

## THE ELECTRONIC SPECTRUM OF THE TROPONE MOLECULE

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**Abstract**—From both theoretical and experimental examination of the first absorption band of the tropone spectrum, it is concluded that the band is composed of two electronic  $\pi \rightarrow \pi^*$  transitions having parallel and perpendicular polarizations with respect to the symmetry axis of the molecule; this is in complete agreement with the results of Weltin *et al.*

The most important thing to account for such an assignment of the tropone spectrum in a theoretical manner is to consider the bond alternate characters.

### INTRODUCTION

THE electronic absorption spectrum of the tropone molecule as a typical non-benzenoid compound has been investigated as the assignment of the first band of the absorption spectrum around 300  $\mu$  has not been well established.

Until recently, the band of the tropone spectrum has been considered to consist of a single electronic transition. In fact, a calculation<sup>1</sup> based on the "molecules in molecules" method has supported the assignment of the first band around 300  $\mu$  as being due to the single electronic  $\pi$  to  $\pi^*$  transition with a polarization perpendicular to the symmetry axis of the molecule.

However, in 1963, from the dichroism of the absorption spectrum induced by the external electric field, Weltin *et al.*<sup>2</sup> established that the band is composed of two different  $\pi \rightarrow \pi^*$  electronic transitions with different polarizations. The authors carried out a theoretical calculation based on the simplified Pariser, Parr and Pople method and obtained results which are in fair agreement with their own experiments.

Lately Julg and Bonnet<sup>3</sup> reported a calculation based on their improved MO method which takes into account the correlative effects between electrons, and obtained two component transitions for the first band of the absorption spectrum.

Recently Inuzuka and Yokota<sup>4</sup> reported the Pariser, Parr and Pople type S.C.F. M.O. calculation and obtained similar results.

Although there appear to be no more problems in connection with the first absorption band of the tropone spectrum, it is necessary to reconsider the experimental results on the dichroism of the tropone spectrum for the following reasons:

First, from the nature of the measurement by Weltin *et al.*, it is difficult to determine whether the perpendicular component of the first band is  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$ , although the parallel component is uniquely determined to be of the  $\pi \rightarrow \pi^*$  type. In the experiment of the dichroism induced by the external electric field, the molecules will orient only their dipoles in the direction of the field. Thus it remains undetermined whether the direction of the transition moment perpendicular to the dipole is in-plane or out-of-plane of the molecule; in the latter case, the transition must be of the  $n \rightarrow \pi^*$  type.

According to the experiment by Weltin *et al.*, the values of the molar extinction coefficients  $\epsilon$  for both component transitions of the first band are about  $\sim 10^3$ . Generally, the  $\epsilon$  values for the symmetry allowed  $n \rightarrow \pi^*$  transitions<sup>5</sup> are known to be in the range of  $10^2 \sim 10^3$ . Accordingly, it is dangerous to make the band assignment of the observed absorption spectra only on the basis of their polarizations and intensities, especially in this experiment.

From these considerations, in this paper we re-examine the assignment of the first band of the tropone absorption spectrum from both theoretical and experimental points of view.

### THEORETICAL CALCULATION

Some properties of the tropone molecules are now well known. For example, it gives an addition compound by the Diels–Alder reaction,<sup>6</sup> and the chemical shifts of its aromatic protons appear at a higher field as compared to those of the benzene molecule.<sup>7,8</sup> All these properties reflect the reduced delocalization of the  $\pi$  electrons of the molecule. Nakajima and Katagiri<sup>9</sup> have pointed out the importance of the bond alternative character, especially in the nonbenzenoid compounds.

As suggested by these observations, it is very important to take into account the reduced delocalization of  $\pi$  electrons into the theoretical calculation of electronic problems of the molecule. In this work, we employed a simple ASMO method, the starting MO of which is Hückel type's. The effect of non-bonding electrons in the  $2p_y$  orbital of the carbonyl oxygen atom is explicitly included according to the formulation by Anno *et al.*<sup>10</sup> The starting Hückel type MO was also varied by the introduction of the bond alternation parameter  $k$  until a good fit of the calculated transition energies with the observed spectral pattern was obtained. The reduced aromatic character of the tropone molecule stated above is incorporated by the introduction of the bond alternation parameter  $k$ , which is defined as the ratio of  $\beta_s$  for a single bond to  $\beta_d$  for a double bond in the Kekulé structure of the molecule.<sup>9</sup> Then  $k = 1$  means the complete delocalization, and  $k = 0$  the complete localization of  $\pi$  electrons.

