attached to the C7 (C7′) atom. For all these isomers, the atoms on each naphthol group keep nearly coplanar, and the two naphthol planes in each isomer are roughly perpendicular to each other. The C2C1C1′C2′ dihedral angle, which approximately measures the relative orientation of the two naphthol planes, was calculated to be 94.0° for ISO1, 83.0° for ISO2, and 75.6° for ISO3.

The calculated structures of 8,8'-BINOL isomers show notable similarities with its 2,2'-diol substituted analogues (2,2'-BINOL). According to the DFT calculation by Sahnoun *et al.*, 2,2'-BINOL, like 8,8'-BINOL, has three S-isomers due to different orientations of OH groups, and each S-isomer has an enantiomer [12]. In comparison with the most stable S-isomer, the energies of the other two S-isomers of 2,2'-BINOL are higher by 17.36 and 31.84 kJ/mol. For all the isomers of 2,2'-BINOL, the two naphthols are almost perpendicular to each other, with the C2C1C1′C2′ dihedral angle being 97.2°, 87.3°, and 88.1° respectively [1]. The maximum difference of C2C1C1′C2′ dihedral angle between the three isomers is 9.9° for 2,2'-BINOL, which is much smaller than the 18.4° for 8,8'-BINOL.

2. Torsional stabilities

The torsion between the two 8-naphthol rings can be approximately described by the C2C1C1′C2′ dihedral angle θ. In order to estimate the ring-to-ring torsional stabilities for the 8,8'-BINOL isomers, we carried out partial optimization for all degrees of freedom except the dihedral angle θ that was fixed at certain values. Figure 2 shows the relative energies of the three S-isomers with the ring-to-ring torsional angle θ varying from 30° to 150°, where the energies at the optimized dihedral angle θ_0 (i.e., 94.0° for ISO1, 83.0° for ISO2, 75.6° for ISO3) were chosen to be zero. As shown in Fig.2, the energy profiles of all the three S-isomer are quite flat around θ_0, which is expectable in view of the single-bonding nature of the C1−C1′ bond. It can be evaluated from the energy profiles that the energy changes are less than 4.18 kJ/mol when $\Delta\theta=\theta-\theta_0$ does not exceed 23°, suggesting a considerable flexibility of 8,8'-BINOL with respect to the ring-to-ring torsion. This hints that the skeleton of 8,8'-BINOL can adapt a quite wide range of θ angle without much expenditure of energy, which makes it possible for various chemical modifications of the OH (O′H′) group while keeping its optical activity.

B. Isomerization of three S-isomers via the re-orientation of OH group

We have studied the isomerization of three S-isomers, ISO1(S), ISO2(S), and ISO3(S), via the rotation of the OH groups around the O−C bonds. The optimized structures of transition states, together with some key structural parameters, are shown in Fig.3. In Fig.4(a), we display the potential energy surface for the OH-orientational isomerizations of 8,8'-BINOL. The interconversions between the three R-isomers via OH rotations were not studied as they are expected to be similar to those between the S-isomers. According to our

