USE OF INFRARED ABSORPTION SPECTRA TO MEASURE THE ENERGY OF THE HYDROGEN BOND FORMED BY SECONDARY AMINES AS PROTON DONORS AND ACCEPTORS

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UDC 543.42

In using IR spectroscopy to study the role of hydrogen bonding in the proton transition during isotopic exchange reactions of hydrogen in liquid systems [1], there arose the problem of making a quantitative estimate of the changes in the proton-donating and proton-accepting capacity of XH functional groups in a number of compounds of similar structure. The present investigation was conducted to determine the thermodynamic parameters, particularly the energy of hydrogen bonds involving participation of the NH group, in the secondary amine series, where this group serves both as a proton donor (NH. . . Y bonding) and a proton acceptor (XH. . . N bonding).

The secondary amine series selected consisted of the aliphatic amines $(C_2H_5)_2NH$, $(C_3H_7)NH$, (iso-$C_4H_9)NH$, and $(C_6H_5 \cdot CH_2)_2NH$ and the aromatic amines $C_6H_5NHCH_3$, $C_6H_5NHC_2H_5$, and $(C_6H_5)_2NH$. Use of these series makes it possible to examine the influence on the properties of the NH functional group of changes in the structure of its electron cloud produced by changes in hydrocarbon-chain length. An increase in the number of methyl groups, which have a positive inductive effect [2], should cause deformation of the electron cloud of the NH group; the resultant intensified proton screening should be accompanied by a reduction in the proton-donating capacity of the functional group and an increase in its proton-accepting capacity. The ionization potentials of molecules are very helpful for characterizing their capacity for hydrogen bonding. Comparison of the proton-accepting properties of compounds with their ionization potentials shows that, in most cases, acceptor properties are more effective as the ionization potential decreases. The ionization potentials of the secondary amines we studied, $I = 8.24$ eV for $(CH_3)_2NH$, 8.01 eV for $(C_2H_5)_2NH$, 7.84 eV for $(C_3H_7)_2NH$, and 7.69 eV for $(C_4H_9)_2NH$ in the aliphatic series [3] and 7.40 eV for $(C_6H_5)_2NH$ and 7.34 eV for $C_6H_5NHCH_3$ in the aromatic series [4], conform to the above hypothesis.

The many studies that have been made of hydrogen bonding of amines by IR spectroscopy have dealt primarily with the change in the spectroscopic characteristics of the substances investigated (the displacement of the associate band with respect to the monomer band after bond formation, the changes in band intensity and half-width, etc.). Thus, a study of the shifts in the NH band of amines in acetone and pyridine [5] showed that proton-donating capacity decreases over the series diphenylamine > methylaniline > ethylaniline in aromatic amines and over the series dibenzylamine > diethylamine in aliphatic amines. Various authors [6-8] reached similar conclusions for aromatic amines. It follows from the data of Pullin and Werner [9] that the displacement and intensity of the νNH band of the associate produced by formation of an NH. . . O=C hydrogen bond increase over the series dialkylamines < N-alkylanilines < diphenylamine. The opposite tendency, i.e., toward an increase in association constant with increasing radical length, was noted in a study of the proton-accepting capacity of trialkylamines from their NMR spectra [10]. The hydrogen-bond energies ΔH for different proton donors and acceptors have been determined in individual cases; thus, it has been shown [8] that the ΔH of the NH. . . N bond to triethylamine is greater for $(C_6H_5)_2NH$ than for $C_6H_5NHC_2H_5$. So far as we know, however, there has been no systematic examination of the donor and acceptor capacities of the NH group in successive series of secondary amines.

Our investigation was conducted with solutions in an inert solvent (CCl_4) containing component concentrations such as to completely preclude the possibility of self-association, as was demonstrated experimentally. The proton acceptor for the entire series of amines was one of the strongest acceptors,

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Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 14, No. 2, pp. 276-281, February, 1971. Original article submitted September 26, 1969; revision submitted June 8, 1970.

