Theoret. chim. Acta (Berl.) 8, 319—333 (1967)

The Electronic Structure and Spectrum of Tropone

HARUO HOSOYA, and SABURO NAGAKURA

Institute of Physical and Chemical Research, Yamato, Saitama, Japan

Received May 22, 1967

The electronic structure and spectrum of tropone were studied by paying special attention to an assignment of the 300 mμ band. The band was shown to have a single $\pi \rightarrow \pi^*$ character overlapped by an $n \rightarrow \pi^*$ transition from the following experimental and theoretical studies: (i) From the comparison of the observed transition energies and intensities with theoretical values obtained by the Pariser-Parr-Pople calculation in which the values of $W_X^{2p\pi}$ (valence state ionization potential of the oxygen atom) and k (bond alternation parameter) taken as guiding parameters were changed widely and their adequateness was carefully examined. (ii) From the correlation among the electronic absorption spectra of tropone, troponeimine, and heptafulvene. (iii) From the finding that the 300 mμ band increases its intensity with the increasing polarity of the solvent. (iv) From the position and intensity of a band newly observed in the vacuum ultraviolet region.

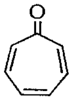
An Tropon wurden Elektronenstruktur und Spektrum untersucht, speziell die 300 mμ-Bande. Diese entsteht aus einem einzigen π-π^*-Übergang, überlagert von einer schwachen n-π^*-Bande, und nicht aus 2 π-π^*-Banden. Als Stütze dienen: 1. eine PPP-Rechnung, bei der das Valenzzustandsionisationspotential von Sauerstoff und der Bindungsalternierungsparameter sorgfältig variiert wurden, 2. die Korrelation der Spektren von Tropon, Troponimin und Heptafulven, 3. der Lösungsmitteleinfluß auf die Bande, 4. eine neuaufgefundene UV-Bande.

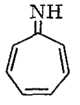
La structure électronique et le spectre de la tropolone ont été étudiés en accordant une attention particulière à l'identification de la bande à 300 mμ. Cette bande a été caractérisée comme résultant d'une transition $\pi \rightarrow \pi^*$ recouverte par une transition $n \rightarrow \pi^*$, à l'aide des arguments théoriques et expérimentaux suivants: 1. à partir de la comparaison des énergies et des intensités de transition observées, avec les valeurs théoriques obtenues par un calcul Pariser-Parr-Pople où les valeurs de $W_X^{2p\pi}$ (potentiel d'ionisation de l'état de valence de l'atome d'oxygène) et de k (paramètre d'alternance des liaisons), considérés comme paramètres régulateurs, ont été largement variées et soigneusement analysées. 2. à partir de la corrélation entre les spectres d'absorption électronique de la tropolone, de la tropolonéimine et de l'heptafulène. 3. à partir du fait que la bande à 300 mμ voit son intensité croitre avec la polarité du solvent. 4. à partir de la position et de l'intensité d'une bande nouvelle observée dans la région de l'ultra-violet lointain.

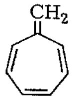
Introduction

The near ultraviolet absorption spectrum of tropone (I, see page 320) is characterized by two bands at 300 and 223 mμ [6]. For the purpose of determining the polarization of these bands, LABHART et al. [25] and also HOSHI et al. [4] measured the ultraviolet absorption of tropone under electric field and in the state adsorbed on a stretched polyvinyl alcohol film, respectively. Their results show that two transition bands polarized perpendicular to each other appear in the 300 mμ region. There are two alternative interpretations for the appearance of the two bands. One of them is that an $n \rightarrow \pi^*$ transition band appears overlapping with the $\pi \rightarrow \pi^*$ transition band in the 300 mμ region. Concerning the other interpretation, several authors [3, 7, 8, 25, 26] pointed out that both transitions have $\pi \rightarrow \pi^*$ characters.

From the theoretical point of view, the calculations carried out so far have some ambiguous points on the choice of parameters concerning both the bond alternation and the valence state ionization potential of the oxygen atom, on which the calculated transition energies and intensities are sharply dependent. In order to check these points carefully and to certify the assignment of the electronic absorption bands, we attempted the reexamination of the π-electron structure of tropone from both theoretical and experimental standpoints, paying special attention to the character of the 300 mμ band.


I


II


III

Pariser-Parr-Pople Calculation of Tropone

The π-electronic structure of tropone was calculated by the Pariser-Parr-Pople method [19, 21], configuration interaction being taken among singly-excited configurations (SCI). In order to clarify the nature of the longest wavelength (300 mμ) band, a number of sets of calculations were performed. It was then found that the lower excited states were sensitive to the two parameters: $- W_X^{2p\pi}$ valence state ionization potential of the terminal oxygen atom, and k $(= \beta_{C-C}/\beta_{C=C})$, the ratio of the core resonance integrals for the single C–C bond to that for the double bond. In Tab. 1 are summarized the other parameters commonly used in the present calculations.

Table 1. *Parameters commonly used in various sets of Pariser-Parr-Pople calculations of tropone*

W_C	-11.22 eV
$\beta_{C=O}$	$-\ 2.40$ eV
(CC | CC) one center	$11.22 - 0.62 = 10.60$ eV
(OO | OO) one center	$17.25 - 2.58 = 14.67$ eV
(pp | qq) two center	Calculated by the quadratic equations
Penetration integrals	Neglected
Geometry of the molecule	See Refs. [6, 9]

The transition energies and oscillator strengths were calculated for the lower excited states, various sets of the $W_X^{2p\pi}$, β_{C-C}, and $\beta_{C=C}$ values being taken. The results are shown in Figs. 1 and 2, where the full and dashed lines are concerned with the transitions polarized parallel and perpendicular, respectively, with regard to the CO bond, and the circle area is proportional to the oscillator strength. For the time being calculated the lower two perpendicular transitions are called I and III, while the parallel ones II and IV.