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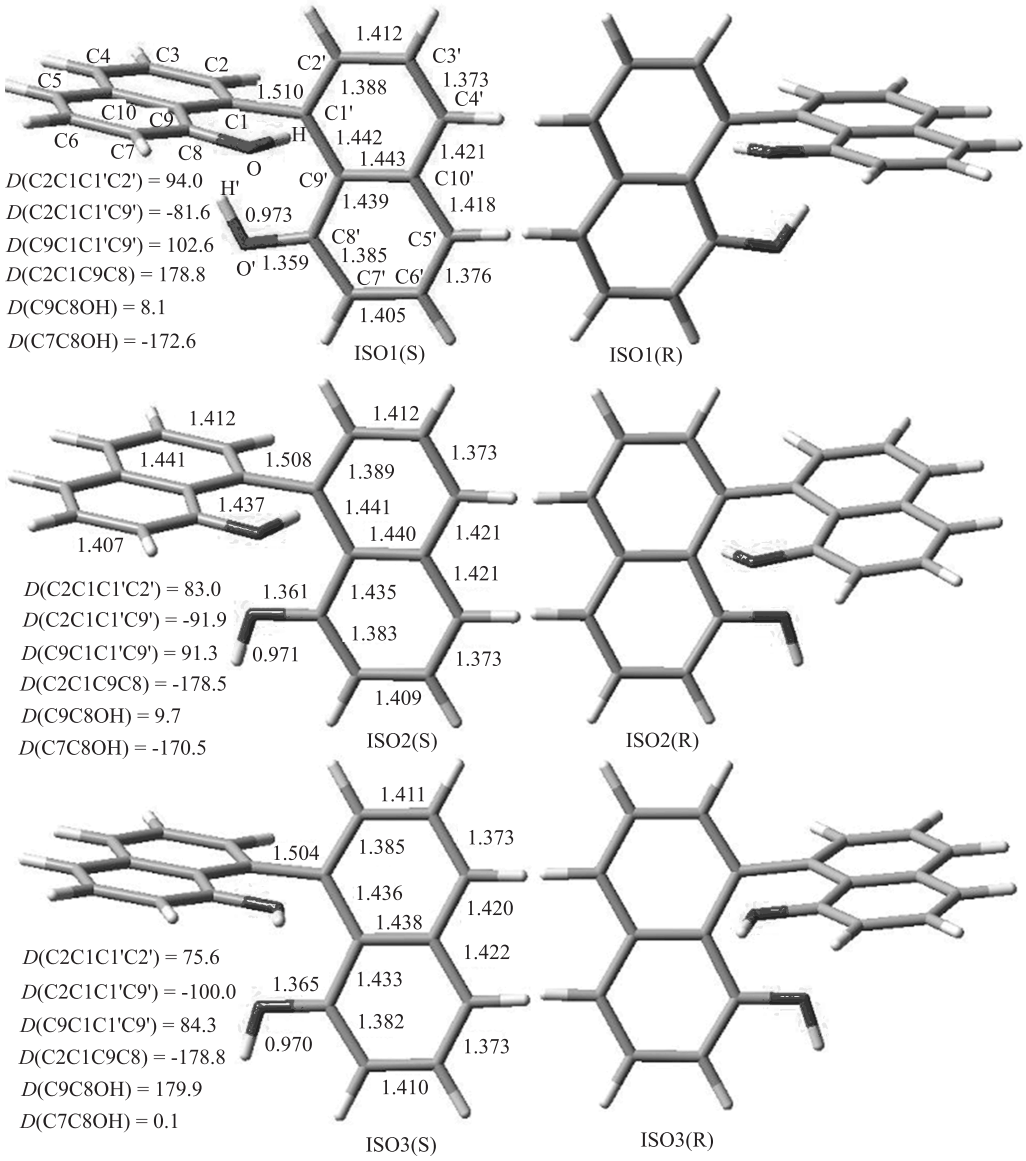

FIG. 1 Optimized ground state structures of the six isomers of 8,8'-BINOL (distances in Å, dihedral-angles in (°)).

DFT calculations, the inter-conversion of ISO1(S) and ISO2(S) can take place via the following two reactions:

$$\text{ISO1(S)} \rightarrow \text{TS1} \rightarrow \text{ISO2(S)} \quad (1)$$

$$\text{ISO1(S)} \rightarrow \text{TS2} \rightarrow \text{ISO2(S)} \quad (2)$$

where reactions (1) and (2) correspond to rotating the O′H′ group by 180° from different sides of the attached naphthyl plane. The structures of the transition states TS1 and TS2 are displayed in Fig.3 (a) and (b), respectively. In both TS1 and TS2, the OH group on C8 atom keeps coplanar with the attached naphthol ring while the O′H′ group on the C8′ atom is nearly perpendicular to the attached naphthol plane. According to our calculations, the barriers of reactions (1) and (2) are 21.03 and 22.84 kJ/mol, respectively; and the imaginary frequencies were calculated to be 351.1i cm^{-1} for TS1 and 382.7i cm^{-1} for TS2.

The inter-conversion of ISO2(S) and ISO3(S) can take place in similar ways:

$$\text{ISO2(S)} \rightarrow \text{TS3} \rightarrow \text{ISO3(S)} \quad (3)$$

$$\text{ISO2(S)} \rightarrow \text{TS4} \rightarrow \text{ISO3(S)} \quad (4)$$

The structures of the transition states TS3 and TS4 are shown in Fig.3 (c) and (d). The barriers of reactions (3) and (4) were calculated to be 20.06 and 20.63 kJ/mol, respectively; and the imaginary frequencies were calculated to be 361.2i cm^{-1} for TS3 and 378.9i cm^{-1} for TS4.

