The Optical Activity of Bis-1,1'-spiroindanes. The Direct Calculation of Optical Rotational Strengths

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A calculation based on Longuet-Higgins and Murrell's method using the MO's of aniline and phenol obtained by the SCF-MO-CI calculation is carried out for the π-electron structures of (—)-6,6'-diamino-(I) and (—)-6,6'-dihydroxy-bis-1,1'-spiroindane (II). These wave functions are then used to calculate the rotation strengths of these compounds. The circular dichroism curves calculated from the results, assuming a Gaussian curve, are compared with the observed spectra; a quantitative agreement with the experimental value is found. The nature of the transitions and the origin of the optical activity are also discussed.

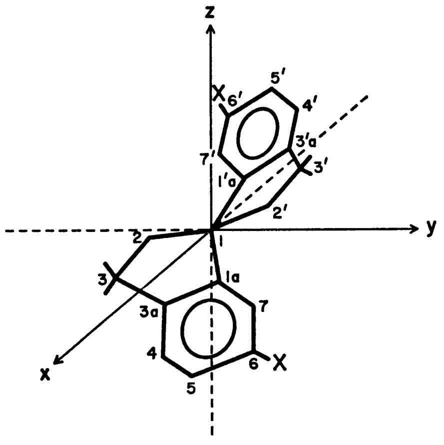
In a previous paper[1] we reported the resolution, the CD spectra, and, from an analysis of the CD spectra, the determination of the absolute configuration of C_2-symmetrical bis-1,1'-spiroindane derivatives. The previous analysis was based on simple dipole-coupling mechanisms. This treatment has been widely used for the determination of the absolute configuration of the chiral molecules considered to be constructed from two or three groups with electric-dipole-allowed transitions.[2] The determination of the absolute configuration of spiroindanes belonging to the classes II and III[3] was based on the quantitative agreement between the observed and calculated rotational strengths associated with the *p*-band. However, the signs of the Cotton effects associated with the α-band are not in agreement with each other; moreover, there are some derivatives in which only one Cotton effect is associated with the α-band. Therefore, in order to satisfy all the electronic absorption regions, the application of simple dipole-coupling mechanisms seems not to be useful; this may be attributed partly to the fact that the value of the spectroscopic moment and the assumption of a point dipole located on the center of the benzene ring are not suitable.

There are also other shortcomings. The transitions correlated with the α- and the *p*-bands are orthogonal to each other and do not mix; also, it is necessary to adopt the configuration interaction among other transitions of the same symmetry and also, in these spiroindanes, to consider the mixing of the transitions through the repulsion force produced from the interaction between the transitions of one isolated chromophore and that of another chromophore. When two π systems are held in perpendicular planes by a common atom of a tetrahedral geometry, the overlap between the *p* orbitals on atoms bound directly to the insulating atom is considerable. Consequently, exchange interactions may become significant and may also produce charge-transfer transitions and a mixing of the local excitations.

In the present paper, we will report on the analysis of the CD spectra of the 6,6'-diamino-(I) and 6,6'-dihydroxy-bis-1,1'-spiroindane (II) by improved theoretical methods.

Method of Calculation

The σ electron, especially at the C-1 position, will influence the π electron framework;[4] in this calculation, however, only π electrons are considered. Therefore, (—)-I and (—)-II can be approximated to the dimers of two anilines and two phenols respectively, set at the spiro position. The five-membered rings of these spiroindanes may not have the envelope form because of the described in the previous paper.[1] Therefore, we have approximated the planar conformation in which the two systems are held in a perpendicular plane by a carbon atom of a tetrahedral geometry, with the S-configuration depicted in Fig. 1, for we believe that the small difference in geometry will not greatly influence the results of the calculated CD spectra.



(-)-I : X=NH_2 (-)-II : X=OH

Fig. 1. The coordinate system employed. The bond lengths are chosen as follows: the aromatic C-C bond, 1.40 Å; the C-C single bond between C_1 and C_{7a} (and also C_1 and $C_{7a'}$), 1.52 Å, the C-O bond, 1.36 Å; the C-N bond, 1.41 Å. A perfect tetrahedral geometry is taken for C_1.

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[1] Part I: S. Hagishita, K. Kuriyama, M. Hayashi, Y. Nakano K. Shingu, and M. Nakagawa, This Bulletin, **44**, 496 (1971).

[2] J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968); H. Eyring, H-C. Liu, and D. Caldwell, *Chem. Rev.*, **68**, 525 (1968).

[3] The spiroindane derivatives were separated into three classes according to the origin of the optical power. In the classes II and III, the contribution of the dispersion force between the two aromatic chromophores is greater than the other effects, and the substituents at the benzene ring have large values in Platt's spectroscopic moment.

