The Intramolecular Interaction between the N–H Group and π-Electrons. II.[1] Intramolecular Interaction in *N*-Phenethylanilines

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In a previous paper[1] the authors have reported that there is an interaction between the N–H group and π-electrons of the benzyl group in *N*-benzylaniline, this fact being confirmed by infrared spectroscopy.

The same type of interaction, i. e., O–H···π interaction, has been reported in a variety of aliphatic and aromatic hydroxylic compounds with π-electrons in appropriate positions.[2] Since both N–H and O–H groups are known to be hydrogen donors, it is expected that the N–H···π interaction may be possible in a compound analogous to a hydroxylic compound which shows the O–H···π interaction.

Phenethyl alcohol and some derivatives of 3-phenylpropyl alcohol,[2e] as well as benzyl alcohol,[2d] have been reported to show the interaction; hence, it may be reasonable to begin with the investigation of *N*-phenethylaniline. Such a study will provide some data on X–H···π interaction in general and will make it possible to compare O–H···π and N–H···π cases.

Experimental

Spectral Measurement and Calculation.—The infrared spectra were recorded on a Perkin-Elmer model 112-G double-pass high precision-grating infrared spectrometer, provided with a 2 cm. quartz cell and a spectral slit width being 1.0 cm^{-1} in the N–H stretching region. Eastman Kodak spectrograde or redistilled carbon tetrachloride was used as a solvent. The concentration of the solution was 0.005—0.007 mol./l., which was dilute enough to exclude associated solute molecules. The temperature was 25±2°C.

The obtained bands were, if necessary, separated into two or more component bands, assuming that each one was expressed by Lorentz function. The integrated intensities were calculated according to the following equation:

$$A=(\pi/2)\cdot\Delta\nu^{a}_{1/2}\cdot\ln(I_0/I)_{max}\cdot l^{-1}\cdot c^{-1}$$

where A is the integrated intensity; $\Delta\nu^{a}_{1/2}$, the half-band width; c, the concentration of the solution (mol./l.), and l, the cell length.

The errors in the values analyzed, especially in the absorption maximum position and the half-band width, are difficult to estimate, since the curves were divided by the "trial and error" method. The band shape was an important factor in determining the ease of division. Thus, the spectrometer allowed an accuracy of 0.1 cm^{-1} for an apparent band maximum, but the analyzed values mentioned above were obtained with an accuracy of only ca. ±0.5 cm^{-1}.

Materials.—The compounds used in the present study were known, unless otherwise stated, and were purified through known methods. Their physical constants agreed well with those reported.

N-Phenethylanilines.—Two procedures were adopted for the preparation of this series of compounds; (a) Phenethyl chloride or bromide (0.1 mol.) and a substituted aniline (0.1 mol.) were heated with 30 ml. of 20% aqueous sodium hydroxide for 30 min. After the unreacted halide and aniline had been removed by steam distillation, the residue was taken up in ether and distilled under reduced pressure; (b) A substituted phenylacetanilide (0.05 mol.), recrystallized from 70% ethyl alcohol, was added in small portions into a stirred solution of 4.0 g. (0.105 mol.) of lithium aluminum hydride in 100 ml. of dry ether. The solution was then further stirred at a refluxing temperature for 6—8 hr., and the excess of lithium aluminum hydride was decomposed with ethyl acetate. The reaction mixture was poured into 150 ml. of 30% aqueous sodium hydroxide and extracted with ether. After the solvent had been distilled off, the residue was distilled under reduced pressure.

The physical constants and elemental analyses of

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[1] Part I: M. Ōki and K. Mutai, This Bulletin, **33**, 784 (1960).

[2] M. Ōki and H. Iwamura, ibid., a) **31**, 770 (1958); b) **32**, 307 (1959); c) **32**, 567 (1959); d) **32**, 955 (1959); e) **32**, 1135 (1959); f) **33**, 681 (1960).