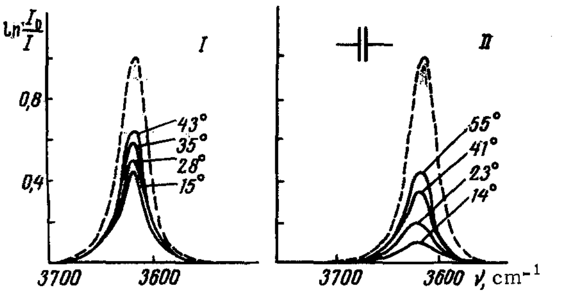

Fig. 1

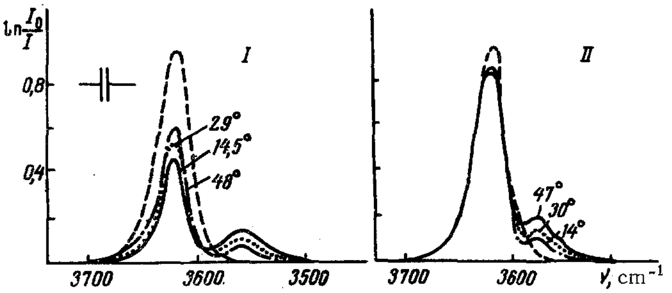

Fig. 2

Fig. 1. Change in νOH band of monomer with temperature in systems consisting of $H(CF_2)_4CH_2OH$ + aliphatic amine in CCl_4. I) $(C_6H_5 \cdot CH_2)_2NH$; II) $(C_3H_7)_2NH$ (the dash line represents the νOH of 0.001 M alcohol solution in CCl_4).

Fig. 2. Change in νOH band of monomer with temperature in systems consisting of $H(CF_2)_4CH_2OH$ + aromatic amine in CCl_4. I) $C_6H_5NHCH_3$; II) $(C_6H_5)_2NH$ (the dash line represents the νOH of 0.001 M alcohol solution in CCl_4).

triethylamine. The proton donor was the fluorinated alcohol $H(CF_2)_4CH_2OH$. The latter was selected because introduction of electronegative fluorine atoms into the alcohol radical causes repulsion of electron density from the functional group and greatly enhances its ability to form a hydrogen bond, serving as a proton donor (OH. . . N), and reduces its proton-accepting capacity, which enables us to avoid formation of an NH. . . O bond, an interfering factor in this case.

The test systems were investigated on the basis of the changes in the valence-vibration absorption bands of the free and bound NH and OH groups with varying temperature. The νOH band of the undissociated alcohol molecule in CCl_4 is represented by the dash line in Figs. 1 and 2 and had the following spectral characteristics: $\nu OH = 3620 \pm 3$ cm^{-1}, a half-width $\Delta\nu_{1/2} = 33 \pm 4$ cm^{-1}, an absorption constant at the band maximum $\varepsilon_0^m = 4700 \pm 100$ liter/mole · cm, and an integral absorption constant $\varepsilon_0^{int} = (1.91 \pm 0.08) \cdot 10^5$ liter/mole · cm^2. The spectra were determined an a UR-20 IR spectrometer and an IKS-11 spectrometer with a PbSe photoresistor cooled with liquid oxygen. The working conditions were selected to produce undistorted absorption bands in each specific case. The temperature-related measurements were made in controlled-temperature cells, using a TS-16 thermostat (over the range 12-70°C); the accuracy of the temperature determinations was ±0.5°C.

