The Infrared Spectra of Troponoid Compounds. VI. The Infrared and Raman Spectra of Tropolone, 3- and 4-Isopropyltropolones

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(Received March 30, 1963)

In Part IV[1] of this series, the infrared and Raman spectra of tropone (I) and their vibrational assignments were described. Analyses of the infrared spectra of many troponoids can be made on the basis of these findings. Yet, however, for the analyses of the infrared spectra of many tropolones, it is desirable to know the characters and the assignments of the infrared and Raman spectra of some typical tropolones. In the present paper, the Raman spectra of tropolone (II), 4-isopropyltropolone (hinokitiol) (III) and 3-isopropyltropolone (α-thujaplicin) (IV) will be measured in carbon tetrachloride, and the vibrational assignments of these spectra will be discussed, together with their infrared spectra. All these tropolones are colorless crystals and are soluble in organic solvents suitable for the measurement of Raman spectra. Although the Raman spectra of II and III in benzene have been reported on already by Imanishi and Ito,[2,3] more detailed results were obtained in the present measurements.

Measurements

Raman spectra were measured with a Shimadzu automatic-grating Raman spectrometer, type GRS-750, using the Hg-e line (4358Å) from the Toronto-type mercury lamp as the exciting line. A solution containing ethyl violet and *p*-nitrotoluene in denatured alcohol was used as the filter for the light source.[1] Each sample was measured in carbon tetrachloride (25~35% conc.) by the use of a Raman tube 8 mm. in inner diameter. As the three tropolones are easily colored on exposure to light, the purified samples were preserved in a dark place and caution was taken to shorten the time required for the measurement. Relative intensities in each spectrum (Tables I—III) are given, taking the peak intensity of the most intense line, around 1500 cm^{-1}, as the standard.

Infrared spectra were measured with a Perkin-Elmer model 21 infrared spectrophotometer, using calcium fluoride, sodium chloride and potassium bromide prisms.

Tropolone (m. p. 51°C), 4-isopropyltropolone (m. p. 52°C) and 3-isopropyltropolone (m. p. 34°C) were purified several times by recrystallization and vacuum distillation.

Results and Discussion

Characteristic Features Appearing in the Raman Spectra of Four Troponoids.—The Raman lines observed on three tropolones are shown in Fig. 1, together with those of tropone measured earlier.[1] All these spectra exhibit the most intense line around 1500 cm^{-1}. Further, some strong lines were found which correspond well in their wave numbers and relative intensities to the intense lines of the

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[1] Y. Ikegami, This Bulletin, 35, 967 (1962).
[2] S. Imanishi and M. Ito, ibid., 28, 75 (1955).
[3] S. Imanishi and M. Ito, ibid., 29, 632 (1956).

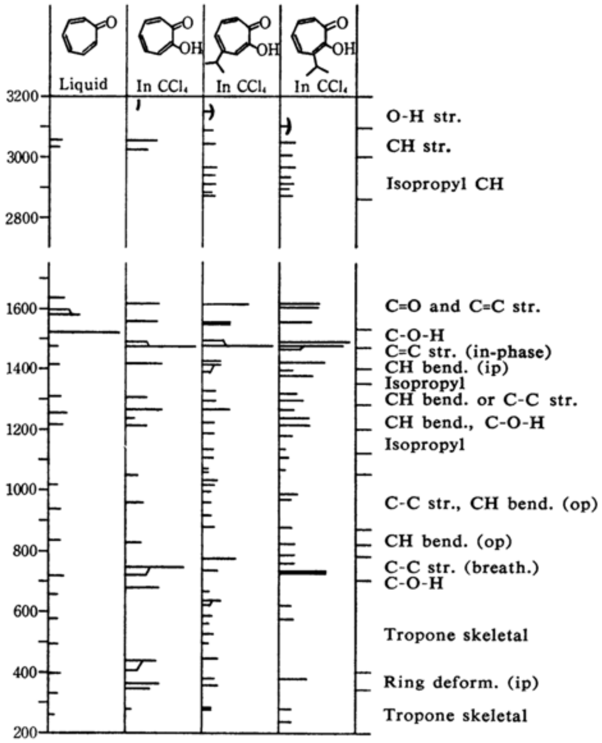
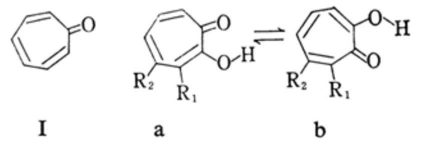


Fig. 1. Raman spectra of four troponoids.

tropone spectrum. Since these characteristic lines in the four troponoids are related to the vibrations of the tropone skeletal part, tentative assignments can be made with reference to the assignments for the spectra of tropone[1] and tropolone[4], as Fig. 1 shows.