[4] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

In this geometry, the resonance integrals between the AO's of the carbon atoms of the two aromatic chromophores must be considered. Assuming appropriate values for the overlap integrals, the wave functions can be obtained for the (—)-I and (—)-II molecules by the SCF–MO treatment. In this calculation, however, the Longuet-Higgins-Murrell formalism[5] is utilized. This method is particularly suitable for the investigation of the nature and origin of the coupling between chromophores and to take account of the configuration interaction effects. Moreover, a fairly well established approximation, such as the SCF-MO-CI method, can be used.

First, it is necessary to obtain the exact wave functions of the local chromophores. Nishimoto and Foster[6] have obtained the wave functions of mono-substituted benzenes by the SCF-CI formalism of the Pariser-Parr-Pople method[7] with variable β approximation. Their results showed that the calculated singlet transition energies and the oscillator strengths of aniline and phenol were in good agreement with the experimental values. Therefore, we adopted these wave functions as the local chromophores (see Appendix 1).

From these wave functions, we took account of only four locally-excited states, from the lowest to the fourth energy level for each chromophore. The resonance integrals between the AO's of the carbon atoms of the two chromophores cannot be neglected, and the energies of the highest occupied and the lowest vacant π MO are very similar to those of the second occupied and the second vacant π MO respectively. Therefore, we took into account an additional eight kinds of charge-transfer configurations, in which an electron is transferred from one aromatic chromophore to another, and *vice versa*. Thus, we considered a total of sixteen configurations for each of the molecules, (—)-I and (—)-II.

Taking the energy of the ground configuration as the standard, the energy values of locally-excited configurations can be directly determined from the results of Nishimoto and Foster.[6]

Neglecting the penetration integrals[8] and assuming a zero differential overlap,[7] the energy for the charge-transfer configuration can be evaluated by the following equation:

$$E_{\mathrm{CT}} = I_{\mu}-A_{\nu}-\sum_{r}\sum_{s}C_{r}{}^{\mu}C_{r}{}^{\mu}C_{s}{}^{\nu}C_{s}{}^{\nu}(rr|ss) \qquad (1)$$

where I_{μ} and A_{ν} are the ionization potential of μth and the electron affinity of the νth level of the MO of the aromatic chromophore respectively, and where C_r^{μ} is the coefficient of the rth AO's of the μth level of the MO. Two-center repulsion integrals of the $(rr|ss)$ type are computed from the Ohno approximation:[9]

$$(rr|ss) = \frac{1}{2}(1\sqrt{R_{rs}^2+1/(rr|rr)^2} + 1\sqrt{R_{rs}^2+1/(ss|ss)^2}) \qquad (2)$$

where the one-center repulsion integrals $(rr|rr)$ are computed from the valence-state ionization potentials, I_r, and the electron affinities, A_r, for carbon, nitrogen, and oxygen by means of Eq. (3):

$$(rr|rr) = I_r-A_r \qquad (3)$$

I_r and A_r are taken from Hinze and Jaffé's table.[10]

As the diagonal matrix elements have been evaluated, it is necessary to consider the off-diagonal matrix elements of the total electric Hamiltonian, each of which represents the magnitude of the interaction between two different configurations. The evaluation of the off-diagonal elements is carried out by the formulations by Pople[11] and Longuet-Higgins and Murrell.[5] In these calculations, the values of the two-center core integrals, β_{CX} (X=C, N, or O), at 1.40 Å for a C–C bond, at 1.38 Å for a C–N bond, and at 1.36 Å for a C–O bond are taken as standard from the literature,[6] while the β_{rs} values are evaluated by means of the following equation:

$$\beta_{rs} = (S_{rs}/S_{\mathrm{CX}})\beta_{\mathrm{CX}} \qquad (4)$$

Here, S_{rs}/S_{CX} is the ratio of the overlap integrals at each distance. The two-center repulsion integrals are also calculated by the Ohno approximation.

Solving the secular equations constructed for each molecule by the use of the matrix elements evaluated above, the energy levels and wave functions shown in Table 1 are obtained.

In this calculation, using the Longuet-Higgins-Murrell formalism, the resonance energy between two aromatic chromophores is very small. The mixing of the locally-excited configurations and charge-transfer configurations by this spiro-conjugation contributes only a little. Therefore, in the other methods, the charge-transfer configurations are neglected and the repulsion among the locally-excited configurations is considered only by the formulation by Pople.[11] Moreover, we have taken twenty and sixteen local configurations for the compounds (—)-I and (—)-II respectively. We name this calculation "Method II"; the results are shown in Table 2.

The CD is governed by the rotational strength, R_i, to which Rosenfeld[12] first applied a quantum mechanical theory. The rotational strength is defined as the imaginary part of the scalar product of the molecular electric dipole moment, $<\psi_0|\vec{\varepsilon}|\psi_i>$, with the magnetic dipole moment of $<\psi_i|\vec{m}|\psi_0>$ for the electric transition under consideration:

$$R_i = Im\langle\psi_0|\vec{\varepsilon}|\psi_i\rangle\langle\psi_i|\vec{m}|\psi_0\rangle \qquad (5)$$

where

$$\vec{\varepsilon} = e\sum_k r_k \text{ and } \vec{m} = \frac{eh}{4\pi imc}\sum_k r_k\times\nabla_k$$

The values of the electric and magnetic moments are not formulated on an equal footing; the rotational strength so calculated is origin-dependent. The evaluation of the electric and magnetic dipole moments is

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[5] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955).

