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Magnetic Circular Dichroism Studies of 4,4′-Disubstituted Biphenyls

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The magnetic circular dichroism (MCD) and ultraviolet (UV) absorption spectra of 4,4′-disubstituted biphenyls were measured. The MCD spectra showed diverse spectral patterns reflecting the natures of the substituent groups. These observed MCD spectra were reproduced by the theoretical calculations based on the Pariser-Parr-Pople-SCF-CI method. The dihedral angles of 4,4′-disubstituted biphenyls were estimated to be about 20° by comparing the observed MCD spectra with the calculated ones. The assignments for the MCD bands of 4,4′-disubstituted biphenyls were given on the basis of these calculations. The substituent effects of biphenyls were interpreted by the use of the coefficients of the configuration interactions.

One of the most interesting aspects of the optical properties of biphenyl and its sterically hindered derivatives has been displayed by the appearance of an intense, structureless absorption band with its maximum at *ca.* 40000 cm^{-1}. The band is well known to be very sensitive to the variation in the torsional angle, θ, around the central carbon-carbon bond of biphenyl (see Fig. 1), giving rise to a change in both the location of the band and its intensity.$^{1)}$ The conjugation between the two benzene rings becomes large with a decrease in the dihedral angle of biphenyl. Thus, if the dihedral angle decreases, this band shows a marked red-shift and an enhancement in its intensity; therefore, it is called the conjugation band. The stable conformation of biphenyl is, in principle, established on the basis of a balance between the two effects, electronic delocalization and electrostatic repulsion between non-bonded atoms.$^{2)}$ Especially, however, repulsion among the hydrogen atoms at ortho positions (2, 6, 2′, and 6′ in Fig. 1) in the biphenyl skeleton is considered to be of primary importance. Accordingly, on substitution by bulky groups at the ortho positions, the dihedral angle of biphenyl increases due to the appreciable increase in steric repulsion, giving rise to a hypsochromic effect on the transition energy and a hypochromic effect on the intensity of the conjugation band. In fact, Beaven *et al.*$^{1)}$ have reported that the conjugation band shifts toward a higher-energy region with a decrease in its intensity on successive substitution by methyl groups at the ortho positions of biphenyl.

On the other hand, the dihedral angle is considered to change only slightly or remain unchanged on substitution at the para positions (4 and 4′ in Fig. 1). Kurland$^{3)}$ gave an equation in which the difference in chemical shift between the protons at the meta and ortho positions of biphenyl was expressed as a function of θ; using that equation, he then tried to estimate the dihedral angles, θ, of the 4,4′-disubstituted biphenyls, including 4,4′-dideuterated biphenyl. The experimental results were well reproduced by taking $\theta=45°$ in his equation. In addition, the dihedral angle is found to be independent of the substituent groups. On the other hand, Suzuki$^{4)}$ tried to elucidate the UV spectra of biphenyl and estimated the dihedral angle, θ, by making use of the core-resonance integral for the central bond as a function of θ. He obtained 0°, 23°, and 43° for biphenyl in gas, solution, and a crystalline state respectively. According to his results, the dihedral angles of 4,4′-disubstituted biphenyls in solution may be expected to take a value of about 20°.

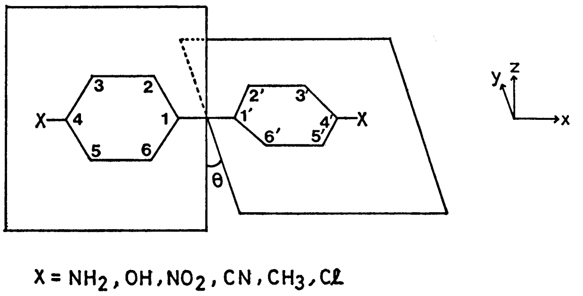

Fig. 1. The nuclear skeleton and coordinate system of 4,4′-disubstituted biphenyl.

So far, MCD studies, which are very useful for the investigation of the electronic states of the compounds, have been carried out on biphenyl, para-substituted biphenyls with electron-donating groups and bridged biphenyls.$^{5,6)}$ The 1st and 2nd MCD bands of the parent molecule, biphenyl, have positive and negative signs respectively, while those of the para-substituted derivatives have the opposite signs. Thus, the MCD spectra of biphenyls show an apparent substituent effect, suggesting that the MCD measurement is more sensitive with respect to the natures of the substituents than the UV measurement, and therefore useful in giving reasonable spectroscopic assignments.

The molecular orbital investigations of biphenyls were limited to those of biphenyl itself, using the Pariser-Parr-Pople method,$^{7,8)}$ molecules in the molecule method,$^{9)}$ and the CNDO/2 method.$^{10)}$

In this work, 4,4′-disubstituted biphenyls with various substituents are investigated by means of UV and MCD spectroscopies in order to examine the substituent effects in a systematic fashion. The calculations for the MCD spectra of these compounds were carried out on the basis of the PPP method so as to reproduce the observed MCD spectra and dihedral angles of 4,4′-disubstituted biphenyls in solutions. It seemed that it would be interesting to see to what extent the observed spectra for hindered biphenyls can be explained by theoretical calculations on the basis of a simple approximation.

