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Optical Activity of Biphenyl Derivatives: The π-π^* and n-π^* Transitions of *o,o'*-Dinitrobiphenyls

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The optical rotatory power for the lower electronic transitions of several *o,o'*-dinitrobiphenyl derivatives is examined on the basis of a theoretical method previously developed and applied to metal chelate compounds and binaphthyl derivatives. The theoretical energy, absorption intensity, and rotational strength are shown to be in reasonable agreement with the observed absorption and circular dichroism spectra, confirming the applicability of the theory to the optical activity of this simple type of dissymmetric molecules. In addition, the origin of the rotational strength for the n-π^* transition is examined in detail. The results indicate that the n-π^* transition gains its intensity and rotatory power through the interaction of the nonbonding electrons in a nitro group with the π electron system in the other nitrobenzene ring.

The optical rotatory dispersion (ORD) and circular dichroism (CD) of organic compounds and of metal complexes have been a subject of increasing interest in relation to their importance in biology as well as in the fundamental theory of molecular electronic structure. Although the general theory for the phenomenon has been established,[1–3] a more extensive study of the electronic origin of the optical activity for each optically active molecule seems to be necessary. It is also desirable to examine in more detail the reliability of the approximations employed in the calculation of the optical activity.

Some years ago, we first tried to use semiempirical electronic wave functions in the calculation of the rotatory strength accompanying the lower electronic transitions in transition-metal chelate compounds and in some binaphthyl derivatives.[4,5] For these two typical types of optically active molecules, the method was revealed to be satisfactory in explaining the observed CD spectra. It was also noticed that the method is capable of treating the rotational strength fully for the "charge-transfer" transition between two chromophors, as well as for the "locally excited" transition in each chromophor, which may be related to the well-known polarizability theory of Kirkwood.[6]

Recently, the optical activity of the biphenyl derivatives, one of the simplest optically active molecules, has been studied in our laboratory in order to clarify the origin of the interaction responsible for the optical activity and in order to examine the applicability of the theoretical method more extensively. Two difficulties have been found in the case of weakly substituted biphenyls (*e.g.*, alkyl- or halogeno-substituted ones); one of them is the vibrationally enhanced electric and magnetic transition moments, which seem to be responsible predominantly for some CD bands. The other is the interaction between the σ and π electrons in a benzene chromophor induced through the interaction with the other. In view of these results, it seems to be desirable to study a biphenyl compound with a strong substituent, for which the above-mentioned effects do not contribute predominantly to the rotational strength.

In the present paper, a theoretical study is presented for *o,o'*-dinitrobiphenyl, and the results are compared with the experimental CD spectra of its derivatives.[7] It is also interesting to study the origin of the CD band accompanying the n-π^* transition since, in this type of compounds, it is not clear whether the n-π^* transition gains its intensity through the vibronic interactions, as in the case of nitrobenzene, or through a purely electronic interaction.

Method of Calculation

The π-π Interaction. Details of the theoretical treatment were given in previous papers.[4,5] Here we will give only an outline of the method and some parameter values characteristic of the compound studied.

The electronic structure of the π electron system of nitrobenzene is calculated by means of the Pariser-Parr-Pople SCFCI method[8] for the geometry given by Trotter.[9] Since there are some ambiguities in the choice of parameter values concerning the nitro group, several choices of the core resonance integrals between nitrogen and oxygen and between nitrogen and carbon are examined in order to determine the best values (see Results and Discussion). The wave functions are then used in the composite-molecule calculation[10] of *o,o'*-dinitrobiphenyl with various dihedral angles (θ). The geometry and coordinate system employed are shown in Figs. 1 and 2. The core resonance integral over the 2pπ AO's (atomic orbitals), χ_1^a and χ_1^b is expressed as a function of θ:

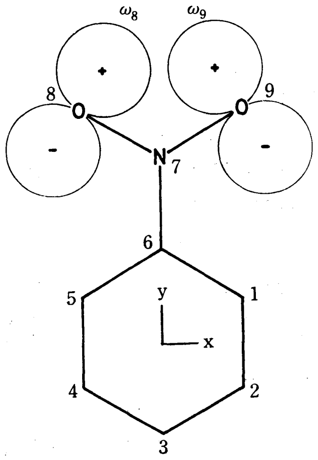


Fig. 1. Numbering of atomic orbitals in nitrobenzene.

