Stretching Vibrations of Amino Group and Inter/Intramolecular Hydrogen Bond in Anilines*

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The IR spectra of *ortho*-substituted anilines with intramolecular hydrogen bond NH$\cdots$O and their complexes with protonoacceptors have been studied in solution. The enthalpy of a complex with a symmetrically perturbed amino group was taken as a definition of the intramolecular bond strength; it increases in the series of substitutes $NO_2 < COOCH_3 < COC_6H_5 < COCH_3 < CO^{2-}$. The influence of the intermolecular bond on the intramolecular bond was estimated by the NH frequency shift of the group involved in the intramolecular bond. In the complexes of *ortho*-substituted anilines this bond is weakened, in those of anthranilic acids it is strengthened on account of the electronic density shift under the influence of protonoacceptor. Solution of the reverse vibrational problem allowed us to find two diagonal force constants, the cross force constant and the HNH bond angle. The calculated frequencies coincide satisfactorily with the experimental ones.

The study of vibrational spectra of substituted anilines with protonoacceptor groups in *ortho*-position and their hydrogen bonded complexes with organic bases makes it possible to ascertain the dependence of amino group frequencies upon the strength of each of two hydrogen bonds formed by this group. The analysis of these data enables the conclusions to be made concerning the energetics of the intramolecular hydrogen bond, the mutual influence of inter- and intramolecular bonds and provides useful material for approbation of the models of vibrational frequencies description of hydrogen bonded complexes. The present paper presents a short review of IR spectra of complexes of *ortho*-substituted anilines with intramolecular hydrogen bond obtained recently in this laboratory, as well as some relevant results concerning compounds of similar structure, which help to argue the principal conclusions.

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* Dedicated to Professor Dušan Hadži on the occasion of his 70th birthday.

Measurements of 2-nitroaniline (*I*), methyl anthranilate (*II*), 2-aminobenzophenone (*III*), 2'-aminoacetophenone (*IV*), anthranilate-anion (*V*) (in the form of tetraoctylammonium salt) and their complexes with protonoacceptor molecules B in CCl_4 solution have been carried out in the region of stretching vibrations for ordinary, deuterated and partially deuterated amino groups.
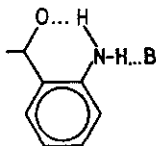
When analyzing the spectra of compounds with intramolecular hydrogen bond formed by amino group, a need often arises for estimates of the strength of intramolecular interaction with an *ortho*-substitute. The problem of determination of the energy of an intramolecular hydrogen bond meets with serious difficulties. In these compounds no equilibrium between forms with and without intramolecular bond is observed, such molecules as *I* or *V* are conformationally strictly uniform. Therefore, the very conception of the energy of intramolecular hydrogen bond needs special definition, related to a priori assumptions.[1]

The free NH_2 group, for example in nonsubstituted aniline, yields, in the region of stretching vibrations, two bands, ν_s and ν_a, of symmetric and antisymmetric vibrations. The semideuterated group NHD yields one band in the νNH region as a consequence of the equivalency of both bonds in the amino group. Formation of the intermolecular hydrogen bond with a protonoacceptor B results in the lowering of both amino group frequencies. With increasing the interaction strength, the shift increases; the effect is stronger for the low-frequency band. The ν(D)NH band of a semideuterated amino group in a complex splits into a doublet; in the doublet the low-frequency component ν_t belongs to NH group, which forms an intermolecular hydrogen bond, the high-frequency component ν_c belongs to the free NH group. The frequency difference $\delta\nu = \nu_t - \nu_c$ can serve as a quantitative measure of bond nonequivalency.