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[9] K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964).

[10] J. Hinze and H. H. Jaffé, *J. Chem. Phys.*, **33**, 1834 (1963).

[11] J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

[12] L. Rosenfeld, *Z. Phys.*, **52**, 161 (1928).

TABLE 1. THE WAVE FUNCTIONS AND ENERGIES OF THE ELECTRONIC STATES OF 6,6'-DIAMINO- AND 6,6'-DIHYDROXY-BIS-1,1'-SPIROINDANE

E(eV)	Symmetry		G	L_1	L_2	L_3	L_4	C_1	C_2	C_3	C_4
Compound (I)											
−0.010	*B*	ϕ_0^D	+0.999	0	0	0	0	+0.016	−0.022	+0.003	0
4.389	*A*	ϕ_1^D	0	−0.706	−0.018	−0.012	+0.016	−0.006	+0.008	−0.009	+0.024
4.410	*B*	ϕ_2^D	+0.001	−0.706	+0.019	+0.009	−0.014	−0.012	+0.009	−0.019	+0.023
5.363	*A*	ϕ_3^D	0	−0.009	+0.632	+0.044	−0.019	−0.020	+0.020	−0.288	+0.116
5.366	*B*	ϕ_4^D	−0.007	−0.032	−0.571	+0.033	−0.013	+0.099	−0.027	+0.376	−0.141
5.437	*A*	ϕ_5^D	0	−0.021	+0.305	+0.018	+0.039	+0.155	−0.040	+0.601	−0.133
5.504	*B*	ϕ_6^D	−0.007	−0.009	+0.410	−0.026	−0.011	+0.099	−0.029	+0.557	−0.100
5.861	*B*	ϕ_7^D	+0.005	+0.017	−0.062	−0.068	−0.039	+0.039	+0.134	+0.162	+0.666
5.865	*A*	ϕ_8^D	0	−0.021	+0.048	−0.049	+0.022	−0.004	−0.140	−0.181	−0.665
6.155	*A*	ϕ_9^D	0	+0.016	+0.017	−0.566	+0.280	+0.220	−0.194	−0.055	+0.106
6.292	*B*	ϕ_{10}^D	−0.011	−0.005	−0.004	−0.463	−0.342	+0.390	+0.023	−0.105	−0.070
Compound (II)											
−0.010	*B*	ϕ_0^D	−0.999	0	0	0	0	+0.016	−0.022	0	−0.002
4.650	*A*	ϕ_1^D	0	−0.705	−0.007	+0.009	−0.013	+0.001	−0.047	−0.006	+0.014
4.624	*B*	ϕ_2^D	+0.001	+0.706	−0.006	+0.012	−0.011	−0.014	−0.030	+0.014	−0.017
5.735	*A*	ϕ_3^D	0	−0.003	+0.647	−0.041	+0.032	+0.108	−0.011	−0.247	+0.078
5.754	*B*	ϕ_4^D	+0.004	−0.009	−0.675	−0.038	−0.031	+0.094	−0.004	+0.158	−0.092
5.879	*B*	ϕ_5^D	−0.005	−0.015	+0.156	−0.002	−0.001	−0.099	+0.017	−0.678	−0.079
5.894	*A*	ϕ_6^D	0	−0.010	+0.263	−0.020	−0.014	−0.038	+0.009	+0.651	−0.072
6.230	*A*	ϕ_7^D	0	−0.018	+0.054	+0.021	−0.051	−0.026	+0.088	−0.102	−0.689
6.230	*B*	ϕ_8^D	−0.001	−0.010	+0.075	−0.038	−0.041	+0.005	+0.088	−0.099	−0.688

L_i represents the *i*th locally excited configuration and
C_i the *i*th charge transfer configuration.
$L_i=\phi_i^{M_a} \pm \phi_i^{M_b}$
$C_i=\phi_k^a\phi_l^b \pm \phi_k^a\phi_l^b$: $k=3$, $l=5$ for $i=1$; $k=3$, $l=6$ for $i=2$; $k=4$, $l=5$ for $i=3$; $k=4$, $l=6$ for $i=4$,
where the minus sign for *A* symmetry and the plus sign for *B* symmetry.

