145. Magnetic Circular Dichroism and Electronic Spectra of Tropothione

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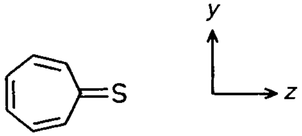
The magnetic circular dichroism (MCD) and electronic absorption spectra of tropothione have been measured. The circular-dichroism (CD) spectrum of the β-cyclodextrin complex with tropothione is also reported. The absorption bands of tropothione are assigned.

Introduction. – Recently, *Machiguchi et al.* [1] have prepared tropothione, which is the iso-π-electron system of tropone and one of the theoretically important members of nonbenzenoid aromatic compounds [2]. The assignment of the electronic absorption spectrum of tropone as a typical troponoid compound was accomplished by several authors [3–8]. The magnetic circular-dichroism (MCD) technique has been tested by various investigators for the elucidation of complicated electronic spectra [9–14]. Recently, the circular dichroism (CD) of the β-cyclodextrin complex has been shown to be a very simple tool for the assignment of absorption spectra [15–17].



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 [18–20]. Therefore, we have investigated the polarization of the absorption bands of tropothione by measuring its MCD spectrum and the CD spectrum of its β-cyclodextrin complex.

Experimental. – Tropothione (= *cyclohepta-2,4,6-trienethione*) was prepared by two of the authors (*T. M.* and *T. H.*) according to the method described in [1] and was isolated as a pure crystalline material [21] (m.p. 20.0–21.0°) by recrystallization with cold Et_2O at −80°. Immediately after the isolation, crystalline tropothione was weighed in a thermostated room at −10° in a rapid succession and was dissolved in ethylene glycol/dist. H_2O 1:1 at the same temp. Commercial β-cyclodextrin was recrystallized three times from dist. H_2O. The soln. of tropothione was added to β-cyclodextrin to form inclusion complexes and stirred, until the complete dissolution (*ca.* 3 min) at −10°. The concentrations of tropothione and β-cyclodextrin were maintained in all experiments at 2.22×10^{-4} and 7.97×10^{-3} M, respectively.

The absorption spectra were recorded on a *Hitachi U-3200* spectrophotometer. The CD spectra were measured using a *Jasco J-600C* spectropolarimeter. To obtain an adequate signal-to-noise ratio, multiple scanning and averaging were accomplished using a microcomputer. The MCD spectra were recorded with a *Jasco J-600C* circular dichrometer with a 1.32-*T* electromagnet. All measurements were carried out at −40.0 ± 0.1° using a *Jasco CS-65* cryostat.

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

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

where ν is the frequency in cm^{-1} and $[\theta]_M$ is the molar ellipticity in 10^{-1} deg $dm^3 \cdot dm^{-1} \cdot mol^{-1} \cdot G^{-1}$ [9] [10].

Results and Discussion. – The absorption and MCD spectra of tropothione are shown in *Fig. 1* together with the CD spectrum of the complex with β-cyclodextrin. The MCD

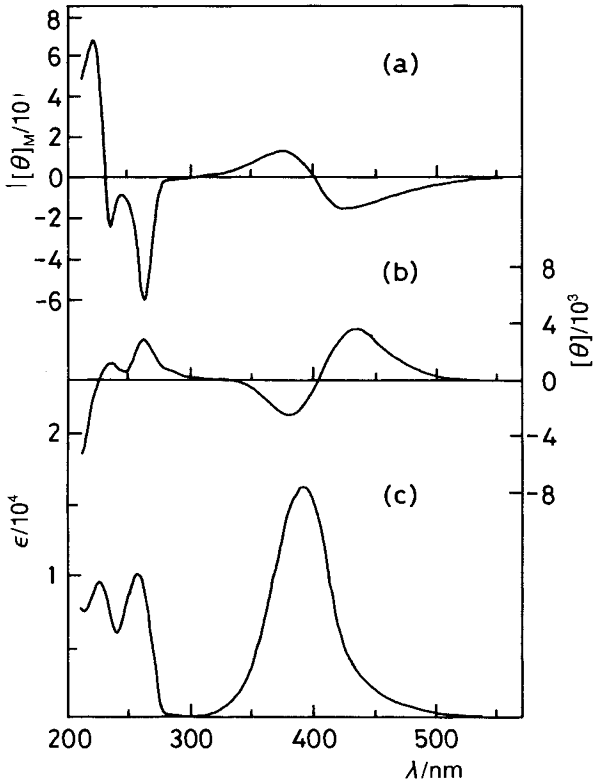


Fig. 1. *The MCD* (a) *and absorption* (c) *spectra of tropothione, and CD spectrum* (b) *of β-cyclodextrin complex with tropothione*

spectrum indicates the +/− signal alternation in the first absorption band (*ca.* 392.0 nm). The *Faraday B* values are 7.05×10^{-3} and -4.77×10^{-3} *Bohr* magneton (Debye)^2 cm^{-1}. As shown by *Larkindale* and *Simkin* [22], two adjacent mutually perpendicular transitions have *Faraday B* values (the sign of the *Faraday B* term is opposite to the one in the MCD spectrum) which are nearly equal in magnitude though opposite in sign.

