Infrared Spectra of Troponoid Compounds. V. Absorption Bands in the Region of 1700~1530 cm^{-1} of Tropone, 2-Chlorotropone and Tropolone[*1]

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Infrared absorption bands due to the vibration of tropone skeleton are generally not present in the higher wave number side than 1651 cm^{-1}, and appear as two or more bands in the region of 1651~1530 cm^{-1} 1). In most reports made to date, the absorption bands with the highest wave number have been treated as that of C=O stretching and the next higher absorption as the C=C stretching mode. Such an assignment, however, has little experimental or evidental basis. Accordingly, it should naturally be considered that $\nu_{C=O}$ might show a lower wave number than $\nu_{C=C}$, as was considered earlier by Kloster-Jensen and others2) with $\nu_{C=O}$ of 2, 7-polymethylene-4, 5-benzotropones.

As shown in the previous reports3,4), the infrared spectrum of tropone (I) in this region shows considerable variation of absorption wave numbers according to the condition of measurement, and the relative intensity of Band I[*2] and Band II[*2] is just reverse, according to whether it is observed in a vapor or liquid state. Such a difference in spectrum may be attributed to the association of molecules. Then, as one of the means for obtaining some informations on the assignment of these bands, the variation of the intensity and the shift of the absorption bands accompanying changes in the state and solvent were examined. Discussions are also given on the results obtained by the measurement of infrared spectra in the region of 1700~1500 cm^{-1}, in various solvents. Besides tropone, 2-chlorotropone (II) and tropolone (III) were also examined.

Measurement

The infrared absorption spectra were measured with a Perkin-Elmer model 21 infrared spectrophotometer equipped with a sodium chloride prism. The measurement on solids were made with the potassium bromide disk method and the sample cell with potassium chloride windows was used for the measurement in solution and liquid. Standard absorption lines of water vapor and polystyrene film were used for wave number calibration. The probable error of the wave number in Tables I, II and III is about ±2 cm^{-1}. Tropone, 2-chlorotropone5), and tropolone were prepared by known methods and purified. The kind of solvents to be used and the concentration of the solution were selected considering the infrared absorption of solvents themselves and the solubility of samples.

Results and Discussion

Tropone.—The spectra measured on tropone are shown in Fig. 1. The spectrum obtained earlier4) in the vapor state is also shown in Fig. 1a. The wave number (ν) of absorption bands found, relative wave number shift ($\Delta\nu/\nu_0$), apparent molecular extinction coefficient (ε^a) at each wave number, and apparent half band width ($(\Delta\nu)_{1/2}{}^a$) are summarized in Table I. The value of $\Delta\nu$ shows the wave number shift ($\nu_0-\nu$) and is given taking the wave number (ν_0) in the vapor state as the standard. The values of ε^a and $(\Delta\nu)_{1/2}{}^a$ are rough values, because the Bands I and II are often accompanied with shoulders. However, these values will be sufficient in knowing the tendency of spectral variation. As a measure to compare the intensities of Bands I and II, the values of r are taken as shown in Table I. These values show $[\varepsilon^a\times(\Delta\nu)_{1/2}{}^a]_I/[\varepsilon^a\times(\Delta\nu)_{1/2}{}^a]_{II}$ and roughly mean the ratio of the area of Band I to that of Band II.

Following features in the spectra are found in Fig. 1 and Table I:

a) The direction of the shift of absorption bands according to changes in the measuring condition is the same in Bands I and II but the magnitude of this shift is greater in Band II (maximum of $\Delta\nu$: 39 cm^{-1}) than in I (maximum of $\Delta\nu$: 18 cm^{-1}). Bellamy and Williams6) discussed the relation between the

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[*1] A part of this work was presented at the 13th Annual Meeting of the Chemical Society of Japan, April, 1960.

1) Y. Ikegami, *Kagaku-no-Ryoiki*, Extra No. **38**, 33 (1959).

2) E. Kloster-Jensen, N. Tarköy, A. Eschenmoser and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).