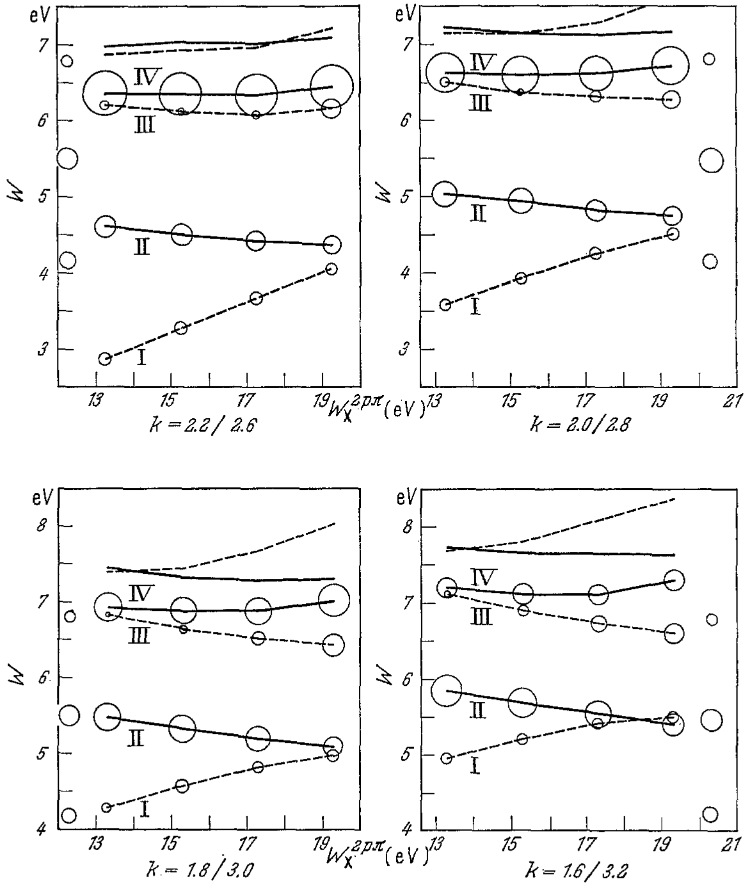


Fig. 1. Diagram showing the k-dependency of the transition energies and intensities of tropone. Full and dashed lines are, respectively, concerned with the transitions polarized parallel and perpendicular to the C=O bond. The circles are drawn in such a way that their areas are proportional to the oscillator strengths. The circles at the right and left sides stand for the experimental values

Fig. 1 shows that,

(i) as the $W_X^{2p\pi}$ becomes deeper, the energies of I and II get closer to each other★.

From Fig. 2 which shows the dependencies of the transition energies and intensities upon k, the following conclusion can be deduced:

(ii) The value of k exerts a great effect upon the calculated transition energy. As the k becomes smaller under the conditions of $\beta_{C-C} + \beta_{C=C} =$ constant, the energies of I and II get larger and their separation smaller.

Apart from these parametric changes, let us consider the possible values of the $W_X^{2p\pi}$ and k. Owing to the electron donating power of the seven-membered ring

---

★ If the electron repulsion integrals are changed simultaneously with the $W_X^{2p\pi}$ (for example, according to the relation $(pp\,|\,pp) = I_p - E_A$ [19]) the separation between I and II tends to be a little smaller.

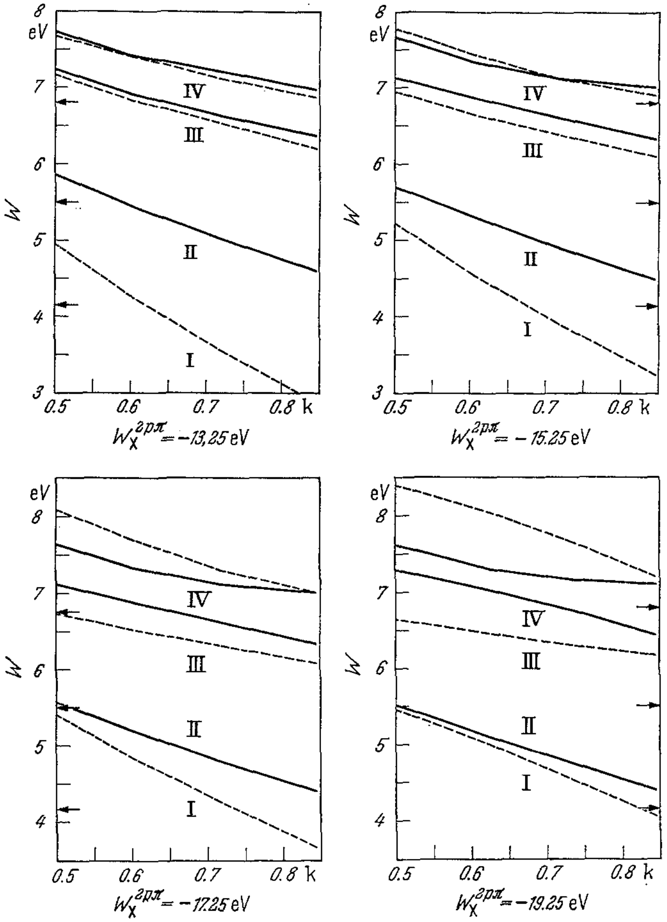


Fig. 2. Diagram showing the $W_X^{2p\pi}$ dependency of the transition energies of tropone. Full and dashed lines are, respectively concerned with the transitions polarized parallel and perpendicular to the C=O bond. The arrows at the right and left sides stand for the experimental values

system, the terminal oxygen atom accepts excess π-electron making the potential $W_X^{2p\pi}$ shallower. The valence state ionization potentials for the isoelectronic oxygen atom and nitrogen mono-negative ion are respectively -17.25 and -3.23 eV (calculated from the table of Pilcher and Skinner [20]). The excess charge of about 0.2 or 0.3 electron on the oxygen atom in tropone may raise the atomic orbital energy by about 2 or 3 eV★. It seems very plausible that the bond alternation in tropone may be smaller (k is larger) than that in butadiene ($k =$ 0.5—0.8), but they do not appreciably deviate from each other. Concerning this point, see the discussion in the next section.

