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A MCD STUDY OF INDENYL ANION
ITS APPLICATION TO THE ASSIGNMENT OF ABSORPTION BANDS

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The magnetic circular dichroism (MCD) spectra of indenyl anion was measured. The Faraday B terms were observed for bands in the range of wavelength 210∿ 400nm. Experimental B/D values were estimated to be $+1.41\times10^{-4}$, $+1.84\times10^{-4}$, $+9.09\times10^{-5}$ and -9.80×10^{-5} (β/cm^{-1}) for four regions of absorption corresponding to electronic transitions $A_1 \rightarrow B_2$, $A_1 \rightarrow A_1$, $A_1 \rightarrow A_1$ and $A_1 \rightarrow B_2$, respectively. Thus MCD technique was shown to be applicable to the assignment of absorption bands.

Not only recent interest in the Faraday effect has led to investigations of π-electronic transitions in aromatic hydrocarbons$^{1)}$ and their ions$^{2)}$, but also it has been well known that the MCD technique is often used as a powerful tool in the assignment of the absorption bands because it gives well resolved spectra in which the symmetries of the ground and excited states of molecules are well reflected.

Although we have already reported the Faraday effect in cyclononatetraenide anion $C_9H_9^-$ with D_{9h} symmetry$^{3)}$, we are also interested in the measurements of the MCD spectra of indenyl anion $C_9H_7^-$ because it is considered to be a slightly perturbed system of cyclononatetraenide anion and iso-electronic with the parent nine-membered monocycle.

On the other hand, Wagner and Ebel$^{7)}$ have recently studied the absorption spectra of alkali metal salts of indenyl anion and reported four regions of absorption. However, these spectra seem to be a superimpose of bands and complicated by an absorption of the solvent, especially the shortest wavelength absorption band of potassium salt is buried in the solvent absorption.

We will show below the utility of the MCD spectra in elucidating the electronic transitions and the nature, especially the magnetic moments, of the excited states of molecules and ions, taking up the potassium salt of indenyl anion as an example.

In the case of an isolated electronic transition o-a of a molecule possessing non-degenerate states, the quantum mechanical expression[4-6] for the Faraday parameter B and the dipole strength D is

$$B_{oa} = \frac{1}{3}\mathrm{Im}\left\{ \sum_{b=o} \frac{m_{bo}}{\nu_{bo}} \cdot \mu_{oa} \times \mu_{ab} + \sum_{b=a} \frac{m_{ab}}{\nu_{ba}} \cdot \mu_{oa} \times \mu_{bo} \right\} \qquad (1)$$

$$D = \mu_{oa}^{2} \qquad (2)$$

where m and μ are magnetic and electric dipole transition moments, respectively. The denominator in Eq.(1) ν_{bo} and ν_{ba} stand for the energy difference between states o-b and b-a. For the C_{2v} symmetry, there exist μ_{oa} and μ_{ob} vectors directed along the two perpendicular axes in the molecular plane (y,z), whereas m_{ab} and m_{oa}, m_{ob} along the x-axis. Therefore if we deal with only π-π^* transitions, the excited states with B_2 symmetries would magnetically couple with totally symmetric ground and excited states, while the excited states with A_1 symmetries would mix with B_2 states.

Table 1. Singlet-singlet transition energies ΔE(eV) and the oscillator strengths f(CGS) of $C_9H_9^-$ and $C_9H_7^-$.

Compd.	Transition	Calc. ΔE(f)	Obs. ΔE(f)
$C_9H_9^-$	$A_1' \rightarrow E_4'$	3.52(forb.)	3.88(0.15)
	$A_1' \rightarrow E_1'$	5.35(3.92)	4.96(2.16)
$C_9H_7^-$	$A_1 \rightarrow B_2$	3.21(0.07)	3.54(0.030)
	$A_1 \rightarrow A_1$	4.18(0.00)	4.31(0.059)
	$A_1 \rightarrow A_1$	5.29(1.34)	5.00(0.71)
	$A_1 \rightarrow B_2$	5.63(0.07)	5.81(0.14)

