229. Magnetic Circular Dichroism and Absorption Spectra of 2-Methyl-1,3-diazaazulene

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Summary

The magnetic circular dichroism and UV. spectra of 2-methyl-1,3-diazaazulene (**2**) have been measured. The UV. spectrum is interpreted by making use of CNDO/S MO CI calculations. Our assignment of the first and second absorption band coincides with one of the corresponding bands of 1,3-diazaazulene (**1**) given by *Small & Burke.* The third and fourth absorption bands are in agreement with those published by *Hiratsuka et al.* and *Tanizaki et al.* for **1** and 2-ethoxy-1,3-diazaazulene, respectively.

Introduction. - The fact that nonbenzenoid hydrocarbons containing an azulene nucleus emit anomalous fluorescence [1-9] led us to investigate the electronic spectra of 1,3-diazaazulene (**1**) and its 2-substituted derivatives. There are four absorption bands in the wave-number region of 20.0×10^3-47.5×10^3 cm^{-1}, around 24.5×10^3, 33.0×10^3, 40.0×10^3 and 45.0×10^3 cm^{-1}. Only the assignment for the third and fourth bands has been well established [6] [7]. From the dichroic spectra of **1** and its 2-ethoxy derivative in a streched polyvinylalcohol sheet, *Hiratsuka et al.* [6] and *Tanizaki et al.* [7] have shown that the first band consist of a $\pi \rightarrow \pi^*$ transition polarized along the y-axis *(Fig. 1)* and a symmetry-forbidden $n \rightarrow \pi^*$ transition, and the second band of a $\pi \rightarrow \pi^*$ transition polarized along the z axis and a symmetry-allowed $n \rightarrow \pi^*$ transition. The polarized absorption, fluorescence and phosphorescence spectra of **1** have been measured in a naphthalene host and only a $\pi \rightarrow \pi^*$ transition polarized along the y axis has been identified in the first band [8]. The polarization in the mixed crystal spectrum shows in the first band a

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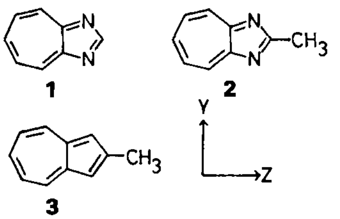

Figure 1. *Numbering of compounds and choice of axis*

$\pi \to \pi^*$ transition with its dipole moment parallel to the y axis, and in the second band two $\pi \to \pi^*$ transitions polarized along the z and y axis [9].

The magnetic circular dichroism (MCD.) is a useful tool for the assignment of complicated electronic spectra and for the investigation of the magnetic properties of the ground and excited states of molecules [10-16]. Expecting that the introduction of a methyl group at the 2 position of **1** would result in a separation of the energies of the $\pi \to \pi^*$ and $n \to \pi^*$ states, we investigated the UV. and MCD. spectra of 2-methyl-1,3-diazaazulene (**2**). The main aim of this paper is to determine the assignment of the first and second absorption band of **2** by means of the MCD. spectra of **2** and 2-methylazulene (**3**) and by comparing the experimental with the theoretical results obtained from the CNDO/S CI method [17] [18].

Experimental Part. - Compound **2** was prepared as reported [19] and was purified by column chromatography on neutral alumina (*Wako Pure Chemical Industries, Ltd.*, W-200) with benzene/acetone 1:1 (*v*/*v*). Compound **3**, supplied by Dr. *Y. Fukazawa*, was recrystallized from cyclohexane then sublimed *in vacuo*. Silica gel 60 H *(Merck)* coated plates were used for thin-layer chromatography. Spots were detected by UV. and fluorescence. The cyclohexane was spectral grade. The UV. spectra were recorded on a *Hitachi* 200-20 recording spectrophotometer. MCD. spectra were obtained with a *JASCO* J-40A recording spectropolarimeter equipped with a 1.52 T electromagnet. All measurements were made on deaerated samples at RT.

MO Calculations. - The transition energies and oscillator strengths of **2** were calculated using the CNDO/S CI method [17] [18]. The molecule was computed with regular seven- and five-rings of bond length 0.14 nm. The bond length of the methyl group was set equal to 0.152 nm. All C,H-bonds were taken to be 0.109 nm. The CI treatment considered 48 singly excited configurations with an energy below 96.0×10^3 cm^{-1} and 45 doubly excited configurations having an energy below 121.7×10^3 cm^{-1}.