Experimental

4,4′-Diaminobiphenyl, 4,4′-dihydroxybiphenyl, 4,4′-dinitrobiphenyl, 4,4′-dicyanobiphenyl, 4,4′-dichlorobiphenyl, and 4,4′-dimethylbiphenyl obtained commercially were recrystallized several times from appropriate solvents.

All the measurements were carried out at room temperature, using ethanol, methanol, or cyclohexane as solvents for the derivatives with strong electron-donating groups, with electron-attracting groups, or with weak electron-donating groups respectively. The MCD and UV spectra were measured on a JASCO-J20A recording spectropolarimeter equipped with a 1.14 T electromagnet and on a Hitachi EPS-3T recording spectrophotometer respectively.

Theoretical

The electronic transition energies, oscillator strengths, and Faraday B values of 4,4′-disubstituted biphenyls were estimated on the basis of the PPP method,[11] including configuration interactions among singly excited configurations with transition energies below 10 eV. One-center-core and repulsion integrals were evaluated from the valence-state ionization potentials and electron affinities. Two-center-core integrals were calculated by the use of the Wolfsberg-Helmholtz equation.[12] Two-center repulsion integrals were evaluated by the use of the Nishimoto-Mataga equation.[13] The repulsion integral, γ_{pq}, within a benzene ring was evaluated according to the usual formula:

$$\gamma_{pq} = \frac{14.397}{R_{pq}+a_{pq}} \text{ (eV)}, \tag{1}$$

$$a_{pq} = \frac{28.794}{\gamma_{pp}+\gamma_{qq}}, \tag{2}$$

where R_{pq} is the distance between the p and q atoms and where γ_{pp} stands for the one-center repulsion integrals. The repulsion integral, γ_{pq}, in which the p and q atoms belong to different benzene rings was calculated using Eq. 1, while modifying a_{pq} as follows:

$$a_{pq} = \frac{28.794}{(\gamma_{pp}+\gamma_{qq})\cos^2\theta+(\gamma'_{pp}+\gamma'_{qq})\sin^2\theta}, \tag{3}$$

$$\gamma'_{pp} = \gamma_{pp} - 6F_2, \tag{4}$$

where θ is the dihedral angle and F_2 is the Slater-Condon parameter. The benzene rings in biphenyl were assumed to be regular hexagons. The coordinate system employed is represented in Fig. 1. The x axis lies along the long molecular axis, and the y axis bisects the dihedral angle, θ. Since the repulsions among orthoprotons in 4,4′-disubstituted biphenyls are considered to be equal to that in biphenyl, their dihedral angles have been assumed to be equal throughout the calculations.

The theoretical Faraday B term associated with an electronic transition, $j \leftarrow a$, is expressed as follows:

$$\begin{aligned} B(j\leftarrow a) = \mathrm{Im}\{ & \sum_{k\neq a} (\langle k|\vec{\mu}|a\rangle/(E_k-E_a))\cdot \\ & \langle a|\vec{M}|j\rangle \times \langle j|\vec{M}|k\rangle \\ & + \sum_{k\neq j} (\langle j|\vec{\mu}|k\rangle/(E_k-E_j))\cdot \\ & \langle a|\vec{M}|j\rangle \times \langle k|\vec{M}|a\rangle\}, \end{aligned} \tag{5}$$

where $\vec{\mu}$ and $\vec{M}$ denote the magnetic and electronic dipole moment operators respectively. The quantities in the denominator, E_k *etc.*, are the energies of the k states. The electric-transition dipole moments were estimated on the basis of the dipole-velocity method. The atomic integrals of the electric and magnetic dipole moments were retained only for the nearest neighbor atoms, while those for the distant atoms were neglected because they were small and expected no decisive effect on the calculated results. The orthogonalized set of atomic orbitals obtained by the Löwdin procedure[14] was used for the calculations of these quantities. The calculations were carried out by using the ACOS-700 computer in the Computer Center of Tohoku University.

Results and Discussion

The UV and MCD spectra of 4,4′-dihydroxybiphenyl are represented in Fig. 2, where ε is the molar extinction coefficient in $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ and where $[\theta]_M$ is the molar ellipticity in degree $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$