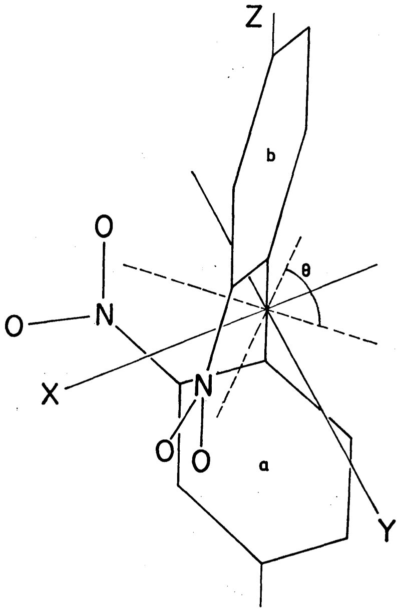


Fig. 2. Numbering and coordinate system for *S*-*o*,*o*′-dinitrobiphenyl.

$$\beta(\chi_1^a, \chi_1^b) = -\beta_0 \cos\theta \qquad (1)$$

Assuming 1.50 Å for the distance between atoms 1a and 1b, β_0 is calculated to be −1.99 eV by means of its proportionality to the benzene value.[8)]

The composite-molecule calculation is performed with 14 LE(locally excited) electron configurations in the electron system of each nitrobenzene fragment and 24 CT (charge transfer) configurations between two π electron systems. The effect of the σ electron in each fragment is neglected.[11)]

The rotational strength[1,2)] for the n-th excited state is given by the following formula:

$$R_{0-n} = -1.187\times 10^2 \tilde{\nu}^{-1}\langle 0|\boldsymbol{\nabla}|n\rangle\cdot\langle n|\boldsymbol{\lambda}|0\rangle \ (\text{Å}^2) \qquad (2)$$

assuming real wave functions. Here, $\boldsymbol{\lambda}=\mathbf{r}\times\boldsymbol{\nabla}$, and the gradient, $\boldsymbol{\nabla}$ and the excitation energy, $\tilde{\nu}$, are expressed in units of Å^{-1} and cm^{-1} respectively. The integrals, $<0|\boldsymbol{\nabla}|n>$ and $<n|\boldsymbol{\lambda}|0>$, are reduced to the integrals over AO's (only the nearest neighbour integrals are retained), the latter being evaluated for nitrobenzene to be[12)]:

$$\nabla_{CC} = -0.417,\ \nabla_{CN} = -0.314 \text{ and}$$
$$\nabla_{NO} = -0.412 \ (\text{Å}^{-1}) \qquad (3)$$

The integral of $\boldsymbol{\lambda}$ over AO's χ_p and χ_q can also be expressed by ∇_{pq}:

$$\begin{aligned}\langle p|\boldsymbol{\lambda}|q\rangle &= \langle\chi_p|\mathbf{r}\times\boldsymbol{\nabla}|\chi_q\rangle\\ &= \langle\chi_p|\mathbf{R}_q\times\boldsymbol{\nabla}|\chi_q\rangle + \langle\chi_p|\mathbf{r}_q\times\boldsymbol{\nabla}|\chi_q\rangle\\ &= \mathbf{R}_q \times \langle\chi_q|\boldsymbol{\nabla}|\chi_p\rangle\\ &= \nabla_{pq}\cdot(\mathbf{R}_q\times\boldsymbol{\sigma}_{pq}) \qquad (4)\end{aligned}$$

where $\mathbf{r}$ and $\mathbf{r}_q$ are the position vectors of an electron measured from a common origin, O, and atom q respectively. $\mathbf{R}_q$ is a vector directed from O to q.