The structural features of the transition states TS1-TS4 are very similar to the isomerization of aryl-

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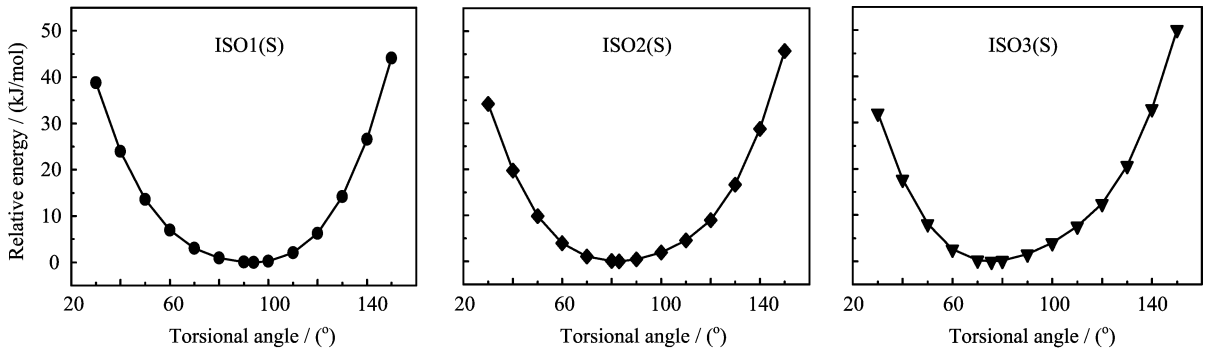

FIG. 2 B3LYP/6-31G(d) calculated relative energies of 8,8'-BINOL (S-isomers) via the change of C2C1C1′C2′ dihedral angle.

