

Optical Rotatory Feature of (*R* or *S*)-1,1'-Binaphthalene-2,2'-diol (BINOL) in Various Solvents

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The changes of the specific rotation and sign of optically active BINOL have been studied in polar/non-polar solvents and at the different pH values of solvent. It is considered that these changes are determined by the equilibrium studies between *cisoid* and *transoid* conformations of BINOL with the same configuration (*R* or *S*) which related to the change of the dihedral angle between two naphthalene ring planes of BINOL.

Keywords 1,1'-binaphthalene-2,2'-diol, solute-solvent interaction, specific rotation, *cisoid* and *transoid* conformation

Introduction

Eliel *et al.*^{1,2} have ever reported that solvent type and concentration would affect the equilibrium of *cis*-3-hydroxythiane-S-oxide conformation which was caused by intermolecular and intramolecular hydrogen bond formed with the interaction between the solute-solvent and the solute-solute in the solution and have important influence on its specific rotation. Up to now it is not very clear, however, whether hydrogen bonding affects specific rotation (in magnitude and occasionally in sign) directly or whether it does so indirectly (by af-

fecting conformation) or both. In the present paper the optical rotatory feature of (*R* or *S*)-(+ or -)-BINOL in various solvents was studied, and the optical phenomenon was explained tentatively.

Results and discussion

Solvent polarity

Table 1 shows the specific rotations of optically active BINOL in various solvents.

It is seen from Table 1 that specific rotation of BINOL in alcohol systems decreased gradually with decreasing of dielectric constant (ϵ) and dipole moment (μ) from methanol to *n*-butanol. In addition, this decrease of optical rotation is very obvious from DMSO to THF. Therefore, it is suggested that solvent polarity would have significant influence on the specific rotation. On the theory of rotational strength it was reported that when the solvent interacts with chromophore of some compounds producing a significant electronic transition

Table 1 Specific rotations of optically active BINOL in various solvents

Solvent	DC ^a ϵ	DM ^b μ (D)	Specific rotation $[\alpha]_D^{20}$ ^c	
			(<i>R</i>)-(-)-BINOL	(<i>S</i>)-(-)-BINOL
Methanol	32.7	1.70	+ 33.2°	- 32.6°
Ethanol	24.6	1.69	+ 30.4°	- 29.8°
<i>n</i> -Propanol	20.3	1.55—1.58	+ 19.2°	- 18.8°
<i>n</i> -Butanol	12.5	1.66	+ 9.8°	- 8.8°
DMSO	47.7—48.9	3.96	+ 158.0°	- 154.4°
THF	7.6	1.78	+ 34.1°	- 33.4°
CHCl ₃	4.8	1.04	- 11.7°	+ 12.0°
Toluene	2.379	0.375	- 47.3°	+ 48.0°
Benzene	2.284	0.424	- 48.6°	+ 48.2°

^a DC: Dielectric constant, from Lide, D. R. Editor-in-chief "Handbook of Chemistry and Physics", 76th edn., pp. 9—42, 1995—1996. ^b DM: dipole moment, from Lide, D. R. Editor-in-chief "Handbook of Chemistry and Physics", 76th edn., pp. 8—16, 1995—1996. ^c $[\alpha]_D^{20}$ unit: deg·cm²·g⁻¹ (c 0.5, at 20 °C).

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accompanying the transition from the ground state to an excited state, the rotational strength would directly depend on the electric and magnetic dipole moments of the matrix elements. Therefore, the more electric and magnetic moments, the more specific rotation.^{3,4} This phenomenon would be called a solvent induction effect. Our results are in correspondence with this theory, according to the rotational values of BINOL in alcohols, DMSO and THF solutions. However, it was very surprising that the rotational sign of (*R*)-(+)-BINOL or (*S*)-(–)-BINOL in non-polar solvent such as chloroform (as compared with THF), toluene or benzene was opposite to the corresponding sign in polar solvent, respectively (Table 1).

It is seen from CD spectra (Fig. 1) that optically active (*R* or *S*)-(+) or (–)-BINOL has two Cotton effects. In general, the sign of first Cotton effect placed in long wavelength shows the rotatory sign of the chiral polymer. First Cotton effect placed at ca. 300 nm might be assigned to the absorption of naphthalene group which is positive sign for (*R*)-(+)-BINOL and negative sign for (*S*)-(–)-BINOL in DMSO and THF solution, and becomes negative and positive for (*R*)-(+)-BINOL and (*S*)-(–)-BINOL in CHCl₃ respectively. These results are in correspondence with Table 1.

