Optical Rotatory Power of 2,2′-Dihydroxy-1,1′-binaphthyl and Related Compounds

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Abstract: The electronic structure and optical rotatory power of 2,2′-dihydroxy-1,1′-binaphthyl were examined from the theoretical and experimental points of view. The theoretical calculation was performed by calculating the electric and magnetic dipole velocities directly on the basis of the electronic wave functions obtained by the Pariser–Parr–Pople and composite-molecule treatments. The observed CD spectrum is shown to be well interpreted on the basis of the theoretical results. The contributions of several types of interactions (such as charge transfer, electrostatic, and exciton type) between the π-electron systems of two aromatic rings to the optical rotatory power are examined in detail. The result shows that the exciton-type interaction is most important to determine the rotational strength, in accordance with the conventional coupled-oscillator model. However, the present analysis shows clearly that the first-order exciton interaction with nearby excited states is important, as well as the zeroth-order exciton interaction. In particular, the former interaction is shown to account predominantly for the circular dichroism spectra accompanying the relatively weak transitions in the longer wavelength region. This point has not been recognized fully in the theoretical calculation of optical activity. Discussion on the determination of the dihedral angle and absolute configuration is given briefly in view of the present theoretical results, together with the discussion on the electronic structure and optical rotatory power of some related binaphthyl derivatives.

The optical rotatory dispersion and circular dichromism (CD) of biaryl compounds have extensively been studied from the experimental point of view.[3] A theoretical consideration has been made on some bianthryl derivatives on the basis of the coupled-oscillator model.[4] Although the strong CD bands in the near-ultraviolet region seem to be well interpreted, the theory seems to fail to interpret quantitatively the weak CD bands in the longer wavelength region. Some qualitative considerations have been made from the viewpoint that the discrepancy is caused by the effect of charge-transfer (CT) interaction between two aromatic rings.[4] The origin and nature of the optical rotatory power accompanying these weak transitions are, however, not quite clear.

Recently, one of the authors has extended the previous CD measurement on binaphthyl derivatives[3a] to some 2,2′- and/or 3,3′-substituted binaphthyls.[5] The results show that their CD spectra are similar to each other, in accordance with the previous results, except for some binaphthyls with the substituents containing carbonyl groups at the 3,3′ positions. This fact indicates the existence of some common mechanism responsible for the CD spectra of these compounds.

In view of these facts, it seems to be necessary to investigate their electronic structures in more detail and to elucidate which kind of electronic interaction is responsible for the observed CD spectra. For this purpose, we take 2,2′-dihydroxy-1,1′-binaphthyl (hereafter abbreviated to DHBN) as a typical example and calculate its electronic structure by means of the composite-molecule treatment,[6] the CT interaction between two aromatic rings being explicitly taken into account in addition to the electrostatic and exciton-type interactions. Using the electronic wave functions obtained in this way, the rotational strength is calculated directly by reducing the matrix elements of the electric and magnetic transition dipoles to the integrals over atomic orbitals. This theoretical procedure is an extension of the theoretical treatment which has been developed and applied to metal chelate compounds by one of the authors.[7]

On the basis of these results, the relative contribution of various kinds of interactions to the rotational strength is analyzed in detail. The absolute configuration and dihedral angle of this compound are determined by comparing the theoretical results with the observed CD and electronic absorption spectra which were measured in the present work in the near-ultraviolet region up to 200 mμ. Discussions are also made on the absolute configuration and dihedral angle for some related binaphthyl derivatives on the basis of the present theoretical results and of the previously reported CD spectra.[3]

Experimental Section

The synthesis of the *R*-optical isomer of DHBN has been described elsewhere.[5,8] Commercially available β-naphthol was recrystallized from a benzene–hexane mixed solvent. Ethyl ether and isopentane were purified according to the standard method.[9]

The electronic absorption spectra of DHBN and β-naphthol were measured in a 1:2 mixture of ethyl ether and isopentane using a Cary Model 14 spectrophotometer. The CD spectrum was taken in the same solvent using a JASCO Model ORD/UV-5 spectrophotometer.

