*Infrared Spectra of Troponoid Compounds. IV. Infrared and Raman Spectra of Tropone**

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Infrared absorption spectrum of tropone (I) has been reported by a number of workers[1-4] but no detailed reports have been made on the assignment of the absorption bands. No work seems to have been done on the measurement of its Raman spectrum. As a part of the studies on the infrared spectra of troponoids, tropone was taken up as a compound having the most fundamental structure of this series. Measurements were made on the infrared spectra in the region of 4000~400 cm^{-1} and on Raman spectrum, and considerations were made on the vibrational assignments for these spectra.

Experimental

Measurement of Infrared Spectra.—Infrared spectra were measured with a Perkin-Elmer model 21 infrared spectrophotometer, using sodium chloride prism for the region of 4000~700 cm^{-1} and potassium bromide prism for the region of 700~400 cm^{-1}. The absorption bands in the region of 4000~1700 cm^{-1} were measured also by using a calcium fluoride prism which has a higher resolution.

Measurement of Raman Spectrum. — Raman spectrum was measured with a Shimadzu automatic grating Raman spectrometer, type GRS-750, using the Hg-e line (4358 Å) from the Toronto type mercury lamp for the exciting line. In this case, a solution containing 0.2 g. of Ethyl Violet and 39 g. of *p*-nitrotoluene in 1.8 l. of denatured alcohol was used as the filter for the light source. This filter solution had a 1 cm. light pass, and the cell was cooled by circulating water to avoid the rise in temperature of the sample cell. Tropone is easily colored on exposure to light, and, in order to avoid this coloration, the sample was preserved in a dark, cool place after purification and caution was taken to shorten the time required for measurement.

Sample. — Tropone used for the measurement was prepared by the known method[5], recrystallized as picrate, and passed through an alumina column to liberate picric acid. The purified tropone was distilled in vacuum more than five times. $n_D^{18}=1.6190$.

Infrared and Raman Spectra of Tropone

Infrared absorption spectrum of liquid tropone is shown in Fig. 1a. This spectrum hardly shows the absorption band at around 3530 cm^{-1} due to the adsorbed moisture always present in the spectra reported to date[2-4]. The spectra of tropone in carbon tetrachloride and carbon disulfide are shown in Fig. 1b. The wave number of absorption bands in these spectra and those in the spectrum measured in a vapor state earlier[4] are listed in Table II.

The Raman spectrum of liquid tropone is shown in Fig. 2, and the wave numbers, their approximate, relative intensities, and depolarization factors are listed in Table II. The relative intensities are given taking the peak intensity of the most intense line at 1520 cm^{-1} as the standard.

Molecular Structure and Vibrational Modes of Tropone

Tropone, C_7H_6O, has the structure of cycloheptatrienone (Ia). Therefore, a structure with all the 14 atoms in the plane and having a symmetric plane including a C=O line perpendicular to that plane can naturally be presumed to be tropone. Under such a presumption, a vibrational spectrum of tropone can be treated as a planar ring structure of C_{2v} symmetry, and, therefore, normal vibrations corresponding to 36 degrees of vibrational freedom can be classified as shown in Table I. In this table, the expected frequency ranges were assigned with reference to the vibrational frequencies of benzene, tropylium cation[6],

* A part of this work was presented at the Tohoku Local Meeting of the Chemical Society of Japan, Sendai, September, 1960.

1) H. J. Dauben and H. J. Ringold, *J. Am. Chem. Soc.*, 73, 876 (1951); A. P. Ter Borg, R. van Helden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chem. Acta*, 43, 457 (1960).

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

3) T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, 28, 477 (1952); T. Nozoe, T. Mukai and K. Takase, *Sci. Repts. Tohoku Univ.*, I39, 164 (1956).

4) S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Research Inst. Tohoku Univ.*, A8, 263 (1956).

5) T. Ikemi, T. Nozoe and H. Sugiyama, *Chem. & Ind.*, 1960, 932.

