2696 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (11), 2696—2698 (1974) [Vol. 47, No. 11

Enthalpies of Hydrogen Bond Formation between Diphenylamines and Dimethyl Sulfoxide

Minoru HIROTA, Kazumasa SHINOZUKA, and Yoshiki HAMADA*
Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama 233
**Department of Pharmacy, Meijo University, Showa-ku, Nagoya 468*

(Received May 21, 1974)

Enthalpies of hydrogen bond formation for the diphenylamine–dimethyl sulfoxide systems were determined by infrared spectroscopic method. The ΔH values for 4-methoxy, 4-methyl, unsubstituted, 3-methoxy, 3-chloro, 3-nitro, and 4-nitro-diphenylamines are −9.6, −10.1, −11.1, −11.2, −12.8, −13.9, and −13.9 kJ mol^{-1}, respectively. The substituent effects are discussed in relation with those on N–H stretching frequencies.

N–H stretching absorptions of amines and amides have been investigated extensively, and a large number of reports were published by many authors.[1–10] The substituent effects on the N–H stretching frequencies were also investigated and were correlated with the Hammett's σ-constants. The N–H frequencies of the substituted anilines and *N*-methylanilines increase as the σ-constants increase.[2] However, the trend of the N–H frequency shift in these amines is reversed when the N–H groups are in substituted amides.[6] The reversed gradients of the Hammett plots in the substituted aniline and the amide series could be interpreted by taking into accounts the change in hybridization of the nitrogen atoms in these series of compounds.[10] Anilines were proved to exist as a non-planar conformation from the dipole moment measurement,[11] and this provides an evidence for the sp^3-like hybridization of the nitrogen atom. On the other hand, the planar sp^2 hybridization is evident for the amide nitrogen atom. Thus, it is of interest to investigate whether the nitrogen atom takes a planar (sp^2) or a non-planar (sp^3-like) hybridization in diphenylamines. The recent investigations of the present authors have provided an evidence for the fact that the diphenylamines with electron-donating substituents are still non-planar but those with electron-withdrawing substituents, such as the nitro group, take planar conformations at the nitrogen atoms.[10,12] On the contrary, the proton chemical shifts of the diphenylamines exhibit a normal σ-constant *vs.* chemical shift plot and this means that the electron density on the imino hydrogen atom decreases linearly with the substituent constant. This, in turn, implies that the hydrogen donating power of the imino group increases linearly with the increase in σ-values when the imino group participates in a hydrogen bond. Thus, in spite of the anomalous ν_{N-H} *vs.* σ plot, the hydrogen bond shift ($\Delta\nu$) and the enthalpy of hydrogen bond formation might increase linearly with increasing σ-value.

To examine the above conclusions experimentally, the intermolecular hydrogen bonding between the diphenylamines and dimethyl sulfoxide was investigated by the infrared spectroscopic method. Since diphenylamines are rather weak proton donor, a strong proton acceptor is chosen so as to keep an enough amount of the associated species to determine the formation constant of the hydrogen-bonded complex at an enough low concentration to prevent the effect of the self-association of the amine.

Experimental

The infrared N–H stretching spectra were recorded with a Hitachi Model 225 grating infrared spectrophotometer, and the absorption frequencies were calibrated by the absorption bands of water vapor at 3447.09 and 3442.41 cm^{-1} in order to keep the accuracy of the wavenumber within 0.5 cm^{-1}. The measurements were carried out on the ternary diphenylamine–dimethyl sulfoxide–carbon tetrachloride system at the temperatures ranging from 280 to 330 K. Throughout each measurement, the temperature of the solution was kept sufficiently constant. (The temperature variation was kept within 0.5 K). The enthalpy of hydrogen bond formation was calculated by plotting logarithms of the intensity ratios of the N–H stretching bands arisen from the free and the hydrogen-bonded species of diphenylamine ($\varepsilon_b/\varepsilon_f$) against the reciprocals of the temperatures ($1/T$).

The diphenylamines were prepared by the known methods[13–16] and carefully purified either by distillation or by recrystallization.

Results and Discussion

After several preliminary experiments on the association between diphenylamine and some hydrogen acceptors (namely acetone, dimethylformamide, diethyl ether, and dimethyl sulfoxide), dimethyl sulfoxide was chosen as an appropriate hydrogen acceptor to investigate, the substituent effect on the hydrogen-donating power of diphenylamines. In diphenylamine (0.005 mol l^{-1})–dimethyl sulfoxide (0.1 mol l^{-1})–carbon tetrachloride systems, the N–H stretching absorptions of the

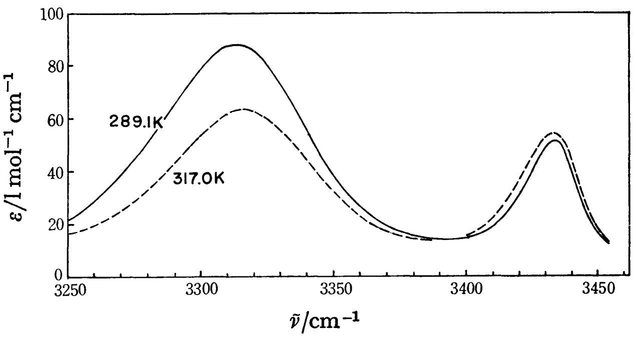

Fig. 1. N–H Stretching absorptions of diphenylamine measured at two temperatures (289.1 K and 317.0 K). The band at 3436 cm^{-1} is assigned to the free species of the amine, and the one at 3314 cm^{-1} to the species associated with dimethyl sulfoxide.

free and the hydrogen-bonded species of diphenylamine are fortunately located separately in the spectra as shown in Fig. 1.

