

Equilibria Between Molecular and Ionic Complexes with an NH···N Hydrogen Bond. Fluorinated Aromatic Amine as a Proton Donor

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Abstract—Ultraviolet absorption spectra in the range 300–200 K were used to study the composition and structure of complexes formed in solutions by the fluorinated amine $(4\text{-CF}_3\text{C}_6\text{F}_4)_2\text{NH}$ as a proton donor with dibutylamine. A program is developed for quantitative analysis of sets of the spectra of equilibrium multicomponent systems, that allow to find spectral and thermodynamic characteristics of the individual components. In the systems in study, 1:1 and 1:2 fluorinated diamine–dibutylamine complexes are formed. The first of them is a molecular complex with an NH···N hydrogen bond, and the second is an ionic proton-transfer complex. The equilibrium constants between the complexes and the free molecules are found, the enthalpies and entropies of formation of both complexes are found, and the spectra of the complexes are measured.

Secondary aromatic amines are most commonly weak proton donors. However, electron-acceptor substituents in the ring, specifically fluorine atoms, may strongly enhance the proton-donor power of the NH group. Simultaneously, fluorination much attenuates the proton-acceptor power of the nitrogen atom, thus attenuating the tendency of the aromatic amine for self-association in solutions. Borisenko *et al.* [1, 2] showed that perfluorinated aromatic amines as proton donors can form complexes with a fairly strong hydrogen bond, while with strong organic bases, such as aliphatic amines, they form complexes with the proton transferred to the acceptor. The referer also found [2] that the UV spectra of the complexes are strongly solvent- and concentration-dependent and proposed that the proton transfer to the aliphatic amine occurs in a complex containing two molecules of the acceptor and one molecule of the proton donor.

In the present work we report the results of a more detailed quantitative UV spectral study in a wide temperature range of the composition, structure, and thermodynamic characteristics of complexes formed in solutions containing bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)amine (**I**) as a proton donor and dibutylamine as an acceptor.

The spectra of solutions containing amine **I** and dibutylamine in the range of the long-wave $\pi \rightarrow \pi^*$ band of amine **I** exhibit a strong dependence on the concentrations of the components. In a solution of amine **I** in isooctane this band which has still retained an ill-defined vibronic structure has a maximum

near 35840 cm^{-1} . Small additions of dibutylamine to a solution containing compound **I** at a concentration of $2 \cdot 10^{-4}\text{ M}$ give rise to a new band shifted to lower frequencies by $\sim 1250\text{ cm}^{-1}$. Its intensity increases with increasing concentration of dibutylamine and reaches a maximum at the concentration of the latter of $\sim 0.1\text{ M}$, when almost all molecules of amine **I** have been complexed (Fig. 1a). This low-frequency band resembles in shape and intensity the band of the free amine **I** but has not so clearly defined vibronic structure. This fact can be considered evidence for a molecular structure of the complex with an NH···N, formed in these conditions. Similar H-bonding-induced changes are characteristic of $\pi \rightarrow \pi^*$ bonds of other OH proton-donor aromatic molecules, such as phenols and naphthols [3, 4].

On further increase in the concentration of dibutylamine, a new band appears near 29680 cm^{-1} , i.e., in a region typical of the anion of compound **I** [2]. In the cited work this band was assigned to a 1:2 complex including one molecule of amine **I** in the anionic form $(4\text{-CF}_3\text{C}_6\text{F}_4)_2\text{N}^-$ and two molecules of dibutylamine, that form a cation. Actually, even at the highest concentrations of compound **I** ($c\ 5 \cdot 10^{-3}\text{ M}$) the band of the anion appears in the spectrum only at a considerable excess of dibutylamine (Fig. 1b), implying a 1:*n* ($n > 1$) structure of the ionic complex of amine **I** with dibutylamine.

