2. G. N. Zhizhin, V. S. Bannikov, M. A. Moskaleva, et al., Poverkhnost', No. 10, 5-8 (1985).
3. F. Gervais and P. Pirious, J. Phys. C, Solid State Phys., 7, 2374-2379 (1974).
4. Yu. M. Gerbshtein and D. N. Mirlin, Fiz. Tverd. Tela, 16, No. 9, 2584-2588 (1974).
5. E. A. Vinogradov, G. N. Zhizhin, and V. I. Yudson, Surface Polaritons [in Russian], Moscow (1985), pp. 105-131.
6. R. G. Greenler, R. R. Rahn, and J. P. Schwartz, J. Catal., 23, No. 42, 856-858 (1971).
7. V. P. Tolstoi, G. N. Kuznetsova, S. I. Kol'tsov, and V. B. Aleskovskii, Dokl. Akad. Nauk SSSR, 242, No. 2, 373-376 (1978).
8. Surface Physics: Vibrational Spectroscopy of Adsorbates [in Russian], Moscow (1984), p. 246.
9. J. F. Rabolt, M. Jurich, and J. D. Swalen, Appl. Spectrosc., 39, No. 2, 269-272 (1985).
10. R. G. Greenler, J. Chem. Phys., 50, No. 5, 1963-1968 (1969).
11. D. A. Bryan, D. L. Begley, K. Bhasin, et al., Surf. Sci., 57, 53-62 (1976).

INFRARED SPECTRA AND ENERGETICS OF COMPLEXES OF NONAFLUORO-TERT-BUTYLAMINE WITH PROTON ACCEPTORS

G. S. Denisov, L. A. Kuzina, and A. L. Smolyanskii

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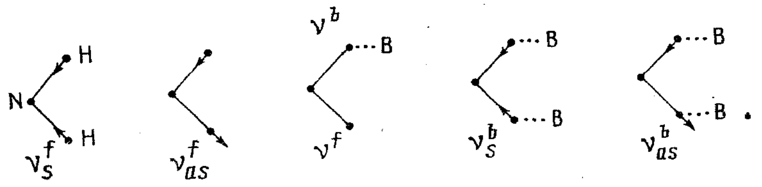
Primary and secondary aliphatic amines can play the role of proton donors and acceptors in a hydrogen bond, forming complexes of type NH...B and AH...N, as well as selfassociates with the NH...N bond. The proton-donor ability of the NH group in aliphatic amines is low. Studies on the NH...B hydrogen bond from the vibrational spectra are complicated due to the low intensity of νNH bands, and the number of such investigations is small [1-5]. There are good prospects for studying the structure and energetics of complexes with the NH...B bond using fluorinated amines, in which the proton-donor ability of the NH group is considerably increased due to the influence of the electronegative fluorine atoms. In the case of primary amines, two types of complexes with proton acceptors, with the participation of one or two NH groups, are possibly formed. In the literature there are papers dealing with the investigation of perturbations during intermolecular interactions of bands of the NH_2 group of trifluoroethylamine $CF_3CH_2NH_2$ [6-8], but no attempts have been made to reveal the spectral characteristics of complexes with a different composition and to evaluate the influence of fluorination on the proton-donor ability of the NH_2 group. In the present article, the results are given of an IR spectral study of the hydrogen bond formed with a proton acceptor by nonafluoro-tert-butylamine $(CF_3)_3CNH_2$ (NFTBA), that probably has the maximum proton-donor ability among the fluorinated aliphatic primary amines. The method for the preparation of NFTBA has already been described in [9]. The spectral parameters of complexes with a 1:1 and 1:2 composition with proton acceptors of different strength have been determined, the energies of the complexes have been measured, and the reciprocal influence of the hydrogen bonds in the 1:2 complex has been evaluated. The types of stretching vibrations of the NH_2 groups and their designations are given according to scheme



Solutions of NFTBA in CCl_4, toluene, acetonitrile, tetrahydrofuran (THF), hexametapol (HMP) and in mixtures of CCl_4 with acceptors have been studied. The investigation was car-