★ According to the VESCF calculation [1] by Gondo [3], the valence state ionization potential of the terminal oxygen atom of tropone was found to be 15.47 eV, while the values for the carbon atoms were in the range of 11.37 – 11.65 eV.

Table 2. *The orbital energies ε_i's and coefficients C_{in}'s of the* SCF-LCAO-MO's *of tropone*[a]

i	Symmetry	ε_i(in eV)	C_{in}[c]				
			1	2	3(8)	4(7)	5(6)
1	S[b]	−15.0580	0.2999	0.3913	0.3598	0.3596	0.3460
2	S	−13.4035	0.5300	0.4730	0.0965	−0.1194	−0.4735
3	A	−13.0449	0.0000	0.0000	±0.4701	±0.5128	±0.1267
4	S	−10.9804	0.5057	0.1727	−0.3639	−0.2967	0.3699
5	S	− 1.0791	0.5076	−0.5099	−0.2316	0.4154	−0.1225
6	A	− 1.0738	0.0000	0.0000	±0.4411	∓0.2878	∓0.4718
7	A	1.9371	0.0000	0.0000	±0.2906	∓0.3927	±0.5112
8	S	2.2077	0.3404	−0.5774	0.4186	−0.3097	0.0655

---

[a] $W_X^{2p\pi} = -15.25$ eV, $k = 1.8/3.0 = 0.600$.

[b] S: symmetric with respect to the plane through the C = O bond perpendicular to the molecular plane; A: antisymmetric.

[c] $n = 1$ for oxygen; $n = 2 - 8$ for carbons around the ring.

Table 3. *Transition energies and wave functions of the lower singlet states of tropone*

a) Parallel transition

Energy (eV)	4 − 5[a]	4 − 8	3 − 6	3 − 7	2 − 5	2 − 8	Oscillator strength
5.3218	0.9443	−0.0987	−0.2929	−0.0128	−0.0277	−0.1090	0.5027
6.8747	0.1592	−0.3557	0.5861	0.0879	0.7021	−0.0626	0.5142
7.3470	0.2249	0.1228	0.7397	0.0818	−0.6168	−0.0030	0.4125
7.8378	0.1534	0.8973	0.1130	−0.1229	0.3531	0.1371	0.1809

b) Perpendicular transition

Energy (eV)	4 − 6	4 − 7	3 − 5	3 − 8	2 − 6	2 − 7	Oscillator strength
4.5717	0.9717	−0.0763	0.2009	0.0499	−0.0442	−0.0713	0.0716
6.6672	0.1963	−0.0566	−0.8953	0.0482	0.3929	0.0042	0.0383
7.4440	0.0382	−0.1239	−0.3782	0.0183	−0.9026	0.1589	0.4211
7.9542	0.0795	0.9665	−0.0996	−0.0377	−0.1207	−0.1837	0.3557

---

[a] Means the coefficient of the configuration caused by the electron excitation from the 4th to the 5th MO.

The results of the calculation with $k = 0.600$ and $W_X^{2p\pi} = -15.25$ eV agree very well with the observed spectrum both in energy and in intensity. The 300 and 223 mμ bands are again assigned to be polarized perpendicular and parallel to the molecular axis, respectively. Tabs. 2 and 3 summarize the typical results of the wave functions and energies obtained by the present authors and Tab. 4 compares the transition energies and oscillator strengths calculated by several authors [2, 7, 8, 25, 26] with those obtained experimentally for the lower excited states of tropone*.

---

* NAKAJIMA et al. [15] and YAMAGUCHI et al. [27] pointed out the double $\pi \rightarrow \pi^*$ character of the 300 mμ band of tropone by perturbation treatment. Tab. 4, however, does not include their results, because their results are very similar to those by YAMAGUCHI et al. [26]. Very recently the authors were communicated by KUNII that he calculated the transition energies of tropone and its derivatives by a modified P.P.P. calculation (variable β method [17]). His results were found to be included in Figs. 1 and 2.

Table 4. *Comparison of the calculated and observed transition energies* (eV) *and intensities (f, in parentheses) of tropone*

