Magnetic Circular Dichroism and Induced Circular Dichroism Spectra of *N*-Bromophthalimide

by **Syuuta Najiwara**, **Masahiro Kawamura**, and **Hiroyuki Yamaguchi***

Department of Materials Science, Faculty of Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi 316-8511, Japan

and **Miwako Higashi**

Cooperative Research and Development, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi 316-8511, Japan

and **Toshitaka Terasaka**

Department of Materials and Biological Sciences, Faculty of Science, Ibaraki University, Mito 310-8512, Japan

The magnetic circular dichroism (MCD), induced circular dichroism (ICD) spectra, and the absorption spectra of *N*-bromophthalimide have been measured. The ICD spectrum of the β-cyclodextrin complex with *N*-bromophthalimide is also reported. The absorption bands of *N*-bromophthalimide are assigned.

Introduction. – The electronic structure of *N*-bromophthalimide has not yet been clarified. The magnetic circular dichroism (MCD) technique has been used by several authors for the elucidation of complicated electronic spectra [1–6]. Recently, the ICD of the β-cyclodextrin complex has been shown to be a very simple tool for the assignment of absorption spectra [7–9].

Polarization investigations have also proved to be powerful in the determination of the symmetries of excited-state wave functions and in studying electronic interactions such as vibronic and spin-orbit coupling [10][11]. Therefore, we have investigated the polarization of the absorption bands of *N*-bromophthalimide by measuring its MCD spectrum and the ICD spectrum of its β-cyclodextrin complex.

Experimental. – *N*-Bromophthalimide was isolated as a pure crystalline material by recrystallization with Et_2O. Commercial β-cyclodextrin was recrystallized three times from dist. H_2O.

The absorption spectra were recorded on a *Jasco Ubest-35* spectrophotometer. The MCD spectra were recorded with a *Jasco J-600C* circular dichrometer with a 1.32-T electromagnet. Spectral-grade solvents (EtOH) were used as received. The stoppered silica cells of 1-cm and 2-mm path-lengths were used.

The ICD spectra were measured using a *Jasco J-600C* circular dichrometer. To obtain an adequate signal-to-noise ratio, multiple scanning and averaging were accomplished using a personal computer. The concentration of β-cyclodextrin was maintained in all experiments at 1.00×10^{-2} M.

The *Faraday* **B** values were extracted from the MCD spectra by use of the formula

$$\mathbf{B} = -(33.53)^{-1} \int_{\text{band}} ([\theta]_M/\nu)\mathrm{d}\nu$$

where ν is the frequency in cm^{-1} and $[\theta]_M$ is the molar ellipticity in 10^{-1} deg · dm^3 · cm^{-1} · mol^{-1} · G^{-1} [1][2].

Results and Discussion. – The geometry of *N*-bromophthalimide calculated by the PM3 method and the molecular-coordinate system are shown in *Fig. 1*. The absorption and MCD spectra of *N*-bromophthalimide are shown in *Fig. 2*, together with the ICD

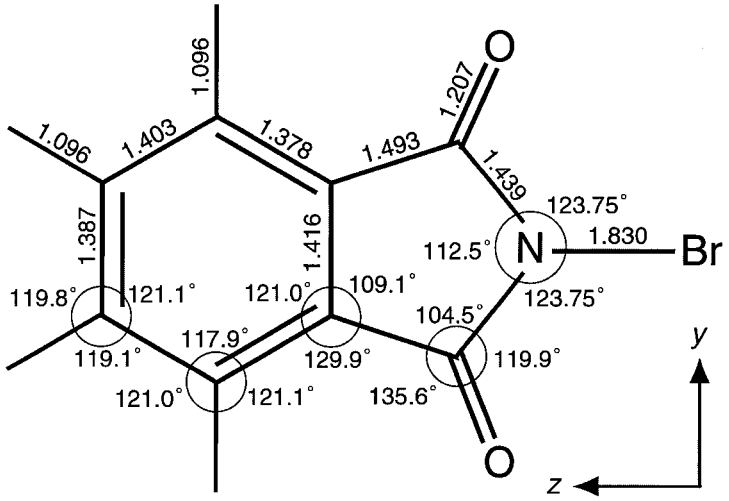

Fig. 1. *The bond lengths and bond angles of* N-*bromophthalimide calculated by the PM3 MO method*

spectrum of the inclusion complex with β-cyclodextrin. The MCD spectra of some quinones were measured and assigned by calculations of the PPP method and the CNDO/S method [5][6]. Well-parametrized PPP calculations turned out to be successful in interpreting the *Faraday* **B** terms of the $\pi \rightarrow \pi^*$ transitions. On the other hand, the position of the $n \rightarrow \pi^*$ transition is well predicted by the CNDO/S method. With the geometry obtained by the MNDO method, we calculated the electronic transition energies, oscillator strengths, and *Faraday* **B** terms using the PPP method [5]. The $n \rightarrow \pi^*$ transition energies were obtained by the CNDO/S method [12]. In *Fig. 2*, the calculated $(-1) \times$ (*Faraday* **B** values) and the calculated oscillator strength values are presented as bars.