Preliminary experiments conducted to find the association constants K of the amine–alcohol systems at room temperature with various component concentrations ($3 \cdot 10^{-4}$-10^{-3} mole/liter of alcohol and 0.04-0.1 mole/liter amine) showed that, within the limits of experimental error, K was independent of the relative compound concentrations (the average values of K are given in Table 1). This enables us to conclude that associates of only one type were formed in the system. In making the temperature measurements to determine ΔH, we selected component concentrations at which there was no self-association and which corresponded to the optimum absorption-band spectral characteristics. Several measurements were made at a given temperature for each system and the average values were then calculated. Figures 1 and 2 show the changes in the νOH band of the unassociated hydroxyl group during formation of an OH. . . N hydrogen bond between the fluorinated alcohol and the aliphatic and aromatic amines. It can be seen that there was a substantial change in band intensity during association and when the system temperature was varied in the case of dialkylamines; the change was far smaller when the amine nitrogen was bound to a benzene ring. The ν_{ass}OH of the systems containing aliphatic amines were not investigated, since these very broad bands ($\Delta\nu_{1/2}$ = 300-400 cm^{-1}) lay in the 2800-3500 cm^{-1} region, overlapping the absorption of the CH and NH groups. The optical density of the maximum of the ν_mOH band was used to determine the monomer concentration (C_m) and the association constant:

$$K = \frac{C_{comp}}{C_m \cdot C_{acc}} = \frac{C_0^{OH} - C_m^{OH}}{C_m^{O}\left(C_0^{NH} - C_m^{OH}\right)} . \qquad (1)$$

Then, proceeding from the well-known relationship between the association constant and hydrogen-bond energy

$$K = A \exp\left(-\frac{\Delta H}{RT}\right) , \qquad (2)$$

TABLE 1. Characteristics of Proton-Accepting Capacity of Secondary Amines in Hydrogen Bond (Concentration of proton donor, $H(CF_2)_4 \cdot CH_2OH$, 0.001 mole/liter)

Amine	C_0^{NH}, mole/liter	Δν, cm^{-1}	$K^{298°}$, liter/mole	$-\Delta H$, kcal/mole	ΔF_0^{298}, kcal/mole	$-\Delta S$, cal/mole · deg
$(C_6H_5 \cdot CH_2)_2NH$	0,075	465	13,7±0,4	6,1±0,3	—1,55±0,05	15±1
$(C_2H_5)_2NH$	0,075	500	55±1	7,8±0,6	—2,37±0,06	18±2
$(C_3H_7)_2NH$	0,075	510	44±1	8,8±0,7	—2,23±0,06	22±2
$(iso\text{-}C_4H_9)_2NH$	0,075	510	49±1	9,3±0,9	—2,30±0,04	24±3
$(C_6H_5)_2NH$	0,1	42	1,3±0,3	1,7±0,3	—0,16±0,04	6±1
$C_6H_5NHCH_3$	0,3	62	2,6±0,3	3,1±0,5	—0,55±0,05	9±2
$C_6H_5NHC_2H_5$	0,3	62	2,7±0,4	3,3±0,4	—0,58±0,07	9±2

the value of ΔH was found graphically (Fig. 3). The data were processed by the method of least squares. In the case of the aromatic amines, where it was possible to make a quantitative measurement from the ν_{ass}OH band, we also determined K from the intensity of this band. It was established that the absorption constants of the ν_mOH and ν_{ass}OH bands were independent of temperature, within the limits of experimental error. The results of independent determinations of K from these two bands were virtually identical. Table 1 gives the thermodynamic parameters of the OH. . . N hydrogen bond: the change in enthalpy ΔH, free energy ΔF, and entropy ΔS, the value of K, the monomer-band displacement, and the experimental conditions. We observed a successive change in all quantities characterizing the strength of the hydrogen bond.

During formation of associates between the alcohol and aromatic amines, hydrogen-bonded complexes of both the OH. . . N and OH. . . amine π-cloud types could be produced. We investigated the spectra of the alcohol–benzene and alcohol–toluene systems with component concentrations comparable to those studied for the amines (10^{-3} mole/liter alcohol and 0.15 mole/liter C_6H_6 or $C_6H_5 \cdot CH_3$). In the vicinity of the νOH bands, we detected very weak low-frequency components displaced with respect to the monomer band by 35 and 30 cm^{-1} for $C_6H_5 \cdot CH_3$ and C_6H_6, respectively. The following values were obtained for the association constants: 0.24 liter/mole for the alcohol–toluene system and 0.17 liter/mole for the alcohol–benzene system (at room temperature). The larger shifts Δν and the fact that the values of K obtained in investigating amine–alcohol association were an order of magnitude larger (Table 1) indicate that we were dealing with an OH. . . N rather than an OH. . . π-bond.