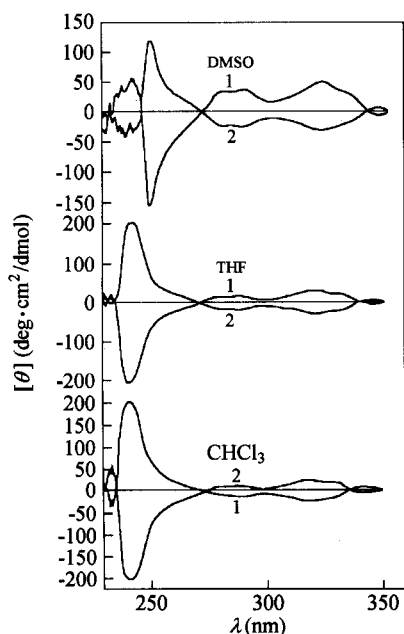
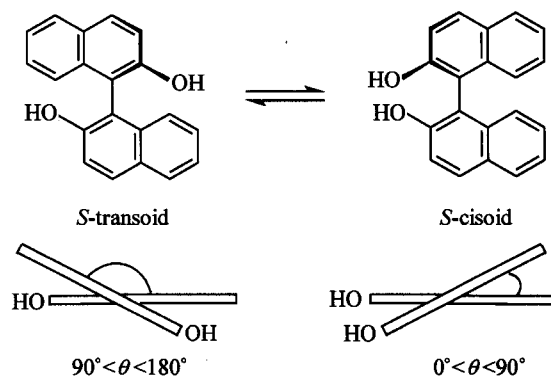


Fig. 1 CD spectra of optically active BINOL in DMSO, THF and CHCl₃ solutions, respectively (concentration 1.2×10^{-5} mol/L). 1, (*R*)-(+)-BINOL; 2, (*S*)-(–)-BINOL.

The above phenomenon might be caused by the change of the conformation of BINOL in special solvents and would be determined by the equilibrium studies between cisoid and transoid conformations of BINOL having *R* or *S* configuration dissolved in special solvents.^{5,6} When a solute is dissolved in some solvents, the solute-solvent interaction would exist generally.⁵⁻⁹ For example, the transoid conformation (Scheme 1) formed by this interaction in polar solvents would lead to increase in the specific rotation of BINOL, but the cisoid con-

formation formed in non-polar solvents to decrease in the specific rotation. The cisoid conformation formed in non-polar solvents might change the rotational sign of BINOL without change in its configuration.

Scheme 1 Equilibrium between cisoid and transoid conformation of optically active BINOL having *S* configuration



Mixture solvent

The changes of the specific rotation and sign in polar/non-polar mixture solvent with various ratios have also been measured and shown in Fig. 2. The specific rotation of (*R*)-(+)-BINOL decreases slowly with decreasing of THF fraction and equals to zero in the ratio 0.43. With increasing of the non-polar solvent (C₆H₆) fraction, the specific rotation and sign change, especially the rotational sign changes, *i. e.*, the rotational sign of (*R*)-(+)-BINOL becomes negative (Fig. 2). For CHCl₃/DMSO mixture solvent system the specific rotation and sign of (*S*)-(–)-BINOL could show similar feature also (Fig. 2).

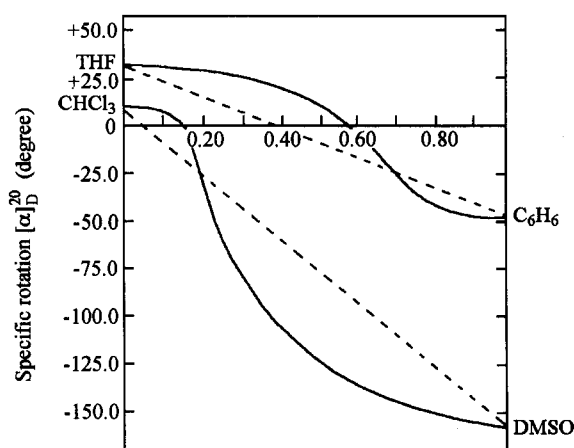
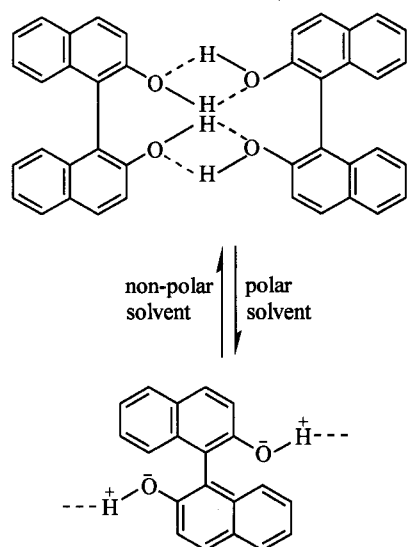


Fig. 2 Change of specific rotation with the ratios of two different mixture solvents. 1, (*R*)-(+)-BINOL-(THF/C₆H₆); 2, (*S*)-(–)-BINOL-(CHCl₃/DMSO).

