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Spectroscopic Studies and VFF Model Calculations on Dynamic and Electrooptic Characteristics of N–H Bonds in Amides

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IR spectroscopic studies of propionamide, n-butyramide, benzamide and 2-(F, Cl, Br)-benzamides within the ν(NH) and δ(HNH) absorption range of -NH_2 group for the "free" (in CCl_4 solutions) molecules and forming complexes with proton acceptor solvents (benzene, toluene, acetonitrile, dimethylformamide, dimethylsulphoxide and hexamethylphosphoramide) have been performed. Modifying the strength of the intermolecular interactions one can achieve the canceling of the primary non-equivalency of the N–H bonds in the -NH_2 group of amides. It allows establishing, for the first time, quantitative measures of dynamic (K(NH)) and electrooptic ($\partial\mu/\partial q$) characteristics of N–H bonds in amides in framework of the R-NH_2 valence force field model. Dynamic and electrooptic non-equivalencies enhance with the increase of the hydrogen bonding strength. For the hydrogen-bonded complexes with acetonitrile, dimethylformamide, dimethylsulfoxide and hexamethylphosphoramide, the dynamic non-equivalency of NH bonds is increased 10–20%, while the electrooptic parameters $\partial\mu_1/\partial q_1$ and $\partial\mu_2/\partial q_2$ grow two or even three times. The electrooptic coupling of the N–H bonds (the parameter $\partial\mu_i/\partial q_j$, where i, j = 1, 2; i ≠ j) increases with the strength of the hydrogen bonding.

Key words: amides, IR-spectra, hydrogen bond, force constants, electrooptic parameters

Hydrogen bonding leads to modification of electron charge distribution of interacting molecules. The magnitude of the change of electrooptic parameters (dipole moments and polarizability of bonds as well as their derivatives in relation to changes of internal coordinates of molecules) upon the hydrogen bond formation is a powerful method in the study of the nature of hydrogen bonding. One of the interesting proton donors in hydrogen bonding is the R-NH_2 group. This appears a unique object in the study the mechanism of intermolecular interactions. Two N–H bonds, which seem to be identical, become non-equivalent due to these interactions. The dynamic – K(NH) and electrooptic – $\partial\mu_i/\partial q_i$ characteristics of the particular N–H bonds can be evaluated from the IR spectra on the basis of simplified four point (R-NH_2), six parameter valence force field VFF model [1]. Such studies were already done for substituted anilines [2–4] and amino pyridines [5].

In this work, the object is the amino group in amides. They are useful model systems of C=O...H–N interactions, so important in biological systems. In these

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compounds, however, the carbonyl group seriously influences the charge distribution in the neighboring -NH_2 group, leading to non-equivalency of N–H bonds, already in the free amino groups. A qualitative study of this problem in the case of the complexes between amides and different proton acceptors has been presented [6–10]. Formation of the 1:1 complexes results in the appearance of two additional, relatively narrow, ν_f(NH) bands located between the $\nu^s(NH_2)$ and $\nu^{as}(NH_2)$ bands of the free molecule, and pretty broad, split ν_c(NH) band at frequencies lower than 3300 cm^{-1}. Appearance of two ν_f(NH) bands is an evidence of the non-equivalency of N–H bonds in the free molecules. It appeared that a convenient method in the study of the N–H bond non-equivalency is the analysis of the shape of valence vibrations of the R-NHD group [6,11,12]. Two types of 1:1 complexes with proton acceptors are formed – with *cis*- and *trans*- NH-groups of amides and thioamides [6,9,10,13]. The field effect of the C=O bond on the *cis*-N–H groups results in a stronger polarization of this group, and makes it a stronger proton donor. However, as was shown in [6,7], the equilibrium between the two forms of 1:1 complexes in solution is shifted to a weaker *trans*-N-H complex, most probably because of steric repulsion of the carbonyl group.

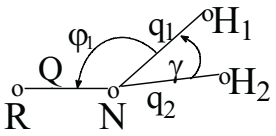
The aim of this work are the experimental and theoretic studies on the influence of substituents in phenyl ring on proton donor ability of N–H bonds in amides and determination of geometric, dynamic and electrooptic parameters of -NH_2 group in amides. The establishing of the correlation between these parameters and spectral characteristics of hydrogen bonded and free molecules is also the purpose of this paper.

The propionamide, n-butyramide, benzamide and 2-(F, Cl, Br)-benzamides were selected. Primary non-equivalency in the free molecules can be modified by intermolecular hydrogen bonding to basic solvents: benzene, toluene, acetonitrile, formamide and hexamethylphosphoramide. For some of them one can observe restoring the equivalency of N–H bonds. Method of modeling of the intermolecular interactions applied in this work allows obtaining quantitative results, which seriously increase the precision in description of physical characteristics of molecules, as well as their modifications upon the formation of hydrogen bonded complexes.

CALCULATIONS

Valence force field calculations for free and hydrogen bonded molecules of amides were solved in framework of six internal coordinates, the simplified four atoms R-NH_2 model (Scheme 1).

For two stretching $\nu^s(NH_2)$ and $\nu^{as}(NH_2)$, and deformational δ(HNH) vibrations the interaction between all internal coordinates, including the common N atom, were accounted, which appeared to be a sufficiently good approximation. In the process of solving of vibrational tasks, the geometric and dynamic parameters of the R-NH_2 moiety were fitted to the best agreement between calculated and



Scheme 1. Internal coordinates in valence force field of R-NH_2 model.

