Absorption Spectra of Nitrobenzene Derivatives. I. Spectral Features of o-, m- and p-Isomers

By Kimio SEMBA*

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It is well known that molecules having electron attracting groups such as nitro, carbonyl and corboxyl groups exhibit intense absorption spectra in the near ultraviolet or visible region$^{1)}$. Recently, Nagakura and Tanaka$^{2)}$ presented a new theory (molecular energy level diagram method) based on the molecular orbital theory treating the electron migration between two π-electron systems. According to their theory, it is possible to interpret strong absorption bands of some aromatic nitro compounds in terms of the intramolecular charge transfer spectra.

The intramolecular charge transfer in nitrobenzene means the interaction of the highest occupied orbital of benzene (H_B) with the lowest vacant orbital of nitro group (V_S). In nitrobenzene derivatives there are appreciable interactions between the molecular orbitals of monosubstituted benzenes and those of the nitro groups$^{3)}$. Considering the energy values and symmetry properties of these orbitals, one sees that the interaction between the highest occupied orbital of the monosubstituted benzene and the lowest vacant orbital (anti-bonding π-orbital) of the nitro group is especially important.

The molecular energy-level diagrams of benzene, aniline and nitromethane$^{2)}$ are shown in Fig. 1. The intramolecular charge transfer transition may occur as a result of interactions between two split orbitals (H_{x1} and H_{x2}) in aniline and the lowest vacant orbital V_s of the nitro group. These transitions are generally accompanied by a large electronic transfer and have been designated as intramolecular charge transfer transition$^{2)}$.

According to Nagakura and Tanaka's theory, there is no interaction between H_{x2} and V_s, and only one transition due to the H_{x1} and V_s interaction can be observed for a *p*-isomer. On the other hand, in *o*- and *m*-isomers the

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* Present address: Research Laboratory, Kurosaki Firebrick Mfg. Co., 535, Fujita, Yawata.

1) L. Dede and A. Rosenberg, *Ber.*, **67**, 147 (1934); W. D. Kumler, *J. Am. Chem. Soc.*, **68**, 1184 (1946).

2) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, ibid., **23**, 1441 (1955).

3) J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1200 (1957).

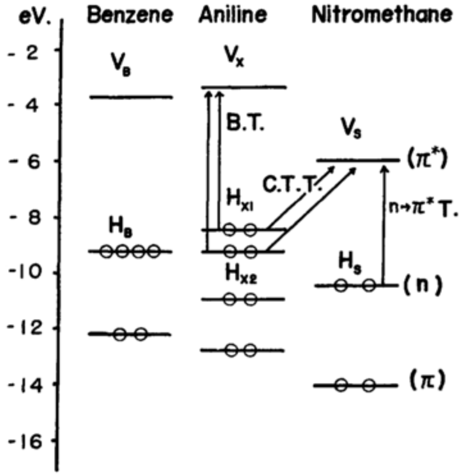

Fig. 1. Molecular energy level diagrams of benzene, aniline and nitromethane.

two orbital H_{x1} and H_{x2} can interact with V_s, and two transfer transitions of the charge transfer type may be expected for these isomers.

In this paper the intramolecular charge transfer spectra (250~400 mμ) of *o*-, *m*- and *p*-nitrophenol, -nitroanisole, -nitroaniline and -nitro-*N*-dimethylaniline are measured in *n*-hexane, and their spectral features together with the effect of substituents on them are discussed according to Nagakura and Tanaka's theory.

The migration effects of electron donating groups on absorption spectra of *o*-, *m*- and *p*-nitroaniline are considered in aqueous and hydrochloric acidic solutions and the existence of simple equilibria between these isomers and protons is indicated.

Experimental

Absorption spectra were recorded by a Hitachi automatic recording spectrophotometer type EPS-2, using quartz cells of 1 cm. in path length. Infrared spectra were obtained by another Hitachi double beam infrared spectrophotometer type EPI-2 with 0.1 mm. rock salt cells.