6) K. Aida, *Sci. Repts. Research Inst. Tohoku Univ.*, A8, 361 (1956); W. G. Fateley, B. Curnutte and E. R. Lippincott, *J. Chem. Phys.*, 26, 1471 (1957).

7) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, 82, 1876 (1960).

8) G. R. Hunts and I. G. Ross, *J. Mol. Spectroscopy*, 3, 604 (1959).

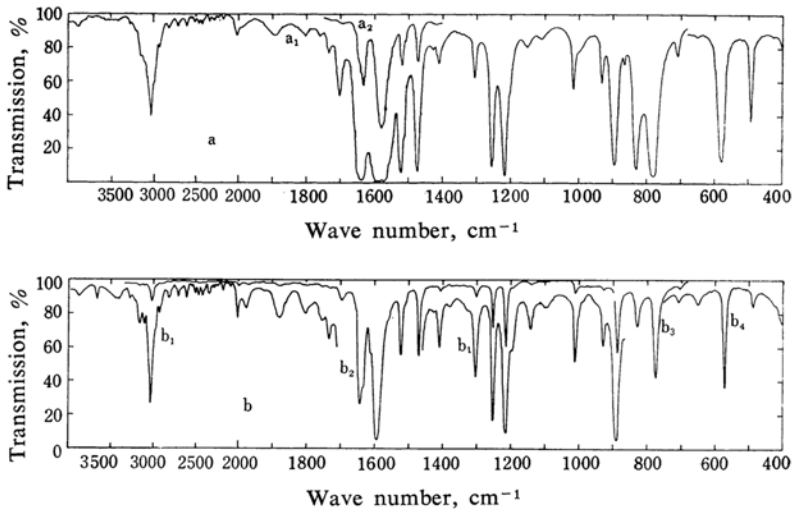


Fig. 1. Infrared spectra of tropone.

a: Pure liquid, a_1; 0.119 mm. thickness, a_2; 0.021 mm.
b: In carbon tetrachloride (4000～880 cm^{-1} range) and in carbon disulfide (900～400 cm^{-1} range), b_1; 6.03% (0.52 mm. thickness), b_2; 2.88% (0.092), b_3; 2.83% (0.092), b_4; 3.86% (0.12).

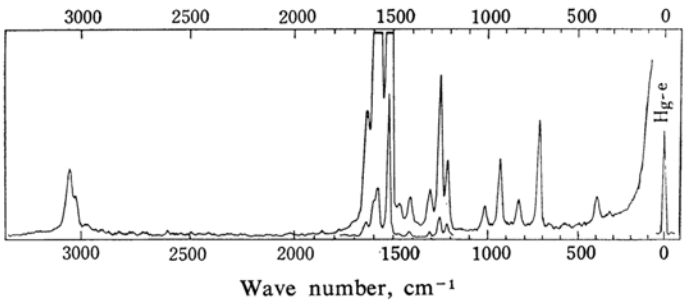


Fig. 2. Raman spectrum of liquid tropone (5100～4340 Å range).

TABLE I. DISTRIBUTION OF VIBRATIONAL FUNDAMENTALS FOR C_{2v} STRUCTURE OF TROPONE

Vibrational mode	Species				Total	Expected range cm^{-1}
	A_1	A_2	B_1	B_2		
In-plane						
CH stretch.	3		3		6	3100～3000
C=O stretch.	1				1	1650～
C=C stretch.	2		1		3	1650～1450
C-C stretch.	2		2		4	1450～ 700
CH bend.	3		3		6	1450～1000
C=O bend.			1		1	1000～?
Ring deform.	2		2		4	900～ 250
Out-of-plane						
CH bend.		3		3	6	1000～ 650
C=O bend.				1	1	1000～?
Ring deform.		2		2	4	700～ 200
Total	13	5	12	6	36	
Activity Infrared	a	ia	a	a		
Activity Raman	p	dp	dp	dp		