The integrals between two fragments are expressed as:

$$\langle\chi_1^b|\nabla_Z|\chi_1^a\rangle = -\nabla_0 \cos\theta,$$
$$\langle\chi_1^b|\lambda_Z|\chi_1^a\rangle = S_0 \sin\theta \text{ (for } S \text{ configuration)}, \qquad (5)$$

where the X and Y components are all vanishing. The quantity ∇_0 is calculated to be −0.359 Å^{-1} by means of the Slater AO.

The n-π Transition.* In the calculation of the rotational strength accompanying the n-π^* transition, it is assumed that the non-bonding AO's (ω_8 and ω_9) are the 2p AO's of oxygen lying in the molecular plane and with their axes perpendicular to the N–O bond. They are taken as their positive directions towards one another (Fig. 1). Taking the symmetry orbitals as:

$$\omega_S = \frac{1}{2}(\omega_8+\omega_9)$$
$$\omega_A = \frac{1}{2}(\omega_8-\omega_9), \qquad (6)$$

one obtains two n-π^* states in nitrobenzene corresponding to the transitions from ω_S and ω_A to the lowest vacant MO(molecular orbital) φ_6. Thus, the following four n-π^* wavefunctions can be constructed for dinitrobiphenyl:

$$\Psi_\tau^{\pm} = (2)^{-1/2}(\Psi_\tau^a \pm \Psi_\tau^b) \quad (\tau=\text{S or A})$$

where Ψ_τ^μ corresponds to transition $\omega_\tau\to\varphi_6$ in the μ-th fragment. The average transition energy for these n-π^* transitions is evaluated to be 3.2 eV on the basis of the ionization potential of the oxygen non-bonding AO, the semiempirical two-center repulsions, and the calculated orbital energy of φ_6. This value is in reasonable agreement with the observation (3.6 eV).[13)]

The n-π^* transitions have an intrinsic (one-center) transition magnetic moment in a direction parallel with the N–O bond. On the basis of ω_S and ω_A, theyare calculated to be:

$$\langle\varphi_6|\lambda_x|\omega_S\rangle = -(3/2)^{1/2}C_{68}$$
$$\langle\varphi_6|\lambda_y|\omega_A\rangle = (2)^{-1/2}C_{68} \qquad (7)$$

where the coordinates, x and y, correspond to those in Fig. 1, and where C_{68} is the coefficient of 2pπ AO χ_8 in MO φ_6. The effect of the mixing of the π-π^* transition on λ can safely be neglected since the one-center magnetic moment is very large. On the other hand, the n-π^* transition may gain ∇ from the π-π^* transition. In the present work, it is proposed that the n-π^* state gains ∇ through the mixing with the π-π^* CT states. In fact, the n-π^* state, $\omega_9^a\to\varphi_6^a$, interacts appreciably with the CT state, $\varphi_i^b\to\varphi_6^a$, through the resonance interaction between ω_9^a and φ_i^b (i=1, 2,⋯,5). The

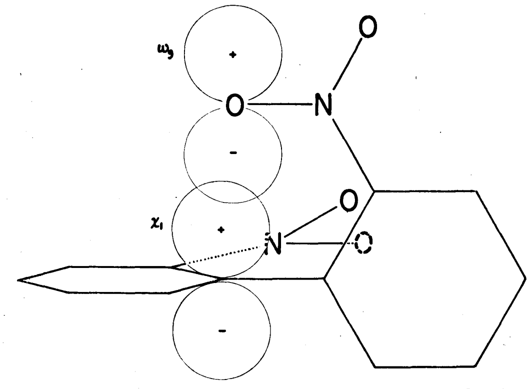


Fig. 3. Interaction of the nonbonding orbital with the 2pπ orbital.