Solvents, *n*-hexane, methanol, ethanol, chloroform and ethyl ether, were purified by the method recommended by Weissberger and Proskauer[4].

o-, *m*- and *p*-Nitrophenol, -nitroanisole and -nitroaniline of Tokyo Chemical Industry Co. special grade were used. *m*- and *p*-Nitro-*N*-dimethylaniline were synthesized according to Fich's method[5] by nitration of *N*-dimethylaniline, and were recrystallized several times from ethanol and benzene, respectively. These samples were thought to be pure enough and no further purification was carried out.

Results and Discussion

Spectral Features of *o*-, *m*- and *p*-Isomers.— Absorption maxima of the nitrobenzene derivatives in *n*-hexane are collected in Table I.

TABLE I. ABSORPTION MAXIMA OF NITROBENZENE DERIVATIVES IN *n*-HEXANE

Molecule	Absorption maxima, mμ			
o-Derivatives				
Nitrophenol	212.6	—	271.0*	347.0*
Nitroanisole	214.5	—	251.2*	307.5*
Nitroaniline	229.0	244.0	269.0*	376.0*
m-Derivatives				
Nitrophenol	222.4	—	258.0*	312.0*
Nitroanisole	225.2	—	261.7*	320.4*
Nitroaniline	229.0	249.0	266.0*	344.0*
Nitro-*N*-dimethylaniline	—	248.0	—	382.5*
p-Derivatives				
Nitrophenol	224.3	—	285.0*	334.0**
Nitroanisole	225.8	—	293.0*	—
Nitroaniline	226.0	—	320.0*	—
Nitro-*N*-dimethylaniline	—	—	348.0*	—

* Intramolecular charge transfer bands.

** Band due to $n \to \pi^*$ transition.

It is noted from Table I and Fig. 2 (the absorption spectra of *o*-, *m*- and *p*-nitroaniline) that the spectra of *o*- and *m*-nitrobenzene derivatives resemble each other in the point that they show two kinds of absorption bands in the ultraviolet and visible regions, one at 260 mμ and the other at 350~380 mμ. On the other hand, the *p*-isomer spectrum is quite different from those of the other isomers, except for the band at 220 mμ.

These spectral characteristics have already been pointed out by Kumler[1], and were interpreted on the basis of the "electron oscillation" theory proposed by Lewis and Calvin[6]. However, Kumler's interpretation must be reconsidered from the standpoint of recent theories.

From the positions and intensities of these absorption bands we may assign the bands at 260 and 350~380 mμ for the *o*- and *m*-isomers and the band at 300 mμ for the *p*-isomer to the intramolecular charge transfer transitions in these molecules. Thus we have two intramolecular charge transfer bands for *o*- and *m*-isomers and only one for the *p*-isomer (Table I). These characteristic features of the intramolecular charge transfer spectra for the three isomers of nitrobenzene derivatives have been well explained by the molecular orbital theories cited above[3].

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4) A. Weissberger and E. S. Proskauer, "Organic Solvent", Interscience Publishers, Inc., New York (1955).

5) H. M. Fich, "Organic Syntheses", Vol. 27, p. 62.

6) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

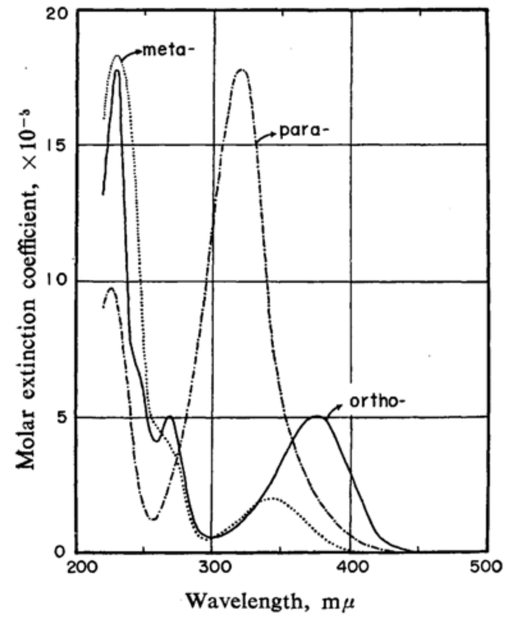

Fig. 2. Absorption spectra of *o*-, *m*- and *p*-nitroaniline, all in *n*-hexane.

