Infrared Spectra of Troponoid Compounds. II. Absorption Band of O–H Stretching Vibration in Some Tropolones[*]

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In the previous report¹⁾, it was shown that the absorption bands assignable to O–H stretching vibration in tropolone (I) appear at around 3210 $\mathrm{cm^{-1}}$ in solid and around 3140 $\mathrm{cm^{-1}}$ in solution or gaseous state, indicating the characteristic properties in absorbing at a lower wave number in dilute solution or gaseous state than in solid. This fact has been explained¹⁻³⁾ on the basis of the intermolecular or intramolecular hydrogen bonding in tropolone, but the nature of these bands was not studied in detail. In this paper, the examinations were made on O–H stretching absorption bands of tropolone, by using a calcium fluoride prism, to see how the absorption bands changed with different concentrations and states. The same examinations were also made on 4-isopropyltropolone (hinokitiol) (II) and 3-bromotropolone (III).

Experimental

Infrared absorption spectra were measured with a Perkin-Elmer model 21 infrared spectrophotometer with a calcium fluoride prism. The solid spectra were obtained by potassium bromide disk or sandwich method, and a cell of 0.109, 0.508, 11.10 or 50.30 mm. thick with potassium chloride windows was used to obtain solution spectra.

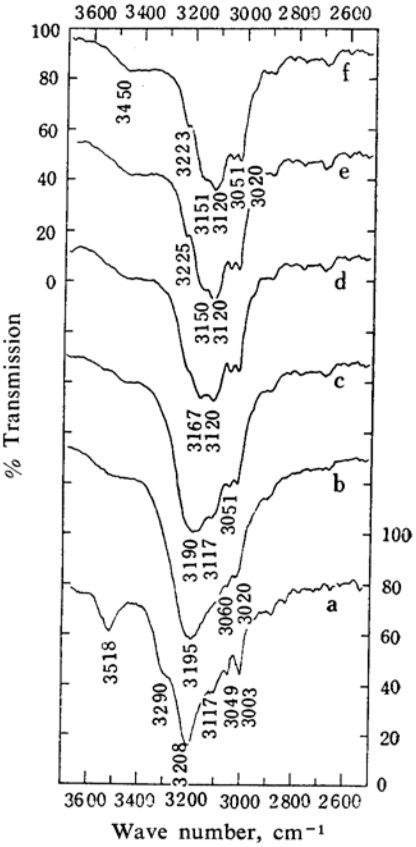

Fig. 1. Infrared spectra of tropolone in the states of solid, liquid and carbon tetrachloride solution (3600∼2600 $\mathrm{cm^{-1}}$ range): a; solid (crystalline film), b; liquid, c; ca. 1.5 mol./l. in $\mathrm{CCl_4}$ (0.109 mm. thickness), d; 0.29 (0.508), e; 0.014 (11.10), f; 0.0029 (50.30).

Results and Discussion

Fig. 1 shows the infrared spectra of tropolone in the region of 3600∼2600 $\mathrm{cm^{-1}}$, measured for solid, liquid and solution in carbon tetrachloride, and shows that there are more absorption bands in this region than had been expected. It also reveals the change in the spectrum accompanying variation of the concentration in solution and of the phase. The two bands in the ranges of 3051∼3049 and 3020∼3003 $\mathrm{cm^{-1}}$ in these spectra correspond to the C–H stretching vibration in the seven-membered ring, which appear with comparative regularity in many of the troponoids⁴⁾. Absorption bands other than these two must be those of O–H stretching vibration in respective states since corresponding bands do not appear in 2-deuteroxytropone⁵⁾ and metal tropolonate⁴⁾.

From the spectra shown in Fig. 1, the following characteristics can be pointed out. a) When measured in the most dilute solution shown in Fig. 1 f, there is no sharp absorption

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

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

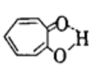
3) H. P. Koch, *J. Chem. Soc.*, **1951**, 512.

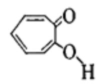
4) Y. Ikegami, unpublished data.

5) Y. Ikegami, This Bulletin, **34**, 94 (1961).

and there are bands at 3151 and 3223 cm^{-1} besides the strongest one at 3120 cm^{-1} and a broad band at 3500∼3300 cm^{-1}. b) The O–H stretching absorption is dependent of the concentration in solution, although it had been reported that the spectrum is independent$^{2)}$, and the bands at 3151 and 3223 cm^{-1} increase their intensity gradually with increasing concentration, which finally merge into the comparatively broad absorption at 3195 cm^{-1} in liquid. c) The spectrum in solid state exhibits shoulders at 3117 and 3290 cm^{-1}, besides the strongest band at 3208 cm^{-1}, and a distinct band at 3518 cm^{-1}. The spectrum obtained in gaseous state$^{1)}$ is the same as that of Fig. 1 f.