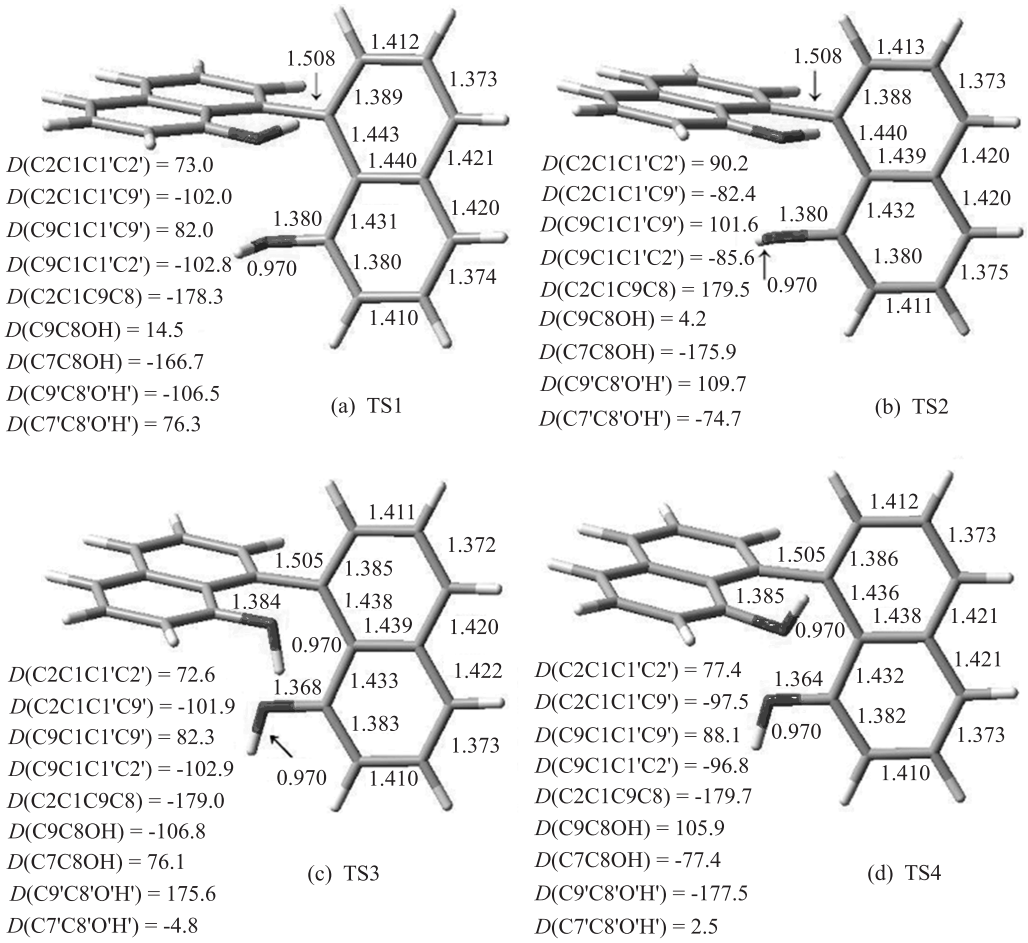

FIG. 3 (a) and (b) Optimized structures of the transition states connecting ISO1(S) and ISO2(S). (c) and (d) Optimized structures of the transition states connecting ISO2(S) and ISO3(S).

hydroxyl, such as phenol or naphthol, through OH rotations. It should be noted that the calculated barriers for TS1-TS4 are close to that of OH rotations of single 8-naphthol molecule calculated at the same level of theory (16.9 kJ/mol).

We did not detect any transition state connecting ISO1(S) and ISO3(S), which suggests that the ISO1(S)↔ISO3(S) inter-conversion is a stepwise process (rather than a concert process) with ISO2(S) as the intermediate.

Due to the small energy differences between the three S-isomers, the low barriers for reactions (1)-(4), and the quite large imaginary frequencies for TS1-TS4, we expect that the equilibrium between the three S-isomers

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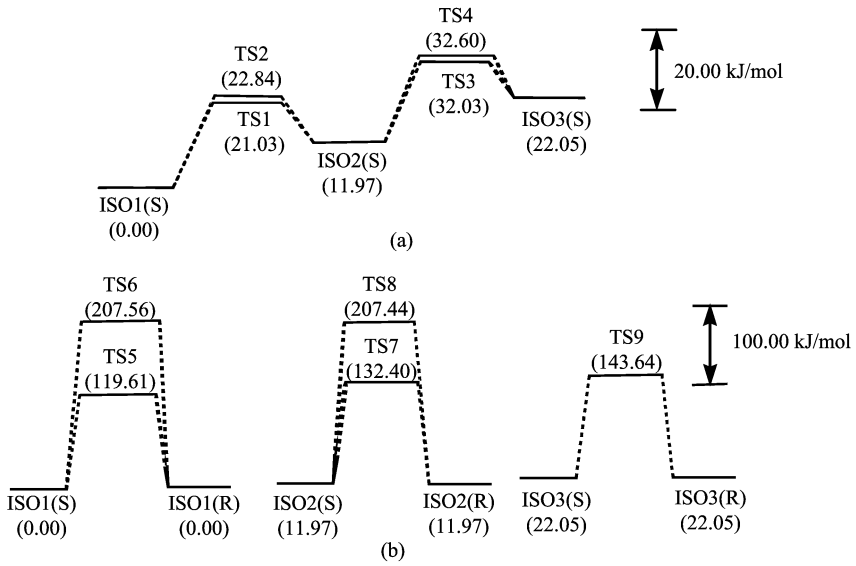

FIG. 4 Profile of potential energy surface calculated at the B3LYP/6-31G(d) level of theory for (a) the OH-orientational isomerizations, (b) the S-R enantiomerization reactions. Relative energies in kJ/mol.

can be readily established in the chirality resolved S-conformational 8,8'-BINOL .

C. Enantiomerization of 8,8'-BINOL

It is well known that the racemization of the binaphthyl derivatives can take place via two ways, i.e., the anti route (or *trans* route) with close contacts of the 2,8' and 2',8 substituents and the syn route (or *cis* route) through a passage of the 2,2' and 8,8' substituents [12,13,26,27]. These two routes are nominated according to the different rotating directions of the two naphthyl rings around the C1−C1′ single bond. We shall demonstrate that, for the racemization of 8,8'-BINOL, the anti routes are energetically more favorable than the syn ones.

