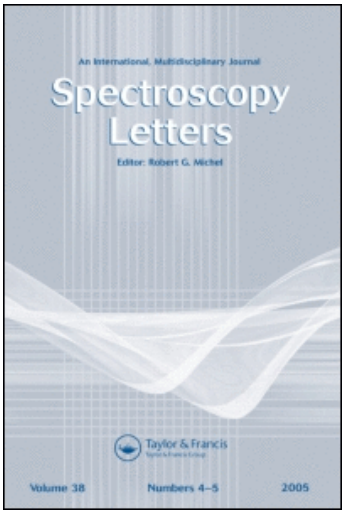


**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Magnetic Circular Dichroism Spectra of p-Disubstituted Benzenes Possessing Both Electron-Donating and Accepting Groups

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**To cite this Article** Teramae, Norio , Higuchi, Seiichiro and Tanaka, Shigeyuki(1977) 'Magnetic Circular Dichroism Spectra of p-Disubstituted Benzenes Possessing Both Electron-Donating and Accepting Groups', Spectroscopy Letters, 10: 12, 979 — 989
**To link to this Article: DOI:** 10.1080/00387017708065035
**URL:** http://dx.doi.org/10.1080/00387017708065035

SPECTROSCOPY LETTERS, 10(12), 979-989 (1977)

# MAGNETIC CIRCULAR DICHROISM SPECTRA OF p-DISUBSTITUTED BENZENES POSSESSING BOTH ELECTRON-DONATING AND ACCEPTING GROUPS

KEY WORDS: Magnetic Circular Dichroism, Molecular Orbital, Pariser-Parr-Pople, p-Disubstituted Benzene

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## ABSTRACT

The magnetic circular dichroism (MCD) and absorption spectra of some p-disubstituted benzenes possessing both electron-donating and accepting groups were measured. The electronic spectra of the above compounds are characterized by the appearance of two absorption bands, one of which appears at 25000-40000 $cm^{-1}$ region with large intensity, and another at 40000-50000 $cm^{-1}$ region with rather small intensity. These absorption bands, especially the latter one, have been investigated by means of the MCD spectra and molecular orbital calculations based on the Pariser-Parr-Pople method.

## INTRODUCTION

In the course of our MCD studies on organic compounds, we have reported the MCD spectra of substituted benzenes[1], mono-[2]

and di-substituted naphthalenes[3]. In the present paper, we report the MCD spectra of p-disubstituted benzenes containing both electron donating and accepting groups, such as p-nitroaniline.

All compounds investigated in this study exhibit two absorption bands, one of which appears in the frequency region of 25000-40000 $cm^{-1}$ with large intensity, and another in the frequency region of 40000-50000 $cm^{-1}$ with rather weak intensity. This spectral feature has been extensively investigated by means of molecular orbital calculations based on the composite molecule[4,5], Pariser-Parr-Pople(PPP)[6-8] and CNDO/s[9] methods, the absorption spectrum of a single crystal[5], the measurement of the electrically induced dichroism[10] and so on. Most of these studies have been concerned with the intense absorption band in the lower wave number region which has been assigned to the intramolecular charge-transfer band[5]. On the other hand, only slight attention has been paid to the weak absorption band in the higher wave number region, although the spectral assignments of nitroaniline and aminobenzoic acid isomers have been discussed by means of the MCD spectroscopic technique[11]. In this study, the measurement of the MCD spectra and molecular orbital calculation based on the PPP approximation have been carried out in order to characterize the above-mentioned absorption bands.

## EXPERIMENTAL

The MCD and absorption spectra were measured on a JASCO J-20 spectropolarimeter equipped with a 14.1-kG electromagnet and on a Shimadzu MPS-50L spectrophotometer, respectively. All the measurement were carried out at room temperature using ethanol as a solvent. All compounds, p-nitroaniline(p-$NO_2$,$NH_2$), p-nitro-N,N-dimethylaniline(p-$NO_2$,$NMe_2$), p-nitrophenol(p-$NO_2$,OH), p-N,N-dimethylaminobenzonitrile(p-$NMe_2$,CN), p-aminobenzoic acid(p-$NH_2$, COOH) and p-N,N-dimethylaminobenzaldehyde(p-$NMe_2$,CHO) were commercially obtained. Their infra-red spectra were measured on a JASCO IRA-2 spectrophotometer and were referred to the published data in order to identify them.