The following features in the spectra are illustrated in Fig. 1.

(1) The Raman lines of the three tropolones corresponding to the vibrations belonging to A_1 species of tropone are strong in general. The Raman line due to the C=C in-phase stretching vibration in each spectrum is most intense, but not so strong as that of tropone in the relative intensity.



I a b

II: $R_1=R_2=H$

III: $R_1=H$, $R_2=$isopropyl

IV: $R_1=$isopropyl, $R_2=H$

(2) In a spectrum of 3-isopropyltropolone, it is noticeable that the line due to the C=C in-phase stretching vibration is separated into two lines, at 1489 and 1476 cm^{-1}, with a similar intensity. This fact suggests two possible tautomeric forms, IVa and IVb, for the structure of 3-isopropyltropolone. In the other region, also, some of the Raman lines are found to form pairs, such as 1618 and 1604, 1318 and 1295, 1263 and 1239, 985 and 965, 785 and 758, 728 and 724, and 275 and 234 cm^{-1}.

The existence of similar tautomeric forms must be considered also for 4-isopropyltropolone, and some paired lines, such as 1554 and 1549, 1426 and 1412, 1328 and 1293, 772 and 731, and 280 and 272 cm^{-1}, are pointed out. On the intramolecular hydrogen bonding of tropolone, it has been suggested that a highly mobile tautomeric hydrogen is located by the two equivalent potential minima.[5] Accordingly, it is natural to interpret the vibrational spectra of tropolones on the basis of a consideration of the tautomerism, except for those cases, such as the 5-monosubstituted tropolones, in which two tautomeric forms have the same structural model.

(3) The vibrations due to the C–O–H group are generally strong in the infrared spectra,[4,6,7] but weaker or indistinct in the Raman spectra.

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[4] Y. Ikegami, ibid., **34**, 94 (1961).

[5] H. P. Koch, *J. Chem. Soc.*, **1951**, 512.

[6] Y. Ikegami, This Bulletin, **34**, 91 (1961).

[7] Y. Ikegami, *J. Japanese Chem.* (*Kagaku-no-Ryoiki*), **38**, 33 (1959).

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

Infrared Solution[a]	Raman In CCl_4	Assignment
3450 vwb		
3151 mb	3229 0.5 b	O–H stretch.[b]
3120 mb		
3051 sh	3053 3.0	CH stretch.
3020 sh	3023 1.8	
2001 w		2×1000
1970 w		1000+953
1903 vw		2×953
1832 vw		2×917 or 1000+828
1817 sh		953+854
1774 w		917+854
1747 w		
1687 sh		919+767 or 854+828
1618 vs	1618 3.8	C=O and C=C stretch.[c]
1555 s	1559 3.2	C=C and C=O stretch.[c]
1490 vs	1490 sh	C–O–H group[b]
1476 vs	1473 10	C=C stretch. (in-phase)
1444 s		C–C stretch. ? or CH bend. (ip)
1425 sh	1418 4.2	CH bend. (ip)
1355 vw		2×675
1317 sh		767+551
1304 m	1304 1.9	CH bend. (ip) or C–C stretch. ?
1267 vs	1265 4.2	CH bend. (ip)
1251 vs	1239 w	C–O–H group[b]
1213 m	1211 1.9	CH bend. (ip)
1048 vw	1049 0.5	C–C stretch.
1000 vw		CH bend. (op)
953 m	957 1.3	C–C stretch.
917 m		CH bend. (op)
873 w		2×434
854 w		CH bend. (op)
	828 1.1	CH bend. (op)
767 m		CH bend. (op)[b]
	744 8.0	C–C stretch. (ring breath.)
726 sb	719 sh	C–O–H group (op)[b]
713 s		
675 w	678 3.9	Skeletal deform.
654 vw		
551 vw		
434 m	439 2.4	Skeletal deform.
404 m	403 sh	
	360 4.0	Skeletal deform. (ip)
	342 2.4	Skeletal deform.
	275 vw	

(vs : very strong, s : strong, m : medium, w : weak, vw : very weak, sh : shoulder, b : broad, ip : in-plane, op : out-of-plane)

a) The region of 3600～2000 cm^{-1} was measured by using a calcium fluoride prism. The spectrum was measured in carbon tetrachloride (4000～900 cm^{-1} range) and in carbon disulfide (900～400 cm^{-1}).

b) Refs. 4 and 6. c) Ref. 9.