1. Enantiomerization between ISO1(S) and ISO1(R)

According to our DFT calculations, direct enantiomerization between ISO1(S) and ISO1(R) can take place via the following reactions:

$$\mathrm{ISO1(S)} \rightarrow \mathrm{TS5} \rightarrow \mathrm{ISO1(R)} \quad (5)$$

$$\mathrm{ISO1(S)} \rightarrow \mathrm{TS6} \rightarrow \mathrm{ISO1(R)} \quad (6)$$

where the reactions (5) and (6) are the anti and syn routes, respectively. The structures of TS5 and TS6 are shown in Fig.5, where the selected key geometrical parameters are also presented. The energy barrier of reactions (5) and (6) are 119.61 and 207.56 kJ/mol, respectively; and the imaginary frequencies were calculated to be 15.4i cm^{-1} for TS5 and 56.2i cm^{-1} for TS6. Both the anti route transition state (TS5) and the syn route one (TS6) show evident non-planar deformation for the two naphthol groups. This non-planar deformation can be roughly considered as the twisting of the naphthol ring around the long axis (the axis passing though the centers of the C2C3 (C2′C3′) and the C6C7 (C6′C7′) bonds), and the deformation is also imposed with a weak folding of the two benzo rings with respect to the C9C10 (C9′C10′) bond. Due to the twist of the naphthol ring, the C1(C1′) atom moves towards one side of the mean-plane of naphthol while the C8(C8′) atom moves towards another side. This leads to the C2C1C9C8 dihedral angles of TS5 (146.4°) and TS6 (145.2°) considerably derivate from 180°. The C2C1C1′C2′ dihedral angle, which measures the ring-to-ring torsion of the two naphthal groups, was calculated to be 171.0° for TS5 (anti route) and 40.9° for TS6 (syn route). In TS6 (Fig.5(b)), the H···O′ distance is 1.660 Å and the O, H, O′ atoms are nearly in the same line, hinting the existence of a weak hydrogen bond between O−H···O′.

2. Enantiomerization between ISO2(S) and ISO2(R)

The direct enantiomerization between ISO2(S) and ISO2(R) can also take place via either the anti route (reaction (7)) or syn route (reaction (8)):

$$\mathrm{ISO2(S)} \rightarrow \mathrm{TS7} \rightarrow \mathrm{ISO2(R)} \quad (7)$$

$$\mathrm{ISO2(S)} \rightarrow \mathrm{TS8} \rightarrow \mathrm{ISO2(R)} \quad (8)$$

The energy barriers of reactions (7) and (8) are 120.43 and 195.47 kJ/mol, respectively; and the imaginary frequencies were calculated to be 21.5i cm^{-1} for TS7 and 64.8i cm^{-1} for TS8. The optimized structures of TS7 and TS8 with selected important geometrical

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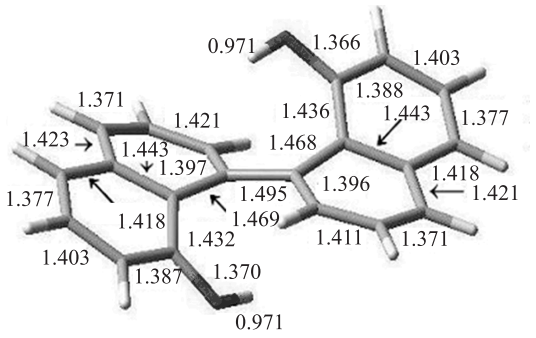
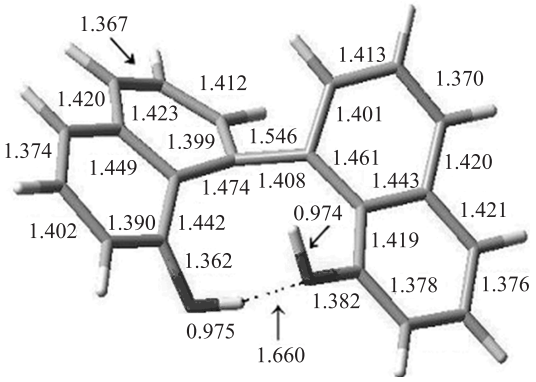


(a) TS5

D(C2C1C1'C2') = -170.9	*D*(C2'C3'C4'C10') = 12.0
D(C2C1C1'C9') = 8.1	*D*(C3C4C10C5) = -170.9
D(C9C1C1'C9') = -169.6	*D*(C3'C4'C10'C5') = 169.5
D(C9C1C1'C2') = 11.2	*D*(C5C6C7C8) = 5.2
D(C2C1C9C8) = 146.4	*D*(C5'C6'C7'C8') = -4.4
D(C2'C1'C9'C8') = -147.4	*D*(C9C8OH) = -2.8
D(C1C2C3C4) = 1.6	*D*(C7C8OH) = 171.8
D(C1'C2'C3'C4') = -0.3	*D*(C9'C8'O'H') = -7.1
D(C2C3C4C10) = -12.6	*D*(C7'C8'O'H') = 177.7