At room temperature (291 K) in a nonpolar inert solvent, isooctane, the equilibrium between the molecular and ionic complexes is to the side of the

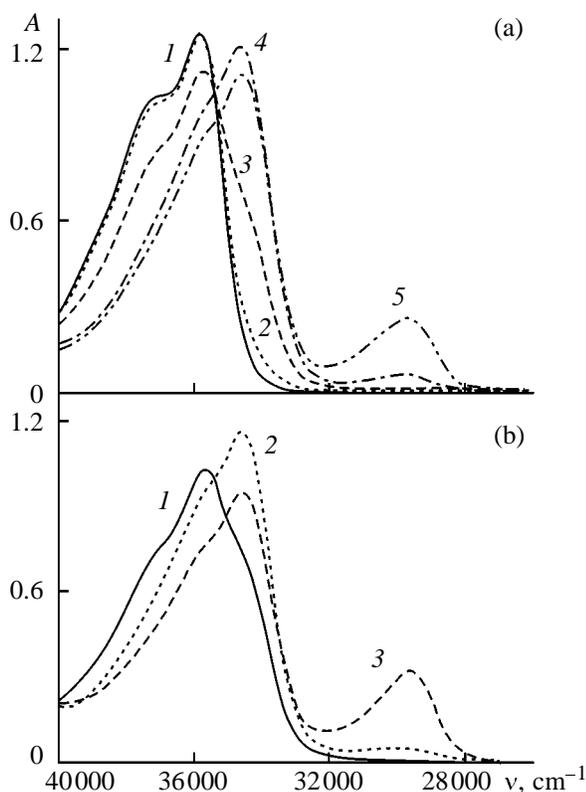


Fig. 1. UV absorption spectra of solutions of amine **I** and dibutylamine in isooctane. (a) Concentration of amine **I** 2×10^{-4} M; concentration of dibutylamine, M: (1) 0, (2) 10^{-4} , (3) 5×10^{-3} , (4) 0.25, and (5) 0.75 (d 2 mm). (b) Concentration of amine **I** 5×10^{-3} M; concentration of dibutylamine, M: (1) 5×10^{-3} , (2) 0.1, and (3) 0.5 (d ~ 0.08 mm).

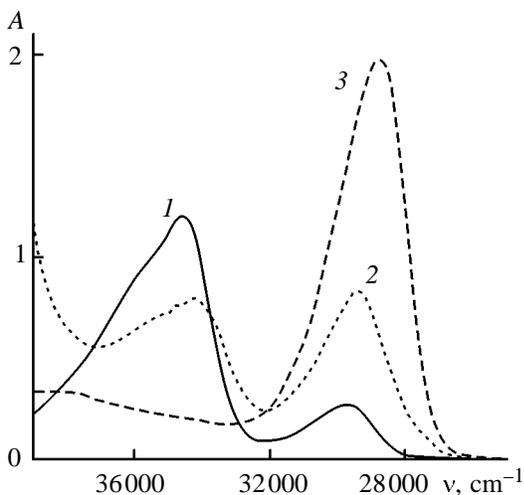


Fig. 2. UV spectra of the system amine **I** (c 2×10^{-4} M) + dibutylamine (c 0.75 M) in (1) isooctane, (2) dichloromethane, and (3) ethanol (d 2 mm).

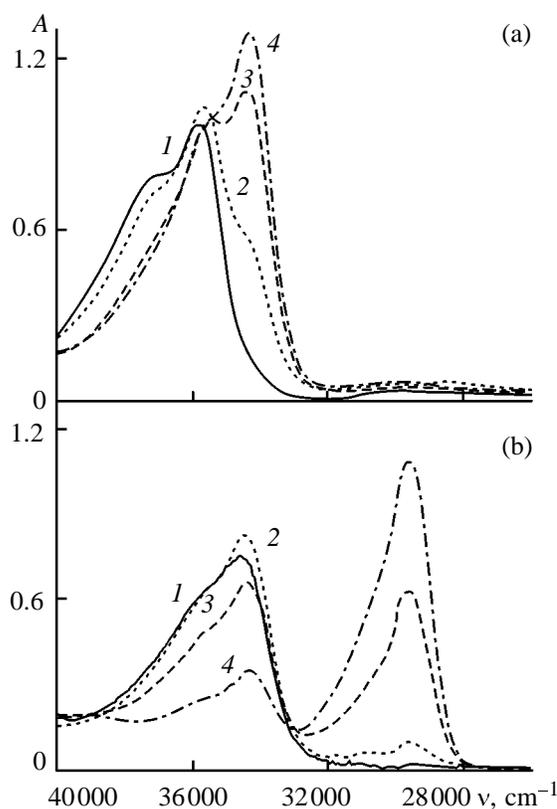


Fig. 3. Variable-temperature UV spectra of amine **I** + dibutylamine solutions. Concentration, M: (a) amine **I** 3.3×10^{-4} , dibutylamine 5×10^{-4} ; and (b) amine **I** 3.3×10^{-4} , dibutylamine 0.1. Temperature, K: (1) 291, (2) 253, (3) 221, and (4) 205 (d ~ 0.9 mm).

