Intramolecular Interaction between N–H Group and π-Electrons in N-Benzylanilines

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(Received December 14, 1959)

The discovery[1] of the rotational isomers and the intramolecular interaction between the hydroxyl group and π-electrons in benzyl alcohol derivatives has prompted the authors to examine the N–H stretching absorption of the benzylamine derivatives, since the situation will be much similar in these two series of compounds. The observation of two ν_{N-H} bands for *N*-benzylaniline was reported by Ōki and Iwamura[1], while Russel and Thompson[2] had reported the presence of two ν_{N-H} bands for *N*-benzylaniline and attributed them to the rotational isomerism. Moritz[3] also noticed the existence of two ν_{N-H} bands for some derivatives of *N*-benzylaniline while the present paper was in preparation and the observation of two ν_{N-H} bands for *N*-allylaniline by Schleyer et al.[4] may also fall into this category.

The present paper deals with the rotational isomers of *N*-alkylanilines in respect of the C_{aliph}–N axis and the intramolecular interaction between the N–H group and π-electrons in N-benzylanilines. Aniline derivatives are not the indispensable choice but are convenient for handling, since they do not absorb carbon dioxide from the air owing to the low basicity.

Experimental

Measurement and Calculation.—They were performed as reported previously[5]. The concentration of the carbon tetrachloride solution ranged from 0.003 to 0.005 mol./l.

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

N-(m-Methoxybenzyl)-aniline.— *m*-Methoxybenzanilide obtained by heating methyl *m*-methoxybenzoate with aniline was reduced with lithium aluminum hydride in ether and the product was purified through fractional distillation. It is a colorless oil, b. p. 200∼202°C/21 mmHg, $n_D^{25.5}$ 1.6039.

Found: C, 78.97; H, 7.34. Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09%.

N-(m-Dimethylaminobenzyl)-aniline.—It was prepared similarly as above, starting from *m*-dimethylaminobenzanilide, and recrystallized from ethanol. It forms colorless needles melting at 60-61°C.

Found: C, 79.65; H, 8.12. Calcd. for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02%.

Results and Discussion

***N*-Alkylanilines.**—The apparent absorption curves for N–H stretching of *N*-alkylanilines are shown in Fig. 1. The curves for *N*-methylaniline is symmetric, while those for N-ethylaniline and for *N*-isopropylaniline are unsymmetric. The unsymmetric curves are divided, assuming that the curve is an overlap of two symmetric curves which can be expressed by the Lorentz function. The results are summarized in Table I.

Inspection of Table I reveals that the positions of absorption curves can be classified as three categories. Namely, band I is located at about 3444 cm^{-1}, band II at about 3421 cm^{-1} and band III, at about 3395 cm^{-1}. The origin of the splitting of the ν_{N-H} absorption cannot be attributed to hydrogen bonding among the solute molecules, because firstly, the low concentration such as 0.005 mol./l.

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[1] M. Ōki and H. Iwamura, This Bulletin, **32**, 955 (1959).

[2] R. A. Russel and H. W. Thompson, *J. Chem. Soc.*, **1955**, 483.

[3] A. G. Moritz, *Spectrochim. Acta*, **12**, 242 (1959).

[4] P. von Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

[5] M. Ōki and H. Iwamura, This Bulletin, **32**, 567 (1959).

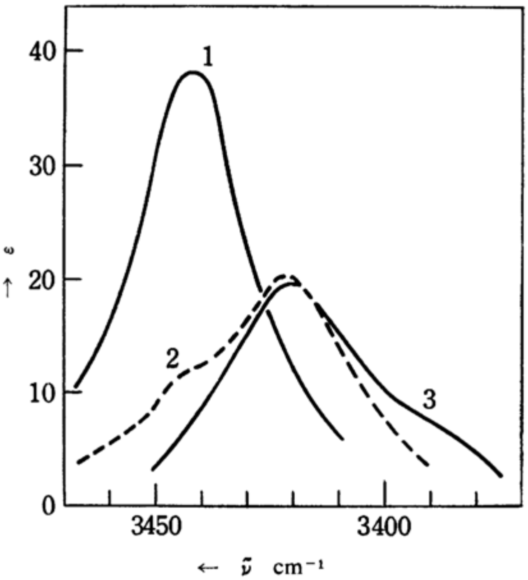

Fig. 1. ν_{N-H} absorptions of methylaniline (1), ethylaniline (2) and isopropylaniline (3).