3) Y. Ikegami, This Bulletin, **35**, 967 (1962).

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

[*2] Each spectrum, referred to in this report, has two strong absorption bands in the region of 1660~1530 cm^{-1}. Hereinafter this band at higher and at lower wave numbers will be designated respectively as "Band I" and "Band II".

5) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, *Sci. Repts. Tohoku Univ.*, **I36**, 126 (1952); S. Seto, ibid., **37**, 275 (1953).

6) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

TABLE I. COMPARISON OF TWO BANDS (I AND II) OF TROPONE IN VARIOUS STATES

Spectral no. and state (Fig. 1)		Band I				Band II				r
		ν cm^{-1}	$\Delta\nu/\nu_0$ $\times 10^3$	ε^a	$(\Delta\nu)_{1/2}{}^a$	ν cm^{-1}	$\Delta\nu/\nu_0$ $\times 10^3$	ε^a	$(\Delta\nu)_{1/2}{}^a$	
a	Vapor	1651				1613				1.19$^{a)}$
b	In n-heptane	1645	3.63	277	14.2	1602	6.82	406	15.0	0.65
c	In diisopropyl ether	1645	3.63	217	20.0	1600	8.06	407	19.8	0.54
d	In triethylamine	1644	4.24	246	19.3	1598	9.30	470	16.5	0.61
e	In carbon tetrachloride	1645	3.63	243	21.5	1595	11.16	513	15.5	0.66
f	In 1-chlorobutane	1645	3.63	211	21.5	1595	11.16	458	19.5	0.51
g	In carbon disulfide	1644	4.24	290	19.5	1593	12.40			
h	In dioxane	1642 1634	5.45	195	23.5	1590	14.26	556	17.5	0.47
i	In acetonitrile	1634	10.30	170	22.5	1585	17.36	545	18.5	0.38
j	In chloroform	1635	9.69	210	13.0	1582	19.22	515	25.0	0.21
k	In ethanol	1633	10.90	209	12.5	1574	24.18	468	31.0	0.18
l	Liquid	1634	10.30		25	1580	20.46		32	0.36

$\Delta\nu/\nu_0$; Relative wave number shifts, were estimated in all cases by reference to the wave number in vapor state.

ε^a; Apparent molecular extinction coefficient at absorption maximum (peak height).

$(\Delta\nu)_{1/2}{}^a$; Apparent half band width, cm^{-1}.

$r = [\varepsilon^a \times (\Delta\nu)_{1/2}{}^a]_{I}/[\varepsilon^a \times (\Delta\nu)_{1/2}{}^a]_{II}$ a); $[\varepsilon^a]_{I}/[\varepsilon^a]_{II}$

TABLE II. COMPARISON OF TWO BANDS (I AND II) OF 2-CHLOROTROPONE IN VARIOUS STATES

Spectral no. and state (Fig. 3)		Band I				Band II				r
		ν cm^{-1}	$\Delta\nu/\nu_0{}^{a)}$ $\times 10^3$	ε^a	$(\Delta\nu)_{1/2}{}^a$	ν cm^{-1}	$\Delta\nu/\nu_0{}^{a)}$ $\times 10^3$	ε^a	$(\Delta\nu)_{1/2}{}^a$	
		(1648)				(1622)				
a	In n-heptane	1642	3.64		11.5	1611	6.78		20.0	1.37
b	In diisopropyl ether	1639	5.46	334	14.5	1609	8.01	281	17.0	1.01
c	In triethylamine	1639	5.46	317	13.7	1610	7.40	234	18.0	1.03
d	In carbon tetrachloride	1636	7.28	284	14.5	1609	8.01	285	17.3	0.84
e	In 1-chlorobutane	1636	7.28	298	13.8	1608	8.63	327	16.3	0.77
f	In carbon disulfide	1634	8.50	318	12.0	1606	9.86	296	16.8	0.77
g	In dioxane	1634	8.50	271	13.0	1605	10.48	340	14.7	0.71
h	In acetonitrile	1632	9.71	218	12.5	1600	13.56	335	19.5	0.42
i	In chloroform	1632	9.71	312	13.0	1597	15.41	411	25.5	0.39
j	In ethanol	1629	11.53	183	16.5	1590	19.73	287	31.8	0.33
k	Solid	1628	12.14		15.4	1591 1583	19.11		30.2	0.26

a); Relative wave number shifts were estimated in all cases by reference to the wave number presumed to vapor state.

