Infrared Absorption Studies of Tropolone and Allied Compounds

by Kenji KURATANI, Masamichi TSUBOI and Takehiko SHIMANOUCHI

(Received March 5, 1952)

Introduction

The chemistry of the seven-membered unsaturated ring has rapidly developed in recent years. A number of new compounds with this ring have been synthesized and their structural formulas determined.(1a) (1b) Of their spectroscopy, however, much work is yet to be done.(2) The present paper describes the infrared absorption spectra of tropolone and the related compounds prepared by Dr. T. Nozoe and his coworkers (Tohoku University, Sendai) who have carried out an extensive work in tropolone chemistry.(1a)

Experimental

Infrared absorption measurements were made by means of the Baird Infrared Spectrophotometer with a NaCl prism. Of the absorptions in the region above 2800 cm.$^{-1}$, measurements were also made by using a quartz spectrometer with higher resolving power, which was described in a previous paper.(3) The absorption curves obtained are shown in Figs. 1—6. Names, and

---

(1a) Nozoe, *Sci. Pap. Tohoku Univ. Ser.* 1, **34**, 199 (1950). *Proc Japan Acad.*, **26**, 30 (1950). Nature, **167**, 1055 (1951). *Chem. and Ind.* (Chem. Soc. Japan), **4**, 348 (1951).

(1b) Cook and Loudon, *Quart. Rev.*, **5**, 99 (1951). Johnson, *Sci Progr.*, **39**, 405 (1951).

(2) Scott and Tarbell. *J. Am. Chem. Soc.*, **72**, 240 (1950). Doering and Knox, *J. Am. Chem. Soc.*, **73**, 828 (1951).

(3) Tsuboi, this Bulletin, **22**, 215 (1949).

melting points of the compounds examined are listed in Table 1. On dissolving the dried sample of tropolone methyl ether in carbon tetrachloride or carbon disulphide, special care was taken to prevent it from being moistened because of its highly hygroscopic property.

Table 1

Substances	Melting points °C.	Absorption curves	References
tropolone	50—51	a	(i)
o-isopropyltropolone	33.2—34	b	(ii)
m-isopropyltropolone	51—52	c	(iii)
p-isopropyltropolone	77—78.5	d	(iv)
o-methyltropolone	49.5—50.5	e	(v)
m-methyltropolone	75—76	f	(v)
p-methyltropolone	108—110	g	(v)
o-bromotropolone	107—108	h	(i)
p-bromotropolone	190—191	i	(i)
o, *o*′-dibromotropolone	159—160	j	(vi)
o, *o*′, *p*-tribromotropolone	125—126	k	(i)
tropolone methyl ether	b.p. 125/5 mm.	l	(vii)
tropolone methyl ether+$^1/_2$H$_2$O	40.5	—	(vii)
tropolone acetate	69.5—70.5	m	(viii)
2-phenyltropone	85.8—86.5	n	(ix)
2-aminotropone	106—107	o	(x)

(i) Nozoe, Seto, Kitahara, Kunori and Nakayama, *Proc. Japan Acad.*, **26** (1950), 38.

(ii) Nozoe, Yasue and Yamane, *Proc. Japan Acad.*, **27** (1951), 15.

(iii) Nozoe and Katsura, *J. Pharm. Soc. Japan*, **69** (1944), 181.

(iv) Nozoe, Seto, Kikuchi and Takeda, *Proc. Japan Acad.*, **27** (1951), 146.

(v) Nozoe, Mukai and Matsumoto, *Proc. Japan Acad.*, **27** (1951), 110; Nozoe, Mukai and Matsui, *Proc. Japan Acad.*, in press.

(vi) Nozoe, Kitahara, Yamane and Yoshikoshi, *Proc. Japan Acad.*, **27** (1951), 18.

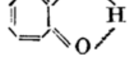
(vii) Nozoe, Seto, Ikemi and Arai, *Proc. Japan Acad.*, **27** (1951), 102.

(viii) Nozoe, Seto and Sato, to be published.

(ix) Nozoe, Mukai and Mineguchi, *Proc. Japan Acad.*, **27** (1951), 419.

(x) Nozoe, Seto, Takeda, Morosawa and Matsumoto, *Proc. Japan Acad.*, **27** (1951), 556.