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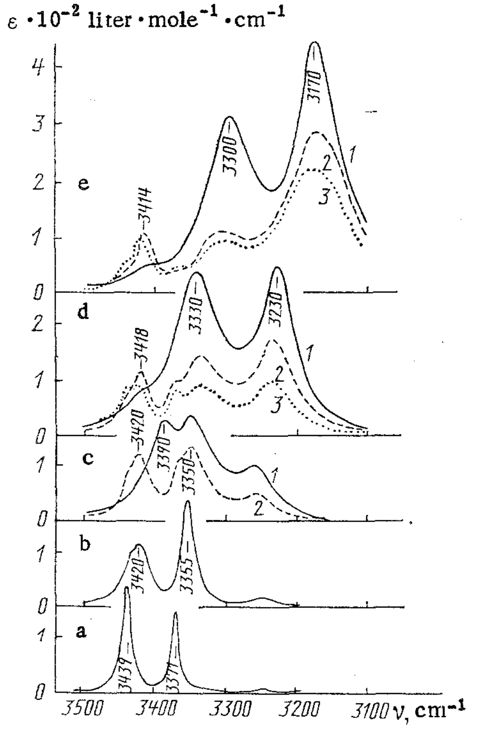

Fig. 1. Spectra of NFTBA solutions in CCl_4 (a), toluene (b), acetonitrile (c), tetrahydrofuran (d), hexametapol (e) — continuous line and in mixtures of CCl_4 with acetonitrile (c), tetrahydrofuran (d), hexametapol (e) — dashed line. Concentration of NFTBA and acceptor, mole/liter: a) 0.2 and 0; b) 0.4 and 9.3; c) 0.4 and 19.0 (1), 1.8 (2); d) 0.2 (1), 0.4 (2, 3), and 12.3 (1), 2.0 (2, 3); e) 0.4 (1), 0.3 (2, 3), and 5.54 (1), 0.88 (2, 3). T = 25 (1, 2) and 72°C (3).

ried out on a UR-20 spectrophotometer, using thermostated cuvettes 0.005-0.5 cm thick for liquids. The spectra were measured in the vibration region of the NH_2 group at temperatures of 25 and 72°C, and the temperature was measured by a copper—constantan thermocouple with an accuracy within ±0.5°C. A solution of proton acceptor in CCl_4 at the same temperature and concentration as for the working solution was placed in the reference channel.

Figure 1 shows the spectra of NFTBA solutions in CCl_4 and proton acceptors and in their mixtures in the νNH_2 bands region. In the spectrum of a solution in CCl_4 (a) bands are observed at $\nu_s{}^f = 3371$ cm^{-1} and $\nu_{as}{}^f = 3439$ cm^{-1} (ε = 140 and 170 liter·mole^{-1}·cm^{-1}), and also a weak band of an overtone of a deformational vibration δ NH_2 at 3250 cm^{-1}. The $\nu_s{}^f$ and $\nu_{as}{}^f$ NH_2 bands in the gaseous phase are shifted by 19 cm^{-1} to the higher frequencies, compared with the case of a solution in CCl_4, and are observed at 3390 and 3459 cm^{-1}. In the spectrum of liquid NFTBA, each of the bands is in the form of a doublet; the high frequency components in the doublets coincide with the frequencies in the gaseous phase and belong to free molecules, while the bands that are shifted by ~15 cm^{-1} to the low frequencies belong to the selfassociates of NFTBA. At NFTBA concentrations lower than 0.3 mole/liter, no self-association was observed, and therefore further work with the NFTBA and proton acceptor solutions was carried out at a concentration that ensured that not more than 0.3 mole/liter of free NFTBA molecule were present in the solution.

On transition to a solution in toluene (Fig. 1b), the ν_s and ν_{as} NH_2 bands are shifted to low frequencies as a result of the formation of NH...π-electrons of the aromatic ring complexes, and are observed at 3355 and 3420 cm^{-1}. The formation of the hydrogen bond leads to 2.2- and 1.3-fold increases in the integral intensities of the ν_s and ν_{as} NH_2 bands, respectively.