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[3] (a) K. Mislow, E. Bannenberg, R. Records, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 1342 (1963); (b) K. Mislow, M. A. W. Glass, R. E. O'brien, P. Rutkin, D. H. Stenberg, J. Weiss, and C. Djerassi, *ibid.*, **84**, 1455 (1962); (c) M. Hagishita and K. Kuriyama, *Bull. Chem. Soc. Jap.*, **44**, 496, 617 (1971).

[4] R. Ginter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 274 (1964).

[5] H. Akimoto, Thesis, The University of Tokyo, 1970.

[6] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S Nagakura, *ibid.*, **23**, 1441 (1954); J. N. Murrell, *Quart. Rev., Chem Soc.*, **15**, 191 (1960).

[7] I. Hanazaki and S. Nagakura, *Inorg. Chem.*, **8**, 654 (1969).

[8] H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.*, 97 (1968); H. Akimoto and Y. Iitaka, *Acta Crystallogr., Sect. B*, **25**, 1491 (1969).

[9] A. Weissberger and E. S. Proskauer, "Organic Solvents," 2nd ed, Interscience, New York, N. Y., 1967.

Theoretical

First of all, the π-electron structure of β-naphthol was calculated by means of the Pariser–Parr–Pople SCF–CI treatment.[10] All nearest-neighbor bond distances, including the C–O distance, are taken to be 1.39 Å.[11] The interatomic electronic repulsion integrals were calculated by means of a modification of the uniformly charged sphere approximation,[10] where the radius of the sphere is adjusted to give the same one-center value as the semiempirical one determined from the valence state ionization potential and electron affinity.[10] All two-center repulsions were calculated with this radius except for that between the nearest-neighbor carbon atoms, for which Pariser's value, 6.9 eV, for naphthalene was used.[12] The following values were adopted as the core resonance integrals: $\beta_{CC} = -2.39$[10] and $\beta_{CO} = -1.68$ eV, the latter being determined by use of the proportionality relation to the overlap integral and ionization potentials. For the one-center core integral of the oxygen 2pπ AO, which participates two electrons with the conjugated systems, a slightly modified value, -29.37 eV, of the oxygen second ionization potential was used. A modified value, 18.52 eV, was also used for the one-center repulsion.[13]

The π-electron structure of DHBN was calculated by means of the composite-molecule method[6] in which the molecule was divided into two β-naphthols, and the configuration interaction calculation was performed among nine locally excited (LE) configurations in each β-naphthol, 18 CT configurations between the π-electron systems of two β-naphthols, and the ground configuration.[15] The geometrical configuration and coordinate system for the *R*-optical isomer, for which the present theoretical calculation and the measurement of CD spectrum was made, are shown in Figure 1. The interatomic distance between the 1 and 1′ carbon atoms is assumed to be 1.50 Å. The core resonance integral between the 2pπ AO's on the 1 and 1′ carbon atoms is calculated by the equation

$$\beta = 1.98 \cos \alpha \text{ (eV)} \qquad (1)$$

where α is the dihedral angle between two aromatic planes. The coefficient on cos α was determined by use of the core resonance integral for benzene, -2.39 eV,[10] and of the proportionality relation to the overlap integral.

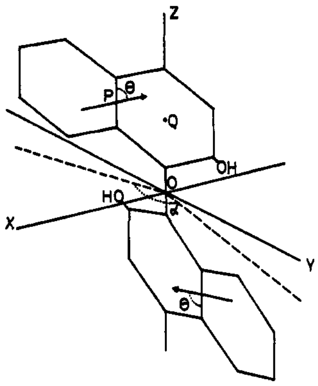

Figure 1. The coordinate system and geometrical configuration of (*R*)-2,2′-dihydroxy-1,1′-binaphthyl.

