

Magnetic Circular Dichroism Spectra of Some *s*-Triazolo[1,5-*b*]isoquinolin-5(*H*)ones, 1,2-Dihydro-6*H*-*s*-tetrazino[2,3-*b*]isoquinolin-6-ones and Related Compounds

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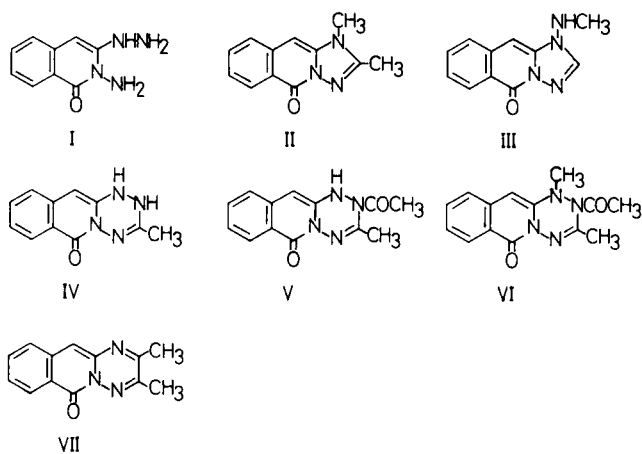
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Magnetic circular dichroism spectra of *s*-triazolo[1,5-*b*]isoquinolin-5(*H*)ones, 1,2-dihydro-6*H*-*s*-tetrazino[2,3-*b*]isoquinolin-6-ones and related compounds were measured. The molecular symmetry of these compounds is so low that the MCD spectra contain only the Faraday parameter B. It appears that the magnitude and sign of the B term depends on the nature of the substituents and of electron migration from *endo*- or *exo*-nitrogen to oxygen, respectively.

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Recently, Goya, *et al.* have synthesized some *s*-triazolo[1,5-*b*]isoquinolin-5(*H*)ones and 1,2-dihydro-6*H*-*s*-tetrazino[2,3-*b*]isoquinolin-6-ones and related compounds (1). The electronic structures of these compounds are of interest from a pharmacological point of view. In this paper, we describe the spectroscopic properties of magnetic circular dichroism (MCD) for compounds I-VII. MCD has some advantages over ordinary spectrophotometric



techniques in that the occurrence of a negative band and the sharp sensitivity to changes in electronic structures are observed. Because of this sensitivity, MCD spectra give valuable information with respect to structural differences between similar compounds (2). According to the quantum theory (3), the observed MCD is composed of a combination of these contributions characterized by the

frequency independent factors "A", "B", and "C" of the Faraday rotation. The molecular symmetry of compounds I-VII is so low that only the Faraday parameter B is extracted from the MCD spectra of these compounds. The

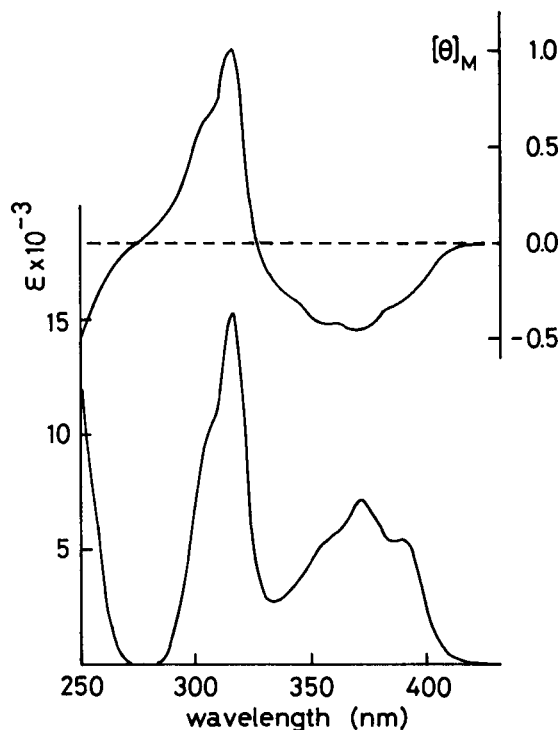


Figure I. MCD (top) and uv (bottom) spectra of IV in ethanol at room temperature.