When acetonitrile is added to a solution of NFTBA in CCl_4 (Fig. 1c), the band intensity of the free molecules decreases and new bands at 3350 and 3420 cm^{-1} appear. With increase in the acetonitrile concentration, the intensity of the 3420 cm^{-1} band first increases and then begins to decrease, and, simultaneously, a new band appears at 3390 cm^{-1}; the intensity of the 3350 cm^{-1} band thus continues to increase. The band at 3420 cm^{-1} is situated between $\nu_s{}^f$ and $\nu_{as}{}^f$ and can be assigned to ν^f vibration of the free NH-group of the 1:1 complex, and the band at 3390 cm^{-1} to the $\nu_{as}{}^b$ vibration of the 1:2 complex, while the absorption with a maximum at 3350 cm^{-1} possibly corresponds to the strongly overlapping $\nu_s{}^b$ and ν^b bands. There is also a 2δ NH_2 band in the spectrum that is intensified by the Fermi resonance with the stretching vibrations of the complex.

A somewhat different pattern is observed for THF, which is a stronger proton acceptor (Fig. 1d): When even commensurable amounts of THF are introduced into an NFTBA solution,

TABLE 1. Spectral Characteristics of Nonafluoro-tert-butylamine and Its Complexes with Tetrahydrofuran and Hexametapol in a CCl_4 Solution

Acceptor	Vibration	ν, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	$S_0 \cdot 10^{-4}$ (25°C), liter·mole^{-1}·cm^{-2}
—	ν_s^f	3371	15	0.27
	ν_{as}^f	3439	17	0.38
THF	ν^f	3418	26	0.69
	ν_{as}^b	3330	80	2.5
	ν^b ν_s^b	3230	60	— —
HMP	ν^f	3414	26	0.55
	ν_{as}^b	3300	70	2.0
	ν^b ν_s^b	3170	90—110	— —

three new bands appear in the spectrum at 3418, 3330, and 3230 cm^{-1}. With increase in the THF concentration, the intensity of the 3418 cm^{-1} band first increases, and then decreases, while the intensities of the other two bands continue to increase. The band at 3418 cm^{-1}, situated between $\nu_s{}^f$ and $\nu_{as}{}^f$, corresponds to the ν^f vibration of the free NH group of the 1:1 complex, and the 3330 cm^{-1} band to $\nu_{as}{}^b$ vibration of the 1:2 complex. The symmetric $\nu_s{}^b$ vibration of the 1:2 complex and the ν^b vibration fo the bound NH group of the 1:1 complex, with similar frequencies, together form a band at 3230 cm^{-1}. The overtone of the deformational 2δ NH_2 vibration, intensified by the Fermi resonance, probably also contributes to this band. With increase in the temperature of the solution, the band intensity of the free NFTBA molecules increases, while that of the complexes, in particular of the 1:2 complex, decreases (Fig. 1d), i.e., the equilibrium is shifted in the direction of free molecules. The spectral parameters of the NH_2 bands in the NFTBA–THF complexes are given in Table 1.

The spectrum of the NFTBA solution in the presence of HMP is similar (Fig. 1e) and the assignment of bands is the same as for THF (Table 1), but the shifts of the νNH_2 bands as a result of the formation of complexes are larger, because HMP is a stronger proton acceptor than THF.

A comparison of the ν^f frequencies of the free NH group of the 1:1 NFTBA complexes with acetonitrile, THF, and HMP shows that with increase in the proton-acceptor ability of the partner, the ν^f band is shifted to lower frequencies and approaches the νNH frequency of the NHD group of NFTBA. The integral absorption coefficient of the ν^f band thus increases and becomes almost twice as high as the mean value for the $\nu_s{}^f$ and $\nu_{as}{}^f$ bands of the free NFTBA molecules. The νNH band of the 1:1 complex of the semideuterated NFTBA with HMP of the HND...B type lies 6-10 cm^{-1} higher than does the νNH band of the free $(CF_3)_3CNHD$ molecule, and hence the formation of the 1:1 complex leads to increase in the force constant of the free NH bond. (The reason for this behavior of the free NH group band may be a kinematic interaction with the vibrations of the bound NH groups of the 1:1 complex, and also the change in the electron density in the NH_2 fragment as a result of the participation of the second NH group in the hydrogen bond).