This allows us to use the absorbance to evaluate the amounts of the free and the hydrogen-bonded species without tedious process to separate the two overlapping bands to obtain the integrated intensities. The ratio of the absorbances of the free and the hydrogen-bonded species ($\varepsilon_b/\varepsilon_f$) was determined at various temperatures ranging from 280 to 330 K, and the enthalpy of the hydrogen-bond formation was estimated from the temperature dependence of the equilibrium constant which is assumed to be proportional to $\varepsilon_b/\varepsilon_f$. An example of $\log(\varepsilon_b/\varepsilon_f)$ *vs.* T^{-1} plots is shown in Fig. 2. As the plot can be approximated by a straight line, the enthalpy is estimated from its slope. The results are shown in Table 1 together with the hydrogen bond shifts $\Delta\nu$ which are defined by the equation $\Delta\nu = \nu_f - \nu_b$, where ν_f and ν_b are the NH stretching frequencies of the free and the hydrogen-bonded species of diphenylamines.

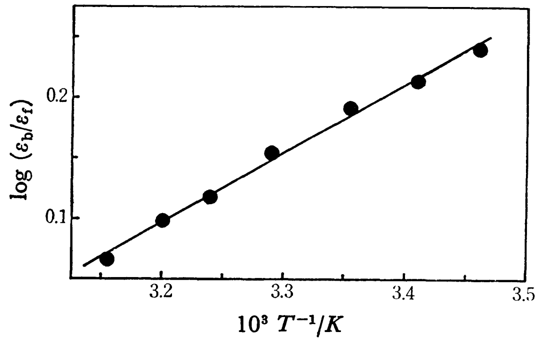

Fig. 2. The temperature dependence of the N–H band intensities of the free and the hydrogen-bonded species of diphenylamine presented as the log ($\varepsilon_b/\varepsilon_f$) *vs.* T^{-1} plot.

Table 1. Hydrogen bond shifts and enthalpies of hydrogen bond formation for diphenylamine–dimethyl sulfoxide–CCl_4 systems

Diphenylamine	ν_{NH}		$\Delta\nu/\mathrm{cm}^{-1}$	$-\Delta H/\mathrm{kJ\cdot mol^{-1}}$
	ν_f/cm^{-1}	ν_b/cm^{-1}		
4-Methoxy	3432	3320	112	9.6±0.6
4-Methyl	3433	3317	116	10.1±0.6
Unsubstituted	3436	3314	122	11.1±0.6
3-Methoxy	3435	3314	121	11.2±0.8
3-Chloro	3433	3308	125	12.8±1.0
3-Nitro	3433	3301	132	13.9±0.6
4-Nitro	3430	3286	144	13.9±0.6

In order to examine the substituent effect, the enthalpies and the hydrogen bond shifts were plotted against σ values and shown in Figs. 3 and 4, respectively. As expected, the linear relations were observed for both $\Delta\nu$ *vs.* σ and ΔH *vs.* σ plots. This shows that the hydrogen-donating abilities of the diphenylamines increase with the increase in σ values. The result agrees with the substituent effect observed in the series of phenols,

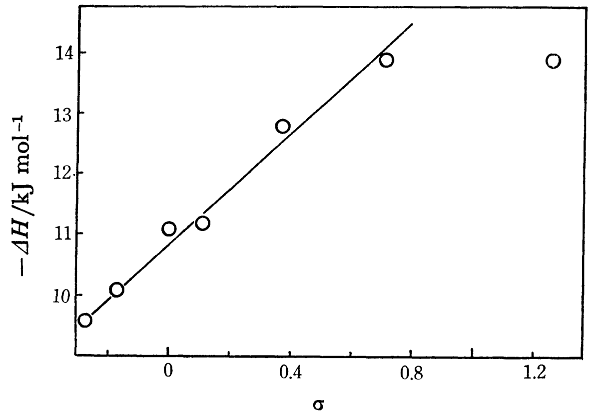

Fig. 3. The ΔH *vs.* σ plot.