Such characters of the O–H stretching absorption band in dilute solution are not essentially different from those of chelated hydroxyquinones$^{6)}$ and enolized β-diketones$^{7)}$ possessing a conjugated chelate system, and can be taken as the characteristics indicating tropolone structure. It is seen from Fig. 1 that the absorption bands shift to the higher wave number side as the concentration increases and as the compound transits liquid or solid. On the other hand, the absorption band at 1618 cm^{-1} in solution appears at a wave number 5 cm^{-1} higher than that in solid$^{1)}$. This is contrary to the direction of the shift of $\nu_{C=O}$ anticipated from that of ν_{O-H} in the hydrogen bonding of $-O-H\cdots O=C<$ type, and then the shift of O–H stretching absorption band can not be explained merely by the strength of hydrogen bonding in this type. Considering the fact that the direction of the shift of C=O stretching absorption band in tropolone according to changes in the states agrees with that in tropone$^{1)}$, it is assumed that the cycloheptatrienone part in tropolones interacts in a manner similar to that in the case of tropone$^{8)}$ and the intramolecular hydrogen bonding is weakend by this interaction. Kuratani et al.$^{2)}$ assumed a dimer form for tropolone in the solid state. However, a wave number 3208 cm^{-1} in tropolone is approximately 700 cm^{-1} higher than that in


Ia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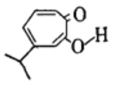
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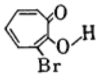
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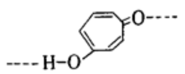
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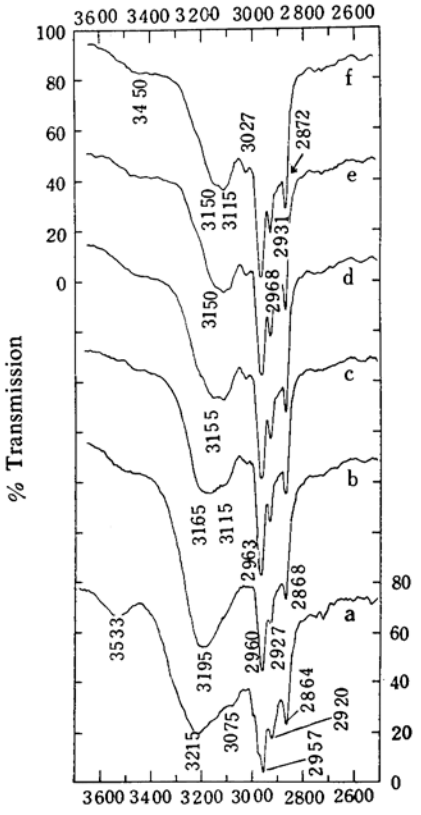

Fig. 2. Infrared spectra of 4-isopropyltropolone in the states of solid, liquid and carbon tetrachloride solution (3600∼2600 cm^{-1} range): a; solid (crystalline film), b; liquid, c; ca. 1.2 mol./l. in CCl_4 (0.109 mm. thickness), d; 0.29 (0.508), e; 0.014 (11.10), f; 0.0029 (50.30).

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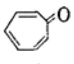
6) D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).

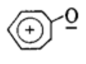
7) S. Bratoz, D. Hadzi and G. Rossmy, ibid., **52**, 464 (1956).

8) Unpublished data. Infrared spectra of tropone in the region of 1700∼1500 cm^{-1} were measured in the states of vapor, liquid and solutions in various solvents. Two strong absorption bands in this region indicated the following wave-numbers, e. g.

vapor	1651 cm^{-1}	1613 cm^{-1}
in *n*-heptane	1645 cm^{-1}	1602 cm^{-1}
in acetonitril	1634 cm^{-1}	1585 cm^{-1}
in ethanol	1633 cm^{-1}	1574 cm^{-1}
pure liquid	1634 cm^{-1}	1580 cm^{-1}.

Also the shape of their bands in liquid tropone is similar to that in such a solvent as acetonitril, differing from it in the vapor state (cf. Ref. 1). From these facts, it is assumed that the tropone in liquid state associates by its polar character of B type as also shown in its large dipole moment (4.17D) (cf. Y. Kurita, S. Seto, T. Nozoe and M. Kubo, This Bulletin, **26**, 272 (1953)).


