

Racemization Barriers of 1,1'-Binaphthyl and 1,1'-Binaphthalene-2,2'-diol: A DFT Study

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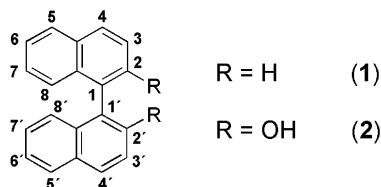
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Density functional theory has been applied to the study of various pathways and transition states for the configurational inversion of 1,1'-binaphthyl (**1**) and 1,1'-binaphthalene-2,2'-diol (**2**). The preferred pathway is found to be anti with centrosymmetric transition state. Whereas the reaction path of **1** goes downhill from transition to ground state, in the case of **2** it contains one unexpected local minimum. Very satisfactory agreement with available experimental values of activation Gibbs energies is achieved.

Introduction

1,1'-Binaphthyl (**1**) and its derivatives exhibit hindered rotation about internuclear bonds, and their enantiomers can be isolated at room temperature. Synthetically useful 1,1'-binaphthalene-2,2'-diol (**2**; BINOL) can be obtained from simple derivatives of **1**.



Enantiomerically pure BINOL is easily obtainable by resolution¹ of low-cost racemate and is one of the most used chiral auxiliaries for asymmetric synthesis.² Rotational barriers of **1** and **2** have been measured³ (Table 1). The racemization barriers of 1,1'-binaphthyl deriva-

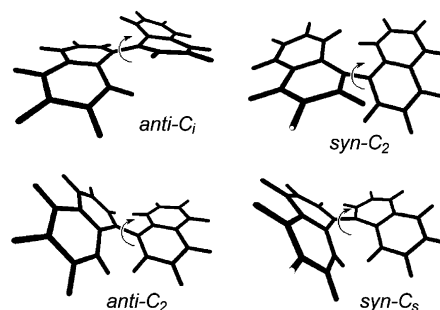


FIGURE 1. Possible racemization pathways of 1,1'-binaphthyl (**1**).

TABLE 1. Racemization of 1,1'-Binaphthyl (**1**) and 1,1'-Binaphthalene-2,2'-diol (**2**)

compd	<i>T</i> (°C)	solvent	$\tau^{1/2}_{\text{rac}}$ (min)	$\Delta G^{\ddagger}_{\text{rac}}$ (kJ/mol)	ref
1	44	benzene	68	100.7	3a
1	50	dimethylformamide	14.5	98.5	3b
2	195	naphthalene	270	155.5	3c,d
2	220	diphenyl ether	60	158	this work

tives have been computed using molecular mechanics⁴ and semiempirical methods.⁵

Racemization of binaphthyl is possible through a passage of 2,8'- and 2',8-substituents (anti route) or 2,2'- and 8,8'-substituents (syn route). Cooke and Harris^{3b} suggested two kinds of anti pathways for racemization

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TABLE 2. Experimental and Calculated C–C Bond Lengths (pm) of **1**

bond	X-ray ⁶	X-ray ⁷	calcd
C(1)–C(1')	147.5	148.6	149.8
C(1)–C(2)	136.5	137.7	138.3
C(2)–C(3)	140.4	140.9	141.5
C(3)–C(4)	136.0	135.8	137.4
C(4)–C(10)	141.3	142.1	142.0
C(5)–C(10)	141.4	142.1	142.2
C(5)–C(6)	134.6	137.0	137.6
C(6)–C(7)	140.4	139.1	141.6
C(7)–C(8)	135.9	136.1	137.6
C(8)–C(9)	141.3	142.6	142.3
C(9)–C(10)	141.6	141.2	143.5
C(1)–C(9)	143.3	143.5	143.5

