Ultraviolet Absorption Spectra of Troponoids⑴

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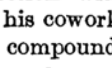
Introduction

In connection with a serial study by T. Nozoe and his coworkers⑵ on "troponoids"—a group of compounds with a seven-membered carbon ring,  (cycloheptatriene-2, 4, 6-one-1),—the present writer has had an opportunity to observe the ultraviolet absorption spectra of more than twenty compounds of this group. It is the purpose of this paper to present what the writer has observed of the general relations between the spectral features and the molecular structures of these compounds and to give explanations concerning these relations.

Data

In Figs. 1—20 are shown graphically the data of the ultraviolet absorption spectra of troponoids, as obtained by means of a Beckman spectrophotometer model DU. Samples used are listed in Table 1, with remarks on them. All of these samples were prepared by Nozoe and his co workers. The structural formulas of most of these compounds were determined

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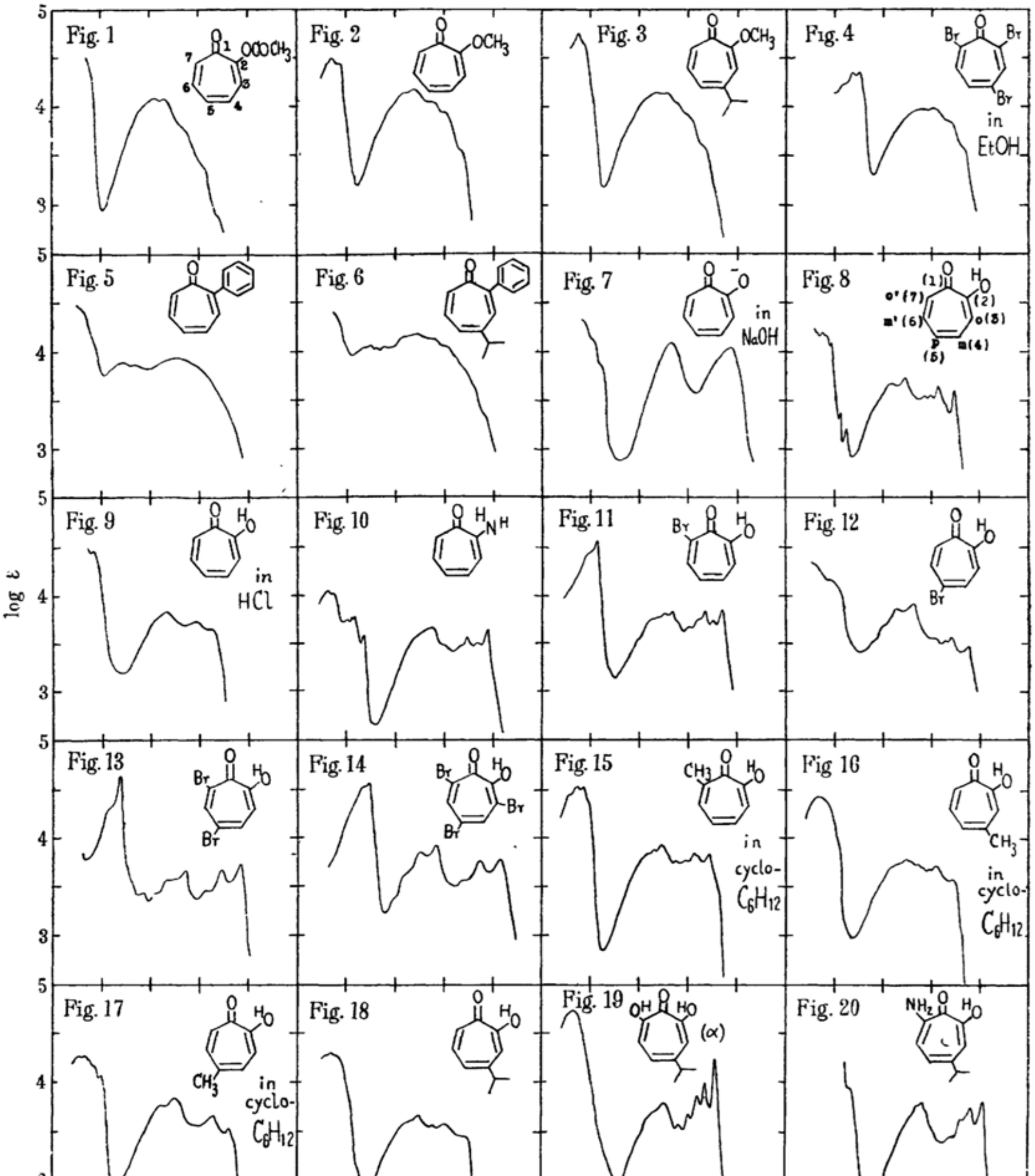
(1) T. Nozoe and his co-workers give the general name "troponoids" to tropone, tropolone, and related compounds.