Hydrogen Bond and Conjugated Double Bonds in the Tropolone Ring.—That tropolone has an intramolecular hydrogen bond of the form:



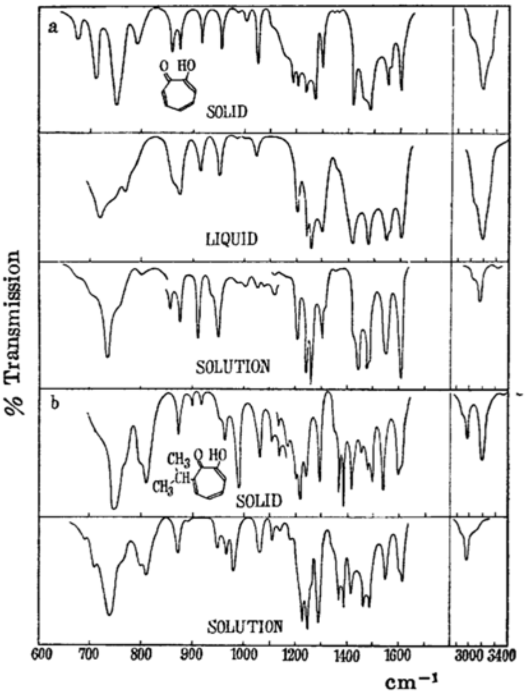


Fig. 1 A.—Infrared spectra of tropolone and *o*-isopropyltropolone.

Spectra in solids: samples molten and solidified between the two sylvine plates.

Spectra in solutions: 1300—630 cm.$^{-1}$, about 5% CS$_2$ solutions 4000—900 cm.$^{-1}$, about 5% CCl$_4$ solutions, cell thickness 0.1 mm.

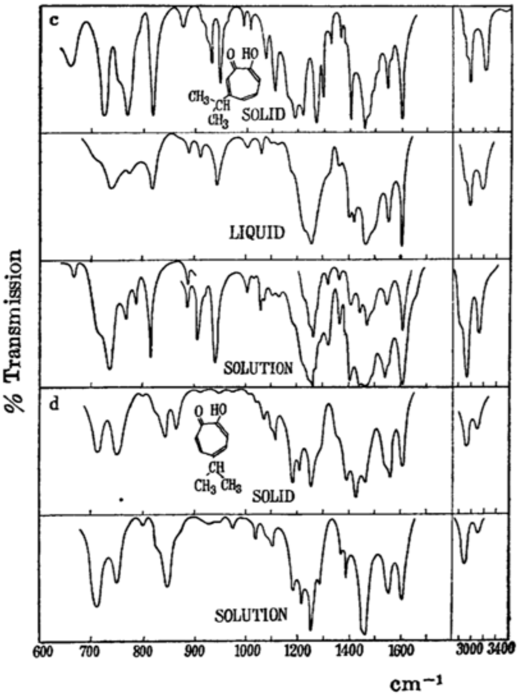


Fig. 1 B.—Infrared spectra of *m*- and *p*-isopropyltropolone.

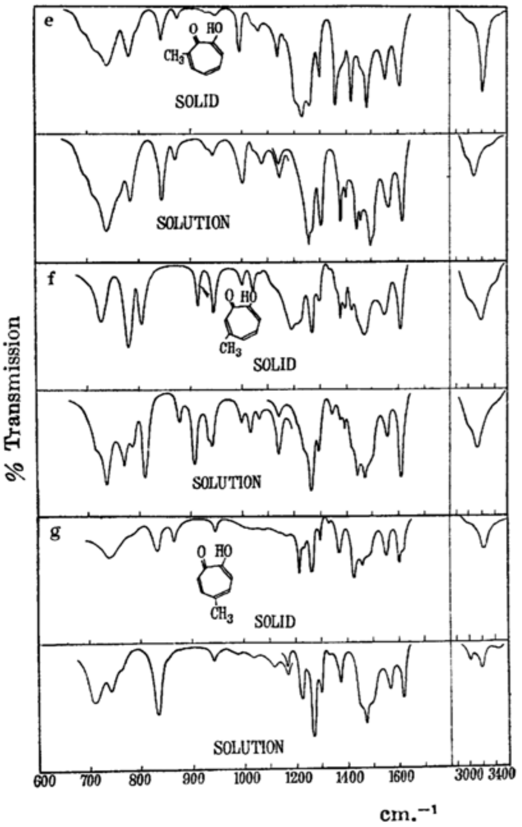


Fig. 1 C.—Infrared spectra of *o*-, *m*- and *p*-methyltropolone.