TABLE I. ν_{N-H} ABSORPTION OF *N*-ALKYLANILINES ($RNHC_6H_5$)

R	Band	ν_{max} cm^{-1}	$\Delta\nu^{a}_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1}·l.·cm^{-2}
CH_3	I	3442.6	29.8	4.13
C_2H_5	I	3445.2	18.2	0.28
	II	3421.4	34.2	2.44
$(CH_3)_2CH$	II	3420.5	31.2	2.19
	III	3394.5	22.0	0.30

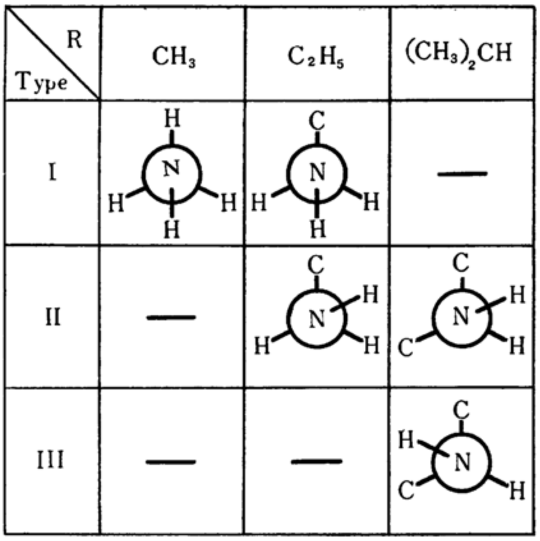

Fig. 2. Classification of rotational isomers in alkylanilines.
The phenyl group is omitted from the diagram for convenience.

would not permit the dimeric form to exist and secondly any kind of association of the molecules does not explain the symmetry of the absorption curve of *N*-methylaniline examined under the similar conditions as the others.

Thus the variation of the curves must be attributed to the variation of the alkyl group attached to the nitrogen atom and the concept of the rotational isomerism about the C_{aliph}-N axis will be valid for the explanation as for a similar phenomenon in the aliphatic alcohols[6].

In Fig. 2, the projection of the molecule through the C_{aliph}-N axis, the nitrogen atom being located at the upper side, is shown. A circle indicates a carbon atom as is customary in Newman projection. It is assumed that the molecule does not take an eclipsed form, thence the hydrogen atom of the N-H group in *N*-methylaniline must be in the same situation, because it always comes between the two hydrogen atoms attached to the alpha-carbon atom, no matter what rotational position is taken. On the other hand, when the alkyl group is an ethyl, there are two posibilities, that the hydrogen atom of the N-H group comes either between the two hydrogen atoms of the alpha-carbon atom or between the carbon and the hydrogen atoms combined with the alpha-carbon atom. Thus two rotational isomers are possible for *N*-ethylaniline. Similarly, *N*-isopropylaniline can take two conformations. Band I may be considered to correspond to rotational isomer I, band II to isomer II and band III to isomer III.

The probability of isomer II is 2/3 for both *N*-ethylaniline and *N*-isopropylaniline. However, the observed values widely differ from those expected and isomer II seems to be an overwhelming majority, since it is probable to assume that the light absorption of a molecule is the same irrespective of its conformation. The reason is not completely understood at the present time but it is clear that the steric effect plays an important role, because the nitrogen atom carries a large phenyl group.

***N*-Arylmethylanilines.**—*N*-Benzylaniline derivatives have two distinct maxima for N-H stretching absorption and the separation of the two bands are much clearer than in *N*-alkylanilines (compare Fig. 3 with Fig. 1). The apparent absorption curves for *N*-(*p*-nitrobenzyl)-aniline, *N*-benzylaniline and *N*-(*p*-dimethylaminobenzyl)-aniline are shown in Fig. 3.