(b) TS6

D(C2C1C1'C2') = 40.8	*D*(C2'C3'C4'C10') = -11.6
D(C2C1C1'C9') = -122.5	*D*(C3C4C10C5) = -171.5
D(C9C1C1'C9') = 76.8	*D*(C3'C4'C10'C5') = -173.3
D(C9C1C1'C2') = -119.7	*D*(C5C6C7C8) = 5.6
D(C2C1C9C8) = 145.2	*D*(C5'C6'C7'C8') = 6.4
D(C2'C1'C9'C8') = 151.5	*D*(C9C8OH) = 51.8
D(C1C2C3C4) = 5.2	*D*(C7C8OH) = -139.0
D(C1'C2'C3'C4') = 3.4	*D*(C9'C8'O'H') = -26.7
D(C2C3C4C10) = -14.4	*D*(C7'C8'O'H') = 148.5

FIG. 5 Optimized transition structures for the ISO1(S)-ISO1(R) enantiomerization via the anti (a) and syn (b) routes.

parameters are presented in Fig.6 (a) and (b). The C2C1C1′C2′ dihedral angles are 170.0° for TS7 (anti route) and 38.3° for TS8 (syn route), which are comparable with the corresponding values for TS5 and TS6. Similar to TS5 and TS6, both TS7 and TS8 show evident out-of-plane deformations for the two naphthol groups, which are dominated with the twisting of the naphthyl rings around the long axes. The C2C1C9C8 dihedral angles were calculated as 147.2° for TS7 and 142.8° for TS8, which accounts for the deviations of C1(C1′) and C8(C8′) atoms to the different sides of the naphthyl mean-planes.

3. Enantiomerization between ISO3(S) and ISO3(R)

We only found the anti route for the direct enantiomerization between ISO3(S) and ISO3(R), with TS9 (C_i symmetry) as the transition state:

$$\text{ISO3(S)} \rightarrow \text{TS9} \rightarrow \text{ISO3(R)} \qquad (9)$$

The barrier of reaction (9) is 121.59 kJ/mol, which is the highest among the three anti routes of enantiomerization. The imaginary frequency of TS9 was calculated to be 24.8i cm^{-1}. The C2C1C1′C2′ dihedral angle in TS9 is 180.0°, which is considerably increased in comparison with the corresponding values of TS5 and TS7. Similar to the cases of TS5-TS8, out-of-plane twisting (together with a slight folding) deformation was also found for the two naphthol groups of TS9. The C2C1C9C8 dihedral angle of TS9 was calculated to be 146.3°.

We did not locate any transition state along the syn route enantiomerization between ISO3(S) and ISO3(R), though several attempts were made by varying the starting geometry of optimization. We found that the optimization from a potential transition structure of syn route enantiomerization always leads to either the stable ISO3(S) or the TS8 that connects ISO2(S) and ISO2(R). It seems that the direct enantiomerization between ISO3(S) and ISO3(R) along the syn route is prevented by the repulsion between the lone-pairs of the oxygen atoms of the two OH groups.

4. Distortion and non-distortion contributions to the active energies

As mentioned above, significant out-of-plane distortions were calculated in all the transition states of 8,8'-BINOL enantiomerization, which is thought to be responsible for a considerable amount of active energies. Kranz *et al.* have suggested that the energy barrier for the racemeriztion of a binaphthyl derivative can be attributed to two effects: the distortion effect that comes from the out-of-plane distortion within the naphthyl

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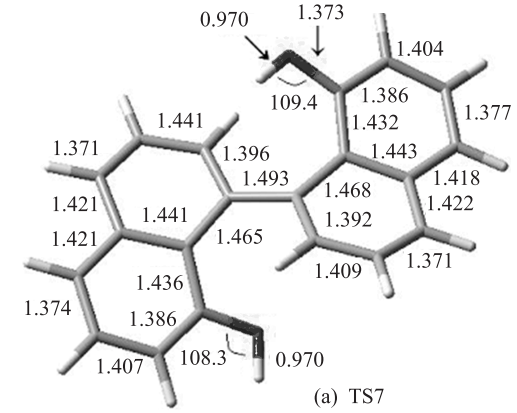
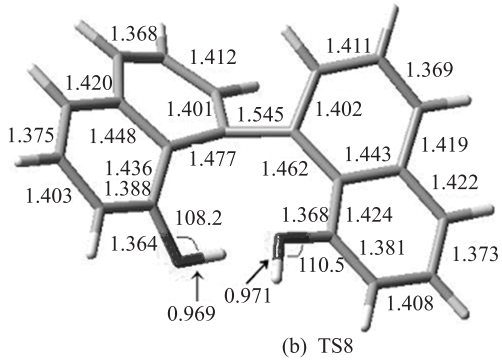