relative wave number shift for C=O stretching absorption band in various ketones and that of acetophenone in various solvents. According to their method, the values of $\Delta\nu/\nu_0$ of tropone in various solvents are plotted against their values of benzophenone, in Fig. 2*3. As is clearly noticed from this figure, an effect, which is similar to that of solvent on the carbonyl group of benzophenone, appears in both Bands I and II of tropone. The effect appeared is smaller in Band I and larger in Band II, than that for the carbonyl group of benzophenone. This effect on Band II is typical as the effect on the usual C=O stretching absorption[6].

b) The Band I is stronger than Band II in a vapor state but Band II is stronger and has wider width in other states.

c) As the Bands I and II shift towards the lower wave number side, the value of ε^a of Band I decreases slightly and that of Band II tends to increase. Consequently, value of r decreases.

d) The spectrum of liquid tropone in this

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*3 Benzophenone was chosen as the standard because two π-electron systems are conjugated with the carbonyl group in a molecule as in tropone. The values of ν/ν_0 of tropone in n-heptane and in diisopropyl ether corresponded respectively to those of benzophenone in n-hexane and in n-butyl ether.

region is similar to that of tropone in ethanol or acetonitrile, generally known as a polar solvent.

On the basis of these features, following discussions are built. There is no doubt that the absorption bands in this region are due to the stretching vibrations of C=O and C=C linkages[7]. According to the consideration on the vibrational assignments of tropone spectrum, one C=O stretching (A_1 species) and two C=C stretching (A_1 and B_1 species) vibrations are expected in the region of 1700~1530 cm^{-1}, as discussed in the preceding paper[3]. That of B_1 species was observed

TABLE III. COMPARISON OF TWO BANDS (I AND II) OF TROPOLONE IN VARIOUS STATES

Spectral no. and state (Fig. 5)		Band I				Band II				r
		ν cm^{-1}	$\Delta\nu/\nu_0$ $\times10^3$	ε^a	$(\Delta\nu)_{1/2}^a$	ν cm^{-1}	$\Delta\nu/\nu_0$ $\times10^3$	ε^a	$(\Delta\nu)_{1/2}^a$	
a	Vapor	1628			31.0	1573 1575			40.0	2.03
b	In *n*-heptane	1622	3.69		16.0	1564	5.72		32.0	1.09
c	In diisopropyl ether	1620	4.91	326	19.0	1565	5.09	166	32.7	1.14
d	In carbon tetrachloride	1618	6.14	297	18.0	1555	11.44	158	37.0	0.91
e	In 1-chlorobutane	1618	6.14	308	18.5	1557	10.17	166	33.0	1.04
f	In carbon disulfide	1617	6.76	343	18.8					
g	In dioxane	1617	6.76	389	14.3	1565	5.09	255	30.3	0.72
h	In acetonitrile	1616	7.37	342	15.0	1553	12.71	167	32.5	0.95
i	In chloroform	1615	7.99	349	15.0	1551	13.99	237	23.5	0.94
j	In ethanol	1614	8.60	336	18.3	1547	16.53			
	In pyrrole[a]	1612	9.83		14.0	1548	15.89		26.8	0.69
k	Liquid	1614	8.60		22.5	1553	12.71		40.0	0.69
l	Solid	1613	9.21		22.5	1548	15.89		36.5	1.04

[a] Concentration; ca. 2.4 mol./l. (0.018 mm. thickness)