The electron-withdrawing group such as the nitro group enhances the band at the higher wave number and diminishes the band at the lower wave number. On the other hand, the electron-donating group such as the dimethylamino group shows just the contrary tendency

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[6] M. Ōki and H. Iwamura, ibid. 32, 950 (1959).

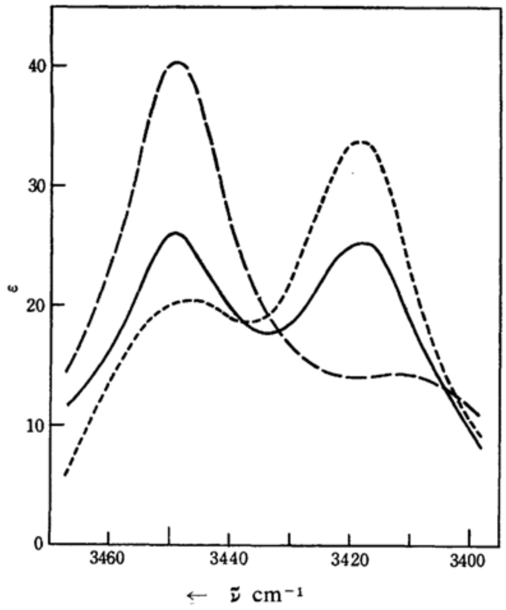

Fig. 3. ν_{N-N} absorptions of benzylaniline (——), *p*-nitrobenzylaniline (----) and *p*-dimethylaminobenzylaniline (------).

and the absorption at the lower wave number forms the main peak. It is again assumed that the curves are the overlaps of the two symmetric curves which obey the Lorentz function and the apparent curves are divided by Ramsay's first method. The results are shown in Table II.

The ratio A_i/A_f, 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 the tendency is indicative of the interaction between the π-electron and the N–H group. The summation of the integrated intensities due to the two forms also changes when the substituent varies, but this fact may be left out, for comparison of the ratio A_i/A_f.

Hammett's σ values[7] of the substituents are taken and the relation with $\log(A_i/A_f)$ is compared. $\mathrm{Log}(A_i/A_f)$ instead of A_i/A_f is taken, because the equilibrium between the interacting and the free forms is the subject of the present discussion. As is seen from Fig. 4, the relation is linear when the σ constants representing the electron density on the carbon atom[8] (C_1), to which the anilinomethyl group is attached, are taken. However, σ values for the other carbon atoms or for the position between two carbon atoms are not proportional to $\log(A_i/A_f)$.

Since the benzylaniline derivatives are secondary amines, which belong to the *N*-ethylaniline type (Fig. 2), they should have two

TABLE II. ν_{N-H} ABSORPTION OF *N*-(ARYLMETHYL)-ANILINES (x-$RC_6H_4CH_2NHC_6H_5$)

R	*x*	Band	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1}·l.·cm^{-2}	$\log(A_i/A_f)$	σ
$(CH_3)_2N$	*p*	i[a]	3418.2	30.5	27.6	3.15	0.382	−0.83
		f[b]	3448.7		24.2	1.31		
	m	i	3419.0	31.8	29.6	2.86	0.276	−0.20 (−0.55)[d]
		f	3450.8		25.6	1.51		
CH_3O	*p*[c]	i	3418.0	32.1	27.8	2.63	0.182	−0.27
		f	3450.1		23.7	1.73		
	m	i	3417.0	32.4	28.4	2.22	0.017	0.12
		f	3449.4		26.8	2.14		
H[c]		i	3417.4	32.8	28.6	2.24	0.025	0.00
		f	3450.2		25.6	2.11		
Cl	*p*	i	3415.3	34.6	37.6	2.76	−0.034	0.23
		f	3449.9		29.2	2.60		
	m	i	3411.9	38.0	27.2	2.23	−0.066	0.37
		f	3449.9		38.4	2.60		
NO_2	*m*	i	3406.6	42.1	45.2	2.03	−0.248	0.71
		f	3448.7		29.4	3.58		
	p	i	3407.9	42.2	51.6	1.94	−0.244	0.78
		f	3450.1		25.2	3.41		

a) i denotes interacting form of the N–H group.
b) f denotes free form of the N–H group.
c) The values are taken from Ref. 1.
d) See the discussion below.