The rotational strength, $R_{0\xi}$, accompanying the transition from the ground state (0) to an excited state (ξ), is expressed by[16]

$$R_{0\xi} = \mathrm{Im}\{\langle 0|\boldsymbol{\mu}_e|\xi\rangle \cdot \langle \xi|\boldsymbol{\mu}_m|0\rangle\} \qquad (2)$$

where Im{····} means to take the imaginary part, $\langle 0|\boldsymbol{\mu}_e|\xi\rangle$ and $\langle \xi|\boldsymbol{\mu}_m|0\rangle$ are the matrix elements of the electric and magnetic dipole moments, respectively. These two types of matrix elements are calculated in a similar manner to the previous treatment of the metal chelate compounds;[7] *i.e.*, the magnetic transition dipoles are reduced into the following integral for intraring nearest-neighbor AO's χ_p and χ_q

$$\langle \chi_p|\nabla_z|\chi_q\rangle = (15/2)A(1 - \tau^2)^{7/2}x^{-5} \times [(3 - 3x + x^2)e^{x} - (3 + 3x + x^2)e^{-x}] \qquad (3)$$

where ∇_z is the *z* component of gradient and

$$A = -(1/15R)\mu^2(3 + 3\mu + \mu^2)e^{-\mu} \qquad (4)$$

The quantities μ, τ, and x are defined by

$$\mu = (\zeta_p + \zeta_q)R/2$$
$$\tau = (\zeta_p - \zeta_q)/(\zeta_p + \zeta_q) \qquad (5)$$

and

$$x = \mu\tau$$

where ζ_p and ζ_q are the orbital exponents of the Slater 2pπ AO's; *R* is the interatomic distance in atomic units. The magnetic transition dipole on the interring bond can be reduced into following two integrals

$$\langle \chi_1|\nabla_z|\chi_{1'}\rangle = -A \cos \alpha \qquad (6)$$

$$\langle \chi_1|\lambda_z|\chi_{1'}\rangle = S \sin \alpha \qquad (7)$$

where λ_z is the *z* component of the rotation; *S* is the overlap integral between the 2pπ AO's on the 1 and 1′ carbon atoms when they are parallel to each other. In all the above equations the *z* axis is defined as directed from atom p (or 1) to atom q (or 1′). In contrast to the previous treatment,[7] the velocity form is retained also for the electric transition dipoles. They are calculated by reducing them to the integrals of the types of eq 3 and 6.

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(10) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(11) H. C. Watson and A. Hargreaves, *Acta Crystallogr.*, **11**, 556 (1958).

(12) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(13) The valence-state ionization potentials to remove a p_z electron from $O[s^2p_x{}^2p_yp_z]$, $O^+[s^2p_xp_yp_z]$, $O^{2+}[s^2p_yp_z]$, $O^-[s^2p_x{}^2p_yp_z{}^2]$, $O[s^2p_xp_yp_z{}^2]$, and $O^+[s^2p_yp_z{}^2]$ are 17.28, 34.15, 54.23, 1.93, 14.61, and 21.41 eV, respectively.[14] From these values, we obtain the following equations

$$I_1 = 2.06q^2 + 14.74q + 14.61$$
$$I_2 = 1.61q^2 + 18.48q + 34.15$$

for the first and second ionization potentials, respectively, where *q* is the charge on oxygen. If we make I_1 equal to the observed ionization potential of methanol, 10.85 eV [K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962)], we obtain $q = -0.265$. Inserting this value into the above equation for I_2, we obtain an estimation of I_2 as 29.37 eV. Hence the one-center repulsion is $I_2 - I_1 = 18.52$ eV.

(14) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

(15) Strictly speaking, the π-electron approximation does not hold for this compound containing two naphthalene rings which are not coplanar. However, since the σ–π interaction does not affect strongly the electronic absorption and CD spectra in the lower energy region, we take into account only the π-electron systems on the two aromatic rings and their interaction.

(16) E. V. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).

Table I. Lower Excited States of β-Naphthol

Calcd Transition energy[a]	Calcd Oscillator strength	θ,[b] deg	Obsd Transition energy[a]	Obsd Oscillator strength
32.53	0.043	40	31.0 31.4 (32.5)	0.030
37.13	0.238	21	34.9 36.4 37.8 39.5	0.102
42.78	0.293	110		
45.99	1.189	99	44.9	1.40
47.84	0.495	134		

[a] In units of 10^3 cm^{-1}. [b] Direction of the transition dipole moment defined in Figure 1.