R	Method	B. p./mmHg	n_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Yield %
N-(2-Arylethyl)aniline ($RC_6H_5CH_2CH_2NHPh$)										
p-CH_3	b	178—179°C /8.5	1.5891 (18°C)	85.26	85.27	8.11	8.18			43
p-Cl	b	158—160°C /3	1.6040 (18°C)	72.47	72.44	6.08	6.11	6.04	5.85	56
m-Cl	b	150—151°C /3	1.6112 (18°C)	72.47	72.39	6.08	6.23	6.04	5.87	65
N-Arylphenethylamine ($PhCH_2CH_2NHC_6H_4R$)										
p-MeO	a	159—161°C /2	1.5956 (16°C)	79.26	79.50	7.54	7.52	6.16	6.13	*
p-CH_3	a	140—144°C /2	1.5896 (20°C)	85.26	85.25	8.11	8.26			*
m-CH_3	a	154—156°C /2	1.5936 (14°C)	85.26	85.49	8.11	8.10			*
p-C_6H_5	b	47— 48°C (m. p.)		87.87	87.58	7.01	7.17			61
p-Cl	a	150—154°C /3	1.6072 (18°C)	72.47	72.42	6.08	6.15	6.04	5.93	*
m-Br	a	175—177°C /3	1.6240 (18°C)	60.88	60.62	5.11	5.20	5.07	5.16	*

* Generally 20—35%

the new compounds are summarized in the following table.

Results and Discussion

***N*-(2-Arylethyl)aniline.** — The *N*-phenethylaniline derivatives containing substituents at the *m*- or *p*-position of phenethyl groups were selected for spectral inspection to avoid the formation of the N–H···X hydrogen bond, which is possible in *o*-substituted compounds. The apparent absorption curves in the N–H stretching region for *N*-phenethylaniline, *N*-(*p*-chlorophenethyl)aniline, and *N*-(*p*-nitrophenethyl)aniline are shown in Fig. 1.

Three curves show that two apparent maxima are present, suggesting that there are at least two bands and, therefore, two isomers. It might be an attractive explanation that they are simple rotational isomers due to the difference in steric conditions caused by the rotation of the N–H hydrogen atom around the N–CH_2 bond axis. The positions of the absorption maxima of the divided bands (see Table I) are at nearly the same wave numbers as those of the rotational isomers in *N*-ethylaniline;[1] this fact may be regarded as supporting evidence for the explanation.

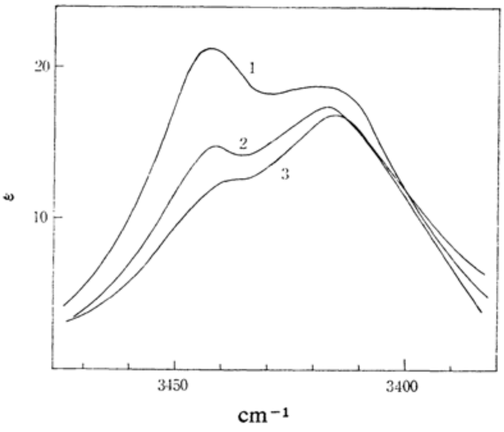

Fig. 1. ν_{N-H} Absorption of *N*-(*p*-nitrophenethyl)aniline (1), *N*-(*p*-chlorophenethyl)aniline (2) and *N*-phenethylaniline (3).

However, it should be noted that a substituent effect is observed in the spectra; the extinction coefficient of the higher wave number band increases at the expense of the lower one as the electron-withdrawing power of the substituent increases. This effect suggests that N–H···π interaction is the more probable interpretation of the presence of two N–H stretching bands, since a *m*- or *p*-substituent in the phenethyl group should not cause an appreciable difference in steric effect on the N–H group. In order to get firmer evidence for this interpretation, the curves of five *N*-(2-arylethyl)anilines were divided, assuming that they were the overlaps of two symmetrical ones expressed by Lorentz function. The results are shown in Table I.

From Table I, it is evident that the A_i/A_f ratio, where A_i is the integrated intensity of the absorption due to the interacting form and A_f, that of the free form, varies with the electron-donating or electron-withdrawing nature of the substituent, and this tendency is indicative of interaction between the N–H

TABLE I. ν_{N-H} ABSORPTION OF *N*-(2-ARYLETHYL)ANILINES, $RC_6H_4CH_2CH_2NHPh$

R	Band	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol$^{-1}\cdot$l$\cdot$cm^{-2}	$\log(A_i/A_f)$
p-CH_3	i[a] f[b]	3414.8 3446.7	31.9	54.4 23.4	3.52 0.41	0.936
H	i f	3415.2 3445.8	30.6	50.2 25.0	2.92 0.43	0.832
p-Cl	i f	3416.6 3446.3	29.7	48.2 24.4	2.85 0.66	0.636
m-Cl	i f	3415.7 3445.5	29.8	44.0 29.0	2.56 0.89	0.458
p-NO_2	i f	3415.0 3444.5	29.5	41.8 29.0	2.34 1.68	0.148

a) i denotes interacting form of N-H group.
b) f denotes free form of N-H group.