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

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

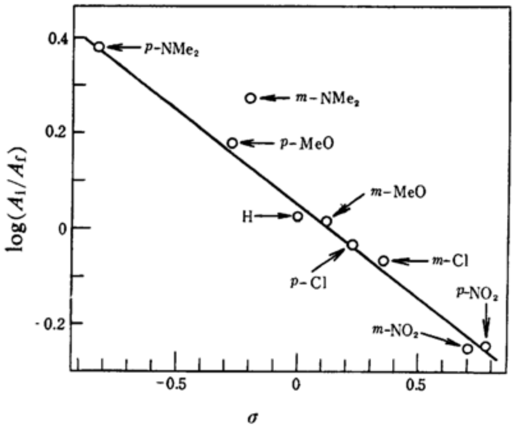


Fig. 4. Comparison of log(A_i/A_f) of *N*-(arylmethyl)-anilines with σ-values.

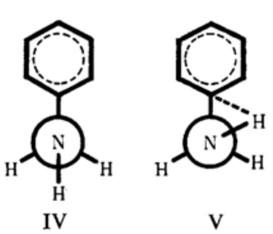


Fig. 5. Possible rotational isomers of benzylaniline (ring B is abbreviated).

rotational isomers. The absorption due to the free form is closely related to type I of *N*-ethylaniline, because it lies at about 3450 cm⁻¹, while type I of *N*-ethylaniline absorbs at 3445 cm⁻¹. Thus, the free form of *N*-benzylaniline corresponds to the rotational isomer IV and the interacting form to structure V in Fig. 5. The interaction takes place between the π-electron on C_1 atom and the N–H group, as judged from the relation between σ constants and log (A_i/A_f). Therefore, the structural formula for the interacting form can be represented by structure V.

One problem remains in the above assignment. That is, the number of molecules of the free form of the *N*-benzylaniline derivatives seem to increase in spite of the expectation that the formation of the internal interaction will lessen the free molecules when compared with the number of molecules belonging to type I in *N*-ethylaniline. In the earlier paper¹⁾, it was pointed out that the internal interaction between the hydroxyl group and π-electrons decreases the number of free molecules. This contradiction may be attributed to the steric effect, since the nitrogen atom carries a large phenyl group. And/or it may be attributed to the difference of the nature of the interactions with the N–H group and with the O–H group series.

The far deviation of the point for *N*(*m*-dimethylaminobenzyl)-aniline might be interpreted in the following way. Jaffé⁷⁾ gave σ value of −0.20 for the *m*-dimethylamino group and this value is taken in Fig. 4. On the other hand, σ value of the *p*-dimethylamino group has been given by Jaffé as −0.60, while the recent paper by McDaniel and Brown⁷⁾ gives −0.83. From an analogous consideration, σ_m given by Jaffé may be smaller than the true and ambiguous, because of lack of examples. The authors obtain −0.55±0.05 for the σ_m of the dimethylamino group from Fig. 4.

Fluctuation of the position for the interacting ν_{H-N} will be discussed in "the nature of the interaction".

N-Benzylarylamines. — The substituent is introduced into the benzene ring which carries the N–H group to understand the electronic effect. It is expected, that the substituent will vary the nature of the N–H bond. The results are given in Table III.

The effect of the substituent on A_i/A_f is not found in Table III. Thus the electron density at the site of hydrogen approach seems

TABLE III. ν_{N-H} ABSORPTION OF *N*-ARYLBENZYLAMINE ($C_6H_5CH_2NHC_6H_4R$-*p*)