former over the entire concentration range (Fig. 1). Enhanced interaction with solvent shifts the equilibrium to the ionic form. Thus the spectrum of an ethanol solution (Fig. 2) of the same concentration as the isooctane solution contains the band of the anion only. A red shift of this band by ~ 1000 cm^{-1} compared with the corresponding band in isooctane can be noted.

Lowering the temperature, too, shifts the equilibrium to the ionic complexes. Figures 3a and 3b show the spectra of amine **I**–dibutylamine solutions with the highest and lowest concentrations of dibutylamine, measured at lowered temperature. In the first case, over the entire temperature range the spectra display no other bands than those of amine **I** and its molecular complex; at 203 K the equilibrium is almost completely shifted to the complexes. In the second case, at room temperature only residual free amine absorption is observed; at lower temperatures these bands dis-

appear, and the spectra contain the bands of the molecular and ionic complexes only.

To find the number and composition of species present in the isooctane solution, to resolve their individual spectra, and to estimate thermodynamic characteristics of equilibria responsible for the observed concentration and temperature trends, we performed a quantitative analysis of a set of various-concentration and various-temperature spectra in the range 300–200 K. The spectra were analyzed by means of a specially developed program (Pascal 7.0) with an algorithm based on the factor analysis technique [5, 6] and approaches proposed in [7, 8]. The program operates with a set of spectra measured at various concentrations and a fixed temperature, and includes two steps.

In the first step the number of spectroscopically resolved components is determined (without *a priori* hypotheses about band shapes and component nature and equilibria). The number of components is measured by a rank r of an absorption matrix \mathbf{D}_{exp} of size $n \times m$ (n is the number of spectral points and m is the number of various-concentration spectra) [6]. The matrix element $\mathbf{D}_{\text{exp}ij}$ is a value A_{ij}/d_j [$A_{ij} = \log(I_0/I)_{ij}$, d_j is the layer thickness] for the j th solution in the i th spectral point v_i . Assuming the validity of Bouguer's law for an r -component solution, the absorption matrix can be represented by product (1):

$$\mathbf{D}_{\text{calc}} = \mathbf{E}\mathbf{C}. \quad (1)$$

Here \mathbf{E} is a matrix of size $n \times r$ of absorption coefficients \mathbf{E}_{il} of each l th individual component in the v_i spectral point; \mathbf{C} is a matrix of size $r \times m$ of concentrations \mathbf{C}_{lj} of these components in each solution. Clearly, in a physical sense, $\mathbf{E}_{il} > 0$ and $\mathbf{C}_{lj} > 0$.

To find the rank r of the matrix \mathbf{D}_{exp} , we used a symmetrical matrix \mathbf{P} of size n [Eq. (2)]:

$$\mathbf{P} = \mathbf{D}_{\text{exp}}\mathbf{D}_{\text{exp}}^{\text{T}}. \quad (2)$$

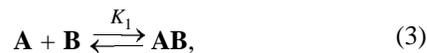
Here $\mathbf{D}_{\text{exp}}^{\text{T}}$ is transposed matrix \mathbf{D}_{exp} . The rank r of the matrices \mathbf{D}_{exp} and \mathbf{P} is equal to the number of nonzero eigenvalues of the matrix \mathbf{P} . Since the data matrix \mathbf{D}_{exp} involves experimental (instrumental) errors, in practice n eigenvalues of the matrix \mathbf{P} are all nonzero. Therefore, the real number of components is obtained by selecting, using known criteria [5, 7], the largest eigenvalues which are above the error level.