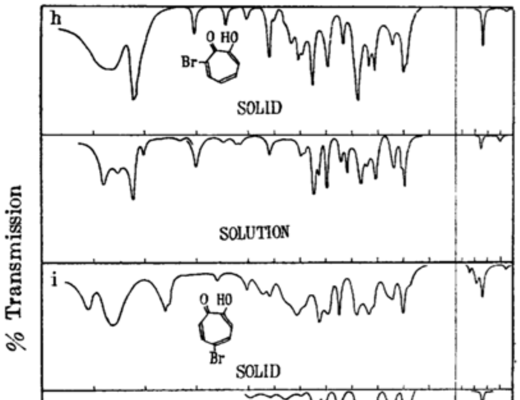


Fig. 1 D.—Infrared spectra of *o*- and *p*-bromotropolone.

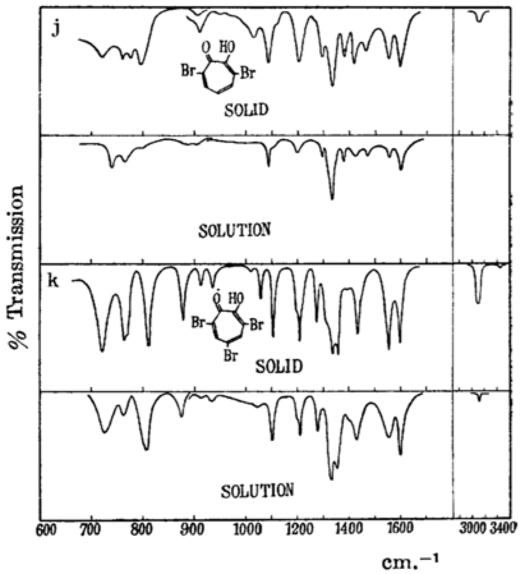


Fig. 1 E.—Infrared spectra of di- and tribromotropolone.

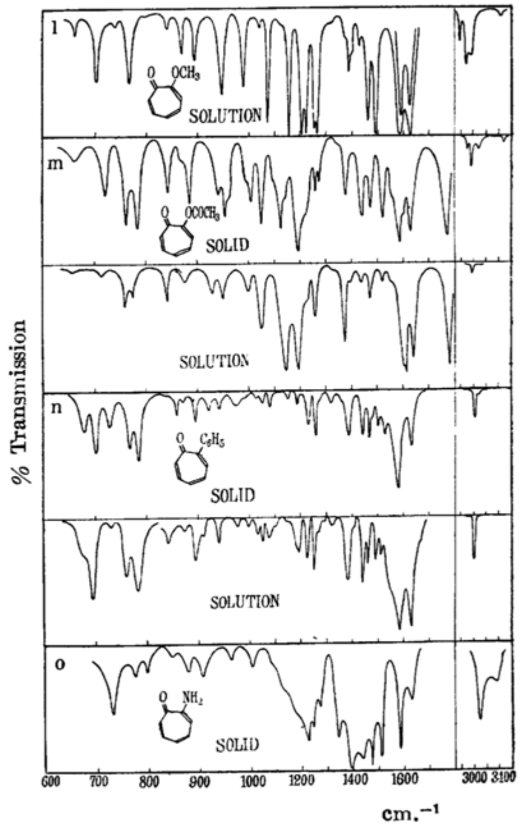


Fig. 1 F.—Infrared spectra of tropolone methyl ether, tropolone acetate, phenyltropone, and aminotropone.