The values of  $\alpha_O = \alpha_C + 0.2 \beta_{C=C}$  and  $\beta_{C=O} = \beta_{C=C}$  were assumed in calculating the Hückel type orbitals for the starting MO in the ASMO method. These values are obtained from comparisons between the experimental and calculated values for both the first ionization potentials and the absorption frequencies of ethylene and formaldehyde molecules. The effects caused by variations of these parameters on the final results were also examined since there was a possibility that they were not the best.

By the standard procedure<sup>11</sup> of the ASMO method, the transition energies from the  $i$ th to the  $k$ th orbitals are given as,

$$\begin{aligned}
 {}^{1,3}E_{i \rightarrow k} - E_0 = & \sum_r \sum_s \{ (C_{kr}C_{ks} - C_{ir}C_{is}) H_{rs}^{\text{core}} \\
 & + \left[ \sum_j (2C_{jr}^2 C_{ks}^2 - C_{jr}C_{kr}C_{js}C_{ks} - 2C_{ir}^2 C_{js}^2 + C_{ir}C_{jr}C_{is}C_{js}) \right. \\
 & \left. - C_{ir}^2 C_{ks}^2 + C_{ir}C_{kr}C_{is}C_{ks} \pm C_{ir}C_{kr}C_{is}C_{ks} \right] \gamma_{rs} \},
 \end{aligned}$$

where the Pariser–Parr approximation<sup>11</sup> with zero differential overlap is assumed, and  $C_{ir}$  etc. are the coefficients of the  $r$ th atomic orbital  $\chi_r$  in the  $i$ th MO, and  $H_{rs}^{\text{core}}$  and  $\gamma_{rs}$  are the usual core and Coulomb integrals, respectively. The penetration integrals

are neglected in the calculation of  $H_{rr}^{\text{core}}$ . The values of  $H_{rr}$  are evaluated from the approximation formula by Kon.<sup>12</sup> One center Coulomb integrals are approximated by the usual formula  $\gamma_{rr} = W_r - A_r$ , where  $W_r$  and  $A_r$  are, respectively, the ionization potential and electron affinity of the valence state of the  $r$ th atom, taken from the data of Prichard and Skinner's paper.<sup>13</sup> Two center Coulomb integrals are calculated from the quadratic equations of the interatomic distances derived by Anno *et al.*<sup>10</sup> and Fumi and Parr.<sup>14</sup> The geometrical data are taken from the work of the electron diffraction on the molecule by Kimura.<sup>15</sup> The values of all integrals used in the calculation are collected in Table 1.

## RESULTS AND DISCUSSIONS

The locations of the excited states thus obtained are shown in Fig. 2 with the various  $k$  values, and in Tables 2 and 3 with  $k = 0.5$ . The Hückel type MO of the tropone molecule, in the case of  $k = 0.5$ , is given in Table 4. In Tables 2 and 3 are shown the results of the full calculations including non-bonding electrons. In Fig. 2 the behaviors of  $n \rightarrow \pi^*$  transitions with  $k$  values are omitted in order to avoid complexity of the figure.

Contrary to our presupposition, the symmetry allowed  $n \rightarrow \pi^*$  transition could not be obtained in the longer wavelength region even though various  $k$  values were assumed. On the other hand, in the neighbourhood of  $k = 0.5$  the two differently polarized  $\pi \rightarrow \pi^*$  transitions appear to reproduce the observed spectrum in a satisfactory manner. These facts show that the perpendicular component of the first band of the tropone spectrum observed by Weltin *et al.* is certainly a  $\pi \rightarrow \pi^*$  transition as shown in Fig. 2, but not an  $n \rightarrow \pi^*$  transition suggested above.

Interestingly, in Fig. 2 it is found that the observed spectral pattern cannot be reproduced with the value of  $k = 1$ . The results reported by Hosoya *et al.*<sup>1</sup> seem to correspond closely to those with  $k = 1$ , where the first band is composed of only one perpendicular  $\pi \rightarrow \pi^*$  transition.