In the present work we analyzed sets of the spectra of isooctane solutions, measured in the range 4000–25000 cm^{-1} . For 291 K, a set of eight spectra at an amine **I** concentration of 2×10^{-4} M and dibutylamine

concentrations of 0.75, 0.5, 0.25, 0.1, 5×10^{-2} , 5×10^{-3} , 5×10^{-4} , and 10^{-4} M. Analysis for 262, 253, 243, 221, and 205 K was performed for sets of six spectra with an amine **I** concentration of 3.3×10^{-4} M and dibutylamine concentrations of 0.5, 0.25, 0.1, 5×10^{-2} , 5×10^{-3} , and 5×10^{-4} M. The number of points in each of the spectra was 300.

Treatment of all experimental data in the range 291–243 K showed that the solutions contain three independent components absorbing in the spectral range in study. At lower temperatures the number of components in the concentration range in study proves equal two, since the free compound **I** is lacking.

At the second step the program finds individual spectra of the components at each temperature. A physically correct solution of this task requires introduction of certain hypotheses or additional conditions [7–9]. For such a hypothesis in the present case we used an assumption that the system in study involves equilibria (3) and (4):



Here **A** is the free form of amine **I**, **B** is the free form of dibutylamine,¹ **AB** is the binary molecular complex, **AB**₂ is the ionic 1:2 proton-transfer complex, and K_1 and K_2 are the equilibrium constants.

With the constraint that equilibria (3) and (4) fit the concentration balance equations and the mass action law, we can find the spectra of components **A**, **AB**, and **AB**₂ and the equilibrium constants from the minimum condition of the regularized functional Φ_α (5):

$$\Phi_\alpha = \sum_{i=1}^{i=n} \sum_{j=1}^{j=m} (\mathbf{D}_{\text{calc}ij} - \mathbf{D}_{\text{exp}ij})^2 + \alpha \|X - X_0\|^2. \quad (5)$$

Here X is the vector of unknown parameters (absorption coefficients of the three forms in each spectral point and the constants K_1 , K_2), X_0 is the initial approximation,² $\|X - X_0\|$ is the norm, and $\alpha > 0$ is the regularization parameter.

¹ Free dibutylamine weakly absorbs in the spectral range in study, and this absorption was compensated for before analysis.

² For the method of minimization, see, for instance, [10]. For optimal choice of initial approximation ensuring fast finding the minimum of functional (5), (10×10) matrix of K_1 and K_2 values is specified. The right-hand part of Eq. (1) is set equal to $\mathbf{D}_{\text{exp}ij}$ and, by means of Eqs. (6) and (7), a point in the matrix and the corresponding matrix **T** are chosen, which give a minimum value for the first term of the right-hand part of Eq. (5).

To reduce the number of unknown parameters, we turned to the principal component analysis [11]. In this method, the absorption coefficient matrix \mathbf{E} is an expansion by the basis \mathbf{S} of size $n \times r$ of eigenvectors of the matrix \mathbf{P} found in the first step simultaneously with eigenvalues [Eq. (6)]:

$$\mathbf{E} = \mathbf{S}\mathbf{T}. \quad (6)$$

Here \mathbf{T} is expansion coefficient matrix of size $r \times r$. Then from Eq. (1) follows Eq. (7):

$$\mathbf{D}_{\text{calc}ij} = \sum_{q=1}^{q=r} \sum_{l=1}^{l=r} \mathbf{S}_{iq} \mathbf{T}_{ql} \mathbf{C}_{lj}. \quad (7)$$

Thus computational expences are much reduced (for details, see [8]).

After the minimum of fuctional (5) has been found, the program, along with absorption coefficients for each form in each spectral point, computes the equilibrium constants K_1 and K_2 . Having performed such computations for sets of variable-temperature spectra, one can find the enthalpies ΔH and entropies ΔS of formation of the complexes by van't Hoff's law.

To test the program, we treated synthetic spectra of a three-component model system with equilibria like (3) and (4). In addition, this procedure allowed estimation of errors in resulting values, arising from superposition on the spectra of accidental noise of various amplitude (Table 1). The errors ΔE and ΔS are averaged over all points and set in % to the corresponding values averaged over the entire ranges; δ is the rms deviation of the absorption spectra reproduced by the program from initial spectra. In the absence of noise, as would be expected, all errors are negligibly small.