The intramolecular charge transfer spectrum of *p*-nitroaniline is much stronger ($\varepsilon \sim 10000$) than those of the *o*- and *m*-nitroaniline (Fig. 2). The coefficient* of the AO at the para-position in the H_{x1}-MO of a monosubstituted benzene (aniline) is greater than those of ortho- and meta-AO's, giving rise to stronger absorption for the *p*-isomer than for other isomers[3]. The intensities of the bands at 260 mμ for the *o*- and *m*-isomers are nearly equal ($\varepsilon \sim 5000$) and the longer wavelength band at 350∼380 mμ for the *o*-isomer is stronger than the band of the *m*-isomer. The same relations among intensities of the intramolecular charge transfer bands can also be observed for the spectra of other nitrobenzene derivatives studied in this paper.

Absorption bands of *o*-nitrophenol and *o*-nitroaniline, due to transitions of the same type appear at longer wavelengths than those of the *m*-isomers. On the other hand, the bands of *m*-nitroanisole appear at longer wavelengths than those of the *o*-isomer. These facts may be explained in terms of intramolecular hydrogen bondings[3] which can be formed in these ortho compounds as shown in Fig. 3. The formations of these intramolecular hydrogen bondings are evident from infrared absorptions as shown in Figs. 4 and 5. The OH group in *o*-nitrophenol shows a very broad infrared absorption band at 3200 cm⁻¹, and the NH_2 group in *o*-nitroaniline shows less broad absorptions at 3510 and 3380 cm⁻¹. On the addition of ethyl ether the former does not shift but the latter groups shift to longer wavelengths. These facts indicate that in *o*-nitrophenol intramolecular hydrogen bonding

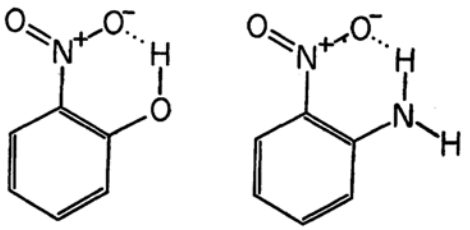

Fig. 3. Intramolecular hydrogen bondings in *o*-nitrophenol and *o*-nitroaniline.

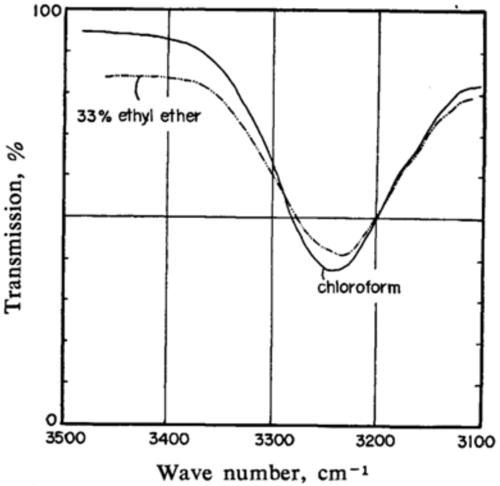

Fig. 4. Infrared absorption of *o*-nitrophenol in chloroform.

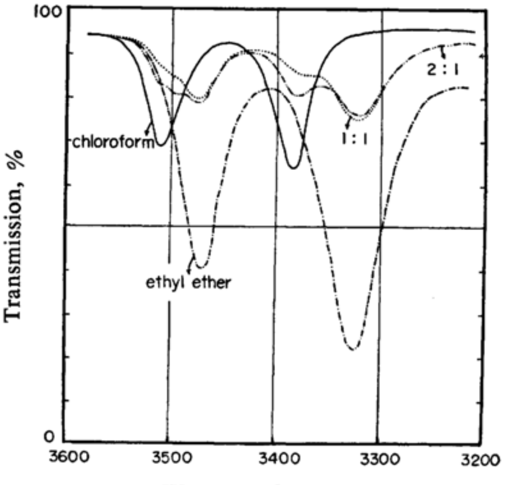

Fig. 5. Infrared absorption of *o*-nitroaniline in chloroform (-·-·- 33% ethyl ether, ······ 50% ethyl ether).