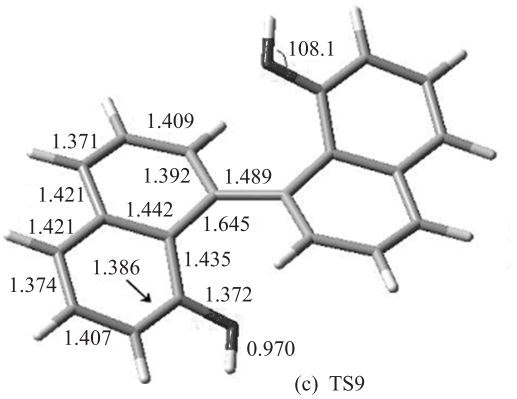
(a) TS7

D(C2C1C1'C2') = 169.9 *D*(C2'C3'C4'C10') = 12.6
D(C2C1C1'C9') = -12.5 *D*(C3C4C10C5) = -169.4
D(C9C1C1'C9') = 168.6 *D*(C3'C4'C10'C5') = 171.2
D(C2C1C9C8) = 147.2 *D*(C5C6C7C8) = 4.4
D(C9C1C1'C2') = -8.9 *D*(C5'C6'C7'C8') = -5.3
D(C2'C1'C9'C8') = -146.9 *D*(C9C8OH) = -173.9
D(C1C2C3C4) = 0.06 *D*(C7C8OH) = 1.3
D(C1'C2'C3'C4') = -2.2 *D*(C9'C8'O'H') = 4.4
D(C2C3C4C10) = -12.0 *D*(C7'C8'O'H') = -170.2



(b) TS8

D(C2C1C1'C2') = 38.3 *D*(C2'C3'C4'C10') = -11.2
D(C2C1C1'C9') = -128.6 *D*(C3C4C10C5) = -169.7
D(C9C1C1'C9') = 69.9 *D*(C3'C4'C10'C5') = -172.2
D(C2C1C9C8) = 142.8 *D*(C5C6C7C8) = 5.7
D(C9C1C1'C2') = -123.0 *D*(C5'C6'C7'C8') = 5.0
D(C2'C1'C9'C8') = 152.0 *D*(C9C8OH) = 34.5
D(C1C2C3C4) = 4.3 *D*(C7C8OH) = -154.8
D(C1'C2'C3'C4') = 2.0 *D*(C9'C8'O'H') = 178.0
D(C2C3C4C10) = -14.9 *D*(C7'C8'O'H') = -7.07



(c) TS9

D(C2C1C1'C2') = 180.0
D(C2C1C1'C9') = -1.0
D(C9C1C1'C2') = 1.0
D(C9C1C1'C9') = 180.0
D(C2C1C9C8) = 146.2
D(C1C2C3C4) = 0.7
D(C2C3C4C10) = -12.4
D(C3C4C10C5) = -169.8
D(C5C6C7C8) = 4.7
D(C9C8OH) = -172.9
D(C7C8OH) = 1.6

FIG. 6 Optimized transition structures for ISO2(S)-ISO2(R) enantiomerization via anti route (a), for ISO2(S)-ISO2(R) enantiomerization via syn route (b), and for ISO3(S)-ISO3(R) enantiomerization via anti route (c).

rings, and the non-distortion effect that comes from the pure steric repulsion between the two naphthyl rings [26]. These authors have proposed a method to evaluate the distortion and the non-distortion contributions to the energy barriers of binaphthyl racemeriztion [26]. According to this procedure, the energy calculation was performed for a single 8-naphthol molecule with the same deformed geometry as the transition-state (or the reactant), where a hydrogen was simply substituted for the second 8-naphthol ring of 8,8'-BINOL. Only the parameters of the newly introduced hydrogen atom were optimized, whereas other atoms of the deformed 8-naphthol ring are frozen so as to be consistent with the transition structure (or the reactant). The energy difference between the 8-naphthol molecule deformed from the transition state and the one deformed from the reactant should give a rough estimate for the deformation energy of a single 8-naphthol moiety in the transition state. In this way, steric repulsions between atoms in the two different 8-naphthol moieties of 8,8'-BINOL are eliminated. By summing the distortion energies of the single 8-naphthol rings and then subtracting that from the respective activation energy, the non-distortion effects of the 8,8'-BINOL can be evaluated.