The results of the treatment of the experimental spectra are given in Fig. 4 and Table 2.

Figure 4 shows the $E(\nu)$ UV spectra of the components at 291 K. The short-wave band in shape and intensity nicely reproduces the spectrum of the free amine \mathbf{I} in the given solvent (Fig. 1a); the long-wave band is close in shape and position to the band of the anion of \mathbf{I} in ethanol (Fig. 2). The band between the above two bands apparently belongs to the molecular complex. Therewith, in the region of the wing of the anion band (near 34500 cm^{-1}) there is a valley. It most probably results from a relatively small fraction of the anions of amine \mathbf{I} in the solutions and from poor stipulation in isosbestic points (~ 33540 and $\sim 35580 \text{ cm}^{-1}$), where all solutions of the given concentration series show an almost the same absorption.

Table 1. Calculated rate constants, rms deviations δ , and errors ΔE and ΔS for a set of synthetic spectra at various values of imposed noise

Noise, transmission %	δ	$K_1, \text{ l mol}^{-1}$	$K_2, \text{ l mol}^{-1}$	$\Delta E, \%$	$\Delta S, \%$
0	5×10^{-13}	225 ± 10^{-1}	9 ± 10^{-12}	10^{-14}	10^{-11}
0.5	3×10^{-3}	225.3 ± 0.8	8.99 ± 0.04	0.25	0.19
1	5×10^{-3}	223.2 ± 1.5	9.17 ± 0.08	0.48	0.37
1.5	8×10^{-3}	216 ± 2	9.33 ± 0.12	0.72	0.55

Table 2. Equilibrium constants and rms deviations δ for the system amine \mathbf{I} + dibutylamine in isooctane at various temperatures

$T, \text{ K}$	δ	$K_1, \text{ l mol}^{-1}$	$K_2, \text{ l mol}^{-1}$
291 ± 1	1.1×10^{-2}	163 ± 2	0.221 ± 0.003
262 ± 1	2.5×10^{-2}	910 ± 8	0.89 ± 0.01
253 ± 1	3.4×10^{-2}	3900 ± 100	1.05 ± 0.01
243 ± 1	4.1×10^{-2}	9400 ± 400	1.09 ± 0.02

At lower temperatures, the same three components result. There spectra are, however, slightly different, i.e., slightly shifted red and have narrower bands and a better defined vibrational structure. Most probably, these changes are of a purely temperature origin. The above valley no longer observed. The ΔE value for the computed band of the free amine \mathbf{I} is $\sim 1\%$ with respect to the experimental band (Fig. 1a). Table 2 lists the equilibrium constants K_1 and K_2 and the δ values at various temperatures, resulting from the

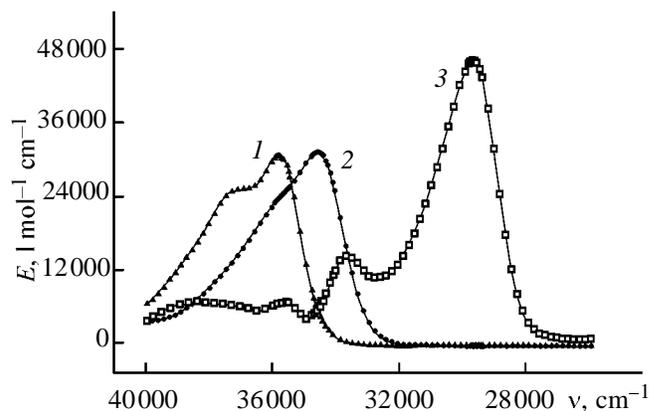


Fig. 4. $E(\nu)$ spectra of (1) the free amine \mathbf{I} and its (2) 1:1 molecular and (3) 1:2 ionic complexes with dibutylamine at 291 K (obtained by treatment of experimental data using the program).

computations. The average error in the absorption coefficients ΔE at various temperatures ranks from $\sim 2 \times 10^{-3}$ to 0.5%; the error in concentration ΔC is from ~ 0.3 to 2%.

