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The MCD Spectrum of the Tropylium Cation

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One of the most interesting monocyclic odd-membered non-benzenoid aromatic hydrocarbons, the cycloheptatrienyl (tropylium) cation, $C_7H_7^+$, which has been shown to have a strong aromatic character due to the delocalization of the six π-electrons, was synthesized as early as 1954 by von Doering and Knox.[1]

Because of the intriguing chemical and physical properties of this cation, several authors[2–4] have attempted to calculate its electronic structures, especially its transition energies, on the basis of the π-electron molecular orbital theory. The N→V spectrum was theoretically studied by Murrell and Longuet-Higgins[2] using the SCF-MO theory. They predicted two transitions, an allowed transition at 6.36 eV ($^1A_1' \rightarrow {}^1E_1'$) and a forbidden transition at 4.33 eV ($^1A_1' \rightarrow {}^1E_3'$). The absorption band at 4.51 eV observed by von Doering and Knox was assigned to the latter transition.

The results of PPP-type calculations by Heilbronner and Murrell[4] of various odd-membered non-alternant hydrocarbons, including $C_7H_7^+$, using perimeter models were reported, along with their experimental data. The agreement between the theory and the experiment was quite good, and their results supported the above assignment of the absorption band of the tropylium cation.

Table 1. Transition energies (eV) of tropylium cation

Symmetry	M-LH[2]	J[3]	H-M[4]	This Work[a]	Obsd[b]
$A_1' \rightarrow E_3'$	4.33	3.6	4.52	4.6(forb.)	4.54(ε=4350)
$A_1' \rightarrow E_1'$	6.36	5.7	5.83	6.3(0.32)	5.73(41000)

a) The values in the parentheses are the calculated oscillator strengths.
b) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957).

We also calculated the transition energies of $C_7H_7^+$ by use of a modified version of the CNDO/2 method parametrized by Tajiri *et al.*,[5] assuming the carbon skeleton to be heptagonal (D_{7h}) and also assuming each bond length to be 1.40 Å. The calculated transition energies are listed in Table 1, along with the observed values. The values predicted within the framework of the CNDO/2 method are in quite good agreement with the experimental data. The results of the previous authors are also included in the table for the sake of comparison.

On the other hand, recently, with the availability of very sensitive photoelectric spectropolarimeters, interest in optical activity measurements in the magnetic field through absorption bands (Magnetic Circular Dichroism: MCD) has been revived. Many authors[6–9] have used the MCD technique in order to extract information on the ground- and excited-states of ions and molecules. According to the theoretical consideration of Schatz and McCafferry,[10] when either the ground- or excited-state of a compound is degenerate, the Faraday A term is observed. The degeneracy of the ground-state causes the Faraday C term. In addition to these two terms, the B term originates from the mixing of the wavefunctions of the ground- and excited-states with some other states. Therefore, the molar ellipticity $[\theta]_M$(in deg·gauss^{-1}·cm^2·mol^{-1}) may be expressed as:

$$[\theta]_M = -21.348\{f_1A + f_2(B + C/kT)\}$$

where f_1 and f_2 are the functions of the frequency, ν, of the incident light (in general, a damped oscillator model is assumed).

Here let us turn again to the discussion of the electronic state of the tropylium cation. We should observe the A term for each band of the cation in question if we believe the predictions of previous authors, who assigned the $^1A_1' \rightarrow {}^1E_1'$ transition to the shorter wavelength absorption, and $^1A_1' \rightarrow {}^1E_3'$ to the longer. Therefore, we tried to measure the UV and MCD spectra of the tropylium cation in order to confirm the above assignment. The purification of the crude BF_4 salt was achieved by adding ether to its acetonitrile solution

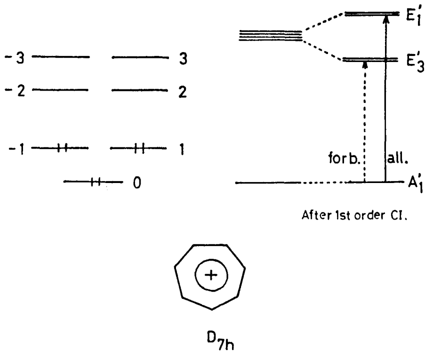

Fig. 1. π-molecular orbitals labeled by the ring quantum number and the electronic states of tropylium cation.

