BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 809—813 (1966)

The Intramolecular Interaction between the N-H Group and π-Electrons. IV.[1] The Energetics of the Interaction[2]

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(Received September 17, 1965)

The thermodynamic parameters for the intramolecular interaction between the N-H group and the π-electrons in *N*-benzylanilines were determined from the temperature dependence of the N-H stretching absorptions. A comparison of the $-\Delta H$'s with those for the O-H···π interaction indicates that there is no appreciable difference between the interactions involving the N-H and the O-H groups. The $-\Delta H$'s are less than 2 kcal./mol., this figure being considered to be a borderline differentiating the X-H···π interaction from the ordinary hydrogen bond. The wave number shift accompanying the interaction cannot be a measure of the $-\Delta H$ in the N-H group, nor be indicative of the difference between two groups. The $-\Delta H$ was found to be closely related with the equilibrium constant in these derivatives.

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[1] Part III of this series: This Bulletin, **38**, 393 (1965).

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

In the previous papers of this series,1),3) the existence of the interaction of the N–H group with π-electrons in *N*-(ω-phenylalkyl)anilines has been confirmed. A comparison of the chain lengths which permit the X–H$\cdots\pi$ interaction has shown that the N–H$\cdots\pi$ interaction is favored over the O–H$\cdots\pi$ interaction, contrary to the general expectation. Although this was presumed to be due mainly to the steric requirement of the phenyl group attached to the N–H nitrogen, it seemed that it would be interesting to compare the other characteristics of the interactions which involve the O–H and the N–H groups. The thermodynamic parameters are the most directly connected, and so they are most appropriate objects of comaprison. Thus the present paper is concerned with the determination of such parameters, on the basis of which the differences or the similarities of the two interactions may be discussed.

Experimental

Spectral Measurements.—A Perkin-Elmer, model 112G, double-pass high-precision grating infrared spectrometer, as has been described previously,3) was used. A carbon tetrachloride solution of a sample (ca. 0.004 mol./l.) was placed in a quartz cell (2 cm. long) covered with a heating coil protected with asbestos. The temperature of the solution was controlled by varying the current through the heating coil; the temperature was kept at each equilibrated temperature within an accuracy of 0.3°C and was read by a thermometer dipped in the solution. The spectrometer being of a single-beam type, a background trace was recorded every time immediately before or after scanning with the solution.

Calculation.—The band obtained was separated into its components and their integral intensities were calculated in a manner described before.3) The observed system can be regarded as being in the equilibrium expressed by Eq. 1, where K is an equilibrium constant:

$$\text{Free form} \overset{K}{\rightleftarrows} \text{Interacting form} \tag{1}$$

Therefore, the well-known van't Hoff equation (2) can be used to obtain the energy difference between the two forms:

$$\ln K = \frac{\varDelta H}{\boldsymbol{R}T} + \frac{\varDelta S}{\boldsymbol{R}} \tag{2}$$

K is given by spectral measurements:

$$K = \frac{c_i}{c_f} = \frac{A_i/a_i}{A_f/a_f} = \frac{a\cdot A_i}{A_f} \tag{3}$$

where a_i and a_f represent the intensities per molecule for the interacting and the free N–H group respectively; a, their ratio, and the A's, the integrated intensities of each form.

By combining Eq. 2 with Eq. 3, Eq. 4 is obtained:

$$\ln\frac{A_i}{A_f} = \frac{-\varDelta H}{\boldsymbol{R}T} + \left(\frac{\varDelta S}{\boldsymbol{R}} - \ln a\right) \tag{4}$$

Assuming that a_i and a_f, or their ratio, a, are independent of the temperature, at least within the 20—70°C range, the interaction energy ($-\varDelta H$) can be determined from the slope of the $\ln(A_i/A_f)$ vs. $1/T$ polt by the least-squares treatment.

Results and Discussion

The effect of the temperature on the N–H stretching frequencies and the intensities of *N*-benzylanilines are summarized in Table I through V.

Some slight changes in the spectral characteristics with the temperature are observed. For instance, $\varDelta\nu_{max}$ (the wave number shift accompanying the interaction) has a tendency to decrease with an increase in the temperature, though the shift is indefinite. The total integral intensity (A_i+A_f) also decreases. The latter phenomenon may be mainly due to the thermal expansion of the solvent, the effect resulting in a decrease of the concentration.