The temperature variations of both the constants are well fitted by functions like $\ln K = -\Delta H/RT + \Delta S/R$. Using a standard procedure, we found the following values of enthalpy and entropy: $\Delta H_1 = -(50 \pm 8)$ kJ mol⁻¹, $\Delta S_1 = -(126 \pm 25) \times 10^{-3}$ J mol⁻¹ K⁻¹ (formation of the 1:1 molecular complex from the free molecules; $\Delta H_2 = -(21 \pm 4)$ kJ mol⁻¹, $\Delta S_2 = -(83 \pm 21) \times 10^{-3}$ J mol⁻¹ K⁻¹ (formation of the ionic complex from the 1:1 molecular complex and one dibutylamine molecule).

Comparing the resulting values with reported enthalpies of formation of molecular and ionic complexes in other systems with a strong hydrogen bond, i.e. those with phenols and carboxylic acids or their chloro and fluoro derivatives as proton donors and aliphatic or aromatic amines, including dibutylamine (see, for example, [12–16]), as acceptors, we can note the following. The enthalpy of formation of a hydrogen-bonded binary molecular complex (50 kJ mol⁻¹), found in the present work, is rather high. For comparison, the enthalpy of formation of a molecular complex formed by dibutylamine with 3,4-dichlorophenol in a nonpolar solvent is 38 kJ mol⁻¹ [12]. This allows a conclusion that amine **I** is a strong hydrogen-bond donor.

At the same time, strongly acidic phenols, such as pentachloro- and pentafluorophenols, form with dibutylamine and other related bases contact proton-transfer ion pairs with an enthalpy of ~ 80 – 84 kJ mol⁻¹, and with 2,4,5- and 2,4,6-trichlorophenols, such ion pairs are in equilibrium with molecular complexes [12, 13]. With amine **I**, as seen from the aforesaid, no proton transfer takes place in the 1:1 complex. For proton transfer to occur, the binary complex should take up one more dibutylamine molecule. Consequently, compound **I** a much weaker proton donor than the above phenols.

The enthalpy of ion-pair formation in carboxylic acid–amine systems is of an almost the same order as in the case of phenols, while the enthalpy of formation of 2:1 complexes is higher than 84 kJ mol⁻¹. Therewith, the proton transfer inside the 1:1 complex or that associated with formation of a greater component complex in such systems decreases the energy by 30–33 kJ mol⁻¹ [14–16]. With compound **I**, the enthalpy of the formation of the ionic complex via addition of a dibutylamine molecule is not so high (~ 21 kJ mol⁻¹). Therewith, the large (by ~ 3 orders of

magnitude) difference between K_1 and K_2 suggests a fairly low probability of formation of the 1:2 complex, on account, probably, a complex configuration of such a ternary complex or by steric hindrance. This conclusion is consistent with the fact that in the nonpolar solvent an appreciable anion band can be observed only with a large excess of dibutylamine.

Thus, we showed that fluorinated aromatic amine **I** is quite a strong proton donor capable of forming strong hydrogen bonds with aliphatic amines. However, in the nonpolar solvent, no proton transfer with ion-pair formation in the binary complex with the aliphatic amine takes place. Our present results provide evidence for the assumption in [1] that the proton transfer occurs only in a complex containing one molecule of amine **I** and two molecules of dibutylamine. The evidence in hand is still not enough for substantiated conclusions concerning the structure (geometry) of such complex. Required information can probably be obtained from UV spectra. We are planning to undertake such studies in near future.

The possibility of formation of an equilibrium mixture of complexes of various composition and structure is a characteristic feature of many hydrogen-bonded systems. The present work has demonstrated the feasibility of our approach to quantitative analysis of spectral data for such systems. We intend to develop special versions of the program for analysis of complex equilibria of different type.

EXPERIMENTAL

The UV spectra were measured on a Specord M-40 spectrophotometer with computer control and data treatment. Room-temperature measurements were performed in standard cells. Low-temperature measurements were performed using a cryostat with CaF₂ windows.

Bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)-amine (**I**) was synthesized as described in [17].

Dibutylamine and solvents were purified by repeated vacuum distillation over KOH; their purity was controlled by the UV and IR spectra.

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