has already been shown from the result of its dipole moment measurement⁽⁴⁾ and from its infrared spectra.⁽⁵⁾ The present studies have afforded further evidence for this conclusion. Thus, the O—H stretching band of tropolone observed in 0.01 mol./l. carbon tetrachloride solution is located at 3.2 μ (Fig. 2A), a position much displaced from that of the free O—H band, 2.8 μ, showing that the OH is hydrogen-bonded. Further, no change has been observed in the feature of the spectrum at all, even the concentration of the solution was changed from 0.004 to 0.1 mol./l., indicating that the hydrogen bonding is intramolecular. The unusually great shift of the O—H band of tropolone from that of free O—H band shows that the hydrogen bonding is correlated with the conjugation of the double bonds in tropolone—in other words, there is a kind of so-called "conjugated chelation"⁽⁶⁾ in tropolone molecule. It may also be seen that the chelation in tropolone is stronger than those of *o*-substituted phenols (with O—H band at about 3.1 μ) and is weaker than those of the enol-forms of acetyl acetone and acetoacetic ethyl ester (with O—H band at about 3.7 μ⁽⁶⁾).

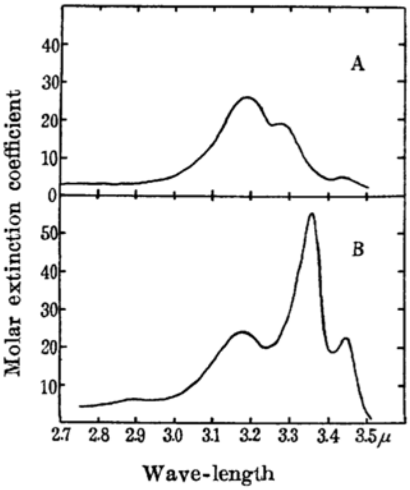


Fig. 2.—Near infrared absorption curves for (A) tropolone and (B) hinokitiol in 0.01 mol./l. CCl_4 solutions.

The C—H stretching absorption of tropolone is found at 3.3 μ but not in the 3.4—3.5 μ region Fig. 2A). This is consistent with the wellknown fact that all the carbon atoms in the tropolone molecule are unsaturated.

The near infrared spectra of *m*-isopropyltropolone (hinokitiol) and *o*- and *p*-isopropyltropolone (α- and γ-thujaplicin) (Fig. 1, b and d) are similar to that of tropolone in most respects, except the presence of the 3.4—3.5 μ bands in the former, which are due to the isopropyl group. Bromotropolones (Fig. 1, h, i, j, and k) exhibit their hydrogen-bonded O—H band 3.2 μ and unsaturated C—H band at 3.3 μ, just as tropolone does. On the other nand, tropolone methyl ether, 2-phenyltropone, and tropolone acetate exhibit no band at 3.2 μ, corresponding to the fact that they have no O—H group. Moreover tropolone methyl ether containing 1/2 H_2O shows its O—H band at 2.86 μ (Fig. 3).

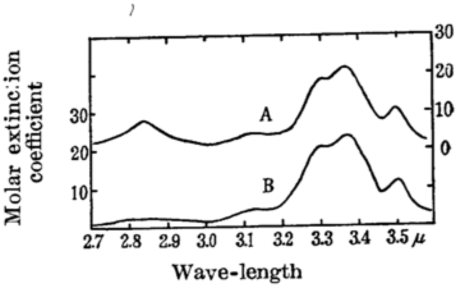
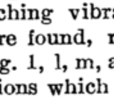


Fig. 3.—Near infrared absorption curves for (A) tropolone methyl ether with $^1/_2$ H_2O and (B) dried tropolone methyl ether in 0.02 mol./l. CCl_4 solutions.

Special attention is called to the double bond region (1700—1500 cm.⁻¹) of the absorption spectra of troponoid⁽⁷⁾ compounds. In tropolone methyl ether as well as tropolone acetate and 2-phenyltropone, the stretching vibrations of the C=O and C=C bonds are found, respectively, at 1630 and 1580 cm.⁻¹ (Fig. 1, l, m, and n), instead of at their normal positions which are respectively at 1720 and 1660 cm.⁻¹. This may be ascribed to the conjugation between the C=C and C=O bonds. Further, in tropolone as well as methyl-, isopropyl- and bromo-tropolones with the intramolecular hydrogen bonds the C=C and C=O frequencies appear in still lower frequency regions —*i.e.* respectively at 1610 and 1560 cm.⁻¹ (Fig. 1, a-k). This fact may be taken as indicating that the intramolecular hydrogen bonding affects the electronic state of the tropolone ring, and, accordingly, affects the force constants of the C=C and C=O bonds in the ring.