experimental frequencies of stretching and deformational vibrations of R-NH_2, R-HND and R-ND_2 species. The same values of valence field parameters were applied for the isotopic substituted molecules. Anharmonicity of vibrations was partially accounted by applying so called spectroscopic masses of hydrogen (1.088 a.u.) and deuterium (2.126 a.u.) [14]. The differences between calculated and experimental frequencies are in average 2 cm^{-1} and do not exceed 8 cm^{-1}. Only in the case of δ(DND) vibrations the difference is 19 cm^{-1}, which can be explained assuming some change of γ(HNH) angle, when going to -ND_2 group. A very high sensitivity of calculated frequencies on γ(HNH) angle allows to estimate the relative value of this angle with precession of 0.25°. Normal coordinates of $\nu^s(NH_2)$, and $\nu^{as}(NH_2)$ are characteristic (do not contain other internal coordinates than of ν(N–H)), which allows the simplification of the model molecule to XY_2, with non-equivalent X–Y bonds. Solving of electrooptic task for more extended models requires a great variety of the number of bands, which integrated intensities should be included into considerations. Because of a large overlapping of the absorption bands and problems with precise estimation of integrated intensity of bands, one can hardly expect an increase of precision in comparison to XY_2 model. In framework of the last model with non-equivalent X–H bonds one has to determine four parameters $\partial\mu_1/\partial q_1$, $\partial\mu_1/\partial q_2$, $\partial\mu_2/\partial q_2$ and $\partial\mu_2/\partial q_1$, which influence the integrated intensity of stretching vibrations of amine group [1]. The number of parameters in this case exceeds the number of equations. In such conditions we have applied three variants of calculations, in which some simplifications were made. It was assumed that, in going from the free molecule to its 1:1 complex, some of the parameters do not change. A more detailed description of the procedure is given in [1].

RESULTS AND DISCUSSION

The valence and deformational vibrations of the amino group in propionamide, n-butyramide, benzamide, 2-(F, Cl, Br)-benzamides and their deuterated analogs (R-NHD, R-ND_2) were measured in CCl_4, benzene, toluene and ethylacetate solutions.

The spectra of partially deuterated amino groups of amides are presented in Fig. 1 within the range of valence ν(NH) and ν(ND) vibrations.

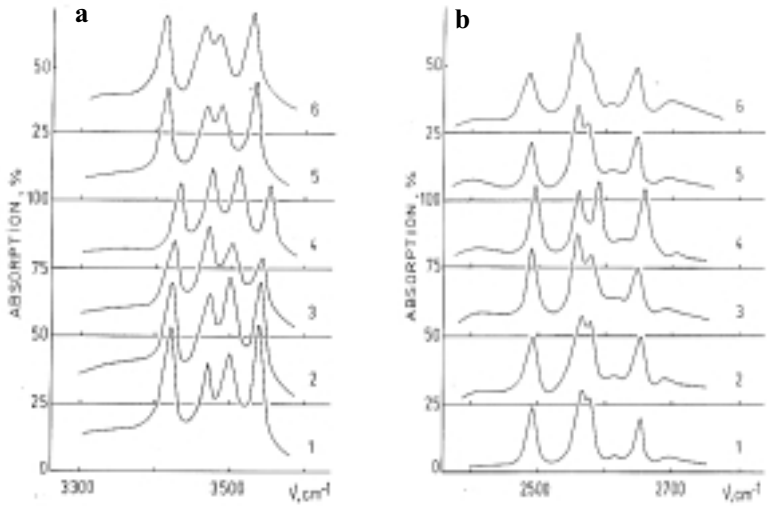
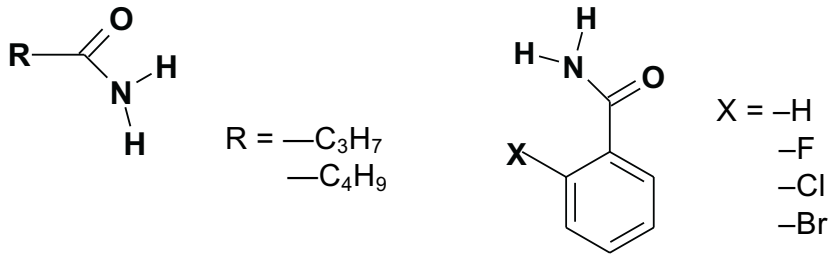


Figure 1. ν(NH) – a, and ν(ND) – b absorption bands of -NH_2, -NHD and -ND_2 groups in partially deuterated: 1: propionamide, 2: n-bytyramide, 3: benzamide, 4: 2-F-benzamide, 5: 2-Cl-benzamide and 6: 2-Br-benzamide in CCl_4 solutions.

Scheme 2



As it is seen from Fig. 1, the four bands appear within the range. Two high frequency bands are assigned to the $\nu^{as}(NH_2)$ and $\nu^{as}(ND_2)$ vibrations, meanwhile the low frequency bands are related to $\nu^{s}(NH_2)$ and $\nu^{s}(ND_2)$ vibrations. The absorption bands located between $\nu^{as}(NH_2)$ and $\nu^{s}(NH_2)$ are assigned to $\nu^{cis}(NH(D))$ (– high frequency component of the doublet) and $\nu^{trans}(NH(D))$ (– low frequency component of the doublet) vibrations of NHD- group of amides. The differences between $\nu^{cis}(ND)$ and $\nu^{trans}(ND)$ bands are clearly smaller than between respective components of the doublet $\nu^{cis}(NH)$, $\nu^{trans}(NH)$, which is connected to an increase of the relative mass of the atoms.

In the association with weak proton acceptors, such as aromatic hydrocarbons, the amides mainly form the *trans*- complexes. This makes possible to select such a proton acceptor, which forms a complex with dynamically equivalent N–H bonds. As a test of equivalency, one can take the lack of the splitting of the ν(NH) and ν(ND) bands in NHD moiety (Figs. 2, 3).