No.	Sym.	H.T.N.	H.N.	H.N.	Obsd.	I.Y.	G.	G.	Y.	J.B.	W.H.L.	Sym.	No.
		[6]	(this paper)		[6]	[7]	[3]	[3]	[26]	[8]	[25]		
I	*A*	4.98 (0.06)	4.57 (0.072)	4.29 (0.02)	4.17 (0.13)	3.03 (0.084) 3.86 (0.194)	3.00 (0.093) 3.92 (0.244)	2.58 (0.062) 3.95 (0.289)	3.63 (0.085) 4.04 (0.695)	4.0 (0.3) 4.3 (1.7)	3.50 weak 4.15 strong	*A* *S*	I II
II	*S*	5.86 (0.41)	5.32 (0.503)	5.56 (0.27)	5.51 (0.37)	5.42 (0.021) 5.81 (1.291)	5.65 (0.008) 5.83 (1.585)	5.68 (0.046) 5.88 (1.667)	4.78 (0.104) 5.71 (0.480)	— 6.9 (0.02)	5.56 weak 5.79 strong	*A* *S*	III IV
III	*A*	—	6.67 (0.038)	5.78 (0.03)		6.60 (0.830)	6.33 (0.349)	6.20 (0.057)	7.16 (0.370)	—	—	*A*	
IV	*S*	—	6.88 (0.514)	6.34 (0.11)	~6.9 (0.1)	6.66 (0.410)	6.68 (0.623)	6.50 (0.002)	6.52 (0.072)	—	—	*S*	
Method[a]		CM	PPP +SCI	PPP +DCI		PPP +SCI	PPP +SCI	VESCF +SCI	PP	PPP′ +SCI	PPP		
$W_X^{2p\pi}$ (eV)		—	−15.25	−15.25		~ −17[b]	−17.25	−15.47	$W_C + 2\beta$	—	$W_C - 2.5$		
k		—	0.60	0.636		1.0	1.0	1.0	0.5	—	0.62[b]		
$-\beta_{C-C}$ (eV)		—	1.80	2.10		2.33	2.33[b]	2.35	1.53[b]	[c]	1.6[b]		
$-\beta_{C=C}$ (eV)		—	3.00	3.30					3.07[b]	[c]	2.6[b]		
Charge Density on O		1.446	1.253	1.199		1.480	1.473	1.303	—	1.335	—		

---

[a] CM: method of composite molecules; PPP: Pariser-Parr-Pople method; PP: Pariser-Parr method; PPP′: LCAO améliorée; SCI: singly excited configuration interaction; DCI: CI using doubly excited configurations too.

[b] Surmised.

[c] $r_{C-C} = 1.45$ Å, $r_{C=C} = 1.35$ Å.

Gondo [3], and Inuzuka and Yokota [7] neglected the effect of bond alternation and took a little deeper $W_X^{2p\pi}$. All the transition energies evaluated by them are generally smaller than the observed values and ours. From Fig. 2 it may be inferred that this discrepancy is principally due to the fact that they neglect the bond alternation and take the k value equal to unity. In actuality Figs. 1 and 2 show that our results corresponding to $k = 1$ coincide well with those of Gondo and of Inuzuka and Yokota. On the other hand, Yamaguchi et al. [26] did not use the SCF procedure and configuration interaction. Therefore their result may be less reliable. Since details of the calculations by Julg and Bonnet [8] and by Weltin et al. [25] are not described in their papers, one cannot find which are the dominating causes for the discrepancy; but the number of the configurations taken by them seems to be too small for estimating correctly the magnitudes of the electron interaction.

As was mentioned above, the separation between W_{I} and W_{II} becomes smaller as the valence state energy of the oxygen becomes deeper (as $|W_X^{2p\pi}|$ becomes larger). In order that the $W_0 \to W_{\mathrm{I}}$ and $W_0 \to W_{\mathrm{II}}$ transition bands overlap with each other and the longest wavelength band has a double $\pi \to \pi^*$ character as assigned by the other authors, it may be deduced from Fig. 1 that the $W_X^{2p\pi}$ value should be deeper than -17 eV and therefore the terminal oxygen atom of tropone should be neutral or somewhat positively charged. This is unlikely because of the large electronegativity of the oxygen atom and electron donating ability of the heptatriene ring, and also from the rather strong basicity of tropone [5].

In order to check the reliability of the present calculation, we have carried out an elaborated calculation including doubly excited configurations* for various sets of $W_X^{2p\pi}$, β and k values. As is clearly seen in Tab. 4, in which the typical results are shown in comparison with those of the singly excited configuration interaction calculation, the elaboration shows a tendency to increase the separation between W_{I} and W_{II}. That is to say, the inclusion of the doubly excited configurations lowers the W_{I} state and lifts the W_{II} state and consequently improves to a great extent the agreement between the experimental and calculated transition energies. Judging from the above-mentioned facts, it may be thought that one $\pi \to \pi^*$ band corresponding to the $W_0 \to W_{\mathrm{I}}$ transition appears in the 300 mμ region.

According to our opinion, another band in this region, the existence of which is certified by polarization experiments [4, 25], may be due to an $n \to \pi^*$ transition. By graphical inspection the 300 mμ band was divided into two parts with the oscillator strengths of 0.13 and 0.01. Therefore, it seems to be reasonable to assign the weaker band to an $n \to \pi^*$ transition. Julg and Bonnet [8], and Yamaguchi et al. [26] calculated the energy of the lowest $n \to \pi^*$ transition to be 4.4 eV (282 mμ) and 4.74 eV (263 mμ), respectively. Furthermore, this band may be expected to be polarized parallel to the $C=O$ bond on consistence with the

---

* The program was written by Mr. Fumihiko Hirota in our laboratory, to whom the authors are indebted for the doubly excited configuration interaction calculation. The results shown in Tab. 4 are obtained by using the following parameters; $W_X^{2p\pi} = -15.25$ eV, $\beta_{C-C} = -2.1$ eV, $\beta_{C=C} = -3.3$ eV, and $\beta_{C=O} = -2.7$ eV. The lowest transition (I) is polarized perpendicular to the C=O axis and is separated from the second lowest transition (II) by more than 1.2 eV. The results of the calculation with other sets of parameters show the same tendency.

polarization observed with one of the 300 mμ bands, if it is intensified by coupling with suitable modes of vibrations.

