STUDY OF INTRAMOLECULAR HYDROGEN BOND IN ORTHO-SUBSTITUTED DERIVATIVES OF TETRAFLUOROANILINE ACCORDING TO IR ABSORPTION SPECTRA

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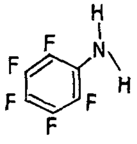
In the present work we studied the intramolecular interaction of the hydrogen atom of the amino group, which in aromatic compounds has substantial proton donor ability, with a proton-acceptor group at the ortho-position in ring fluorinated aniline derivatives. The aim of the investigation was to discover whether an NH...B intramolecular hydrogen bond (IHB) exists in compounds in which group B has a varying proton-accepting ability; to establish the manifestation of this bond in ν NH_2 bands; and to clarify the character of the influence of fluorination on the IHB. Introduction of fluorine atoms into the aromatic ring often leads to a change in the reactivity of the functional groups, which arouses great interest in these compounds [1]. Moreover, it appeared to be expedient using the example of tetrafluoroanthranilic acid to attempt to use the IHB for detecting changes in electron density distribution in the vicinity of the acceptor center B due to intermolecular perturbations.

Pentafluoroaniline (I), tetrafluoro-2-hydroxyaniline (II), tetrafluoro-2-methoxyanoline (III), tetrafluoro-2-nitroaniline (IV), tetrafluoroanthranilic acid (V) and its methyl ester (VI) having the following structures: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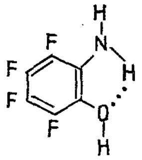
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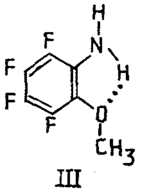
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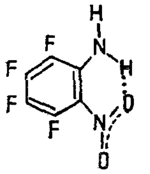
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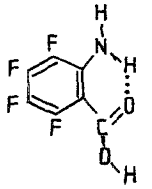
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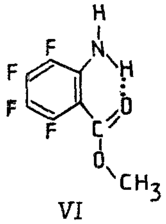
VI

were selected as the subjects of the investigation. Compounds I, IV, V; II; and VI were obtained according to methods described in [2], [3], and [4], respectively. Compound III [5] was obtained in 80% yield by reduction of 3,4,5,6-tetrafluoro-2-nitroanisole by iron according to methods described in [2].

The frequencies of the symmetric ν_s and antisymmetric ν_a vibrations of the NH_2 group decrease on both symmetric and asymmetric perturbation, when the two NH bonds become nonequivalent. The NH...B IHB in the compounds studied leads to an asymmetric perturbation of the NH_2 group, and for its identification it is sufficient to establish the fact of the nonequivalency of the two NH bonds. A method proposed in [6] was used to do this. This method was used by authors of [7-10], namely, to measure the spectrum of partially deuterated samples, i.e., containing a half deuterated DNH group. In the νNH and νND region, compounds with equivalent NH bonds in the NH_2 group thus give one band each, and those with nonequivalent

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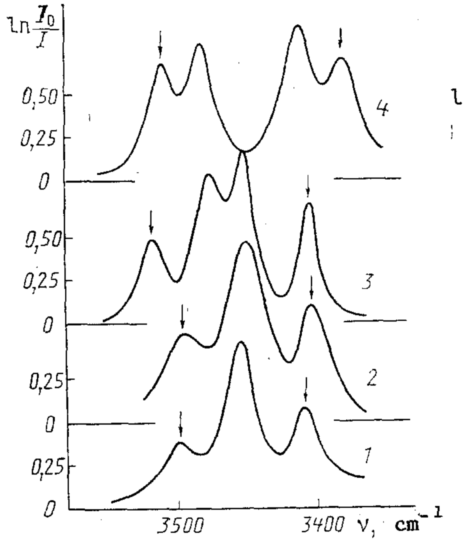