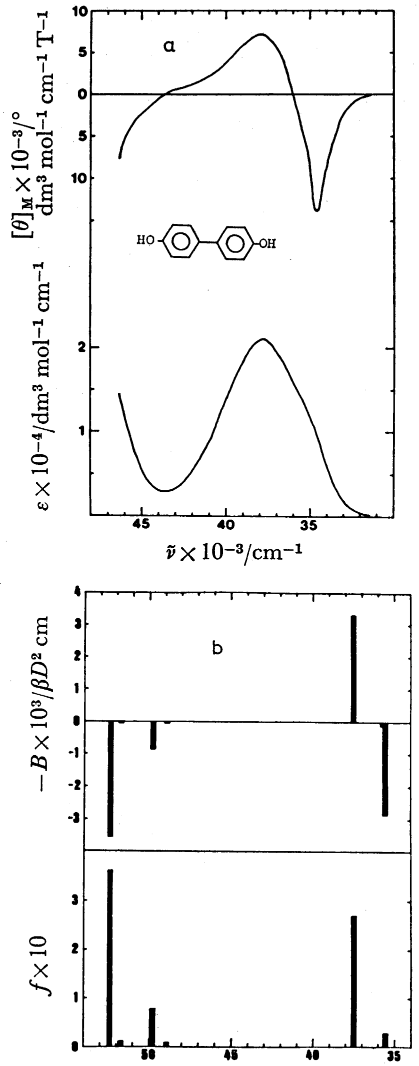

Fig. 2. The observed and calculated results of 4,4′-dihydroxybiphenyl.
(a) The MCD (top) and UV (bottom) spectra in ethanol measured at room temperature. (b) The calculated Faraday B value (top) and oscillator strength (bottom).

T^{-1}. The UV spectrum shows a single peak with its maximum at 37800 cm^{-1}, whereas the MCD spectrum exhibits a negative peak at 34600 cm^{-1} and a positive peak at 38000 cm^{-1}. 4,4′-Diaminobiphenyl shows a spectral profile (Fig. 3) similar to that of the dihydroxy derivative— a negative band at a lower frequency and a positive at a higher, but its MCD peaks shift toward a frequency region higher by about 2000 cm^{-1} in comparison with the dihydroxy derivative.

On the contrary, the MCD spectra of nitro and cyano derivatives show a positive band in the lower-frequency region and a negative in the higher, while the MCD extrema of the former are observed in a frequency region lower by about 3000 cm^{-1} than that of the latter (Figs. 4 and 5).

Furthermore, the signs of the MCD spectra of the methyl and chloro derivatives are all negative in the corresponding spectral region (Figs. 6 and 7). Thus, the UV spectrum of each compound is apparently observed as a single peak in the spectral region of 35000—40000 cm^{-1}, whereas the MCD spectra show various spectral patterns corresponding to the natures of the substituent groups.

The estimated Faraday B values (B) and oscillator strengths (f) are represented in Figs. 2—7. The longitudinal axis takes $-B$, since the Faraday parameter, B, appears as $-B$ in the expression of the molar ellipticity $[\theta]_M$. The estimated Faraday B values for the hydroxy and amino derivatives show positive signs in the lower-frequency region and negative signs in the higher, whereas those for the nitro and cyano derivatives are negative in the lower region and positive in the higher. The methyl derivatives are all predicted to have positive B values. The transition energies of hydroxy, amino, nitro, and methyl derivatives are in fairly good agreement with the experiments. However, in the cyano derivative the energy separation between the 1st and 2nd MCD bands is too small in comparison with the observed

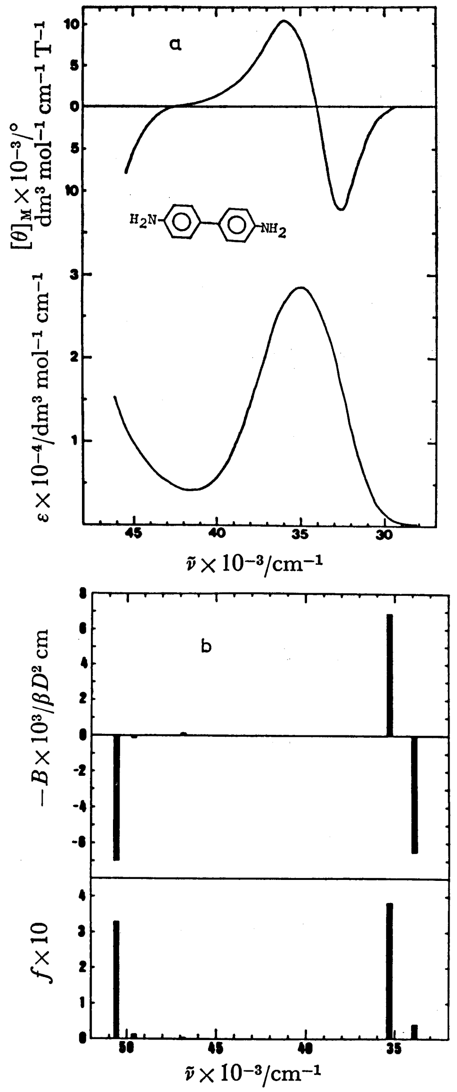

Fig. 3. The observed and calculated results of 4,4′-diaminobiphenyl.
(a) The MCD (top) and UV (bottom) spectra in ethanol measured at room temperature. (b) The calculated Faraday B value (top) and oscillator strength (bottom).