Table 1. Core resonance integral between $\omega_9{}^a$ and $\chi_p{}^b$ (eV)$^{a)}$

p	(deg.)$^{b)}$ 60	80	91	100
1	0.71	0.30	0.11	0.07
2	0.57	0.65	0.66	0.65
3	0.03	0.07	0.12	0.30

a) $\beta(\omega_9{}^b, \chi_p{}^a)=\beta(\omega_9{}^a, \chi_p{}^b)$. b) Dihedral angle.

same holds for the interaction between $\omega_9{}^b \rightarrow \varphi_6{}^b$ and $\varphi_i{}^a \rightarrow \varphi_6{}^b$. The schematic drawing of the interaction is given in Fig. 3. The core resonance integrals between $\omega_9{}^a$ and the 2pπ AO's, $\chi_1{}^b$, $\chi_2{}^b$, and $\chi_6{}^b$, and those between $\omega_9{}^b$ and $\chi_1{}^a$, $\chi_2{}^a$ and $\chi_6{}^a$, are evaluated on the basis of their proportionality to the overlap integral and the valence-state ionization potential.[14,15] They are summarized in Table 1 for several dihedral angles. The effects of the mixing are calculated by the first-order perturbation treatment.

Results and Discussion

Nitrobenzene. The transition energies and oscillator strengths for some lower electronic transitions of nitrobenzene calculated by means of the SCFCI method are given in Table 2, together with the observed values obtained by Nagakura and his coworkers[16] and by Labhart.[17] The theoretical results given in the table are calculated with $\beta_{CN}=-2.4$ and $\beta_{NO}=-2.7$ eV, which seem to give a reasonable agreement with the experimental results. It should be noted that the oscillator strength for nitrobenzene shown in Table 2 is calculated on the basis of the transition dipole moment:

$$f_m = 1.085\times 10^{-5}\tilde{\nu}|\langle 0|\mathbf{r}|n\rangle|^2 \tag{8}$$

whereas the f value for the dinitrobiphenyls given below (Tables 4, 5, and 6) is calculated by means of the dipole velocity:

$$f_v = 4.16\times 10^{4}\tilde{\nu}^{-1}|\langle 0|\nabla|n\rangle|^2 \tag{9}$$

It has been pointed out that f_m generally gives a considerably larger value, whereas f_v gives a favorable agreement with the experimental results.[18] In view of this, the present result for nitrobenzene is fairly satisfactory.

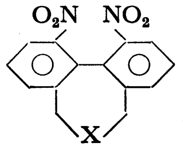
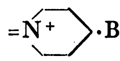
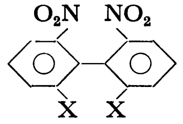
Table 2. Calculated and observed transitions for nitrobenzene

Transition Energy (10^3 cm^{-1}) Obsd$^{a)}$	Calcd$^{b)}$	Oscillator Strength Obsd$^{a)}$	Calcd$^{b)}$
30$^{c)}$	—	0.004$^{d)}$	—
35.3	35.6	0.01	0.04
41.2	37.8	0.17	0.37
51.8	44.9	0.38	0.17
	48.4		0.25
	48.5		0.40
61.0	57.8	0.87	0.61
	57.8		1.11

a) Ref. 16 except for the n-π^* transition. b) Calculated on the basis of the transition dipole moment; Eq. (8). c) The n-π^* transition. Taken from Ref. 17. The oscillator strength is estimated from the spectrum given in the reference.

o,o′-Dinitrobiphenyl (Type I). There are two types of *o,o′*-dinitrobiphenyl derivatives for which the CD spectra have been measured by Mislow *et al.*;[7] one has a bridge between the 2 and 2′ positions (Type I), and the other has substituents at the 2 and 2′ positions (Type II). The compounds for which the CD measurement was made are summarized in Table 3. The dihedral angle for the latter compounds is not known and may fluctuate around a stable position. On the other hand, the former compounds have a well-defined dihedral angle. It seems reasonable to take $\theta\approx 60°$ for the compounds studied here.[19]