The spectrum of the *p*-nitro derivative (Table V) behaves unusually; the $\log(A_i/A_f)$ changes irregularly with the temperature, and a new, third band appears at a higher temperature, as shown in Fig. 1.4) The experiment was repeated twice for this case; the results were qualitatively similar, as is shown in Fig. 2 (the data given in Table V are those of one case). It may be supposed that the compound which is rather unstable in a solution would react with the solvent carbon tetrachloride, and that the product at this reaction would be the origin of the new band. However, the room temperature spectrum of the solution which had been heated to a high temperature showed no appreciable difference from that before heating.

For the origin of the new band at the high temperature, there are several possibilities: 1) the appearance of a new conformer, one which is unstable at room temperature; 2) the existence of a new product from the solute and the solvent which is

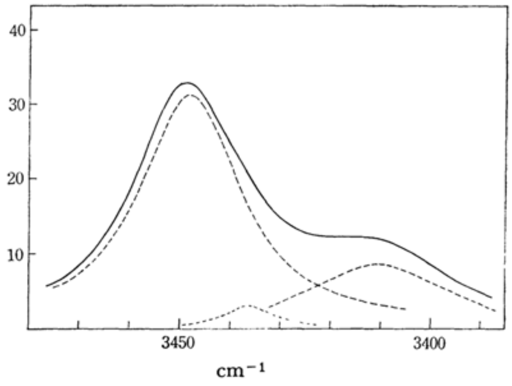

Fig. 1. $\nu_{\text{N-H}}$ Absorption of *N*-(*p*-nitrobenzyl)aniline at 74°C.

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3) M· Ōki and K. Mutai, This Bulletin, **38**, 387 (1965).

4) It is assumed that the curves are expressed by Lorentzian equation. This assumption is hold throughout this paper.

THE EFFECT OF THE TEMPERATURE ON ν_{N-H}'S OF BENZYLANILINES

TABLE I. *N*-(*p*-DIMETHYLAMINOBENZYL)ANILINE

Temperature $1/T\times10^3$ (°K^{-1})	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	$\ln(A_i/A_f)$
3.38	3448.7 3418.2	30.5	24.2 27.6	1.30 3.14	0.878
3.18	3450.8 3419.8	31.0	26.6 24.8	1.43 2.86	0.695
3.03	3449.5 3418.8	30.7	26.4 24.4	1.53 2.64	0.548
2.90	3448.8 3419.5	29.3	31.4 26.6	1.60 2.58	0.475

TABLE II. *N*-(*p*-METHOXYBENZYL)ANILINE

Temperature $1/T\times10^3$ (°K^{-1})	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	$\ln(A_i/A_f)$
3.34	3450.2 3418.6	31.6	28.6 29.2	2.16 2.70	0.223
3.18	3449.7 3418.5	31.2	26.6 26.4	1.87 2.19	0.161
3.03	3449.1 3418.4	30.7	27.6 24.8	1.87 1.99	0.079
2.91	3448.1 3417.9	30.2	30.8 26.2	1.94 1.98	0.018

TABLE III. *N*-BENZYLANILINE

Temperature $1/T\times10^3$ (°K^{-1})	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	$\ln(A_i/A_f)$
3.34	3449.4 3417.7	31.7	26.4 27.0	2.03 1.99	−0.018
3.22	3448.9 3417.4	31.5	25.8 26.0	2.18 2.07	−0.055
3.10	3448.5 3417.3	31.2	27.4 26.2	2.22 2.02	−0.092
3.01	3448.1 3418.0	30.1	27.2 24.0	2.10 1.77	−0.154
2.89	3448.2 3417.2	31.0	28.4 24.0	2.18 1.81	−0.186

TABLE IV. *N*-(*m*-CHLOROBENZYL)ANILINE

Temperature $1/T\times10^3$ (°K^{-1})	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	$\ln(A_i/A_f)$
3.35	3449.0 3413.2	35.8	28.2 34.2	2.93 2.11	−0.324
3.18	3448.4 3413.5	34.9	26.8 29.8	2.63 1.84	−0.354
3.06	3448.3 3413.3	35.0	27.6 30.2	2.66 1.83	−0.370
2.92	3448.4 3413.3	35.1	28.8 30.4	2.61 1.74	−0.405