Effect of Bond Alternation

There is another factor complicating the assignment of the electronic spectrum of tropone; namely, it is the effect of the bond alternation [12, 16, 18]. Each set of the present calculations (SCI) for tropone is not self-consistent with respect to the relation between the bond order and the resonance integral. There are proposed several empirical relationships among the bond order (p_{pq}), bond length (r_{pq}), overlap integral (S_{pq}), and core resonance integral (β_{pq}) [11, 12, 14, 16, 17]. Some of them (β in eV and r in Å) are as follows:

$$\beta_{pq} = \beta_0 \exp \{a(1.397 - r_{pq})\} ,$$

$$a = 4.5988 \text{ [14]} , \tag{1}$$

$$a = 3.2196 \text{ [12]} ; \tag{1'}$$

$$\beta_{pq} = -17.765/r_{pq} \text{ [11]} ; \tag{2}$$

$$\beta_{pq} = \beta_0 \, S_{pq}/S_0 ; \tag{3}$$

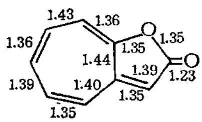
$$r_{pq} = b - c \, p_{pq} , \quad b = 1.52, c = 0.19 \text{ [14]} , \tag{4}$$

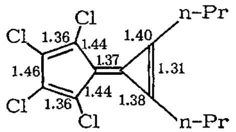
$$b = 1.50, c = 0.15 \text{ [12]} ; \tag{4'}$$

where we chose the benzene as the standard, i.e., $\beta_{pq} = \beta_0 = -2.39$ eV for $r_{pq} = 1.397$ Å [19]. Fig. 3 shows these bond length dependencies of β_{pq}.

The best k value was estimated as follows. First the wave functions of tropone were calculated with trial values of $\beta_{\mathrm{C-C}}$ and $\beta_{\mathrm{C=C}}$*. Then β_{pq} values were evaluated by the use of one of the relations (1)—(3), with (4) or (4′) as an auxiliary relation. The β's were found to be well grouped in two groups: i.e., single and double CC bonds corresponding to the Kekulé type structure (I). The ratio k of the mean $\beta_{\mathrm{C-C}}$ and $\beta_{\mathrm{C=C}}$ values was compared with the trial one. With another parameter $W_X^{2p\pi}$ fixed, the self-consistent k value for each assumption was obtained as is graphically shown in Fig. 4. The results from the different assumptions are listed in Tab. 5 and compared with the corresponding values of butadiene. The latter values were estimated by substituting the observed bond lengths into the relations (1)—(4).

It is noteworthy, however, that the best k value is dependent on the $\beta - p$ relation chosen, and their deviation is considerably large (0.6—0.8). If we assume the values of $k = 0.7$, $\beta_{\mathrm{C-C}} + \beta_{\mathrm{C=C}} = 2\,\beta_0$, and the relation (1′) or (2), $r_{\mathrm{C-C}}$ and $r_{\mathrm{C=C}}$ are obtained as 1.46 and 1.35 Å, respectively. The following two compounds are demonstrated by X-ray crystal analysis experiment to show the bond alternating character of the odd-membered conjugated ring systems [22, 23]:





---

* In practice we assumed an additional restriction that $(\beta_{\mathrm{C-C}} + \beta_{\mathrm{C=C}})/2 = -2.40$ eV, which seems a little arbitrary but not unreasonable.

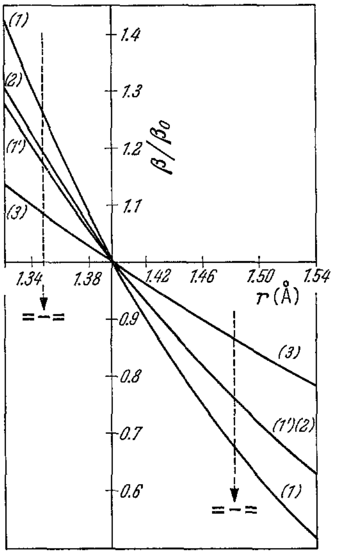


Fig. 3. The relations between β and r. Curves (1), (2), (1') and (3) correspond to the Eqs. (1), (2), (1') and (3) in the text, respectively

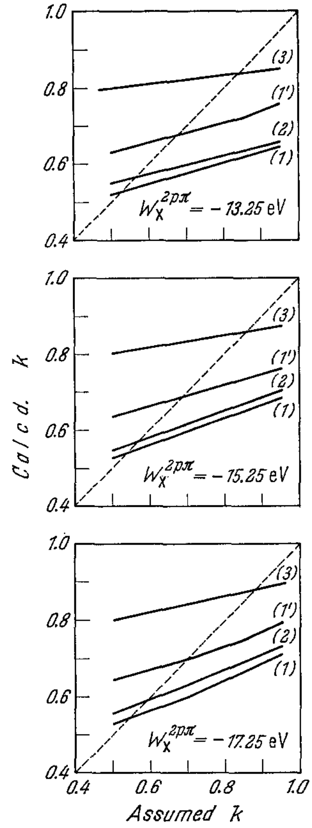


Fig. 4

Fig. 4. Diagram for obtaining the self-consistent k value. The calculation with the parameter k taken from the crossing point gives the results which are self-consistent with respect to the bond alternation if one of the $\beta - r$ relations (1) − (3) is valid

Table 5. *Best k values estimated from different assumptions*

Assumption	Tropone $W_X^{2p\pi}$ (eV)			Butadiene
	−13.25	−15.25	−17.25	
(1) (4)	0.53	0.54	0.55	0.52
(1') (4')	0.68	0.69	0.70	0.64
(2) (4)	0.56	0.57	0.59	0.62
(3) (4)	0.84	0.86	0.88	0.79

The present theoretical consideration on the bond alternation of tropone is in favor of these experimental values. However, the only experimental data for the structure of tropone were based on the assumption that the seven-membered ring is regular [9]. Both theoretical and experimental refinements are wanted to settle this problem.

