

OPTICAL ACTIVITY IN 1, 1'-BINAPHTHLYLS

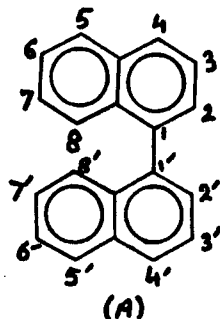
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ABSTRACT

A general discussion of the optical activity and the optical stability of 1, 1'-binaphthyls is presented. Determination of the absolute configuration in such systems with the help of asymmetric synthesis, optical displacement rule and Cotton effects associated with the shortwave band of the electronic absorption spectra is discussed.

AFTER the problem of the origin of optical activity in biphenyls^{1,2,3} was solved, the same principles were applied to 1, 1'-binaphthyls (A)⁴. 1, 1'-Binaphthyls are 'atropisomers' in which under normal conditions the achievement of planarity becomes improbable; thus they possess optical activity. 1, 1'-Binaphthyl-2, 2'-dicarboxylic acid once resolved, did not racemise⁴. 1, 1'-Binaphthyl-8, 8'-dicarboxylic acid^{5,6,7} was prepared in an optically active form; it exhibits a remarkably low optical



stability. The curious fact is that 1, 1'-binaphthyl-5, 5'-dicarboxylic acid⁸⁻¹¹, which has no carboxylic acid group in the interfering positions (e.g., 8, 8' and 2, 2') is optically more stable than 8, 8'-dicarboxylic acid. Another similar example, where the amino groups are not substituted in the interfering position of 1, 1'-binaphthyl, is 4, 4'-naphthidine¹². The deamination of optically active 4, 4'-naphthidine at low temperatures yields optically active 1, 1'-binaphthyl (half life 13 min. at 50° in N, N-dimethyl formamide^{13,14}). The spontaneous crystallisation of optically active 1, 1'-binaphthyl from its racemic melt¹⁵ has been reported.

The degree of optical stability of chiral 1, 1'-binaphthyls depends mainly upon the effective size of the blocking barriers but the 8, 8'-dicarboxylic acid and its esters (flat groups) are exceptions. It was thus evident that an explanation of the low optical stability of 8, 8'-dicarboxylic acid, with two -COOH groups in blocking positions, must be sought outside the bounds of the simple obstacle theory of restricted rotation. A suggestion was advanced¹⁴ that intramolecular overcrowding⁸ in this acid

produces a state of strain which is relieved by distortions; these distortions are favourable to the occurrence of optical inversion by decreasing the barrier. On the basis of the studies on a set of 8, 8'-disubstituted compounds it was concluded that the energy of racemisation (E_{rac}) is influenced by the following factors, viz., steric barrier (E_{ster}) to restricted rotation, the gain in resonance energy (E_r) in the transition state, and the ground-state strain (E_{gs}) of the molecule; $E_{rac} = E_{ster} - E_r - E_{gs}$. The entropy of activation and the conformation of the transition state also modify E_{rac} .

A large number of chiral compounds in the biphenyl series and some in the 2, 2'-positions of 1, 1'-binaphthyl series with a bridge running from one ring to the another have been reported during last 25 years. In such cases, the overlap of the substituents in the suitable positions is not the only principal cause of the restricted rotation¹⁻³; the angular strain in the transition state of racemisation is also responsible. Before 1972, only the 2, 2'-bridged compounds were known as the optically active 1, 1'-binaphthyls; they are formed in such a manner that a ring larger than a five-membered one results. A six-membered bridged compound, 9, 10-dihydro-3, 4, 5, 6-dibenzophenanthrene¹⁶ is optically active (E_{rac} 30.8 kcal. mole⁻¹). This is described as a dissymmetric nonasymmetric* molecule. When the 2, 2'-positions are joined with a saturated chain resulting in a seven-membered ring, the compounds are optically more stable than those with six-membered rings¹⁰. The optical stability of the 2, 2'-bridged 1, 1'-binaphthyls cannot be compared with that of unbridged 1, 1'-binaphthyls, because the *trans*-passing route is not available. The low optical stability is in fact a dramatic change in the 2, 2'-bridged 1, 1'-binaphthyl series as the corresponding unbridged 2, 2'-disubstituted 1, 1'-binaphthyls are completely optically stable. The reason for this low stability in bridged compounds is that the passage through the planar transition state is

* For an explanation of the significance of this term see Mislow, K., *Introduction to Stereochemistry*, Benjamin, Inc., New York, 1965, p. 27.