Fig. 1

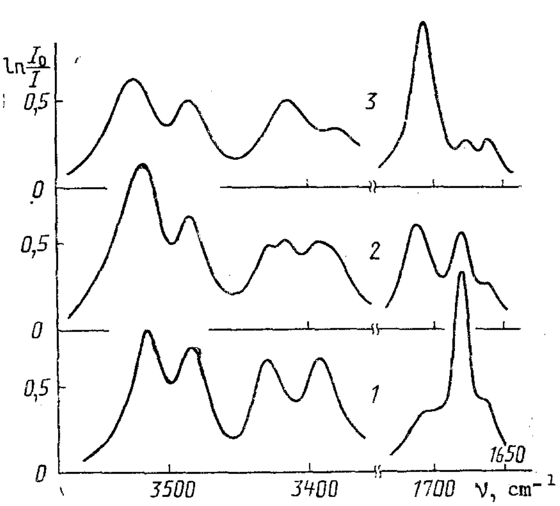


Fig. 2

Fig. 1. Spectra of solutions in CCl_4 of half-deuterated compounds: 1) pentafluoroaniline (I); 2) tetrafluoro-2-methoxyaniline (III), 3) tetrafluoro-2-nitroaniline (IV), 4) methyl tetrafluoroanthranilate (VI). C = 0.3 (1), 0.2 (2), 0.02 (3), and 0.13 mole/liter (4); T = 25°C.

Fig. 2. Spectra of solutions in CCl_4 of half-deuterated tetrafluoroanthranilic acid. C = 0.02 (1, 2) and 0.003 mole/liter (3); T = 25 (1) and 75°C (2, 3).

bonds give two bands. The high-frequency band ν_t corresponds to a free NH group present in the trans-position relative to B, while the low frequency ν_c corresponds to the NH group interacting with the group B present in a cis position with respect to it. The distance between these bands $\delta\nu = \nu_t - \nu_c$ serves as a measure of nonequivalency of the NH bonds, and in the present case, a measure of perturbation due to the formation of a hydrogen bridge. The results obtained are presented in Figs. 1-3 and in Tables 1, 2.

Figure 1 shows the spectra of partially deuterated compounds I, III, IV, VI in the νNH region. For the ease of graphical representation, absorption curves of samples are shown in which there is an appreciable amount of the RNH_2 form. The ν_s, ν_a bands of this form are indicated by arrows, while further deuteration leads to weakening of these bands relative to the bands of the half-deuterated DNH group, lying between ν_s and ν_a of NH_2. In the spectrum of compound I, the single ν(D)NH band lies half-way between ν_s and ν_a of NH_2. This means that the two bonds of NH_2 are equivalent, and no preferential orientation of one of the NH groups with respect to the neighboring ortho-fluorine atom is observed. In the spectra of compounds II, III, there is also only a single νD(NH) band, but is somewhat broader than in I. This suggests the presence of two strongly overlapping components of the band, corresponding to different orientations of the NH bond with respect to the proton-accepting group —OR. Hence it follows that NH...O interaction in the five-membered ring is slight and results in a low-frequency shift of the νNH band of not more than 5-6 cm^{-1}.

In the spectrum of compound IV, the ν(D)NH band has the form of a doublet with splitting of 23 cm^{-1}, and here we can already consider the NH...O interaction as a typical IHB. The splitting of the νD(NH) band is still greater for methyl tetrafluoroanthranilate VI, i.e., the extent of the interaction increases on transition to the O═C acceptor group, as in the case of the nonfluorinated compounds [7].

Because of the high proton-donor ability of the OH group of acid V, a virtually stoichiometric series of complexes of compound V with proton acceptors of variable strength can be obtained at room temperature and in an inert solvent, and thus a step-wise shift of the electron density to carbonyl group oxygen atom can be realized. This leads to increase in the NH...O═C intramolecular interaction, which in the experiment is manifested by the increase in the splitting of the νD(NH) band. This effect is first of all observed on transition from concentrated solutions of the acid to dilute solutions, and with increase in temperature, when there is a considerable shift of the equilibrium in the direction of the monomer. Parallel measurements of the spectra in the 1650-1750 cm^{-1} region make it possible