TABLE 2. THE WAVE FUNCTIONS AND ENERGIES OF THE ELECTRONIC STATES OF 6,6'-DIAMINO- AND 6,6'-DIHYDROXY-BIS-1,1'-SPIROINDANE, NEGLECTING THE CHARGE TRANSFER CONFIGURATIONS

E(eV)	Symmetry		G	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9	L_{10}
Compound (I)													
0.0		ϕ_0^D	1.0	0	0	0	0	0	0	0	0	0	0
4.390	*A*	ϕ_1^D	0	−0.706	−0.020	−0.014	+0.017	+0.011	0	+0.002	+0.002	−0.002	0
4.412	*B*	ϕ_2^D	0	+0.707	−0.017	−0.009	+0.014	+0.007	0	+0.002	+0.002	−0.002	0
5.388	*A*	ϕ_3^D	0	−0.022	+0.704	+0.054	−0.015	−0.025	+0.005	+0.005	−0.004	−0.001	+0.022
5.416	*B*	ϕ_4^D	0	−0.016	−0.705	+0.041	0	−0.017	+0.004	+0.005	−0.002	−0.002	−0.002
6.230	*A*	ϕ_5^D	0	+0.019	+0.059	−0.650	+0.254	+0.089	−0.059	−0.028	+0.018	−0.009	+0.006
6.408	*B*	ϕ_6^D	0	+0.003	+0.037	+0.645	+0.286	+0.027	+0.007	+0.013	+0.008	−0.007	−0.001
6.638	*A*	ϕ_7^D	0	+0.012	−0.004	+0.265	+0.650	+0.075	−0.021	−0.024	+0.008	+0.001	+0.008
6.713	*B*	ϕ_8^D	0	+0.015	+0.013	+0.278	−0.638	+0.117	−0.021	−0.021	+0.015	−0.002	+0.008

E(eV)	Symmetry		G	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8
Compound (II)											
0.0		ϕ_0^D	1.0	0	0	0	0	0	0	0	0
4.615	*A*	ϕ_1^D	0	−0.707	0.007	+0.015	−0.015	0	+0.005	−0.001	−0.004
4.629	*B*	ϕ_2^D	0	+0.707	−0.006	+0.010	−0.012	0	+0.004	0	−0.003
5.770	*A*	ϕ_3^D	0	−0.008	+0.706	−0.042	+0.006	+0.002	−0.006	+0.003	0
5.785	*B*	ϕ_4^D	0	+0.006	+0.706	+0.029	+0.008	−0.002	+0.003	−0.003	+0.002
6.421	*A*	ϕ_5^D	0	−0.021	−0.039	−0.603	+0.359	+0.014	−0.060	+0.022	+0.030
6.655	*B*	ϕ_6^D	0	+0.004	−0.024	+0.426	+0.564	−0.008	0	−0.017	+0.008
6.851	*A*	ϕ_7^D	0	+0.006	−0.016	−0.362	−0.606	−0.011	+0.010	−0.022	+0.004
7.011	*B*	ϕ_8^D	0	−0.015	−0.017	+0.559	−0.422	+0.020	−0.083	+0.030	+0.032

The symbol G and L_i are used in the same manner as in Table 1.

achieved in the following way:[13]

$$\langle\psi_0|r|\psi_i\rangle = \frac{h}{4\pi^2 m\nu_{i0}}\langle\psi_0|\nabla|\psi_i\rangle \tag{6}$$

where

$$h\nu_{i0} = E_i - E_0$$

The wave functions obtained above can be written in the form:

$$\psi_i{}^{\mathrm{D}} = \sum_i C_i{}^i \psi_i{}^{\mathrm{M}} + \sum_k C_k{}^i \psi_k{}^{\mathrm{CT}} \tag{7}$$

where $\psi_i{}^{\mathrm{M}}$ and $\psi_k{}^{\mathrm{CT}}$ represent the *i*th wave function of the monomer chromophore and the *k*th wave function of the charge-transfer transition respectively. The monomer wave functions can be rewritten as a linear combination of configurations:

$$\psi_i{}^{\mathrm{M}} = \sum_l \sum_m C^i{}_{lm}(\psi_l{}^{-1}\psi_m) \tag{8}$$

Then, the electric dipole moments of the monomer may be approximated as follows:

$$\langle\psi_0{}^{\mathrm{M}}|\nabla|\psi_i{}^{\mathrm{M}}\rangle \doteqdot \sqrt{2}\,C^0{}_{00}\sum_l \sum_m C^i{}_{lm}\langle\psi_l|\nabla|\psi_m\rangle \tag{9}$$