It is noteworthy that the different value  $\alpha + \beta$  for the Coulomb integral of the carbonyl oxygen atom, which is usually used,<sup>22</sup> could not explain the spectrum even when procedures similar to those employed in the above theoretical scheme were adopted. From Table 3 the location of the lowest triplet level is seen to be at very low frequencies, which may provide an explanation for the nonappearance of the phosphorescence of the molecule.<sup>16</sup>

In Fig. 3 are shown the changes of the Hückel orbital energies of the heptafulvene molecule accompanying changes of the Coulomb integrals of the terminal carbon atom, based on a simple perturbational calculation. The relation between the spectra of heptafulvene and tropone is well illustrated by the figure. With an increase of the Coulomb integral of the terminal carbon atom of heptafulven, the two transitions corresponding to the bands 280  $\mu\mu$  (parallel) and 430  $\mu\mu$  (perpendicular)<sup>17</sup> first approach each other, then overlap, and finally exchange their positions.

These simple considerations also serve to illustrate not only the importance of the value of the Coulomb integral of the terminal atom for the understanding of the spectral change from heptafulvene to tropone, but also the justification in assigning the first band of the tropone spectrum to the two component transitions with different polarizations.

In Table 5 are collected some theoretical works on the band assignments of the tropone spectrum with experimental data.

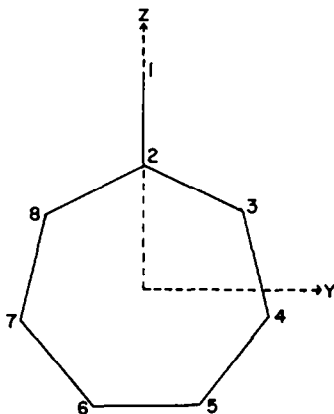


FIG. 1 Coordinate system and numbering of the atoms in tropone molecule.

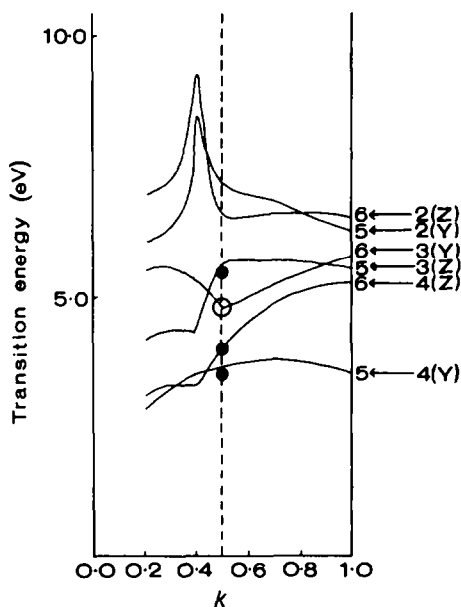


FIG. 2 The variation of the lower singlet excited states with  $k$  values. The figures at the extreme right show the pair of the orbitals among which the transitions take place. The vertical dotted line is drawn at  $k = 0.5$ . The intersection of this line with each curve should be compared with the experimental values shown by black circles. The white circle is the value taken from the data by Tanizaki<sup>20</sup> on the dichromatic character of tropone derivatives adsorbed on the extended polyvinyl alcohol.