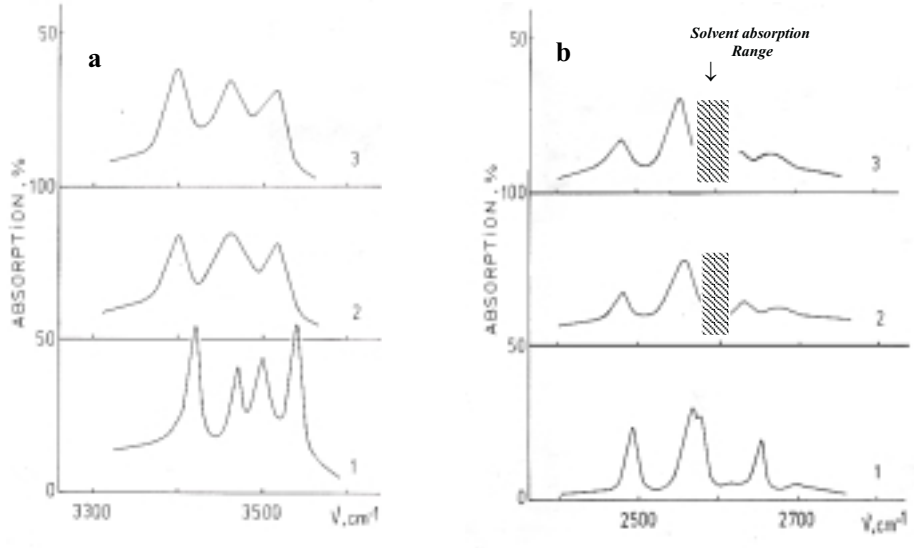


Figure 2. ν(NH) – a, and ν(ND) – b absorption bands in partially deuterated propionamide in different solvents: 1: CCl_4 (C = 0.004 M), 2: benzene (C = 0.01 M) and 3: toluene (C = 0.01 M).

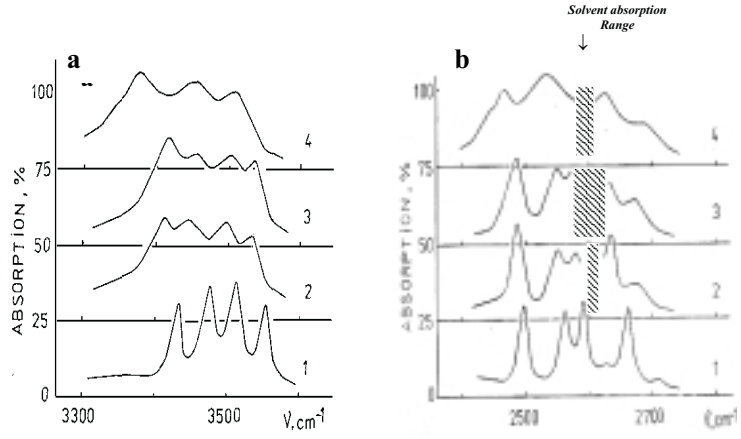


Figure 3. ν(NH) – a, and ν(ND) – b absorption bands of partially deuterated 2-F-benzamide in different solvents: 1: CCl_4 (C = 0.004 M), 2: benzene (C = 0.01 M), 3: toluene (C = 0.01 M) and 4: ethylacetate(C = 0.3 M).

Experimental studies show that the dynamic equivalency of the NH bonds can be reached in the 1:1 complexes of propionamide, n-butyramide, benzamide, 2-(Cl,Br)-benzamide with benzene and toluene, while for 2-F-benzamide with ethylacetate.

The absorption bands of the deformational vibrations δ(HNH) of amides are observed within the range 1600–1650 cm^{-1} (Fig. 4). A comparative analysis of the spectra of solutions in CCl_4 of non-deuterated and deuterated (-NHD, $-ND_2$) amides allowed the assignment of the bands with maximum at 1609 and 1608 cm^{-1} as δ(HNH) of propionamide and 2-F-benzamide, respectively.

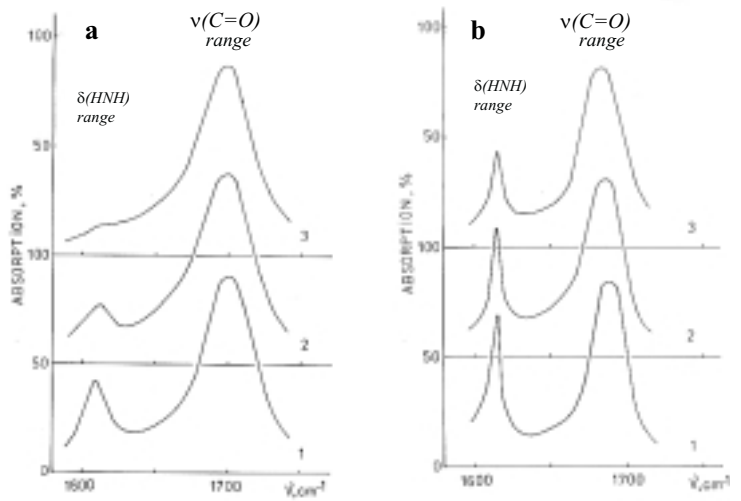


Figure 4. Deformational δ(HNH) absorption band range of 1: non-deuterated, 2, 3: partially deuterated of a – propionamide and b – 2-F-benzamide in CCl_4 solutions (C = 0.004 M), the content of deuterated species in 2 and 3 differs by a factor of 2.

The calculations of normal vibrations of HND-amide, performed within the VFF model, predicted the location of the δ(HND) band within the range of 1410–1440 cm^{-1}. The assignment of this band appears, however, to be difficult due to the complex pattern of the vibrational spectra of amides within this range. Comparison of the spectra of non-deuterated and partially deuterated species allows to make univocal assignment of the δ(HND) vibrations in the experimental spectra. For the propionamide and 2-F-benzamide, the δ(HND) frequencies are equal to 1428 and 1423 cm^{-1}, respectively.

Fig. 5 presents the absorption spectra of 2-F-benzamide and its deuterium analogues within the range of deformational δ(DND) vibrations. Because the increase of the intensity of the band located at 1157 cm^{-1} with degree of deuteration, this band is assigned to δ(DND) vibrations. Nearly the same frequency of deformational vibrations is observed for other benzamides.

