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Infrared Absorption Intensities of Out-of-plane CH Bending Vibrations of Substituted Benzenes. IV. Solvent Effect on the Intensities of the Bands of Aniline

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The infrared absorption intensities of out-of-plane CH bending and ring out-of-plane deformation vibrations of aniline have been measured in an acetone solvent mixed with various quantities of acetic acid. When such solvents are used, new peaks attributable to aniline interacting with the acid appear as shoulders of each of the original bands. A marked decrease in the sums of the intensities of the above two modes (A_0) has been observed for the bands of aniline interacting with the acid. It is demonstrated that the degree of such a decrease in intensity depends on the molar ratios of aniline and the acid. When there exists enough the acid in comparison with aniline, the values of A_0 become minimum. On the other hand, when the numbers of the exsiting acetic acid molecules are much smaller than those of aniline, the values of A_0 are considerably greater than those in the former case. In this case, a farily long time is needed until the interaction reaches an equilibrium state. Finally, when a very large amount of the acid is added, the bands attributable to aniline interacting with the acid are no longer observed. An attempt has been made to interpret these phenomena in terms of the state of the aggregation of aniline, acid and acetone molecules in the solutions.

In our previous studies, we examined the infrared absorption intensities of the out-of-plane CH bending and ring out-of-plane deformation vibration bands of various monosubstituted (PhX-, Ph_2X-, and Ph_3X-type molecules) and meta disubstituted benzenes and discussed the intensities of those bands in terms of several basic factors, *i. e.*, the forms of group vibrations, the C–H bond dipole moment, and the structural factors, including the angles of rotation of benzene rings (in case of Ph_n X-type molecules) and the conformational isomerism.[1–3] Several conclusions have been drawn from these studies. Those of them essential to the

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1. S. Higuchi, K. Nakamori, S. Tanaka, and H. Kamada, *Nippon Kagaku Zasshi*, **89**, 565 (1968).
2. Y. Gōda, S. Higuchi, S. Tanaka, and H. Kamada, *ibid.*, **92**, 21 (1971).
3. S. Higuchi, Y. Gōda, S. Tanaka, and H. Kamada, *ibid.*, **92**, 670 (1971).

present problem are enumerated below.

1) The forms of group vibrations corresponding to the two strong bands in the 800—670 cm^{-1} region are determined by strong coupling of the two vibrational modes, *i.e.*, out-of-plane CH bending and ring out-of-plane deformation vibrations. As a result of this, there occurs an intensity borrowing between these two vibrational modes.

2) The degree of coupling of the above two modes is sensitive to slight changes in the structure of substituents attached to the benzene ring. Thus, the forms of the group vibrations corresponding to each of the bands are not characteristic of the series of related compounds.

3) Considering that the moment induced by the ring out-of-plane deformation mode is much smaller than that by the out-of-plane CH bending mode (in the case of monosubstituted benzenes, we can estimate the former to be about one-fifth of the latter, thus, in intensity, it is about 4 percent of the latter.), the sums of the intensities of the two bands in question can be regarded as approximately corresponding to an out-of-plane CH bending vibrational mode similar to that of benzene, which is the in-phase vibration of all the hydrogen atoms attached to the benzene ring.

4) The vibrational coordinates corresponding to these sums of intensities can be considered characteristic of the series of the related compounds.[1] Consequently, the differences in the intensity sums among the compounds can be discussed in terms of the alterations in the C–H bond moment, the electric factor of the intensities of the vibrations in question. From the correlations between the intensity sums and the wavelength of the benzenoid bands in the UV spectra, it was pointed out that, when there is *n*-π conjugation between substituents and the benzene ring, the intensity sums (hence, the C–H bond moment) increase considerably with the effect, while, otherwise, they stay approximately constant.

On the basis of these results, we have examined this time the effect of solvents on the intensity sums, which we will hereafter call the group characteristic intensities, A_0. As the solute molecule, we have selected aniline. In this molecule, the effect of *n*-π conjugation, which has been found to be the major factor in determining the magnitude of the C–H bond moment, is considerably pronounced; it is interesting to examine the solvent dependences of A_0 in relation to the effect of solvents on the *n*-π conjugation between the substituent and the benzene ring. Thus, in this study, we have tried to consider from this viewpoint the factors attributable to the media and responsible for the changes in A_0.