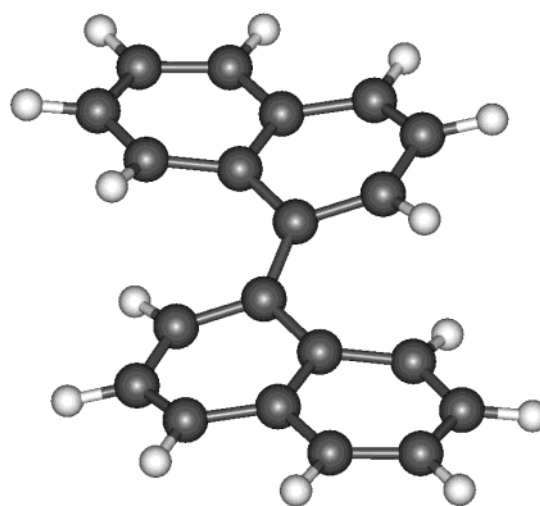
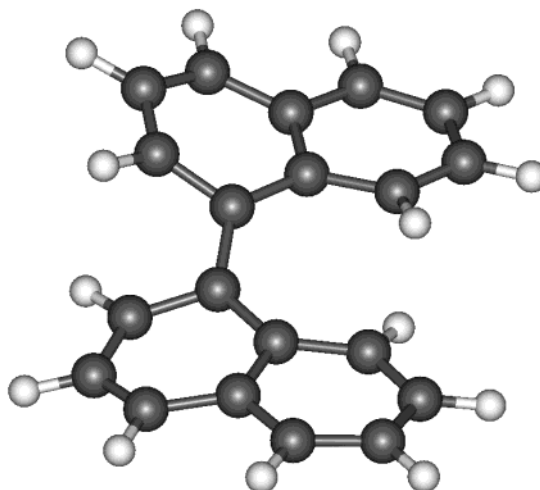
of substituted binaphthyl—“mesoid” (*anti-C_i* in Figure 1) and “racemoid” (*anti-C₂* in Figure 1). Carter and Liljefors^{4d} added syn analogues of these routes (*syn-C₂* and *syn-C_s* in Figure 1). They investigated all four racemization pathways of **1** and showed *anti-C_i* to be the preferred route with one *C_T*-symmetric local minimum. Tsuzuki et al.^{4e} found this *anti-C_i* pathway to have no local minimum but *C_T*-symmetric saddle point by MM2' and the same result we report for **1** and **2** in this paper. Kranz et al.⁵ excluded *anti-C_i* route from consideration and investigated *syn-C₂* and *anti-C₂* pathways of **1** by MNDO, AM1 and PM3. They preferred slightly the *anti-C₂* over *syn-C₂* route in conclusion. To the best of our knowledge racemization of **2** was not computationally investigated before.

Results and Discussion

1,1'-Binaphthyl (**1**). Ground-State Conformation.

Calculated bond lengths of **1** are compared to those from X-ray analyses (Table 2). Deviations from experimental values do not exceed 2 pm. X-ray structures of racemate and pure enantiomer of **1** were determined having C(2)–C(1)–C(1')–C(2') dihedral angles 68°^{6,7} and 103°,⁷ respectively. Our calculated *C₂*-symmetric structure has an energy minimum at 75°.

Transition Structures. Four types of racemization pathways, which were taken in consideration, are schematically drawn in Figure 1. However, we were able to locate only two transition structures—*anti-C_i* and *syn-C₂* (Figure 2). Table 3 shows relative energies and selected geometrical parameters of these transition states. Our *anti-C_T*-TS energy (96 kJ/mol) agrees almost exactly with the experimental values, whereas semiempirical AM1 and PM3 underestimate⁸ (84 and 75 kJ/mol) and ab initio Hartree–Fock (HF) overestimates⁸ (127 kJ/mol) the value of the racemization barrier. IRC calculation of *anti-C_T*-TS (Figure 3) shows simple downhill path to the ground state. During racemization starting from one GS enantiomer, atoms H(2) and H(8') initially pass each other with closest contact of 155 pm, then their non-bonded contact reaches 179 pm in the TS, and finally atoms H(2') and H(8) pass each other to give the opposite GS enantiomer.

*anti-C_i*-TS*syn-C₂*-TS**FIGURE 2.** Computed transition structures of **1**.

Binaphthalene-2,2'-diol (2**).** Ground state conformation. Calculated bond lengths of **2** are compared to those from X-ray analyses in Table 4. Deviations from the experimental values do not exceed 3 pm. Experimental C(2)–C(1)–C(1')–C(2') dihedral angles are 88° for racemate and 77° for pure enantiomer of **2**.⁹ Our calculated *C₂*-symmetric structure has an energy minimum at 95°.

Transition structures. Again, all four types of racemization pathways (Figure 1) were investigated. However, we were able to find only three transition structures—*anti-C_i*, *syn-C₂* and *anti-C₂* (Figure 4). Their relative energies and important structural parameters are shown in Table 5. Like **1**, the lowest in energy is the *anti-C_T*-TS (158 kJ/mol agrees excellently with the experimental values; AM1 and PM3 underestimate⁸ – 129 and 144 kJ/mol – and HF highly overestimates⁸ – 210 kJ/mol – the height of the rotational barrier). This centrosymmetric transition structure has both hydroxy groups in syn conformation (!), having short H(2)–C(8') nonbonded