In order to discuss the sign of the *Faraday B*-term for the first electronic transition of **2** from the viewpoint of a perturbational treatment [20], we calculated the MO's and MO energies of the unperturbed system of molecule **3** using standard parameters [21] [22] within the PPP approximation [23] [24]. The change ($\delta\varepsilon_i$) of the ith MO energy due to the introduction of the two N-atoms at the 1 and 3 positions was given by the simple perturbational formula, $\delta\varepsilon_i = 2\,c_{i1}^2\delta\alpha_1$. The change ($\delta\alpha_1$) of the *Coulomb* integral was estimated by the formula [25], $\delta\alpha_1 = 0.6\,\beta_0$, where the value of β_0 was taken as -2.38 eV [22].

Results and Discussion. - The UV. and MCD. spectra of **2** are shown in *Figure 2.* The transition energies and oscillator strengths calculated by the CNDO/S MO CI method are listed in the *Table.* The MCD. spectrum indicates that the first absorption band at about 24.0×10^3 cm^{-1} consists of an electronic transition. The MO calculations *(Table)* show that the electronic transition has a transition dipole

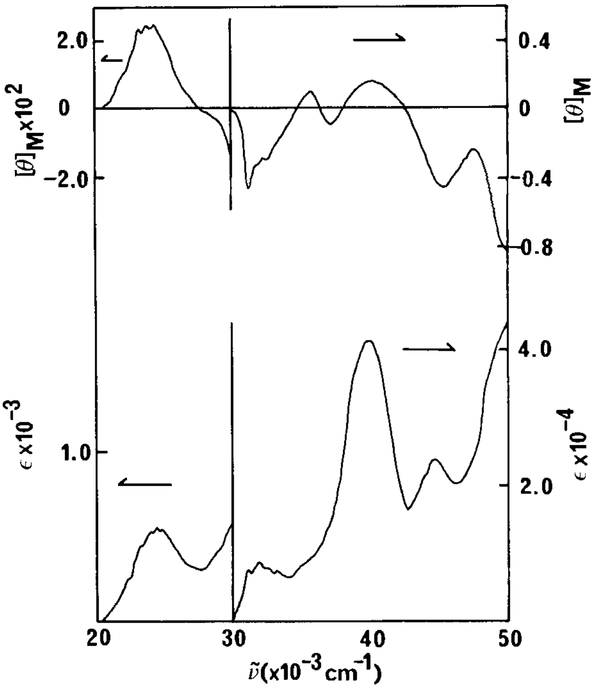

Figure 2. *Magnetic circular dichroism* (top) *and absorption* (bottom) *spectra of 2-methyl-1,3-diazaazulene* (**2**) *in cyclohexane*

moment parallel to the y-axis of **2**. From the negative and positive peaks of the MCD. spectrum at 32.0×10^3 and 35.8×10^3 cm^{-1} respectively, one expects that the second absorption band contains at least two electronic transitions. In the *Table* are listed two allowed $\pi \rightarrow \pi^*$ transitions and a forbidden $n_- \rightarrow \pi^*$ transition in the region of the second absorption band. The forbidden $n_- \rightarrow \pi^*$ transition may probably be too weak to be observed. The CNDO/S calculations indicate that the third absorption band consists of four electronic transitions, *i.e.*, an $n_- \rightarrow \pi^*$, a $\pi \rightarrow \pi^*$ parallel to the z-axis, a forbidden $n_- \rightarrow \pi^*$ and an allowed $n_+ \rightarrow \pi^*$ transition. These $n \rightarrow \pi^*$ transitions obtained by calculation might be hidden under the strong absorption band at 40.0×10^3 cm^{-1}. The *Table* strongly supports the conclusion that the fourth absorption band (45.0×10^3 cm^{-1}) consists of the $n_+ \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, and the fifth band (above 48.0×10^3 cm^{-1}) of a $\pi \rightarrow \pi^*$ transition polarized parallel to the z-axis.

Our assignment for the first absorption band is not in agreement with that given by *Hiratsuka et al.* [6] for **1** and by *Tanizaki et al.* [7] for the 2-ethoxy derivative of **1** but it fits the interpretation given by *Burke et al.* [8] and *Small & Burke* [9] for **1**. The attribution of the second absorption band agrees with [9]. Our assignment for the third and fourth absorption band is consistent essentially with [6] and [7].

