*Infrared Spectra of Troponoid Compounds. III. Tropolone and 2-Deuteroxytropone**

By Yusaku IKEGAMI

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Absorption of O–H stretching vibration of tropolone (I) in solid, liquid and carbon tetrachloride solution was described in the preceding paper[1]. In the present paper the spectra of tropolone, chiefly in finger-print region, will be described. Infrared spectra of tropolone have been reported earlier by Koch[2], Kuratani[3], Kinumaki[4] and others, and its Raman spectrum by Imanishi and Ito[5], but only a few vibrations, such as those of C=O, C=C and C–H out-of-plane, have been assigned in the finger-print region. In order to clarify the absorption bands originating in C–O–H group in the spectrum of tropolone, an infrared spectrum of 2-deuteroxytropone (II) was measured and compared with that of I. On heating I with heavy water, a compound III, in which the deuterium atom had entered the seven-membered ring, was obtained and brief mention will be made of this compound. Further, some considerations were given to the spectrum of I in the finger-print region.

Results and Discussion

Comparison of the Infrared Spectra of 2-Deuteroxytropone and Tropolone.—2-Deuteroxytropone (II) was obtained by recrystallization of tropolone (I) from heavy water. The infrared spectra of I and II in carbon tetrachloride and carbon disulfide solutions are shown in Fig. 1, a and b. The presence of an absorption due to hydroxyl compound can not be denied in the spectrum of Fig. 1b but most of it is in the spectrum of II.

In the spectral curve of Fig. 1b, the O–H stretching absorption around 3150 cm^{-1} in 1a has shown drastic decrease of its intensity and a new absorption originating in the O–D bond has appeared at around 2400 cm^{-1}. This band has two peaks at 2400 and 2342 cm^{-1} and the shape of this band is similar to that of tropolone in which the O–H stretching absorption is not sharp even in the state of dilute solution. The ratio of the wave numbers of ν_{O-H} and ν_{O-D} is indicated in Table I together with values obtained in 3-bromo- and 3-methyl-tropolones. These values are in good agreement with the values (1.33~1.34) obtained by Keussler et al.[6] on deuteration of phenols

TABLE I. ν_{O-H}/ν_{O-D} VALUES FOR SOME TROPOLONES

Compounds		ν_{O-H} cm^{-1}	ν_{O-D} cm^{-1}	ν_{O-H}/ν_{O-D}
Tropolne	solid	3208	2385	1.345
	in CCl_4	3167	2400	1.320
		3120	2342	1.332
3-Bromotropolone	solid	3208	2390	1.342
3-Methyltropolone	solid	3202	2394	1.338

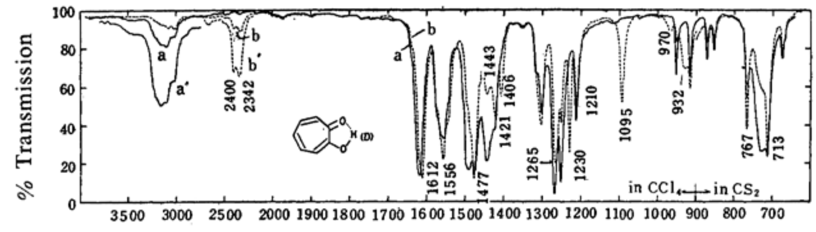

Fig. 1. Infrared spectra of tropolone (a : 3%, a′ : 10%) and 2-deuteroxytropone (b : 3%, b′ : 9%) in the solution of carbon tetrachloride (4000~900 cm^{-1} range) and of carbon disulfide (900~650 cm^{-1}) (0.12 mm. thickness).

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* A part of this work was presented at the 10th Annual Meeting of the Chemical Society of Japan, April 4, 1957.

1) Part II: Y. Ikegami, This Bulletin, 34, 91 (1961).

2) H. P. Koch, *J. Chem. Soc.*, 1951, 512.

3) K. Kuratani, M. Tsuboi and T. Shimanouchi, This Bulletin, 25, 250 (1952).

4) Part I: S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Research Inst. Tohoku Univ., Ser.* A, 8, 263 (1956).

5) S. Imanishi and M. Ito, This Bulletin, 28, 75 (1955); 29, 632 (1956).

6) V. von Keussler und G. Rossmy, *Z. Elektrochem.*, 60, 136 (1956).

possessing a conjugated chelate structure as tropolone.