TABLE II. OBSERVED FREQUENCIES (cm^{-1}) AND THEIR POSSIBLE ASSIGNMENTS FOR TROPONE

Infrared			Raman			Assignment	
Liquid	Solution	Vapor	Liquid		ρ	Vibrational mode	Species
3205 sh							
3141 sh	3162 w						
3110 sh	3114 w	3100 sh					
3073 sh	3077 sh						
3050 sh	3055 sh		3055	0.5	0.38		A_1
		3048 s				CH stretching	
3024 m	3031 m		3031	0.3	0.61		B_1
2988 sh	3006 sh	3000 sh	2984	vw			
	2975 sh		2972	0.1			
2013 w	2005 w	2011 w				2×1000 ca.	
1980 sh	1973 w						
1892 w	1881 w					1000+893	
1808 w	1807 w	1805 w				934+867 ?	
1763 w	1757 w					934+830 or 893+867	
1737 m	1736 m	1735 sh				2×867	
1702 m	1702 m	1687 sh	1704	w		867+830	
1648 sh						867+779	
1634 vs	1645 vs	1651 vvs	1637	1.0	0.59	C=O and C=C stretch.	A_1
	1636 sh						
	1614 sh						
			1598	sh		C=C stretch.	B_1
1580 vvs	1595 vvs	1613 vvs					
			1580	3.4	0.51	C=C and C=O stretch.	A_1
1521 s	1525 s	1516 s	1520	10.0	0.30	C=C stretch.	A_1
1512 sh	1512 sh					932+577	
1473 s	1473 s	1465 s	1473	0.1	0.7	C-C stretch. ?	B_1
1429 w	1427 vw					779+650 or 2×712	
1411 m	1409 w	1405 w	1412	0.3	0.87	CH bend. (in-plane)	B_1
	1379 vw		1380	w		712+664 ?	
1345 vw							
	1328 sh					2×664	
1305 m	1304 m	1305 m	1309	0.4	0.78	CH bend. (in-plane)	B_1
1253 s	1253 s	1251 m	1254	1.3	0.37	CH bend. (in-plane)	A_1
1216 s	1215 s	1208 s	1217	0.6	0.72	CH bend. (in-plane)	B_1
1204 sh	1200 sh	1185 w				CH bend. (in-plane)	A_1?
1151 w	1142 w	1145 wb				CH bend. (in-plane)	A_1?
1108 w	1100 vw	1086 w				712+396 or 779+329	
1015 m	1013 m	1010 w	1017	0.2	0.79	C-C stretch. ?	B_1
1000 sh	990 sh	999 w	990	sh		CH bend. (out-of-plane)	A_2
932 m	930 m		934	0.6	0.44	CH bend. (out-of-plane) ?	A_2
						C-C stretch.	A_1
893 s	889 s	882 s				CH bend. (out-of-plane)	B_2
867 w						CH bend. (out-of-plane)	A_2
830 s	830 s	827 m	833	0.3	0.56	CH bend. (out-of-plane)	B_2
779 vs	776 vs	767 s				CH bend. (out-of-plane)	B_2
712 w	709 w	703 w	716	0.9	0.29	C-C stretch.	A_1
			664	vw		Skeletal deform.	A_2
650 vw	653 w	650 vw	653	0.1	0.7	Skeletal deform.	B_1
			644	w		Skeletal deform.	A_2
577 s	574 s		576	0.1	0.8	Skeletal deform.	B_2
492 m	490 m		492	0.1	0.8	Skeletal deform.	B_2
402 w	405 m						
			396	0.3	0.72	Skeletal deform.	A_1
			386	sh		Skeletal deform.	B_1?
			329	0.1	0.8	Skeletal deform.	B_1?
			259	vw		Skeletal deform.	?

(vs : very strong, s : strog, m : medium, w : weak, vw : very weak, sh : shoulder)
ρ : Depolarization factor

tropilidene[7], and azulene[8] whose vibrational spectra had already been analyzed.