In *ortho*-substituted anilines with protonoaccepting substitutes the intramolecular hydrogen bond disturbs the symmetry of the amino group, and in the spectrum of a free molecule the νNH (and νND) band of a semideuterated group is split into a doublet.[2,3] In Figure 1, the dependence of stretching frequencies of NH_2 and NHD groups on the strength of intermolecular interaction is shown schematically for the νNH region. For compounds *I – V* the $\delta\nu$ value, measured in inert surroundings, is taken as a measure of the strength of intramolecular perturbation.[3] In the figure, the levels are shown with respect to the solution in CCl_4, which was taken as a reference point. The formation and gradual strengthening of intermolecular hydrogen bond NH$\cdots$B, formed by free NH group, causes a decrease of frequency ν_t, which becomes equal to ν_c frequency of the group involved in the intramolecular hydrogen bond, and goes on to decrease with subsequent increasing of protonoaccepting power of B. The intermolecular bond becomes stronger than the intramolecular bond, the difference $\delta\nu$ changes its sign. In the complex in which $\delta\nu \approx 0$, the amino group is perturbed symmetrically by two hydrogen bonds. In the diagram of Figure 1, the strength of the intramolecular bond is taken as a parameter. It has been determined by the properties of *ortho*-substituent and the amino group itself, and its protonodonating ability in these compounds changes as well. Thus, the scale of the protonoaccepting power of molecules B
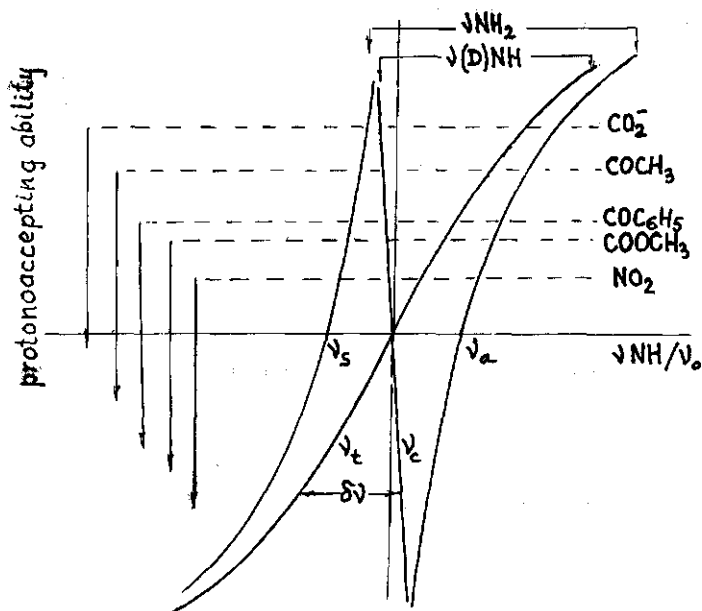
Figure 1. Dependence of amino group frequencies on the strength of inter- and intramolecular hydrogen bonds.

is shifted along the ordinate individually for each compound. Since the symmetrical structure of NH_2 group for different compounds is reached at different values of frequency v_o, it is expedient to take the dimensionless independent variable, the ratio vNH/v_o, and then this diagram gets universal. A similar diagram can be built for vND frequencies of ND_2 and NHD groups.

Thus, the absence of splitting of the $v(D)NH$ (and/or $v(H)ND$) band of the semi-deuterated amino group serves the experimental criterion of equality of the strength of inter- and intramolecular bonds, formed by NH_2 group. The energy of the intramolecular hydrogen bond in such a complex with a symmetrically perturbed amino group can be accepted as the definition of the energy of an intramolecular hydrogen bond.[1] The enthalpy of such complexes can be measured experimentally by traditional procedures.

As the measurements in vNH and vND regions showed, the bands v_t and v_c do not resolve into a doublet and are registered as singlet in the spectra of the following complexes: I + chlorobutane and toluene, II + ethyl acetate and acetonitrile, III + methyl ethyl ketone, IV + diethyl ether, V + hexamethylphosphoramide (HMP). The enthalpy ΔH of the formation of these complexes
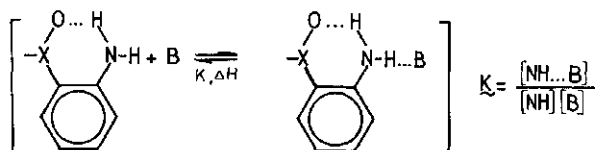
was determined by temperature dependence of the equilibrium constant K in an interval of 25 ° – 72 °C using the van't-Hoff law. The concentration of free protonodonor molecules [NH] was measured by the intensity of the νNH band, the other values were found from equations of balance. The results[4,5] are presented in Table I, where the enthalpy values estimated independently from the empirical equation[6] $-\Delta H = 12.2$ $\Delta A^{1/2}$ (A-the νXH integrated intensity) are also given. It is seen from these data that ΔH values correlate with the differences $\delta\nu$ (solution of $I - V$ in CCl₄) both in νNH and νND regions and change more or less in accordance with the protonoaccepting power of oxygen atom in the *ortho*-substitute. The ΔH values agree, in general, with the known enthalpies of intermolecular complexes of aromatic amines with the usual organic bases. It is important to emphasize that the procedure used gives the enthalpy of the intramolecular hydrogen bond in a complex with acceptor B; it can be markedly lower than the enthalpy of the intramolecular bond in the free molecule on account of the mutual influence of two hydrogen bonds. The data obtained throw some light on this interesting and important phenomenon in the energetics of hydrogen bond, their nonadditivity or, as it is often called, cooperativity.[7]