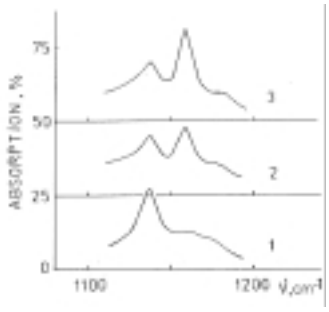


Figure 5. Deformational δ(DND) absorption bands of 1: 1 complexes of 1: non-deuterated, 2, 3: partially deuterated 2-F-benzamide in CCl_4 solutions (C = 0.004 M). Degree of deuteration in 3 is nearly 2 times higher than in 2.

The difference between ν(NH) frequencies calculated within the VFF model and the locations of the first spectral moments $M^{(1)}$ (NH_2) does not exceed 2–3 cm^{-1}, what demonstrates a high quality of the model applied. The force constants K_1(NH) and K_2(NH) of the studied amides in various solvents as well as the values of the valence angles γ(HNH), calculated within this model, are collected in Table 1. Dynamic non-equivalency of the N–H bonds of the free amide molecules in CCl_4 is less than 1–2%. On passing from alkyl amides to benzamides, the dynamic non-equivalency of the N–H bonds in the amino group of the free molecules increases. In benzene and toluene N–H bonds become equivalent.

Table 1. Dynamic characteristics of the N–H bonds and the valence γ(HNH) angles of the NH_2 groups of amides in different solvents.

Compound	Solvent	γ(HNH) [γ(DND)], degree	K_1(NH)·10^{-6} [K_1(ND)·10^{-6}], cm^{-2}	K_2 (NH)·10^{-6} [K_2 (ND)·10^{-6}], cm^{-2}	ΔK(NH)·10^{-6}* [ΔK(ND)·10^{-6}]
propionamide	CCl_4	110.1 [111.2]	11.267 [11.289]	11.160 [11.165]	0.107 [0.124]
	benzene	109.8 [110.0]	11.096 [11.104]	11.096 [11.104]	0 [0]
	toluene	109.0 [109.4]	11.078 [11.096]	11.078 [11.096]	0 [0]

Table 1 (continuation)

n-butyramide	CCl_4	110.0	11.277	11.170	0.107
		[110.6]	[11.306]	[11.184]	[0.124]
	benzene	109.6	11.104	11.104	0
		[109.9]	[11.113]	[11.113]	[0]
	toluene	109.0	11.083	11.083	0
		[109.4]	[11.094]	[11.094]	[0]
benzamide	CCl_4	109.7	11.293	11.177	0.116
		[110.6]	[11.295]	[11.169]	[0.126]
	benzene	109.2	11.124	11.124	0
		[109.5]	[11.128]	[11.128]	[0]
	toluene	109.0	11.100	11.100	0
		[109.5]	[11.115]	[11.115]	[0]
2-F-benzamide	CCl_4	110.8	11.370	11.175	0.195
		[112.1]	[11.407]	[11.210]	[0.197]
	benzene	111.6	11.284	11.124	0.160
	toluene	112.4	11.241	11.104	0.137
	ethylacetate	113.3	10.958	10.958	0
		[113.4]	[10.996]	[10.996]	[0]
2-Cl-benzamide	CCl_4	110.2	11.256	11.126	0.130
		[110.9]	[11.289]	[11.150]	[0.139]
	benzene	110.6	11.093	11.093	0
		[110.7]	[11.103]	[11.103]	[0]
	toluene	109.8	11.050	11.050	0
		[110.0]	[11.085]	[11.085]	[0]
2-Br-benzamide	CCl_4	109.6	11.209	11.088	0.121
		[110.5]	[11.250]	[11.121]	[0.129]
	benzene	109.6	11.055	11.055	0
	toluene	109.1	11.010	11.010	0
		[110.2]	[11.067]	[11.067]	[0]

*$\Delta K(NH) = K_1(NH) - K_2(NH)$; $\Delta K(ND) = K_1(ND) - K_2(ND)$.

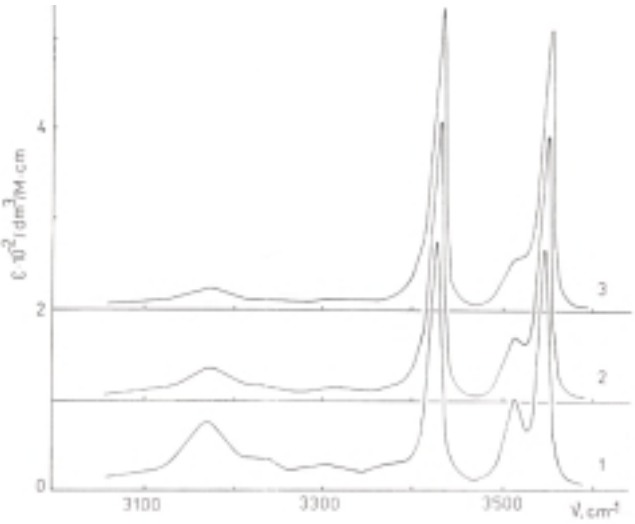


Figure 6. Dependence of the shape of valence vibration absorption bonds of the amino groups on the concentration of n-butyramide in CCl_4. 1: C = 0.002 M; 2: C = 0.001 M; 3: C = 0.0005 M.

The majority of the amides reveal a tendency to self-association, even at so low concentration in CCl_4 as 10^{-4} M. Fig. 6 shows the dependence of the shape of the valence absorption bands of the amino groups on the concentration of n-butyramide in CCl_4. The $\nu_f(NH)$ absorption band (~3520 cm^{-1}) is observed even at a concentration of $5 \cdot 10^{-4}$ M. On the increase of the concentration, the intensity of the $\nu_c(NH)$ and $\nu_f(NH)$ bands of the self-associates grows. Taking this into account, in the course of determination of the integrated intensity B_m of the free molecules of amides in CCl_4, we have used the results extrapolated to zero concentration of solute.