Table 3. *o,o′*-Dinitrobiphenyls

Type		Compound	X
I		Ia	$=C(COOC_2H_5)_2$
		Ib	$=CHOH$
		Ic	 $\cdot Br^-$
II		IIa	CH_3
		IIb	CH_2Br
		IIc	CH_2OH
		IId	COOH
		IIe	$COOCH_3$

The calculated results for the *S*-isomer with $\theta=60°$ are summarized in Table 4, together with the CD and absorption spectra observed by Mislow *et al.* for Ia. Since the methylene bridge is expected to work as a very weak substituent, the experimental results for this compound can be compared with the theoretical results in which the effect of bridge is not taken into account. This conclusion is also supported by the fact that the CD spectra for the related compounds with different X are almost the same in their shape, indicating that the rotational strength is predominantly determined by the nitrobenzene groups and their relative orientation.

Except for the n-π^* transition, which will be discussed below, the characteristic features of the CD spectrum seem to be explained by the present calculation—that is, a positive Cotton effect around 35000 cm^{-1} and a stronger negative one in the higher-energy region. The experimental rotational strength for the latter is -2.7×10^{-4} (Å^2), whereas the calculated one is -5.62×10^{-4} (Å^2). The calculated rotational strength for the lower-energy transition is correct in its sign. It is, however, too large compared with the corresponding CD band, although the mixing with the n-π^* transition reduces the theoretical rotational strength to some extent (see below). One reason for this inconsistency may lie in the fact that the nitro group twists to some extent. The first LE state in nitrobenzene is of a CT character (benzene to the nitro group). The first three calculated rotational strengths for dinitrobiphenyl, which have the LE$_1$ state as main components, are sensitive to the twist. In fact, the X-ray crystal analysis of nitromesitylene[20] shows that the nitro group twists by 66° from the

TABLE 4. RESULTS FOR (*S*)-*o,o'*-DINITROBIPHENYL WITH $\theta=60°$

Calcd				Obsd a)				
				Absorption		CD		
E (cm^{-1}) b)	f c)	R (Å^2) d)	Remarks	E(cm^{-1}) b)	ε	E(cm^{-1}) b)	$\Delta\varepsilon$	R(Å^2) d)
—	—	—	n-π^*			30.3×10^3	17	1.7×10^{-4}
34.72×10^3	0.05	3.82×10^{-4}	LE$_1$, LE$_2$					
36.28	0.01	0.27	LE$_1$			34.6	5	0.2
36.40	0.12	3.37	LE$_2$, LE$_1$					
37.95	0.18	−5.62	LE$_2$	38×10^3	7100	39.1	−32	−2.5
41.57	0.03	0.49	CT$_{46}$					
41.71	0.00	−0.25	CT$_{46}$					
43.25	0.00	−0.07	CT$_{56}$					
43.91	0.06	1.75	CT$_{56}$	43.5	17000			
46.00	0.00	0.12	CT$_{36}$					
46.03	0.00	−0.05	CT$_{36}$					
47.61	0.02	1.42	LE$_3$					
47.84	0.09	−0.45	LE$_5$, LE$_3$, LE$_4$					
48.56	0.24	10.62	LE$_3$, LE$_5$					

a) Observed for Ia; Ref. 7. b) Transition energy or peak energy. c) Oscillator strength calculated on the basis of dipole velocity; Eq. (9). d) Rotational strength.

benzene plane. The angle of twist must be much smaller in the present case, since the steric hindrance due to the *ortho* substituent (in the present case, a phenyl group) is expected to be much weaker than that for nitromesitylene.