In the region of 1700∼650 cm^{-1}: — In this region, the absorption band at 1618 cm^{-1} in I shifts to the lower wave number side by 6 cm^{-1} in II, and a certain amount of difference is observed between I and II below 1500 cm^{-1}. New bands have appeared at 1406, 1230, 1095, 970 and 932 cm^{-1} in the spectrum of Fig. 1b. On the other hand, the absorption bands at 1490, 1444, 1251, 953 and 726 cm^{-1} in I do not appear in II, and the intensity of the absorption at 1267 cm^{-1} is weaker. These bands in Fig. 1a are considered to have some relation, either directly or comparatively closely, to the vibration of the C–O–H group.

Identification of absorption bands originating in the C–O–H group by conversion of hydroxyl to deuteroxyl compound has been reported already by Hadzi, Mecke and others in carboxylic acids[7], chelated hydroxyquinones[8], enolized β-diketones[9,10] and phenols[11]. These results point out that the distribution of absorption bands which shift by deuteration and their interpretation vary according to the shape of a molecule, even in the same C–O–H group. In the case of tropolone, a storng absorption band at 1490 cm^{-1} disappeared and a new band appeared at 1095 cm^{-1} (1086 cm^{-1} in solid) by deuteration, and these wave numbers are close to those which were assigned to the O–H and O–D deformation vibrations in enolized β-diketones (around 1435 and 1090 cm^{-1} respectively)[9]. Moreover, the other band which can be assigned to the O–D deformation vibration appeared at

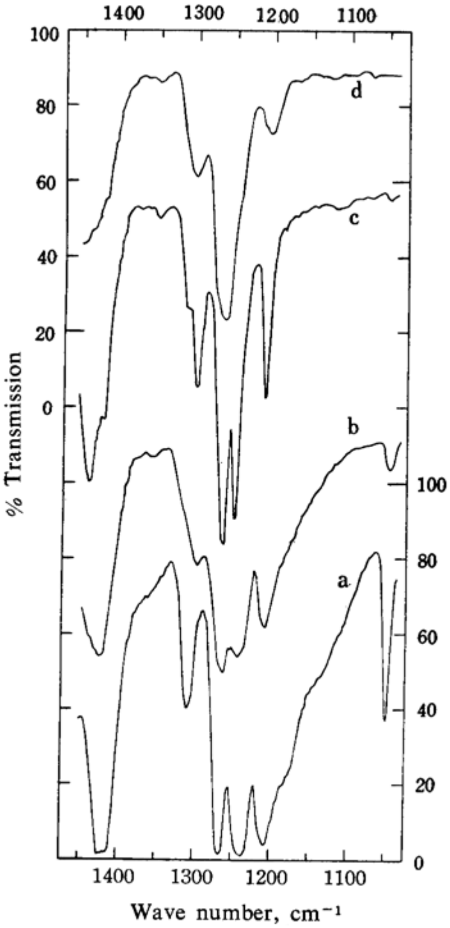

Fig. 2. Infrared spectra of tropolone in the states of solid (a), liquid (b), CCl$_4$ solution (c) and vapor (d) (1450∼1050 cm^{-1} range).

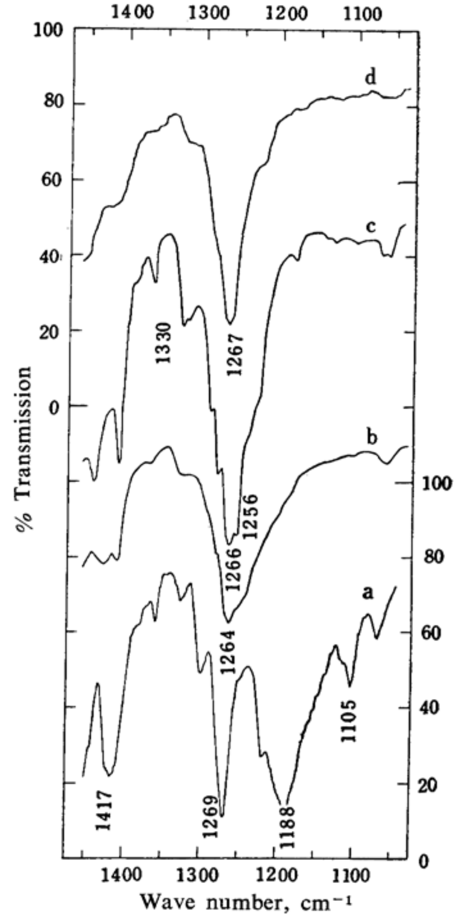

Fig. 3. Infrared spectra of 4-isopropyltropolone in the states of solid (a), liquid (b), CCl$_4$ solution (c) and vapor (d) (1450∼1050 cm^{-1} range).