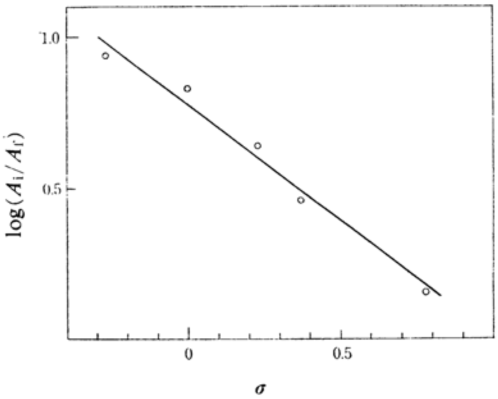

Fig. 2. The relationship between σ-constant and $\log(A_i/A_f)$ for *N*-(2-arylethyl)aniline.

group and π-electrons. The summation of the integrated intensities due to the two forms also changes slightly with the substituent, but this is not a significant factor in comparing the A_i/A_f ratio, since the substituent seems to have nearly the same effect on both intensities.

The $\log(A_i/A_f)$ value was plotted against the Hammett σ value[3] of the substituent. The σ value is believed to be closely related to the electron density[4] at an appropriate carbon atom in a substituted benzene nucleus. As may be seen in Fig. 2, a linear relationship is gained when the σ value is so taken as to represent the reactivity of the ring carbon atom which is attached to the anilinoethyl group. As the A_i/A_f ratio corresponds to an equilibrium constant of the system between the two forms and changes with the electron density, the two component bands should be assigned to the interacting and the free forms of the N-H group, the forms corresponding to the higher and lower wave number bands respectively, as denoted in Table I.

A difference may be found between the data in Table I and those obtained with phenethyl alcohol derivatives. The displacement ($\Delta\nu_{max}$) of the absorption maximum of the O-H group by the O-H$\cdots\pi$ interaction has a tendency to increase as the σ value of the substituent decreases, the phenomenon being far more evident than in *N*-phenethylaniline; when the substituent varies from *p*-CH_3 to *p*-NO_2, the difference of $\Delta\nu_{max}$ is 12.2 cm^{-1} in the O-H$\cdots\pi$ interaction, while the corresponding difference in the N-H$\cdots\pi$ interaction is only 2.4 cm^{-1}, though the change is in the same direction. There has been general acceptance of a proposal that $\Delta\nu_{max}$ provides an index of the strength of the hydrogen bond (ΔH, the enthalpy of hydrogen bonding),[5] though exceptions to this rule are not rare and the matter should be treated carefully. A comparison of the ΔH's of the O-H$\cdots\pi$ interaction in several hydroxylic compounds[6] with those of some derivatives of *N*-benzylaniline[7] has shown that there is no remarkable difference between the two groups. Thus, it must be emphasized that the $\Delta\nu_{max}$ difference between O-H and N-H groups cannot be directly related to the interaction energy.

Another striking difference is the value of $\log(A_i/A_f)$. In *N*-phenethylaniline, even the value of the most unfavorable derivative for the interaction among the compounds investigated, i.e., *N*-(*p*-nitrophenethyl)aniline, does not fall to the minus region. This means that if the absorption strength per molecule is the same for both free and interacting forms, the

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[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York (1940); H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953); D. M. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[4] H. H. Jaffé, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952); H. H. Jaffé *J. Am. Chem. Soc.*, **76**, 5843 (1954).

[5] For instance, G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Cal. (1960). pp. 67—141.

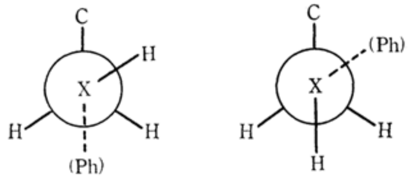
[6] M. Ōki and H. Iwamura, This Bulletin, **33**, 717, 1599 (1960).

[7] M. Ōki and K. Mutai, Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[8] M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

interacting form is always favored over the free one. On the contrary, in phenethyl alcohol the interaction is of little advantage and a fairly strong electron-donating group such as a *p*-amino substituent can only make the interacting form exceed the free one by a factor of 1.14.