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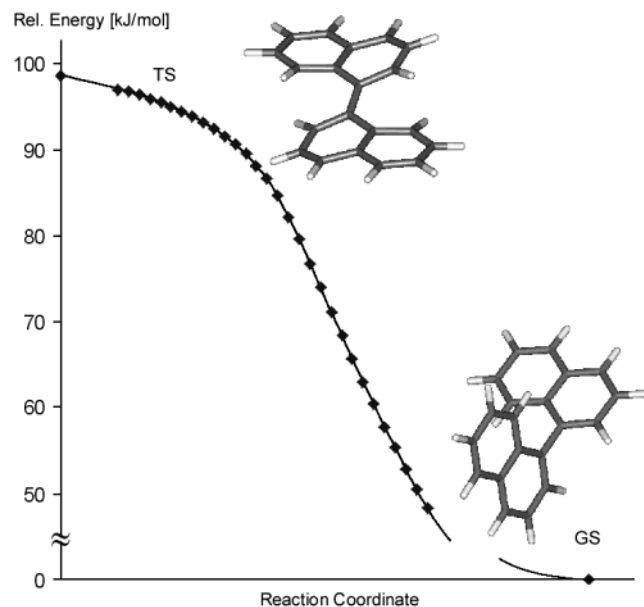
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TABLE 3. Relative Energies and Geometrical Parameters of Stationary Points of 1

structure	rel energy (kJ/mol)	angle C(2)–C(1)–C(1')–C(2') (deg)	distance (pm)			
			C(1)–C(1')	H(2)–H(8')	H(2)–H(2')	H(8)–H(8')
GS	0	75.0	150	373	313	325
<i>anti</i> -C _T -TS	96.1	180	150	179		
<i>syn</i> -C ₂ -TS	133.0	26.4	153		201	163

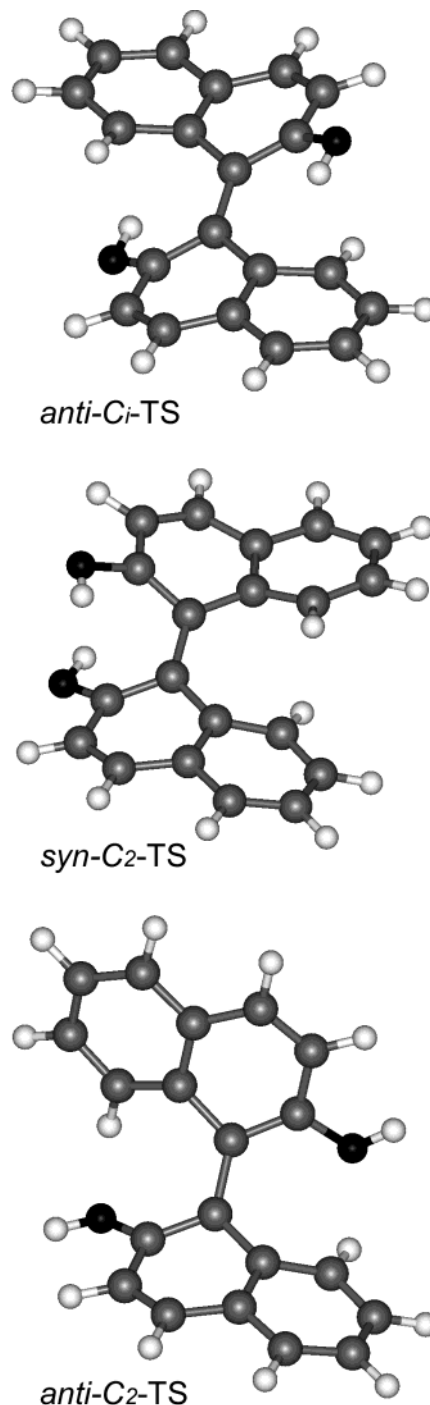
**FIGURE 3.** B3LYP 6-31G racemization path of 1.**TABLE 4. Experimental and Calculated C–C and C–O Bond Lengths (pm) of 2**

bond	X-ray rac ⁹	X-ray enant ⁹	calcd
C(1)–C(1')	148.9	150.1	149.8
C(1)–C(2)	138.8	137.5	139.2
C(2)–C(3)	141.5	141.7	141.9
C(3)–C(4)	135.3	135.4	137.1
C(4)–C(10)	141.0	140.7	142.2
C(5)–C(10)	141.9	141.9	141.9
C(5)–C(6)	135.4	134.9	137.7
C(6)–C(7)	139.9	141.1	141.5
C(7)–C(8)	136.3	135.4	137.8
C(8)–C(9)	141.5	141.7	142.2
C(9)–C(10)	142.9	142.5	143.4
C(1)–C(9)	141.9	142.7	143.7
C(2)–O(1)	136.8	136.1	135.9

distance (209 pm). IRC calculation starting from the *anti*-C_T-TS (Figure 5) exhibits one local minimum (M) between TS and GS, which differs from GS in one H(2)–O(2)–C(2)–C(1) dihedral angle and is by 18 kJ/mol above the GS. The shortest nonbonded contact between H(8') and O(2) during TS→M transformation is 190 pm (234 pm for TS itself).