To study the influence of the hydrogen bond on other NFTBA bands, spectra of the NFTBA solutions in CCl_4 in the presence of HMP (or HMP-D_9) were recorded in the 400-1700-cm^{-1} region. The δNH_2 band at 1630 cm^{-1} in the complex is shifted to 1635 cm^{-1}, while its width increases more than twofold. The 922 cm^{-1} band ($\varepsilon \sim 200$ liter·mole^{-1}·cm^{-1}), which was tentatively assigned to the stretching vibration of the CN group, and which in the 1:1 complex is shifted to 928 cm^{-1}, was found to be very sensitive to the formation of the hydrogen bond. The remaining NFTBA bands located in a region accessible to observation do not undergo any noticeable changes.

The quantitative determinations of the equilibrium constants of the reactions of formation of the 1:1 (1) and 1:2 (2) complexes were carried out for the NFTBA–THF and NFTBA–HMP systems in CCl_4 according to the intensity of the νNH_2 bands:

$$A + B \rightleftarrows AB, \quad K_1 = [AB]/[A][B], \tag{1}$$

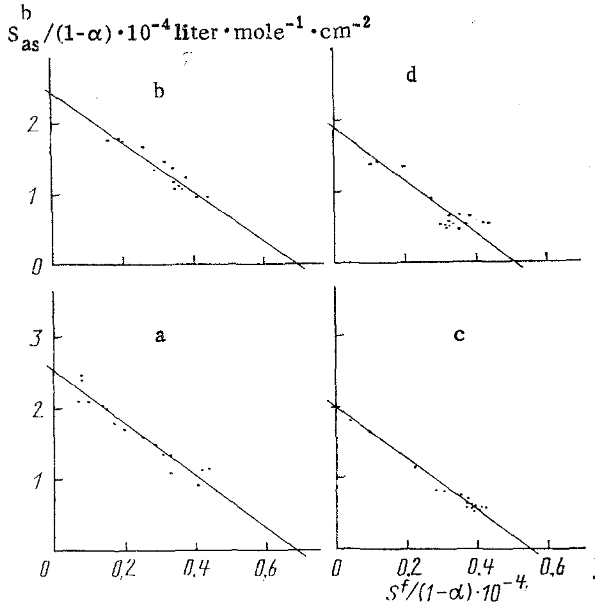

Fig. 2. Dependence (5) for the integral intensities S_{as}^{b} and S^{f} ($S = \int D d\nu / d\,[A_0]$) of the $\nu_{as}{}^{b}$ and ν^{f} bands of the NFTBA–THF (a, b) and NFTBA–HMP (c, d) systems. T = 25 (a, c) and 72°C (b, d). On abscissa $S^{f}/(1-\alpha)\cdot 10^{-4}$ in liter·mole^{-1}·cm^{-2}.

TABLE 2. Thermodynamic Characteristics of Complexes of Nonafluoro-tert-butylamine with Tetrahydrofuran and Hexametapol

Acceptor	K_1	K_2	$-\Delta H_1$	$-\Delta H_2$	$-\Delta S_1$	$-\Delta S_2$
	liter·mole^{-1}, 25°C		kcal·mole^{-1}		cal·mole^{-1}·K^{-1}	
THF	1,7	0.62	3,0	2,7	9,0	10,0
HMP	27	0,66	5,3	3,1	11,2	11.2

$$AB + B \rightleftarrows AB_2, \quad K_2 = AB_2/[AB]\,[B]. \tag{2}$$

Here [A], [B] are concentrations of free molecules of proton donor and acceptor; [AB], $[AB_2]$ are concentrations of complexes with a 1:1 and 1:2 composition, respectively. By using the balance equations (3), (4), the number of values required for the determination of K_1, K_2, which should be measured according to the band intensities, can be reduced to two:

$$[A_0] = [A] + [AB] + [AB_2], \tag{3}$$

$$[B_0] = [B] + [AB] + 2\,[AB_2] \tag{4}$$

($[A_0]$, $[B_0]$ are initial concentrations of the proton donor and acceptor). For these values, we selected [A] and [AB] which can be conveniently determined from $\nu_s{}^{f}$ and ν^{f} bands. After the graphical separation of the bands, the value of [A] was determined from the intensity at the maximum of the $\nu_s{}^{f}$ band, the absorption coefficient of which is known from the spectra of NFTBA solutions in CCl_4. However, to determine [AB], a preliminary measurement of the absorption coefficient of the ν^{f} band was necessary, and the following procedure was used. By expressing the [AB] and $[AB_2]$ concentrations as optical densities of the bands D (ε is absorption coefficient, d is optical path) and by introducing $\alpha \equiv [A]/[A_0]$ (the fraction of the free proton donor molecules), Eq. (3) can be represented in the form