In the sequence of complexes with different protonoacceptors, strengthening of the intermolecular bond is accompanied with a high-frequency shift of the ν_c band of *cis*-group taking part in the intramolecular hydrogen bond (for a semideuterated amino group), Figure 2; the effect is shown schematically in Figure 1. This shift shows the weakening of the intramolecular bond NH···O under the influence of protonoacceptor B, and it is accounted for by the distortion of the electronic cloud of amino group towards the *cis*–NH–bond. The magnitude of shift $\Delta\nu_c$ in complexes with the given protonoacceptor increases with the strength of the intramolecular hydrogen bond in the row $I - V$, *i. e.* the influence of protonoacceptor B on the intramolecular bond is stronger in the spectra of compounds with a stronger intramolecular bond. It is a typical example of mutual weakening of hydrogen bonds, a case of »negative« cooperativity, or anti- cooperativity.[8]

The influence of an intermolecular hydrogen bond on the intramolecular bond formed by amino group can be well retraced in the spectra of complexes of anthranilic and tetrafluoroanthranilic acids with protonoacceptors,[9-11] Table II. Here, the effect has the opposite sign, the intramolecular bond gets stronger on account of the shift

TABLE I

Enthalpy of the intermolecular hydrogen bond in symmetrical complexes of ortho-*substituted* anilines 2-X-C₆H₄NH₂ (I–V) *with protonoacceptors*

Substitute X		Acceptor	$-\Delta H^*$	$-\Delta H^{**}$	$\delta\nu^{***}$/cm⁻¹	
			kJ/mol	kJ/mol	NH	ND
I	NO₂	2-chlorobutane	–	1.3	31	17
I	NO₂	toluene	–	1.5		
II	COOCH₃	acetonitrile	4.2	4.2	64	43
II	COOCH₃	ethyl acetate	4.6	3.8		
III	COC₆H₅	methyl ethyl ketone	7.5	8.0	84	51
IV	COCH₃	diethyl ether	12	9.7	100	62
V	CO₂-[N⁺Oct₄]	hexamethylphosphoramide	12	18	190	145

*From the van't-Hoff law.
**From empirical equation $-\Delta H = 12.2 \ (\Delta A)^{1/2}$.[6]
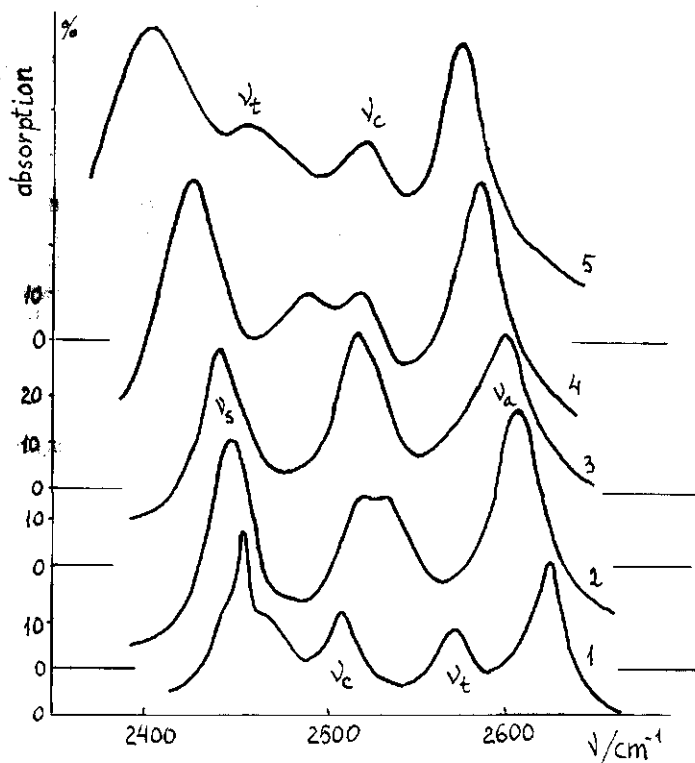***Solution $I - V$ in CCl₄.