The effect of intramolecular hydrogen bonding upon the electronic state of tropolone ring is also shown from the observation of its ultraviolet spectrum. Tropolone methyl ether and tropolone acetate exhibit one strong absorption band at about 320 mμ in the near ultraviolet region, while tropolone anion:



exhibits two bands at 330 and 393 mμ. The ultraviolet absorption spectra of tropolone and

---

(4) Kurita, Nozoe and Kubo, this Bulletin, **24**, 10 (1951).

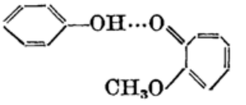
(5) Koch, *J. Chem. Soc.*, 512 (1951).

(6) Rasmussen, Tunnicliff and Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949).

(7) Dr. Nozoe gives a name "troponoids" to the allied compounds of tropone.

hinokitiol with intramolecular hydrogen bond possess features intermediate between those of tropolone methyl ether (or tropolone acetate) and tropolone anion, indicating that they are intermediate in electronic state.⁽⁸⁾

The Proton-Accepting Powers of Tropolone Methyl Ether and Hinokitiol Methyl Ether.—As has been mentioned above, tropolone has the stronger intramolecular hydrogen bond than o-substituted phenols. In order to obtain further information about the hydrogen-bond-forming powers of the compounds with the seven-membered unsaturated ring, the methyl ethers of tropolone and hinokitiol were compared with benzaldehyde as to their proton-accepting powers, by the method described in a previous paper.⁽⁹⁾ The hydrogen-bonded complexes:



and

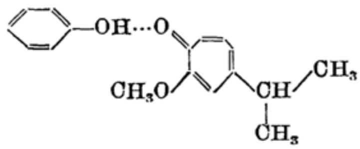
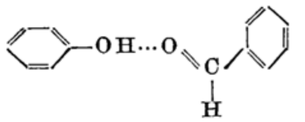


exhibit O—H bands at 3.00 and at 3.02 μ in dilute carbon tetrachloride solutions respectively (Fig. 4), while the complex:



exhibits O—H band at 2.89 μ. From the amount of these complexes in the solutions (estimated from the intensity measurement of these O—H bands) and from the amount of shifting of these O—H bands from free-phenol O—H band (2.77 μ), it is concluded that the proton-accepting powers of the methyl ethers of tropolone and hinokitiol are stronger than that of benzaldehyde.

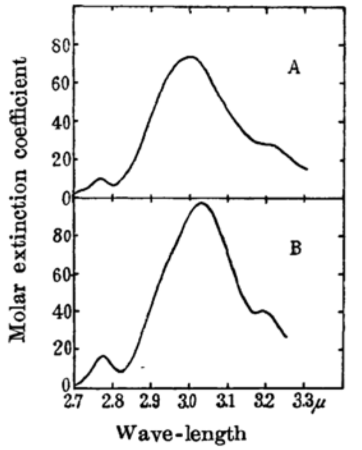


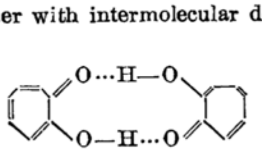
Fig. 4.—Near infrared absorption curves of phenol in (A) phenol (0.01 mol./l.)+tropolone methyl ether (0.02 mol./l.)+CCl₄ and in (B) phenol (0.01 mol./l.)+hinokitiol methyl ether (0.02 mol./l.)+CCl₄

The Vibrational Spectra and the Structure of Troponoid Compounds.—Corresponding to the arrangement of the substituent groups of benzene, characteristic absorption bands due to the out-of-plane C—H deformation vibrations are found in the region of 900—750 cm.⁻¹.⁽¹⁰⁾ In the case of sevenn-membered unsaturated ring compounds, similar strong characteristic bands are found as shown in Table 2. The data given in the table will be useful for the determination of the structural formulas of the tropolone derivatives.