Therefore, it is fairly difficult to distinguish the vibrations of the tropone skeletal part in the infrared spectra, especially in the fingerprint region, because of the overlap with the strong and broad absorptions due to the C–O–H group. On the contrary, almost all of the skeletal vibrations are observed distinctly in the Raman spectra.

(4) In the spectra of 4- and 3-isopropyltropolones, the Raman lines due to the isopropyl group[8] are found in the 2968～2872, 1393～1375 and 1188～1132 cm^{-1} regions.

On the basis of these features, the following

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[8] R. N. Jones and C. Sandorfy, " Chemical Application of Spectroscopy", Ed. by W. West, Interscience Publishers, New York (1956), pp. 336, 356.

TABLE II. OBSERVED FREQUENCIES (cm^{-1}) AND THEIR POSSIBLE ASSIGNMENTS FOR 4-ISOPROPYLTROPOLONE

Infrared				Raman In CCl_4	Assignment
Solid[a,b]	Liquid[b]	Solution[b,c]	Vapor[d]		
3533 vwb	3450 sh	3450 sh			
3215 sb	3195 sb	3150 m	3140 w	3231 3181 wb 3146	O-H stretch.
		3115 mb			
		3027 w		3088 w 3043 0.4	Ring CH stretch.
2995 sh					
2971 sh					
2957 m	2960 m	2968 s	2980 s	2968 0.7	Asym. CH_3 stretch.
2920 w	2927 w	2931 w	2940 sh	2940 0.5	CH_3 stretch. or 2×1475
				2911 0.5	1616+1293 ?
				2883 w	Tert. CH stretch.
2864 w	2868 w	2872 w	2890 w	2872 0.4	Sym. CH_3 stretch.
		1997 vw			2×998
		1972 vw			
		1900 vw			2×951
1818 w	1804 w	1804 w	1800 w		911+890
		1775 vw			2×890
		1700 vw			
1609 vs	1615 vs	1617 vs	1625 vs	1616 5.9	C=O and C=C stretch.
1547 vs	1551 s	1560 s 1546 s	1563 s	1554 1549 3.1	C=C and C=O stretch.
1487 vs	1499 sh	1496 vsb	1498 vs	1495 sh	C-O-H group
1479 vsb 1462 vs	1474 vsb	1472 vsb	1475 vsb	1475 10	C=C stretch. (in-phase)
1449 sh		1442 s	1460 sh		CH_3 degen. deform.
1425 sh	1427 s			1426 1.3	Ring CH bend. (ip)
1417 s			1422 m		
1412 sh	1412 s	1410 s		1412 1.3	
1385 sh		1385 vw		1389 sh	CH_3 sym. deform.
			1370 sh		
1360 w	1369 w	1367 w			
1328 w	1325 w	1330 m		1328 0.7	Ring CH bend. (ip) or C-C stretch. ?
		1320 m	1320 sh		
		1299 sh			
1301 m		1291 sh	1290 sh	1293 0.7	
		1281 m			
1269 vs	1264 vs	1266 vs	1267 vsb	1266 3.0	Ring CH bend. (ip)
	1250 shb	1256 vsb			C-O-H group
1220 sh	1225 sh	1230 sh	1229 sh	1222 0.5	Ring CH bend. (ip)
1188 vsb					C-O-H group
	1185 sh	1182 w	1176 vw	1188 0.4	Isopropyl group
		1142 vw			
		1130 vw		1132 0.2	
1113 w					
1105 m		1100 vw		1106 0.2	
1070 m	1057 w	1066 w	1060 w	1068 vw	
		1058 w		1058 vw	
1013 w	1011 vw	1024 vw 1009 w	1003 w	1030 0.7 1014 0.5	Ring C-C stretch.
998 vw				991 w	Ring CH bend. (op)
960 sh	954 sh	951 sh		957 w	Ring CH bend. (op)
950 s	947 s	946 s	943 m		Ring CH bend. (op)
933 m	913 m	911 m	905 m	914 w	
877 w	891 m	890 m		878 0.3	Ring C-C stretch.
820 s	824 s	821 s	820 m		Ring CH bend. (op)
	790 sh	790 m			