Table II. Calculated Energies and Rotational Strengths for DHBN at Various Dihedral Angles

Assignment[a]	α = 60°[b] E[c]	α = 60°[b] R[d]	α = 75°[b] E[c]	α = 75°[b] R[d]	α = 90°[b] E[c]	α = 90°[b] R[d]	α = 105°[b] E[c]	α = 105°[b] R[d]	α = 120°[b] E[c]	α = 120°[b] R[d]
V_1^-	31.8	−0.093	32.1	−0.071	32.2	−0.046	32.1	−0.019	31.7	0.013
V_1^+	33.1	0.039	32.8	0.063	32.6	0.091	32.6	0.115	32.8	0.131
V_2^-	34.7	−0.033	35.4	−0.044	36.0	0.001	35.6	0.040	34.9	0.025
V_2^+	38.7	0.112	38.2	0.234	37.9	0.397	37.6	0.503	37.3	0.505
CT_1^+	40.5	0.056	39.8	0.032	39.4	0.000	39.3	0.070	39.4	0.277
CT_1^-	40.6	−0.010	40.0	−0.012	39.4	0.000	39.7	0.089	40.4	0.132
V_3^+	43.7	0.018	43.0	−0.144	42.5	−0.198	42.8	−0.084	43.3	0.344
V_3^-	44.0	0.086	43.1	0.206	42.9	0.227	43.0	0.172	43.5	0.151
V_4^-	43.5	−4.007	44.2	−4.360	45.0	−4.037	45.4	−3.097	45.7	−2.101
V_4^+	47.5	1.285	46.9	2.345	46.2	3.094	45.7	3.090	45.5	2.197

[a] V_i^+ and V_i^- indicate that the main component of the excited states is V_i of β-naphthol (see Table I). CT_i^+ and CT_i^- indicate that the main components are the *i*th CT configurations (CT from aromatic rings a to b and the corresponding one from b to a). Superfices + and − indicate that the excited states belong to the irreducible representations A and B, respectively, of symmetry group C_2. [b] Dihedral angle. [c] Transition energy in units of 10^3 cm^{-1}. [d] Rotational strength for the *R* isomer in units of 10^{-3} Å^2.

For the purpose of comparison, the rotational strength was calculated also by means of the coupled-oscillator model. Although the treatment is similar to that reported,[4] a little more general expression is used in the present work for the rotational strength

$$R_{\pm} = \pm \pi \nu Q^2 a \sin \alpha \sin^2 \theta [1 + (b/a)/\tan \theta] \times 10^{-8}\ (\text{Å}^2) \quad (8)$$

where ν is the transition energy in cm^{-1}, a and b (both in units of Å) are distances $\overline{OQ}$ and $\overline{PQ}$, respectively, shown in Figure 1, Q is the magnitude of the transition dipole moment in Å, and θ is the direction of the transition dipole moment as defined in Figure 1. R_+ and R_- correspond to the states belonging to irreducible representations A and B, respectively, of symmetry group C_2. They correspond to the *R*-optical isomer shown in Figure 1.

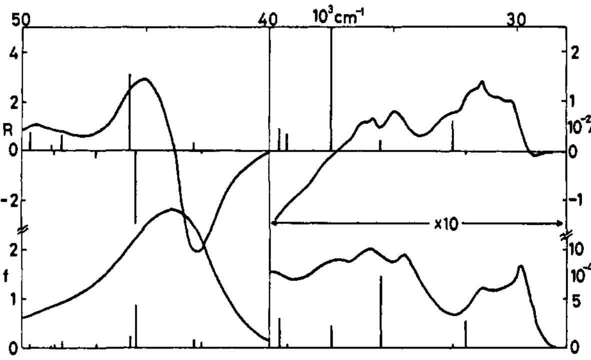

Figure 2. The observed CD spectrum (upper) and the electronic absorption spectrum (lower) of (*R*)-2,2′-dihydroxy-1,1′-binaphthyl. Calculated rotational strength *R* (in units of Å^2) and oscillator strength *f* for α = 105° are shown by vertical lines. All results in the right half of the figure are expanded by a factor of 10.

Result and Discussion

The result of the SCF–CI calculation for β-naphthol is shown in Table I together with the observed values. The electronic configurations, the energies of which are below 7 eV, are taken into account in the calculation. The agreement between the theoretical and observed values is satisfactory. The result is also coincident with the calculation by Forster and Nishimoto[17] with a different set of parameters.