The small hydrogen-bond energy in the $(C_6H_5)_2NH-H(CF_2)_4CH_2OH$ system could not be measured from the changes in the monomer νOH band in the temperature region investigated. The 3620 cm^{-1} band of the unbound alcohol molecules became weaker (Fig. 2, II) when a proton acceptor (diphenylamine) was added, but no temperature-related changes were detected (within the limits of experimental error). In this case, the quantities K and ΔH were determined from the change in the ν_{ass}OH associate band; the monomer and complex bands were separated graphically. A series of experiments conducted at room temperature with different amine and alcohol concentrations yielded the value ε_{ass}^{m} = 6100 ± 100 liter/mole · cm. The Lambert–Beer rule was used to calculate the associate concentration for different temperatures and association constants:

$$K = \frac{C_{ass}}{\left(C_0^{OH} - C_{ass}\right)\left(C_0^{NH} - C_{ass}\right)}. \tag{3}$$

The value obtained for ΔH (Fig. 3, VII) was 1.7 ± 0.3 kcal/mole.

In determining the ΔH of the amines investigated with a given proton acceptor (triethylamine), the optical density at the maximum of the monomer νNH band, D_m, remained constant (within the limits of experimental error) when the temperature was varied, while the optical density of the associate band D_{ass} changed very substantially (Fig. 4). This can be related to the fact that the absorption constant of the complex was considerably greater than that of the monomer [11]. Thus, the ε_{ass}^{m} values for the NH bands of the aliphatic amines were 9.0 ± 0.5, 16 ± 2, 12.0 ± 0.9, and 17.8 ± 0.7 liter/mole · cm for $(C_2H_5)_2NH$, $(C_3H_7)_2NH$, $(iso\text{-}C_4H_9)_2NH$, and $(C_6H_5 \cdot CH_2)_2NH$, respectively, while the ε_0^{m} values were 2.5 ± 0.1, 3.7 ± 0.3, 2.8 ± 0.3, and 4.8 ± 0.3 liter/mole · cm, respectively. The hydrogen-bond energies for all the systems were determined from the dependence of ln D_{ass}/D_m on temperature. Expressing Eq. (1) in terms of the optical densities and absorption constants of the bands, we obtain

$$K = \frac{C_{ass}}{C_m \cdot C_{acc}} = \frac{\varepsilon_0^{m} D_{ass}}{\varepsilon_{ass}^{m} D_m C_{acc}}.$$

TABLE 2. Characteristics of Proton-Donating Capacity of Secondary Amines in Hydrogen Bond

Amine	C_0^{NH}, mole /liter	C_0^{N}, mole /liter	$\Delta\nu$, cm^{-1}	$K^{303°}$, liter /mole	$-\Delta H$, kcal/mole	$\Delta F_0^{303°}$, kcal/mole	$-\Delta S$, cal/mole · deg
$(C_6H_5 \cdot CH_2)_2NH$	0,075	0,75	67	0,30±0,06	2,0±0,4	0,7±0,1	9±2
$(C_2H_5)_2NH$	0,075	0,3	58	0,16±0,04	1,6±0,3	1,1±0,3	9±2
$(C_3H_7)_2NH$	0,075	0,3	48	0,10±0,02	1,3±0,3	1,4±0,3	9±2
$(iso\text{-}C_4H_9)_2NH$	0,075	0,3	46	0,10±0,02	1,2±0,2	1,4±0,3	8±2
$(C_6H_5)_2NH$	0,1	3,0	183	0,6 ±0,1	4,8±0,7	0,30±0,06	17±2
$C_6H_5NHCH_3$	0,15	3,0	151	0,24±0,08	3,7±0,6	0,90±0,30	15±5
$C_6H_5NHC_2H_5$	0,15	3,0	126	0,23±0,03	2,9±0,4	0,90±0,09	12±2