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* See ref. 3.

is too strong to allow an intermolecular hydrogen bonding between the solute and ethyl ether molecules but in *o*-nitroaniline the intermolecular hydrogen bonding is formed to a large extent, as shown in Fig. 6.

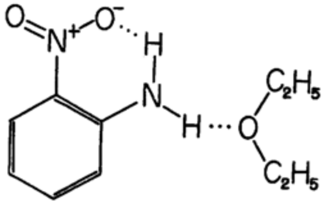

Fig. 6. Intermolecular hydrogen bonding between *o*-nitroaniline and ethyl ether.

The band at 220 mμ in the spectra of *o*-, *m*- and *p*-isomers may be associated with the transition of another charge transfer type[7]. Absorption shoulders are observed at 240～250 mμ for *o*- and *m*-nitroaniline (Table I).

Effect of Substituents on Absorption Spectra. —Next we shall study the effect of electron donating groups on the absorption spectra in nitrobenzene derivatives. Usually this effect is divided into resonance and inductive effects. In the present case only the resonance effect is of interest, and so we neglect the inductive effect.

According to the perturbation theory the resonance effect is associated with the transfer of an electron from a π-orbital of the substituent into a vacant orbital of the conjugated system. The effect of the substituents on absorption spectra of benzene derivatives has been explained in terms of the relative stabilization of the ground and excited states[8]. The stabilization energies of these states are closely connected with electron migration from the substituents into the ring, and as generally the stabilization is much greater in the excited state, red shifts of absorption bands are expected with the increasing electron migration.

As seen from Table I, the absorption bands of the *m*- and *p*-isomers shift to the longer wavelengths in the order of OH, OCH_3, NH_2 and $N(CH_3)_2$ groups. These spectral shifts are very similar to those of monosubstituted benzene derivatives. However, the shifts for *o*-isomers are of somewhat different nature on account of ortho-effects involving effects of intramolecular hydrogen bonding and of steric hindrance.

On comparing nitrophenol with nitroaniline the ionization energy of the NH_2 group is much smaller than that of the OH group[9], leading to a much larger electron migration from the NH_2 group than from the OH group. Consequently nitroaniline shows a red shift of absorption maximum as compared with nitrophenol. The same type of shifts has been observed for monosubstituted benzenes, phenol and aniline, the latter showing the absorption at the longer wavelength.

On the other hand, we find the absorption maximum of nitrophenol on the blue side of the nitroanisole maximum. Matsen et al.[10] found that the O–O band of phenol is at a longer wavelength than that of anisole and from this they concluded that the resonance of the OH group with the benzene ring is much stronger than that of an alkoxy group (OCH_3 or OC_2H_5). However, from our result we can assume that the electron migration from the OCH_3 group is greater than that from the OH group because of the hyperconjugation effect of the CH_3 group. The same consideration may be taken for the NH_2 and $N(CH_3)_2$ groups, as the absorption maximum of nitro-*N*-dimethylaniline appears at the longer wevelength than that of nitroaniline.

Effect of Electron Migration on Absorption Spectra. — As mentioned above, the shifts of intramolecular charge transfer spectra are very much influenced by the amount of electron migration from electron donating substituents into the benzene ring. For the sake of simplicity we limited our consideration to the case of nitroaniline in aqueous or hydrochloric acidic solution.

The amount of electron migration from the NH_2 group of nitroaniline will decrease by addition of hydrochloric acid to the aqueous solution, since the lone pair electrons of the N-atom in the NH_2 group will be fixed by a proton according to the following scheme

$$-NH_2+H^+ \rightleftharpoons -NH_3^+$$

and the electron migration into the ring will be arrested. Then the absorption spectrum of nitroaniline will resemble that of nitrobenzene.