On the basis of the above-mentioned SCF–CI wave functions for β-napththol, the composite-molecule calculation was performed[18] for the *R*-optical isomer of DHBN at dihedral angle α = 60, 75, 90, 105, and 120°. The calculated rotational strengths for the lower excitations are summarized in Table II. An examination of the change of rotational strengths with α reveals that the best agreement with the observation is obtained at $\alpha \approx 100°$. In Table III are summarized the details of the result for α = 105°, the nearest to the best value of α, together with the observed electronic absorption and CD spectra. They are also shown in Figure 2. The agreement of the calculated result with the observed one is fairly good. From this result, we can determine the absolute configuration of the optical isomer studied in the present study to be the *R* type shown in Figure 1. This result is in accordance with the absolute configuration of the optically active DHBN derived from the chemical correlation to 2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxylic acid, the absolute configuration of which has been determined by the X-ray crystal analysis.[5,8]

A pair of strong transition bands (hereafter designated as band C) is predicted to appear around 45,000 cm^{-1}. They can be correlated to the transition to V_4 of β-naphthol (Table I). The predicted separation of

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(17) L. S. Forster and K. Nishimoto, *J. Amer. Chem. Soc.*, 87, 1459 (1965).

(18) The calculations were performed by use of a FACOM 270-30 electronic computer at the Institute of Physical and Chemical Research.

Table III. Theoretical and Observed Results for the *R* Isomer of DHBN

	Calcd			Obsd			
				Circular dichroism		Electronic absorption	
Assignment[a]	Transition energy, 10^3 cm^{-1}	Oscillator strength	Rotational strength, 10^{-3} Å^2	Transition energy, 10^3 cm^{-1}	Rotational strength, 10^{-3} Å^2	Transition energy, 10^3 cm^{-1}	Oscillator strength
V_1^-	32.08	0.054	−0.019	29.3	−0.0005	29.8	0.086
V_1^+	32.64	0.009	0.115	(30.3)	0.0869	(30.2)	
				31.4		31.1	
				(31.9)		(31.9)	
				(32.7)			
V_2^-	35.57	0.137	0.040	35.0	0.0347	34.5	0.216
				35.9		35.9	
V_2^+	37.58	0.043	0.504	(36.2)		37.3	
				(37.8)		(38.8)	
CT_1^+	39.33	0.006	0.070				
CT_1^-	39.70	0.059	0.090				
V_3^+	42.75	0.105	−0.084				
V_3^-	43.01	0.131	0.172				
V_4^-	44.35	0.829	−3.097	42.9	−0.655	44.0	3.21
V_4^+	45.70	0.225	3.090	45.0	0.519		
V_5^-	46.99	0.074	−0.270				
V_5^+	48.30	0.101	0.573	49.4			
V_6^-	48.73	0.031	−0.169				
V_6^+	48.84	0.010	0.119				

[a] See footnote *a* in Table II.

these bands is very small, accounting for the fact that a single band is observed in this region of the electronic absorption spectrum. The observed magnitude of each CD band is considerably smaller than the theoretical value. This is attributable, at least partly, to the strong cancellation of two nearby CD bands with opposite signs.

A pair of weak transitions (V_1^- and V_1^+) corresponding to the transition to V_1 of β-naphthol can be assigned to the observed band in the $29 \sim 33 \times 10^3$ cm^{-1} region (hereafter designated as band A). Although the existence of the vibrational structure makes it a little difficult to compare the theoretical and experimental results, we can compare the overall areas of the positive and negative CD bands in this region with the calculated rotational strengths. The theoretical values are -1.89×10^{-5} and 1.15×10^{-4} Å^2, whereas the observed ones are -4.7×10^{-7} and 8.69×10^{-5} Å^2, respectively. The ratio of the observed negative rotational strength to the positive one is much smaller than the corresponding theoretical value. This indicates that most part of the observed negative rotational strength is cancelled by the positive one.