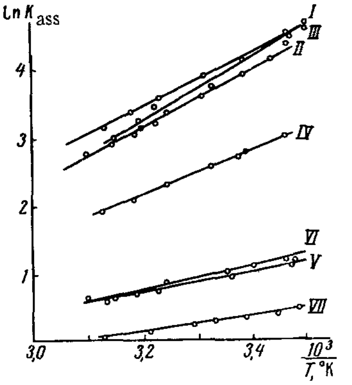

Fig. 3

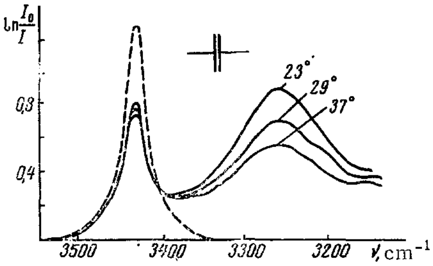

Fig. 4

Fig. 3. Determination of hydrogen-bond energy in alcohol–amine system. I) $(C_2H_5)_2NH$; II) $(C_3H_7)_2NH$; III) $(iso\text{-}C_4H_9)_2NH$; IV) $(C_6H_5 \cdot CH_2)_2NH$; V) $C_6H_5NHCH_3$; VI) $C_6H_5NHC_2H_5$; VII) $(C_6H_5)_2NH$.

Fig. 4. Infrared spectrum of $(C_6H_5)_2NH-(C_2H_5)_3N$ system in CCl_4 at different temperatures.

Hence

$$K = \ln \frac{D_{ass}}{D_m} + \ln \frac{\varepsilon_0^m}{\varepsilon_{ass}^m} - \ln C_{acc} \tag{4}$$

Because of the large excess of proton acceptor in the systems (Table 2), the third term in Eq. (4) can be treated as constant. The second term was also assumed to be independent of temperature. Unfortunately, experimental verification of this assumption was difficult; we could only show that the ε_0^m of the amines investigated was constant over the temperature range studied. Table 2 gives the values found graphically for ΔH and the other thermodynamic and spectral characteristics.

The results obtained show that there is a clear reduction in proton-donating capacity and an increase in proton-accepting capacity as the hydrocarbon radical becomes larger over the series of aliphatic and aromatic amines selected. Our hypothesis that the alkyl group has a positive inductive effect is thus confirmed. As can be seen from Tables 1 and 2, dibenzylamine, in which the two rings are separated from the N atom by methylene (CH_2) groups, has properties intermediate between those of aliphatic (the class to which it belongs) and aromatic amines.

Comparison of the aromatic and aliphatic amines shows that the hydrogen-bond energy of aromatic amines serving a donor function is greater than that of aliphatic amines, while the energy of aromatic amines serving an acceptor function is lower. This pattern can be explained by taking into account the change in the electronic structure of the NH group. In aliphatic amines, the outer electrons of the nitrogen atom have sp^3 hybridization, while those in aromatic amines have almost sp^2 hybridization [12]. In the second case, the free electron pair occupies a pure or almost pure p orbital and is conjugated with the π-electrons of the ring. The degree of electron-cloud asymmetry of the free pair with respect to the nucleus of the N atom determines the efficiency of the interaction. The increase in the degree of asymmetry on moving from aromatic to aliphatic amines leads to an increase in electron density in the vicinity of the free pair. The conjugation of the p orbital with the ring results in development of an effective positive charge on the nitrogen atom. Thus, both the change in hybridization and the presence of conjugation lead to an increase in the proton-donating capacity and a decrease in the proton-accepting capacity of the NH group in aromatic amines, as was confirmed experimentally.

The data obtained show that the consequences of the intermolecular interaction can be explained on the basis of qualitative concepts of the electronic structure of the molecular partners.

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