This expectation is satisfactorily supported by the experimental results as shown in Figs. 7, 8 and 9. The absorption spectra of *o*-, *m*- and *p*-nitroaniline in aqueous solutions approach to that of nitrobenzene with the increasing concentration of hydrochloric acid, and finally they all become the same as the spectrum of nitrobenzene with respect to absorption intensities and wavelengths.

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[7] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1114 (1958).

[8] K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947); W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5252 (1950); H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 72 (1951); M. Tuboi, This Bulletin, **25**, 369 (1952); K. Semba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 333, 338 (1956).

[9] W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

[10] W. W. Robertson, A. J. Seriff and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 1539 (1950).

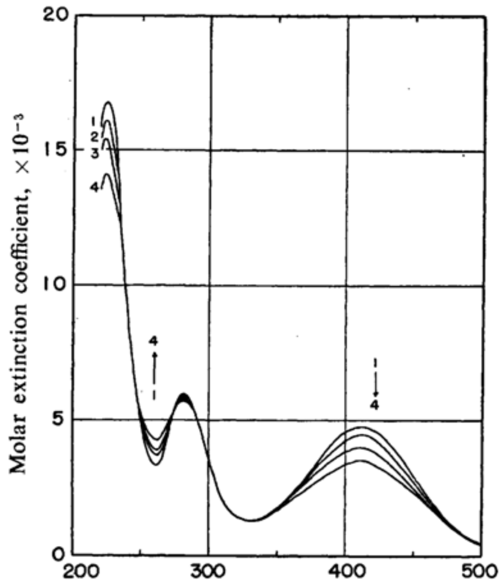


Fig. 7. Absorption spectra of *o*-nitroaniline (4.18×10^{-5} mol./l.) in water in the presence of hydrochloric acid, at 29°C.
Curve 1: aqueous solution.
Curve 2: concentration of hydrochloric acid 9.16×10^{-2} mol./l.
Curve 3: 2.75×10^{-1} mol./l.
Curve 4: 4.58×10^{-1} mol./l.

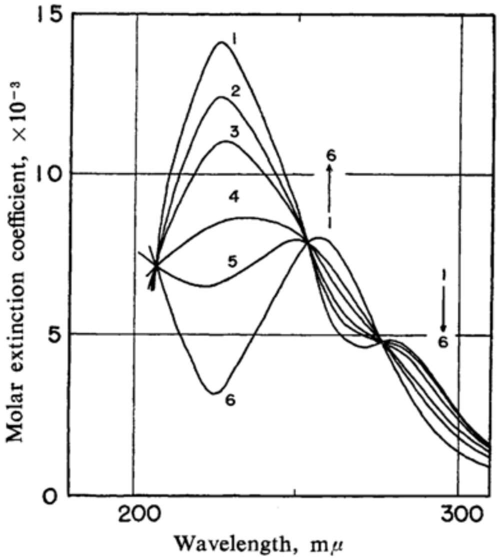


Fig. 8. Absorption spectra of *m*-nitroaniline (5.78×10^{-5} mol./l.) in water in the presence of hydrochloric acid, at 29.5°C.
Curve 1: aqueous solution.
Curve 2: concentration of hydrochloric acid 9.16×10^{-4} mol./l.
Curve 3: 1.83×10^{-3} mol./l.
Curve 4: 4.58×10^{-2} mol./l.
Curve 5: 9.16×10^{-2} mol./l.
Curve 6: 4.58×10^{-1} mol./l.