TABLE I
 Substituted 1, 1'-binaphthyls which racemise

Sl. No.	Substituent at position		E_{rac} kcal. mole ⁻¹	$\log_{10}A$	$\Delta F \neq$ kcal. mole ⁻¹	$\Delta H \neq$ kcal. mole ⁻¹	$\Delta S \neq$ e.s.u.	Ref.
	8	8'						
1.	H	H	22.2	12.1	23.5	21.9	-5.2	14
2.	H	COOH	22.4	12.0	23.5	21.8	-5.5	14
3.	COOH	COOH	22.1	11.3	24.4	21.5	-9.1	14
4.	COOMe	COOMe	22.0	11.6	23.8	21.4	-7.5	14
5.	COOH	COOMe	21.6	11.4	23.7	20.9 (5)	-8.4	14
6.	CH ₂ OH	CH ₂ OH	29.2	12.6	29.8	28.4	-3.4	17
7.	CH ₃ OH	COOMe	25.8	12.0	27.2	25.1	-6.2	17
8.	CH ₃	CH ₃	27.6	11.0	30.4	26.8	-9.4	17
9.	COO ⁻	COO ⁻	26.0	15.2	22.5	25.4	+9.2	14
10.	COO ⁻	COOEt	25.7	14.0	24.0	25.1	+3.2	14
11.	H	COOMe	23.6	12.5	24.1	22.9	-3.5	18
12.	H	CH ₂ OH	26.0	12.4	26.7	25.3	-3.8	18
13.	H	CH ₃	25.3	11.7	27.2	24.6	-7.3	18
14.	COOH	CH ₃	25.3	11.6	27.4	24.6	-7.7	20
15.	CH ₂ COOH	CH ₂ COOH	32.0	14.3	29.6	31.2	+3.6	32
	5	5'						
16.	COOH	COOH	24.1	12.3	25.4	23.5	-5.9	14, 19
17.	COO ⁻	COO ⁻	24.9	12.9	24.8	24.3	-1.5	14, 19
18.	COOMe	COOMe	23.8	12.2	24.8	23.2	-5.1	14

mainly due to considerable reduction in the degree of interplanar angle in their ground state compared with the unbridged ones, thus the molecule requires lesser energy to pass through the transition state. On the basis of optical stability 1, 1'-binaphthyls can be divided into two categories:

1. Those which racemise (Table I).
2. Those which do not racemise (Table II).

 TABLE II
 Substituted 1, 1'-binaphthyls which do not racemise

Substituent at positions						Ref.
2	2'	3	3'	5	5'	
COOH	COOH	H	H	H	H	4, 16
NH ₂	NH ₂	H	H	H	H	21
CH ₂ OH	CH ₂ OH	H	H	H	H	16
SO ₃ H	SO ₃ H	H	H	H	H	22
OH	OH	COOH	COOH	H	H	23
NO ₂	NO ₂	H	H	SO ₃ H	SO ₃ H	24

STEREOCHEMICAL CORRELATIONS

Mainly the following methods have been applied to skewed biaryls (inherently dissymmetric) to determine absolute configuration.

(1) *Asymmetric Synthesis*.—In this method asymmetry is introduced in the course of a reaction, which involves the preferential formation of one or the other diastereoisomer in the reaction of *dl*-substance with an unsymmetrical reagent ($k_l \neq k_d$) where k_l is the reaction rate constant for levorotatory isomer and k_d is the reaction rate constant for dextrorotatory isomer. The reagent approaches the part of the molecule to be reduced from the less hindered side. Meerwein-Ponndorf-Verley (M-P-V) reduction of a keto group has proved effective²⁵. A binaphthyl ketone (IV) (Fig. 1) has been reduced²⁶, by centrally asymmetric alcohols of known absolute configuration and resulted in configurational determination of biphenyls and later of 2, 2'-substituted 1, 1'-binaphthyls²⁷. The stereospecificity of this method is generally applicable one. The ketone (IV) differs from ketones $RR'C=O$ in the classical M-P-V reduction in two ways: (a) it can exist in enantiomeric forms, (b) hydrogen transfer to either face of the

carbonyl group in a given enantiomer produces the same alcohol. This is because, ketone (IV) is dissymmetric nonasymmetric. From inspecting models of the transition state, one expects that reduction of the R-isomer in S-octanol would take place quicker than that of the S-isomer. As S-(+)-2-octanol produces R-(−)-alcohol (V in Fig. 1) which is derived from (+)-1, 1'-binaphthyl-2, 2'-dicarboxylic acid (I in Fig. 1); this process relates the R-configuration for the corresponding optical isomers of the compounds in Fig. 1.