Another point to be discussed here is the origin of the peak at 43500 cm^{-1} in the absorption spectrum. The band is very intense ($f\approx 0.6$) if it is considered as a single transition. The strong transitions predicted to appear between 47000—50000 cm^{-1} are unlikely to be responsible for the observed peak; they are mainly composed of LE$_3$, LE$_4$, and LE$_5$ in nitrobenzene (see Table 2), the calculated energies of which are somewhat lower than the observed one. Since we have calculated the electronic structure of dinitrobiphenyl on the basis of the calculated energies for nitrobenzene, the predicted energies (47000—49000 cm^{-1}) for the LE transitions must be somewhat lower than the actual energies. The most reasonable interpretation is that the peak is due to the CT transition predicted to appear at 43910 cm^{-1} overlapping on the tail of the strong absorption bands in the higher-energy region. It is desirable to extend the absorption and (especially) CD measurements to a higher-energy region in order to clarify this point.

o,o'-Dinitrobiphenyl (Type II). The calculated results for the (*S*)-*o,o'*-dinitrobiphenyl with $\theta=91°$ are summarized in Table 5, together with the observed results[7] for (*S*)-2,2'-dimethyl-6,6'-dinitrobiphenyl (IIa). Again, the lowest CD band at 29000 cm^{-1} is the n-π^*

TABLE 5. RESULTS FOR (*S*)-*o,o'*-DINITROBIPHENYL WITH $\theta=91°$

Calcd				Obsd a)				
				Absorption		CD		
E (cm^{-1}) b)	f c)	R (Å^2) d)	Remarks	E(cm^{-1}) b)	ε	E(cm^{-1}) b)	$\Delta\varepsilon$	R(Å^2) d)
—	—	—	n-π^*	29×10^3	(500) e)	28.6×10^3	−0.7	−0.8×10^{-5}
34.30×10^3	0.07	0.10×10^{-4}	LE$_1$	33	(4000) e)			
34.87	0.00	0.30	LE$_1$					
35.75	0.13	−10.01	LE$_2$			33.6	−2.7	−4.4
36.64	0.18	7.25	LE$_2$	38.6	10000	40.0	4.9	3.8
38.86	0.00	0.00	CT$_{56}$					
38.86	0.00	−0.01	CT$_{56}$					
42.03	0.00	0.00	CT$_{46}$					
42.03	0.00	0.00	CT$_{46}$					
44.33	0.01	1.66	LE$_3$					
46.50	0.05	0.11	LE$_4$, LE$_3$					
46.87	0.30	−2.13	LE$_3$, LE$_4$					
47.79	0.01	0.28	LE$_4$					
48.11	0.10	−5.28	LE$_5$					
48.40	0.26	8.64	LE$_5$					

a) Observed for IIa; Ref. 7). b) Transition energy or peak energy. c) Oscillator strength calculated on the basis of dipole velocity; Eq. (9). d) Rotational strength. e) Shoulder.

transition, and the remaining two CD bands with opposite signs are qualitatively consistent with the theoretical third and fourth transitions, which are of an LE_2 character. The sum of the theoretical oscillator strengths for the first four transitions ($f\approx0.38$) is also in reasonable agreement with the observed one ($f\approx0.3$). However, the magnitude of the two CD bands ($R=-1.00\times10^{-3}$ and 7.25×10^{-4} Å^2) are too large compared with the corresponding observed CD bands ($R\approx-4.4\times10^{-5}$ and 3.8×10^{-5} Å^2 respectively). In view of the agreement between the theoretical and experimental f values, the most probable reason for this discrepancy is the mutual cancellation of the positive and negative CD bands. The effect of the cancellation should be remarkable for the dihedral angle of $\sim90°$, since the energy separation becomes smaller. This viewpoint may also be supported by the fact that the rotational strength of the n-π^* transition, in which the algebraic sum of R's for four transitions is responsible for the observed single peak, is in reasonable agreement with the observation (see below).