The sum of theoretical rotational strengths of the transitions to V_2^- and V_2^+ amount to 5.4×10^{-4} Å^2, whereas the corresponding one observed in the $35 \sim 36 \times 10^3$ cm^{-1} region (hereafter designated as band B) is 0.35×10^{-4} Å^2. The discrepancy can be interpreted as due to the cancellation by the strong negative tail of band C. The theoretical splitting between the transitions to V_2^- and V_2^+ is $2000 \sim 4000$ cm^{-1}, depending on α. If we take account of the vibrational structure, the splitting will be reduced to a few tenth of the above value, since the splitting is mainly determined by the exciton-type interaction between the transition dipoles and the latter is divided for each vibronic state. This explains the fact that the energy of each vibrational band in the electronic absorption spectrum, which is mainly due to the transition to V_2^-, is almost coincident with the corresponding one in the CD spectrum, which is mainly due to the transition to V_2^+.

The theoretical calculation predicts a pair of interring CT transitions to appear near 40,000 cm^{-1}. This could not be detected experimentally. They are probably hidden in the strong tail of band C. The optical isomer of the binaphthyl derivative in which the 2 and 2′ carbon atoms are connected by a bridge $-CH_2-R-CH_2-$, where R is $>C{=}O$, $>CHOH$, $>C(COOC_2H_5)_2$, or $-OCH_2O-$, shows a distinct negative CD peak in this region.[3,5] This band may be assigned to the CT transition since no corresponding band can be found in the CD spectra of unbridged compounds. The dihedral angle of the bridged compound is restricted to $50 \sim 70°$, for which the CT interaction is stronger than that for DHBN. The theoretical results for DHBN indicate that the rotational strength of the longer wavelength CT band is always positive and stronger than that of the shorter wavelength counterpart for all dihedral angles studied. Hence the apparent negative peak around 40,000 cm^{-1} of the *R*-optical isomers of the bridged binaphthyls is likely the result of mutual cancellation of the positive CD peak due to the CT transition and the negative tail of band C.

It seems to be interesting at this point to examine the relative importance of several kinds of interaction on the rotational strength. Table IV demonstrates some results of the analysis. The calculation by the coupled-oscillator treatment (eq 8) shown in column 4 predicts a pair of CD bands with the same magnitude and opposite signs for each pair of transitions. This is not the case experimentally except for band C. The marked discrepancy between the observed rotational strength of bands A and B and the corresponding values calculated by the coupled-oscillator treatment cannot be attributed to the effect of the CT interaction, since, as is clear in column 3 of Table IV, the removal of the CT interaction from the present calculation (column 2) results in only a minor change of rotational strengths except for the disappearance of the CT bands. This result (column 3) was obtained by the same composite-molecule calculation as before except that the CT interaction was not taken into account. The interaction

Table IV. Rotational Strengths of DHBN by Various Kinds of Calculation (in Units of 10^{-3} Å^2)

Assignment	Present calculation[a]	Exciton interaction alone[b]	Coupled oscillator[c]
V_1^-	−0.019	−0.028	−0.180
V_1^+	0.115	0.109	0.180
V_2^-	0.040	0.013	−0.459
V_2^+	0.504	0.540	0.459
CT_1^+	0.070		
CT_1^-	0.090		
V_3^+	−0.084	−0.156	−1.24
V_3^-	0.172	0.248	1.24
V_4^-	−3.097	−3.269	−6.32
V_4^+	3.090	3.459	6.32

[a] Taken from Table III. [b] Calculated taking into account only the exciton interaction between two aromatic rings (see text for details). [c] Calculated by means of eq 8.

of the ground state charge distribution on a β-naphthol with the LE transition in the other was also not taken into account. Hence this result is essentially the same as those of the conventional coupled-oscillator model (column 4) except for the inclusion of the first-order exciton interaction between nonequivalent excited states, *e.g.*, those between bands A and C, and bands B and C, etc.[19]

Therefore we can conclude that the first-order exciton interaction is essentially important in explaining the weak CD bands in the longer wavelength region. In fact, the marked unbalance of the positive and negative CD strengths accompanying relatively weak transitions (like bands A and B) can well be accounted for by the first-order exciton interaction with nearby strong transitions (such as band C). This type of interaction is effective because even a slight mixing of excited states with high rotatory power into one with weak rotatory power results in a remarkable change of the rotatory power of the latter. Although the first-order exciton interaction has been considered in the original theory[20] and has actually been taken into account for the optical rotatory power of polymers,[21] no quantitative examination of its effect has been undertaken on the optical activity of relatively small molecules.[22]