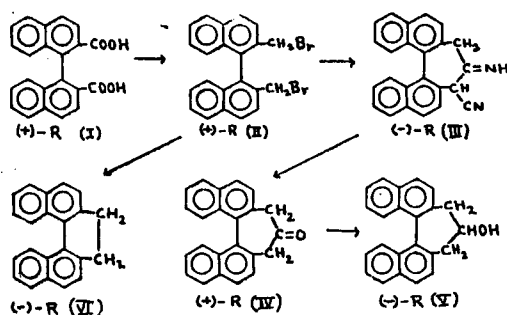


FIG. 1. Structures of some 2, 2'-disubstituted 1, 1'-binaphthyls. The R-configuration has been assigned on the basis of asymmetric synthesis and chemical correlation²⁷.

(2) *Optical Displacement.*—The success of Freudenberg's displacement rule in the centrally asymmetric chiral molecules has been discussed²⁸ in terms of the similarity in the size and the shape of the molecules to be compared. It is suggested that similar shifts in optical rotation take place in related derivatives of biaryls of the same configuration, and they make a basis for a chemical correlation. Using polarisability theory of optical rotatory power, the S-configuration has been assigned to (+)-9, 10-dihydro-3, 4, 5, 6-dibenzophenanthrene (VI). Therefore, its synthetic precursor, (−)-2, 2'-dicarboxylic acid (I), has also S-configuration. The absolute configurations of these compounds²⁷ confirm the validity of this rule. 2, 2'-Bridged compounds derived from S-(−)-6, 6'-dinitro-2, 2'-diphenic acid²⁸ and S-(−)-6, 6'-dichloro-2, 2'-diphenic acid²⁸ have stronger dextrorotatory power than their parent unbridged acids. 2, 2'-Bridged compounds derived from S-(+)-6, 6'-dimethyl-2, 2'-diphenic acid again show considerably larger dextrorotation. On the basis of these findings it has been proved²⁸ that going from unbridged to 2, 2'-bridged biaryls which involves a change in the interplanar angle, reflects a characteristic change in the sign and the magnitude of the optical rotation. It follows the general 'optical displacement rule' that

a symmetrically substituted hindered biaryl has the S- or the R-configuration, if in going from an unbridged to a bridged system, the optical activity suffers a marked shift in the positive or the negative direction respectively.

(3) *Chiroptical Effects.*—The detailed study of optical rotatory dispersion (ord) furnishes useful information about configurational assignment²⁷. The usefulness of ord curves for such a purpose in optically active ketones of known absolute configuration has been tested. Circular dichroism (cd) of inherently dissymmetric chromophores (skewed biaryls) is extremely useful in separating the individual electronic transitions responsible for the total Cotton effect²⁹. From the results of these two optical properties of chiral molecules it is concluded that the Cotton effect is related to the configuration of compounds. An enantiomeric pair of molecules have similar Cotton effects of opposite sign.

OPTICAL ROTATORY DISPERSION AND ABSOLUTE CONFIGURATION OF 1, 1'-BINAPHTHYLS

Spectroscopic observations³⁰ have been collected for a series of unbridged and bridged biphenyls and unbridged and bridged 2, 2'-disubstituted 1, 1'-binaphthyls. Their configurations have been related to the compounds whose absolute configurations were already assigned by some other standard method. A change in *conformation* brings about a characteristic change in ord Cotton effect curve. The long-wave Cotton effect of the 2, 2'-bridged biaryls is generally accompanied by a Cotton effect at shorter wavelength, of opposite sign and of greater amplitude. The Cotton effect at the shorter wavelength usually dominates the sign of rotation in the visible region. For 2, 2'-bridged biaryls having the R-configuration, the sign of the long-wave Cotton effect is negative for 6, 6'-dinitro-derivatives and positive for 6, 6'-dichloro and 6, 6'-dimethyl derivatives of biphenyl and 2, 2'-disubstituted 1, 1'-binaphthyls.