The n-π^* Transition. Before discussing the rotational strength of the n-π^* transition, it is necessary to consider the splitting of the n-π^* excited states. McEwen[21] has calculated the n-π^* states of nitromethane by taking account of the interaction of two nonbonding AO's (ω_8 and ω_9) with the nitrogen σ AO's. The results show that the orbital energy of ω_S is higher than that of ω_A by about 400 cm^{-1}. The result of configuration interaction predicts that the n-π^* state in which an electron has been removed from ω_S will lie at an energy lower by 1200 cm^{-1}. In view of these results, it may be reasonable to assume that the energies of these n-π^* transitions are very close to each other. The remarkable asymmetry observed by Labhart[17] for the n-π^* band of nitrobenzene may be taken as an indication of the overlapping of these two bands.[22] The splitting into the $\Psi_\tau{}^+$ and $\Psi_\tau{}^-$ states (τ=S or A) in dinitrobiphenyls is very small and can safely be neglected for the present purposes.

The rotational strengths and oscillator strengths for the n-π^* transitions are summarized in Table 6 for several dihedral angles. In view of the calculated R values for four n-π^* transitions, the observed single CD band is predominantly accounted for by the transition to $\Psi_S{}^-$, while those to $\Psi_A{}^+$ and $\Psi_A{}^-$ must give small negative contributions on the longer-wavelength tail of the spectrum. The calculated total rotational strength for $\theta=60°$ is 2.85×10^{-4} Å^2, which is in reasonable agreement with the observation, 1.8×10^{-4} Å^2, given in Table 4.

Table 6. Calculated results for the n-π^* transitions of (*S*)-*o*,*o*′-dinitrobiphenyl

	n-π^* State	θ (deg.)[a]			
		60	80	91	100
	$\Psi_S{}^+$	0.50	0.19	−0.019	−0.020
	$\Psi_S{}^-$	2.62	0.98	−0.12	−1.48
R[b] $\times10^4$ (Å^2)	$\Psi_A{}^+$	−0.50	−0.19	0.019	0.020
	$\Psi_A{}^-$	0.23	−0.005	−0.006	−0.11
	total	2.85	0.98	−0.13	−1.59
	$\Psi_S{}^+$	0.97	0.18	0.0022	0.27
	$\Psi_S{}^-$	7.10	0.95	0.013	1.78
f[c] $\times10^3$	$\Psi_A{}^+$	0.97	0.18	0.0022	0.27
	$\Psi_A{}^-$	7.10	0.95	0.013	1.78
	total	16.2	2.3	0.03	4.1

a) Dihedral angle. b) Rotational strength. c) Oscillator strength calculated from Eq. (9).

The calculated total oscillator strength for $\theta=60°$ is 0.016. Comparing this value with that of nitrobenzene ($f\approx0.004$[17]; presumably of vibronic origin), one can conclude that the present mechanism of the interaction between the nonbonding AO and the π electron system determines predominantly the intensity of the n-π^* transition for this compound, although the vibronic intensity borrowing may give rise to an additional effect. Unfortunately, the n-π^* band is much weaker than the nearby π-π^* transitions and cannot be observed as distinct peaks in the absorption spectrum. However, the very long tail on the longer-wavelength side of the absorption spectrum of Ia can be taken as an indication of the overlapping of absorption bands with $\varepsilon\approx10^3$, which is in order-of-magnitude agreement with the calculated intensity (f=0.016).

The observed n-π^* rotational strength for Compound IIa is -7.9×10^{-6} Å^2. If one supposes that the observation corresponds to a pure optical isomer, this result indicates that the dihedral angle for this compound is only slightly larger than 90°. In fact, the calculated result, $R=-1.3\times10^{-5}$ Å^2 for $\theta=91°$, is in reasonable agreement with the observation.[23] This conclusion is also consistent with the above discussion of the π-π^* transition bands.

In view of these results, it can be concluded that the rotational strength and oscillator strength for the n-π^* transition are due to direct interaction between the non-bonding AO of the nitro group and the π electrons in the adjacent benzene ring.

