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## 24. Naofumi Ōi: The Infrared Characteristic Absorption Bands of Mono- and Di-substituted Anthraquinones in the Region of 650~900 cm<sup>-1</sup>.

(Research Department, Osaka Works, Sumitomo Chemical Company\*)

Generally speaking, aromatic compounds show strong characteristic absorption bands in the region of 650~900 cm<sup>-1</sup>, originating in the out-of-plane deformation vibration of the ring hydrogen. In the case of substituted benzenes, an extensive investigation has been made, and it has been shown that the principal factor determining their frequencies is the number of free hydrogen atoms in the ring which are adjacent to one another.<sup>1)</sup> However, in the case of substituted anthraquinones the data are not available.

Anthraquinone derivatives are very useful substances as an intermediate of various dyes, but they are mostly not pure and contain their isomers. It is very difficult to analyse such a mixture by means of usual chemical methods.

The purpose of the present paper is to establish the correlation between the position of mono- and di-substituents in anthraquinone ring and characteristic absorption frequencies in the region of 650~900 cm<sup>-1</sup> for use in the analysis.

The infrared spectra of 10 monosubstituted anthraquinones and 23 disubstituted anthraquinones were determined under the same conditions, and the characteristic absorption bands in the region of 650~900 cm<sup>-1</sup> could be correlated respectively with their structures.

### I. Monosubstituted Anthraquinones

The position and intensity of characteristic absorption bands of 10 monosubstituted anthraquinones are shown in Fig. 1.

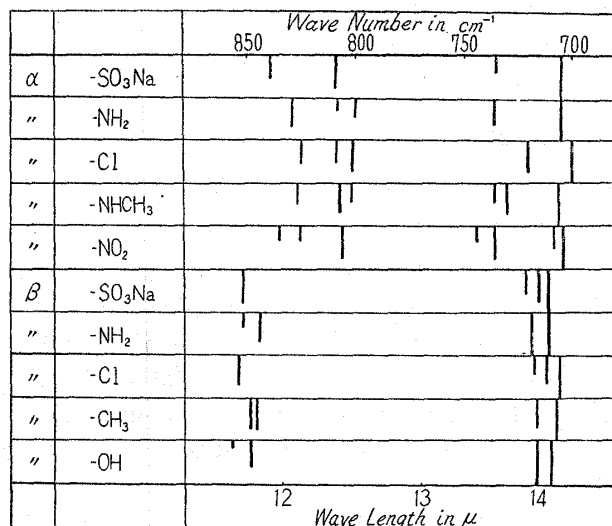


Fig. 1. Position and Intensity of the Absorption Bands of Monosubstituted Anthraquinones (650~900 cm<sup>-1</sup>)

(i) 1-Substituted Anthraquinones: Five standard substances were measured and they showed characteristic absorption bands at 820~840 cm<sup>-1</sup>, 800~810 cm<sup>-1</sup>, 730~740 cm<sup>-1</sup>, and 700~710 cm<sup>-1</sup>. All the bands near 700 cm<sup>-1</sup> were of large intensity and small dispersion, but 2-substituents also have strong absorption bands in this position. Therefore in the analysis of 1-substituted anthraquinones, the characteristic bands at 800~810 cm<sup>-1</sup> or 730~740 cm<sup>-1</sup> are available.

(ii) 2-Substituted Anthraquinones: Five standard substances were measured and

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1) N. B. Colthup: J. Opt. Soc. Amer., 40, 397(1950).

they showed coincident characteristic absorption bands at  $840\sim 860\text{ cm}^{-1}$  and  $700\sim 720\text{ cm}^{-1}$ . They are both available for use in the analysis and it is noted that the bands of  $700\sim 720\text{ cm}^{-1}$  are not a singlet but a strong doublet or triplet.

## II. Disubstituted Anthraquinones

In Fig. 2, the position and intensity of characteristic absorption bands of 23 disubstituted anthraquinones in the region of  $650\sim 900\text{ cm}^{-1}$  are shown.