Relation of Tropone to Heptafulvene and Troponeimine

Next let us examine the relation among the spectra of tropone (I), troponeimine (II), and heptafulvene (III). The spectrum of troponeimine [10]* resembles that of tropone [6] except for the longer wavelength side than 350 mμ (see Fig. 5). A shoulder is distinct at 360 mμ for troponeimine.

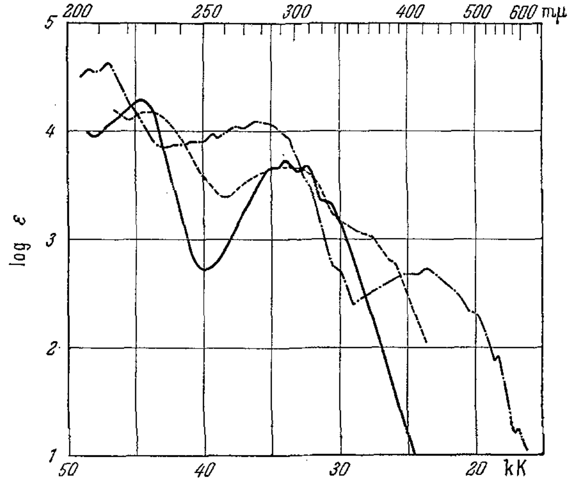


Fig. 5. Ultraviolet absorption spectra of tropone (—) [6], troponeimine (- - -) [10], and heptafulvene (·—) [2]

Table 6. *Calculated and observed transition energies* (eV), *intensities (f, in parentheses), and π-electron density on the terminal carbon atom of heptafulvene*

H. N. Present work	N. K. [16]	I. Y. [7]	Obsd. [2]
3.31 (0.035)	2.82 (0.057)	2.31 (0.051)	2.91 (0.02)
4.46 (0.434)	4.53 (0.89)	4.02 (0.310)	4.43 (0.4)
5.94 (0.236)	—	5.66 (0.015)	5.82 (~0.5)
π-Electron density on the terminal carbon atom			
1.034	1.043	0.963	—

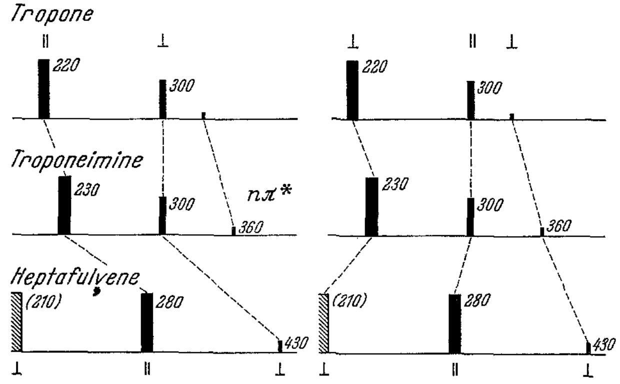
Next let us correlate them with the transitions of heptafulvene [2]. The π-electronic structure of heptafulvene was calculated by the Pariser-Parr-Pople method, with the parameters mostly in common with the case of tropone. As is

---

* The authors wish to express their sincere thanks to Professor I. KITAHARA, Tohoku University, for his kindness in informing them of the data of the absorption spectrum of troponeimine prior to publication.

evident in Tab. 6, all the calculated energies and intensities by the different authors [7, 16] agree fairly well with the experimental values except for the minor discrepancy due to the different choice of parameters. The fact that INUZUKA and YOKOTA [7] got smaller transition energies is again attributed to the neglect of the bond alternation.

There are two possibilities for interpreting the correlation among the absorption bands of heptafulvene, troponeimine and tropone. One of them is that the 300 mμ band of tropone may be the $\pi \to \pi^*$ band corresponding to the 430 mμ band of heptafulvene overlapped with the $n \to \pi^*$ transition band [6]*. The other is the view that the 300 mμ band may consist of the two $\pi \to \pi^*$ transition bands corresponding to the 430 mμ and 280 mμ bands of heptafulvene [4, 7, 15, 25, 26]. The correlation diagrams from the former and latter view-points are respectively shown in Figs. 6a and 6b.



(a) (b)

Fig. 6. Diagrams representing the correlations of the lower transition energy bands among tropone, troponeimine, and heptafulvene: a) the present authors' assignments and b) the alternative. The numerals represent the observed peak wavelengths in mμ. The area of a block is proportional to the intensity

From theoretical consideration shown in Fig. 1, it is clear that the longest wavelength band (430 mμ) of heptafulvene shifts to shorter wavelengths and increases its intensity as the $W_X^{2p\pi}$ becomes deeper. This conclusion is also supported by the elaborated calculation including the doubly excited configurations. From this it may be concluded that the component band polarized perpendicular to the C=O bond of the 300 mμ band of tropone can be regarded as the shifted band of the 430 mμ band of heptafulvene.

Concerning the 280 mμ band of heptafulvene, the correlation is more complicated. According to our opinion, the band corresponds to the 223 mμ band of tropone and to the 230 mμ band of troponeimine; namely, it shifts to shorter wavelengths in the order of heptafulvene < troponeimine < tropone, and therefore shifts monotonously to shorter wavelengths with the increasing $| W_X^{2p\pi} |$

---

* It is known that the oscillator strength of an $n \to \pi^*$ transition can be increased up to the order of 10^{-2}, when the $n \to \pi^*$ chromophore is perturbed by some unsaturated system [13]. The f values of 0.01 and 0.015 of the weaker band in the 300 mμ region observed with tropone and troponeimine, respectively, are not extraordinary.

value. On the other hand, according to the other authors' opinion, the 280 mμ band of heptafulvene corresponds to one component of the 300 mμ bands of tropone and troponeimine, and is interpreted to shift to longer wavelengths with the increasing $| W_X^{2p\pi} |$ value.