Experimental

A Japan Spectroscopic Company Model DS-403G Infrared Spectrophotometer was used for the measurement of the intensities. The spectra were recorded in absorbance with a frequency scale in cm^{-1}, and the integrated areas were obtained directly from the instrumental charts. The concentration range was about 0.3—1.0 mol/*l*, and the cell thickness, 33 and 38 μm. The solvents used were cyclohexane, dioxane, carbon disulfide, acetone, nitromethane, acetonitrile, and mixed solvents of acetone and various carboxylic acids (acetic acid, *n*-propionic acid, *n*-butyric acid, and *p*-hydroxybenzoic acid). The slit width, $S/\Delta\nu_{1/2}$, was kept between 0.2 and 0.1. The scanning speed was about 10 cm^{-1}/min.

As will be shown later, two bands overlap for each of out-of-plane CH bending and ring out-of-plane deformation vibration modes, and it becomes necessary to divide these overlapping bands into components. In this study, such curve resolution was made by the use of a Du Pont 310 Curve Resolver, assuming the Lorentzian band contour for each component. The bands of aniline in the acetone solvent have shapes relatively close to those of Lorentzian curves. However, it should be noted that, strictly speaking, the asymmetric character of the band shapes is slightly more pronounced in the case of the acetone solvent than in the case of nonpolar solvents; moreover, the wings of the bands do not fit so well with the Lorentzian contours. Taking these facts into consideration, it may be necessary to make allowance for errors of 10—15 percent in the measured areas through the use of this procedure of curve resolution.

The root-mean-square difference between the individual intensity values and their mean was found to be less than 10 percent.

Results and Discussion

1. *The Behaviour of A_0 of Aniline in Usual Polar and Nonpolar Solvents.* Table 1 lists the observed intensities of the out-of-plane CH bending (A_1) and ring out-of-plane deformation vibration bands (A_2), and their sums (A_0) of aniline in six different solvents. These values of A_0 are plotted in Fig. 1 against the corresponding "reaction-field constant" $(\varepsilon-1)/(2\varepsilon+1)$, which is used here as a quantitative measure of the polarity of the solvents. These plots show distinctly that A_0 is little influenced by the polarity of solvents in the usual sense of the word. Such a situation has also been observed in the cases of other monosubstituted benzenes. Figure 1 shows the plots for toluene for the sake of comparison. Although the absolute magnitudes of A_0 are different between aniline and toluene, a difference which is attributable to the difference in the substituent effect between NH_2 and CH_3 groups, the behaviour of the A_0 according to the polarity of the solvents is always similar. This may be due to the facts that the major factor in determining the values of A_0 is the conjugation effect between the substituent and the benzene ring and that the solvents used here can not be expected to affect this very much.

TABLE 1. THE OBSERVED INTENSITIES A_1, A_2 AND THEIR SUM A_0 OF ANILINE IN VARIOUS SOLVENTS

Solvent	A_1	A_2	A_0
Cyclohexane	4270	1790	6060
Dioxane	4350	1950	6300
Carbon disulfide	4190	1860	6060
Acetone	4070	1950	6020
Nitromethane	4330	1800	6130
Acetonitrile	4320	1890	6210

Unit of intensities: $[\text{cm}^{-2}\cdot l\cdot\text{mol}^{-1}]$

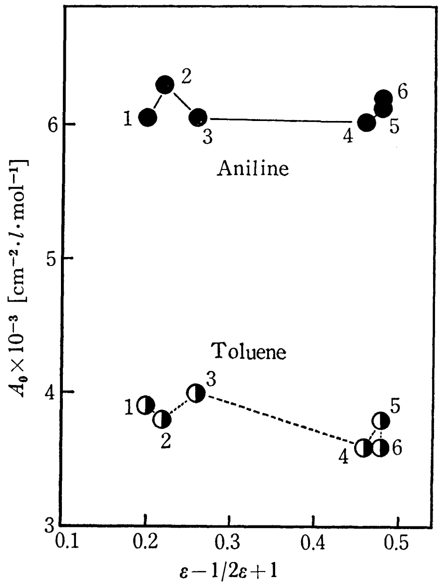

Fig. 1. The behaviors of A_0 of samples in polar and nonpolar solvents, 1: cyclohexane, 2: dioxane, 3: carbon disulfide, 4: acetone, 5: nitromethane, 6: acetonitrile.

2. *The Behavior of A_0 of Aniline in Acetone Mixed with Various Quantities of Acetic Acid.* From above experimental results, the marked changes in A_0, if any, may be expected when the solvent contains some chemical species which have a strong interaction with the n-electrons on the NH_2 group. Thus, we next examined the behaviour of A_0 of aniline in a mixed solvent consisting of acetone and organic acids.