TABLE V. *N*-(*p*-NITROBENZYL)ANILINE

Temperature $1/T\times10^3$ (°K^{-1})	ν_{max} cm^{-1}	$\Delta\nu_{max}$ cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-3}$ mol^{-1} l. cm^{-2}	$\ln(A_i/A_f)$
3.32	3448.9 3410.5	38.4	24.6 36.0	3.57 1.25	−1.04
3.18	3448.9 3410.9	38.0	24.6 37.0	3.32 1.24	−0.984
3.06	3448.4 3432.1 3410.3	38.1	23.4 18.0 32.4	3.21 0.12 1.10	−1.10 (−1.07)*
2.88	3448.2 3436.3 3410.2	38.0	24.4 12.6 33.0	2.75 0.13 1.03	−1.03 (−0.981)*

* The values in parentheses are those calculated by ignoring the intensity of a new band at ca. 3432—3436 cm^{-1}.

Table VI. Thermodynamic parameters of N-benzylanilines. $RC_6H_4CH_2NHC_6H_5$

Substituent, R	$-\Delta H$, kcal./mol.	$\Delta S/R-\ln a$	$\Delta\nu_{max}$,[a] cm^{-1}	$\ln(A_i/A_f)$[c] (at 300°K)
p-Me_2N	1.69 ± 0.07	-2.01 ± 0.12	30.4	0.828
p-MeO	0.96 ± 0.03	-1.38 ± 0.05	30.9	0.226
H	0.77 ± 0.04	-1.31 ± 0.07	31.1	−0.014
m-Cl	0.35 ± 0.03	-0.93 ± 0.04	35.2	−0.331
p-NO_2	0.02 ± 0.12[b]	-1.06 ± 0.19[b]	38.1	−1.028

a) Average of the values at various temperatures.
b) Calculated from the data of two runs.
c) Read from the line of $\ln(A_i/A_f)$ vs. $1/T$ plot drawn by least-squares treatment.

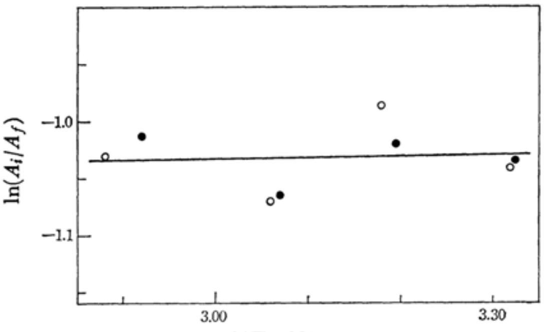

Fig. 2 Intensity ratios of N-(p-nitrobenzyl)aniline at various temperatures. Filled and open circles show the values of two runs.

only present at the higher temperature; 3) a change in the absorption curve shape which allows a third band to find its place as a result of the somewhat indefinite calculation method (the trial and error method), etc. The band intensity, however, is very small, the position of its maximum is uncertain, and its existence is much limited by the compound and the temperature. Therefore, the authors have not yet tried to make a choice among the possibilities. It is difficult to determine whether the third band should be classified as the interacting or the free form, but it was temporarily assumed to be the free form. At any rate, the classification matters little to the intensity ratio.

Table VI summarizes the thermodynamic parameters obtained by applying Eq. 4 to the data in Tables I through V.

In Table VI it may be seen that the $-\Delta H$ values are all smaller than that for the ordinary hydrogen bond, which is more than 2 kcal./mol. In this connection it is interesting and significant that the N–H group is similar to the O–H group[5),6)] in the intramolecular interaction with π-electrons. The interaction energy ($-\Delta H$) of both groups is generally less than 2 kcal./mol., this small ΔH value may be the best criterion for differentiating the X–H$\cdots\pi$ interaction from the ordinary hydrogen bonding, not only for the O–H group but also for the N–H group.

In this connection, it would be interesting to examine the thermodynamic data for the intermolecular N–H$\cdots\pi$ interaction. Recently Whetsel and Lady[7)] reported that the energies of the intermolecular N–H$\cdots\pi$ interactions in N-methylaniline - benzene and aniline - benzene systems were 1.5 and 1.6 kcal./mol. respectively, the value being again in the range for X–H$\cdots\pi$ interaction. They also reported that the C–H$\cdots\pi$ interaction energy in a chloroform - benzene system was 2 kcal./mol. In conclusion, all the data so far available confirm the above criterion to be reliable. The small $-\Delta H$ values are probably due to the weak electron-donating power of the π-electron system of benzene.