As can be seen from this table, all the vibrational modes are Raman active, and 31 of them except those of A_2 species are also infrared active. However, the observed spectra show that the number of Raman lines are much smaller than the anticipated number and this is probably due to the non-observation of weak Raman lines by the afore-mentioned defect in the measurement and also to the superposition of adjacent lines.

Vibrational Assignment

From the distribution of vibrational modes and the spectral data, the following considerations were made on the vibrational assignments for tropone. Results are summarized in Table II.

Around 3000 cm^{-1}.—Six vibrations due to the CH stretching mode, active both in the infrared and Raman spectra, can be anticipated in this region, which should not be higher than 3100 cm^{-1} but higher than 3000 cm^{-1}. The observed spectra show the bands assignable to CH stretching vibrations as an absorption of strong intensity with 3~4 shoulders in the infrared spectrum and as two lines at 3055 and 3031 cm^{-1} in the Raman spectrum. These bands are probably the six vibrations overlapped due to the low resolution of the spectrometer. The infrared spectrum using a calcium fluoride prism does not give an excellent separation. It should further be noted that, in this region, the foot of CH stretching absorption bands in the infrared spectra is extended outside the region of 3100~3000 cm^{-1}, with several shoulders, and that a distinct band has been recorded at 2972 cm^{-1} in the Raman spectrum. Such bands, extending outside the expected range, should naturally be explained in most cases, as the combination bands or over-tones of the vibrations in the lower frequency region, especially in the region of 1660~1450 cm^{-1}, where the bands of strong intensity appear in both the infrared and Raman spectra. This Raman line at 2972 cm^{-1} is not improbable as a CH stretching vibration, refering to the assignment of naphthalene spectrum[9], but there is no evidence to support this assignment. A Raman line at 3055 cm^{-1} belongs to A_1 species by its depolarization factor.

Region of 1660~1450 cm^{-1}. — It is noticed that the bands in this region are very strong in both infrared and Raman spectra, as compared with those of tropilidene (II)[7] which has the same C_{2v} symmetry as tropone. Of the stretching vibrations anticipated from the tropone skeleton, the four vibrational modes due to C=O and C=C bonding are expected to appear in a higher side in this region. A most intense, polarized Raman line at 1520 cm^{-1} is assigned to the C=C in-phase stretching vibration belonging to A_1 species, and is analogous to the most intense Raman lines of tropilidene and tropolone (1535[7] and 1473 cm^{-1} [10] respectively). In the higher side than this line, there are three distinct lines in the Raman spectrum, as anticipated, and two absorption bands of strong intensity with several shoulders are observed in the infrared spectrum. The nature and assignment of these bands will be discussed in a later paper[11] with consideration of the infrared spectra measured in various solvents. A Raman line at 1598 cm^{-1} belongs to B_1 species and other two bands in the region of 1651~1580 cm^{-1} are explained as the vibrations whose main components are the C=O and C=C stretching modes.

The shoulder at 1512 cm^{-1} is thought to correspond to the combination band, 932+577 cm^{-1}. Another distinct band at 1473 cm^{-1}, in both infrared and Raman spectra, may be assigned to the C–C stretching vibration belonging to B_1 species, although it locates rather higher, compared to that in tropilidene[7].

Region of 1450~700 cm^{-1}.—Absorptions of CH out-of-plane bending vibrations belonging to B_2 species and present in the region below 1000 cm^{-1} are generally expected to have strong intensity in the infrared spectrum but weak or indistinct in the Raman spectrum. The three bands at 893, 830 and 779 cm^{-1} are assigned to this vibration. The strong lines at 934 and 716 cm^{-1} in Raman spectrum are assigned to the C–C stretching modes belonging to A_1 species because of their depolarization factors. The latter is analogous to the strong Raman line at 744 cm^{-1} in tropolone[10,12].

The CH out-of-plane bending vibration belonging to A_2 species should be weak in the Raman spectrum and only observed as forbidden bands in the infrared spectrum. In accordance with this presumption the band at 867 cm^{-1} is assigned to this bending vibration. The characteristic weak bands in the region of 2000~1600 cm^{-1} in benzenoids, depending on the position of substituents, are explained

9) E. R. Lippincott and E. J. O'Reilly, *J. Chem. Phys.*, 23, 238 (1955); A. L. McClellan and G. Pimentel, ibid., 23, 245 (1955).