(2) T. Nozoe, *Sci. Rep. Tohoku Univ.*, Ser. I, **34**, 199 (1950); *Nature*, **167**, 1055 (1951); *Chem and Chem. Industry (Chem. Soc. Japan)*, **4**, 348 (1951).



Figs. 1—20.—Ultraviolet Absorption Spectra of Troponoids
(Solvent: iso octane unless otherwise stated)

Table 1

Substances	Melting Points, °C.	References	Structural Formulas and Ultraviolet Absorption Spectra
Tropolone acetate	69.5-70.5	(3)	Cf. Fig. 1
Tropolone methyl ether	(oil)	(4)	Cf. Fig. 2
Hinokitiol methyl ether	(oil)	(5)	Cf. Fig. 3
2, 4, 7-Tribromotropone	185	(6)	Cf. Fig. 4
2-Phenyltropone	85-86	(7)	Cf. Fig. 5
2-Phenyl-4-(or 6)-isopropyl-tropone	93-94	(7)	Cf. Fig. 6
Tropolone	50-51	(8)	Cf. Figs. 7, 8 and 9
2-Aminotropone	106-107	(9)	Cf. Fig. 10
o-Bromotropolone	107-108	(8) and (10)	Cf. Fig. 11
p-Bromotropolone	190-191	(8)	Cf. Fig. 12
o, *p*-Dibromotropolone	152-153	(10)	Cf. Fig. 13
o, *o*′, *p*-Tribromotropolone	125-126	(8)	Cf. Fig. 14
o-Methyltropolone	51	(11)	Cf. Fig. 15
m-Methyltropolone	76	(12)	Cf. Fig. 16
p-Methyltropolone	110	(5)	Cf. Fig. 17
Hinokitiol (β-Thujaplicin) (*m*-Isopropyl-tropolone)	51-52	(13)	Cf. Fig. 18
o′-Hydroxyhinokitiol	60(α), 52(β), 46(γ)	(14)	Cf. Fig. 19(α)
o′-Aminohinokitiol	99	(15)	Cf. Fig. 20

also by them.(3)~(15) In the present experiments, iso-octane was used as the solvent in most cases, but in the cases where the measurements corresponding to Figs. 4, 7, 9, and 15—17 were made, ethanol, NaOH solution, HCl solution, and cyclohexane were used respectively as the solvents.

Discussion

I. General Features.—Each of the absorption spectra of troponoids so far observed is divisible, without exception, into two parts—one ranging from 200 to 300 mμ which is composed of the absorption bands with ε-values of 10^4-10^5. and the other ranging from 300 to 400 mμ which is composed of the absorption bands a little weaker in intensity ($\varepsilon=10^3$-10^4). This is a characteristic feature common to all the troponoids spectra.

In detail, however, the spectra of troponoids may be classified into two types:

Type A (Tropone type)—This is represented by the spectrum of tropone, which shows only one electronic band in the 300-400 mμ region.(16) The spectra of Figs. 1—6 belong to this type. All of these spectra are of tropone derivatives with no hydrogen bonds.