## METHOD OF CALCULATION

The electronic transition energies, oscillator strengths and polarizations were calculated by the PPP approximation[12,13], including configuration interaction among all singly excited configurations. One-center electron repulsion and core integrals were evaluated from valence state ionization potentials and electron affinities. Two-center repulsion integrals were obtained by means of the Nishimoto-Mataga formula[14], and optimum parameters suggested by several authors[8,15-18] were used for two-center resonance integrals. All molecules were assumed to be planar. It was assumed that all bond angles were $120^{\circ}$ except for

the case of C-C≡N and N-C≡$H_3$ in which they were taken to be 180°. Methyl group was treated with the pseudo-atom approximation[15]. Calculations were carried out using a HITAC 8700/8800 computer in the computer center of Tokyo University.

## RESULTS AND DISCUSSIONS

The calculated electronic transition energies, oscillator strengths and polarizations of p-$NO_2$,$NH_2$, p-$NO_2$,$NMe_2$, p-$NO_2$,OH and p-$NMe_2$,CN are summarized in TABLE 1. All molecules are assumed to belong to $C_{2v}$ point group within the framework of the pi electron approximation. According to these calculations, the intense absorption band in the lower wave number region includes two $\pi$-$\pi^*$ transitions polarized parallel (Y) and perpendicular (X) to the long molecular axis. As for the absorption band in the higher wave number region, it can be considered to be composed of two transitions with mixed polarizations for p-$NO_2$,$NH_2$ and p-$NO_2$,$NMe_2$. On the other hand, for p-$NO_2$,OH and p-$NMe_2$,CN, it can be considered to be composed of a single transition polarized along the X-axis. In contrast with our calculations, Labhart and Waginiere[10] assigned by means of the electrically induced dichroism and molecular orbital calculations that the absorption band in the higher wave number region of p-$NO_2$,$NMe_2$ molecule was composed of a single transition. In order to examine the above-mentioned calculated results for the polarizations of the absorption bands, the MCD

TABLE 1

Calculated Transition Energies, f-Values and Polarizations, and Observed Values Obtained from Absorption and MCD Spectra.

| Compounds | Calculated Values E(eV) | f-Val. | Pol. | Observed Values Absorption E(eV) | log ε | MCD E(eV) | B-Values* |
|---|---|---|---|---|---|---|---|
| p-$NO_2$,$NH_2$ | 3.86 | 0.658 | Y | 3.33 | 4.16 | 3.72 | +2.68 x$10^{-4}$ |
| | 4.34 | 0.002 | X | | | 4.19 | -2.48 |
| | 5.16 | 0.143 | X | 5.40 | 3.77 | 5.02 | +3.11 |
| | 5.67 | 0.004 | Y | | | 5.49 | negative |
| p-$NO_2$,$NMe_2$ | 4.02 | 0.676 | Y | 3.21 | 4.29 | 3.37 | +5.73 |
| | 4.25 | 0.017 | X | | | 4.04 | -3.81 |
| | 5.38 | 0.095 | X | 5.37 | 3.96 | 4.93 | +4.38 |
| | 5.48 | 0.003 | Y | | | 5.43 | -1.36 |
| p-$NO_2$,OH | 4.26 | 0.454 | Y | 3.97 | 4.03 | ** | |
| | 4.41 | 0.005 | X | | | | |
| | 5.57 | 0.037 | X | 5.55 | 3.87 | 5.55 | positive |
| p-$NMe_2$,CN | 4.48 | 0.001 | X | 4.25 | 4.51 | 3.99 | +24.4 |
| | 4.65 | 0.818 | Y | | | 4.34 | -25.7 |
| | 5.75 | 0.060 | X | 5.58 | 4.02 | 5.60 | +16.2 |

*) B-Value : $Debye^2 \cdot Bohr\ magneton/cm^{-1}$

**) Values could not be listed because of strong superimposition of two MCD bands with opposite signs.

spectra of these compounds have been measured, since the MCD technique has been known to be a powerful tool for elucidating the complicated electronic spectra[1-3,11,19-22].