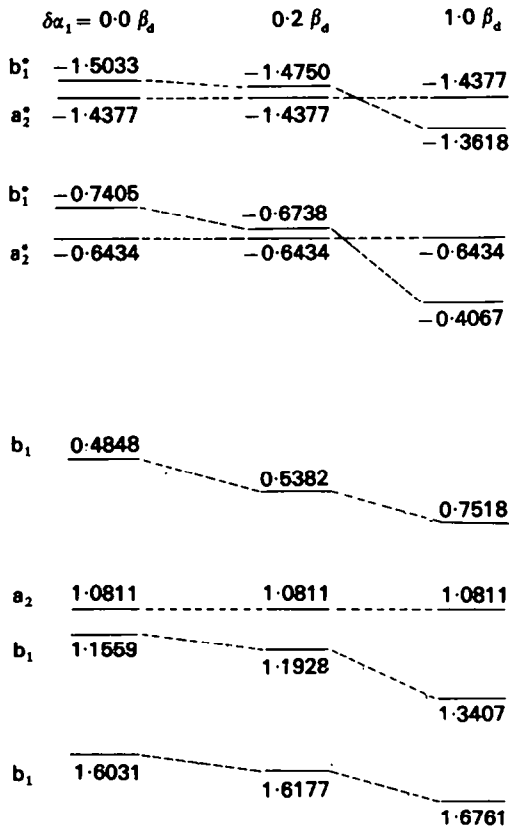


FIG. 3 The changes of the orbital energies of heptfulvene ( $k = 0.57$ ) with the Coulomb integral of the terminal carbon atom. The value of  $k = 0.57$  for the molecule was taken from Ref. 17.

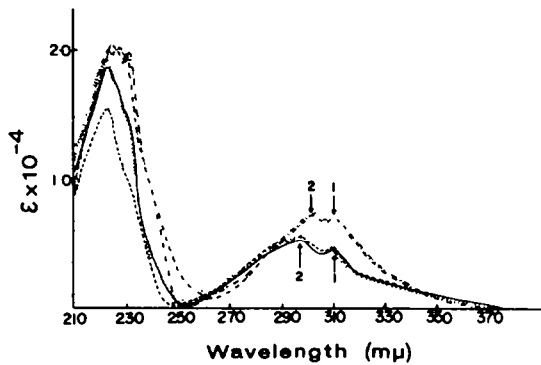


FIG. 4 The absorption spectra of tropone in isopentane (—), n-hexane (---), methylcyclohexane (·····), ethanol (-·-·-), and methanol (- - - -).

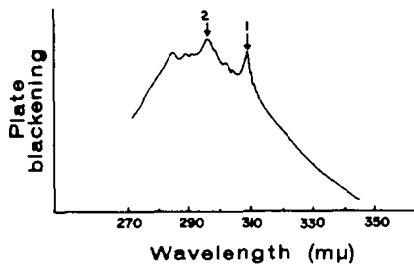


FIG. 5 The absorption spectrum of tropone vapour at 60°.

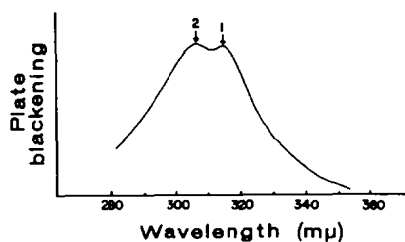


FIG. 6 The absorption spectrum of tropone in mixed solvent (the mixture of isopentane and methylcyclohexane with the volume ratio of 2:3) at -170°.

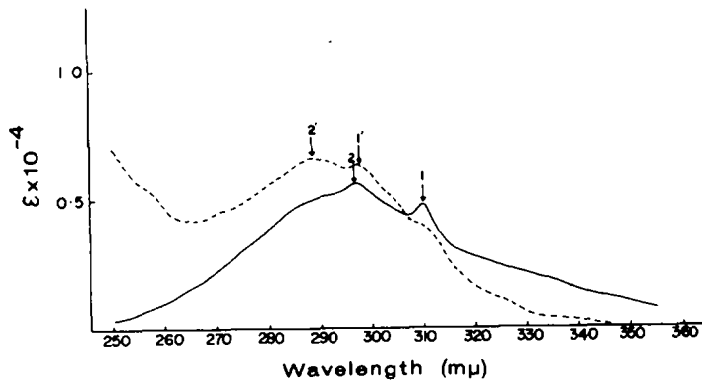


FIG. 7. The absorption spectra of tropone (—) and tropone-oxime (----) in n-hexane.