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[7] D. Hadzi and N. Sheppard, *Proc. Roy. Soc.*, **216A**, 247 (1953).

[8] Idem., *Trans. Faraday Soc.*, **50**, 911 (1954).

[9] S. Bratoz, D. Hadzi and G. Rossmy, ibid., **52**, 464 (1956).

[10] R. Mecke and E. Funck, *Z. Elektrochem.*, **60**, 1124 (1956).

[11] R. Mecke and G. Rossmy, ibid., **59**, 866 (1955).

932 cm^{-1} (896 cm^{-1} in solid) by deuteration, while the band at 1267 cm^{-1} weakened. These wave numbers are close to those of chelated hydroxyanthraquinones, in which two bands characteristic to the deuteroxyl group had been recognized at around 980 and 930 cm^{-1} 8). Anyway, these facts indicate that the bands at 1490 and 1267 cm^{-1} in tropolone originate in the C–O–H group, although the definite assignments of these bands are indistinct.

It is clear that the bands at 1490 and 1267 cm^{-1} in Fig. 1a are related to the vibration of the C–O–H group, not only because these bands shift by deuteration but because 2-halotropones, which have no C–O–H group, do not have strong absorptions this wavenumber region12). The fact that the absorption at around 1267 cm^{-1} in tropolone has the character of O–H deformation is also understandable by comparing the spectra in solid, liquid, solution and gaseous states. The spectra in these states in the region of 1450∼1050 cm^{-1} are shown in Fig. 2, and the spectra of 4-isopropyltropolone, for the comparison with those, are also shown in Fig. 3. From the spectra in Fig. 3, it is clear that the broad absorption at 1188 cm^{-1} in solid has shifted to the higher wave number side, merging in the position at around 1265 cm^{-1} in other states. In the same manner, the broad absorption in the region of 1208∼1100 cm^{-1} in solid tropolone (Fig. 2a) shifts to the higher wave number side in other states and is assumed to correspond to the strong absorption at 1265 cm^{-1} in the gaseous. The direction of such a shift of absorptions according to changes in the state agrees with the direction of the shift of δ_{O-H} anticipated from that of ν_{O-H} as stated in the preceding report1).

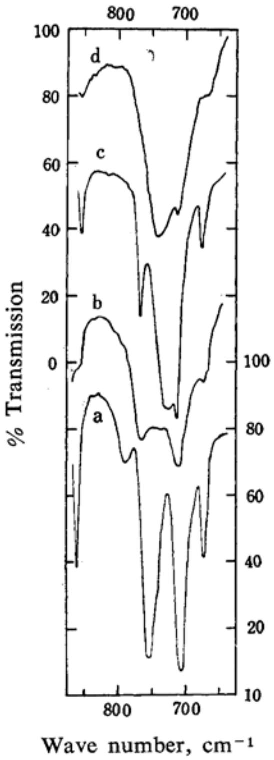

Fig. 4. Infrared spectra of tropolone in the states of solid (a), liquid (b), CS$_2$ solution (c), and vapor (d) (850∼650 cm^{-1} range).

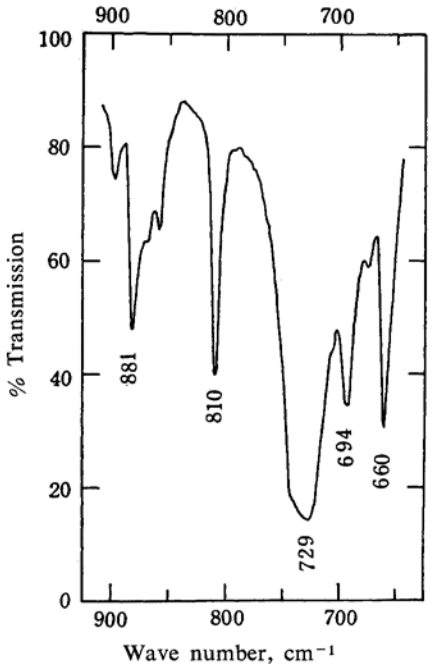

Fig. 5. Infrared spectrum of deuterated tropolone (III) in carbon disulfide (ca. 8%) (900∼650 cm^{-1} range).