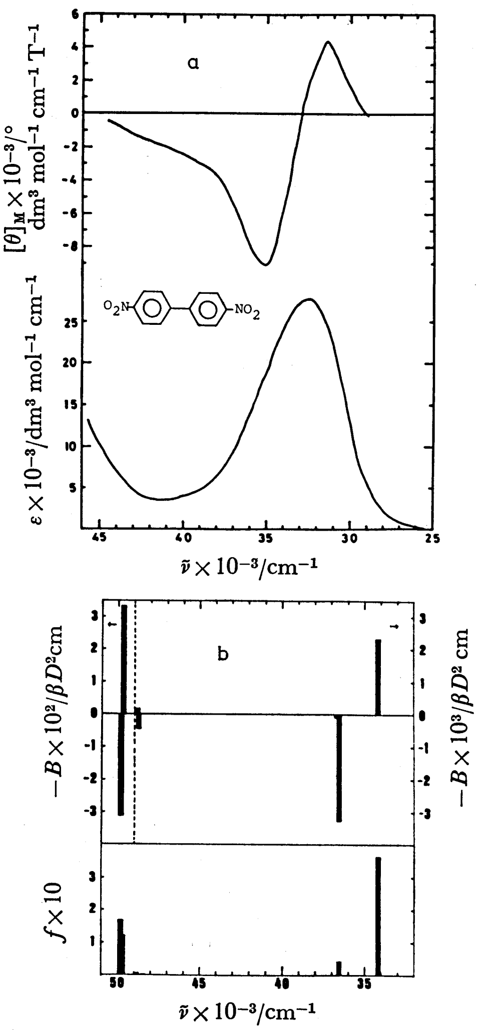

Fig. 4. The observed and calculated results of 4,4′-dinitrobiphenyl.
(a) The MCD (top) and UV (bottom) spectra in methanol measured at room temperature. (b) The calculated Faraday B value (top) and oscillator strength (bottom).

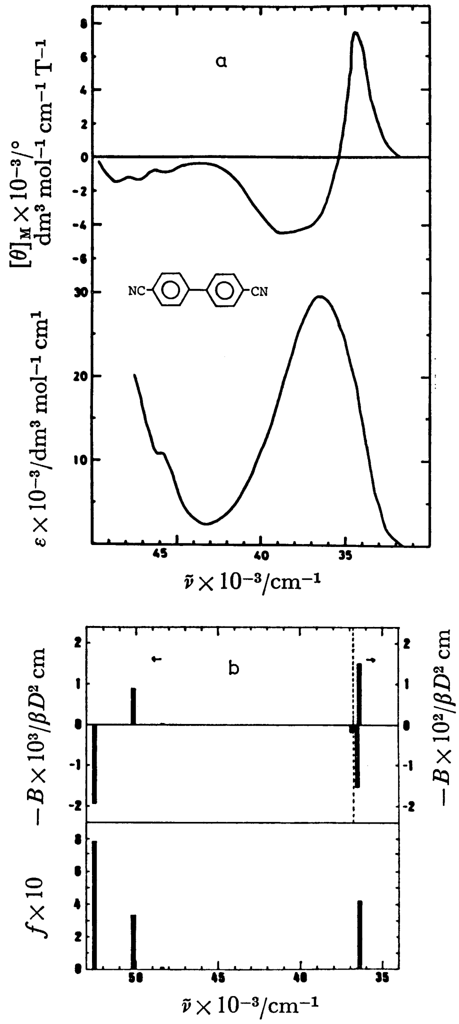

Fig. 5. The observed and calculated results of 4,4′-dicyanobiphenyl.
(a) The MCD (top) and UV (bottom) spectra in methanol measured at room temperature. (b) The calculated Faraday B value (top) and oscillator strength (bottom).

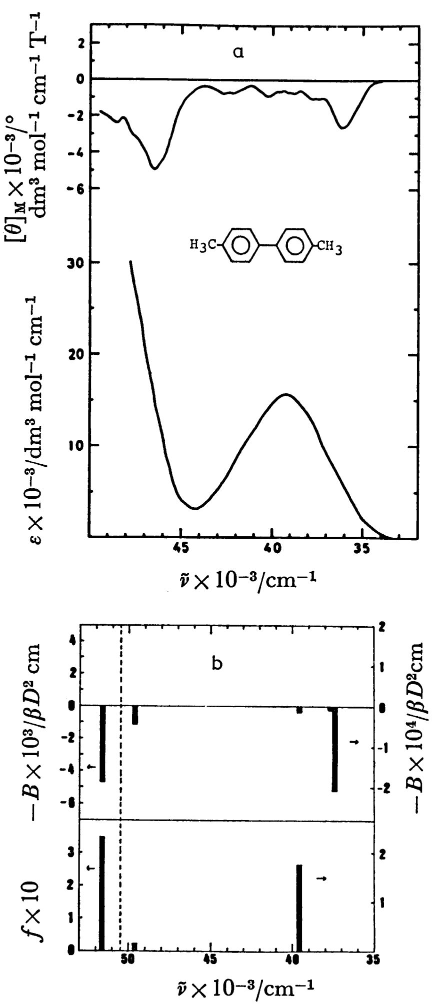

Fig. 6. The observed and calculated results of 4,4′-dimethylbiphenyl.
(a) The MCD (top) and UV (bottom) spectra in cyclohexane measured at room temperature. (b) The calculated Faraday B value (top) and oscillator strength (bottom).

one, and the experimental MCD signs of the chloro derivative are not reproduced. The disagreement between the calculations and experiments in cyano and chloro derivatives is mainly due to the parametrizations for atomic integrals in the present calculations.