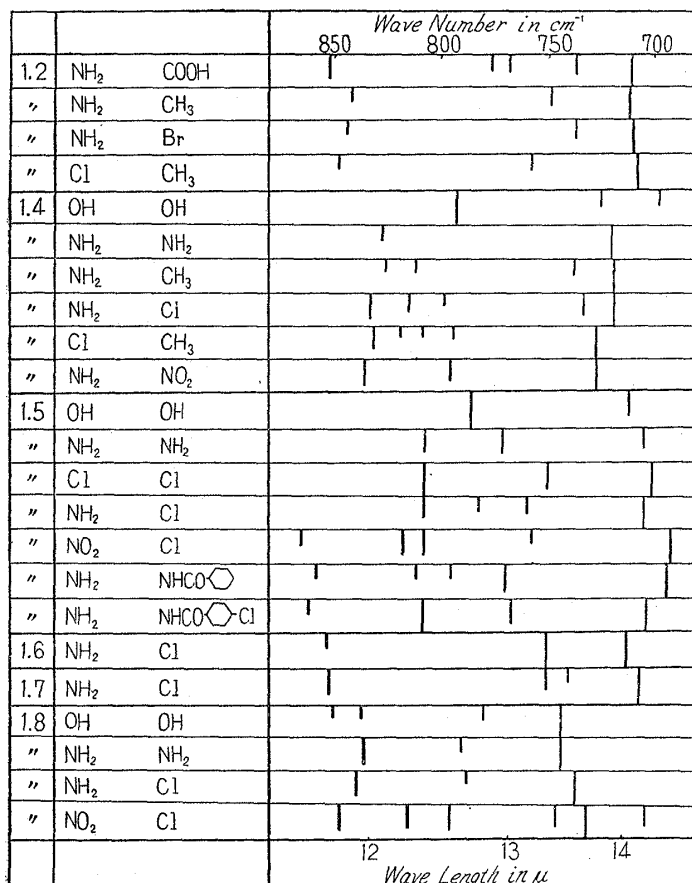


Fig. 2. Position and Intensity of Absorption Bands of Disubstituted Anthraquinones ( $650\sim 900\text{ cm}^{-1}$ )

(i) 1,2-Substituted Anthraquinones : Four standard substances were measured and they showed characteristic absorption bands at  $840\sim 850\text{ cm}^{-1}$  and  $700\sim 710\text{ cm}^{-1}$ .

(ii) 1,4-Substituted Anthraquinones : Six standard substances were measured and they showed characteristic absorption bands at  $820\sim 840\text{ cm}^{-1}$  and  $720\sim 730\text{ cm}^{-1}$ . The position of bands in the region of  $720\sim 730\text{ cm}^{-1}$  have small deviation and they are available for use in the analysis. However, dihydroxy compound is an exception to the regularity.

(iii) 1,5-Substituted Anthraquinones : Seven standard substances were measured and they showed coincident characteristic absorption bands at  $800\sim 820\text{ cm}^{-1}$  and  $690\sim 710\text{ cm}^{-1}$ , and they are both available for use in the analysis. However, it is noteworthy that dihydroxy compound has no absorption band near  $810\text{ cm}^{-1}$ . The reason of such specificity at 1,4- and 1,5-dihydroxy substituents is not clear. It may be due to the fact that the two hydroxyl groups form intramolecular hydrogen bonds with two carbonyl groups of the anthraquinone ring and the  $\pi$ -electron system in the molecule is affected strongly.

(iv) 1,8-Substituted Anthraquinones : Four standard substances were measured and they showed characteristic absorption bands at  $830\sim 850\text{ cm}^{-1}$  and  $730\sim 750\text{ cm}^{-1}$ , and they are both available for use in the analysis.

In this series, the dihydroxy compound is not an exception to the regularity, and it is assumed to be due to the fact that only one carbonyl group of anthraquinone ring forms a hydrogen bond with the hydroxyl group.

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### Experimental

The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer, using a sodium chloride prism. The spectra of all substances were obtained as mulls in mineral oil.

Most of the compounds studied were either commercially available or were supplied by members of this Research Department. These compounds were used without further purification unless doubt existed as to their purity. If purification was necessary, standard methods of recrystallization from suitable solvents and sublimation were used.

### Summary

The infrared spectra of 10 monosubstituted and 23 disubstituted anthraquinones were determined in the region of  $650\sim 900\text{ cm}^{-1}$ , and the strong characteristic absorption bands obtained were found to be correlated to their structures.

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## 5-2 25. Naofumi Ōi : The Infrared Characteristic Absorption Bands of Monosubstituted Naphthalenes in the Region of $1650\sim 2000\text{ cm}^{-1}$ .

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Normally, the spectral region of  $1650\sim 2000\text{ cm}^{-1}$  is not very interesting unless carbonyl groups or triple bonds are present, but this region has been used by Young, DuVall, and Wright<sup>1)</sup> for the characterization of substituted benzene compounds, and its usefulness in the analysis has been confirmed by Bellamy.<sup>2)</sup> Whiffen<sup>3)</sup> presented evidence that the stronger infrared absorption bands from  $1650\sim 2000\text{ cm}^{-1}$  in benzene derivatives normally arise from summation tones of the out-of-plane CH bending vibrations.

In substituted naphthalene compounds, such investigation has not yet been shown, but it is well known that they have strong characteristic bands in the region of  $650\sim 900\text{ cm}^{-1}$  as in benzene ring originating in the out-of-plane deformation vibration of the ring hydrogen, so it is supposed that monosubstituted naphthalenes will show characteristic absorption bands in the region of  $1650\sim 2000\text{ cm}^{-1}$ .

As was expected, these substances showed strong characteristic absorption bands in this region and the pattern of these bands of ten monosubstituted naphthalenes is shown in Fig. 1. These patterns are more complex than monosubstituted benzenes, but it is known that these bands can be correlated with their structure.

\* Kasugade-cho, Konohana-ku, Osaka (大井尙文).

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2) L. J. Bellamy : "The Infrared Spectra of Complex Molecules," Methuen & Co., London (1954).

3) D. H. Whiffen : *Spectrochim. Acta*, **7**, 253(1955).