$$\frac{D^{f}}{\varepsilon^{f} d\,(1-\alpha)\,[A_0]} + \frac{D_{as}^{b}}{\varepsilon_{as}^{b} d\,(1-\alpha)\,[A_0]} = 1. \tag{5}$$

It can be seen that by plotting the intensities of the ν^f and $\nu_{as}{}^b$ bands, obtained at different concentrations of the donor and acceptor in the $D^f/d(1 - \alpha)\ [A_0]$, $D_{as}{}^b/d(1 - \alpha)\ [A_0]$ coordinates, we obtain a line that cuts sections on the axes equal to the absorption coefficients of these bands. The same procedure can also be applied for the determination of the integral absorption coefficients of the ν^f and $\nu_{as}{}^b$ bands; the values of the concentrations [AB], determined from the integral and peak intensities of the ν^f band, were found to be similar. Figure 2 shows the corresponding dependences, plotted from the integral intensities of the bands at 25 and 72°C. The integral absorption coefficients S_0 of the ν^f and $\nu_{as}{}^b$ bands, found in this way for the complexes of NFTBA with THF and HMP, are listed in Table 1. With increase in the temperature from 25 to 72°C, these values decrease by 2-7%.

In the calculation of the values of K_1, K_2, the following factors were taken into account. Firstly, in the calculation of K_1, we did not use experiments with a large excess of proton acceptor, where equilibrium (1) is shifted strongly to the right and the value of [A] is low; secondly, for the calculation of K_2, we used experiments in which the fraction of the NFTBA molecules in the 1:1 complexes was higher than 10%, and in the 1:2 complexes higher than 30% (the error in the determination of $[AB_2]$ according to (3) is higher than [AB] measured directly according to the ν^f band); and thirdly, the experiments with less than double excess of HMP were excluded, since in this case the value of the error in the determination of [B] according to (4) is high. The values of K_1, K_2, averaged from 5-9 experiments, are given in Table 2, and their accuracy was estimated as 20-30%. A correction was introduced in the calculations for the dependence of the density of solvent on temperature.

The changes in the enthalpy ΔH and entropy ΔS in processes (1) and (2) were calculated according to the van't Hoff equation, and the results are given in Table 2. The error in the determination of these values is ~10-20%. It is seen that for the NFTBA–HMP system, the energy of formation of the second hydrogen bond is lower than that of the first one, i.e., the proton-donor ability of the second NH group appreciably decreases during the formation of the first hydrogen bond NH...B. However, for complexes of NFTBA with the weaker proton-acceptor THF, the reciporocal influence of the two hydrogen bonds is not as high and the energy of one hydrogen bond in the 1:2 complex (within the experimental error) does not differ from that of the 1:1 complex.

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LITERATURE CITED

1. E. L. Zhukova and I. I. Shman'ko, Opt. Spektrosk., 25, No. 4, 500-505 (1968).
2. E. L. Zhukova and I. I. Shman'ko, Opt. Spektrosk., 26, No. 4, 532-536 (1969).
3. A. E. Lutskii and E. I. Goncharova, Zh. Fiz. Khim., 40, No. 11, 2735-2742 (1966).
4. H. Wolff and G. Gamer, J. Phys. Chem., 76, No. 6, 871-876 (1972).
5. B. R. Friedman and M. Schwartz, Spectrosc. Lett., 15, No. 12, 945-952 (1982).
6. H. Wolff and D. Horn, Ber. Bunsenges. Phys. Chem., 71, No. 5, 467-478 (1967).
7. I. F. Bertran, Rev. Cienc., Quim., 13, No. 1, 9-12 (1982).
8. I. F. Bertran and B. S. Torres, Spectrochim. Acta, 40A, No. 7, 687-689 (1984).
9. Yu. V. Zeifman, L. T. Lantseva, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 401-406 (1986).