We applied the above procedure for all the transition states of 8,8'-BINOL S-R enantiomerizations. According to our calculations, the distortion effect contributes about 86%, 63%, 88%, 67%, and 96%, respectively, to the active energies of TS5, TS6, TS7, TS8, and TS9. This suggests that the distortion effect over-

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whelmingly dominates the reaction barriers of the anti routes of enantiomerization, whereas both the distortion and non-distortion effects are important for the syn routes of enantiomerization. The non-distortion effect, which associates with the steric repulsion between the two naphthol rings, is expected to significantly increase the C−C′ bond of the transition structure. This is consistent with our DFT calculations, which show clearly elongated C−C′ bonds for the TS6 (1.546 Å) and TS8 (1.545 Å) as compared with TS5, TS7, and TS9 (1.463-1.489 Å).

D. Comparison of various enantiomerization routes

Figure 4(b) displays the potential energy diagram of various enantiomerization routes. Our DFT calculations demonstrated that S-R enantiomerization of ISO1 and ISO2 can take place through either anti or syn routes, with the barriers of the anti routes lower than those of the syn ones by 87.95 and 75.03 kJ/mol, respectively. The S-R enantiomerization of ISO3 occurs only via the anti route. All these suggest that the anti routes take place much more easily than the syn ones. Furthermore, the barriers for the anti S-R enantiomerization of all the three isomers are quite close in energy (119.61, 120.43, and 121.59 kJ/mol, respectively). On the other hand, the isomerization between the three S-isomers (or between the three R-isomers) can take place easily due to the very low barriers for reactions (1)-(4). Thus, we consider that all the three anti route processes (reactions (5), (7), and (9)) play critical roles in the racemization of 8,8'-BINOL. Therefore, the 8,8'-BINOL racemization can be attributed to a parallel reaction mechanism, where the direct S-R enantiomerizations via the anti routes take place for all the three OH-orientational isomers.

Comparison of the isomerization of 8,8'-BINOL with that of 2,2'-BINOL reveals some significant distinctions between the two sister compounds. According to the DFT calculation by Sahnoun *et al.*, the racemization of 2,2'-BINOL is a multi-step isomerization/enantiomerization process [12]. The direct interconversion between the most stable enantiomer pair of 2,2'-BINOL was found to be energetically unfavorable [12]. This is in contrast with the 8,8'-BINOL for which the direct inter-conversion between the most stable enantiomer (ISO1(S)-ISO1(R)) has the lowest barrier. In addition, Sahnoun *et al.* found that the racemization can take place between the different OH-orientational isomers of 2,2'-BINOL. For 8,8'-BINOL, however, we did not find any S-R racemization reaction (neither anti nor syn route) connecting different OH-orientational isomers. The different racemization mechanisms between 2,2'-BINOL and 8,8'-BINOL indicate that the positions of the OH substituents have a significant influence on the steric repulsion between the two naphthol rings.

IV. CONCLUSION

The isomerization and enantiomerization processes of 1,1'-binaphthalene-8,8'-diol were theoretically investigated using density functional theory. Three pairs of enantiomer were identified for 8,8'-BINOL due to different orientations of OH groups. The inter-conversion between three S-isomers (or between three R-isomers) were found to have quite low barriers owing to the nearly free rotation around the O−C single bonds. The S-R enantiomerization of ISO1 and ISO2 can take place through the ring-ring torsion around the C1−C1′ single bond, either in the anti-rotation manner or in the syn-rotation manner. The barriers of the anti routes are lower than those of the syn routes by 87.95 and 75.04 kJ/mol. For the S-R enantiomerization of ISO3, only the anti route is possible. Significant out-of-plane distortions were found for the TS structures of S-R enantiomerization. The barriers for the anti-rotation enantiomerizations of ISO1, ISO2, and ISO3 are 119.61, 120.43, and 121.59 kJ/mol, respectively. A parallel reaction mechanism, where the direct S-R enantiomerizations via the anti routes take place for all the three OH-orientational isomers, is proposed for the 8,8'-BINOL racemization.

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