Figure 2. IR spectra of partially deuterated 2'-aminoacetophenone solutions in carbon tetrachloride (1), ethyl acetate (2), diethyl ether (3), tetramethylurea (4), 20% solution of hexamethylphosphoramide in CCL$_4$ (5) in the νND region, c = 0.35 mol/dm^3.

TABLE II

Frequencies νNH of the semideuterated amino group in the complexes RCOOH:B of anthranilic and tetrafluoroanthranilic acids with protonoacceptors B (solution in CCl$_4$).[9]

Complex	2-DNHC$_6$H$_4$COOH ν(D)NH/cm^{-1}			2–DNHC$_6$F$_4$COOH ν(D)NH/cm^{-1}		
	ν_t	ν_c	$\delta\nu$	ν_t	ν_c	$\delta\nu$
dimer	3480	3427	53	3484	3431	53
monomer	3481	3418	63	3486	3416	70
B: terahydrofuran	–	–	–	3485	3399	86
hexamethylphosphoramide	3477	3391	86	3486	3386	100
tributylamine	3477	3387	90	3478	3334	144
dibutylamine	3471	3360	111	3482	3314	168

of electronic density in a complex towards carbonilic oxygen. In contrast, dimerization of an acid causes the weakening of the intramolecular bond as a result of the competitive influence of two hydrogen bonds in the dimer. The first bond decreases and the second bond increases the electronic density of the oxygen lone pair; the influence of the nearest bond is stronger and it determines the sign of the whole effect. The same results have been obtained for tetrafluoroanthranilic acid, for which the perturbation of the intramolecular bond is stronger than for the nonsubstituted acid, obviously owing to the higher protonodonating power of the carboxylic group and a much stronger intermolecular bond with the same protonoacceptor B.

The influence of intermolecular bond COOH$\cdots$B upon the intramolecular bond NH$\cdots$O$=$C can be more directly observed in the spectra of complexes formed by *N*-monosubstituted anthranilic acids, *N*-methyl- and *N*-phenyl anthranilic acids,[12] Table III. In the row of complexes, the νNH band shifts to lower frequencies showing a

TABLE III

Frequencies νNH of the complexes RCOOH:B of N-methyl- and N-phenylanthranilic acids with protonoacceptors B

Complex	2-(CH$_3$NH)C$_6$H$_4$COOH		2-(C$_6$H$_5$NH)C$_6$H$_4$COOH	
	νNH	$\Delta\nu$NH	νNH	$\Delta\nu$NH
	cm^{-1}		cm^{-1}	
dimer	3396	−13	3344	−10
monomer	3383	0	3334	0
B: acetonitrile	3383	0	3320	14
methyl ethyl ketone	3373	10	3310	24
diethyl ether	3371	12	3309	25
tetrahydrofuran	3370	13	3306	28
dimethyl sulfoxide	3368	15	3303	31
tetramethylurea	3365	18	3300	34
hexamethylphosphoramide	3357	26	3294	40
tributylamine	3345	38	3260	74
dibutylamine	3302	81	3230	104

TABLE IV

Enthalpy of the formation of the first HNH$\cdots$B ΔH$_1$ and the second B$\cdots$HNH$\cdots$B ΔH$_2$ hydrogen bonds by fluorinated amines with tetrahydrofuran (THF) and hexamethylphosphoramide (HMP)

Donor	Acceptor	−ΔH$_1$	−ΔH$_2$
		kJ/mol	
t–C$_4$F$_9$NH$_2$	THF	13	12
	HMP	22	13
C$_6$F$_5$NH$_2$	THF	14	12
	HMP	22	13.5
4–NC$_5$F$_4$NH$_2$	THF	15.5	12
	HMP	24	13
4-NO$_2$C$_6$F$_4$NH$_2$	THF	16	11
	HMP	25	13

strengthening of the intramolecular bond. For N-phenylanthranilic acid, the νNH frequency itself is lower, and its shifts in the spectra of the complexes are larger than for N-methyl substituted acid, so that the cooperative effect is reflected more strongly in the spectra of molecules with stronger intramolecular bond.