The MCD and absorption spectra of p-$NO_2$,$NH_2$, p-$NO_2$,$NMe_2$, p-$NO_2$,OH and p-$NMe_2$,CN are shown in Figs. 1 and 2. In these figures, $[\theta]_M$ is molar ellipticity per unit magnetic field and

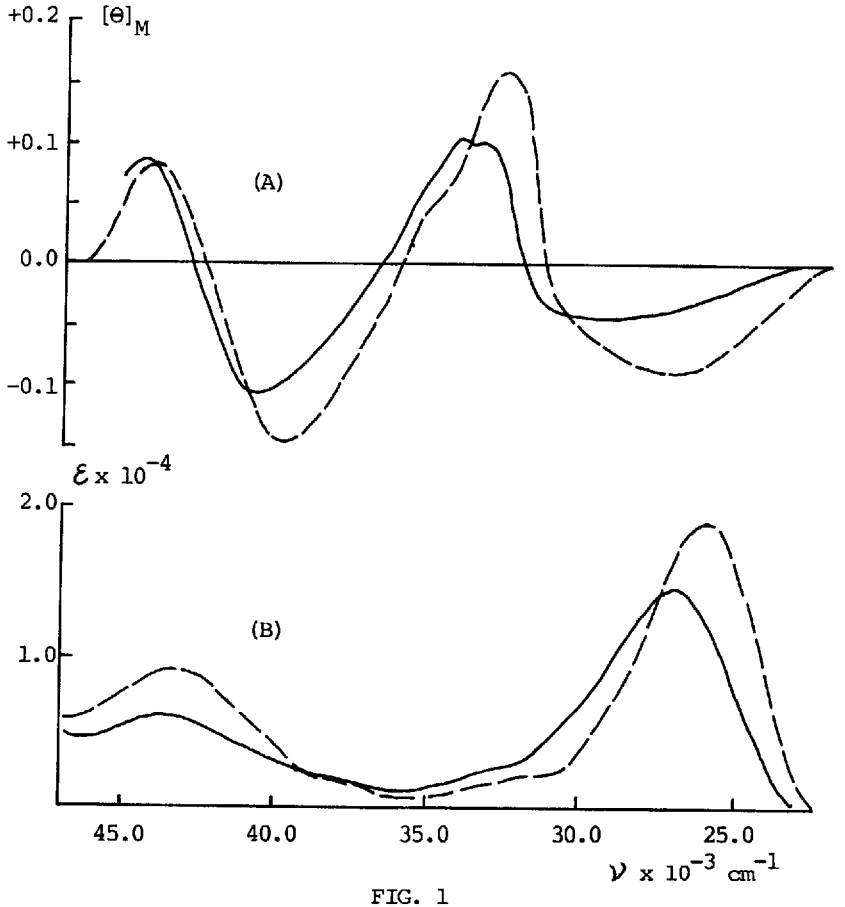


FIG. 1

MCD (A) and absorption (B) spectra of p-nitroaniline( ———— ) and p-nitro-N,N-dimethylaniline( – – – – – )

is expressed in degree·gauss$^{-1}$·cm$^{2}$·mole$^{-1}$ unit. The observed values are tabulated at the right side in TABLE 1.