TABLE II. (Continued)

Infrared				Raman in CCl_4	Assignment
Solid[a,b]	Liquid[b]	Solution[b,c]	Vapor[d]		
767 m	769 m	769 m		772 3.9	Ring C–C stretch. (ring breath.)
756 mb				756 ?	
	735 mb	735 sb	742 mb		C–O–H group (op)
				731 0.9	
726 m	707 m	722 sh			
655 m	658 s	660 m	658 m	662 vw	Tropone skeletal
	633 sh			635 1.4	
598 m	612 m	610 w		620 sh	
580 sh	582 sh			582 w	
	556 sh			560 vw	
530 sh	522 sh			524 0.3	
503 w	491 w			494 vw	
448 m	444 m			(444 (1)[e])	Ring deform.
				378 0.5	Ring deform.
				353 0.9	
				280 0.2	Ring deform.
				272 0.2	

a) The region of 4000~2000 cm^{-1} was measured as a crystalline film (Ref. 6) and the region lower than 2000 cm^{-1} was measured in a potassium bromide disk.

b) The region higher than 2000 cm^{-1} was measured by using a calcium fluoride prism.

c) In carbon tetrachloride (4000~900 cm^{-1} range) and in carbon disulfide (900~600 cm^{-1}), ca. 5% conc.

d) Ref. 10. e) Ref. 3.

remarks can be made concerning the assignments for the observed frequencies of tropolone, 4- and 3-isopropyltropolones.

Tropolone.—The observed frequencies of tropolone and their assignments are summarized in Table I. The infrared spectra of tropolone in the solid, liquid and vapor states and the assignments regarding the C–O–H group, the CH-stretching and some of the CH-bending vibrations have already been described in Parts II[6] and III[4].

In the 1650~1450 cm^{-1} region, the most intense Raman line, at 1473 cm^{-1}, may easily be assigned to the totally symmetric stretching vibration of three C=C bonds. The two bands at 1618 and around 1555 cm^{-1} may be explained as resulting from the participation of both C=O and C=C stretching vibrations, as has been described in the preceding paper.[9] These frequencies are considerably lower than those of the corresponding bands in tropone as a result of the conjugated chelation in a tropolone structure.

When the Raman spectrum in the 1450~1000 cm^{-1} region is compared with that of tropone, the following lines corresponding to each other in frequency and relative intensity are found:

Tropone; 1412 (0.3), 1309 (0.4), 1254 (1.3), 1217 (0.6), 1017 cm^{-1} (0.2).
Tropolone; 1418 (4.2), 1304 (1.9), 1265 (4.2), 1211 (1.9), 1049 cm^{-1} (0.5).

The vibrational frequencies due to the tropone skeletal part in tropolone are not greatly different from those of tropone. Therefore, the above frequencies can be assigned to the same vibrational modes as those of tropone, as is indicated in Table I. The band at 1265 cm^{-1} is assumed to be related to the vibration of the C–O–H group,[4] and thus this band may be considered the overlap of two bands. The band at 1444 cm^{-1} is assumed to correspond to the band at 1473 cm^{-1} of tropone.

The infrared absorptions at 767 and 726 cm^{-1} are assigned to the CH and OH out-of-plane bending vibrations respectively.[4] Of the remaining frequencies in the 1000~700 cm^{-1} region, the two bands at 957 and 744 cm^{-1} can be assigned to the C–C stretching vibrations, since these bands are strong in the Raman spectrum and correspond well to the vibrations belonging to A_1 species of tropone. The latter was also assigned similarly by Imanishi and Ito.[2,3] The other frequencies observed in this region are assumed mainly to be due to the CH bending vibrations, as indicated in Table I.

The bands in the region lower than 700 cm^{-1} are assigned to the deformation vibrations of the tropone skeleton. Of these, the distinct Raman lines at 678, 360 and 342 cm^{-1} are probably due to vibrations similar to the bands at 653, 396 and 329 cm^{-1} of the tropone spectrum.[1]

4-Isopropyltropolone.—The observed frequencies, obtained from the infrared spectra in the

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[9] Y. Ikegami, This Bulletin, 35, 972 (1962).