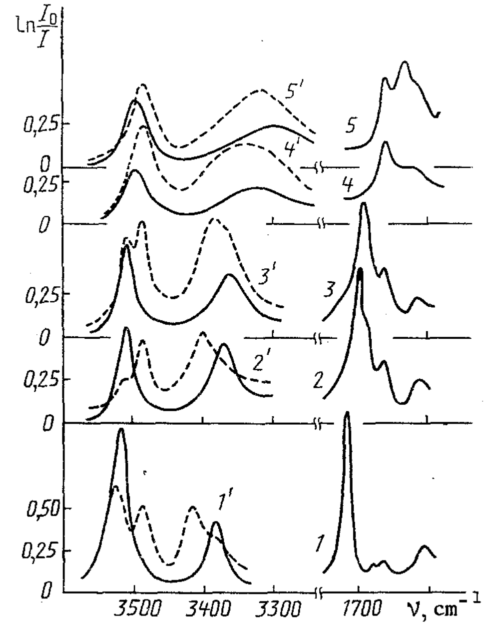
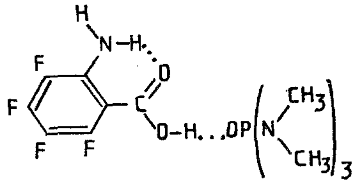


Fig. 3. Spectra of solutions of tetrafluoroanthranilic acid in CCl_4 without a proton acceptor (1), and with the addition of THF (2), HMP (3), TBA (4) and DBA (5). Contious line) nondeuterated; dashed line) half-deuterated samples. Concentrations of acid (proton acceptor) C = 0.001 (0) (1); 0.1 (0.3) (2, 2'); 0.02 (0.02) (3-5, 3'-5') and 0.003 mole/liter (0) (1'); T = 75 (1, 1') and 25°C (2-5, 2'-5').

to monitor the position of the equilibrium according to the $\nu C{=}O$ bands of the dimers at 1683 cm^{-1} and of monomers at 1717 cm^{-1} (Fig. 2). Figure 2 shows that on transition from the dimer of the acid to a monomer, the splitting value $\delta\nu NH$ increases in discrete amounts from 53 to 70 cm^{-1}. The weaker perturbation of the $\nu(D)NH$ band in the dimer is caused by a decrease in the electron density of the unshared pair of the C=O group as the result of the formation of a second hydrogen bond C=O...H—O in the dimer. This case is an obvious graphical example of nonadditivity in the hydrogen bond system, while the simultaneous participation of the carbonyl group in two hydrogen bonds, intra- and intermolecular, is accompanied by their mutual weakening.

In complexes of acid V with the proton acceptors hexametapol (HMP) and tetrahydrofuran (THF), the carbonyl group of the acid does not participate directly in the intermolecular hydrogen bond. Due to the influence of the acceptor, the electron density in the carbonyl group shifts and increases on the carbonyl oxygen atom. This leads to intensification of the NH...O=C interaction and to increase in the $\delta\nu NH$ splitting compared with the monomer. In solutions with an equimolar content of the acid and HMP, a complex with a 1:1 acid—HMP composition predominates, and the fraction of the monomers and dimers of the acid is small. In the spectrum of the $\nu C{=}O$ region (Fig. 3, curve 3), a single band of a mixed complex is observed at 1689 cm^{-1}, i.e., at not very high dilutions of the solutions containing equimolar amounts of V and HMP, only their complex exists in the form



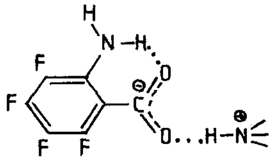
In this complex, the differences between the frequencies $\delta\nu NH$ is 100 cm^{-1}. For the weaker acceptor THF, this stoichiometric interaction does not occur at the working concentrations of 0.01-0.1 mole/liter, and a two- to threefold excess of THF must be introduced into the solution in order to suppress the dimerization; in this case, the band of the mixed 1:1 complex at 1698 cm^{-1} predominates in the $\nu C{=}O$ region (Fig. 3, curve 2), and lies between

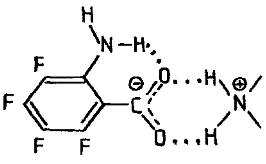
TABLE 1. Frequencies νNH (cm^{-1}) in IR Spectra of Pentafluoroaniline I and Its 2-Substituted Derivatives II-VI (Solution in CCl_4)