Type B (Anion type)—This is represented by the spectrum of tropolone anion (Fig. 7), which is observed when tropolone is dissolved in an alkaline solution. Each of the spectra of this type shows two electronic bands in the 300-400 mμ region. The spectra of Figs. 8—20 belong to this type. All of these spectra are of tropone derivatives which have either OH or NH_2 radical on the 2-carbon atom (C_2) (carbon atom adjacent to the carbonyl carbon atom) and an intramolecular hydrogen bond between the OH or NH_2 and the carbonyl oxygen atom.

All the compounds examined have C=O and C=C's conjugated with each other. According to McMurry,(17) it is expected, with such compounds, that two kinds of electronic bands will

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(3) T. Nozoe, S. Seto, and T. Sato, to be published.

(4) T. Nozoe, S. Seto, T. Ikemi, and T. Arai, *Proc. Japan Acad.*, **27**, 102 (1951).

(5) T. Nozoe, *Science of Drugs*, **3**, 171 (1949).

(6) T. Nozoe, Y. Kitahara, T. Ando, and S. Masamune, *Proc. Japan Acad.*, **27**, 415 (1951); H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, **73**, 876 (1951).

(7) T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Japan Acad.*, **27**, 419 (1951).

(8) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama, Ibid., **26**, 38 (1950).

(9) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, Ibid., **27**, 556 (1951).

(10) T. Nozoe, Y. Kitahara, K. Yamane and A. Yoshikoshi, Ibid., **27**, 18 (1951).

(11) T. Nozoe, T. Mukai, and K. Matsui, Ibid., **27**, 646 (1951).

(12) T. Mukai, M. Kunori, H. Kishi, T. Muroi, and K. Matsui, Ibid., **27**, 410 (1951).

(13) T. Nozoe, *Science of Drugs*, **3**, 174 (1949); *Sci. Rep. Tohoku Univ.*, **34**. 199 (1950).

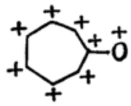
(14) T. Nozoe, Y. Kitahara, and K. Doi, *Proc. Japan Acad.*, **27**, 156 (1951).

(15) T. Nozoe, Y. Kitahara, and K. Doi, *J. Am. Chem. Soc.* **73**, 1895 (1951).

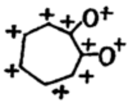
(16) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**. 876 (1951).

(17) H. L. McMurry, *J. Chem. Phys.*, **9**. 231, 241 (1941); Cf. also M. Kasha, Discussions of the Faraday Society, 1950, p. 14.

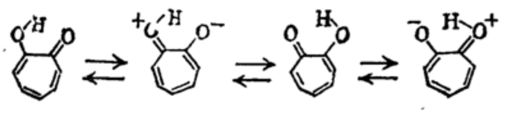
appear: one due to the N→V_n type transitions and the other due to the N→E_n type transitions. The bands of the first kind are related to the π-electrons extending along the entire system of conjugated bonds and are strong in intensity ($\varepsilon \doteqdot 10^4$); while the bands of the second kind are related to the electrons in the non-bonding molecular orbital, largely localized on the oxygen atom and are weak in intensity ($\varepsilon \doteqdot 10^1$). All the observed bands of the compounds now at issue are strong in intensity ($\varepsilon \doteqdot 10^4$), and hence may be assigned to the transitions of the N→V_n type, but not to the transitions of the N→E_n type.

The two bands in the 300—400 mμ and 200—300 mμ regions in the spectra of type A may be regarded as due respectively to N→V_1 and to N→V_2 transitions in a seven-sided ring system composed of conjugated three C=C's and one C=O, viz. a system composed of the field; 

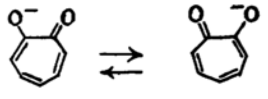
and eight π-electrons. Octatrienal, which has also conjugated three C=C's and one C=O, shows a band at 306 mμ, and this was explained by McMurry⁽¹⁷⁾ as due to the N→V_1 transition. The 300 mμ band in the spectra of type A may be of the same nature as this 306 mμ band.

