Raman Spectrum of Hinokitiol (m-Isopropyltropolone)

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Introduction

In a previous paper[1] the Raman spectrum of tropolone in benzene solution was studied, and the more important vibrational frequencies there found were compared with infra-red and vapor ultra-violet absorption data[2], together with known facts about benzene, and the types of vibrational modes in the tropolone molecule having these frequencies were discussed qualitatively. Up to the present no complete theoretical calculation of normal vibrational modes of any cycloheptatriene derivatives has been attempted, preventing unambiguous interpretation of all the vibrational frequencies found in the Raman spectrum to be given. In this paper the Raman effect for hinokitiol was studied in order to obtain further experimental information regarding the characteristic frequencies common to " tropolonoid " molecules.

Experimental

The hinokitiol sample used in this experiment was prepared in the Medical Department of Kumamoto University, and was kindly placed at our disposal by Prof. K. Sebe. The sample was expected to be sufficiently pure, so no further purification was attempted. Five grams of the sample was dissolved in 20 cc. of pure benzene, and with this solution a Wood's tube of 1 cm. bore and 15 cm. length was filled. The Wood's tube has an outer jacket through which a saturated solution of sodium nitrite was circulated to cut off ultra-violet radiations of wave-lengths below 4047Å completely, and the Hg 4047Å line partially.

Filtering the mercury radiations with sodium nitrite solution appeared to help suppress photochemical coloring of hinokitiol markedly. However, after a prolonged irradiation with two quartz mercury lamps, burning at 10 amp. each, the sample ultimately turned red-brown as in the case of tropolone, and the effective time of exposure must have been much shorter than the twenty hours' used in the experiment.

The spectrograph employed had two dense flint glass prisms each of 13 cm. height and 22 cm. side length. The camera lens was of 60 cm. focal length, giving an effective aperture of F/5 and a linear dispersion of about 20Å/mm. at 4359Å. Kodak " Plus X " panchromatic film was used to record the scattered spectrum. The microphotometer trace of the spectrum is reproduced in Fig. 1, together with those of tropolone and the solvent (benzene). The Raman lines due to benzene are marked with arrows. The original

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[1] S. Imanishi and M. Ito, This Bulletin, 28, 75 (1955).

[2] S. Imanishi and M. Ito, to appear in *J. Chem. Phys.*, 1956.

traces were made with a recording microphotometer supplied by the former Institute of Physical and Chemical Research, Tokyo. It is seen in this figure that in the hinokitiol spectrum the long wave end is superposed by a strong background, making eye observation of weak Raman lines not easy. Wave-lengths of Raman lines were determined against those of Fe comparison lines. Their wave-number shifts from the exciting Hg line 4359Å, as well as estimates of their relative intensities, are given in Table I.

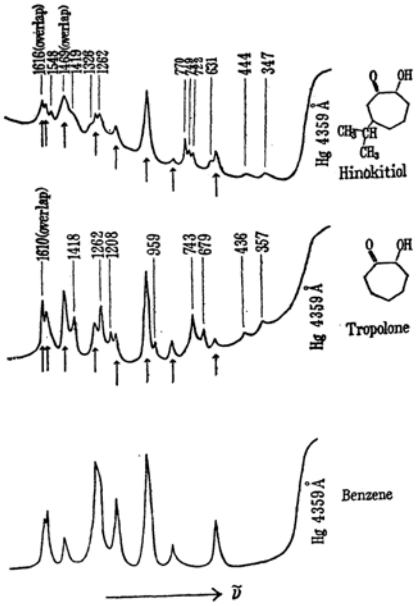

TABLE I

VIBRATIONAL FREQUENCIES IN HINOKITIOL (cm^{-1})

Hinokitiol Raman C_6H_6 Solution	Infra-red Absorption* Liquid	Tropolone[1] Raman C_6H_6 Solution
347 (2)		357 (2)
444 (1)		436 (1)
631 (2)		679 (2)
722 (2)	730 (m)	
749 (2)		
770 (3)	770 (w)	743 (3)
	820 (m)	
	890 (w) = 2×444	
	910 (w)	
	940 (m)	959 (1)
	990 (w) = 347+631	
	1050 (w) = 347+722	
	1100 (w) = 347+749	
		1208 (2)
1264 (4)	1250 (s)	1262 (4)
1326 (3)	1350 (w)	
1419 (4)	1410 (m)	1418 (5)
1469 (5)	1470 (s)	
1548 (4)	1560 (m)	
1616 (5)	1600 (s)	1610 (5)

* The frequencies and intensities in this column are those estimated from the published absorption curve of ref. (3).