Compound, substituent	ν NH_2			ν (D) NH		
	ν_a	ν_s	Δν	ν_t	ν_c	δν
I	3500	3410	90	3455		<5
II, OH	3496	3403	93	3451		<6
III, OCH_3	3496	3402	94	3450		<6
IV, NO_2	3518	3406	112	3476	3453	23
V, dimer, COOH	3517	3394	123	3484	3431	53
VI, $COOCH_3$	3511	3380	131	3482	3413	69
V, monomer	3516	3381	135	3486	3416	70
V, complex with THF	3510	3368	142	3485	3399	86
V, complex with HMP	3508	3358	150	3486	3386	100
V, complex with TBA	3493	3314	179	3478	3334	144
V, complex with DBA	3492	3296	196	3482	3314	168

the monomer and dimer bands. Under these conditions, as can be noted from the νNH_2 bands, practically no binding occurs between the free NH group of the acid and excess THF, and the measured value of δνNH 85 cm^{-1} belongs in fact to an equimolecular complex.

The greatest increase in the proton-accepting ability of the oxygen atom of the acid can be obtained by the ionization of the carboxylic group as a result of the reaction of V with strong organic bases — the aliphatic amines. In the presence of equimolar amounts of di- and tributylamine (DBA and TBA) the νC=O bands of the molecular forms of the acid disappear, and a band at 1630 cm^{-1} appears, which belongs to the ν_a CO_2^- of the carboxylate anion (Fig. 3, curves 4, 5). It is clear that the complex of the acid with amines has the structure of an ion pair, formed as a result of a transfer of the proton from the COOH group of the acid to the nitrogen atom of the amine. In the series of the compounds studied (see Table 1), in the spectrum of the ion pairs of acid V with TBA and DBA, the ν_s and ν_a bands of the NH_2 group are the most strongly shifted to the lower frequencies, and the distances between them Δν is maximal. In this series, with intensification of the IHB, the vibrations of the two NH bonds in the amino group become increasingly independent, the contribution of the movement of the trans-hydrogen atom to the low-frequency ν_s band decreases, and this band becomes increasingly corresponding to the vibration of the cis-NH bond, which participates in the IHB. With intensification of the IHB, the width of this band increases, and for ion pairs of the acid with DBA, it reaches ~120 cm^{-1}. The ν_a band, which for the ion pairs of acid V with amines almost completely corresponds to the vibrations of the trans-NH group, can be interpreted in the same way. In the spectrum of the half-deuterated amino group, in the ion pairs the δνNH difference increases from 144 to 168 cm^{-1} as a result of the intensification of the IHB due to the appearance of a negative charge on the oxygen atom in the anion. The extent of the HNH...O$^-$ interaction in the ion pair of acid V with a secondary amine is higher than with a tertiary amine, which indicates an appreciable difference in the distribution of the electron cloud of the CO_2^- group in these complexes. A qualitative explanation can be proposed on the basis of a model of ion pairs, in which the NH^+ group of the tertiary amine cation is bound by a hydrogen bond with one oxygen atom of the anion, while the NH_2^+ group of secondary amine cation is bound to two oxygen atoms [11]:





In the first case, the hydrogen bond with the cation leads to increase in the electron density on the oxygen atom to which the cation is coordinated, and to its decrease on the oxygen atom participating in the IHB. In the second case, two almost equivalent hydrogen bonds in the NH^+...O$^-$ ion pair fix in the first approximation the symmetric distribution of the charge in the anion, so that the NH...O$^-$ IHB is more strongly manifested.