Tropolone anion may be regarded as a system composed of a field; 

and ten π-electrons. According to Dewar's molecular orbital treatment,⁽¹⁸⁾ the two bands in the 300—400 mμ region as well as the bands in the 200—300 mμ region may be explained as due to the N→V_n transitions in the system just mentioned. The fact that tropolone and its derivatives exhibit spectra of type B, as tropolone anion, may be taken as indicating that they bear a closer resemblance in the electronic state to tropolone anion than to tropolone methyl ether and tropolone acetate, which exhibit spectra of type A. This may in turn indicate that there is a resonance in tropolone somewhat similar,



which resembles the resonance in tropolone anion,



The resonance as above cannot occur in tropolone methyl ether and tropolone acetate, there being no intramolecular hydrogen bond in these compounds. The spectrum of aminotropone (Fig. 10) belongs also to the "Anion type" (type B), indicating that its electronic state resembles that of tropolone anion. The intramolecular N-H...O bonding in this compound seems to act like the O-H...O bonding in tropolone.

II. Effect of Substitution on the Positions of the Bands.—Though, as has been stated above, various spectra belonging to both type A and type B resemble one another in their general feature, they differ from ons another in the positions of their corresponding bands. Of the spectra of type A, that of tropone shows the bands at the shortest wave-lengths, and when Br, isoC_3H_7, OCH_3, or $OCOCH_3$ are substituted for the hydrogen atoms of tropone, they shift toward longer wave-lengths. Of the pectra of type B, that of tropolone shows thee bands at the shortest wave-lengths, and the substitution of Br, CH_3, etc. for the hydrogen atoms of tropolone also causes the shifting of the bands toward longer wave-lengths.⁽¹⁹⁾ The amounts of these shifts ($\varDelta\nu$) are shown in Table 2. As may be seen from the table, the shift of the bands is greatest when the substituent is NH_2, and it becomes less in the order of OH, Br, and alkyl radicals. This order of the amount of shift for different substituent radicals is reverse to the order of the ionization potentials of the radicals.⁽²⁰⁾ There is a tendency that *p* (or 5)-substitution of tropolone (Figs. 12 and 17) gives in general a larger red-shift than *m* (or 4)- or *o* (or 3)-substitution (Figs. 11, 15, and 16); and the amount of the red-shift is approximately additive when two or more radicals are substituted for the hydrogen atoms in one tropolone ring.

These shifts of the bands caused by substitution may be explained as due to the electron migration from the substituent radicals toward the seven-membered ring of the tropone. K. F. Herzfeld⁽²¹⁾ advanced a general theory on the electron migration from the substituent radicals toward the conjugated double-bond

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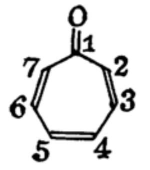
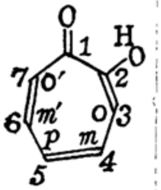
(18) M. J. S. Dewar, *Nature*, **166**, 790 (1950).

(19) *O* (or 3)-and *m* (or 4)-alkyl substitutions are exceptional; they cause a little shifting of the bands toward shorter wave-lengths.

(20) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(21) K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947).