Finally it is necessary to discuss the possibility of determining the absolute configuration from the CD spectrum. For the *R* isomer of DHBN, the sum of the rotational strengths corresponding to band B (transitions to V_2^+ and V_2^-) is positive irrespectively of the dihedral angle studied. Therefore we can determine the absolute configuration by observing the overall sign of band B. According to the empirical rule,[3a] the *R* isomers of the 2,2′-substituted 1,1′-binaphthyls commonly exhibit a positive CD band in the 280 ~ 300-mμ region. This result can be understood in view of the present result at least for weak 2,2′ substituents such as OH, CH_3, NH_3Cl, and CH_2OH,[3,5] since their electronic structures seem to be much the same. It is a little striking that the stronger substituents like NH_2, COOH, $COOCH_3$, and $CONH_2$ at the 2,2′ positions exhibit a similar CD spectrum. Perhaps the 2,2′ substitution does not bring about such a change of the electronic structure as to affect the rotational strength remarkably. This point seems to require a further theoretical study.

In view of the present theoretical result, we can also infer that the dihedral angle is much the same for the above-mentioned binaphthyl derivatives, since, as shown in Table II, the CD spectrum should change appreciably if the dihedral angle were changed by 15° or more. The CD spectra of the 2,2′-bridged binaphthyls in the longer wavelength region are not so much different from those of the unbridged ones, except that band B shifts to longer wavelength,[3,23] and a new CD band appears at ~250 mμ due to the interring CT transition. This latter point has already been discussed above. The red shift of the former is likely caused by the stronger interaction with the CT configurations.

It is difficult to determine the absolute configuration by use of band C because the order of the energies of the components changes along with the dihedral angle (V_4^- and V_4^+ in Table II). However, if the absolute configuration is known by examining band B, the dihedral angle may be estimated by comparing the calculated rotational strength and exciton splitting of band C with those observed. On the other hand, it may be possible to determine the absolute configuration by inspecting band C if the dihedral angle can be estimated independently (*e.g.*, in the case of the bridged biaryls mentioned above). Although this latter procedure is restricted to bridged compounds, it may be more reliable than that utilizing band A or B, since the strong band like band C is hardly affected by the interaction with the other transitions.

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(19) The result in column 4 differs from that in column 3 also in the approximation employed. The former is calculated by use of eq 8; *i.e.*, the electric and magnetic dipoles are calculated in the dipole moment form, not in the dipole velocity as employed in the latter calculation. In the former, the local magnetic moment around the local origin in one of β-naphthols (point P in Figure 1) is also neglected according to the ordinary coupled-oscillator treatment. However, these differences do not affect the essential feature (*e.g.*, the unbalance of positive and negative rotational strengths) of the calculated rotational strength.

(20) A. S. Davydov, "Theory of Molecular Excitons," translated by M. Kasha and M. Oppenheimer, Jr., McGraw-Hill, New York, N. Y., 1962.

(21) I. Tinoco, Jr., *Advan. Chem. Phys.*, **4**, 113 (1962); *J. Chim. Phys.*, **65**, 91 (1968); C. A. Bush and J. Brahms, *J. Chem. Phys.*, **46**, 79 (1967).

(22) Bush and Brahms[21] refer to conservative and nonconservative interactions, by dividing the interaction into one within the "near uv" region and one with the "far uv" transitions. There is, however, an ambiguity in choosing the critical energy to divide two regions. Our concept is believed to be much clearer from the theoretical point of view to distinguish the effect of two types of interaction on the rotational strength accompanying each electronic transition.

(23) Band A was not observed for the 2,2′-bridged binaphthyls studied so far. Perhaps their electronic structures are not so much different from that in naphthalene itself, since the bridging groups are very weak substituents like $-CH_2OCH_2-$, $-CH_2COCH_2-$, $-CH_2CHCOCH_2-$, and $-CH_2C(COOC_2H_5)_2CH_2-$.