The MCD. spectrum of **3** is shown in *Figure 3*, together with the absorption spectrum. As a whole, the MCD. spectrum of **3** resembles that of azulene except

Table. *Transition energies* (ΔE) *and intensities* (f) *of 2-methyl-1,3-diazaazulene* (**2**)

Theory			Experiment
ΔE ($\times 10^3$ cm^{-1})	Sym.	f	ΔE ($\times 10^3$ cm^{-1})
25.7	$^1A''$ ($\pi \to \pi^*$)	0.0002	24.5 (logε = 2.73)
33.2	$^1A'$ ($\pi \to \pi^*$)	0.0146	33.0 (logε = 3.93)
34.5	$^1A''$ ($\pi \to \pi^*$)	0.0990	
35.1	$^1A''$ ($n_- \to \pi^*$)	0.0001	
36.6	$^1A'$ ($n_- \to \pi^*$)	0.0002	40.0 (logε = 4.61)
38.3	$^1A'$ ($\pi \to \pi^*$)	0.5678	
39.9	$^1A''$ ($n_- \to \pi^*$)	0.0000	
41.7	$^1A'$ ($n_+ \to \pi^*$)	0.0001	
47.4	$^1A'$ ($n_+ \to \pi^*$)	0.0000	45.0 (logε = 4.38)
47.6	$^1A''$ ($\pi \to \pi^*$)	0.0369	
48.5	$^1A'$ ($\pi \to \pi^*$)	0.1786	

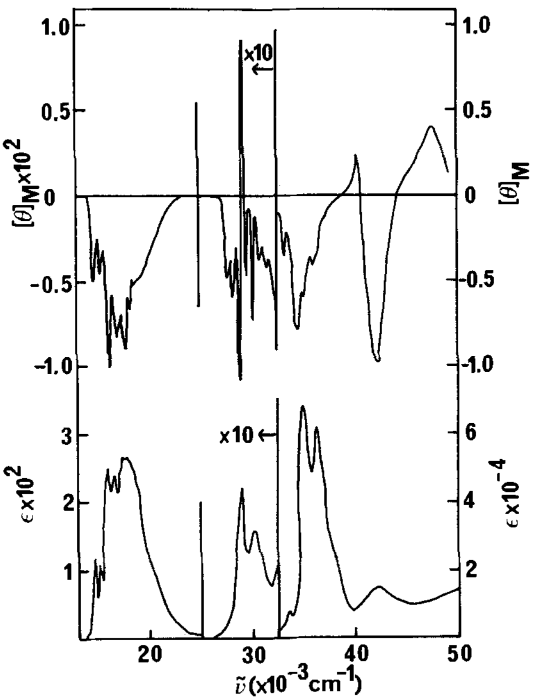

Figure 3. *Magnetic circular dichroism* (top) *and absorption* (bottom) *spectra of 2-methylazulene* (**3**) *in cyclohexane*

for the sign of the second band which is opposite to that of the same band of azulene [26–28]. The PPP SCF MO CI calculations for **3** indicate that the lowest singlet excited (S_1) state can be represented by $|1 \to -1\rangle$ and the second excited (S_2) state by the linear combination $a|1 \to -2\rangle - b|2 \to -1\rangle$. Bonding molecular orbitals are numbered in the order of decreasing, antibonding orbitals by negative integers in the order of increasing energy. The contribution of the *B*-term of the $S_0 \rightarrow S_1$ transition which arises from the magnetic mixing of S_1 and S_2 states is then equal to $B(S_1 \text{ from } S_2) = (a^2 - b^2)\,\mathrm{Im}\{\langle 2|\hat{\mu}|1\rangle \cdot \langle 1|\hat{m}|-1\rangle \times \langle 1|\hat{m}|-2\rangle / \Delta E\}$ where ΔE is the energy difference between the S_2 and S_1 states, $\hat{\mu}$ the magnetic and $\hat{m}$ the electric dipole moment operator [20]. The perturbation due to the introduction of two N-atoms instead of C(1) and C(3) of **3** makes the energy of $|1 \rightarrow -2\rangle$ higher than that of $|2 \rightarrow -1\rangle$, so $a^2 < b^2$. The sign of the *Faraday B*-term of **2** will be negative in the first electronic transition. In fact as shown in *Figure 2*, the MCD. spectrum of **2** has a positive curve (the sign of the *Faraday B*-term is opposite to the sign of the MCD. spectra) in the first absorption band.

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