The changes of specific rotation and sign could be explained by the equilibrium between the cisoid and transoid conformation of BINOL with the same configuration (*R* or *S*) in polar/non-polar mixture solvents with various ratios. It is

explained that the transoid conformation having some configuration of BINOL might exist in polar solvent with strong solute-solvent interaction and the cisoid conformation in apolar solvents with weak solute-solvent interaction. The cisoid conformation with high twisting power caused by intermolecular or intramolecular hydrogen bond interaction could be overcome by the strong interaction of solvent with solute resulting in formation of transoid conformation having some configuration (*R* or *S*) of BINOL shown in Scheme 2.

Scheme 2 Conformation change of optically active BINOL due to solute-solvent and solute-solute interaction in organic solvents



In fact, the change between the cisoid and transoid conformation with the same configuration (*R* or *S*) of BINOL would reflect the change of the dihedral angle between two naphthalene rings of BINOL. Therefore, it is suggested that the zero specific rotation would not mean configurational racemization in the presence of mixture solvent but would reveal the intermediate state placed in two conformation equilibria. Because after evaporating off the solvent the solute, BINOL, would possess the original configuration (*R* or *S*) and normal rotation values.

pH values of solvents

The acid-base behavior of the solvent (*i. e.*, pH value) would have a significant influence on the equilibrium between the cisoid and transoid conformation of BINOL with some configuration (*R* or *S*). It is known that BINOL, which is considered as a weak binary acid, might possess the cisoid conformation in acidic methanol solution and partly dissociate into the oxygen anion and hydrogen cation with changing of the pH values (adjust using HCl and KOH). But the dissociation of hydroxyl groups of BINOL accompanying with increase of pH values (pH < 10) does not give rise to larger change of specific rotation. However, with further increase of pH values (pH > 10) the dissociation of hydroxyl groups of BINOL into more oxygen anions in the base solution will lead to transfer from the cisoid to the transoid conforma-

tion of BINOL because two like electric charges repel one another to overcome the twisting power. In this case, significant change in the specific rotations and sign of (*R*)-(+) -BINOL would take place^{10,11}. It is apparent that the NMR has provided an especially sensitive and useful tool for the study of inter- and intra-molecular interactions. The assignment of ¹H NMR spectra of BINOL in the four deuterium-substituted solvent has been shown in Table 2, where it is seen that in the four solvents according to polarity (ϵ), for example, the specific rotation ($[\alpha]_D^{20}$) at pH about 12 could reach negative values over 880° shown in Fig. 3.

Table 2 Chemical shifts of aromatic protons of (*R*)-(+) -BINOL in deuterium-substituted solvents

Aromatic proton	Chemical shift (δ)			
	DMSO- <i>d</i> ₆	THF- <i>d</i> ₈	CDCl ₃	C ₆ D ₆
H-3,3'	7.32	7.24	7.37	7.17
H-4,4'	7.85	7.83	7.93	7.56
H-5,5'	7.81	7.79	7.86	7.52
H-6,6'	7.25	7.20	7.28	7.18
H-7,7'	7.18	7.15	7.25	7.23
H-8,8'	6.74	7.04	7.18	7.20
H-9,9'	9.20	7.53	4.95	4.70

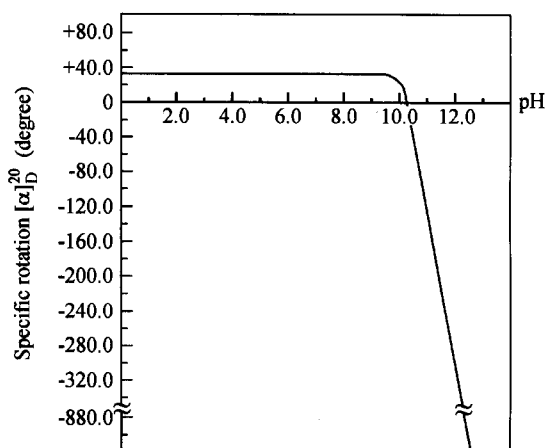


Fig. 3 Relationship between the specific rotation of (*R*)-(+) -BINOL and the pH values of the solution.

¹H NMR spectra of BINOL

The interaction between solvent and BINOL would be explained by formation of hydrogen bond. The fluctuation of H-bond formed from hydroxyl groups in various solvents has to be considered fully and might be characterized by ¹H NMR order: DMSO-*d*₆ > THF-*d*₈ > CDCl₃ > C₆D₆ (Table 2). The chemical shifts of H-9,9' of BINOL (protons of —OH group) were gradually shifted toward upfield from δ 9.20 to δ 4.70.