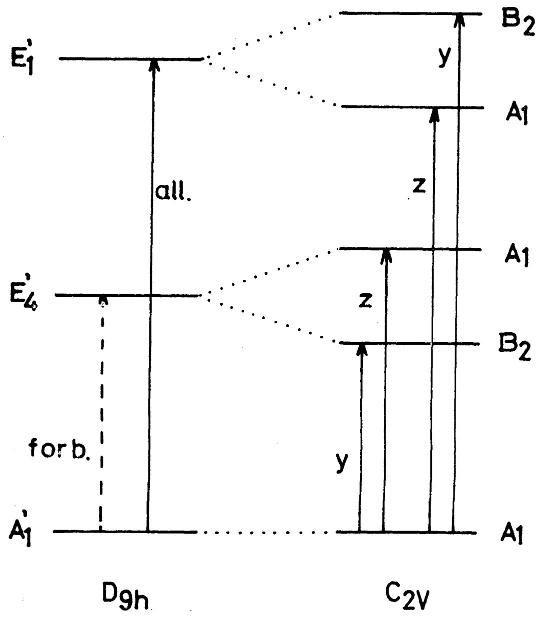

Fig. 1 A correlation diagram of the states in $C_9H_9^-$ and $C_9H_7^-$.

Before MCD measurement, we calculated electronic spectra of indenyl anion by use of PPP[8] method in order to see how they were affected by a symmetry reduction from D_{9h} to C_{2v}. The results are listed in Table 1, showing a good agreement with experimental data. The degeneracy of the excited state in D_{9h} structure is removed by an introduction of a cross bond and split into B_2, A_1 in C_{2v} structure. A splitting pattern of the states is depicted in Fig.1.

Newly distilled indene in ether was treated with potassium tip in an evacuated glass tube fitted with a quartz cell having light path of 1mm. The ethereal solution turned to pale yellow on contact with the metal. An anion formation was confirmed by observing a new absorption band, with its maximum at 350nm, which was absent in the neutral molecule. As for the MCD measurement, an electromagnet supplying a field strength of 12.5KG was used.

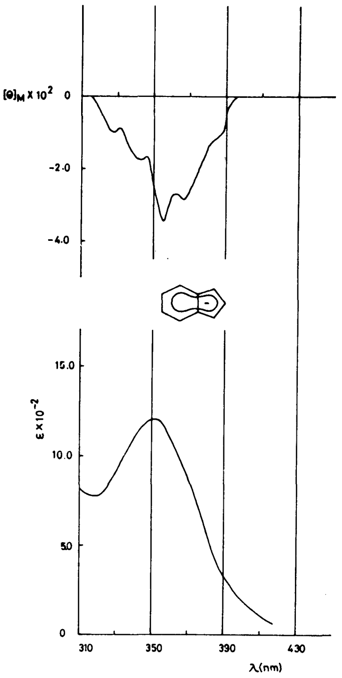

Fig.2 The MCD(top) and UV(bottom) spectra of indenyl anion in ether, at room temperature.

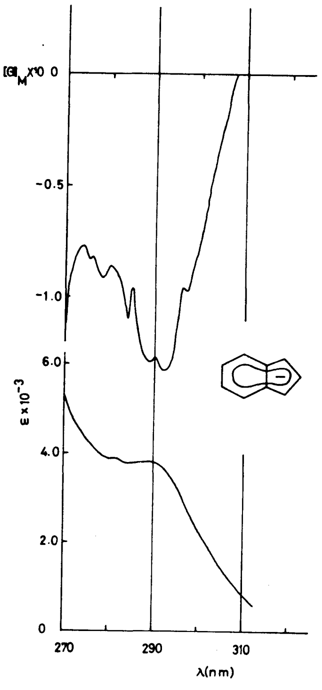

Fig.3 The MCD(top) and UV(bottom) spectra of indenyl anion in ether, at room temperature.

In Fig. 2 MCD(top) and UV(bottom) spectra of indenyl anion in the range of wavelength 310∿400nm are shown. A MCD minimum coincides with an absorption maximum within the limit of the experimental error. Vibrational structures which are absent in the UV spectrum are clearly observed in the MCD spectrum. This longest wavelength MCD band is considered to be the Faraday B term which arises from the magnetic mixing of the first excited B_2 state with the ground and excited states of A_1 symmetries.