Here, it seems appropriate to add some data characterizing the order of value of nonadditivity in the energetics of hydrogen bonds formed by amino group.[11,13,14] In Table IV, the enthalpy values of addition of the first ΔH_1 and the second ΔH_2 molecules of protonoacceptor to NH_2 group of fluorinated amines are given. One can see that the energy of the second hydrogen bond is smaller than the energy of the first bond, and the difference increases with the bond strength. It is important to take account of the following circumstance. Though the energies of formation of the first and second hydrogen bonds in the complex of 1:2 composition differ by 1.5–2 times, in the equilibrium (i. c. completely relaxed) complex their energies are equal; for the strongest complex the energy of one bond reaches $(25 + 13)/2 \approx 19$ kJ/mol. Spectral characteristics of the perturbation (frequency shift, intensity increase, change in chemical shift *etc.*) correspond just to the bond energy in the equilibrium complex, which may not be coincident with the energy of the complex formation determined by the van't-Hoff law. Supposing the connection between the enthalpies of the two hydrogen bonds in the complex $V+$HMP to be the same as in complexes of tetrafluoro-4-NO$_2$-aniline with one and two molecules of HMP, one can assume the enthalpy of intramolecular bond in the free anion V to be about 20–25 kJ/mol, and the energy of each bond in equilibrium symmetric complex $V+$HMP is 17–20 kJ/mol. This value is obtained by the empirical relationship between enthalpy and the increase of integrated intensity of the νNH band. Using the data from Table IV one can make corrections for anti-cooperativity in the complexes of compounds $I - IV$ as well and obtain the energy values of intramolecular hydrogen bond in free molecules $I - IV$: ~1.5; ~6.5; ~10; ~15 kJ/mol, respectively.

Collection of experimental data concerning the stretching vibration frequencies of amino group in compounds $I - V$ and their complexes with protonoacceptors enabled a simple solution of the inverse vibrational problem.[15] It was done using the following approximations:

1. Only stretching vibrations NH were considered, their coupling with the other vibrations was neglected. Stretching vibrations were assumed to be characteristic.

2. The anharmonicity was taken into account by the spectroscopic mass method; it was assumed to be independent of the strength of the intermolecular hydrogen bond.

In these approximations the problem is redundant – there are twice as many experimental values (8 frequencies, or 6 for the symmetric complex) as unknown parameters of amino group. These parameters are: the diagonal force constants K_1, K_2, the off-diagonal force constant K_{12} and the NHN angle θ. For the symmetric case $K_1 = K_2$ there are three unknown parameters. The unknown parameters were searched by means of minimization of the functional

$$S = \sum_{i=1}^{8} (\nu_i^e - \nu_i^c)^2$$

where ν_i^e– the experimental frequency, ν_i^c – the frequency calculated by the solution of the direct vibrational problem, depending on the sought parameters.

The redundance of the system allows one to estimate the accidental error of calculations. The discrepancy between ν_i^c and the final values of ν_i^c is about (4–6) cm^{-1} for a weak hydrogen bond and (10–15) cm^{-1} for strongest complexes. These values are comparable with the experimental uncertainty in the measurements of the band maximum or of the center of gravity for comparatively wide bands of complexes. The error of the force constants, estimated by the differences of calculated and experimental frequencies, is (0.01–0.03) 10^6 cm^{-2}, the error of the valence angle $2° – 4°$.

To estimate the systematic error related to the neglect of all but two vibrational degrees of freedom, a more complete calculation was carried out. The calculation was done for the symmetric complex, taking into account two more vibrations most strongly coupled with νNH, the HNH bending and CN stretching vibrations. It was found that the systematic error does not exceed the accidental error and does not depend on the strength of hydrogen bond.