TABLE 1. THE VALUES OF VARIOUS TYPES OF INTEGRALS USED IN THE PRESENT WORK

$\gamma$ integrals (eV)		
$\gamma_{11} = 14.52$	$\gamma_{22} = 11.08$	$\gamma_{92} = 7.9212^c$
$\gamma_{12} = 8.5280^a$	$\gamma_{23} = 7.5019^b$	$\gamma_{93} = 5.8953^c$
$\gamma_{13} = 6.0432^a$	$\gamma_{24} = 5.3951^b$	$\gamma_{94} = 3.9370^d$
$\gamma_{14} = 3.9389^d$	$\gamma_{25} = 4.4484^d$	$\gamma_{95} = 3.2394^d$
$\gamma_{15} = 3.2401^d$	$\gamma_{91} = 12.62$	$\gamma_{99} = 14.75$
		$\delta_{19} = 0.95^e$
$\alpha$ integrals (eV)		
$\alpha_1 = -W_{2p}^0 - \gamma_{12} - 2\gamma_{13} - 2\gamma_{14} - 2\gamma_{15} - 2\gamma_{91}$		
$\alpha_2 = -W_{2p}^c - \gamma_{12} - 2\gamma_{23} - 2\gamma_{24} - 2\gamma_{25} - 2\gamma_{92}$		
$\alpha_3 = -W_{2p}^c - \gamma_{13} - 2\gamma_{23} - 2\gamma_{24} - 2\gamma_{25} - 2\gamma_{93}$		
$\alpha_4 = -W_{2p}^c - \gamma_{14} - 2\gamma_{23} - 2\gamma_{24} - 2\gamma_{25} - 2\gamma_{94}$		
$\alpha_5 = -W_{2p}^c - \gamma_{15} - 2\gamma_{23} - 2\gamma_{24} - 2\gamma_{25} - 2\gamma_{95}$		
$\alpha_9 = -W_{2p}^c - \gamma_{91} - 2\gamma_{92} - 2\gamma_{93} - 2\gamma_{94} - 2\gamma_{95} - \gamma_{99}$		
$\beta$ integrals (eV)		
$\beta_{12} = -2.2013$		
$\beta_{23} = -2.3194$		

<sup>a</sup>  $\gamma_{12}, \gamma_{13}$  are approximated by the equation

$$(CC|OO) = 12.80 - 3.8837 r + 0.3914 r^2,$$

where  $r$  is the internuclear distance in Å.

<sup>b</sup>  $\gamma_{23}, \gamma_{24}$  are approximated by the equation

$$(CC|CC) = 11.08 - 2.9226 r + 0.26203 r^2.$$

<sup>c</sup>  $\gamma_{92}, \gamma_{93}$  are approximated by the equation

$$(CC|O^*O^*) = 11.23 - 2.9506 r + 0.25760 r^2.$$

<sup>d</sup> These integrals are calculated explicitly from Roothaan's formula<sup>21</sup> using the effective nuclear charges of 3.25 and 4.55 for the carbon and oxygen atoms, respectively.

<sup>e</sup>  $\delta_{19}$  is an abbreviation of the integral

$$\delta_{19} = (19|19) = \int \chi_1^*(1)\chi_9^*(1)e^2/r_{12}\chi_1(2)\chi_9(2) d\tau_1 d\tau_2.$$

TABLE 2. THE LOCATION OF THE LOWER EXCITED SINGLET STATES CALCULATED BY TAKING ACCOUNT OF  $n$ -ELECTRONS OF OXYGEN ATOM (THE CASE OF  $k = 0.5$ )

Transition type*	Transition energy (eV)	Oscillator strength
$^1B_2 \leftarrow A_1$ (Y) $5 \leftarrow 4$	3.63	0.085
$^1A_1 \leftarrow A_1$ (Z) $6 \leftarrow 4$	4.04	0.695
$^1B_2 \leftarrow A_1$ (Y) $6 \leftarrow 3$	4.78	0.104
$^1A_1 \leftarrow A_1$ (Z) $5 \leftarrow 3$	5.71	0.480
$^1A_1 \leftarrow A_1$ (Z) $6 \leftarrow 2$	6.52	0.072
$^1B_2 \leftarrow A_1$ (Y) $5 \leftarrow 2$	7.14	0.370
$^1A_2 \leftarrow A_1$ (forb.) $6 \leftarrow n$	4.74	
$^1A_2 \leftarrow A_1$ (forb.) $8 \leftarrow n$	6.67	
$^1B_1 \leftarrow A_1$ (X) $5 \leftarrow n$	8.14	

\* The letter in bracket shows the direction of the polarization, and (forb.) the forbidden character of the transition. The designation  $6 \leftarrow 4$ ,  $6 \leftarrow n$ , etc mean the transition from the orbital 4 or  $n$  to the orbital 6, etc.