As shown in Figs. 1 and 2, two MCD bands with opposite signs appear for the absorption band at 25000-40000 cm$^{-1}$ region. It is

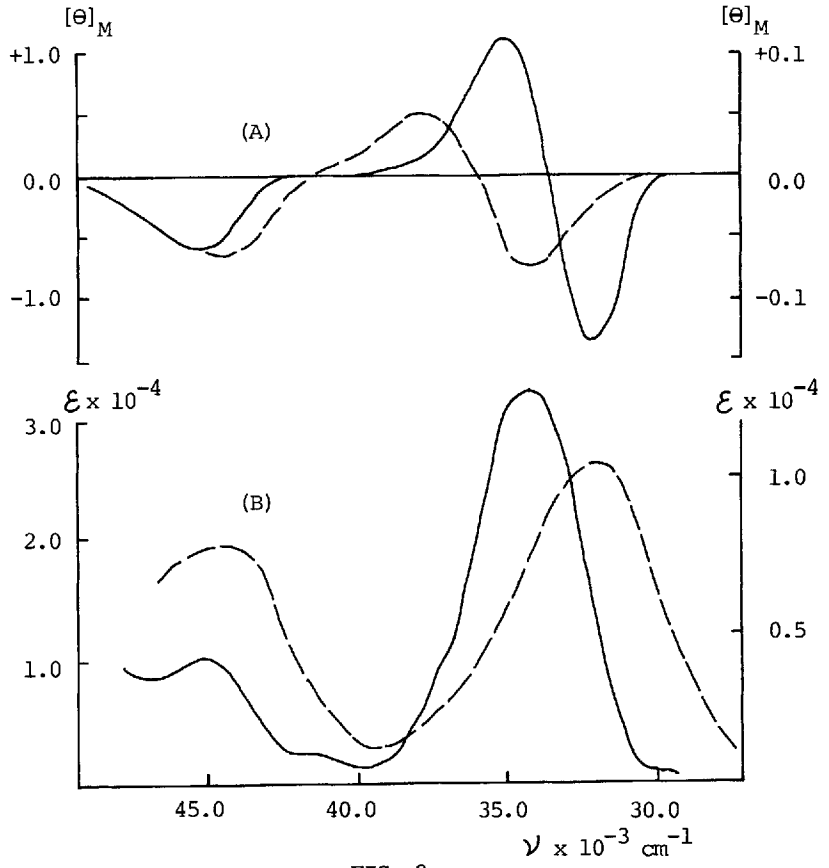


FIG. 2
MCD (A) and absorption (B) spectra of p-nitrophenol( - - - - - - - ) (right scale) and p-N,N-dimethylaminobenzonitrile( ———— ) (left scale).

clear, therefore, that this absorption band is composed of two transitions with mixed polarizations. As for the absorption band at 40000-50000 $cm^{-1}$, two MCD bands appear with opposite signs for p-$NO_2$,$NH_2$ and p-$NO_2$,$NMe_2$, although only single MCD band appears

for p-$NO_2$,OH and p-$NMe_2$,CN. On the basis of this MCD spectral feature, it is concluded that this absorption band is composed of two transitions with mixed polarizations for p-$NO_2$,$NH_2$ and p-$NO_2$, $NMe_2$, and of a single transition for p-$NO_2$,OH and p-$NMe_2$,CN. This conclusion is consistent with the prediction obtained by the molecular orbital calculations tabulated at the left side in TABLE 1.

The calculated transition energies and oscillator strengths of p-$NH_2$,COOH and p-$NMe_2$,CHO are tabulated at the left side in TABLE 2. The observed values of these compounds are also tabulated in its right side, and the MCD and absorption spectra are shown in FIG. 3. As shown in this figure, a single MCD band is



TABLE 2

Calculated Transition Energies and f-Values, and Observed Values Obtained from Absorption and MCD Spectra.