The systematic error arising from an approximate account of anharmonicity was estimated by more detailed consideration of the complexes of *I* and *IV*. It showed that the anharmonicity increases with the strength of hydrogen bond. It means that the low-frequency band shift occurs on account of two causes – decrease of a harmonic force constant of NH bond, and increase of the vibration anharmonicity. The calculation with the fixed spectroscopic mass leads to a systematic gradual decrease of the force constant with increasing the bond strength. The estimates show that for not very strong hydrogen bonds the anharmonicity correction is no more than 20% and, therefore, does not influence the general conclusions of the calculations.

In Table V calculation results are presented for methyl anthranilate (*II*) as an example; K_1 refers to the NH group involved in intramolecular hydrogen bond, K_2 refers to the NH group forming intermolecular bond, or free. From the analysis of all results one can conclude that:

1. A regular decrease of the diagonal force constants K_1 (in the row of free molecules $I – V$) and K_2 (in the rows of complexes of each compound $I – V$ with protonoacceptors) occurs with the strengthening of intra- and intermolecular hydrogen bonds, respectively.

TABLE V

The force constants of NH bonds and the valence angle HNH in methyl anthranilate and its complexes with protonoacceptors

acceptor	K_1	K_2	K_{12}	$\theta°$
		cm$^{-2} \cdot 10^6$		
carbon tetrachloride	10.82	11.23	–0.01	115
2-chlorobutane	10.85	11.13	0.02	118
toluene	10.85	11.09	0.02	117
mesitylene	10.87	11.03	0.01	117
acetonitrile	10.92	10.92	0.04	118
ethyl acetate	10.92	10.92	0.04	119
methyl ethyl ketone	10.88	10.88	0	118
diethyl ether	10.90	10.71	0.04	120
tetrahydrofuran	10.88	10.62	–0.02	117
tetramethylurea	10.92	10.41	–0.09	112
dimethyl sulfoxide	10.87	10.40	–0.27	105
hexamethylphosphoramide	10.93	10.10	–0.20	108

2. In free molecules I-IV, the K_2 constants of the free NH bond are practically equal ((11.21–11.24)$\cdot 10^6$ cm^{-2}); in anion V, with the strongest intramolecular bond, K_2 is markedly lower ($11.07 \cdot 10^6$ cm^{-2}).

3. The weak increase of the K_1 constant occurs with the strengthening of the intermolecular hydrogen bond. This influence gets stronger with strengthening the intramolecular hydrogen bond (Figure 3). The same result was obtained for the shifts of ν_c band in semideuterated compounds.

4. For not very strong hydrogen bonds, the value K_{12} is near zero; it is negative and increases in absolute value with the strengthening of the intermolecular hydrogen bond. The maximum value of K_{12} for I-IV lies near $\Delta K \approx 0$, when intra- and inter-molecular bonds are comparable (Figure 4).

5. A similar dependence is obtained for the valence angle HNH in complexes of I-IV: the maximum value $\theta \sim 120^\circ$ is reached at $\Delta K \approx 0$. It allows one to assume the planar structure of fragment CNH$_2$ in the complexes with symmetrically perturbed amino group.

6. Rather different results were obtained for the anthranilate anion V: the off-diagonal force constant $K_{12} \approx -0.4 \cdot 10^6$ cm^{-2} is approximately the same in complexes with all protonoacceptors and considerably larger in absolute value than for compounds I-IV; the angle $\theta \sim 90^\circ$ – 100°, i. e. markedly smaller than for I-IV. It can probably be accounted for by the strong intramolecular hydrogen bond in V and the localization of the negative charge in CO$_2^-$ group closing this bond.
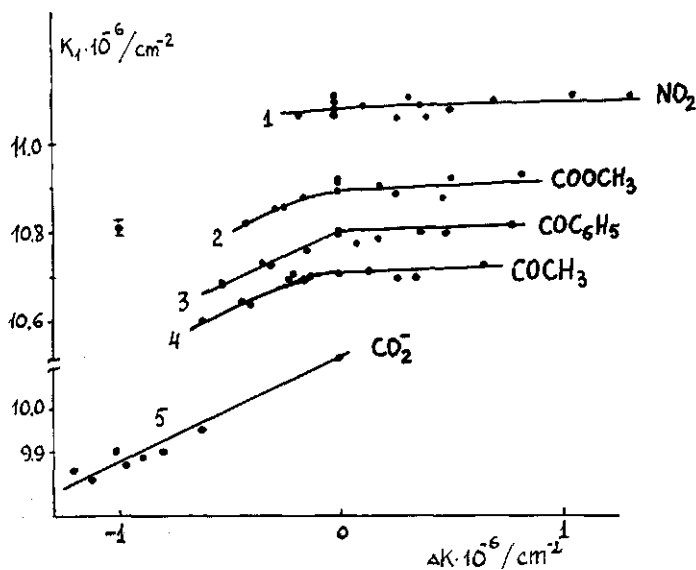