Spectral characteristics of the $\nu^s(NH_2)$ and $\nu^{as}(NH_2)$ bands of free molecules of amides in CCl_4 are given in Table 2. The "effective" half-widths of the bands are related to second central moment $M^{(2)}$ by: $(\Delta\nu_{1/2})_{eff} = 2(M^{(2)})^{1/2}$ [15].

It was found that the spectral moments $M^{(1)}_{s,m}$ of the amides in CCl_4 correlate quite well with the parameters $(K_1\ (NH))^{1/2}$ and $(K_2\ (NH))^{1/2}$:

$$M^{(1)}_{s,m} = 1.063\ (K_2\ (NH))^{1/2} - 130.7 \qquad n = 6,\ r = 0.993 \qquad (1)$$

$$M^{(1)}_{as,m} = 0.935\ (K_1\ (NH))^{1/2} + 396.8 \qquad n = 6,\ r = 0.979 \qquad (2)$$

The difference $\Delta M^{(1)}_m = M^{(1)}_{as,m} - M^{(1)}_{s,m}$ correlates with the valence angle γ(HNH):

$$\Delta M^{(1)}_m = 5.620\ \gamma(HNH) - 500.9 \qquad n = 6,\ r = 0.993 \qquad (3)$$

The parameters of the (1) – (3) correlations for amides are remarkably different from corresponding parameters for anilines [16–18], which is the result of the influence of polar carbonyl group on the charge distribution of amino group in amides. The electrooptic task (*cf*. [16]) can be solved unequivocally for systems with equivalent N–H bonds. The spectral characteristics of the absorption bands $\nu^s(NH_2)$ and $\nu^{as}(NH_2)$ of amides in toluene are also collected in Table 2 (given in parentheses).

Table 2. Spectral characteristics of the absorption of the $\nu^s(HN_2)$ and $\nu^{as}(HN_2)$ bands of various amides in CCl_4 and toluene (in parantheses).

Compound	$\nu^s(HN_2)$			$\nu^{as}(HN_2)$		
	$M^{(1)}$, cm^{-1}	$2(M^{(2)})^{1/2}$, cm^{-1}	$B^s \cdot 10^{-3}$, $dm^3 \cdot M^1 \cdot cm^2$	$M^{(1)}$, cm^{-1}	$2(M^{(2)})^{1/2}$, cm^{-1}	$B^{as} \cdot 10^{-3}$, $dm^3 \cdot M^1 \cdot cm^{-2}$
propionamide	3417 (3398)	33.3 (33.5)	7.01 (8.32)	3535 (3511)	36.6 (37.4)	6.84 (8.18)
n-butyramide	3419 (3399)	33.4 (33.6)	6.74 (8.22)	3536 (3512)	33.6 (35.2)	6.58 (8.10)
benzamide	3421 (3401)	34.5 (39.8)	8.65 (10.37)	3537 (3515)	34.8 (40.2)	7.24 (8.41)
2-F-benzamide	3424 (3407)	30.1 (33.1)	7.21 (8.96)	3546 (3533)	32.2 (35.7)	8.50 (10.02)
2-Cl-benzamide	3413 (3392)	35.4 (39.7)	8.27 (9.20)	3531 (3508)	34.7 (41.9)	9.66 (10.50)
2-Br-benzamide	3408 (3387)	34.0 (38.3)	8.43 (9.25)	3523 (3501)	38.2 (39.4)	9.86 (10.67)

The electrooptic parameters $\partial\mu/\partial q$ (derivative of the dipole moment with respect to the length of a given N–H bond) and $\partial\mu/\partial q'$ (derivative of the dipole moment with respect to the length of adjacent bond) are presented in Table 3. These data allow the estimation of the electrooptic non-equivalency of the bonds N–H of amides in CCl_4.

Table 3. Electrooptic parameters of the amino group (in $D\text{Å}^{-1}$) of various amides in toluene (the NH bonds of $-NH_2$ groups are equivalent).

Molecules	$\partial\mu/\partial q$,	$\partial\mu/\partial q'$,
propionamide	1.79	0.33
n-butyramide	1.78	0.33
benzamide	1.92	0.41
2-Cl-benzamide	1.95	0.30
2-Br-benzamide	1.96	0.29

Table 4. Electrooptic parameters $\partial\mu_1/\partial q_1$, $\partial\mu_1/\partial q_2$ and $\partial\mu_i/\partial q_j$ (in $D\text{Å}^{-1}$) of amino group of amides in CCl_4 (the NH bonds are dynamically symmetric).

Molecule	Variant A		Variant B	
	$\partial\mu_1/\partial q_1$,	$\partial\mu_1/\partial q_2$,	$\partial\mu_1/\partial q_1$,	$\partial\mu_i/\partial q_j$,
propionamide	1.54	0.28	1.54	0.31
n-butyramide	1.47	0.25	1.48	0.30
benzamide	1.67	0.36	1.67	0.39
2-Cl-benzamide	1.81	0.25	1.82	0.28
2-Br-benzamide	1.83	0.25	1.84	0.27

The $\partial\mu/\partial q$ and $\partial\mu/\partial q'$ parameters, calculated for the free amides in CCl_4, by two different methods, are presented in Table 4. In variant A it was assumed that the electrooptic parameters $\partial\mu_2/\partial q_2$ and $\partial\mu_2/\partial q_1$ of the free N–H bonds do not change on passing to the complexes for amides of 1:1 stoichiometry with toluene:

$$\partial\mu_2/\partial q_2 = \partial\mu/\partial q = \text{const (in toluene)}; \qquad \partial\mu_2/\partial q_1 = \partial\mu/\partial q', \text{(in toluene)} \tag{4}$$

In B version it was assumed that, on passing to hydrogen bonded (1:1) molecules, the parameter $\partial\mu_2/\partial q_2$ remains unchanged, while the parameters $\partial\mu_i/\partial q_j$ ($i, j = 1, 2; i \neq j$) are changed, but remain equal to each other:

$$\partial\mu_2/\partial q_2 = \partial\mu/\partial q = \text{const (in toluene)}; \qquad \partial\mu_1/\partial q_2 = \partial\mu_2/\partial q_1 \tag{5}$$

The third variant, which was previously used by us for anilines [16–18], appeared non acceptable for amides because lack of solution of the equations set [16].