According to the CNDO/S calculation, there are two $n \rightarrow \pi^*$ transitions in the wavelength region 315–335 nm. One is the allowed $^1B_1$ (x-direction) at 332 nm and the other is the forbidden $^1A_2$ transition at 318 nm. The MCD spectrum of *N*-bromophthalimide shows the negative band (positive *Faraday* **B** term) around 330 nm. In the ICD spectra of β-cyclodextrin complexes, it has been shown that the transition of the guest molecules with a transition dipole moment parallel to the molecular axis of β-cyclodextrin results in a positive CD value. On the other hand, the transition with a transition dipole moment perpendicular to the axis of β-cyclodextrin results in a negative CD value [7–9]. The geometric structure of β-cyclodextrin excludes the formation of an equatorial inclusion complex in the case of *N*-bromophthalimide [13][14]. Thus, the long molecular axis (z-axis) is parallel to the molecular axis of β-cyclodextrin. The ICD spectrum of *N*-bromophthalimide shows that the transition around 330 nm is polarized perpendicularly to the z-axis. Accordingly, it can be concluded that the band around 330 nm consists of the allowed $^1B_1$ ($n \rightarrow \pi^*$) transition.

In the first absorption band (250–310 nm), the MCD spectrum indicates a positive band. One positive ICD band is also observed in the same wavelength region. According to the PPP calculation, there are two $\pi \rightarrow \pi^*$ transitions, which are $^1A_1$ (z-