TABLE 3. THE LOCATION OF THE LOWER EXCITED TRIPLET STATES CALCULATED BY TAKING ACCOUNT OF  $n$ -ELECTRONS OF OXYGEN ATOM

Transition type	$k$			
	0.5	0.6	0.7	1.0
$^3A_1 \leftarrow A_1$ ; $6 \leftarrow 4$	1.90	1.98	2.06	2.18
$^3B_2 \leftarrow A_1$ ; $5 \leftarrow 4$	2.80	2.89	2.92	2.62
$^3A_2 \leftarrow A_1$ ; $6 \leftarrow n$	4.11	4.10	4.03	3.49
$^3B_1 \leftarrow A_1$ ; $5 \leftarrow n$	8.14	7.67	7.07	4.77

TABLE 4. HÜCKEL TYPE MO'S AND THEIR ENERGIES OF TROPONE WITH THE PARAMETERS,  $\alpha_1 = \alpha + 0.2\beta_d$  AND  $k = 0.5$ .

Energy, $e_i$	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$	$C_7$	$C_8$	Symmetry
1.5448	0.3379	0.4544	0.3641	0.3353	0.3077	0.3077	0.3353	0.3641	$b_1$
1.1641	0.4803	0.4631	0.0587	-0.1632	-0.4973	-0.4973	-0.1632	0.0587	$b_1^1$
1.0624	0.0	0.0	0.4773	0.5071	0.1229	-0.1229	-0.5071	-0.4773	$a_2$
0.5874	-0.4761	-0.1844	0.3677	0.3082	-0.3734	-0.3734	0.3082	0.3677	$b_1$
-0.6817	0.0	0.0	0.4376	-0.2983	-0.4685	0.4685	0.2983	-0.4376	$a_2^1$
-0.6902	-0.5599	0.4984	0.2159	-0.3982	0.1178	0.1178	-0.3982	0.2159	$b_1^1$
-1.3808	0.0	0.0	0.2841	-0.3923	0.5151	-0.5151	0.3923	-0.2841	$a_2^1$
-1.4061	0.3391	-0.5447	0.4268	-0.3277	0.0681	0.0681	-0.3277	0.4268	$b_1^1$



TABLE 5. THE BAND ASSIGNMENT AND THE EXCITATION ENERGIES OF TROPONE SPECTRUM BY SEVERAL WORKERS

H. Hosoya	A. Julg	E. Weltin	K. Inuzuka	This work	Observed <sup>a</sup>
			3-034(Y)		
		3-55(Y)		3-63(Y)	3-5(Y)
			3-863(Z)		
	4-0(Y) 4-3(Z)	4-2(Z)		4-04(Z)	4-0(Z)
4-98(Y)	↑			4-78(Y)	4-6 ∫ (Y) <sup>b</sup> 5-0
	5-3(Z)				
		5-5(Y) 5-7(Z)	5-423(Y)	5-71(Z)	5-5(Z)
5-86(Z)	5-9(Z)		5-813(Z)		
	↓		6-602(Y) 6-663(Z)	6-52(Z)	
	6-9(Z)			7-16(Y)	

<sup>a</sup> These experimental values are taken from the data of Ref. (2).

<sup>b</sup> The polarization of this band is due to the work of Ref. (20).

TABLE 6. THE FREQUENCIES OF THE PEAKS 1 AND 2 OF TROPONE SPECTRA IN VARIOUS SOLVENTS

Solvent	Dielectric constant $\epsilon$	$\nu_1$ (cm <sup>-1</sup> )	$\nu_2$ (cm <sup>-1</sup> )	$\Delta\nu_{12}$ (cm <sup>-1</sup> )
Isopentane	1.84	32,260	33,750	1490
Hexane	1.89	32,260	33,660	1400
Methylcyclohexane	2.02	32,260	33,620	1360
Ethanol	24.30	32,130	33,100	970
Methanol	32.63	32,130	33,060	930

TABLE 7. THE FREQUENCY SHIFTS OF THE PEAKS 1 AND 2 OF TROPONE SPECTRA AT VARIOUS STATES

	Vapour	Solution		
	60°	20°	-60°	-170°
$\nu_1$ (cm <sup>-1</sup> )	32,410	32,140	32,070	31,790
$\nu_2$ (cm <sup>-1</sup> )	33,870	33,600	33,460	32,720
$\Delta\nu_{12}$ (cm <sup>-1</sup> )	1460	1460	1390	930