Figures 2 and 3 show the spectra of aniline in acetone and in an acetone-acetic acid mixed solvent. As is shown in Fig. 3, two new bands, 1′ and 2′, appear as shoulders of the original peaks, 1 and 2, when the mixed solvent is used. These four bands can be interpreted as follows. The 1 and 2 bands are assigned, respectively, to out-of-plane CH bending and ring out-of-plane deformation vibrations of aniline not interacting with the acid, and the 1′ and 2′ bands, to the corresponding vibrations of aniline interacting with the acid. As has already been mentioned, these overlapping bands have been divided into components with a Lorentzian band contour, using a Du Pont 310 Curve Resolver. An example of such curve resolving is shown in Fig. 3.

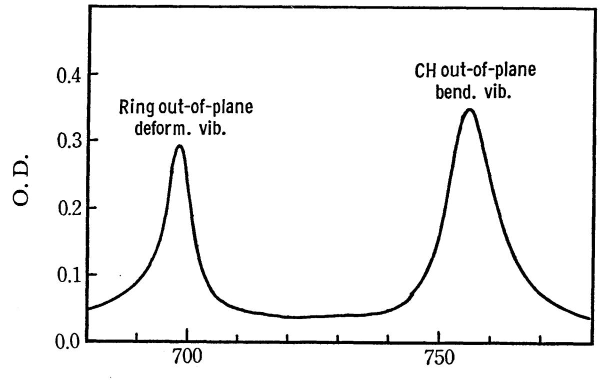

Fig. 2. The spectrum of aniline in acetone solvent.

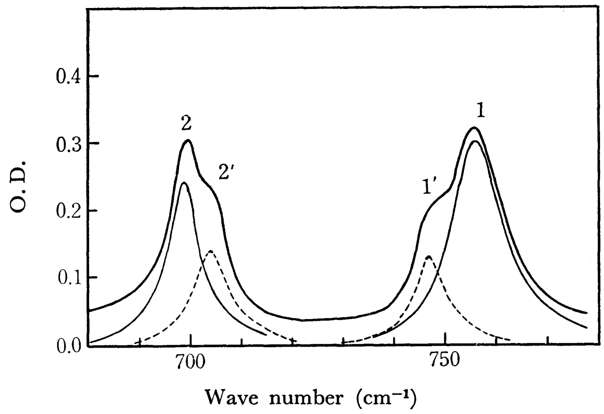

Fig. 3. The spectrum of aniline in the mixed solvent.

TABLE 2. THE KINDS OF ADDED ACIDS AND A_0 OF ANILINE INTERACTING WITH THE ACID

Acid	pK_a	A_0
Acetic acid	4.76	3500
n-Propionic acid	4.85	2900
n-Butyrlic acid	4.82	3400
p-Hydroxybenzoic acid	4.54	3300

Unit of intensities [cm^{-2}·l·mol^{-1}]

In order to calculate the intensities of each of the four bands, it is necessary to estimate the concentrations of aniline interacting and not interacting with the acid. For this purpose, the concentrations of aniline not interacting with the acid have been obtained from the areas of each of the two bands attributed to this kind of chemical species. In doing this, it was assumed that the concentration of not-interacting aniline corresponding to a certain area of a band is equal to that corresponding to the same area of the band of aniline in an acetone solvent. From the results of this procedure, the concentration of aniline interacting with the acid has been determined. It may be worth mentioning that the concentrations determined from the two different bands agree with each other within the limits of experimental error.

Figure 4 shows the plots of the intensity sums, A_0, of aniline interacting with the acid against the cor-

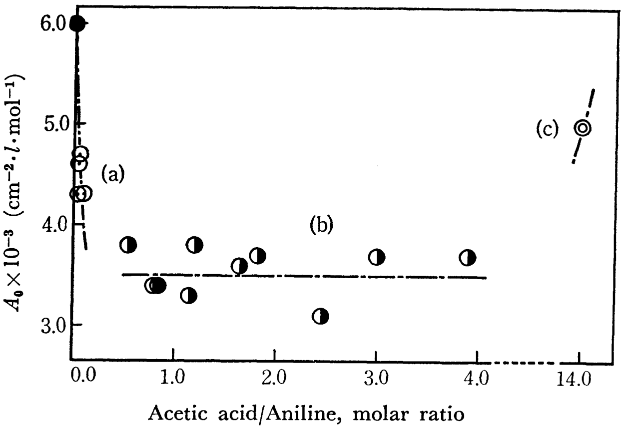

Fig. 4. The dependence of A_0 on the concentrations of the acid.

responding molar ratios of aniline and acetic acid. It can be seen from this figure that the intensity behavior can be classified into at least three categories, (a), (b) and (c). We will now consider these types of intensity behavior individually.