To discuss the matter more fully, some comments should be made on the rotamer ratio in the corresponding compounds with no π-electron system available for interaction. The A(C–H)/A(H–H) ratio in *N*-ethylaniline is 8.7[1] and that in ethyl alcohol,[8] 0.56, where A(C–H) denotes the integrated intensity of the rotamer which has its X–H group hydrogen between carbon and hydrogen in the Newman projection (Fig. 3, I), and A(H–H), one with the X–H hydrogen between two hydrogens (Fig. 3, II).



I II

Fig. 3. Possible rotamers with regard to CH_2–X bond in C–CH_2–X–H.

The band at ca. 3445 cm^{-1} shown in Table I should be assigned to the rotamer II. The fact that the ratio in *N*-ethylaniline is greater by the factor of ca. 15 than that of the alcohol may reasonably be explained by the steric effect of the phenyl group attached to the nitrogen, since the conformation with phenyl between two hydrogens (I) will be favored over one with the group between carbon and hydrogen (II) on account of the greater steric repulsion in the latter.

A comparison of the data in Table I with those of *N*-benzylanilines also shows two interesting points. First, the slope of the line obtained by plotting $\log(A_i/A_f)$'s against Hammett σ values is remarkably steeper in *N*-phenethylaniline ($\rho=-0.85$) than that in *N*-benzylaniline ($\rho=-0.40$). Second, the $\log(A_i/A_f)$ values for the latter take both positive and negative signs, but those for the former take only the positive. These are rather abnormal phenomena, because in the *N*-phenethyl derivative the N–H group is separated farther by a methylene group when compared with benzylaniline and, therefore, the situation is unfavorable for the interaction (vide supra). The reasons for these unexpected results can be one or more of the following three: (1) The lower frequency band assigned to the interacting form is, in fact, composed of two bands, due to the interacting form and to the free rotamer, with the absorption maxima of the two at nearly the same position. (2) The absorption intensity per molecule of the interacting form is considerably higher than that of the free form. (3) On establishing the interaction, four- and five-membered rings are formed in *N*-benzyl- and *N*-phenethylaniline respectively. In view of ring strain and the bond angle of p_π–H–N in the rings, electronic interaction may be more fully effected in the larger ring, the effect leading to a real increase in the number of interacting molecules in spite of the statistical disadvantage.

The maximum positions of the bands due to the rotamers in *N*-ethylaniline are at 3445.2 and 3421.4 cm^{-1}, the latter being shifted to a wave number higher by ca. 6 cm^{-1} than the maximum position of the interacting form in *N*-phenethylaniline. If this type of rotamer really exists, especially with a broad band width, it will be difficult to distinguish the bands at 3421 and 3415 cm^{-1}. It is even possible that they might in the calculations be regarded as one band in view of the technical uncertainties involved in dividing composite spectra. However, it is noteworthy that Fig. 2 shows a good linear correlation between $\log(A_i/A_f)$ and σ values. This may reflect the fact that the contribution of the rotamer to the intensity A_i is small for the reasons to be elucidated below. Let us consider an equilibrium:

$$\mathrm{f}_1 \overset{K_i}{\rightleftarrows} \mathrm{f}_2 \overset{K_f}{\rightleftarrows} \mathrm{i}$$

where f and i denote the free and the interacting states respectively, and f_1 corresponds to the rotamer I and f_2 to the rotamer II in question. K_f and K_i are equilibrium constants. If it is true that the band at the lower wave number corresponds to the sum of the interacting and the free f_2 forms, $(f_2+i)/(f_1)$ rather than $(i)/(f_1+f_2)$ should be adopted as A_i/A_f. Therefore, $(A_i/A_f)=(f_2+i)/(f_1)=[K_f(f_1)+K_fK_i(f_1)]/(f_1)=K_f(1+K_i)$. In the above equation it is K_i which is directly dependent on the substituent. On the other hand, K_f changes indirectly and may be only a little dependent on the effect. Therefore, the conformity to a linear correlation for the wide range of $\log(A_i/A_f)$ values, as observed in Fig. 2, probably indicates the absence or the presence in only a small portion of f_2 in the equilibrium; at any rate the amount of f_2 cannot lead to the destruction of the linearity. However, there remains a possibility that K_f and K_i change so that $\log K_f(1+K_i)$ is linear with σ. Hence, postulate 1 cannot be obviated completely, but it probably is not a major factor.