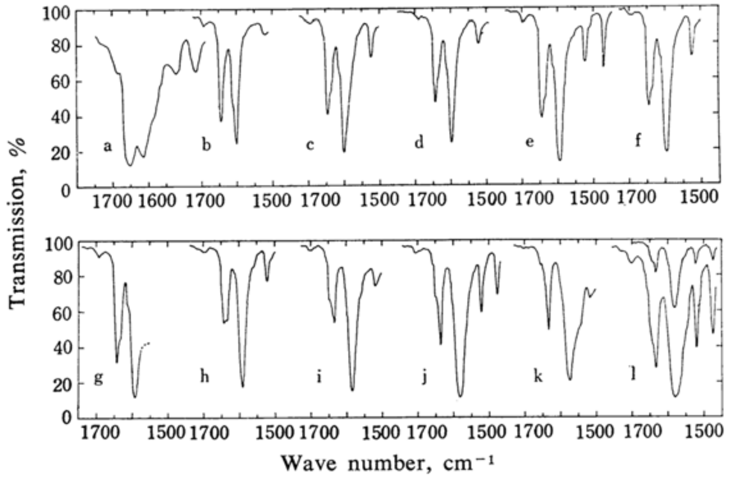

Fig. 1. Infrared spectra of tropone in the states of vapor and liquid, and in various solvents (1700~1500 cm^{-1} range): a; vapor, b; in *n*-heptane, 0.029 mol./l. (0.524 mm. thickness), c; in diisopropyl ether, 0.185 (0.095), d; in triethylamine, 0.141 (0.092), e; in carbon tetrachloride, 0.185 (0.092), f; in 1-chlorobutane, 0.185 (0.095), g; in carbon disulfide, 0.182 (0.092), h; in dioxane, 0.147 (0.092), i; in acetonitrile, 0.160 (0.092), j; in chloroform, 0.185 (0.095), k; in ethanol, 0.153 (0.092), l; liquid.

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[7] That the $\nu_{C=O}$ in tropone is less than 1651 cm^{-1} is generally explained as follows. The $\nu_{C=O}$ of saturated cycloheptanones is between 1708 and 1698 cm^{-1}, according to many references. When the molecule has a double bond conjugated with a C=O group, the frequency is less than this value by ca. 40 cm^{-1} (for example, eucarbone: 1660 cm^{-1}). Therefore, the $\nu_{C=O}$ of tropone is expected at the lower than 1650 cm^{-1} because tropone has a longer conjugated system and the polar character of Ib type. Moreover, from the the length of C=O bond, which was determined as 1.26 Å by electron diffraction analysis, we can expect the $\nu_{C=O}$ of tropone at around 1610 cm^{-1} because of the relation between the bond length and the frequencies reported by Leyton et al. (Cf. K. Kimura, S. Suzuki, M. Kimura and M. Kubo, This Bulletin, **31**, 1051 (1953); E. M. Leyton, R. D. Kross and V. A. Fassel, *J. Chem. Phys.*, **25**, 135 (1956).)

distinctly at 1598 cm^{-1} in the Raman spectrum but it is not so clear in the infrared spectra and is probably superposed in Band II. Consequently, Bands I and II both must belong to the A_1 species, as they are also supported from their depolarization factors[3].

It is well known in general that the C=O stretching vibration appears strongly in infrared spectra and the wave number of absorption band and the intensity are easily affected by the internal or external effects[8]. Such properties are found in both of Bands I and II in tropone, although often more in Band II than I, as shown in the foregoing a)—c). On the other hand, it is hardly expected that the out-of-phase C=C stretching vibration of tropone appears strongly, because of the fact that the absorption of tropilidene[9], which has the same C_{2v} symmetry as tropone, is very weak in this region. The wave number 1580 cm^{-1} in the liquid tropone, for example, is too low for pure out-of-phase C=C stretching vibration belonging to A_1 species, compared with that of tropilidene (1609 cm^{-1})[9] and of tropylium cation (1594 cm^{-1})[10].