First, we will discuss the molar ratio range, (b), where the magnitude of A_0 becomes lower than in the case of the acetone solvent. In this case, the intensity value, $3500 \pm 200\ \mathrm{cm}^{-2} \cdot l \cdot \mathrm{mol}^{-1}$, has been obtained as the A_0 value of aniline interacting with the acid; this value is remarkably lower than that of $6000 \pm 100 \mathrm{cm}^{-2} \cdot l \cdot \mathrm{mol}^{-1}$ when no acetic acid is added. This lowering of the intensity is considered to be due to a decrease in the interaction of n-electrons on the NH_2 group with π-electrons of the benzene ring as a result of a strong interaction of the acid with n-electrons of the substituent.

The validity of the above discussion of the physicochemical mechanism of the decrease in intensity can be inferred from the correlations of A_0 with the wavelengths of the benzenoid bands in the UV spectra. Fig. 5 shows the correlations for several monosubstituted benzenes. It is known that the maximum absorption of aniline occurs at 288 nm in the case of a neutral solution, while, in the case of an acidic solution, it appears at 254 nm.[4] It can be seen that the values of A_0 for aniline in acetone-acetic acid mixed solvents are well on the correlation curve in Fig. 5 when plotted against the data for the wavelength quoted above. The shift to the shorter wavelength in the case of an acidic solution is said to be due to the decrease in the conjugation between the NH_2 group and the benzene ring, resulting from the interaction of the substituent with the acid. Thus, this result supports the first assumption that such an effect of acidic substances will cause a marked change in the C–H bond moment and, therefore, in the magnitude of A_0.

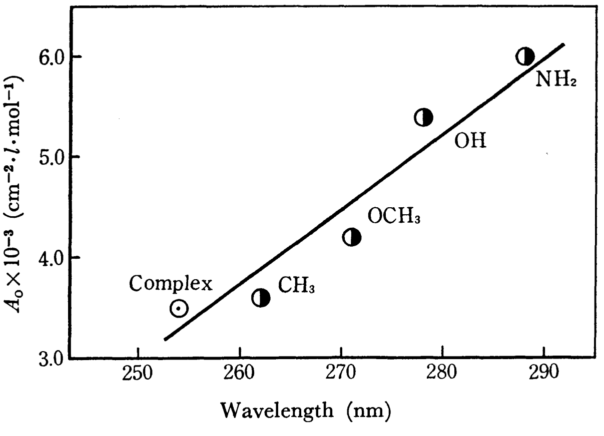

Fig. 5. The comparison of A_0 of aniline with that of its complex in terms of the correlation with UV spectra.

A similar decrease in intensity has been observed when different acidic substances are added to acetone. Table 2 lists the data for A_0 of aniline interacting with various carboxylic acids having similar pK_a values. These results show that there is no wide difference among these acids in their effects on the aniline molecule, regardless of the substituents attached to the COOH group.

Quite different phenomena have been observed in the molar ratio range (a), where the existing acetic acid molecules are much fewer than the aniline molecules. First, a considerable amount of time is required until the interaction reaches the equilibrium state (about two hours after sampling). The change of the spectra with the time is demonstrated in Fig. 6. Second, the group characteristic intensity, A_0, is $4500 \pm 200\ \mathrm{cm}^{-2} \cdot l \cdot \mathrm{mol}^{-1}$, considerably larger than that in the (b) range. Third, the molar concentration of aniline molecules interacting with the acid is much greater than that of the added acid molecules. From these experimental facts, it can be guessed that the state of the aggregation of aniline, acid, and acetone molecules is different from that in the case of (b).

In the molar ratio range (c), where a very large quantity of the acid is added to acetone, the following phenomena can be observed, although, in this case, the observed spectra are not clear enough for a precise estimation of the intensities. The new bands attributable to aniline interacting with the acid can no longer be observed in this case, and the intensity sum, A_0, estimated roughly from the observed bands becomes near to that of aniline not interacting with the acid. These experimental results show clearly that, in this concentration range, the acid becomes almost inactive to the aniline molecule.