The rotational strength of the π-π^* type transition is also affected by the interaction with the n-π^* states. This is caused by the mixing of the intrinsic transition magnetic moment of the n-π^* transition into the π-π^* transition. For instance, the rotational strengths for the first, third, and fifth transitions for Compound Ia change from 3.82, 3.37, and 0.49×10^{-4} Å^2 to 1.93, 4.20, and -0.19×10^{-4} Å^2 respectively, while the second and fourth transitions remain unchanged. This brings the theoretical results in Table 4 into better agreement with the observed CD spectrum, although the effect of the twisting of nitro groups mentioned above may also be responsible.

The unoccupied orbitals, φ_7 and φ_8, of nitrobenzene lie at higher energies than φ_6 by 1.82 and 2.35 eV respectively. Hence, the second and third n-π^* transitions to these π^* orbitals may appear in the 45000—50000 cm^{-1} region. Although, in the present treatment, we focus on the lowest n-π^* transition at 30000 cm^{-1}, these higher n-π^* transitions may have some effect on the calculated rotational strengths.

Related Compounds. The CD spectra of two additional compounds of Type I (Ib and Ic) have been recorded by Mislow *et al.*[7] Their spectra resemble that of Ia quite well, so their electronic structures can be regarded as almost the same as that of Ia. The result also indicates that the substituent on the bridge does not bring about any significant effect on the optical activity. Among the Type II compounds (IIb—IIe), IIb and IIc show CD spectra similar to that of IIa, while a remarkable deformation is observed for IId and IIe. The latter is undoubtedly due to the strong substituent effect of carboxyl groups at the 2 and 2′ positions. Finally, the present theoretical results for the *S* configuration are consistent with the observed CD spectra for the optical isomers, determined to have the same absolute configuration on the basis of the chemical correlation.[7,24] This confirms the reliability of the present theoretical treatment in determining the absolute configuration in this type of compound.

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11) The effect of the σ-π* and π-σ* excited states in the benzene chromophor will be discussed in a forthcoming paper.

12) The quantity ∇_{pq} is defined by:

$$\langle \chi_p | \nabla | \chi_q \rangle = \nabla_{pq} \boldsymbol{\sigma}_{pq}$$

where $\boldsymbol{\sigma}_{pq}$ is the unit vector directed from atom q to atom p. It is calculated nonempirically for the Slater AO's (see Eq. (3) of Ref. 5).

13) The other type of n-π* transition which may take part in the interaction between the n-π* and π-π* states is the transition from ω_8 or ω_9 of one nitrobenzene to the lowest vacant MO of the other. Its transition energy is estimated in a similar manner to be about 8 eV. Hence, its effect is ignored in the present treatment.

14) The interactions between ω_9 and χ_3, χ_4, and χ_5 are ignored.

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19) A calculation based on the molecular model indicates $\theta = 55$—$60°$, whereas the estimation based on the electronic absorption spectra indicates $\theta = 46°$ for bridged biphenyls with no substituent at the 2,2′ positions (H. Suzuki, This Bulletin, **32**, 1357 (1959)). In the present calculation, we assume $\theta = 60°$ taking account of the repulsive interaction between two nitro groups.

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22) On the other hand, a recent photoelectron study [T. Kobayashi and S. Nagakura, *Chem. Lett.*, **1972**, 903; *Bull. Chem. Soc. Jpn.*, **47**, 2563 (1974)] shows that the third peak at 11.01 eV for nitrobenzene corresponds to the ionization from ω_S, whereas the energy of the ionization from ω_A is not lower than 12.65 eV Since the splitting between the n-π* excited states is not the same as that between the non-bonding orbitals, this result cannot be taken as definite evidence for a large separation between the n-π* states. Even if the splitting is large, our conclusion will not be altered essentially, since the main contribution to the rotational strength arises from Ψ_S^-, one of the lower n-π* states.

23) Since two benzene rings are not fixed in this compounds, the dihedral angle may fluctuate over a considerably wide range. The estimated value of θ corresponds to a weighted mean value.

24) When the actual spectrum is shown for the *R* optical isomer, the same spectrum with a reversed sign is taken for the *S* isomer.