R	Band	ν_{max} cm⁻¹	$\Delta\nu_{max}$ cm⁻¹	$\Delta\nu^a{}_{1/2}$ cm⁻¹	$A\times10^{-3}$ mol⁻¹·l.·cm⁻²	A_i/A_f	σ
CH_3O	i f	3405.6 3442.7	37.1	35.8 30.5	1.93 1.74	1.11	−0.27
CH_3	i f	3413.5 3448.3	34.8	34.6 28.0	2.34 1.79	1.30	−0.17
H[a)]	i f	3417.4 3450.2	32.8	28.6 25.6	2.24 2.11	1.06	0.00
Cl	i f	3420.7 3451.8	31.1	26.6 23.0	2.55 2.32	1.10	0.23
Br	i f	3421.5 3451.5	30.0	27.4 23.6	2.75 2.54	1.08	0.23
NO_2	i f	3431.8 3455.0	23.2	17.6 17.4	5.45 4.05	1.34	0.78

a) The values are taken from reference 1.

to determine the number of internally interacting molecules.

The things which vary with the varying substituent are the individual absorption peak of the free and the interacting molecules, and the difference of positions of peaks ($\Delta\nu_{max}$) corresponding to each species of the molecule. The absorption maxima of both free and interacting forms move to higher frequencies as the substituent becomes more electronegative, although the relation between the σ constants and the frequencies of absorption is not perfectly linear. This result roughly agrees with the data obtained by others[9] who have revealed the relationship in aniline derivatives.

One thing noticeable is that $\Delta\nu_{max}$ between the free and the interacting forms relates linearly with the σ value of the substituent (Fig. 6), although the rate of increase or decrease of the frequencies of the free and the interacting forms is not the same and the straight lines, which show the relation between σ value and ν_{max}, are not parallel to each other. The phenomenon will be discussed in "the nature of the interaction".

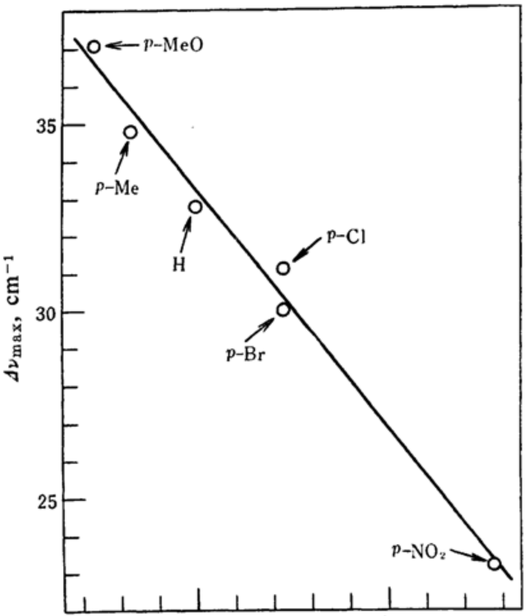
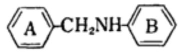


Fig. 6. Comparison of $\Delta\nu_{max}$ of *N*-arylbenzylamines with σ-values.

Nature of the Interaction.—It is now known from Table II that the ν_{N-H} absorption due to the interacting form does not always appear at the constant wave number, when the substituent is introduced into the benzene ring (ring A) which is included in the benzyl group. This is the striking difference when the situation of the benzyl alcohol derivatives is considered, of which interacting hydroxyl groups absorb at a reasonably constant frequency. As was already pointed out, the free form absorbs at the constant wave number, ca. 3450 cm^{-1}, irrespective of the substituent, indicating the effect of the substituent through the methylene group is negligible.



The relation between $\Delta\nu_{max}$ and σ values for the compounds carrying a substituent in ring A, is shown in Fig. 7, which reveals, that the slope of the straight line is not constant but shows a crease at some point. When the electron density on ring A is decreased, σ constants and $\Delta\nu_{max}$ are in linear relation, the slope being positive. On the other hand, when σ value is below 0.00~0.10, the slope of the straight line is almost zero, i. e., $\Delta\nu_{max}$ seems to have no connection with the substituent.