Conclusions

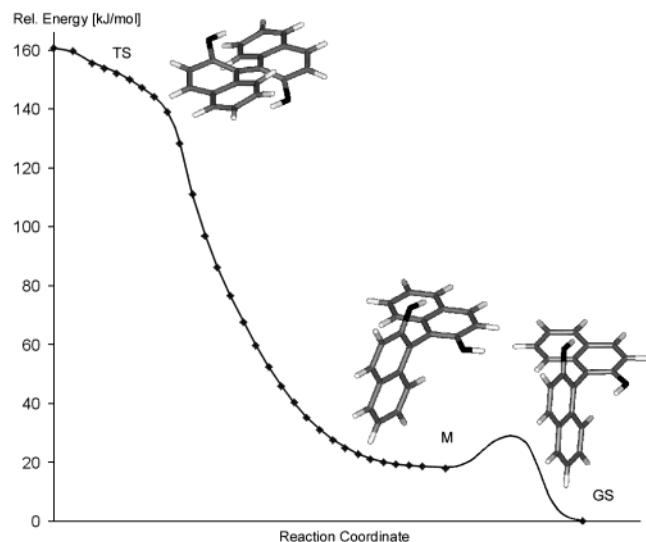
We have shown that density functional computations are excellent for calculating the racemization barriers of binaphthyls. The preferred racemization route is *anti*-C_T for both investigated compounds. Nevertheless, *syn*-C₂ racemization path might be important for other 2,2'-disubstituted binaphthyls (*syn*-C₂ is only 17 kJ/mol over preferred *anti*-C_T for BINOL 2). Racemization of both

**FIGURE 4.** Computed transition structures of 2.

investigated binaphthyl compounds does not affect the internuclear C(1)–C(1') bond length. Energy increase of TS is mainly caused by nonplanar geometries of aromatic rings.

TABLE 5. Relative Energies and Geometrical Parameters of Stationary Points of **2**

structure	rel energy (kJ/mol)	angle C(2)–C(1)–C(1')–C(2') (deg)	distance (pm)			
			C(1)–C(1')	H(2)–H(8')	H(2)–H(2')	H(8)–H(8')
GS	0	94.8	150	327	336	375
<i>anti</i> -C ₂ -TS	158.3	180	149	218	dist C(8)–H(2') 209	
<i>syn</i> -C ₂ -TS	175.3	25.6	150		255	202
<i>anti</i> -C ₂ -TS	249.4	172.7	152		dis. O(1)–H(8') 201	

FIGURE 5. B3LYP 6-31G racemization path of **2**.

Experimental Section

Racemization barrier of BINOL was determined as follows:

Solution of 25 mg (*S*)-BINOL in 500 mg diphenyl ether in a test tube was placed to an oil bath at (220±1) °C. Samples were analyzed at Chiralpak AD column (250 × 4.6 mm, solvent 5% 2-propanol in hexane, flow 0.5 mL/min, detection UV 254 nm) to give following results (ret. times of enantiomers: $t_R=29$ min, $t_S=31$ min):

time (min)	0	40	80	120
ee (%)	94	55.5	36	24.5

from which $k=1.93 \times 10^{-4} \text{ s}^{-1}$ (calculated by the first-

order rate equation: $k = \sum t_i^{-2} \sum t_i \ln(ee_0/ee_i)$ with the ee_0 at the time $t=0$ and ee_i at t_i , respectively), and $\Delta G_{\text{rac}}^{\ddagger}=(158\pm 1) \text{ kJ/mol}$.

The density functional calculations of B3LYP quality with basis sets 6-31G(d,p) were carried out using the GAUSSIAN 98¹⁰ program suite. Transition structure optimizations have been done using the STQN procedure without any geometry constraints. Second derivative (frequency) calculations proved the nature of stationary points (exactly 1 negative eigenvalue). The reaction path was determined by IRC calculations (at somewhat smaller 6-31G basis sets) for selected structures.

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Supporting Information Available: Cartesian coordinates and electronic energies of all stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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