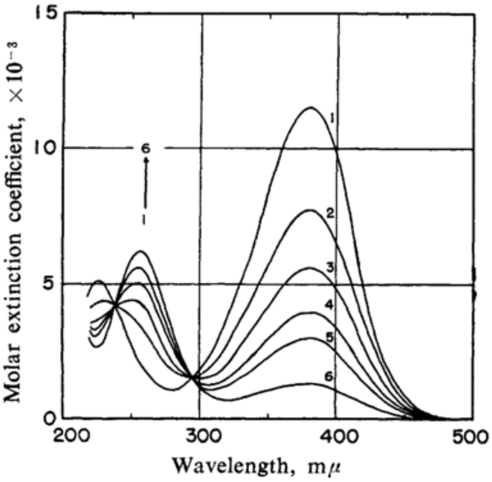
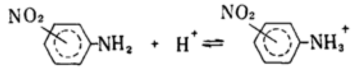


Fig. 9. Absorption spectra of *p*-nitroaniline (1.02×10^{-4} mol./l.) in water in the presence of hydrochloric acid, at 26°C.
Curve 1: aqueous solution.
Curve 2: concentration of hydrochloric acid 4.58×10^{-2} mol./l.
Curve 3: 9.16×10^{-2} mol./l.
Curve 4: 1.83×10^{-1} mol./l.
Curve 5: 2.75×10^{-1} mol./l.
Curve 6: 6.41×10^{-1} mol./l.

Isosbestic points observed for the spectra of all the isomers can be explained by assuming the following equilibrium

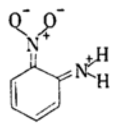


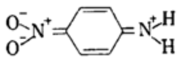
From the experimental results the equilibrium constants and differences of free energy are evaluated, as listed in Table II.

TABLE II. EQUILIBRIUM CONSTANTS AND FREE ENRGY DIFFERENCES FOR *o*-, *m*- AND *p*-NITROANILINE

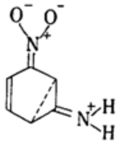
Molecule	Equilibrium constant	Free enrgy difference kcal./mol.
o-Nitroaniline	3.5	−0.75 (at 29°C)
m-Nitroaniline	200	−3.3 (at 29.5°C)
p-Nitroaniline	10.8	−1.4 (at 26°C)

The equilibrium constant for the *m*-isomer is much larger than those for other isomers, and the *m*-isomer requires a very small amount of hydrochloric acid to reach equilibrium. This may be due to the meta-directing property of the NO_2 group. The meta-position is more negative compared with other positions as the NO_2 group has the meta-directing power, and the proton affinity of the N-atom in the *m*-isomer is large (formation of *m*-nitroanilinium ion). The same conclusion may be reached from the viewpoint of the resonance theory. In the *o*- and *p*-isomers the *o*- and *p*-quinoid structures





contribute largely, while in the *m*-isomer the contribution of the *m*-quinoid structure



is expected to be small. From this fact we may conclude that the electron migrations from the NH_2 group in the *o*- or the *p*-isomer are large, and that in the *m*-isomer a proton may easily be bonded to the N-atom.

The small value of the equilibrium constant for the *o*-isomer is probably due to steric hindrance.

$n\rightarrow\pi^*$ Transition— The absorption band of nitrobenzene due to the $n\rightarrow\pi^*$ electronic transition was observed by Wolf and Herold[11] and by Wenzel[12]. The absorption due to the $n\rightarrow\pi^*$ transition is characterized by its weak intensity and so can not be observed if a strong absorption band lies in the same wavelength region.

In the present work the absorption shoulder with the molar extinction coefficient of about 1000 is observed for *p*-nitrophenol at about 334 mμ. Although this absorption shoulder shifts to the longer wavelengths, in methanol, ethanol and water, it may be assigned to the $n\rightarrow\pi^*$ transition owing to its weakness of intensity. However, we could not observed this weak band in detail owing to the disturbance of the strong intramolecular charge transfer band which overlaps the weak band.

Summary

The intramolecular charge transfer spectra of some nitrobenzene derivatives were measured in *n*-hexane. The general features of the absorption spectra and the effect of substituents on the absorption spectra were considered from the concept of the intramolecular charge transfer. The migration effect of electron donating groups was discussed for the nitroaniline in aqueous and hydrochloric acidic solutions. Also other absorption due to the $n\rightarrow\pi^*$ transition of nitro group was considered.

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Department of Chemistry
Faculty of Science
Kyushu University
Hakozaki, Fukuoka

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