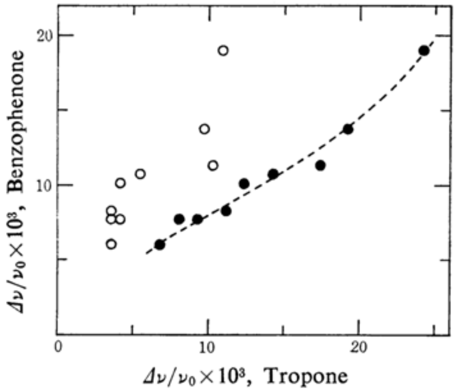

Fig. 2. Relation between the values of $\Delta\nu/\nu_0$ of Bands I and II in tropone and of $\nu_{C=O}$ in benzophenone in various solvents. ○ ; Band I, ● ; Band II

Considering the facts described above, it is natural to assume that both Bands I and II have contributions from the C=O and C=C stretching vibrations, which belong to A_1 species and both are expected at around 1600 cm^{-1}. If such is the case, there would be relative variation in the frequency, intensity, and width of absorptions in both Bands I and II as the C=O bond is polarized by external effects, and the foregoing characteristics a)—c) in spectra should mean that the character of C=O stretching vibration in Band II is greater than that in Band I, except in a vapor state. If the Ib character of a tropone skeleton becomes stronger and the double bond character of C=O bond becomes smaller, it is likely that the $\nu_{C=O}$ appears in a further lower wave number region. For example, Buchanan

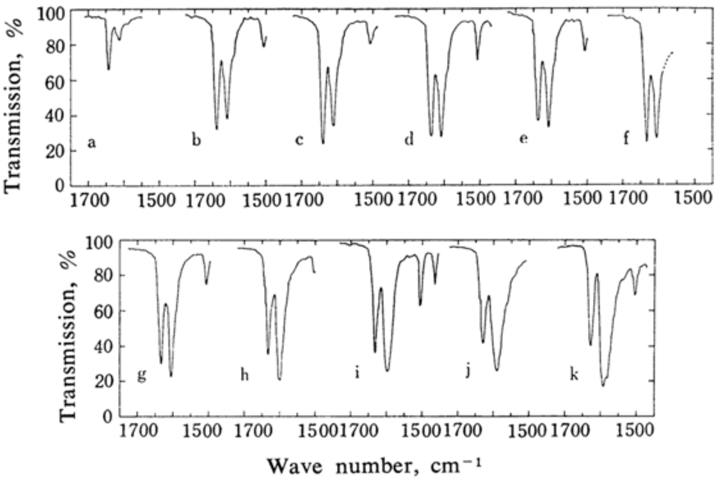

Fig. 3. Infrared spectra of 2-chlorotropone in the state of solid and in various solvents (1700∼1500 cm^{-1} range) ; a ; in *n*-heptane, saturated (0.13 mm. thickness), b ; in diisopropyl ether, 0.146 mol./l. (0.10), c ; in triethylamine, 0.149 (0.13), d ; in carbon tetrachloride, 0.146 (0.13), e ; in 1-chlorobutane, 0.146 (0.10), f ; in carbon disulfide, 0.146 (0.13), g ; in dioxane, 0.142 (0.13), h ; in acetonitrile, 0.153 (0.13), i ; in chloroform, 0.149 (0.095), j ; in ethanol, 0.153 (0.13), k ; solid.

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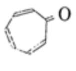
8) R. N. Jones and C. Sandorfy, "Chemical Application of Spectroscopy", Ed. by W. West, Interscience, New York (1956), p. 443.

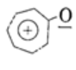
9) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **82**, 1876 (1960).

10) W. G. Fateley, B. Curnutte and E. R. Lippincott, *J. Chem. Phys.*, **26**, 1471 (1957).

and others[11] assumed that the strong absorption at 1540～1470 cm^{-1} in associated 4-hydroxy-2, 3-benzotropone is that of the C=O bond, and the same treatment was also made regarding to the band at 1465 cm^{-1} in associated 4-hydroxytropone[1].