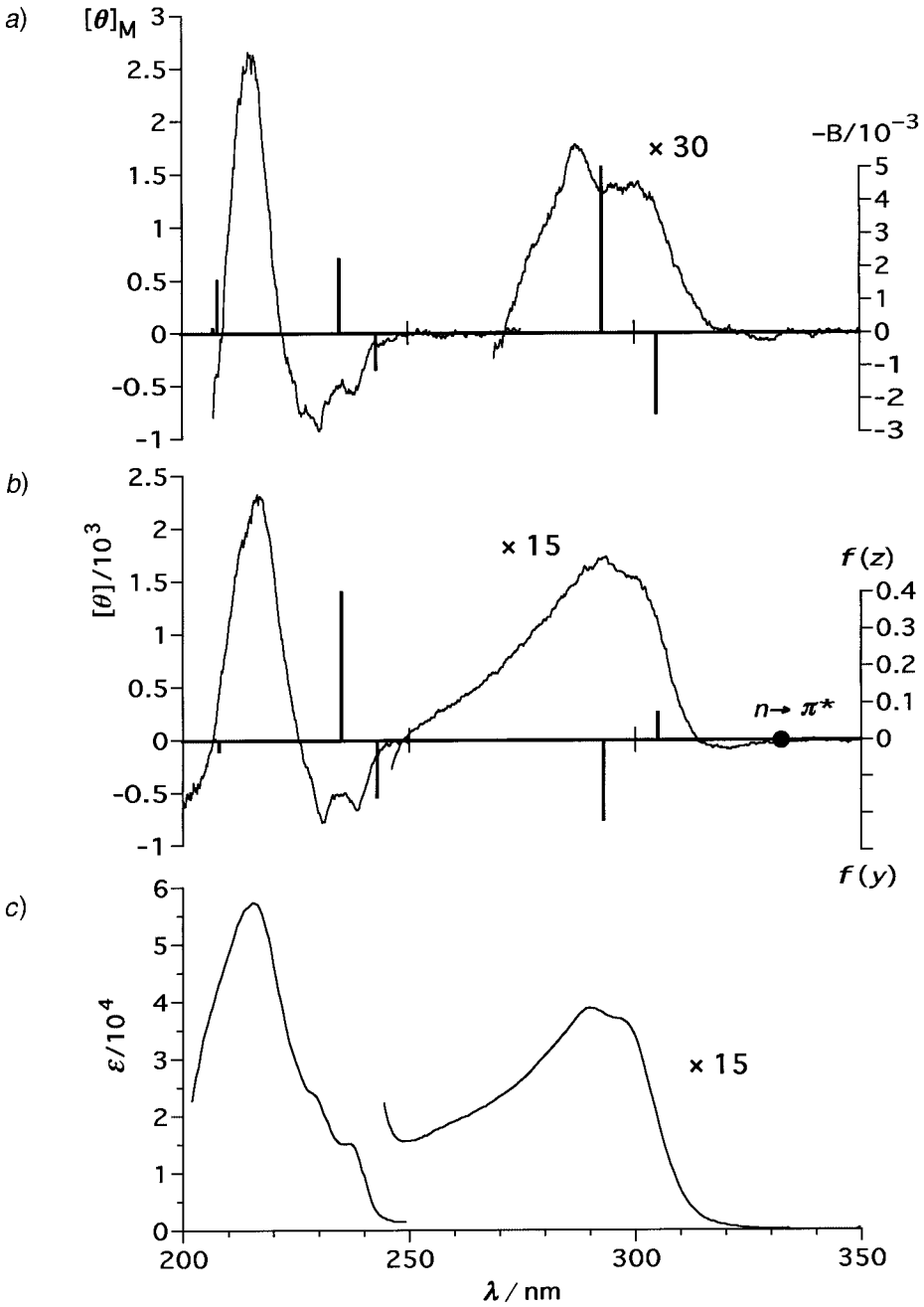

Fig. 2. *The MCD spectrum* (*a*) *and absorption spectrum* (*c*) *of* N-*bromophthalimide in EtOH, and ICD spectrum* (*b*) *of the* β*-cyclodextrin complex with* N-*bromophthalimide in 20% aq. EtOH soln*. The bars are calculated (– **B**) values (*a*) and calculated oscillator strengths (*b*) for the $\pi \rightarrow \pi^*$ transitions. For the oscillator strengths, the negative bars represent the *y*-polarized transitions, and positive bars represent the *z*-polarized transitions.

direction) and $^1B_2$ transitions (*y*-direction) and have mutually opposite *Faraday* **B** terms. The MCD ($^1A_1$) or ICD ($^1B_2$) bands may be hidden by the other strong band.

In the second absorption band (210–250 nm), the MCD spectrum indicates the +/− signal alternation. The *Faraday* **B** values extracted from the MCD spectra are -2.81×10^{-3} and 1.47×10^{-3} *Bohr* magneton (*Debye*)^2 cm^{-1}. The calculated *Faraday* **B** values are -2.24×10^{-3} ($^1A_1$ transition) and 1.08×10^{-3} ($^1B_2$ transition) *Bohr* magneton (*Debye*)^{2}cm^{-1}. As shown by *Larkindale* and *Simkin* [15], two adjacent mutually perpendicular transitions have Faraday **B** values (the sign of the Faraday **B** term is opposite to that in the MCD spectrum) that are nearly equal in magnitude but opposite in sign. In the ICD spectrum, the negative and positive strong bands appear in the second absorption band. The calculation and ICD spectrum show that the positive (λ_{max} 217 nm) and negative (λ_{max} 231 nm) bands are assigned to the $^1A_1$ and $^1B_2$ ($\pi \rightarrow \pi^*$) transitions, respectively.

REFERENCES

[1] A. D. Buckingham, P. J. Stephens, *Ann. Rev. Phys. Chem*. **1966**, *43*, 1427.
[2] P. N. Schatz, A. J. McCaffery, *Q. Rev. Chem. Soc*. **1969**, *23*, 552.
[3] D. Caldwell, J. M. Thorne, H. Eyring, *Ann. Rev. Phys. Chem*. **1971**, *22*, 259.
[4] M. Higashi, H. Yamaguchi, *J. Chem. Phys*. **1979**, *70*, 2198.
[5] A. R. Meier, G. H. Wagnière, *Chem. Phys.* **1987**, *113*, 287.
[6] J. Frei, H. Yamaguchi, J. Tsunetsugu, G. H. Wagnière, *J. Am. Chem. Soc.* **1990**, *112*, 1413.
[7] H. Yamaguchi, S. Abe, *J. Phys. Chem*. **1981**, *85*, 1640.
[8] H. Yamaguchi, A. Uchida, F. Yoneda, H. Baumann, *J. Chem. Soc.*, *Faraday Trans. 2*, **1981**, *77*, 947.
[9] H. Yamaguchi, M. Fukuda, H. Takeshita, H. Mametsuka, H. Baumann, *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 193.
[10] T.-S. Lin, J. R. Braum, *Chem. Phys.* **1978**, *28*, 379.
[11] J. J. Dekkers, G. P. Hoornweg, W. P. Cofino, M. Maclean, N. H. Velthorst, *Chem. Phys. Lett*. **1979**, *67*, 24.
[12] H. Baumann, CNDUV (QCPE No. 333), 1977.
[13] M. M. Harding, J. M. Maclenman, R. M. Paton, *Nature (London)* **1978**, *274*, 621.
[14] W. Saenger, *Angew. Chem.*, *Int. Ed*. **1980**, *19*, 344.
[15] J. P. Larkindale, D. J. Simkin, *J. Chem. Phys.* **1971**, *55*, 5668.

Received March 13, 2000