Postulate 2 is very improbable. If the absorption intensity per molecule of the interacting form were appreciably larger than that of the free form, the sum of the intensities, i. e., $A_i + A_f$, should have increased with the increasing proportion of the interacting form. As is seen in Table I, however, the total intensities of the *p*-methoxyl and *p*-nitro derivatives are 3.93×10^3 and 4.02×10^3 mol^{-1}·l.·cm^{-2} respectively, within the limit of experimental uncertainties. Hence, the postulate may be disregarded.

On the other hand, the remaining explanation, (3), seems to be more probable. A scale model shows a larger angle of p_π-N-H for *N*-phenethylaniline. Unfortunately, no literature has been published concerned with the experimental correlation between the hydrogen bond energy and the linearity of the bond in the non-crystalline state, but some theoretical estimations[9] seem to lend support to the explanation that in the hydrogen bond, the larger the deviation angle from linearity, the less the bond energy. The explanation is really consistent with the data obtained. It is probably the most significant factor in the effects; at least it is a major factor.

One further difference between the spectral characteristics of these homologs is concerned with $\Delta\nu_{max}$ values. In *N*-benzylanilines the values range from 30 to 42 cm^{-1}, whereas in *N*-phenethylanilines the range is from 29 to 32 cm^{-1}. This sharp contrast in the $\Delta\nu_{max}$ range may serve as a key to elucidate the mechanism of the interaction, but no convincing explanation has been obtained so far.

***N*-Arylphenethylamines.** — Since the intramolecular interaction between the N-H group and π-electrons has been proved to exist in *N*-phenethylanilines, it seemed of interest to introduce various kinds of substituents into the aniline ring of the compound. The substituents might have an effect on the N-H group through resonance and induction, and, in turn, the effect may appear in the property of the interaction. For this purpose, four derivative were synthesized and their spectra investigated. Their absorption curves are shown in Fig. 4.

A comparison of Fig. 4 with Fig. 1 shows some differences between the spectral features of these series of derivatives. The absorption curves in Fig. 4 do not show two clear maxima. the presence of the latter two having been one of the characteristics of the interaction between the N-H group and the π-electrons. Additionally, three apparent characteristics can be pointed out in relation to the electronic effect of the substituent; as the electron-withdrawing power of a substituent increases (as the Hammett σ value inrceases), (a) the maximum intensity increases, (b) the half-band width decreases, and (c) the apparent maximum position shifts to a higher wave number. These characteristics, however, are not always peculiar to the N-H···π interaction, because they are also observed in *N*-arylethylamines, which lack a π-electron source for the interaction, as is shown in Fig. 5, and in *N*-methylanilines.[10] Although the substituent effects reveal just the same trend, a close examination of the change in band shape draws attention to the fact that the introduction of a phenyl group to the ethyl group in *N*-arylethylamines produces some changes in shape. The absorption curve of an *N*-arylphenethylamine shows a broader band with a little lower maximum intensity than that of an *N*-arylethylamine with the same substituent. This difference seems to come from the different shape of the side band which appears in the lower wave number region. In *N*-arylethylamines the shape of the band is due to a rotamer, as has already been discussed. On the other hand, the band should be assigned to the interacting N-H group in *N*-arylphenethylamine, though a band due to the free rotamer absorbing in nearly the same region may be a contributing factor.

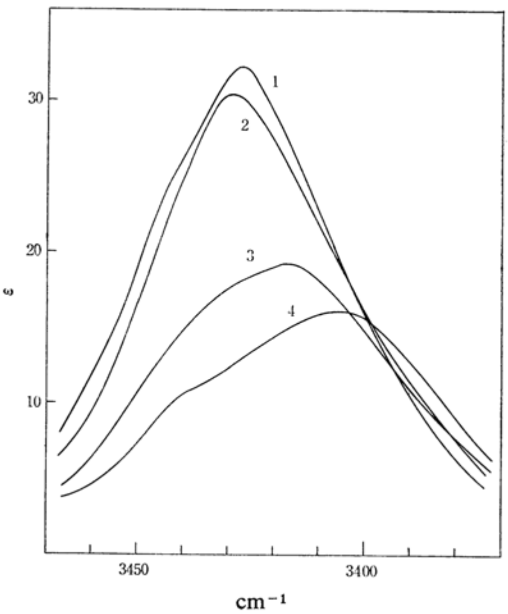


Fig. 4. ν_{N-H} Absorptions of *N*-(*m*-bromophenyl)- (1), *N*-(*p*-chlorophenyl)- (2), *N*-*p*-tolyl- (3) and *N*-*p*-anisyl-phenethylamines (4).