Similarly, the magnetic moments are approximated as follows:

$$\langle\psi_i{}^{\mathrm{M}}|\vec{m}|\psi_0{}^{\mathrm{M}}\rangle = \frac{eh}{4\pi imc}\cdot\sqrt{2}\,C^0{}_{00}\sum_m \sum_l C^i{}_{ml}\langle\psi_m|r\times\nabla|\psi_l\rangle \tag{10}$$

where $\boldsymbol{r}$ is the radius vector to the electron under consideration. The MO's, ψ_i and ψ_m, are written as linear combinations of AO's (X):

$$\psi_l = \sum_\alpha C_\alpha{}^l \chi_\alpha \tag{11}$$

Therefore,

$$\langle\psi_l|\nabla|\psi_m\rangle = \sum_{\text{all bond}} C^{lm}_{\alpha\beta}\langle\chi_\alpha|\nabla|\chi_\beta\rangle \tag{12}$$

$$\langle\psi_l|r\times\nabla|\psi_m\rangle = \sum_{\text{all bond}} C^{lm}_{\alpha\beta} r_{\alpha\beta}\times\langle\chi_\alpha|\nabla|\chi_\beta\rangle \tag{13}$$

where $C^{lm}_{\alpha\beta}$ is the transitional bond order ($C^{lm}_{\alpha\beta}=C_\alpha{}^l C_\beta{}^m - C_\beta{}^l C_\alpha{}^m$) and where $\vec{\boldsymbol{r}}_{\alpha\beta}$ is the radius vector to the mid-point of the bond. We also made similar calculations on the charge transfer, but the electric and magnetic dipole moments are very small. Therefore, these quantities for the charge-transfer configuration are neglected. By these procedures, we found the rotational strengths which are origin-independent. Using the MO's, the rotational strengths can be calculated on the basis of these formulations.

On the other hand, the rotational strength can be calculated by using Eqs. (5) and (11′) for the wave-function of method II:

$$\langle\psi_i|\vec{m}|\psi_0\rangle = \frac{\pi\nu_{i0}}{C}i\sum_k \boldsymbol{R}_k\times\langle\psi_i|er_k|\psi_0\rangle \tag{11′}$$

where $\boldsymbol{R}_k$ is the radius vector to the center of gravity of π-electrons in the ground state of the aromatic chromophore. By this procedure (named method III), we could also find the rotational strengths which are origin-independent.

TABLE 3. COMPARISON OF THE OBSERVED AND CALCULATED SPECTRA OF (S)-6,6′-DIAMINO-(I) AND (S)-6,6′-DIHYDROXY-BIS-1,1′-SPIROINDANE (II)

	Found (in MeOH)				Theoretical							
	UV		CD		Method I			Method II			Method III	
	λ (mμ)	D ($\times 10^{-36}_{cgs}$)	λ (mμ)	R ($\times 10^{-40}_{cgs}$)	λ (mμ)	D ($\times 10^{-36}_{cgs}$)	R ($\times 10^{-40}_{cgs}$)	λ (mμ)	D ($\times 10^{-36}_{cgs}$)	R ($\times 10^{-40}_{cgs}$)	D ($\times 10^{-36}_{cgs}$)	R ($\times 10^{-40}_{cgs}$)
	296	5.95	298.5	−7.23	281.8	1.94	−7.27	282.4	3.20	−7.18	6.91	+28.4
					280.5	0.04	+0.03	281.0	0.11	+0.27	0.27	−21.3
	236	17.2	244.0	−8.70	231.1	7.99	−225.0					
			233.0	+14.6	230.6	3.75	+155.0	230.0	10.1	−262.0	20.8	−812.0
I					226.1	0.99	−27.9	228.9	6.63	+257.0	13.8	+787.0
					224.8	2.13	+90.8					
	207	58.2	220.0	−204.0	211.2	0.05	−1.28	199.0	21.3	+25.3	36.2	+80.4
					211.0	0.11	+0.31	193.5	0.03	+44.3	0.15	+90.5
					201.1	9.90	−52.3	186.8	20.9	−485.0	42.2	−1560.0
					197.7	1.05	+120.0	184.7	14.7	+534.0	29.8	+1640.0
	289	5.22	291.5	−4.30	268.6	1.29	−2.13	268.6	2.06	−2.25	4.16	+31.7
	284		270.0	+0.63	267.6	0.02	−0.02	267.7	0.08	−0.07	0.19	−19.5
	220^t	8.40	236.0	−0.02	215.8	4.07	−124.0					
			228.0	+2.38	215.0	2.92	+136.0	214.8	4.27	−117.0	9.50	−291.0
					210.5	0.13	+5.18	214.3	2.99	+123.0	6.68	+325.0
II					210.0	0.35	−10.9					
			209.0	−18.6	198.6	0.62	−4.88	193.1	29.4	−27.5	43.7	+288.0
					198.6	~0	−0.10	186.3	4.55	+439.0	10.4	+1263.0
								180.9	35.7	−527.0	69.9	−1588.0
								176.8	16.1	+178.0	33.5	−152.0

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[13] M. Wolfsberg, *J. Chem. Phys.*, **23**, 793 (1955).

Results and Discussion

From the results of the compounds (—)-I and (—)-II given in Table 1, the contribution of the configurations to the excited states can be estimated, and we can see the nature of the transitions. By method I, the first and the second excited states can be said to be mainly composed of the ϕ_1^{M} configuration (α-band) of the monomer and to have A and B symmetries respectively. In the third and fourth excited states, although the main configuration is the ϕ_2^{M} (*p*-band) of the monomer, the charge-transfer configuration contributes to these states only to some extent. On the contrary, the main configuration of the fifth and sixth excited states is the charge-transfer configuration. This means that these transitions involve a large amount of electron transfer between the aromatic chromophores.