The calculated results are summarized and listed in Table 1. The 4,4′-disubstituted biphenyls belong to the point group, D_2, as well as the parent molecule. The 1st, 2nd, and 3rd $\pi^*\leftarrow\pi$ transitions of the hydroxy, amino and methyl derivatives are calculated to be $^1B_2\leftarrow{}^1A$, $^1B_1\leftarrow{}^1A$, and $^1B_3\leftarrow{}^1A$ respectively, whereas those in the nitro and cyano derivatives to be $^1B_3\leftarrow{}^1A$, $^1B_2\leftarrow{}^1A$, and $^1B_1\leftarrow{}^1A$. Therefore, the 1st and 2nd MCD bands of the derivatives with electron-donating groups are assigned to the $^1B_2\leftarrow{}^1A$ and $^1B_3\leftarrow{}^1A$ transitions respectively, and those of derivatives with electron-attracting groups, to the $^1B_3\leftarrow{}^1A$ and $^1B_2\leftarrow{}^1A$ transitions. The $^1B_1\leftarrow{}^1A$ transitions in the lower-frequency region of all the compounds are considered to be too weak to be distinctly observed.

In the above MCD calculations, the dihedral angles of all the compounds were assumed to be 20°. On the contrary, according to Kurland,$^{3)}$ the dihedral angles of 4,4′-disubstituted biphenyls were supposed to be 45°; in that way the observed NMR spectra were well explained. The calculation of the transition energies and Faraday B parameters was carried out for the hydroxy, amino, and nitro derivatives, in which the dihedral angles were taken to be 45°. The results are summarized and listed in Table 2, along with the results with $\theta=20°$. The results calculated with $\theta=45°$ seemed to be in poor agreement, especially with respect both to the excitation energies and Faraday B values, with the experimental values. Accordingly, it is concluded that the dihedral angles of 4,4′-disubstituted biphenyls in solution are about 20°.

In Fig. 8 the molecular orbitals of biphenyl, 4,4′-diaminobiphenyl, and 4,4′-dinitrobiphenyl are schematically illustrated in order to show the interaction between biphenyl and the substituents. In the derivatives with electron-donating groups, the molecular orbitals of substituents interact, preferably with

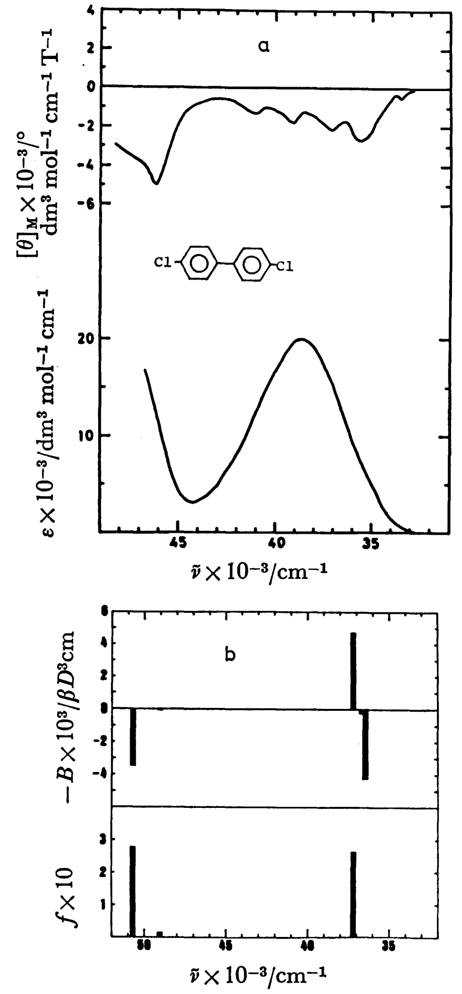

Fig. 7. The observed and calculated results of 4,4′-dichlorobiphenyl.
(a) The MCD (top) and UV (bottom) spectra in cyclohexane measured at room temperature. (b) The calculated Faraday *B* value (top) and oscillator strength (bottom).