TABLE III. OBSERVED FREQUENCIES (cm^{-1}) AND THEIR POSSIBLE ASSIGNMENTS FOR 3-ISOPROPYLTROPOLONE

Infrared[a)]		Raman In CCl$_4$	Assignment
Liquid	Solution		
3450 wb			
		3102 w	O-H stretch.
3170 mb	3095 wb	3083 w	
	3040 vw	3049 1.0	Ring CH stretch.
	3008 vw	3007 0.5	
2960 s	2962 s	2967 1.0	Asym. CH$_3$ stretch.
2925 sh	2925 sh	2934 0.3	CH$_3$ stretch. or 2×1463 ?
		2913 0.7	
2890 sh	2888 sh	2896 w	Tert. CH stretch.
2865 m	2866 m	2872 0.5	Sym. CH$_3$ stretch.
1618 s	1621 s	1618 5.2	C=O and C=C stretch.
1603 s	1603 s	1604 5.0	
1551 vs	1554 vs	1553 3.7	C=C and C=O stretch.
1493 vs	1495 vs		C-O-H group
		1489 10	C=C stretch. (in-phase)
		1476 9.0	
1465 vs	1465 vs	1463 sh	CH$_3$ degen. deform.
1425 s	1427 s	1420 6.0	Ring CH bend. (ip)
1394 vs	1395 vs	1393 0.8	CH$_3$ sym. deform., Ring CH bend. (ip)
1377 s	1378 s	1375 3.8	
	1365 sh		
1350 sh	1345 sh		Tert. CH deform.
1319 vw	1319 vw	1318 1.4	Ring CH bend. (ip) or C-C stretch. ?
1292 s	1295 vs	1295 2.3	
1265 sh	1265 sh	1263 1.0	C-O-H group, Ring CH bend. (ip)
1253 vs	1254 vs		
1233 vs	1237 vs	1239 3.5	
1210 sh	1210 sh	1214 3.4	Ring CH bend. (ip)
1183 w	1182 w	1179 0.6	Isopropyl group
1132 w	1130 w	1132 vw	
1105 w	1105 w	1106 w	
1060 m	1061 m	1065 w	
984 sh	984 m	985 1.4	Ring C-C stretch.
967 m	968 m	965 0.4	
958 sh	953 m		Ring CH bend. (op)
894 sh	888 vw		
875 m	873 m	877 0.6	Ring C-C stretch.
		822 1.2	Ring CH bend. (op)
809 s	809 s		Ring CH bend. (op)
801 sh	799 m		
		785 1.1	Isopropyl group
	764 sh	758 1.0	
742 sb	739 vs		C-O-H group (op)
720 m	713 m	728 724 6.2	Ring C-C stretch. (ring breath.)
689 m	690 w		
659 m			
622 m		618 0.6	Tropone skeletal
569 m	572 0.7		
547 vw			
529 vw			
502 vw			
462 m			
426 m			
		376 3.0	Ring deform. (ip)
		275 0.6	Ring deform.
		234 0.6	

a) The region higher than 2000 cm^{-1} was measured by using a calcium fluoride prism.

solid, liquid, solution and vapor states[10] and from the Raman spectrum, are shown in Table II, together with their possible assignments. The OH and CH-stretching absorptions have already been discussed in Part II.[6] Frequencies in the 1650∼1470 cm^{-1} region are due to the tropone skeletal stretching and C–O–H group vibrations, as in the case of tropolone.

The bands in the 1460∼1442, 1389∼1360 and 1188∼1130 cm^{-1} regions are assigned, respectively, to the CH_3 degenerate deformation, the symmetric deformation and the skeletal vibrations of the isopropyl group.[8,11] These bands are very weak in both infrared and Raman spectra. The assignments of the remaining bands in the 1470∼1000 cm^{-1} region were given with reference to those of tropolone and after consideration of the variation of absorptions according to the changes of state.[4] The Raman lines at 1030 and 1014 cm^{-1}, as well as those at 1426 and 1412 cm^{-1}, are considered to be doublets due to the existence of two tautomeric forms, IIIa and IIIb.

It is possible to assign the intense Raman lines at 878 and 772 cm^{-1} to the ring C–C stretching, and the absorption bands at 950, 820 and 790 cm^{-1},[12] to the CH out-of-plane bending vibrations, which are expected to have a strong intensity. The broad absorption band at 735 cm^{-1} is the OH out-of-plane vibration. The weak bands at 998 and 951 cm^{-1} are probably assigned to the CH out-of-plane vibrations, which are to be expected in this region. The weak absorptions at 1997 and 1900 cm^{-1} can be explained as the overtones of these vibrations.