The results of the Pariser-Parr-Pople calculation considering only singly excited configurations made by the present authors (see Fig. 1) and also of the simple perturbation treatment made by NAKAJIMA et al. [15] prospect that the 280 mμ band of heptafulvene should shift to longer wavelengths with an increasing $| W_X^{2p\pi} |$ value. However, the more elaborated calculation considering the doubly excited configurations made by the present authors truns out to show the reverse tendency, namely blue shift with increasing $| W_X^{2p\pi} |$ value. Therefore, in the present state of the theoretical study, it may be said that our interpretation on the correlation of the 280 mμ band of heptafulvene seems to be more probable, though not conclusive, than the alternative interpretation.

Furthermore, according to our interpretation shown in Fig. 6a, the corresponding bands shift monotonously to shorter wavelengths with increasing $| W_X^{2p\pi} |$ value (280, 230 and 223 mμ for heptafulvene, troponeimine and tropone, respectively). On the other hand, according to the alternative interpretation shown in Fig. 6b, the wavelength shifts of the corresponding bands become complicated; that is to say, the 230 mμ band of troponeimine and the 223 mμ band of tropone may be regarded as red-shifted bands of 210 mμ band of heptafulvene, and the magnitude of the red-shift is smaller for tropone than for troponeimine, while the oxygen is in general more electronegative than the nitrogen. Therefore it turns out in this case that the corresponding bands do not shift monotonously with the $W_X^{2p\pi}$ value. This might be unlikely to occur, though not impossible. The above-mentioned facts on the wavelength shifts seems to support our interpretation that the 300 mμ band of tropone is composed of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition bands.

Experimental Results Newly Obtained

Vacuum ultraviolet absorption spectrum of tropone was measured with a vacuum spectrophotometer constructed in our laboratory [24] (Fig. 7)*. One more band was found in the shorter wavelength side of the 223 mμ band. It is located at about 180 mμ (6.9 eV). It appears as a shoulder of a very strong absorption of higher energy, and the intensity is a little smaller than the 223 mμ band. This new information is also in favor of our calculation and assignments. According to our assignment, the new shoulder corresponds to the transition to the W_{III} state. As clearly seen from Figs. 1 and 2, the W_{IV} state is located just above the W_{III} state and the transition to the former is much stronger than that to the latter. This is well coincident with the experimental fact that the 180 mμ band appears as a shoulder of the strong band at the shorter wavelength side. On the other hand, the alternative assignment, according to which the 180 mμ band corresponds to the transition to the W_{IV} state, shows the discrepancy even qualitatively from the

---

* We thank Dr. KOJI KAYA for the measurement of the vacuum ultraviolet absorption spectrum of tropone. We are also indebted to Professor YOSHIE TANIZAKI and Dr. TOSHIHIKO HOSHI of Tokyo Institute of Technology, and also Sankyo Pharmaceutical Co. for the gift of tropone.

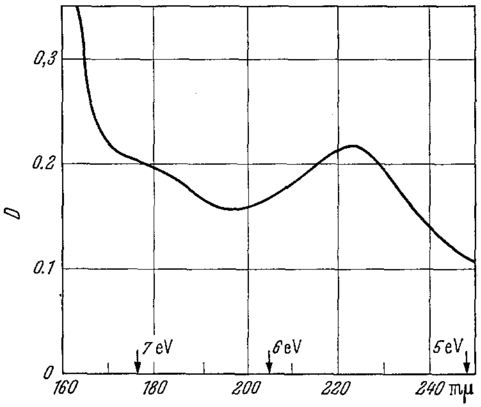
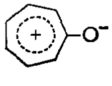


Fig. 7. Vacuum ultraviolet absorption spectrum of tropone vapor

above-mentioned observation. That is to say, from this assignment and the theoretical results shown in Figs. 1 and 2, it might be expected that the 180 mμ band should have absolutely strong intensity and at least be stronger than the 223 mμ band. However the actual observation is completely reverse.

For the purpose of obtaining further information about the assignment of the bands in the 300 mμ region, we measured the absorption spectrum of tropone in various solvents like water, ethanol, ether, acetonitrile, dichloromethane and *n*-heptane. The results are shown in Fig. 8. From this figure it is clear that the 300 mμ band remarkably increases its intensity with the increasing dielectric constants of solvents. Since it may be expected that the electron transfer in the ground state from the heptatriene ring to the oxygen atom increases with the increment in the dielectric constant of solvents*, the above-mentioned findings on the solvent effect means that the 300 mμ band increases its intensity with the increasing electronegativity (or $|W_X^{2p\pi}|$ value) of the X atom. The combination of this fact with the theoretical study shown in Fig. 1 leads to the conclusion that the 300 mμ band has the same character as is expected for the $W_0 \rightarrow W_{\mathrm{I}}$ transition (therefore the 430 mμ band of heptafulvene) and exhibits the completely reverse character expected from that for the $W_0 \rightarrow W_{\mathrm{II}}$ transition (therefore the 280 mμ band of heptafulvene). This means that the $W_0 \rightarrow W_{\mathrm{I}}$ transition band is the main and stronger one in the 300 mμ region of the tropone spectrum. This may be difficult to be understood from the other authors' interpretation that the 300 mμ band of tropone is composed of the weaker 430 mμ band and stronger 280 mμ band of heptafulvene which correspond to the $W_0 \rightarrow W_{\mathrm{I}}$ and $W_0 \rightarrow W_{\mathrm{II}}$ transitions, respectively. Thus, the solvent effect experiment seems to support our interpretation that the 300 mμ band is due to the $W_0 \rightarrow W_{\mathrm{I}}$ transition overlapped with the weak $n \rightarrow \pi^*$ transition.