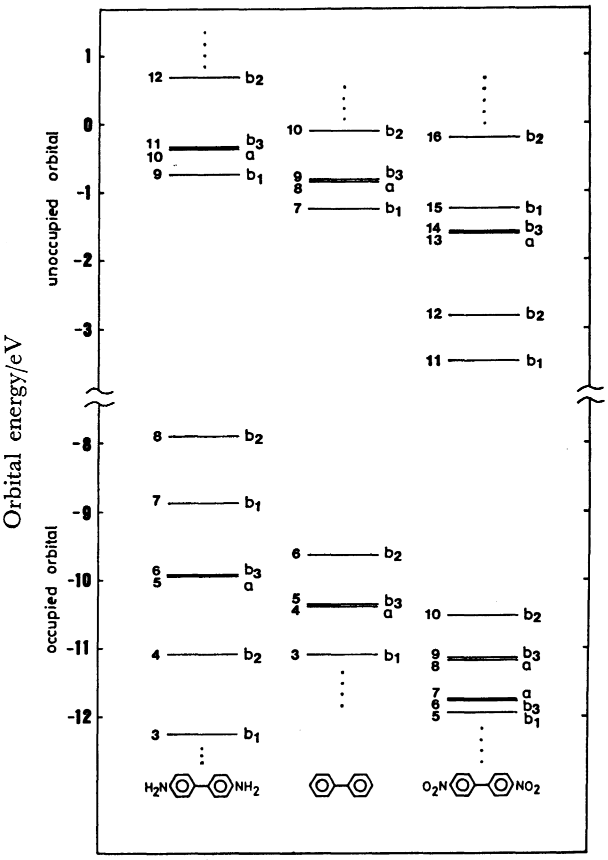

Fig. 8. The molecular orbitals of biphenyl, 4,4′-diaminobiphenyl, and 4,4′-dinitrobiphenyl.

the upper occupied orbitals of biphenyl, so that some of the occupied orbitals of biphenyl are destabilized. On the contrary, in the derivatives with electron-attracting groups, the molecular orbitals of substituents preferably interact with the lower unoccupied orbitals of biphenyl.

In Table 3 the wave functions which describe the three lowest excited states of biphenyl, 4,4′-diaminobiphenyl, and 4,4′-dinitrobiphenyl are shown, where $\phi_{k\to l}$ denotes a singly excited configuration from the k-th molecular orbital to the l-th. As is expected from Fig. 8, the lowest-energy excited state is considered to make a dominant contribution to the singly excited configuration arising from the LUMO← HOMO transition in each molecule. However, the lowest B_3 state is not able to be the lowest because of the weak configuration interaction with the higher B_3 states. On the contrary, the strong configuration interaction between $\phi_{5\to7}$ and $\phi_{6\to8}$ and that between $\phi_{4\to7}$ and $\phi_{6\to9}$ lower the B_2 and B_1 states below the B_3 state. This is also true for the amino derivative. In the nitro derivative, there exists a configuration with B_3 symmetry, $\phi_{5\to12}$, close to the $\phi_{10\to11}$ arising from the single excitation from the HOMO to the LUMO. The energy level of the B_3 state is lowered appreciably due to the configuration interaction, whereas the effect of the configuration interaction among the B_2 states, and also that among B_1 configurations, does not exceed the stabilization of the B_3 states. Consequently, the B_3 state is the lowest energy state in the nitro derivative.

The discrepancy of the MCD signs between the derivatives with the strong electron-donating groups and those with the attracting groups can then be explained. Here, only the strong MCD bands in the lower-frequency region in both derivatives are considered; they are assigned to the $^1B_2 \leftarrow {}^1A$ and $^1B_3 \leftarrow {}^1A$ transitions in the former and to $^1B_3 \leftarrow {}^1A$ and $^1B_2 \leftarrow {}^1A$ in the latter. As can clearly be seen from Eq. 5, the contribution of the 2nd term is considered to be of primary importance in the calculation of the Faraday *B* values because of its appreciable contribution to Eq. 5 thanks to the small energy difference in the denominator. Furthermore, the matrix element of the nearest neighboring state is of crucial importance; for example, the B_2 state mixes with B_3, and *vice versa.*

The excited electronic-wave functions of biphenyl derivatives are considered to be expressed for the lowest B_2 and B_3 states by a slight modification of the wave functions of biphenyl itself:

TABLE 1. THEORETICAL TRANSITION ENERGIES ($\tilde{\nu}$), OSCILLATOR STRENGTHS (f), AND FARADAY B VALUES (B) OF 4,4′-DISUBSTITUTED BIPHENYLS