3-Isopropyltropolone.—The observed frequencies and their possible assignments are summarized in Table III. The bands observed in the 2967∼2865 and 3049∼3007 cm^{-1} regions belong to the CH stretching vibrations, and their frequencies differ little from those of 4-isopropyltropolone. The broad infrared absorption in 3450∼3095 cm^{-1} is assigned to the OH stretching vibration, and the corresponding Raman lines are very weak. This OH absorption, which is strongest at 3170 cm^{-1} in liquid, shifts to 3095 cm^{-1} and its intensity decreases in carbon tetrachloride. The direction of the shift of absorption caused by the change of state agrees with that in the case of tropolone, but the frequencies in each state are lower by about 50 cm^{-1} than those of many tropolones. Such lower frequencies are also observed in the spectra of 3,7-dibromotropolones[13] and 3-quinonyltropolone (3090 cm^{-1}),[14] all of which have a bulky substituent at the 3-position of the tropolone ring.

Frequencies in the 1650∼1470 cm^{-1} region are assigned in the same manner as in the case of 4-isopropyltropolone. The Raman line at 1463 cm^{-1} is assigned to the CH_3 degenerate deformation vibration, and the corresponding infrared band shows a strong intensity because of the overlap with the strong and broad absorption due to the C–O–H group. Two bands in 1395∼1375 cm^{-1}, one shoulder at 1345 cm^{-1} and two band in 1183∼1130 cm^{-1} are all assigned to the vibration due to the isopropyl group. Of these, the strong intensity of the infrared absorption band at 1394 cm^{-1} indicates the overlapping with the ring CH bending absorption, as its to be expected from the fact that 3-bromotropolone shows the absorption band at 1375 and 1353 cm^{-1} (in carbon tetrachloride).

The broad absorption band at 1233 cm^{-1} in the liquid spectrum appears to be related to the C–O–H group. In carbon tetrachloride, this band shifts to the higher wave number side, merging around 1254 cm^{-1}, as in cases of tropolone and 4-isopropyltropolone.[6] The remaining bands in the 1470∼1000 cm^{-1} region have been assigned with reference to the assignments for the spectra of tropolone and 4-isopropyltropolone.

As may be seen in Fig. 1, a line at 877 cm^{-1} and two paired Raman lines at 985 and 965 cm^{-1} and at 728 and 724 cm^{-1} are assigned to the ring C–C stretching vibrations. The broad absorption band, strongest at 742 cm^{-1} in the liquid spectrum, shifts to 739 cm^{-1} in carbon tetrachloride; this is assigned to the OH out-of-plane vibration. Among the remaining bands in the 1000∼700 cm^{-1} region, those which are strong in the infrared spectrum and weak in the Raman spectrum are probably to be assigned to the CH out-of-plane bending vibrations, as Table III indicates. The two Raman lines at 785 and 758 cm^{-1} are assumed to be due to the isopropyl group.[8] The Raman lines at 618 and 376 cm^{-1} and the paired ones at 275 and 234 cm^{-1}, which are all distinct in the Raman spectrum, are probably to be assigned to the same vibrations as those of tropone at 653, 396 and 259 cm^{-1} respectively.

The author wishes to express his deep gratitude to Professor Susumu Kinumaki, Professor

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[10] S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Research Inst., Tohoku Univ., Ser. A*, **8**, 263 (1956).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London (1958), pp. 13, 26.

[12] From the results of spectral measurement made on various 2,4- and 2,6-disubstituted tropones, Takase et al. concluded that the absorption bands at 820 and 790 cm^{-1} correspond to the structures of IIIa and IIIb respectively. (K. Takase, M. Yasunami and T. Nozoe; Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.)

[13] K. Ogura and Y. Ikegami, *Bull. Chem. Research Inst. Non-Aqueous Solutions, Tohoku Univ.*, **9**, 23 (1959).

[14] S. Seto, Y. Ikegami and H. Sato, ibid., **11**, 85 (1962); S. Seto and H. Sato, This Bulletin, **35**, 349 (1962).

Shuichi Seto and Professor Koyo Aida for their unfailing guidance during the course of this work. He is also indebted to Miss Hisako Minegishi for her technical cooperation in the spectral measurements.

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