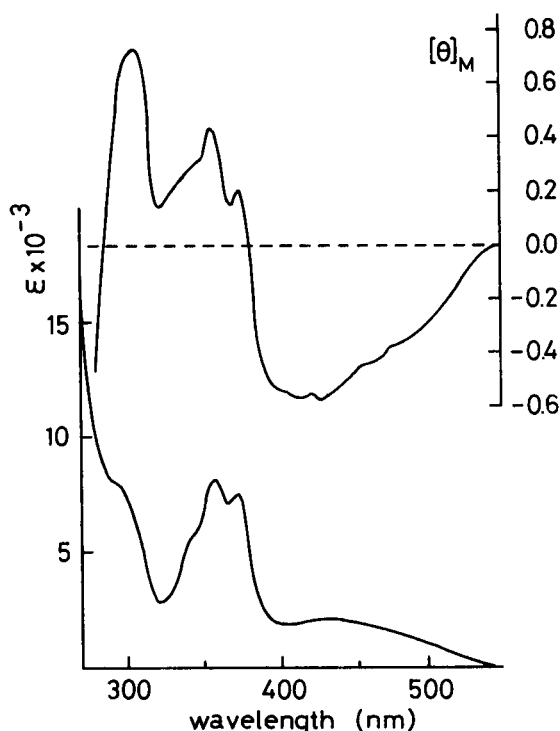


Figure II. MCD (top) and uv (bottom) spectra of VII in ethanol at room temperature.

MCD and uv spectra of compounds I, II, III, IV, V, and VI resemble each other, and compound VII differs from these compounds in the MCD and uv spectra. The MCD and uv spectra of compounds IV and VII are given in Figures I and II. The Faraday B term is often discussed by comparing its ratio to the dipole strength D. The B and D values were evaluated as in reference (4)

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

$$D = 9.1834 \times 10^{-3} \int_{\text{band}} (\epsilon/\nu) d\nu$$

where ν is frequency in cm^{-1} , $[\theta]_M$ is molar ellipticity per unit field in units of $\text{deg l m}^{-1} \text{ mole}^{-1} \text{ gauss}^{-1}$, and ϵ is molar extinction coefficient. The uv and MCD spectra were analyzed assuming Gauss-type absorption bands with the method described by Badoz, *et al.*, (5). The experimentally extracted Faraday parameters are summarized in Table I.

MCD spectra show unambiguously two B terms of opposite sign for compounds I-VI and three B terms for compound VII through the 270-450 nm range. The MCD spectra clearly demonstrate the presence of two and three absorption bands for compounds I-VI and VII, respectively. In the uv spectra, the two bands of compounds I-VII in the 270-400 nm region have nearly the same shape and λ max. On the other hand, the MCD spectra of com-

Table I
Experimental Faraday Parameters

Compound Number	λ max nm	B (a)	D (b)	B/D (c)
I	302	-2.2	13.5	-1.6
	368	1.7	5.7	3.0
II	316	-2.0	10.5	-1.9
	371	0.73	8.7	0.83
III	316	-6.0	9.1	-6.6
	375	5.3	8.9	5.9
IV	316	-2.1	9.6	-2.2
	373	2.0	9.0	2.2
V	310	-8.5	8.9	-9.5
	366	0.71	9.9	0.72
VI	309	-3.3	8.7	-3.8
	363	3.0	9.8	3.1
VII	304	-1.6	7.8	-2.1
	357	-1.2	9.5	-1.3
	433	3.6	4.9	7.4

(a) In 10^{-3} debye² Bohr magneton/ cm^{-1} . (b) In debye². (c) In 10^{-4} Bohr magneton/ cm^{-1} .

pounds I-VI show two bands with the + - sign alternation, while compound VII exhibits two positive bands. The band of compounds I-VI and VII in the 370 nm region may originate in a transition involving an electron migration from *exo*-nitrogen to oxygen as indicated in IVa and from *endo*-nitrogen to oxygen as indicated in VIIa, respectively. The compounds I-VI are different from com-

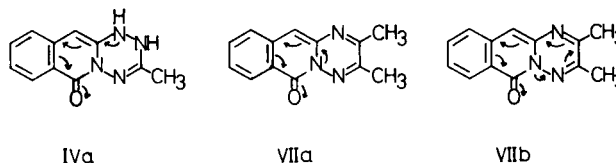


Chart 2

pound VII not in uv spectra but in the sign of the MCD spectra since the conjugated system along which an electron moves is different. The band in the shortest wave lengths corresponds to the same electron migration in compounds I-VII. The band at the longest wavelengths is observed only in the spectra of compounds VII. This band may correspond to a transition involving an electron migration from *endo*-nitrogen to oxygen as shown in VIIb. Compounds I-VI do not exhibit the band in the 450 nm region since an electron cannot move as shown in VIIb. A comparison of compounds IV, V, and VI shows that the difference between B/D values of two bands increases in the case of acetyl substitution and decreases in the case of methyl substitution. It may be considered that MCD spectra provide significant information concerning the

effect of substitution on electronic structure and electron migration.

EXPERIMENTAL

Chemicals.

Compounds I-VII were supplied by Professor S. Goya and Dr. A. Takadate. These compounds were crystallized twice from ethanol. Ethanol was carefully purified according to the descriptions in reference (6).

Measurements.

The uv spectra were taken on a Hitachi EPS-3T recording spectrophotometer. The MCD spectra were measured on a JASCO J-20A recording spectropolarimeter equipped with a 12.2 k gauss electro-magnet. All measurements were made on deaerated samples at room temperature.

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