The geometrical structure of β-cyclodextrin excludes the formation of an equatorial inclusion complex in the case of tropothione [23] [24]. Thus, the CD spectrum of the β-cyclodextrin complex with tropothione is attributed to the structure of an axial inclusion complex. It has been shown that the transition of the guest molecule in the cavity of β-cyclodextrin with a transition dipole moment perpendicular to the molecular axis of β-cyclodextrin results in a negative CD value and the transition with a transition dipole moment parallel to the axis in a positive one [15–17]. Accordingly, it can be concluded that the first absorption band (around 300–500 nm) consists of at least two electronic transitions with polarizations parallel and perpendicular to the *z* axis.

The CNDO/S calculation [25] also shows that there are two $\pi \rightarrow \pi^*$ transitions in the first absorption band. One is the A_1 transition (*z*-direction) at 371 nm and the other is the

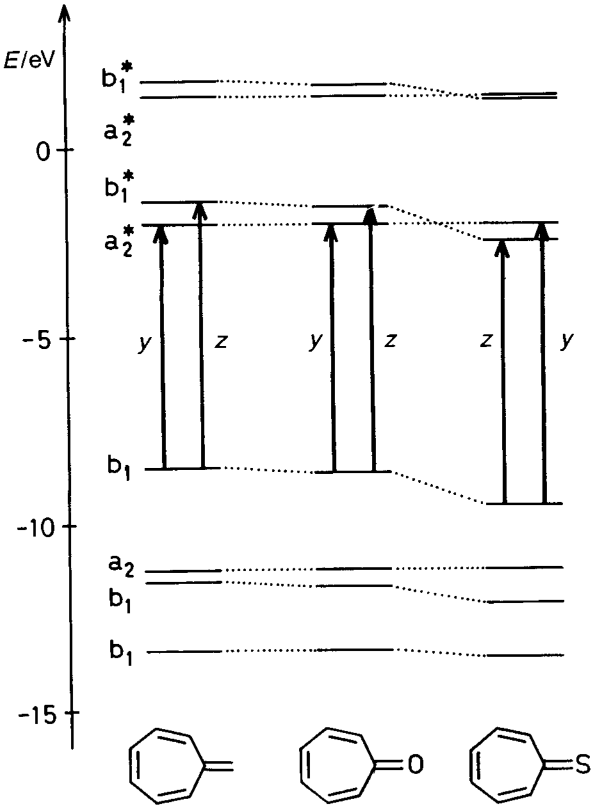


Fig. 2. *The changes of the orbital energies of heptafulvene, tropone, and tropothione with the* Coulomb *integral of the terminal C-atom.* The arrows indicate the main components of the first and second electronic $\pi \rightarrow \pi^*$ transitions.

B_2 transition (y-direction) at 362 nm. According to the CNDO/S calculation, there are two additional $n \rightarrow \pi^*$ transitions in the longest wavelength region. The first $n \rightarrow \pi^*$ transition is the forbidden A_2 transition at 503 nm, and the second is the B_1 (x-direction) transition at 398 nm. The calculation supports the assumption that the two weak bands at 610 and 682 nm in non-polar solvent [1] may be $n \rightarrow \pi^*$ transitions.

The MCD spectrum shows +/− signal alternation in the second absorption band (around 210–280 nm). The absorption, MCD, and CD spectra below 210 nm cannot be measured due to the absorption of solvent. There are peaks at 235.6 nm in the MCD and CD spectra. The CD spectrum of the second absorption band indicates another positive peak at 262.0 nm. The peak at 235.6 nm is assigned to the totally symmetric vibration [15]. The CD spectrum suggests that there is an electronic transition with a transition dipole moment perpendicular to the z-axis below 210 nm. Thus, at least two transitions with different polarizations exist in the second absorption band.

The assignment of the first absorption band of tropothione will now be discussed from a different point of view. The electronic absorption spectrum of heptafulvene has shown bands at 430 nm (perpendicular to the z-axis) and 280 nm (parallel to the z-axis) [26]. *Fig. 2*, based on a simple perturbation calculation [27], shows the changes of the orbital energies of heptafulvene, due to changes of the *Coulomb* integrals of the terminal C-atom. With the geometry obtained by the MNDO method [28], we calculated the molecular-orbital energies by using PPP MO method [13]. With an increase of the *Coulomb* integral of the terminal C-atom of heptafulvene, the two transitions, corresponding to the bands 430 nm (perpendicular) and 280 nm (parallel), first approach each other (in the case of tropone) [7] [8] and finally exchange their positions (in the case of tropothione).

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