A


B

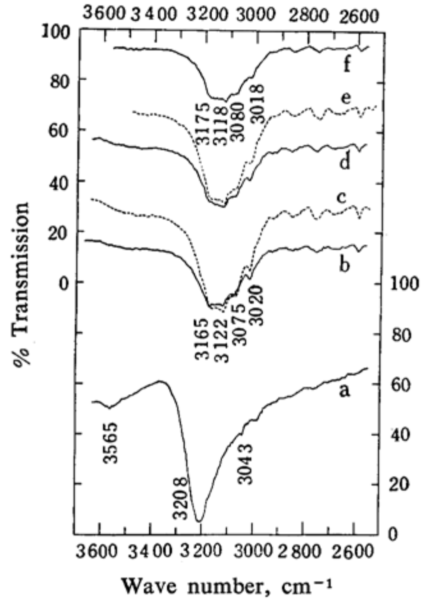


Fig. 3. Infrared spectra of 3-bromotropolone in the states of solid and carbon tetrachloride solution (3600∼2600 cm^{-1} range): a; solid (KBr disk), b; 0.1 mol./l. in CCl_4 (0.508 mm. thickness), c; 0.01 (11.10), d; 0.005 (11.10), e; 0.002 (50.30), f; 0.001 (50.30).

4-hydroxytropone[9,10] (IV) (ν_{O-H}; 2920 (w.) and 2530 cm^{-1} (v.s., broad)) and 3-hydroxytropone[11], which form a strong intermolecular hydrogen bond in solid and show the higher melting points and less volatilities than those of tropolone. Therefore, even though solid tropolone forms a dimer, it is not easy to explain why the hydrogen bonding in the dimer form is weaker than that in hydroxytropones. In addition, a distinct band at 3518 cm^{-1} in Fig. 1a indicates the existence of unchelated O–H group as Ib type.

The absorption spectra of 4-isopropyltropolone (II) and 3-bromotropolone (III) are respectively indicated in Figs. 2 and 3. The spectra in Fig. 2 are essentially the same, with the exception of the bands due to isopropyl group, as the spectra in Fig. 1. 3-Bromotropolone is sparingly soluble in carbon tetrachloride. Its spectra in higher concentrations have not been measured, but the mode of change in the form of absorption can be learned similarly. It is therefore possible to discuss the absorption of these compounds in the same manner as in the case of tropolone.

The characters of O–H absorption bands above-mentioned will generally be observed in compounds possessing the skeletal structure of tropolone[12], but those forming a strong intermolecular hydrogen bonding such as 4- and 5-hydroxytropolones[13] and those showing extremely low intensity such as 3, 7-dibromo- and 3, 5, 7-tribromo-tropolones[14] do not show the typical O–H absorption band of tropolones.

Summary

Infrared spectra of tropolone, 4-isopropyltropolone and 3-bromotropolone in the solid, liquid and solution in carbon tetrachloride were measured with a calcium fluoride prism in the region of 3600∼2600 cm^{-1}. The absorptions of O–H stretching vibration in these compounds in dilute solution are strongest at around 3120 cm^{-1} with numerous branches, and these bands shift gradually to the higher wave number side with 100∼88 cm^{-1}, as the concentration increases and the compound transits to the liquid or solid state. This character was explained by the assumption that the tropolone skeleton has a stable chelate system and that the intermolecular action increases with the increase of concentration. In the solid state, a distinct band corresponding to the O–H group of Ib type was also observed at around 3540 cm^{-1}.

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9) T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. & Ind.*, **1955**, 66; R. S. Coffey and A. W. Johnson, *J. Chem. Soc.*, **1958**, 1741.

10) Y. Ikegami, *J. Japan. Chem.* (*Kagaku-no-Ryoiki*), Extra No. 38, 46 (1959).

11) R. B. Johns, A. W. Johnson and M. Tisler, *J. Chem. Soc.*, **1954**, 4605.

12) Unpublished data. According to the results of spectral measurement made on about 40 kinds of tropolones, the O-H absorption bands appear in the region of 3260∼3160 cm^{-1} (s.) in the solid state, and in the region of 3225∼3095 cm^{-1} (m. or w.) in solution. Further, a very weak band generally appears in the region of 3640∼3500 cm^{-1} in the solid.

13) Y. Kitahara, *Sci. Repts. Tohoku Univ., Ser.* **I**, **39**, 258 (1956).

14) K. Ogura and Y. Ikegami, *Bull. Chem. Research Inst. Non-Aqueous Solutions, Tohoku Univ.*, **9**, 23 (1959); Ref. 10, p. 60.