Solvation effect on C=O bond in tropone, as far as it appears in $\nu_{C=O}$, is similar to that on the carbonyl group in benzophenone, as clearly noticed in Fig. 2. The fact d) that the spectrum of liquid tropone is similar to that in a polar solvent, which generally has a strong effect on the C=O bond, means that tropone itself is strongly associated with the Ib type polar character. The polar character of tropone is distinctly seen in its large dipole moment (4.17 D)[12].


Ia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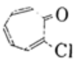
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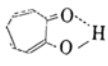
III

2-Chlorotropone.—Figure 3 shows the spectra obtained with 2-chlorotropone (II). In the same way as with tropone, the values of ν, $\Delta\nu/\nu_0$, ε^a, $(\Delta\nu)_{1/2}{}^a$, and r are summarized in Table II. The value of ν_0 was presumed from the frequencies in solutions, as it is not known in the vapor state. Plotting of the values of $\Delta\nu/\nu_0$ against those of $\nu_{C=O}$ in benzophenone, Fig. 4 is obtained. The tendency of spectral variation, as observed from these figures and table, is essentially the same as that of tropone, and the assignment of Bands I and II can be discussed by the coupling of $\nu_{C=O}$ and $\nu_{C=C}$ in the same way as in tropone. Further, the followings are clear from the comparison with tropone.

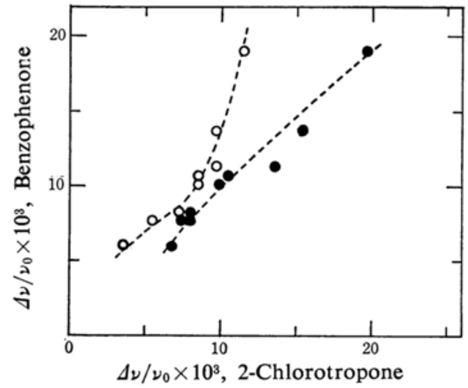

Fig. 4. Relation between the values of $\Delta\nu/\nu_0$ of Bands I and II in 2-chlorotropone and of $\nu_{C=O}$ in benzophenone in various solvents.
○ ; Band I, ● ; Band II

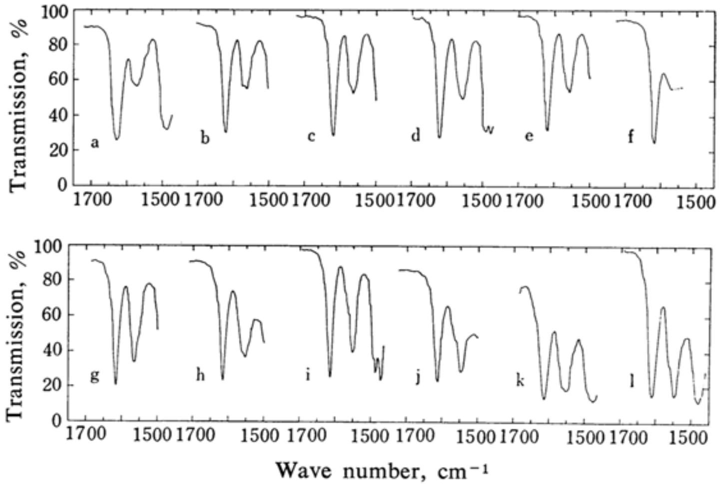

Fig. 5. Infrared spectra of tropolone in the states of vapor, liquid, solid, and in various solvents (1700～1500 cm^{-1} range) : a ; vapor, b ; in *n*-heptane, saturated (0.102 mm. thickness), c ; in diisopropyl ether, 0.172 mol./l. (0.095), d ; in carbon tetrachloride, 0.24 (0.12), e ; in 1-chlorobutane, 0.164 (0.095), f ; in carbon disulfide, 0.164 (0.102), g ; in dioxane, 0.164 (0.102), h ; in acetonitrile, 0.164 (0.102), i ; in chloroform, 0.176 (0.095), j ; in ethanol, 0.164 (0.102), k ; liquid, l ; solid.