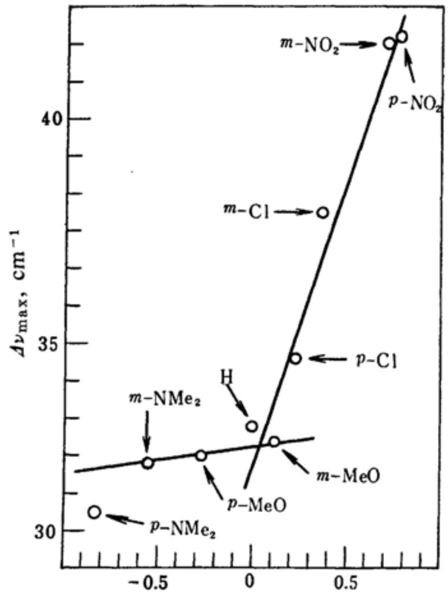


Fig. 7. Comparison of $\Delta\nu_{max}$ of *N*-(arylmethyl)-anilines with σ-values.

Yet, splitting of the ν_{N-H} band into two distinct maxima must be attributed to the intramolecular interaction between the N–H group and the π-electron, no matter which ring carries the substituent. The mechanism of the interaction must also be common in both series of compounds and will satisfy the following conditions. 1) The larger the σ constant, the

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[9] M. St. C. Flett, *Trans. Faraday Soc.*, **40**, 767 (1944); S. Califano and R. Mocca, *Gazz. chim. ital.*, **86**, 1014 (1956); P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc.*, **A243**, 143 (1957).

smaller is the $\Delta\nu_{max}$, when the benzene ring (ring B), which carries the N–H group, bears the substituent. In the case of the substituent involved in ring A, $\Delta\nu_{max}$, increases as the σ value increases, as far as the σ value is larger than 0.1. 2) When a substituent of which the σ-constant is less than 0.1 is introduced into ring A, $\Delta\nu_{max}$ changes to a negligible extent, regardless of the substituent.

It must be noticed that condition 1 is just the contrary to the case mentioned in ω-arylalkanols[10], In the case of ω-arylalkanols, the hydrogen atom of the hydroxyl group possesses at least a proton-like character and the increasing electron density in the benzene nucleus favors the interaction. The above considerations lead to an idea that is quite different from that developed for the interaction between the hydroxyl group and π-electrons.

That is, one of the possibilities which will explain the results is the idea of "flow-in" of the electron from the N–H group to ring A. If this idea were taken into consideration, above conditions 1 and 2 would be explained in the following way. The greater the electron-density gap between ring A and the N–H group, the easier the flow of the electron of the latter into the former, as far as the electron density of the N–H group is higher, Thus the force constant of the N–H group is lessened to result in appearance of the N–H band at a lower wave number and also in more $\Delta\nu_{max}$. If the difference of electron densities between ring A and the N–H group approaches zero or the electron density of ring A is higher than that of the latter, the electron of the N–H group does not "flow-out". Then, it will be the field effect that plays the most important role, and $\Delta\nu_{max}$ may appear at the constant wave number, irrespective of the substituent.

Furthermore, if the above assumption is made, it is easier to understand the phenomenon found in *N*-benzylarylamines. When an electron-withdrawing substituent is introduced into ring B, the electron of ring B is attracted to the substituent, hence the electron of the N–H group flows into ring B. The lack of the electron in the N–H group results in a smaller electron-density difference between ring A and the N–H group. This permits the flow of the electron from the N–H group to ring A to a very limited extent, the interaction between π-electron and N–H group becoming weaker. Thus the strength of the interaction or $\Delta\nu_{max}$ may be proportional to σ constant of the substituent, when the substituent is introduced into ring B.

In the above hypothesis, it is assumed, that the interaction takes place as a mere probability. The interaction must be caused by an overlap of the orbitals belonging to the electrons of the N–H group and the π-electrons of ring A. And the overlap of orbitals will occur more easily, when the electron density of ring A is heightened by the presence of an electron-repelling group. Accordingly, the molecular species which has the internal interaction increases when the electron density of ring A is higher, although the electron flows out of the N–H group into ring A.

A support to the above hypothesis is being sought.

The authors are thankful to Professor Y. Urushibara and Professor T. Shimanouchi for their valuable advice and encouragement and to Mr. H. Iwamura for his technical assistance. The authors are also indebted to the Ministry of Education for the Grant in Aid for the Fundamental Scientific Research.

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[10] M. Ōki and H. Iwamura, This Bulletin, 32, 1135 (1959).