The electrooptic parameters $\partial\mu_1/\partial q_1$ and $\partial\mu_i/\partial q_j$ of the amino groups of amides, which were calculated according to the A and B variants, are similar (*cf.* Table 4). It proves the reliability of the estimation of the electrooptic parameters of the *trans* N-H group in the free molecules of amides. The electrooptic task was not solved, for the free molecules of 2-F-benzamide, because of the lack of reliable experimental data concerning the intensities of the 1:1 complexes with ethylacetate in consequence of the strong overlapping of the bands (Fig. 3).

The electrooptic non-equivalency of the N–H bonds of the amino group in the free molecules of amides is about 10–15% (*cf.* Tables 3 and 4). This demonstrates that the

electrooptic parameters of the amino groups of amides, similar to anilines, appear more sensitive to intermolecular interactions than the dynamic parameters of the N–H bonds.

Fig. 7 shows how the various proton acceptors influence the valence vibration bands of the amino group of the free and hydrogen bonded (1:1) molecules of n-butyramide and benzamide in CCl_4 solutions. In the spectral range between the $\nu^{s}_{m}(NH_2)$ and $\nu^{as}_{m}(NH_2)$ bands of monomers a single or double band of ν_f(NH) for complexes of 1:1 composition is observed. The ν_c(NH) band with a structured shape is located lower than 3400 cm^{-1}.

It is interesting to follow the evolution of the structure of the ν_f(NH) bond in the series of proton acceptors: CH_3CN, DMF, DMSO, HMPA.

Complexes of amides with one of the weakest proton acceptor (CH_3CN) reveal the single ν_f(NH) band located at 3515 cm^{-1}. In the complexes with DMF, DMSO and HMPA, the doublet character of this band appears, which is seen most clearly in 1:1 complex with the strongest base – HMPA. The intensity of both components of the doublet is here comparable, which suggests that in solutions there exist nearly equal amounts of the *cis*- and *trans*- 1:1 complexes. The low-frequency component of the doublet can be assigned to the absorption of the *cis*- complex [6]. The intensity increase of the low frequency component of the ν_f(NH) doublet (Fig. 7) indicates that strengthening of the hydrogen bond shifts the equilibrium in the direction of *cis*-complexes.

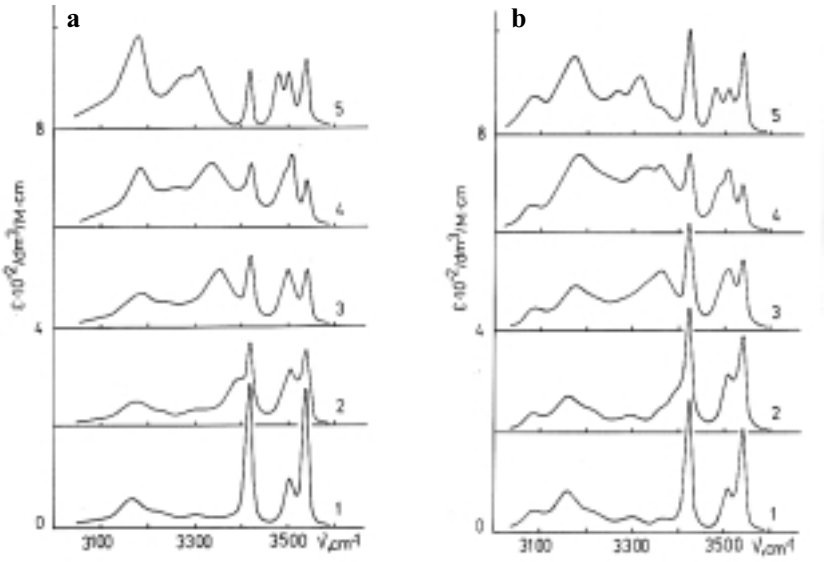


Figure 7. Stretching vibration absorption bands of amino groups in:
a – n-butyramide (C = 0.005 M) in: 1: CCl_4 (C=0.002M); 2: CH_3CN (C = 0.2 M); 3: DMF (C = 0.1 M); 4: DMSO (C = 0.1 M); 5: HMPA (C = 0.02 M);
b – benzamide (C = 0.002 M) in 1: CCl_4, 2: CH_3CN (C = 0.1 M), 3: DMF (C = 0.05 M) , 4: DMSO (C = 0.05 M); 5: HMPA (C = 0.01 M).

The half width of the single band in the complexes with CH_3CN is much higher than the half widths of the components of the doublet, which suggests that also in the complexes with CH_3CN there are *cis*- and *trans*- forms in equilibrium.

Total integrated intensity of the doublet $B_f^{trans+cis}$ is presented in Table 5. It contains also the values of the equilibrium constants K_{298} determined in ternary systems in CCl_4 solutions. Formal concentrations of amide and proton acceptor are given in this table. Concentration of free amide form in equilibrium was determined from integrated intensity of $\nu^s(NH_2)$ band. The equilibrium constants K_{298} given in this table characterize the association process without the splitting into *cis*- and *trans*- complexes. The equilibrium constants of the alkyl amides are larger than those of the benzamides (Table 5).

Table 5. Formation constants K_{298} and spectral characteristics of the absorption bands $M^{\cdot(1)}$, $2(M^{\cdot(2)})^{1/2}$ (in cm^{-1}) and integrated intensities B (in $10^3 dm^3/Mcm^2$) of the valence vibrations of amino groups in the 1:1 complexes of amides with different proton acceptors in CCl_4.