When the intramolecular charge-transfer configurations are neglected, the results given in Table 2 also show the mixing of the locally-excited configurations and the A and B symmetry of the transitions respectively. The first and the second excited states have mainly the ϕ_1^{M} configuration, while the third and the fourth excited states have again the ϕ_2^{M} configurations; in higher excited states, a mixing of the configurations is clearly observed.

When the excitation energies obtained by the two methods are compared with those of the experiments, the experimental results show still lower energies. This may be explained by the fact that the local excitation energies are adopted from aniline and phenol directly instead of from 6-amino- and 6-hydroxy-indane.

When the observed and the calculated CD spectra are compared, it is important to consider any mutual cancellation or addition of bands in areas where they overlap. The rotational strength, *R*, of an isolated, optically-active transition can be defined in the terms of directly observable properties, such as the ellipticity, $[\theta]_\lambda$[14]:

$$R = \frac{hc}{48\pi^2 N}\int[\theta]_\lambda \mathrm{d}\ln\lambda \text{ (integration taken through the bond)} \tag{15}$$

If the ellipticity has a Gaussian dependence on the wavelength,

$$[\theta]_\lambda = [\theta]_{\max}\exp\left[-\left(\frac{\lambda-\lambda_i}{\Delta_i}\right)^2\right] \tag{16}$$

where $[\theta]_{\max}$ is the maximum value of the ellipticity, Δ_i is the half-width, and λ_i is the wavelength corresponding to the maximum ellipticity. Furthermore, one obtains a direct relation between the ellipticity, $[\theta]_\lambda$, and the rotational strengths, R_i:

$$[\theta]_\lambda = \frac{1}{1.233\times10^{-42}}\sum_i R_i\frac{\lambda_i}{\Delta_i}\exp\left[-\left(\frac{\lambda-\lambda_i}{\Delta_i}\right)^2\right] \tag{17}$$

In this calculation, the values of the half-widths, Δ_i, are different in every transition, but we approximate the λ_i/Δ_i value to a constant. Using this equation and this assumption, we plot the theoretical CD curves in Figs. 2 and 3.

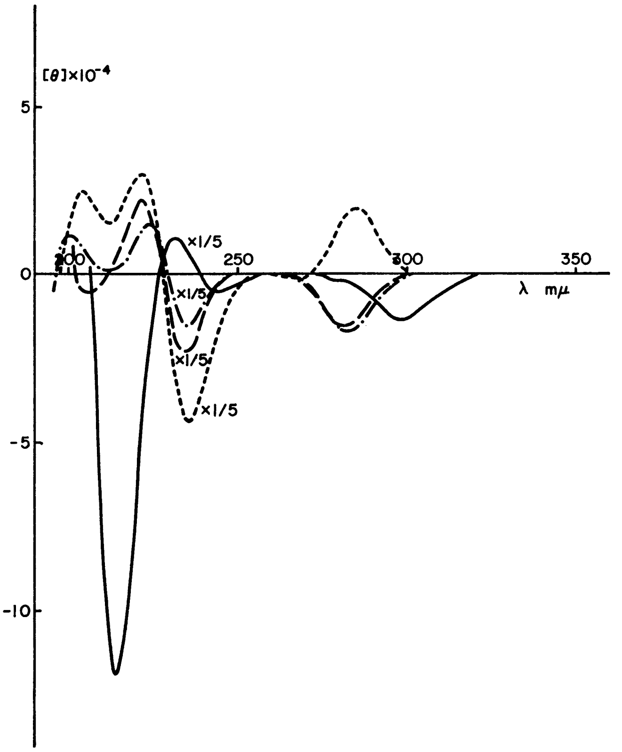

Fig. 2. CD spectra of (—)-3,3,3′,3′-tetramethyl-6,6′-diamino-bis-1,1′-spiroindane. Found (——), method I (– – –), method II (–·–·–), and method III (······).