Figure 3. Dependence of force constant K_1 of the NH bond involved in the intramolecular hydrogen bond on $\Delta K = K_1 - K_2$ for 2-nitroaniline (1), methyl anthranilate (2), 2-aminobenzophenone (3), 2'-aminoacetophenone (4), anthranilate-anion (5).
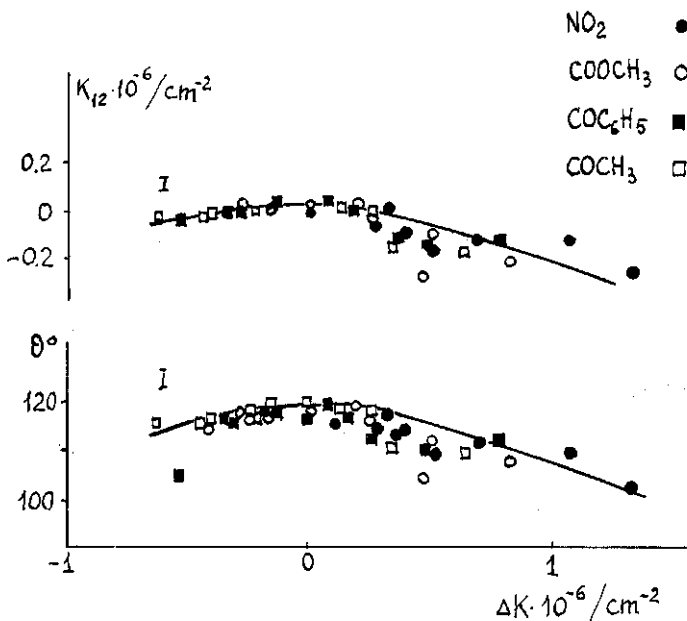
Figure 4. Dependence of the off-diagonal force constant K_{12} and the HNH angle θ on $\Delta K = K_1 - K_2$ for the compounds 1-4 (see Figure 3).

In conclusion, the dependence of the calculated frequency upon $\Delta K = K_1 - K_2$ is given for 2-aminobenzophenone (*III*) as an illustration (Figure 5). A similar picture is obtained for all five compounds *I–V* in the νNH and νND regions. It is seen that the model used gives a satisfactory description of the experimental frequencies (shown by points) measured in the wide range of the inter- and intramolecular bond strength. The general disposition of the frequencies is in good accordance with the scheme of Figure 1.