| Calculated Values | | | Observed Values Absorption | | MCD | |
|---|---|---|---|---|---|---|
| Compounds | E(eV) | f-Val. | E(eV) | log $\varepsilon$ | E(eV) | B-Values* |
| p-$NH_2$COOH | 4.35 | 0.016 | 4.28 | 4.36 | 4.08 | +16.2 x$10^{-4}$ |
| | 4.56 | 0.594 | | | 4.46 | -13.5 |
| | 5.75 | 0.177 | 5.61 | 4.01 | 5.61 | positive |
| p-$NMe_2$,CHO | 4.45 | 0.095 | 3.67 | 4.46 | 3.69 | +31.1 |
| | 4.51 | 0.564 | | | 4.12 | -31.8 |
| | 5.72 | 0.027 | 5.14 | 3.84 | 5.14 | +12.3 |

*) B-Value : $Debye^2 \cdot Bohr\ magneton/cm^{-1}$

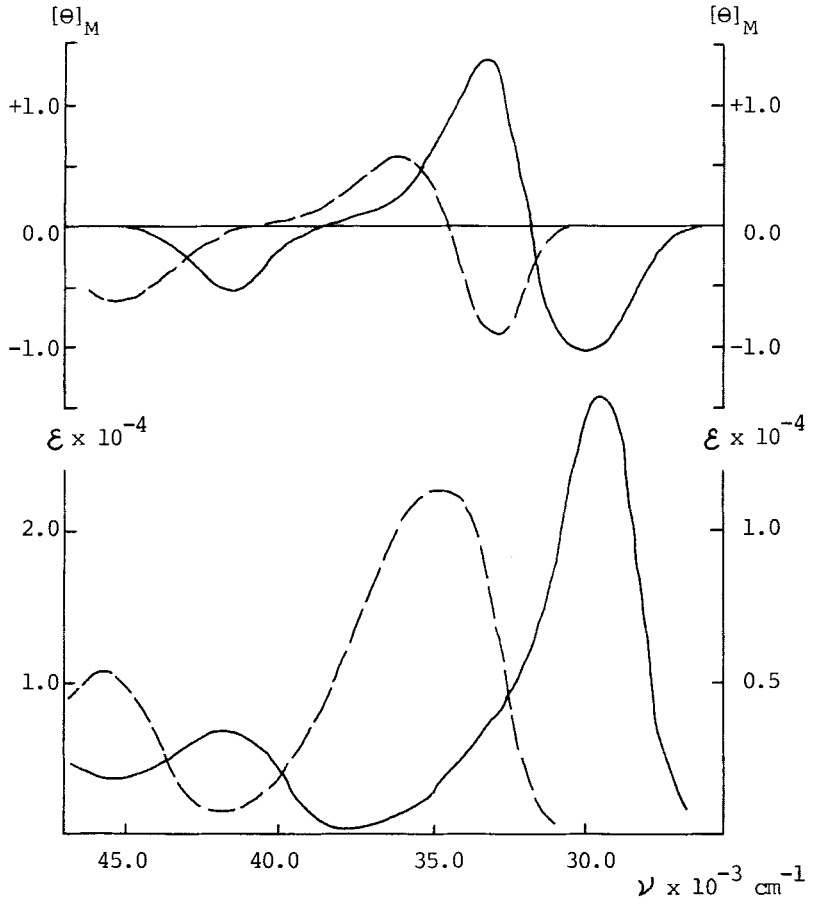


FIG. 3

MCD(A) and absorption(B) spectra of p-N,N-dimethylaminobenzaldehyde( ———— )(left scale) and p-aminobenzoic acid ( - - - - - )(right scale).

observed for the absorption band in the higher wave number region. It is concluded, therefore, that this absorption band is composed of a single transition for p-$NH_2$,COOH and p-$NMe_2$,CHO.

By means of the MCD spectra, the hidden transitions in strongly overlapped absorption bands are detected, and it is clarified that, for p-disubstituted benzenes investigated in this study, the absorption band in the lower wave number region is composed of two transitions, and that the absorption band in the higher wave number region is composed of two transitions for p-$NO_2$,$NH_2$ and p-$NO_2$,$NMe_2$, and of a single transition for p-$NO_2$,OH, p-$NMe_2$,CN, p-$NH_2$,COOH and p-$NMe_2$,CHO.



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Received: 9-16-77
Accepted: 9-21-77