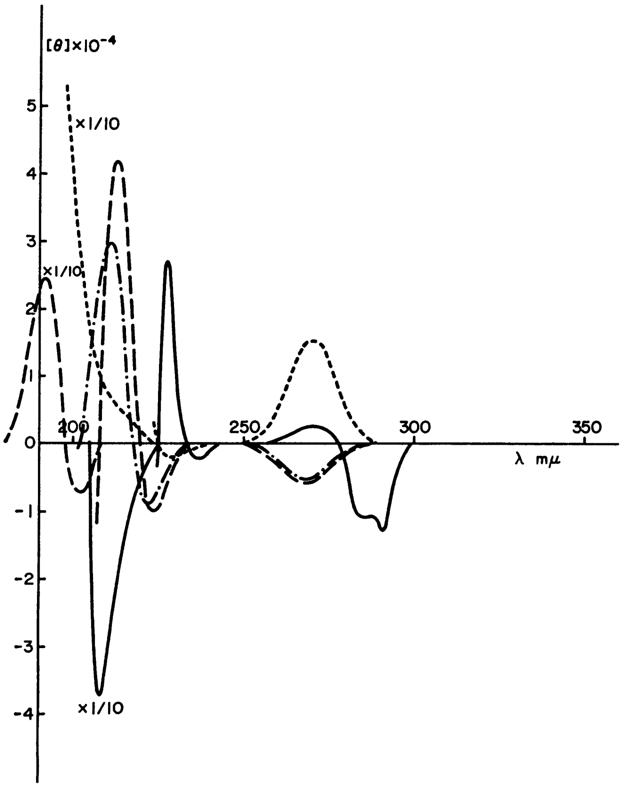

Fig. 3. CD spectra of (—)-3,3,3′,3′-tetramethyl-6,6′-dihydroxy-bis-1,1′-spiroindane. Found (——), method I (– – –), method II (–·–·–), and method III (······).

As has been mentioned above, the calculated excitation energies are higher than the observed ones. By comparing the observed and calculated CD spectra cited in Fig. 2, the calculated Cotton effect centered at

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[14] W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

ca. 280 mμ can be considered to be correlated with the observed Cotton effects at *ca.* 300 mμ. Although the simple dipole-coupling mechanisms and method III could not predict the correct signs and magnitudes of the Cotton effect in this region, the results of methods I and II predict almost quantitatively the sign and the magnitude of the Cotton effect.

In (—)-II, we can see two oppositely-signed Cotton effects at 291.5 and 270 mμ, but the CD spectra calculated by methods I and II in Fig. 3 show only the negatively-signed Cotton effect, while that calculated by method III shows only a positively-signed one at *ca.* 269 mμ. Although these methods, I and II, cannot predict the small Cotton effect of a positive sign, the large, negatively-signed Cotton effect corresponds to the results of the calculation. The results are, therefore, not so unsatisfactory, while method III gives an unsatisfactory result from the same point of view.

In the shorter-wavelength regions, the observed rotational strengths at 244 and 233 mμ of (—)-I are correlated with the four calculated strengths at 231.3, 230.6, 226.1, and 224.8 mμ by method I or with the two at 230.0 and 228.9 mμ by the method II, and the calculated magnitudes are much larger than those observed. However, it is considered that many bands overlap with each other in this region, giving rise to a mutual cancellation or addition of band areas; the validity can be judged by means of the calculated CD curves.

From the CD curves depicted in Fig. 2, the observed Cotton effects centered at 244 and 233 mμ of (—)-I can be correlated with those calculated at *ca.* 235 and 225 mμ respectively. Similarly, in Fig. 3 the observed Cotton effects at 236 and 228 mμ of (—)-II can be correlated with those calculated at *ca.* 225 and *ca.* 210 mμ respectively.

In the method I, the charge-transfer configurations are mixed to some extent in the third and fourth excited states; also, the fifth and sixth excited states have the character of a charge-transfer overlap in these band areas, the results calculated by methods I and II, however, show almost the same CD spectra. From these result, the contribution of the charge-transfer transition can be considered to be small. It cannot, however, be denied that the bands in these regions have the character of a mixture of a number of configurations. The signs and the magnitudes of the observed Cotton effects and those calculated by these three methods agree almost quantitatively.

APPENDIX 1. THE WAVE FUNCTIONS AND ENERGIES OF THE ELECTRONIC STATES OF ANILINE

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7
ϕ_1	+0.45480	+0.55958	+0.36985	+0.27380	+0.23770	+0.27380	+0.36985
ϕ_2	+0.58562	+0.25924	−0.10110	−0.39351	−0.50961	−0.39351	−0.10110
ϕ_3	0	0	+0.50308	+0.49690	0	−0.49690	−0.50308
ϕ_4	+0.60660	−0.33600	−0.36972	+0.14232	+0.45305	+0.14232	−0.36972
ϕ_5	0	0	−0.49690	+0.50308	0	−0.50308	+0.49690
ϕ_6	+0.24973	−0.57031	+0.23492	+0.30299	−0.56427	+0.30299	+0.23492
ϕ_7	+0.14101	−0.42604	+0.40139	−0.39765	+0.40017	−0.39765	+0.40139