The absorption bands which shift by deuteration are recognized at 1444, 1251 and 953 cm^{-1}, but these bands have also disappeared in the compound III, as will be described below. In these bands, the absorption at 1251 cm^{-1} is assumed to correspond to that at 1230 cm^{-1} in Fig. 1b, from their similar shape.

In the region of 800∼700 cm^{-1}, there are three strong absorption bands in the state of solution. Of these, the band at around 720 cm^{-1} was assigned by Koch2) and Kuratani et al.3) to the out-of-plane vibration of hydrogen atoms in the seven-membered ring. On the other hand, Imanishi and Ito5,13) assigned the Raman line at 743 cm^{-1} to the breathing vibration of the seven-membered ring. Moreover, the following considerations are possible

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12) Y. Ikegami, unpublished data.

13) S. Imanishi and M. Ito, *J. Chem. Phys.*, **24**, 1272 (1956).

from the spectra indicated in Fig. 1. The comparatively broad absorption at 726 cm^{-1} in I is no longer visible in II and, therefore it can be assigned to the out-of-plane deformation vibration of C–O–H expected in this region. Analogous absorption bands have been recognized in carboxylic acids[7], chelated β-diketones[9] and hydroxyquinones[8]. This is also understandable since a broad absorption is seen in this region in tropolones in general but not in tropones[12]. The absorption at 767 cm^{-1} can be assigned to the C–H out-of-plane deformation vibration as the majority of 1,2-disubstituted troponoids show strong absorption in this region[12] and because this absorption band has disappeared in deuterated tropolone (III), as shown in Fig. 5. Aside from such considerations in solution, the spectra in other states show a marked difference in shape, as shown in Fig. 4, and this fact indicates that such absorptions are easily affected by intermolecular action.

On Deuterated Tropolone. — Deuterated tropolone was obtained by heating a mixture of I and heavy water in a sealed tube at 150°C for a few hours. The compound III, obtained

TABLE II. OBSERVED FREQUENCIES (cm^{-1}) OF TROPOLONE

Infrared				Raman[d]	
Solid[a]	Liquid[a]	Solution[b,a]	Vapor[c]	In benzene	
3518 w	3450 vw	3450 vw			O–H stretch.
			3245 sh		
		3151 m			
3208 s	3195 s		3140 w		
		3120 m			
3049 vw	3060 vw	3051 sh	3055 w		C–H stretch.
3003 vw	3023 vw	3020 sh	3030 w		
1613 s	1614 vs	1618 vs	1628 vs	1610 (5)	C=O and C=C stretch.
1548 vs	1553 s	1555 s	1573 s		
1480 vs		1490 vs	1490 vs		C–O–H
	1476 vs				
1469 sh		1476 vs	1470 sh		C–C stretch.
		1444 s	1450 s	1418 (5)	
1425 vs	1426 vs				
		1425 sh	1425 sh		
1363 vw	1360 vw	1355 vw	1357 vw		2×675
		1317 sh			
1310 m	1300 m	1304 m	1305 s		
1266 vs	1264 vs	1267 vs	1265 vs	1262 (4)	C–O–H or C–H in-plane deform.
1238 vs	1245 vs	1251 vs	1250 sh		
1208 vs	1210 s	1213 m	1208 m	1208 (2)	
1049 m	1048 w	1048 vw			357+679[d]
1009 vw	990 vw	1000 vw			
958 m	956 m	953 m	940 m	959 (1)	
919 m	920 m	917 m	908 m		
874 w	871 m	873 w			2×436[d]
860 m	860 sh	854 w	860 w		
789 w					357+436
	769 s	767 m			CH out-of-plane deform. C–C stretch.[d] OH out-of-plane deform.
754 s			738 s	743 (3)	
	740 s	726 s			
708 s			710 m		
	711 s	713 s			
672 m	675 m	675 w	675 w	679 (2)	C–C–C ring deform.
531 vw					
433[e] m				436 (1)	C–C–C ring deform.
				357 (2)	C–C–C ring deform.