Table 2

Types of substitutions	Examples	Frequencies
1, 2-substituted	tropolone	735 cm.⁻¹
	tropolone methyl ether	770
	tropolone acetate	750 or 770
1, 2, 3-substituted	*o*-isopropyltropolone	800
	o-methyltropolone	782
	o-bromotropolone	770
1, 2, 4-substituted	*m*-isopropyltropolone	820
	m-methyltropolone	812
1, 2, 5-substituted	*p*-isopropyltropolone	850
	p-methyltropolone	830
	p-bromotropolone	850

Spectra of Troponoids in the Solid State.—Infrared spectra of tropolone and isopropyltropolones in the solid state are considerably different from those in solutions (Fig. 1, a—d). When they are brought from the solutions into the solid state, some of their absorption bands increase in relative intensity (for example, 1190—1210 cm.⁻¹ bands probably due to O—H deformation vibrations contained in them) and some become doublets (Fig. 1, b and c). The hydrogen-bonded O—H bands become, on solidification, stronger (in comparison with the C—H bands) and sharper, and at the same time shift towards shorter wave lengths (Fig. 1, b, e, f, g; Fig. 2 and 5). This indicates that the correlation between conjugation and hydrogen bonding in tropolonoid molecules is less remarkable in solid states than in solutions. According to the private communication of Prof. I. Nitta and Dr. K. Osaki, the presence of ring dimer with intermolecular double hydrogen bonds:



---

(8) Ultraviolet absorption studies of troponoids will be published elsewhere.

(9) Tsuboi, this Bulletin, **25**, 60 (1252).

(10) For example, Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

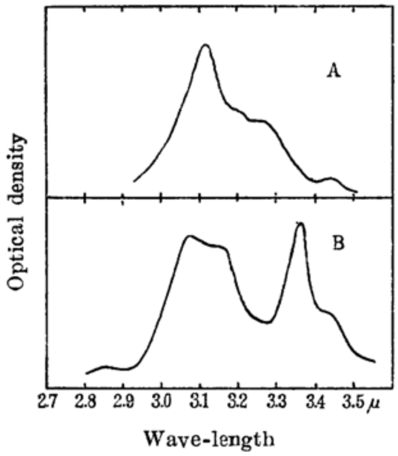


Fig. 5.—Near infrared absorption curves for (A) tropolone and (B) hinokitiol in solid states.

in tropolone crystal is recently proved from its x-ray analysis. Since tropolone in solutions has an intramolecular hydrogen bond and is in monomeric state, there must be a change in the behavior of hydrogen-bonding on its solidification. The observed changes in the spectra of tropolone and the allied compounds may be attributed to such changes in the behavior of hydrogen-bonding. A fact, perhaps worthy of note in this connection, is that the spectra of tropolone and hinokitiol in liquid states are closer to those in solutions than to those in the solid state, as may be seen from the comparison of the absorption curves shown in Fig. 1, a and c. The infrared spectra of some of the bromo-substituted tropolones are almost independent of their phase changes (Fig. 1, h—k).

Spectrum of Aminotropone.— Aminotropone exhibits two N—H stretching absorption bands at 2.83 μ (3530 cm.$^{-1}$) and 2.97 μ (3360 cm.$^{-1}$) (Fig. 6). This fact may be explained from the structure of this compound:

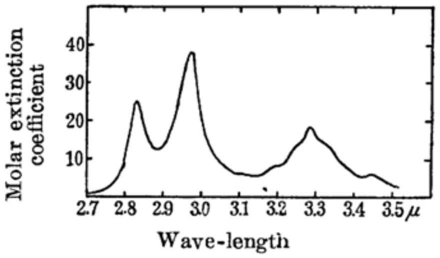
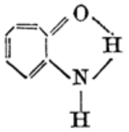


Fig. 6.—Near infrared absorption curve for aminotropone in 0.02 mol./l. CCl_4 solution.



the former band being assigned to the free N—H vibration and the latter to the hydrogen-bonded N—H vibration. On the other hand, double-bond absorption bands observed for this compound are situated at 1624 and 1590 cm.$^{-1}$ (Fig. 1, o)——positions not much displaced from those observed for tropolone methyl ether. This shows that the internal hydrogen bond of aminotropone is weak.

In conclusion the writers wish to express their sincere thanks to Professor San-ichiro Mizushima for his kind guidance in this work, and to Professor Tetsuo Nozoe, Shuichi Seto, Yoshio Kitahara, Toshio Mukai, and other members of the Laboratory of Organic Chemistry, Faculty of Science, Tohoku University for their placing the samples at the writers' disposal and for their valuable suggestions. The cost of this work has been partly defrayed by a grant from the Ministry of Education.

Department of Chemistry,
Faculty of Science, University of Tokyo.