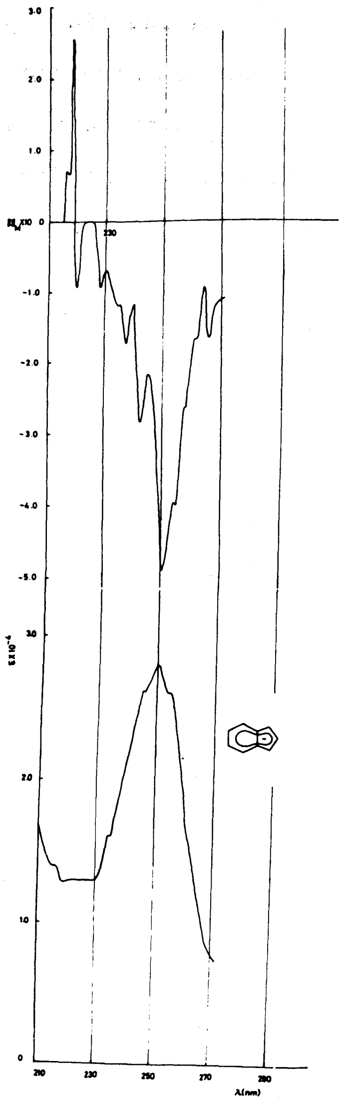

Fig.4 The MCD(top) and UV(bottom) spectra of indenyl anion in ether, at room temperature.

Although in the range of wavelength 270∿310nm (Fig.3) an absorption corresponding to the electronic transition $A_1 \rightarrow A_1$ appears as a shoulder in the UV spectrum, the MCD spectrum with fine structures shows more clearly an existence of this band than the UV spectrum does. The negative MCD peak is again considered to be the B term due to the mixing of the second excited state A_1 with the other excited states with B_2 symmetries.

There lie two absorption bands in the wavelength range of 210∿270nm as is clearly seen from the MCD spectrum in Fig.4. There is no hesitation of assigning the $A_1 \rightarrow A_1$ electronic transition to the band with its maximum(UV) or minimum(MCD) at 250nm, and this, in turn, permits one to assign the fourth $\pi-\pi^*$ transition $A_1 \rightarrow B_2$ to the shortest wavelength band.

The Faraday parameter B is often discussed by taking its ratio to the dipole strength D in Eq.(2). The experimentally extracted Faraday parameters are summarised in Table 2.

Table 2 Extracted Faraday Parameters

transition	$\lambda_{max.}$(nm)	$[\theta]_M$	B/D(β/cm^{-1})
$A_1 \rightarrow B_2$	350	-0.026	$+1.41\times10^{-4}$
$A_1 \rightarrow A_1$	290(s)	-0.127	$+1.84\times10^{-4}$
$A_1 \rightarrow A_1$	250	-0.489	$+9.09\times10^{-5}$
$A_1 \rightarrow B_2$	218(s)	+0.256	-9.80×10^{-5}

s: shoulder band

The B/D values for the lower two transitions are larger than those for the higher two. Furthermore it should be noted that the sign alternation (-,-,-,+) of the MCD spectra could not be explained by a simple model considering a mixing between only two excited states; e.g. between B_2 and A_1 derived from E_4' and between A_1 and B_2 from E_1' in the D_{9h} structure. When only two excited states are concerned, a MCD spectrum which is equal in magnitude but opposite in sign is expected. The sign alternation encountered is considered as a result of the multiple coupling among the excited states because of their small energy difference.

While the present MCD measurement shows us that the results of Wagner and Ebel[7)] for the assignment of the absorption bands in indenyl anion are reasonable, in addition to that it seems to reveal the electronic spectra of molecules and ions in more details than the absorption measurement does, in such a sense as an appearance of a hidden band (or a shoulder), and also of vibrational structures absent in the UV spectra.

References

1) P.J.Stephens, P.N.Schatz, A.B.Ritchie and A.J.McCaffery, J. Chem. Phys., 48, 132(1968)

2) P.J.Zandstra, D.J.Scholtens and R.E.Koning, ibid., 57, 3821(1972)

3) A.Tajiri and M.Hatano, to be submitted in Chem.Phys. Letters.

4) P.N.Schatz and A.J.McCaffery, Quart. Rev., 23, 552(1969)

5) A.D.Buckingham and P.J.Stephens, Ann. Rev. Phys. Chem., 17, 399(1966)

6) B.Briat, D.A.Schooley, R.Records, E.Bunnenberg, C.Djerassi and E.Vogel, J. Amer. Chem. Soc., 90, 4691(1968)

7) B.O.Wagner and H.F.Ebel, Tetrahedron, 26, 5155(1970)

8) R.Pariser and R.G.Parr, J. Chem.Phys., 21, 446,767(1953)
J.A.Pople, Trans. Faraday Soc., 49, 1375(1953)

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