Unbridged 1, 1'-binaphthyls possess complex u.v. absorption spectra³¹ dominated by maxima at about 285 and 230 nm. It corresponds to the complex ord spectra. Two ord Cotton effects for 1, 1'-binaphthyls with -CH₂OH, -CH₂Br, -CH₃, -COOH, -COOMe, -CONH₂ groups substituted in the 2, 2'-positions, centred at 285 nm and below 250 nm respectively, were observed³⁰. In all the cases a positive or a negative 285 nm Cotton effect corresponds to the R- or the S-configuration respectively. A study of u.v. absorption spectra of 1, 1'-binaphthyl³³ and 8, 8'-disubstituted 1, 1'-binaphthyls³² between 200–320 nm in ethanol has revealed more details. The ord spectrum of (+)-1, 1'-binaphthyl³³

at 8° C in ethanol exhibits a negative Cotton effect centred at 285 nm confirming its S-configuration in conformity with X-ray crystallographic studies³⁴. The ord spectra of twelve optically active 8, 8'-disubstituted 1, 1'-binaphthyls³² exhibited in addition to a positive or a negative Cotton effect for R- or S-configuration respectively, a very strong negative or positive Cotton effect associated with the short wavelength u.v. absorption band.

Bridging with a saturated chain containing two carbon atoms incorporating the 2, 2'-positions of 1, 1'-binaphthyl changes bathochromically the u.v. absorption pattern compared with the unbridged compounds particularly at long wavelengths; bands at 320, 328, 335 and 348 nm appear³⁵. Compound (VI in Fig. 1) shows a bathochromic shift of Cotton effect associated with its u.v. absorption shift; its Cotton effect is of enormous amplitude (1,570,000°) centred near 250 nm. In contrast, the ord curves of the bridged compounds, forming a seven-membered ring with the 2, 2'-positions, have u.v. absorption spectra dominated by maxima at 220, 232 and 306 nm. The bathochromic shift of the long wavelength absorption band at 283 and 293.5 nm of 1, 1'-binaphthyl³³ itself, in comparison with these bridged compounds also appears in ord curves yielding two Cotton effects of opposite sign, centred near 300 nm and below 240 nm respectively. A positive 300 nm Cotton effect corresponds to the R-configuration.

CIRCULAR DICHROISM AND ABSOLUTE CONFIGURATION OF 1, 1'-BINAPHTHYLS

As pointed out earlier the cd curves are extremely useful in identifying the electronic transitions which are solely responsible for the individual Cotton effects. Intensity in the cd curves is analogous to extinction coefficient in the absorption spectrum and amplitude in the ord curve. All of them together characterise the internal chirality of chromophores present in a molecule. The sign of the cd curves corresponds to that of the related ord curve. The advantage of cd over ord is that the overlap of the tails in the bands of the latter is reduced in the former. It assists in the identification of weak optically active transitions generally not seen in ord. The cd studies have been undertaken in 2, 2'- and 8, 8'-disubstituted 1, 1'-binaphthyls²⁹⁻³². Unbridged 2, 2'-disubstituted and 8, 8'-disubstituted 1, 1'-binaphthyls have a negative 285 nm Cotton effect corresponding to the S-configuration. All the 1, 1'-binaphthyls bridged in the 2, 2'-positions provide cd curves at 270 and 310 nm of opposite signs; they correspond to the oppositely signed ord curves centred near 265 and 300 nm respectively. Like in ord, a negative 300 nm cd Cotton effect corresponds to the S-configuration. Furthermore, a negative cd band at shortest wavelength (~ 220 nm) and a positive one 15-20 nm higher, is characteristic of S-configuration³⁶ (Table III).

TABLE III
Correlation of configuration through cd in the short wavelength (214-240 nm) region³³

Substituents at positions	Sign of rotation at 589 nm	Negative extremum	Wavelength at $[\theta] = 0$	Positive extremum	Configuration derived by cd
8 H	8' H	(+) 214* (-590,000)	220	225* (+825,000)	S
Me	Me	(+) 218* (-320,000)	222.5	229.5* (+1200,000)	S
COOH	COOH	(-) 223* (-5000,000)	232.5	240* (+420,000)	S
CH ₂ Br	CH ₂ Br	(+) 228* (-760,000)	238	241* (+142,000)	S
CH ₂ COOH	CH ₂ COOH	(+) 220* (-340,000)	226	230* (+135,000)	S
CH ₂ (Py)+I ⁻	CH ₂ (Py)+I ⁻	(+) 214* (-940,000)	222.5	231* (+280,000)	S
2 Me	2' Me	(+) 221* (-590,000)	224.5	228.5* (+1240,000)	S

* Wavelength in nm.

Number in the parentheses represent the molar ellipticity $[\theta]$.

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