Discussion

The only data pertaining to the vibrational spectrum of hinokitiol so far published and available for comparison are those we owe to Shimanouchi et al[3] which deal with the infra-red absorption. Approximate positions and relative intensities of absorption maxima observed by these authors are listed in column 2 of Table I. In the Raman spectrum of hinokitiol three new bands are found in the low frequency region below 650 cm^{-1}, which were not found infra-red absorption. In the high frequency region above 1200 cm^{-1} agreement with infra-red data is very good. As any Raman frequency associated with a considerable intensity must be regarded as a fundamental, all of the twelve Raman shifts given in the Table are here taken as such. On the basis of this assumption, in fact, many of the weak maxima measured in the infra-red in the intermediate frequency region can be interpreted as overtones and combinations as indicated in the Table.

The two low frequencies 357 cm^{-1} (2) and 436 cm^{-1} (1) in tropolone (Table I) are preserved in hinokitiol [347 cm^{-1} (2) and 447 cm^{-1} (1)], almost unaffected by the substitution with the isopropyl group. From their magnitudes these frequencies are very probably of out-plane torsional vibrations of the tropolone ring. The strong Raman shifts of 1262, 1419 and 1616 cm^{-1} in hinokitiol coincide exactly with the 1262, 1418 and 1610 cm^{-1} shifts in tropolone, allowing for errors in measurement. As absorption bands of almost the same frequencies as these three are invariably found in infrared absorption of many tropolone derivatives it is apparent that these also belong to vibrations characteristic of the tropolone skeleton. Among them the strongest 1616 cm^{-1} is attributed to the C=O stretching vibration[4], although the value is considerably lowered from that of the ordinary C=O frequency ($\gtrsim$1700 cm^{-1}). On the other hand the frequencies between 1262 and 1548 cm^{-1}, which are considered to be of C—C stretching vibrations of the ring, are as a whole higher than the corresponding frequencies in benzene compounds. These facts support Koch's[5] view that in molecules with the heptatriene ring C=O bond forces are weaker and C—C bond forces are stronger than those in benzenoids. These changes in bond forces may have been

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

[4] Scot and Tarbel, *J. Am. Chem. Soc.*, **72**, 240 (1950). Doering and Knox, ibid., **73**, 828 (1951).

[5] Koch, ibid., **73**, 512 (1951); Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London (1954), p. 75.

caused on the one hand by resonance, or what amounts to the same thing, by the electron migration from the carbonyl O atom into the ring, and on the other by the formation of intramolecular hydrogen bonding between the two O atoms of the tropolone molecule. Furthermore these facts seem to suggest that the heptatriene ring in tropolone owes its stability to the attachment of the carbonyl group.

The comparatively strongly observed Raman shift 770 cm^{-1} corresponds to the strong 743 cm^{-1} in tropolone. This frequency is also found in infra-red absorption, but there it was found as a shoulder to the strong absorption peak at 730 cm^{-1}. By analogy with tropolone the vibrational mode with this frequency is assumed to be the totally symmetric breathing vibration of the molecule, to which in-plane ring deformation contributes considerably. This conclusion is supported by the hinokitiol vapor ultra-violet absorption(6), in which three strong and board bands form a progression with $\sim$600 cm^{-1} interval, starting from the O, O band on its shorter wave side. Then this $\sim$600 cm^{-1} frequency must represent the excited (electonic) state value of the 770 cm^{-1} fundamental of the ground state. In tropolone the excited state value of the corresponding 743 cm^{-1} breathing vibration is 643 cm^{-1}. Apart from the above evidence from ultra-violet absorption, we have calculated the two totally symmetric vibration frequencies of the cycloheptatrienyl (tropylium) ion $(CH)_7^+$ with D_{7h} symmetry, using force constants borrowed from benzene, in order to check the magnitudes of these vibration frequencies in a seven-membered ring compound. They came out to be 863 cm^{-1} (C and H in phase) and 3038 cm^{-1} (C and H in reversed phase), showing that the in-plane breathing frequency is considerably lowered from 992 cm^{-1} in benzene (D_{6h}). These vibrations should be strictly infra-red inactive and the most Raman-active. In fact, in the infra-red data reported by Doering and Knox(7) there is no absorption near the calculated 863 cm^{-1} region, just as expected.

Now, it can be seen in analogy with benzenoids that this type of vibration will gain intensity in infra-red absorption with still lowered frequency by the substitution of H atoms with heavy radicals as in tropolonoids, with the consequent loss of the D_{7h} symmetry. These arguments also support our assignment regarding the breathing vibrations in tropolone and hinokitiol, and make understandable their intensity relation in infra-red and Raman spectra.

The ramaining Raman frequencies 722 and 749 cm^{-1} in hinokitiol have no corresponding shifts in tropolone, so that they may be attributed to internal vibrations of the isopropyl radical.

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6) S. Imanishi and M. Ito, Orally communicated to the Chem. Soc. Japan Meetings, 1952.

7) Doering and Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).