With these values in mind, it may be easily explained why Moritz[8)] could not find any detectable change in the N–H stretching bands of N-benzylaniline with a varying temperature. Generally a small intensity change accompanying a small $-\Delta H$ is difficult to detect, especially when it is not the extinction coefficient but the half-band width that determines the value of the integral intensity.

In view of the $-\Delta H$ values and the frequency shifts ($\Delta\nu_{max}$) in Table VI, it is evident that there is no generally supposed linear relationship between the two. On the contrary, a large $-\Delta H$ value is accompanied by a small $\Delta\nu_{max}$ value (for instance, the $-\Delta H$ of the p-dimethylamino derivative is 1.7 kcal./mol. and the $\Delta\nu_{max}$, 30.4 cm^{-1}, whereas the $-\Delta H$ and $\Delta\nu_{max}$ of p-nitro derivatives are nearly zero and 38.1 cm^{-1} respectively). It should be emphasized that this anomaly is observed in a group of substituted benzylanilines, since in this group of compounds steric, electronic and other factors are nearly equal, and it may generally be expected that the stretching frequency of the N–H group would be predominantly affected by the strength of the interaction, namely, the energy of the interaction, $-\Delta H$. Considering this anomaly, it sould not be safe to discuss the interaction energies by using the $\Delta\nu_{max}$ value only.

On the other hand, the energy is closely related to the intensity ratio. As may be seen in Fig. 3,

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5) M. Ōki and H. Iwamura, This Bulletin, **33**, 717 (1960).
6) M. Ōki and H. Iwamura, ibid., **33**, 1600 (1960).
7) K. B. Whetsel and J. H. Lady, *J. Phys. Chem.*, **69**, 1596 (1965).
8) A. G. Moritz, *Spectrochim. Acta*, **16**, 1176 (1960).

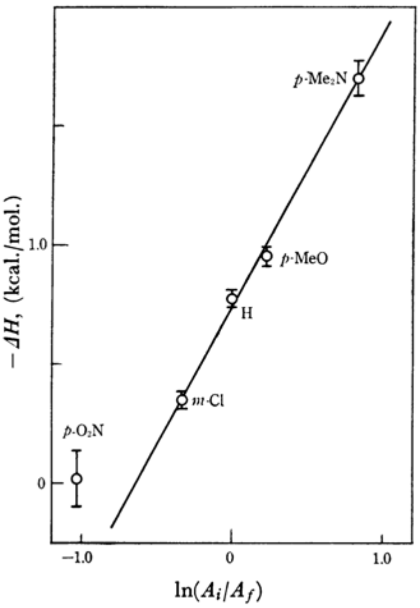

Fig. 3. Relation of $\ln(A_i/A_f)$ with interaction energy ($-\Delta H$).

a plot of $-\Delta H$ against $\ln(A_i/A_f)$ shows a linear correlation, except for the value for the *p*-nitro derivative. In this group of compounds, it may safely be said that the equilibrium constant, *K*, is affected mainly by $-\Delta H$, with some part compensated for by the entropy.

The entropy change of the interaction (ΔS) could not be determined, because we do not know the *a* value. Strictly speaking, for the calculation of the entropy change another standard band, common in frequency and in molecular absorption coefficient with both interacting and free forms, must be used together with these two bands.[9] The value, $\Delta S/R-\ln a$, obtained as an intercept from the plot is, therefore, only a rough measure of the true ΔS, and no fruitful discussion can be expected from these data.

The $-\Delta H$ value of *p*-nitro derivative is nearly zero, and there remains a possibility of its being negative (ΔH is positive). This possibility is also supported by extending the line of the $-\Delta H$ vs. $\ln(A_i/A_f)$ plot (see Fig. 3), though the value obtained is obscured by large errors. Taking this into account, together with the N–H···π interaction which will cause some stability, it is suggested that there are some factors other than the N–H···π interaction which affects the total energy. The problem seems to be closely connected with the conformations of the two forms. An explanation for this phenomenon will be published in a forthcoming paper.

The authors are indebted to Professor Yoshiyuki Urushibara and Professor Takehiko Shimanouchi for their valuable discussions and encouragement. They are also indebted to the Ministry of Education for a grant-in-aid for Fundamental Scientific Research.

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[9] S. Mizushima, T. Shimanouchi, K. Kuratani and T. Miyazawa, *J. Am. Chem. Soc.*, **74**, 1378 (1952).