Table 2

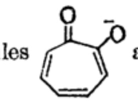
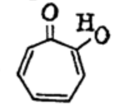
Fundamental System	Substituents	Positions of Absorption Peaks of the Longest Wave-Lengths mμ	cm^{-1}	Shiftings due to the Substitution (Δν), cm^{-1}
	Nothing	310	32200	—
	2-$OCOCH_3$	317	31500	−700
	2-OCH_3	321	31100	−1100
	2-OCH_3-4-isoC_3H_7	325	30700	−1500
	2, 4, 7-Br_3	349	28600	−3600
	Nothing	374	26700	—
	o(or 3)-CH_3	372	26800	+100(19)
	m(or 4)-CH_3	372	26800	+100(19)
	p(or 5)-CH_3	379	26400	−300
	m(or 4)-isoC_3H_7	372	26800	+100(19)
	o(or 3)-Br	385	25900	−800
	p(or 5)-Br	389	25700	−1000
	o, *p*(or 3, 5)-Br_2	392	25500	−1200
	o, *p*, *o'*(or 3, 5, 7)-Br_3	407	24500	−2200
	m(or 4)-isoC_3H_7-*o'*(or 7)-OH	379	26400	−300
	m(or 4)-isoC_3H_7-*o'*(or 7)-NH_2	402	24800	−1900

system, and H. Baba and S. Nagakura(22) made a correction and a supplement to it. According to this theory, the lower the ionization potential of the substituent is, the greater must be the extent of the migration, and accordingly the greater must be the shift of the band caused by the migration; and when the substituent radicals are more than one, the amount of the shift must be the sum of the shifts caused by respective radicals. All these consequences of the theory are in good agreement with what has been observed of the shifts of the bands due to substitutions in tropone and tropolone.

The Baba-Nagakura theory claims that the band due to N→En transition should shift on substitution toward shorter wave-lengths. Then, the fact that all the bands of tropone and tropolone that have been treated in this paper shift on substitution toward longer wave-lengths must be, according to the theory, an indication that these bands are not due to N→En transitions. This is what has already been concluded from the intensity measurements of these bands (page 372).

III. Miscellanies.—Some interesting facts which have come to the writer's notice in the course of the present work are recorded below:

(1) The spectrum of 2-phenyltropone as well as that of 2-phenyl-4 (or 6)-isopropyltropone corresponds nearly to the superposition of the spectra of tropone and benzene. This fact shows that there is but little interaction between π-electrons of the seven-membered ring and the benzene ring in 2-phenyltropone or 2-phenyl-4 (or 6)-isopropyl-tropone.

(2) The spectrum of tropolone in neutral water corresponds exactly to the superposition in a certain proportion of the spectra of tropolone in NaOH (Fig. 7) and of tropolone in HCl (Fig. 9). This fact shows that in the aqueous solution of tropolone two forms of molecules  and  coexist.

(3) The absorption bands of tropolone acetate (Fig. 1) are situated at slightly shorter wave-lengths than those of tropolone methyl ether (Fig. 2). An explanation of this fact may be that the nonbonding electrons on the oxygen atom attached to the 2-carbon atom (C_2) in tropolone acetate migrate partly toward the acetyl group and partly toward the seven-membered ring, while those of tropolone methyl ether migrate exclusively toward the seven-membered ring.

(4) The vibrational structures of the spectra of *o*-, *m*-, and *p*-methyl tropolones are considerably different from one another (Figs. 15, 16, and 17), while they bear a striking resemblance respectively to those of *o*-, *m*-, and *p*-isopropyl tropolones (α, β, and γ-thujaplicins).(23) Similarly the vibrational structures of the spectra of *o*- and *p*-methyl tropolones

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(22) H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, **72**, 72, 74 (1951).

(23) A. Aulin-Erdtman, *Acta. Chem. Scand.*, **4**, 1031 (1950).

resemble respectively to those of *o*-, and *p*-bromotropolones (Figs. 11 and 12). In general, the features of the vibrational structures in the spectra of the tropolone ring appear to be determined by the positions, rather than the kinds, of the substituent radicals.

(5) Of *o'*-hydroxyhinokitiol (Fig. 19), three isomers, α(m. p. 60°C.), β(m. p. 52°C.), and γ(m. p. 46°C.) have been obtained by T. Nozoe et al.(14) The spectra of these three isomers are exactly alike in the positions of all the absorption peaks, but differ from one another in the absorption intensities of the bands. According to the present writer's near infra-red absorption studies, there is evidence which indicates that these three isomers differ from one another in the state of their intramolecular hydrogen bonds.

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