(vs : very strong, s : strong, m : medium, w : weak, vw : very weak, sh : shoulder)

a) The region of 3600~2600 cm^{-1} was measured by using CaF_2 prism; see Ref. 1.

b) Fig. 1a. c) Ref. 4. d) Ref. 5.

e) The region of 650~400 cm^{-1} was measured by using KBr prism only in solid (KBr disk).

by treating I twice with 99.78% heavy water for 5 hr., melted at 50°C, alone and in admixture with I. The ultraviolet spectrum of III is also very similar to that of I but their infrared spectra are very different. The absorption bands of III appeared at 3180, 1616, 1556, 1472, 1227 (in carbon tetrachloride) and 729 cm^{-1} (in carbon disulfide), all corresponding to those in Fig. 1a with similar shape. The absorption of C–H stretching vibration in I has become indistinct and appears as a weak band of C–D stretching vibration at 2266 cm^{-1} in III. Further, the strong absorptions at 1444, 1251 and 767 cm^{-1} in I have all disappeared and appear at around 1370, 1084 and 810 cm^{-1} in III (partly shown in Fig. 5), also indicating that these bands are closely related to the C–H bond in the seven-membered ring in I. However, there is not sufficient evidence to determine the position and number of deuteration.

Considerations Regarding Vibrational Spectrum of Tropolone.—The infrared absorption bands of tropolone, wave numbers of Raman lines reported by Imanishi[5], and their assignments are summarized in Table II. These assignments were chiefly based on the considerations of the foregoing deuteration and previously reported data[2-5]. Further, the weak absorptions at 1355 and 789 cm^{-1} were assumed to correspond respectively to the overtone, 2×675 cm^{-1}, and combination tone, $357+436$ cm^{-1}. The spectrum of tropylium cation[14], which has the most fundamental form among tropoids, was compared with that of tropolone and bands corresponding well were recognized in the lower wave number region. The vibration due to the seven-membered ring in the cation should not differ greatly from that of tropolone. It is expected to indicate similar wave numbers. Therefore, the absorptions at 675 and 433 cm^{-1} and Raman line at 357 cm^{-1} can be assigned to the ring deformation vibration. The few medium intensity bands observed clearly in the region of 1300∼1200 cm^{-1}, which are characteristics of tropoids, may be assigned to the C–H deformation vibration of the seven-membered ring.

Experimental

Materials. — Recrystallization of tropolone (I), m. p. 50∼51°C, was repeated several times from a mixed solvent of dioxane, dehydrated by metallic sodium, and 99.78% heavy water or from heavy water alone and 2-deuteroxytropone (II) was obtained as colorless needles, m. p. 51°C. Admixture of II and I showed no depression of the melting point. II easily reverted to I by the presence of a slight amount of moisture. Corresponding deuteroxyl compounds were also obtained by the same procedure from 3-bromotropolone, m. p. 108°C, and 3-methyltropolone, m. p. 50°C.

A mixture of 100 mg. of I and ca. 2 ml. of heavy water was heated in a sealed tube at 150°C for 5 hr. This procedure was repeated twice with fresh heavy water each time. The product purified by sublimation and recrystallization to colorless prisms (III), m. p. 50°C alone and in admixture with I.

U. V. $\lambda_{\max}^{\text{cyclohexane}}$: 226, 239, 247 (sh.), 308 (sh.), 322, 355 and 374 mμ[15].

Infrared Absorption Spectra.—All infrared spectra were measured by a Perkin-Elmer model 21 infrared spectrophotometer equipped with a sodium chloride prism. The solid spectra were obtained by the potassium bromide disk method and solution spectra in carbon tetrachloride, purified several times by dehydration with phosphorus pentoxide, or carbon disulfide.

Summary

In order to find infrared absorption of tropolone, especially the absorption that can be assigned to the C–O–H group, the spectrum of 2-deuteroxytropone was measured and there were discussions chiefly on absorptions in the finger-print region. The absorption bands at around 3150, 1490, 1267 and 726 cm^{-1} were assigned to the vibration of C–O–H group. In this connection, some mention was made on deuterated tropolone and considerations were made on the assignment of vibrational spectra of tropolone, as summarized in Table II.

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The Chemical Research Institute of
Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai

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[14] K. Aida, *Sci. Repts. Research Inst. Tohoku Univ., Ser. A*, 8, 361 (1956); W. G. Fateley, B. Curnutte and E. R. Lippincott, *J. Chem. Phys.*, 26, 1471 (1957).

[15] U. V. spectrum was measured by a Hitachi EPU-2A spectrophotometer.