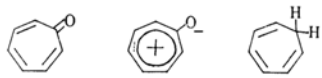
10) Y. Ikegami, unpublished data. The Raman spectra of tropolone and 3- and 4-isopropyltropolones were measured in carbon tetrachloride solution and the spectra showed the most intense Raman lines respectively at 1473, 1489 and 1475 cm^{-1}.

11) Y. Ikegami, Part V, This Bulletin, 35, 972 (1962).

12) S. Imanishi and M. Ito, ibid., 28, 75 (1955); 29, 632 (1956); *J. Chem. Phys.*, 24, 1272 (1956).

as the combination bands or over-tones of CH out-of-plane bending vibrations[13]. If such an interpretation were to apply in the case of planar tropone skeleton, the infrared absorption band at 2013 cm^{-1} would probably by the anticipated over-tone of CH out-of-plane bending vibration at around 1000 cm^{-1}, because, if this band is the combination of two fundamental frequencies, one of these must be higher than the expected frequency range to the CH out-of-plane bendings. This vibration belongs to A_2 species and corresponds to the shoulder of a band at 1017 cm^{-1}. Under such consideration, the probable combination, 934+867 cm^{-1}, is assumed to be a weak band at 1808 cm^{-1}. Accordingly, another CH out-of-plane bending vibration belonging to A_2 species probably exists at around 934 cm^{-1} together with the C–C stretching vibration.

It is noticed that, in this region, the CH out-of-plane bendings of tropone appear at 120~150 cm^{-1} higher than those of tropilidene (II)[7]*.



Ia Ib II

In the region higher than 1000 cm^{-1}, there should be one C–C stretching (B_1 species) and six CH in-plane bending vibrations. Of the observed frequencies, the band at 1253 cm^{-1} can be assigned to the vibration belonging to A_1 species from its depolarization factor. The four bands at 1412, 1309, 1217 and 1017 cm^{-1} are considered to belong to B_1 species, and one of them would be assigned to the C–C stretching vibration. Although there are no definite grounds, the line at 1017 cm^{-1} may probably be assigned to the C–C stretching vibration, since many troponoids show the characteristic absorption band, independent of substituents, in this region[14]. Of the remaining bands, those weak in both infrared and Raman spectra may be assigned as combination bands or over-tones, as indicated in Table II, and distinct bands at 1204 and 1151 cm^{-1} are assumed to belong to A_1 species though indistinct in Raman spectrum.

Region Lower than 700 cm^{-1}.—The bands in this region are assigned to the deformation vibrations of the tropone skeleton. A Raman line at 396 cm^{-1} is assigned to the vibration of A_1 species, similar to that of tropilidene at 420 cm^{-1} and that of tropylium cation at 433 cm^{-1}, although this is doubtful in its depolarization factor. The bands at 576 and 492 cm^{-1} which are strong in the infrared spectrum and weak in the Raman spectrum are assigned to that of B_2 species, and the bands at 644 and 664 cm^{-1}, indistinct in infrared and weak in Raman, are probably assigned to those belonging to the A_2 species. The remaining bands at 653, 386 and 329 cm^{-1} distinct in Raman spectrum were assumed to be assigned to the B_1 species.

Others.—Due to the lack of reliable data, two deformation modes of oxygen atom have been excluded. Of the remaining observed absorption, combination bands or over-tones in the region higher than 1650 cm^{-1} are included in Table II.

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13) Y. Kakiuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1839 (1956); *Kagaku-no-Ryoiki*, Extra No. 38, 1 (1959).

* The structural difference between tropone and tropilidene is known as the aromatic character of tropone due to some contribution from ionic structure Ib and the quasi-aromatic character of tropilidene due to the conjugation of its three double bonds.

14) Y. Ikegami, unpublished data.