Proton donors (M)	Proton acceptors (M)	ν_f(NH)			ν_c(NH)			K_{298} $dm^3\,M.^{-1}$
		$M_f^{(l)}$	$2(M._f^{(2)})^{1/2}$	$B_f^{trans+cis}$	$M_c^{(1)}$	$2(M._c^{(2)})^{1/2}$	$B_c^{trans+cis}$	
propionamide (0.005)	CH_3CN(0.2)	3499	44	8.91	3280	172	20.09	7.59
	DMF(0.1)	3497	44	8.55	3278	172	26.39	10.15
	DMSO(0.1)	3496	42	7.58	3257	173	42.36	33.63
	HMPA(0.02)	3487	46	7.16	3239	181	44.07	106.19
n-bytyramide (0.005)	CH_3CN(0.2)	3499	43	8.23	3290	173	19.45	8.36
	DMF(0.1)	3498	42	7.40	3288	170	25.54	22.73
	DMSO(0.1)	3499	40	7.14	3278	174	38.97	39.29
	HMPA(0.02)	3490	45	7.05	3246	177	41.44	176.87
benzamide (0.002)	CH_3CN(0.1)	3503	42	9.16	3271	183	25.80	6.54
	DMF(0.05)	3500	42	8.72	3265	184	38.01	23.70
	DMSO(0.05)	3499	39	7.85	3253	184	49.13	36.28
	HMPA(0.01)	3490	44	7.72	3234	187	54.41	107.38
2-F-benzamide (0.002)	CH_3CN(0.1)	3519	38	8.81	3265	165	20.81	3.50
	DMF(0.05)	3518	38	8.14	3257	164	28.92	10.93
	DMSO(0.05)	3516	35	7.80	3223	172	44.76	17.33
	HMPA(0.01)	3516	37	7.52	3203	176	46.88	48.99
2-Cl-benzamide (0.002)	CH_3CN(0.1)	3496	38	8.99	3250	173	21.45	3.89
	DMF(0.05)	3495	40	9.05	3246	173	29.12	16.18
	DMSO(0.05)	3491	39	7.95	3215	175	46.92	35.55
	HMPA(0.01)	3480	40	7.86	3190	182	51.89	67.54
2-Br-benzamide	CH_3CN(0.1)	3492	42	9.04	3248	177	26.56	4.06
	DMF(0.05)	3488	45	8.22	3243	176	38.52	16.66
	DMSO(0.05)	3488	43	8.48	3214	178	54.37	29.66
	HMPA(0.01)	3478	44	7.98	3191	186	57.11	79.21

Despite this, the integrated intensities B_c and the shifts of ν_c(NH) band in the complexes of benzamide with proton acceptors are greater than in the complexes of propionamide and n-butyramide with CH_3CN, DMF, DMSO and HMPA.

Vibrational and electrooptic tasks for the complexes of amides with proton acceptors were solved with accounting for the dynamic and electrooptic non-equivalency of the N–H bonds of the amino group. The dynamic parameters K(NH) for ν_c(NH) and ν_f(NH) are presented in Table 6. Normalized coefficients of normal vibrations q_1 and q_2 were calculated. Contribution of the stretching of particular N–H bonds in

$\nu^{as}(NH_2)$ and $\nu^{s}(NH_2)$ modes is different by 15–20% in CCl_4 solutions and becomes identical in toluene. In the complexes with stronger bases (CH_3CN, DMF, DMSO, HMPA) the $\nu_c(NH)$ and $\nu_f(NH)$ vibrations appear to be much stronger localized on particular N–H bonds; relations of q_1 q_2 are 1:0.3 in $\nu_c(NH)$ and 0.3:1 in $\nu_f(NH)$ vibrations, respectively.

Table 6. Dynamic – K(NH) and electrooptic $\partial\mu/\partial q$ parameters (in $DÅ^{-1}$) of amino groups in amides forming the 1:1 complexes with proton acceptors.

Proton donors	Proton acceptors	*K(NH) $\cdot 10^{-6}$ cm^{-2}	Variant 1		Variant 2		Variant 3	
			$\partial\mu_1/q$	$\partial\mu_1/\partial q_2$	$\partial\mu_1/\partial q_1$	$\partial\mu_2/\partial q_2$	$\partial\mu_1/\partial q_1$	$\partial\mu_i/\partial q_j$
propionamide	CH_3CN	10.086 (11.252)	2.93	0.27	2.92	1.71	2.93	0.29
	DMF	10.073 (11.240)	3.31	0.45	3.34	1.59	3.33	0.42
	DMSO	9.934 (11.244)	4.08	0.80	4.19	1.34	4.17	0.66
	HMPA	9.820 (11.190)	–	–	4.25	1.31	4.24	0.71
n-butyramide	CH_3CN	10.153 (11.246)	2.87	0.36	2.88	1.62	2.87	0.35
	DMF	10.139 (11.245)	3.21	0.62	3.29	1.43	3.26	0.53
	DMSO	10.075 (11.253)	3.91	0.86	4.04	1.25	4.00	0.69
	HMPA	9.864 (11.214)	–	–	4.13	1.28	4.11	0.69
benzamide	CH_3CN	10.022 (11.289)	3.27	0.44	3.27	1.77	3.27	0.43
	DMF	9.983 (11.278)	3.90	0.69	3.96	1.61	3.95	0.60
	DMSO	9.903 (11.277)	–	–	4.48	1.45	4.46	0.80
	HMPA	9.784 (11.223)	–	–	4.70	1.41	4.68	0.84
2-F-benzamide	CH_3CN	9.983 (11.399)	–	–	2.96	1.68	2.95	0.39
	DMF	9.929 (11.394)	–	–	3.47	1.52	3.45	0.58
	DMSO	9.711 (11.394)	–	–	4.26	1.43	4.27	0.58
	HMPA	9.587 (11.398)	–	–	4.35	1.40	–	–
2-Cl-benzamide	CH_3CN	9.890 (11.248)	–	–	3.02	1.69	2.97	0.52
	DMF	9.863 (11.249)	–	–	3.48	1.64	3.45	0.59
	DMSO	9.667 (11.235)	–	–	4.37	1.42	–	–
	HMPA	9.513 (11.168)	–	–	4.57	1.40	–	–
2-Br-benzamide	CH_3CN	9.876 (11.225)	–	–	3.32	1.66	3.29	0.57
	DMF	9.842 (11.208)	–	–	3.98	1.46	3.93	0.80
	DMSO	9.658 (11.215)	–	–	4.68	1.43	–	–
	HMPA	9.522 (11.152)	–	–	4.79	1.38		–

*Values in parentheses concern $\nu_f(NH)$ bands, while without parentheses – the $\nu_c(NH)$ bands.