Compound	Symmetry	Theoretical			Experimental	
		$\tilde{\nu}\times10^{-3}$ / cm^{-1}	f	$-B\times10^{5}$ / $\beta D^2/\mathrm{cm}^{-1}$	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	$[\theta]_M^{\max}\times10^{-3}$
4,4′-Dihydroxybiphenyl	$^1B_2\leftarrow{}^1A$	35.54	0.028	−286.3	34.60	−13.84
	$^1B_1\leftarrow{}^1A$	35.69	0.001	−11.7	—	—
	$^1B_3\leftarrow{}^1A$	37.54	0.270	331.9	37.88	7.10
4,4′-Diaminobiphenyl	$^1B_2\leftarrow{}^1A$	33.87	0.043	−652.8	32.68	−12.23
	$^1B_1\leftarrow{}^1A$	33.90	0.002	−24.2	—	—
	$^1B_3\leftarrow{}^1A$	35.31	0.381	689.1	36.10	10.37
4,4′-Dinitrobiphenyl	$^1B_3\leftarrow{}^1A$	34.20	1.346	233.6	31.45	4.36
	$^1B_2\leftarrow{}^1A$	36.64	0.139	−327.2	35.10	−9.01
	$^1B_1\leftarrow{}^1A$	36.72	0.005	−11.6	—	—
4,4′-Dicyanobiphenyl	$^1B_3\leftarrow{}^1A$	36.46	0.421	1512	34.36	7.44
	$^1B_2\leftarrow{}^1A$	36.61	0.003	−1546	38.50	−4.41
	$^1B_1\leftarrow{}^1A$	36.93	0.0002	−22.0	—	—
4,4′-Dimethylbiphenyl	$^1B_2\leftarrow{}^1A$	37.40	0.0003	−20.8	36.01	−2.51
	$^1B_1\leftarrow{}^1A$	37.71	0.000	−0.76	—	—
	$^1B_3\leftarrow{}^1A$	39.57	0.176	−1.50	39.30	−0.62
	$^1B_1\leftarrow{}^1A$	49.63	0.016	−4.59	46.51	−4.89
4,4′-Dichlorobiphenyl	$^1B_2\leftarrow{}^1A$	36.45	0.009	−425.6	35.52	−2.65
	$^1B_1\leftarrow{}^1A$	36.74	0.0004	−26.7	—	—
	$^1B_3\leftarrow{}^1A$	37.24	0.265	468.3	38.61	−2.16
	$^1A\leftarrow{}^1A$	46.83	forb.	—	—	—
	$^1B_1\leftarrow{}^1A$	49.04	0.014	−8.85	46.08	−4.95

TABLE 2. THE CALCULATED RESULTS OF HYDROXY, AMINO, AND NITRO DERIVATIVES WITH THE DIHEDRAL ANGLES OF 20° AND 45°

Compound	20°		45°		Experimental	
	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	$B\times10^{5}$ / $\beta D^2/\mathrm{cm}^{-1}$	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	$B\times10^{5}$ / $\beta D^2/\mathrm{cm}^{-1}$	$\tilde{\nu}\times10^{-3}$ / cm^{-1}	$B\times10^{5}$ / $\beta D^2/\mathrm{cm}^{-1}$
4,4′-Dihydroxy-	35.54	286.3	36.16	171.9	34.60	338.0
	35.69	11.7	36.17	28.7	—	—
	37.54	−331.9	39.98	−197.4	37.88	−436.0
4,4′-Diamino-	33.87	652.8	34.45	257.8	32.68	456.0
	33.90	24.2	34.40	51.1	—	—
	35.31	−689.1	37.55	−346.5	36.10	−531.0
4,4′-Dinitro-	34.20	−233.6	36.17	−636.0	31.45	−161.0
	36.64	327.2	37.32	620.2	35.10	642.3
	36.72	11.6	37.30	116.8	—	—

TABLE 3. THE WAVE FUNCTIONS OF THE $\pi^*\leftarrow\pi$ STATES OF BIPHENYL AND 4,4′-DISUBSTITUTED BIPHENYLS

Compound	State	Wave function
Biphenyl	$^1B_2$	$0.639\ (\phi_{5\to7}-\phi_{6\to8})+0.303\ (\phi_{4\to10}-\phi_{3\to9})$
	$^1B_1$	$0.634\ (\phi_{4\to7}+\phi_{6\to9})+0.312\ (\phi_{5\to10}+\phi_{3\to8})$
	$^1B_3$	$0.986\ \phi_{6\to7}+0.077\ (\phi_{6\to11}+\phi_{2\to7})+0.080\ \phi_{4\to9}+0.070\ \phi_{5\to8}$
4,4′-Diamino-	$^1B_2$	$0.813\ \phi_{8\to10}-0.376\ (\phi_{6\to9}+\phi_{7\to11})+0.222\ \phi_{5\to12}$
	$^1B_1$	$0.824\ \phi_{8\to11}-0.392\ \phi_{7\to10}+0.340\ \phi_{5\to9}-0.211\ \phi_{6\to12}$
	$^1B_3$	$0.981\ \phi_{8\to9}-0.152\ \phi_{7\to12}$
4,4′-Dinitro-	$^1B_3$	$0.969\ \phi_{10\to11}+0.233\ \phi_{5\to12}+0.040\ (\phi_{9\to13}+\phi_{8\to14})$
	$^1B_2$	$0.814\ \phi_{9\to11}+0.422\ \phi_{8\to12}-0.395\ \phi_{10\to13}$
	$^1B_1$	$0.824\ \phi_{8\to11}+0.441\ \phi_{9\to12}-0.352\ \phi_{10\to14}$

$$\begin{aligned}\Psi_{B_2} &= C_1\psi_{5\to7} - C_2\psi_{6\to8} + C_3\psi_{4\to10} - C_4\psi_{3\to9}\\ \Psi_{B_3} &= \psi_{6\to7},\end{aligned} \tag{6}$$

where the coefficients, C_1—C_4, are taken to be positive. In biphenyl, C_1 is equal to C_2, and C_3 to C_4.