## EXPERIMENTAL

In order to confirm experimentally the above theoretical assignments, the absorption spectra of the tropone molecule were re-examined by several methods differing from that of Weltin *et al.* For this purpose, we followed the following three methods: The first is the use of the "solvent effect" on the absorption spectra, the second the use of different spectral shifts of different electronic bands according to the states in which the spectra are observed, and finally the use of the "oxime effect"<sup>18</sup> on the  $n \rightarrow \pi^*$  absorption bands.

(a) *Purification.* EtOH, MeOH, n-hexane, methylcyclohexane and isopentane were used as solvents for the absorption spectra in soln. Their purifications were carefully carried out according to descriptions in "Organic Solvents".<sup>19</sup>

Tropone was freshly prepared and carefully purified in each step of the measurements of the spectra by Prof. S. Ito and co-workers, Organic Chemistry Department, Tohoku University.

(b) *Measurements.* The soln spectra were measured by a Cary Model 14 spectrometer. For measurements of gas spectra, and the soln spectra at liquid air temp, a Shimadzu GE 100 Grating Spectrometer was used, and the spectra photographed on Fuji spectroscopic plates were then analysed by a Riken B-type microphotometer.

*Experimental results and discussions*

(a) *Solvent effects on the spectra.* The first absorption band around 300 m $\mu$  in the tropone spectrum has two rather sharp peaks as indicated by arrows in Fig. 4. We shall call these two as peaks 1 and 2 throughout the discussions. The frequencies of these peaks in each soln spectrum are listed in Table 6, with the dielectric constants of the solvents used. With an increase of the polar character of the solvents, both peaks shifted toward the red, with a larger red shift for peak 2 than for peak 1.

If one assumes that the so-called first band is due only to a single electronic transition, both peaks 1 and 2 should be assigned to the vibrational fine structures associated with the same electronic transition, and also the frequency differences between them should be almost constant in the solution spectra in various solvents.

On the contrary, the frequency differences of both peaks in these spectra are far from constant, changing rather largely as shown in Table 6. These facts are not consistent with the assumption that these peaks are both vibrational members of a single electronic transition.

On the basis of the usual conception of the solvent effect leading to red shifts of the  $\pi \rightarrow \pi^*$  absorption bands in polar solvents, it is concluded that both peaks should be of  $\pi \rightarrow \pi^*$  types and belong to different electronic transitions.

(b) *Spectra measured in different states.* In Figs 5 and 6 are shown the absorption spectra of tropone in gas (at 60°) and soln (in the mixed solvent of isopentane and methylcyclohexane with a volume ratio of 2:3, at liquid air) states. The frequencies of both peaks 1 and 2 in these spectra are given in Table 7.

From the Table, one can find the frequency differences between peaks 1 and 2 also to be far from constant. Accordingly, for the reason stated in the preceding section, one can also conclude that peaks 1 and 2 should belong to different electronic transitions.

(c) *Oxime effect.* Finally, we examined the oxime effect which is often used for the confirmation of the existence of  $n \rightarrow \pi^*$  transition in the longer wavelength region of absorption spectra.

In the compounds which have carbonyl groups as their composite members, e.g. acetone, benzaldehyde and fluorenone, it is well known that the  $n \rightarrow \pi^*$  transitions are observed in the region of the longer wavelength end of their spectra. However, these  $n \rightarrow \pi^*$  bands are not found in the absorption spectra of their oxime derivatives, while the other  $\pi \rightarrow \pi^*$  bands are preserved in the spectra of the oxime. These phenomena are called the "oxime effect on the  $n \rightarrow \pi^*$  absorption spectra", and have been used to check whether the observed band is due to an  $n \rightarrow \pi^*$  transition or not.

The absorption spectra of tropone and tropone-oxime are shown in Fig. 7. Although the two spectra naturally differ slightly, one cannot find any serious changes in both spectra, specially in the neighborhood of the longer wavelength region.

According to the above conception of the oxime effect, it is concluded that no such  $n \rightarrow \pi^*$  transition existed originally in this region.

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