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1) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

2) J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23**, 2347 (1955).

3) A. Julg, *J. Chim. Phys.*, **59**, 567 (1962).

4) E. Heilbronner and J. N. Murrell, *Mol. Phys.*, **6**, 1 (1963).

5) A. Tajiri, N, Ohmichi, and T. Nakajima, This Bulletin, **44**, 2347 (1971).

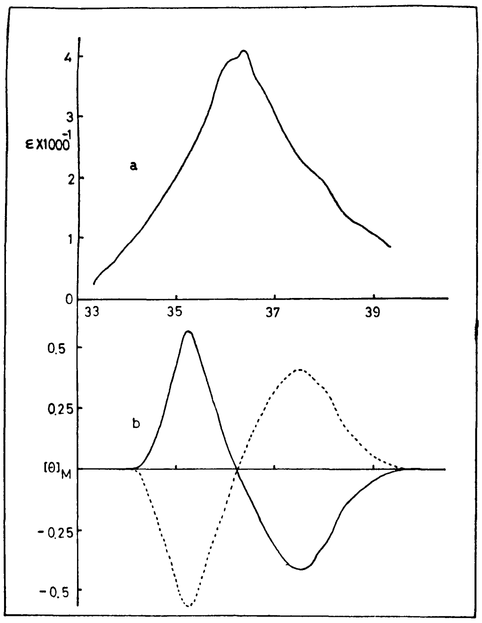
6) B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 6170 (1967).

7) B. Briat, D. A. Schooley, R. Records, E. Bunnerberg, and C. Djerassi, *ibid.*, **89**, 7062 (1967).

8) B. Briat, D. A. Schooley, R. Records, E. Bunnerberg, C. Djerassi, and E. Vogel, *ibid.*, **90**, 4691 (1968).

9) P. J. Stephens, P. N. Schatz, A. B. Ritchie, and A. J. McCafferry, *J. Chem. Phys.*, **48**, 132 (1968).

10) P. N. Schatz and A. J. McCafferry, *Quart. Rev.*, **23**, 552 (1969).



Frequency (kK)

Fig. 2. (a) Molar extinction coefficient of tropylium cation in N/10 HCl solution at room temperature (300°K). (b) Molar ellipticity per unit magnetic field of tropylium cation in N/10 HCl solution at room temperature (300°K). The dotted line is obtained when the current in the magnet is reversed.

until white crystals formed. The concentration of this salt in the N/10 HCl solution was found to be 2.01×10^{-4} mol/l. For the measurement of the MCD spectrum, we employed a JASCO ORD/UV-5 recording spectropolarimeter provided with a CD measuring attachment and a 10 KG electric magnet.

Figure 1 shows the π-molecular orbitals and a schematic diagram of the two excited states caused by the lowest electronic transition from the degenerate HOMO to the degenerate LVMO. In Fig. 2 the UV and MCD spectra are shown. Unfortunately, however, because of the difficulties of the MCD measurement in the shorter-wavelength region, we were obliged to limit our measurement to the wavelength region longer than 230 nm.

A clear Faraday A term is shown in Fig. 2; its inflection point coincides with the absorption maximum (4.5 eV) within the limits of experimental error. This, in turn, shows that the lowest excited state of the tropylium cation, corresponding to the longest-wavelength absorption band, which is forbidden by the symmetry but which is partially allowed by the vibrational process, belongs to the $^1E_3'$ irreducible representation of the D_{7h} point group. Furthermore, the ground-state is totally symmetric and non-degenerate because of the lack of the Faraday C term, which should have an extreme in the MCD spectrum near the absorption maximum.

Actually the Faraday A term should be discussed in terms of an A/D which gives the parameters of theoretical interest and, in turn, the magnetic moment of the excited-state, where D is the dipole strength of the particular spectral line. From the observed MCD and UV spectra for this cation, we obtained the A/D value, which was estimated to be $-1.40\ \beta$ by use of the method of Briat *et al.*[6] At the same time, $[B+C/kT]/D$ was found to be negligibly small.

We conclude that the MCD measurements help in the direct assignment of an absorption band and, accordingly, provide us with information on the nature of the ground- and excited-states of ions and molecules.

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