By comparing Table 6 with Table 1 one can mention that the formation of 1:1 complexes leads to a 10% decrease of $K_1(NH)$ in comparison to free molecules, while the $K_2(NH)$ parameters of the free N–H group practically do not change.

A linear correlation between the $M_c^{(1)}$ values and the parameter $(K_1(NH))^{1/2}$, describing the "active" N–H bond, is observed for all of the amides forming 1:1 complexes with proton acceptors

$$M_c^{(1)}\ (1{:}1) = 0.979\ (K_1(NH))^{1/2} + 168.8 \qquad n = 24,\ r = 0.999 \qquad (6)$$

The variant 1 [16] is improper for the strongest (1:1) complexes of amides with proton acceptors, because of the assumption that the $\partial\mu_2/\partial q_2$ parameters of the non bonded N–H group do not change on complexation. In the case of the strongest complexes, not only the polarization of the lone electron pair of the proton acceptor takes place, but

also the polarization of the amino group of amides by the influence of the proton acceptor.

All the 1–3 variants (Table 6) give practically the same values of the $\partial\mu_1/\partial q_1$ parameters of the groups active in hydrogen bonding. With an increase of the strength of the hydrogen bond in the series of the proton acceptors CH_3CN, DMF, DMSO and HMPA, the parameter $\partial\mu_i/\partial q_j$ increases, while the $\partial\mu_2/\partial q_2$ parameter decreases.

A dependence between the $\partial\mu_1/\partial q_1$ and the $(K_1(NH))^{1/2}$ parameters of the amino group of amides in 1:1 complexes with various proton acceptors was investigated. An attempt to perform a linear correlation gives:

$$\partial\mu_1/\partial q_1\ (1{:}1) = 1.6166\cdot10^{-2}\cdot(K_1(NH))^{1/2} + 54.64 \qquad n = 24,\ r = 0.762 \qquad (7)$$

Use of the parabolic approximation leads to equation:

$$\partial\mu_1/\partial q_1\ (1{:}1) = -4.2082\cdot10^{-5}\cdot(K(NH)) + 2.4773\ (K_1(NH))^{1/2} - 359.04$$
$$n = 24,\ r = 0.765 \qquad (8)$$

One can mention that the correlation factor is low and practically does not depend on the form of equation. With the increase of the hydrogen bond strength for the 1:1 complexes, the electrooptic interaction between the N–H bonds of the amino groups increases ($\partial\mu_i/\partial q_j$ parameter grows (Table 6)) in the series CH_3CN, DMF, DMSO, HMPA. From the experiments performed it follows that the electrooptic parameters of the amino group of amides are more sensitive to the formation of an intermolecular hydrogen bond than the dynamic characteristics of the bonds.

CONCLUSIONS

Spectral characteristics of the stretching and deformational vibration absorption bands of the free ($R\text{-}NH_2$, R-NHD, $R\text{-}ND_2$) groups and in the 1:1 complexes with benzene, toluene, acetonitrile, dimethylformamide, dimethylsulfoxide and hexamethylphosphoramide have been measured for molecules of propionamide, n-butyramide, benzamide and 2-(F, Cl, Br)-benzamides. Formation constants of the complexes were established on the basis of these experimental data. Electrooptic parameters were calculated within the model of the valence force field (VFF). Dynamic characteristics of the bonds K(NH), valence angles γ(HNH) and electrooptic parameters $\partial\mu/\partial q_{NH}$, $\partial\mu/\partial q'_{NH}$ were estimated.

It was found that the dynamic non-equivalency of N–H bonds in the free amino groups does not exceed 1%, when electrooptic non-equivalency reached up to 10%. In the majority of the amides studied, the NH bonds become dynamically equivalent in the result of trans (in relation to C=O bond) complexes formation with benzene and toluene. In the case of 2-F-benzamide, such an equivalency is achieved in associates with ethylacetate. Stronger proton acceptors, *e.g.* – acetonitrile, dimethylformamide, dimethylsulfoxide and hexamethylphosphoramide, at low concentrations of donor molecules (C_D<0.01M) and acceptor molecules (C_A<0.1M) form the 1:1 complexes

with amides of *trans*- and *cis*- configuration of roughly equal population, in which the dynamic non-equivalency of NH bonds becomes of the order of 10–20%, while the electrooptic parameters $\partial\mu_1/\partial q_1$ and $\partial\mu_2/\partial q_2$ in such a case differ two or even three times. It follows that the electrooptic parameters of the amino group of amides are more sensitive to the formation of an intermolecular hydrogen bond than the dynamic characteristics of the bonds. On passing from the free to bonded amides, the electrooptic coupling of the N–H bonds (the parameter $\partial\mu_i/\partial q_j$, where $i, j = 1, 2; i \neq j$) is enhanced. The effect increases when the hydrogen bonding becomes stronger.

VFF model, applied in this work, allows a systematic description of the complex spectra of -NH_2 groups involved as proton donors and provides qualitative characteristics of dynamic and electrooptic consequences of the hydrogen bonding formation. It deepens our understanding of internal modification of geometric and electrooptic structure of molecules upon forming hydrogen bonded complexes.

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