At the top of the scheme the intramolecular bond is strong, the intermolecular bond is weak, and the frequencies ν_c and ν_t differ considerably. Strengthening of the intermolecular bond causes a decrease of ν_t and an increase of ν_c and they become equal at equal perturbation of the amino group by the intra- and intermolecular bonds ($\delta\nu \approx 0$, $\Delta K \approx 0$). With subsequent strengthening of the intermolecular bond, the frequency ν_t goes on decreasing and asymptotically approaches the position of the low-frequency vibration of the NH$_2$ group. Frequency ν_c also draws together with the frequency of the second stretching vibration of NH$_2$ group and they approach the common limit. Simultaneously, the form of both stretching vibrations of NH$_2$ group changes: at $\Delta K \approx 0$ ($\nu_c \approx \nu_t$), the vibrations of *cis-* and *trans-*groups NH make almost equal contributions to the modes ν_s and ν_a. At $\Delta K > 0 (\delta\nu < 0)$, the intermolecular bond is stronger than the intramolecular one; the larger contribution to the form of the low-frequency mode is due to the NH group linked by the intermolecular bond, whereas that for the high-frequency mode comes from the NH group involved in the intramolecular
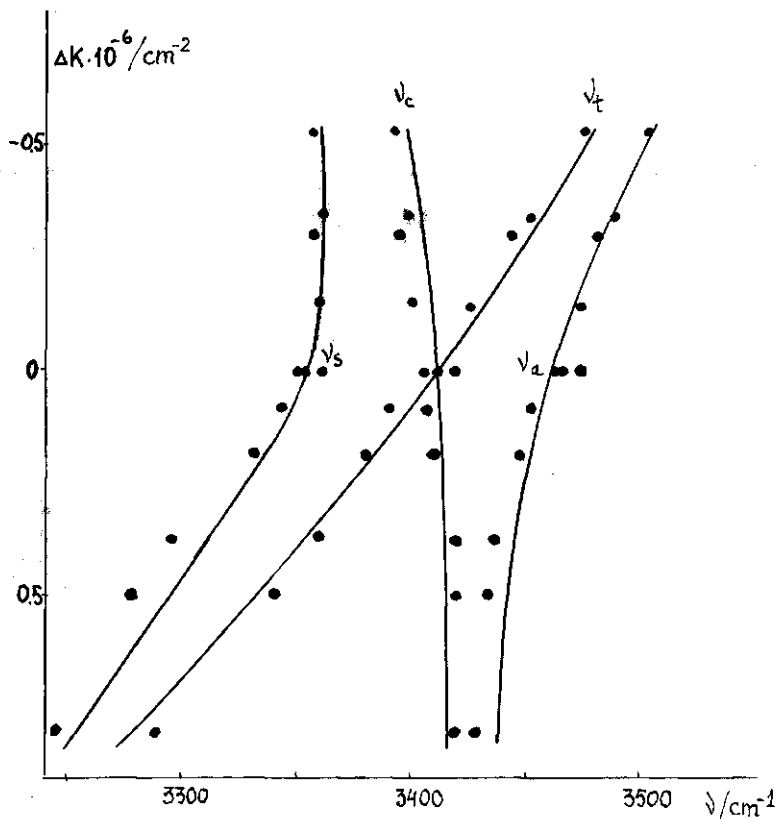
Figure 5. Dependence of the calculated (solid line) and experimental (circles) frequencies ν_s, ν_a, ν_c and ν_t on $\Delta K = K_1 - K_2$ for 2-aminobenzophenone in the νNH region.

bond. At $\Delta K < O(\delta \nu > O)$, the intermolecular bond is weaker than the intramolecular one, and the character of vibrations becomes opposite. In any case, the low-frequency mode depends primarily upon the NH group forming a stronger hydrogen bond, and the high-frequency mode depends upon the NH group forming a weaker hydrogen bond.

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SAŽETAK

Vibracije rastezanja amino skupine i inter/intramolekulska vodikova veza u anilinima

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Proučavani su infracrveni spektri otopina *orto*-supstituiranih anilina s intramolekulskom vodikovom vezom $NH\cdots O$ i njihovih kompleksa s akceptorima protona. Entalpija kompleksa sa simetrično poremećenom amino-skupinom uzeta je kao usporedbeni standard, za jačinu intramolekulske veze. Ona raste u nizu supstituenata: $NO_2 < COOCH_3 < COC_6H_5 < COCH_3 < CO^{2-}$. Utjecaj intermolekulske veze na intramolekulsku vezu procijenjen je iz pomaka frekvencije rastezanja veze NH na skupinu uključenu u intramolekulsku vezu. U kompleksima *orto*-supstituiranih anilina ta je veza oslabljena, u onima pak antranilne kiseline ona je ojačana na račun pomaka elektronske gustoće pod utjecajem protonskog akceptora. Rješenje obrnutoga vibracijskog problema omogućava nalaženje dviju dijagonalnih konstanti sile, interakcijske konstante sile i valentnog kuta HNH. Proračunane frekvencije dobro se slažu s eksperimentalnima.