TABLE 2. Frequencies νNH (cm^{-1}) in IR Spectra of 2-Substituted Derivatives of Aniline 2-X-$C_6H_4NH_2$ (Solution in CCl_4)

Substituent X	ν NH_2			ν (D) NH		
	ν_a	ν_s	$\Delta\nu$	ν_t	ν_c	$\delta\nu$
OH	3488	3397	91	3442		<6
OCH_3	3489	3398	91	3444		<6
NO_2	3523	3404	119	3481	3450	31
COOH, dimer	3513	3389	124	3480	3427	53
$COOCH_3$	3509	3380	129	3480	3416	64
COOH, monomer	3512	3381	131	3481	3418	63
COOH, complex with HMP	3503	3362	141	3477	3391	86
COOH, complex with TBA	3498	3353	145	3477	3387	90
COOH, complex with DBA	3486	3320	166	3471	3360	111

A similar case is observed in the 2400-2700 cm^{-1} region, in which the νND_2 and ν(H)ND bands of the deuterated compounds are located. In compounds I-IV the $\nu_s ND_2$ band has a doublet structure; the data for I are similar to the results obtained in [12], whose authors attributed the splitting of the $\nu_s ND_2$ band to Fermi-resonance interaction with a composite vibration $\delta ND_2 + \nu CN$. In V and VI, the $\nu_s ND_2$ band is single and its width is much narrower than that for the NH_2 analogs. The ν(H)ND band of the half-deuterated amino group, as in the νNH region, is single for I-III; its splitting, indicating considerable interaction with the ortho-substituent, appears in the spectrum of IV, and increases in the same sequence as for the ν(D)NH band (Table 1).

Similar measurements were carried out with nonfluorinated 2-substituted derivatives of aniline 2-X-$C_6H_4NH_2$, analogs of compounds II-VI. The results are given in Table 2. It can be seen that the νNH frequencies in the two series of compounds are similar. The $\nu_a NH_2$ values for the fluorinated compounds are 2-8 cm^{-1} higher than the nonfluorinated ones (except for IV); the values of $\nu_s NH_2$ for the fluorinated compounds, which at the beginning of the series also exceed the ν_s values of nonfluorinated compounds by 2-6 cm^{-1}, have a tendency to decrease in the series of compounds listed in Tables 1 and 2, and for the ion pair of V with DBA, the ν_s are 24 cm^{-1} lower than in the case of its hydrogen containing analog. A similar tendency is also observed in the change in the ν_t and ν_c frequencies of the DNH group: the ν_t value of the fluorinated compounds is 2-11 cm^{-1} higher than for the nonfluorinated compounds (with the exception of IV); the ν_c values at the beginning of the series exceed by 3-9 cm^{-1}, and at its end are a few cm^{-1} lower than the values for the fluorinated analogs, but for the ion pair with DBA, this difference increases to 29 cm^{-1}.

In conclusion, we shall compare the influence of the ring fluorination on the $\delta\nu$(D)NH values, characterizing the degree of perturbation of the νNH frequency due to IHB. One characteristic is not observed: for compounds with a strong IHB, the fluorination leads to increase in the NH...O interaction, and with weakening of the IHB, the difference between the flourinated and nonfluorinated compounds decreases, while for IV, the value of $\delta\nu$ is lower than for the nonfluorinated 2-nitroaniline. On transition from the dimer to monomer of the anthranilic acid, the $\delta\nu$ value increases more strongly for the fluorinated than for the nonfluorinated form. This can be attributed to a stronger deformation of the electronic cloud of the acceptor oxygen atom of the C=O group by the action of the intermolecular hydrogen bond in the dimer because of the higher proton-donor ability of the OH group in V than in the nonfluorinated acid. As the result, the proton-accepting ability of the oxygen atom of C=O group of V increases more strongly during the decomposition of the dimer. The same reason may possibly determine the change in the value of $\delta\nu$, which also occurs during the formation of complexes of the acids with HMP and DBA, where this effect increases. However, for the weak IHB in IV, the increase in the proton-donor ability of the NH_2 group during the ring fluorination does not compensate for the decrease in the proton-accepting ability of the NO_2 group; a similar pattern is known for the intermolecular bond in dimers of halogen-substituted acids from acetic to trifluoroacetic acid [13]. The establishment of the characteristics of the influence of fluorination on the proton-donor and proton-acceptor ability of groups present in the ortho-position could possibly be furthered by the study of spectra of compounds with a weaker NH...X IHB than in IV.

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