The Faraday *B* terms of the B_2 and B_3 states are expressed as follows within this nearest-neighbor approximation:

$$\begin{aligned}B(B_2 \leftarrow A) &= -\mathrm{Im}<B_2|\mu_z|B_3><A|M_y|B_2>\\ &\qquad \times <B_3|M_x|A>/(E_{B_3}-E_{B_2})\\ B(B_3 \leftarrow A) &= \mathrm{Im}<B_3|\mu_z|B_2><A|M_x|B_3>\\ &\qquad \times <B_2|M_y|A>/(E_{B_2}-E_{B3}).\end{aligned} \tag{7}$$

As can clearly be seen from Eq. 7, $B(B_2 \leftarrow A) = -B(B_3 \leftarrow A)$. In amino derivatives the following equations hold for the energies and the off-diagonal matrix element of the μ_z operator:

$$E_{B_2} < E_{B_3} \tag{8}$$

$$\begin{aligned}\mathrm{Im}<B_2|\mu_z|B_3> &= \beta\{C_1<\phi_5|\vec{r}\times\vec{\nabla}|\phi_6>_z\\ &\qquad -C_2<\phi_8|\vec{r}\times\vec{\nabla}|\phi_7>_z\}\\ &\approx \beta\{0.7C_1+1.1C_2\} > 0,\end{aligned} \tag{9}$$

where β is the Bohr magneton and where ϕ_k denotes the *k*-th molecular orbital of biphenyl.

The configurations, $\psi_{5\to7}$, $\psi_{6\to8}$, $\psi_{4\to10}$, and $\psi_{3\to9}$, in biphenyl correspond to $\psi_{6\to9}$, $\psi_{8\to10}$, $\psi_{5\to12}$, and $\psi_{7\to11}$ respectively in the amino derivative. If the para-positions of biphenyl are replaced by the electron-donating groups, such as $-NH_2$ or $-OH$, the energy levels of $\psi_{6\to8}$ and $\psi_{3\to9}$ are found to be lower than those of $\psi_{5\to7}$ and $\psi_{4\to10}$ respectively, as may be seen from Fig. 8 and Table 3. This means that $C_1 < C_2$ and $C_3 < C_4$. Then, the off-diagonal matrix element of M_y, $<A|M_y|B_2>$, is expressed as:

$$\begin{aligned}<A|M_y|B_2> &= \sqrt{2}\{C_1<\phi_5|m_y|\phi_7>-C_2<\phi_6|m_y|\phi_8>\\ &\qquad + C_3<\phi_4|m_y|\phi_{10}>-C_4<\phi_3|m_y|\phi_9>\}\\ &\approx \sqrt{2}\{(C_1-C_2)m_1+(C_3-C_4)m_2\} < 0,\end{aligned} \tag{10}$$

where;

$$<\phi_5|m_y|\phi_7> \approx <\phi_6|m_y|\phi_8> \equiv m_1 > 0,$$

and

$$<\phi_4|m_y|\phi_{10}> \approx <\phi_3|m_y|\phi_9> \equiv m_2 > 0.$$

In addition, the matrix element, $<B_3|M_x|A>$, is calculated to be:

$$<B_3|M_x|A> = \sqrt{2}<\phi_6|m_x|\phi_7> > 0. \tag{11}$$

From Eqs. 7—11, the Faraday *B* values for the derivatives with strong electron-donating groups are found to be:

$$B(B_2 \leftarrow A) = -B(B_3 \leftarrow A) > 0. \tag{12}$$

On the contrary, in the nitro derivative,

$$E_{B3} < E_{B_4}. \tag{13}$$

Equations 9 and 11 hold for the nitro derivative as well as the amino derivative, but with $C_1 > C_2$ and $C_3 > C_4$ the matrix element, $<A|M_y|B_2>$, of the nitro derivative has the opposite sign of that of the amino derivative. Therefore, this leads to the following relationship:

$$<A|M_y|B_2> > 0. \tag{14}$$

From Eqs. 9, 11, 13, and 14, the signs of the Faraday *B* values of the nitro derivative are shown to be the same as in Eq. 12; *i.e.*,

$$B(B_2 \leftarrow A) = -B(B_3 \leftarrow A) > 0.$$

Equation 12 implies that the MCD band which is assigned to the $^1B_2 \leftarrow {}^1A$ transition must be negative and that the MCD band which is assigned to the $^1B_3 \leftarrow {}^1A$ transition must be positive. In the hydroxy and amino derivatives, the electronic transitions are $^1B_2 \leftarrow {}^1A$ and $^1B_3 \leftarrow {}^1A$ in the increasing order of energy; therefore the MCD profile is negative for the 1st band and positive for the 2nd band. In the nitro and cyano derivatives, the situation is completely reversed; the MCD profile is positive for the 1st MCD band and negative for the 2nd band because of the inversion of the B_2 and B_3 excited states in these molecules.

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