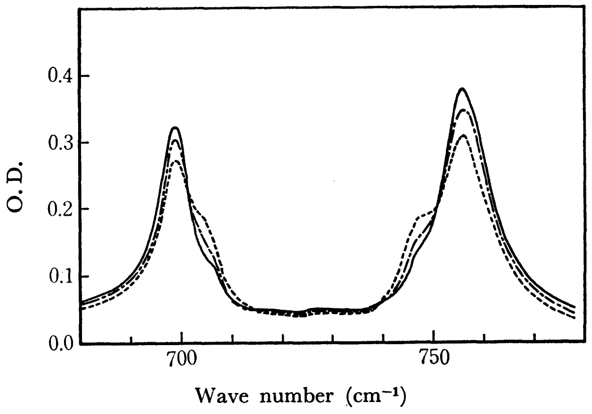

Fig. 6. The change of spectra with time, ——: immediately after sampling, ———: 30 min. after sampling, ……: 120 min. after sampling.

3. *The Relation between the Behavior of* A_0 *and the State of Aggregation for the Molecular Systems in Question.* The above-mentioned experimental results clearly suggest that the factor determining the behaviour of A_0 is the state of aggregation for the molecular systems in question. Therefore, in this paragraph, we will try to present some details on the state of molecules in the solutions, expressed so far in the rather ambiguous term "interacting", and will discuss the changes in A_0 from that viewpoint. The molecular systems treated here are very complex, and there are several kinds of possible molecular associations. That is, the following five kinds of combinations of the molecules are considered to be possible in this case; (1)

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[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", John Wiley and Sons, Inc., New York London (1962), p. 257.

aniline-aniline, (2) aniline-acetone, (3) aniline-acid, (4) acid-acid, and (5) acid-acetone. Since, in general, primary amines are very weak proton donors, the (1) and (2) associations are, if present at all, weak. On the other hand, the (3), (4) and (5) associations may be inferred to be considerably stronger. In the solutions, these molecular associations are considered to be in certain equilibrium states, resulting from complicated mutual interferences among them.

First, we will consider the state of aggregation when no acetic acid is added; here the only possible molecular associations are (1) and (2). The information on the formation of such a state of aggregation will be given by the spectra in the wavenumber region of NH_2 stretching vibrations. Those spectra are shown in Fig. 7. It can be seen that the NH_2 stretching bands of aniline in the acetone solvent show no shift of wavenumbers, even when the concentrations of the solute are made about twenty five times smaller than those used in the measurements of the intensities of the out-of-plane bending vibrations in question. This fact proves that there is no self-association (1) among aniline molecules. However, it is also observed that the wavenumbers in the case of the acetone solvent are about 20 cm^{-1} lower than those in the case of carbon tetrachloride, suggesting that there occurs a weak association (2) by hydrogen bonding between the aniline and the acetone molecules. In fact, it has been reported in the literature that amines associate with carbonyl compounds by weak hydrogen bonding.[5,6] Thus, it can be concluded that the state of aggregation in this case is the associated complex of a certain number of aniline molecules with carbonyl groups between them. Since, in the formation of this type of complex, the hydrogen atoms of the NH_2 group act the principal role, while the *n*-electrons on the group do not, this interaction has no effect on the intensity sum, A_0, resulting in no marked changes in A_0 among the different solvents, as is demonstrated in Table 1 and Fig. 1.

When acetic acid is added to the acetone solvent, three molecular associations, (3), (4), and (5), may all be realized. In this case, it is natural to consider that the acid added to the solvent interacts with the NH_2 groups involved in the complex originally formed between the aniline and the acetone molecules, and that, in this interaction, *n*-electrons on the NH_2 group act the principal role, resulting in the great changes in A_0 described in the foregoing paragraph. At the same time, the added acid molecules will associate with themselves (4) and with acetone molecules (5). These three associations, (3), (4), and (5), will reach some equilibrium state determined by the relative concentration of each of the component molecules. Since the A_0 values of the aniline interacting with the acid change with the concentration of the acid, as is demonstrated in Fig. 4, the strength of the (3) interaction can be thought to change with the alterations in the equilibrium relations among the (3), (4), and (5) associations. In a very simple picture, however, it may safely be said that the degree of the interaction, which has appeared as the change in the A_0 of aniline, is regulated by the degree of the competing associations, (4) and (5), in the equilibrium state at each concentration of the acid. On the basis of this simple model, the following qualitative interpretations of the behaviours of A_0 shown in Fig. 4 are possible, though no quantitative discussion of the chemical equilibria in question here are possible at present. As has already been mentioned, the interaction determining the behaviour of A_0 is between the acid and the associated complex of a certain number of aniline molecules with carbonyl groups between them. In the molar ratio range (b), where there is enough of the acid, each of the NH_2 groups in the complex undergoes sufficient interaction with the acid, resulting in the lowest magnitude of A_0. The experimental results demonstrated in Fig. 5 and Table 2 suggest that, in this case, aniline molecules interacting with the acid exist in the solutions as anilinium ions or a similar state of molecular aggregation. As the concentrations of the acid become higher, the dimerization of the acid (4) gradually becomes pronounced. However, at least in the concentration range (b) examined in the present study, the effect of this dimerization does not appear in the values of A_0; A_0 keeps approximately constant within the limits of experimental error. This suggests that, in this range of concentration of the acid, the dimerization of the acid molecules competes only with the association between the acid and acetone molecules (5), and that the association (3) is not much influenced until the concentration of the acid becomes much higher, though no quantitative and decisive discussion of this phenomenon can be given here.