	$\phi_4\phi_5$	$\phi_4\phi_6$	$\phi_4\phi_7$	$\phi_3\phi_5$	$\phi_3\phi_6$	$\phi_3\phi_7$	$\phi_2\phi_5$
ϕ^{M}_1	+0.87889	0	0	0	−0.46840	−0.01702	−0.08864
ϕ^{M}_2	0	+0.95475	+0.05865	+0.28526	0	0	0
ϕ^{M}_3	+0.46231	0	0	0	+0.79468	−0.02994	+0.38804
ϕ^{M}_4	0	−0.26055	−0.15385	+0.93659	0	0	0
ϕ^{M}_5	−0.11400	0	0	0	−0.38099	−0.12893	+0.90830
ϕ^{M}_6	0	−0.08423	+0.96971	+0.11769	0	0	0
ϕ^{M}_7	0	−0.11478	+0.10289	+0.16420	0	0	0
ϕ^{M}_8	+0.00337	0	0	0	−0.05146	+0.91400	+0.11491
ϕ^{M}_9	−0.02879	0	0	0	−0.03583	−0.38315	−0.05790
ϕ^{M}_{10}	0	+0.01756	−0.14818	+0.02469	0	0	0

	$\phi_2\phi_6$	$\phi_1\phi_5$	$\phi_1\phi_6$	E(eV)		f	
				Calcd	Found	Calcd	Found
ϕ^{M}_1	0	−0.00342	0	4.404	4.40	0.056	0.028
ϕ^{M}_2	+0.05726	0	−0.01918	5.408	5.39	0.366	0.140
ϕ^{M}_3	0	+0.05734	0	6.379	6.40	0.478	0.510
ϕ^{M}_4	−0.17416	0	−0.03020	6.645	6.88	0.890	0.570
ϕ^{M}_5	0	−0.01493	0	7.614	7.87	0.546	(0.68)
ϕ^{M}_6	0.12418	0	+0.15261	7.651			
ϕ^{M}_7	+0.97291	0	−0.05213	7.973			
ϕ^{M}_8	0	+0.38568	0	8.755			
ϕ^{M}_9	0	+0.92070	0	9.406			
ϕ^{M}_{10}	+0.06642	0	+0.98626	9.744			

Appendix 2. THE WAVE FUNCTIONS AND ENERGIES OF THE ELECTRONIC STATES OF PHENOL

	χ_1	χ_2	χ_3	χ_4	χ_4	χ_6	χ_7
ψ_1	+0.71851	+0.53215	+0.26534	+0.15244	+0.11526	+0.15244	+0.26534
ψ_2	+0.48242	−0.02488	−0.27207	−0.43389	−0.49202	−0.43389	−0.27207
ψ_3	0	0	−0.50280	−0.49717	0	+0.49718	+0.50280
ψ_4	+0.43788	−0.44910	−0.36616	+0.19584	+0.51159	+0.19584	−0.36616
ψ_5	0	0	−0.49718	+0.50280	0	−0.50280	+0.49718
ψ_6	+0.20913	−0.57444	+0.24199	+0.30393	−0.56958	+0.30393	+0.24193
ψ_7	+0.12469	−0.42957	+0.40366	−0.39721	+0.39811	−0.39721	+0.40366

	$\psi_4\psi_5$	$\psi_4\psi_6$	$\psi_4\psi_7$	$\psi_3\psi_5$	$\psi_3\psi_6$	$\psi_3\psi_7$	$\psi_2\psi_5$	$\psi_2\psi_6$	E(eV)		f	
									Calcd	Found	Calcd	Found
ψ_1^M	+0.83038	0	0	0	+0.55359	+0.01448	−0.06164	0	4.624	4.59	0.036	0.023
ψ_2^M	0	+0.89721	+0.01654	−0.43873	0	0	0	+0.04744	5.780	5.76	0.180	0.175
ψ_3^M	−0.55509	0	0	0	+0.81528	−0.02817	−0.16247	0	6.718	6.68	0.908	0.585
ψ_4^M	0	+0.43146	+0.06106	+0.89498	0	0	0	+0.09550	6.771	6.90	1.125	0.371
ψ_5^M	0	−0.00895	+0.93443	−0.02152	0	0	0	−0.35539	8.049			
ψ_6^M	−0.04614	0	0	0	+0.16600	+0.29736	+0.93909	0	8.050			
ψ_7^M	0	−0.09363	+0.35049	−0.07786	0	0	0	+0.92862	8.401			
ψ_8^M	−0.01460	0	0	0	−0.03606	+0.95424	−0.29650	0	8.905			

In the even-shorter-wavelength regions, the CD bands could not be predicted from these calculations. This may be due to the neglect of the higher energy states in method I and of the π–σ^* transitions, which may contribute to the CD spectra in these regions.

From the quantitative agreement between the experimental and the calculated results obtained by the methods, I and II, these methods can be considered to be suitable for the determination of the absolute configuration and for the estimation of the order of the rotational strengths of compounds with two or more chromophores composed of π-electrons. It must be noted that, for the same good wave-functions, methods II and III give different rotational strengths; method III especially shows incorrect signed Cotton effects in the α-band region. The difference in these results may be caused by the choice of the center of the transition dipole in method III, but the true reason for the failure of method III and for the success of method II does not appear to be understood at present. From our present studies, however, it could be concluded, for π-electron systems, that the rotational strengths calculated by method II are more likely to give a good agreement with the experimental data.