---

* This may correspond to the fact that the contribution of the polar resonance structure such as  increases with the increasing dielectric constants of solvents.

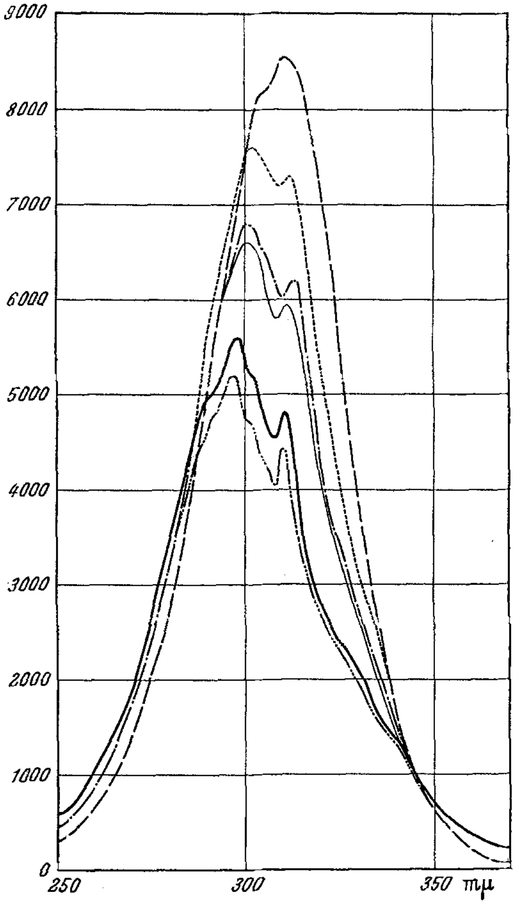


Fig. 8. Solvent effect of the 300 mμ band of tropone. The solvents are H_2O (– –), C_2H_5OH (·········), CH_2Cl_2 (– · – ·), CH_3CN (——), $(C_2H_5)_2O$ (——), and n-C_7H_{16} (– · · ·)

Finally we should like to add that the final conclusion on the assignment of the 300 mμ band of tropone may be reserved until reliable experimental information on the bond alternation and therefore on the bond lengths of tropone can be obtained. Further, it may be pointed out that polarization measurements of the electronic absorption bands of various tropone derivatives are important for settling this problem.

References

1. Brown, R. D., and M. L. Heffernan: Trans. Faraday Soc. **54**, 757 (1958).
2. Doering, W. von E., and D. W. Wiley: Tetrahedron **11**, 183 (1960).
3. Gondo, T.: Private communication.
4. Hoshi, T., T. Kobayashi, Y. Tanizaki, and S. Ueda: Presented at the Annual Meeting of the Chemical Society of Japan, Osaka (1965).
5. Hosoya, H., and S. Nagakura: Bull. chem. Soc. Japan **39**, 1414 (1966).
6. —, J. Tanaka, and S. Nagakura: Tetrahedron **18**, 859 (1962); see the references therein.
7. Inuzuka, K., and T. Yokota: J. chem. Physics **44**, 911 (1966).
8. Julg, A., and M. Bonnet: Tetrahedron **20**, 2243 (1964).

9. Kimura, K., S. Suzuki, M. Kimura, and M. Kubo: Bull. chem. Soc. Japan **31**, 1051 (1958).
10. Kitahara, Y.: Private communication.
11. Kon, H.: Bull. chem. Soc. Japan **28**, 275 (1955).
12. Longuet-Higgins, H. C., and L. Salem: Proc. Roy. Soc. (London) **A257**, 445 (1960).
13. Murrell, J. N.: The theory of the electronic spectra of organic molecules, p. 165. London: Methuen Co. Ltd. 1963.
14. Nakajima, T.: Bull. chem. Soc. Japan **38**, 83 (1965).
15. —, S. Kouda, and K. Kikuchi: Presented at the Symposium on Molecular Structure, Osaka 1966.
16. —, and S. Katagiri: Mol. Physics **6**, 149 (1963).
17. Nishimoto, K., and L. S. Forster: Theoret. chim. Acta **4**, 155 (1966).
18. Ooshika, Y.: J. physic. Soc. Japan **12**, 1246 (1957).
19. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
20. Pilcher, G., and H. A. Skinner: J. inorg. nucl. Chem. **24**, 937 (1962).
21. Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953). — Proc. phys. Soc. (London) **A68**, 81 (1955).
22. Sasada, Y.: Bull. chem. Soc. Japan **32**, 171 (1959).
23. —, H. Shimanouchi: Presented at the Symposium on Non-Benzenoid Aromatic Compounds, Sendai (1966).
24. Tsubomura, H., K. Kimura, K. Kaya, J. Tanaka, and S. Nagakura: Bull. chem. Soc. Japan **37**, 417 (1964).
25. Weltin, E., E. Heilbronner, and H. Labhart: Helv. chim. Acta **46**, 2041 (1963).
26. Yamaguchi, H., T. Azumi, Y. Amako, and H. Azumi: Presented at the Symposium on Molecular Structure, Nagoya (1965).
27. —, Y. Amako, and H. Azumi: Presented at the Symposium on Molecular Structure, Osaka (1966).

Prof. Dr. S. Nagakura
The Institute for Solid State Physics
The University of Tokyo
Azabu Minato-ku, Tokyo, Japan