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[9] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Cal. (1960), pp, 242–245.

[10] P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc.*, A243, 143 (1957).

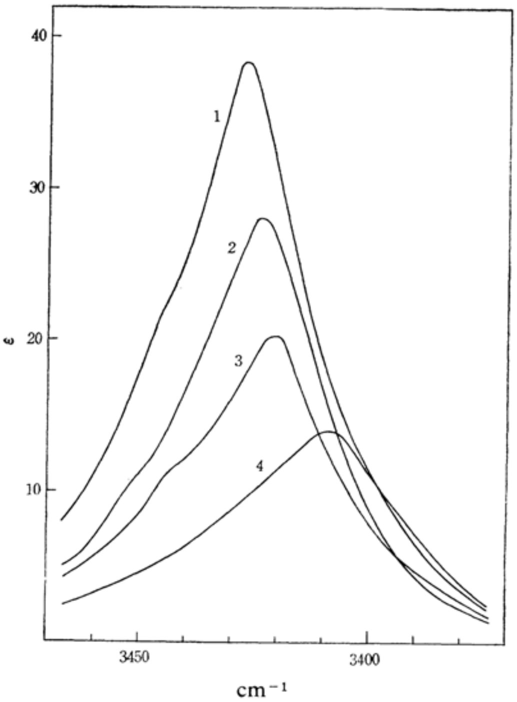

Fig. 5. ν_{N-H} Absorptions of *m*-bromophenyl- (1), *p*-chlorophenyl- (2), phenyl- (3) and *p*-anisyl-ethylamines (4).

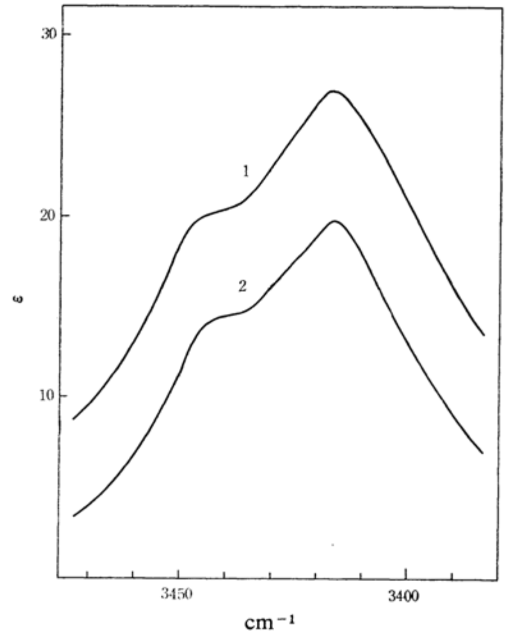

Fig. 6. ν_{N-H} Absorptions of *N*-*m*-tolyl-(1) and *N*-*p*-biphenylyl-phenethylamines (2). Curve (1) is displaced upward by 5 units.

The different features of the curves in Figs. 1 and 4 deserve comment. As has been reported previously,1) the half-band width of the interaction band and the $\Delta\nu_{max}$ value in *N*-arylbenzylamine increase as a substituent becomes more electron-donating. Assuming that this relation still holds true in *N*-arylphenethylamine, a derivative with an electron-donating substituent should show a broader interaction band, with a larger $\Delta\nu_{max}$. The overlapping of the interaction band with the free results in a band with only one apparent maximum, on account of a broad band width in the case of an electron-donating substituent. On the other hand, although the half-band width is small in the case of an electron-withdrawing substituent, $\Delta\nu_{max}$ is also small, thus giving the apparent one band. Consequently, *p*-chloro and *m*-bromo derivatives show apparent narrower curves with an obscure shoulder in the higher wave number region, while *p*-methyl and *p*-methoxy derivatives show apparent broad curves. Although clear evidence for these explanations could be obtained by dividing the curves into their components, the band shape precludes this approach. Moreover, even if the division could be made, the experimental uncertainties could not be reduced to a level sufficiently low to permit a confident discussion of the results.

It should, in addition, be noted that the derivatives with a substituent of a nearly zero σ value, e. g., *p*-phenyl (-0.01) and *m*-methyl (-0.07), show band shapes similar to that of unsubstituted *N*-phenethylaniline (see Fig. 6). This phenomenon suggests that the fact that the two maxima are indistinguishable in *N*-arylphenethylamine is not caused by a loss of a hydrogen atom from the benzene ring, but by the electronic effect of a substituent.

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