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[11] G. L. Buchanan and J. K. Sutherland, *J. Chem. Soc.*, **1956**, 2620.

[12] Y. Kurita, S. Seto, T. Nozoe and M. Kubo, This Bulletin, **26**, 272 (1953).

e) The difference in wave number (27～39 cm^{-1}) in Bands I and II is much less than that in tropone (38～59 cm^{-1}).

f) Band I is stronger than II in non-polar solvents and Band I is weaker than II in polar solvents. The variation of relative intensity is noticeble.

The fact e) suggests that the carbonyl group in 2-chlorotropone is less affected by the external effects than that of tropone. Also, comparing the fact f) with Fig. 4, it is found, that the $\Delta\nu/\nu_0$ values of the two bands are close to each other when the intensities of Bands I and II are nearly equal, but the variation of $\Delta\nu/\nu_0$ is generally larger with a stronger band than with a weaker band. This may be indicated that the one with larger character of C=O stretching vibration shows more variation in wave number.

Tropolone.—In tropolone (III), the carbonyl group is fixed by a intramolecular hydrogen bond. So it is of interest to examine how the effects of solvents appear in the spectra. Figure 5 shows the spectra measured in various states and solvents, as well as in vapor state obtained earlier[4]. The various values obtained from Fig. 5 are shown in Table III, and the relative wave number shifts are given in Fig. 6.

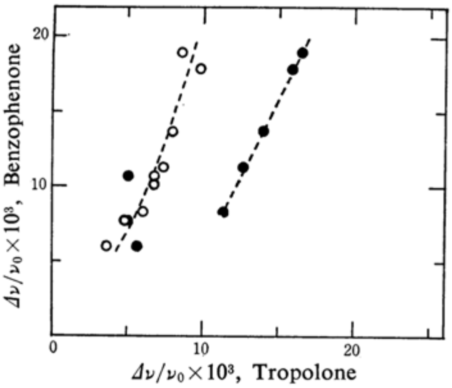

Fig. 6. Relation between the values of $\Delta\nu/\nu_0$ of Bands I and II in tropolone and of $\nu_{C=O}$ in benzophenone in various solvents.
○ ; Band I, ● ; Band II.

From these results the following features are found.

g) In accordance with the results on tropone, the direction of shift is the same for both of Bands I and II and the degree of shift of Band II is larger than that of Band I. However, the peak intensity of Band I is larger than that of II and Band II is broader.

h) The wave numbers of Bands I and II are smaller than those of tropone by 23～21 and 38～27 cm^{-1}, respectively.

i) The values of $\Delta\nu/\nu_0$ of Bands I and II in polar solvents are smaller than those of tropone, 2-chlorotropone, and $\nu_{C=O}$ of benzophenone.

j) ε^a of Band II does not show the tendency to decrease with the shift to the lower wave number side. As is noticed from the values of r, the variation of the intensity of Band II is less than that of tropone, though the values of intensity are not sufficiently reliable because of the absorption of the solvent itself and the broad absorption at around 1490 cm^{-1} due to a C–O–H group[13].

The variation of spectrum is thus the same in tendency as in the cases of tropone and 2-chlorotropone but is very small in its degree. This means that the C=O stretching absorption shifts to the lower side than that of tropone by 23～40 cm^{-1} by the effect of intramolecular hydrogen bond and that, by this hydrogen bond, the carbonyl group is affected little by the external actions at any state of measurement. This effect is comparatively large in polar solvents.

Summary

Infrared absorption spectra of tropone, 2-chlorotropone, and tropolone in the region of 1700～1500 cm^{-1} were measured in various states and in various solvents, and the variation of two strong Bands I and II in the region of 1700～1530 cm^{-1} was investigated. The data are shown in tables and figures. These two bands are explained as the participation of both of the C=O and C=C stretching vibrations in a tropone skeleton. The variation of the spectrum of tropolone with the measuring condition is much smaller than that of tropone. This is because the carbonyl group in tropolone is fixed by the intramolecular hydrogen bond.

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