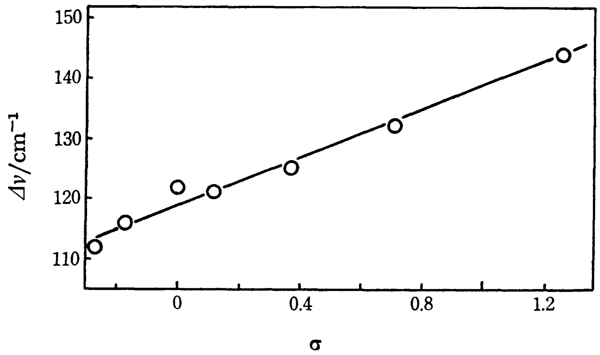

Fig. 4. The $\Delta\nu$ *vs.* σ plot.

The substituent effect on the enthalpies results from the change in acidities of the diphenylamines. In general, a stronger acid forms a stronger hydrogen bond when other conditions are similar. From the electrostatic point of view, this phenomenon is explained that the larger N–H dipole of a diphenylamine carrying an electron-withdrawing substituent attracts more intensely the S–O dipole of dimethyl sulfoxide. By the concept of the charge transfer interaction, the results are interpreted as follows. Lower electron density on the N–H group stablizes its anti-bonding σ^*-orbital, and then the unshared electrons of the proton acceptor can interact more easily with the σ^*-orbital. Hence, the stronger hydrogen bond is formed when the substituent on the diphenylamine is more electron attracting.[19]

The hybridization of the imino nitrogen atom changes so as to increase the s-character of the nitrogen orbital when the substituent becomes more electronegative. As the s-character of the N atomic orbital increases, the resulting N–H molecular orbitals tend to be lower in energy. This again favors for the hydrogen bond formation. Somewhat convex curvatures of the plots may be caused by the reinforced effect of the electronegativity and the hybridization in the negative σ region. However, further investigation is necessary to estimate their effect separately. A considerable deviation from the line is observed with 4-nitrodiphenylamine, and this may be attributed to the strong conjugation between the nitrophenyl and the imino groups which enforces the both groups planar, Enthalpies of hydrogen bond formation of the unsubstituted diphenylamine have been measured by several authors employing various hydrogen acceptors. Among the hydrogen acceptors investigated, triethylamine forms the strongest hydrogen bond of which enthalpy is estimated to be $-18.8\,\mathrm{kJ\,mol^{-1}}$. The N–H···O hydrogen bond of diphenylamine is by far weaker. The enthalpies of formation were reported to be -10.0, -10.5, and $-11.7\,\mathrm{kJ\,mol^{-1}}$, respectively, when the acceptors are dioxane, acetone, and methyl acetate.[17,18)] Thus, the results of the present authors seem to be consistent with the previous reports. The hydrogen bonding of substituted diphenylamines has never been reported.

The present investigation was partly supported by a Scientific Research Grant from the Ministry of Education of Japan for which the authors are grateful.

References

1) H. C. Flett, *J. Soc. Dye. Colour.*, **68**, 59 (1952).

2) D. Hadzi, "Infrared Spectroscopy and Molecular Structure," ed. by M. Davies (1962), p. 236.

3) T. L. Brown, *J. Phys. Chem.*, **61**, 820 (1957).

4) P. J. Krueger, *Can. J. Chem.*, **40**, 2300 (1962).

5) P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc. Ser. A*, **243**, 143 (1957).

6) H. W. Thompson and D. A. Jameson, *Spectrochim. Acta*, **13**, 236 (1958).

7) J. Itier and A. Casadevall, *Bull. Soc. Chim. Fr.*, **1969**, 2342, 2355, and 3523.

8) M. G. W. Bell, M. Day, and A. T. Peters, *J. Chem. Soc., C*, **1967**, 132.

9) H. Levitsky, G. Norwitz, and D. E. Chasan, *Appl. Spectroscopy*, **22**, 493 (1968).

10) M. Kasai, M. Hirota, Y. Hamada, and H. Matsuoka, *Tetrahedron*, **29**, 267 (1973).

11) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1936**, 599.

12) T. Mizuno, M. Hirota, Y. Hamada, and Y. Ito, *Tetrahedron*, **27**, 6011 (1971).

13) V. Merz and W. Weith, *Ber.*, **13**, 1299 (1880); **14**, 2345 (1881).

14) F. Ullmann and R. Dahrmen, *ibid.*, **41**, 3477 (1908).

15) R. Willstatter and H. Kubli, *ibid.*, **42**, 4138 (1909).

16) A. V. Iogansen, G. A. Kurkchi, and B. V. Rassadin, *Zh. Prikl. Spektrosk.*, **11**, 1054 (1969).

17) A. E. Lutskii, A. A. Axtyrskaya, and V. N. Konel'skaya, *Zh. Obshch. Khim.*, **42**, 1827 (1972).

18) S. F. Bureiko and G. S. Denisov, *Zh. Prikl. Spektrosk.*, **14**, 276 (1971).

19) On the importance of the charge transfer contribution in hydrogen bonding, see a) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971) and b) S. Bratoz, *Advan. Quantum Chem.*, **3**, 209 (1966).