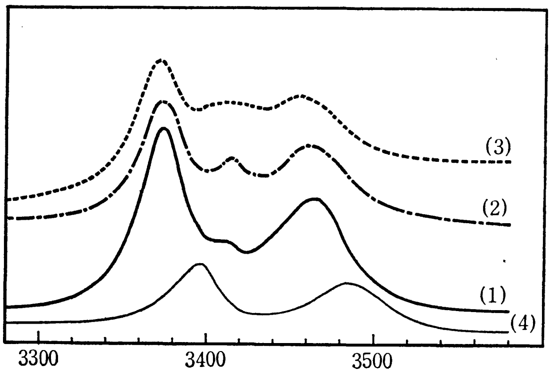

Fig. 7. The spectra of aniline in NH_2 stretching region, (1), (2), (3): in acetone, (4): in carbon tetrachloride, rough concentrations: (1) 0.5 mol/*l*, (2) 0.1 mol/*l*, (3) 0.02 mol/*l*.

In relation to the above discussions, the phenomenon observed in the molar ratio range (c), where a very large amount of the acid is added to acetone, can be interpreted easily. That is, in this concentration range, the effect of the dimerization of the acid is extremely pronounced; as a result, the acid molecules become inactive not only to acetone, but also to aniline molecules, resulting in the disappearance of the bands attributable to aniline interacting with the acid.

As has already been mentioned, the results for the

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5. E. A. Cutmore and H. E. Hallam, *Trans. Faraday Soc.*, **58**, 40 (1962).
6. J. Lauransan, P. Pineau, and M. L. Josien, *Ann. Chim.* (Paris), **9**, 213 (1964).

molar ratio range (a) suggest that the state of aggregation of the molecules in this case is different from that in the case of (b). Also, in this case, the interaction in question is considered to occur between the associated complex [aniline-acetone] and the acid molecules. However, there is a difference in this case in that there does not exist enough of the acid as compared with aniline. From the experimental results, it may be supposed that, in the (a) range, NH_2 groups in the complex exist not as a state similar to anilinium ions (1 : 1 association), as in the case of (b), but as a state such as when one acid molecule interacts with several NH_2 groups simultaneously. On the basis of this model, the relatively greater values of A_0 observed in this concentration range can be understood easily, for, under such circumstances, the action of the acid which the n-electrons of each of the NH_2 groups in the complex receive in the equilibrium state becomes weaker on the average. Although a more detailed microscopic image of the molecular associations in this case cannot be given at present, the assumption of the possibility of the above-mentioned state of aggregations is consistent with all the phenomena observed in the (a) range. Be that as it may, it can at least be said that the experimental facts presented here are very suggestive as to the elucidation of the state of molecules in solutions similar to those in question here.

Conclusion

It has been demonstrated that the present experimental results are all consistent with the concept that the n-π conjugation between the substituent and benzene ring is the major factor in determining the magnitude of the C–H bond moment. The conclusion was drawn originally from the studies of the substituent effect; this time, it has been confirmed by discussion of the state of aggregation of the solute and solvent molecules. The authors realize that more detailed experimental and theoretical research over a wide range of related compounds is required before a more general rule as to the influences of media on the intensities in question can be set up. We realize also that there remain considerable ambiguities concerning the explanations of the state of molecules in the solutions in question. However, we believe that the experimental results demonstrated in this paper will be of value in stimulating the advancement of more detailed and exact studies of this subject.

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