It is known that the basicity of the solvents measured using the ¹H NMR spectrum in an inert reference solvent (cyclohexane) was δ 1.32, δ 0.79 and δ 0.2 for DMSO, THF and CHCl₃, respectively,¹² which means the polarity order. The chemical shift fluctuation of hydrogen bond, formed

between BINOL and solvent, shifted toward downfield δ 9.20 (Lit.¹¹ δ 9.25) for polar solvent, DMSO- d_6 , and upfield δ 4.95 (Lit.¹¹ δ 4.69) for non-polar solvent, $CDCl_3$. Therefore, DMSO possesses not only a strong polarity, but also a much stronger basicity, and hydrogen bond acceptor ability and chloroform might be a weak hydrogen bond donor. Hence, the interaction degree of solvent-solute would be determined by the chemical shift of the hydrogen bond formed. These results have shown that the chemical shift of the strong H-bond formed in strong polarity solvent as DMSO- d_6 is shifted toward downfield and that of the weak H-bond in non-polar solvent as $CDCl_3$, C_6D_6 shifted toward upfield.

In the process of formation of hydrogen bond, the equilibrium between transoid and cisoid conformations would be determined by the polarity of the solvents. The configuration isomer of BINOL as a chiral molecule, *i. e.*, *R* or *S* configuration is very stable in normal case due to restricted rotation of hydroxyl group and the hydrogen at H-8,8'¹³ around 1,1'-asymmetric axis of BINOL. But in the case of unrestricted rotation around 1,1'-asymmetric axis, *i. e.*, the opposite direction which produces the cisoid or transoid prevailing conformation of BINOL might be influenced closely by special solvent used.

The equilibrium between the cisoid and transoid conformations should have directly reflected the corresponding change of the dihedral angle between two binaphthalene rings. The change of the dihedral angle would have closely related to the chemical shift of H-8,8'. The chemical shift of H-8,8' of BINOL in special solvent would have reflected directly the conformation change. Zhong *et al.*¹⁴ have indicated that when the dihedral angle become small the resonance of H-8,8' markedly moves toward downfield and vice versa. Because the H-8,8' resonance of BINOL is very sensitive to the shielding effects of the circular electric current upper the naphthalene ring plane and the change of the dihedral angle between two naphthalene rings, the chemical shift of H-8,8' of BINOL was shifted toward downfield with decreasing of polarity, *i. e.*, from δ 6.74 to δ 7.20 for DMSO- d_6 to C_6D_6 as shown in Table 2. The chemical shift at δ 6.74 for DMSO means that the dihedral angle becomes larger resulting in higher specific rotation and the chemical shift at δ 7.20 for C_6D_6 means that the dihedral angle becomes smaller resulting in lower specific rotation. These results are in agreement with our above-mentioned suggestion.

Conclusion

The specific rotation and sign of optically active BINOL in various solvents would be determined by the solvent polarity. The larger the polarity, the higher the specific rotation. The opposite change in rotational sign of BINOL would take place in non-polar solvents. The influence of the pH values of the solvent on the specific rotation and sign of BINOL would be related to the dissociation of —OH groups of BINOL in basicity condition. The mentioned results would in

fact reflect the change of the dihedral angle between two naphthalene rings of BINOL in the special solvents, *i. e.*, the equilibrium state between the cisoid and transoid conformation. In polar solvents the larger the dihedral angle, the higher the specific rotation. The BINOL with some configuration (*R* or *S*) would exist as the transoid conformation in polar solvents, on the contrary, as the cisoid conformation in non-polar solvents.

Experimental

The optically active isomers (*R*)-(+)—BINOL and (*S*)-(—)—BINOL can be conveniently resolved from racemic BINOL according to reported paper¹⁵ and recrystallized from ethanol, m.p. 209—211 °C for (*S*)-(—)—BINOL; m.p. 210—212 °C for (*R*)-(+)—BINOL. All solvents were distilled from CaH_2 prior to use. Optical rotation measurements were carried out on a WZZ-15 spectropolarimeter at 20 °C. The pH values of the methanol solution of BINOL which were adjusted by KOH and HCl methanol solution were recorded on an ORION ion selective pH meter (Model 818). CD spectrum was recorded in a 0.01-cm cell at room temperature on a JASCO-720 spectro-polarimeter. All ¹H NMR chemical shifts were given from added Me_4Si in four deuterium-substituted solvents and were recorded on a Varian XL-200 (200 MHz) spectrometer.

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