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EFFECT OF FLUORINE ATOMS ON THE SPECTRAL PARAMETERS AND THE ENERGY OF HYDROGEN BOND IN 2-NITRO-3,4,5,6-TETRAFLUOROANILINE AND METHYL 2-AMINO-3,4,5,6-TETRAFLUOROBENZOATE

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

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The proton-donor power of the amino groups in intermolecular hydrogen bonding and the enthalpy of intramolecular hydrogen bond were estimated from the IR spectra (N—H and N—D stretching vibration region) of solutions of 2-nitro-3,4,5,6-tetrafluoroaniline and methyl 2-amino-3,4,5,6-tetrafluorobenzoate and their NHD and ND_2 *derivatives in* CCl_4. *The intermolecular hydrogen bond exerts a weak effect on the intramolecular hydrogen bond. The intramolecular hydrogen bond in methyl 2-amino-3,4,5,6-tetrafluorobenzoate is stronger, as well as in the case of nonfluorinated analogs; fluorination insignificantly increases its strength. The opposite effects of fluorine atoms on the proton-donor power of the NH group and on the proton-acceptor power of the ortho substituent compensate for each other.*

Investigation of vibrational spectra of H complexes between proton acceptors B and the NH group of substituted anilines in which the amino group is simultaneously involved in intramolecular H bond with the *ortho* substituent Y allowed us to introduce a criterion of the strength of the NH···Y intramolecular H bond and to propose a procedure for estimating its energy [1]. In [1—3] we analyzed stretching vibration frequencies of the NH and ND groups in complexes of several *ortho*-substituted anilines with various proton acceptors, determined the enthalpies of inter- and intramolecular H bonds in these complexes, and estimated the mutual influence of the H bonds. The occurrence of inter- and intramolecular H bonds frequently plays a determining role in the reactivity of such compounds.

Using the same approach, in the present work we examined the IR spectra of 2-nitro-3,4,5,6-tetrafluoroaniline (I) and methyl 2-amino-3,4,5,6-tetrafluorobenzoate (II) and compared the spectral and thermodynamic parameters of complexes involving these compounds and their nonfluorinated analogs (Ia, IIa) in order to estimate the effect of fluorine atoms on the proton-donor and proton-acceptor powers of the active groups and the weakening of the intramolecular H bonds upon formation of intermolecular H bonds (anticooperative effect). We measured the IR spectra of compounds (I, II) and their complexes with various proton acceptors in CCl_4 in the region of stretching vibrations of N—H and N—D bonds for NH_2, NHD, and ND_2 derivatives. The concentrations of solutions of (I) and (II) were about ~0.1 M to prevent self-association. The frequencies of the absorption maxima are given in Tables 1 and 2. These data, together with those for nonfluorinated compounds (Ia) and (IIa) [1] led us to the following conclusions.

The NH_2 and ND_2 absorption frequencies of (Ia) and (IIa) are slightly higher than those of the corresponding fluorinated derivatives. For the free molecules and weak complexes the difference is 2—5 cm^{-1}, which is typical of compounds like Ar_FX [4]. As the intermolecular H bond becomes stronger, the difference increases to 10—30 cm^{-1}. The complex shape of the bands often makes comparison difficult. Figure 1 gives the spectra of partially deuterated compound (II) in various solvents as an example. In these cases two (or sometimes three) maxima are observed. For compounds (I, II) the difference $\Delta\nu = \nu_a - \nu_s$ is, as a rule, somewhat lower than for their analogs (Ia, IIa), but it increases in the case of the strongest complexes.

With growing strength of the intermolecular H bond, the ν_c and ν_t frequencies (*cis* and *trans* orientation with respect to the *ortho* substituent Y) of the NH and ND bonds in the semideuterated

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Table 1. Amino Group Absorption Frequencies in the IR Spectra of Solutions of 3,4,5,6-tetrafluoro-2-nitroaniline (I) and Its Complexes with Proton Acceptors in CCl_4 (cm^{-1})

Proton acceptor	NH_2			(D)NH			ND_2			(H)ND		
	ν_s	ν_a	$\Delta\nu$	ν_c	ν_t	$\delta\nu$	ν_s	ν_a	$\Delta\nu$	ν_c	ν_t	$\Delta\nu$
–	3406	3518	112	3453	3476	23	2514, 2489, 2425	2640	151	2546	2569	23
Ethyl trifluoroacetate	3400	3509	109	3463		0	2488, 2520	2635	147	2551		0
Butyl chloride	3395	3506	111	3454		0	2483, 2515	2632	149	2546		0
Toluene	3395	3505	110	3450		0	2482, 2510	2632	150	2546		0
Mesitylene	3391	3501	110	3455	3435	−20	2481, 2508	2631	150	2545	2535	−10
Ethyl acetate	3354	3480	126	3455	3390	−65	2422, 2462	2609	147	2550	~2490	−60
Acetonitrile	3200, 3361	3484	123	3455	3390	−65	2426, 2467	2613	146	2545	~2485	−60
Methyl ethyl ketone	3200, 3348	3480	132	3458	3380	−78	2419, 2462	2608	146	2550	~2485	−65
Acetophenone	3190, 3344	3474	130	3455	3370	−85	2418, 2462	2607	145	2545	2480	−65
Diethyl ether	3200, 3325	3476	151	3458	3330	−128	2400, 2410	2603	190	2550	2458	−92
Tetrahydrofuran	3190, 3320	3472	190	3456	3315	−141	2396, 2408	2601	200	2550	2453	−97
Tetramethylurea	3190, 3305	3466	200	3456	3260, 3320	−170	2370	2590	220	2550	2444	−106
Hexamethylphosphoric triamide	3130, 3260	3463	300	3457	3160, 3260	−280	2350, 2500	2587	230	2548	2350	−200

Table 2. Amino Group Absorption Frequencies in the IR Spectra of Solutions of Ethyl 2-Amino-3,4,5,6-tetrafluorobenzoate (I) and Its Complexes with Proton Acceptors in CCl_4 (cm^{-1})

Proton acceptor	NH_2			(D)NH			ND_2			(H)ND		
	ν_s	ν_a	$\Delta\nu$	ν_c	ν_t	$\delta\nu$	ν_s	ν_a	$\Delta\nu$	ν_c	ν_t	$\Delta\nu$
–	3380	3511	131	3413	3482	69	2476	2631	155	2526	2573	47
Mesitylene	3376	3489	113	3417	3445	28	2473	2623	150	2528	2555	27
Acetonitrile	3374	3478	104	~3420		~0	2468	2612	144	2531	2540	9
Methyl ethyl ketone	3362	3466	104	~3420		0	2408, 2462	2603	143	2530		0
Diethyl ether	3342	3455	113	3418	3380	−38	2405, 2450	2590	150	2530	~2480	−50
Tetrahydrofuran	3180, 3335	3450	135	3418	~3335	−73	2403, 2445	2590	160	2530	~2475	−65
Dimethyl sulfoxide	3170, 3310	3440	180	~3425	~3320	−105	2390, 2437	2575	165	2530	2460	−70
Hexamethylphosphoric triamide	3150, 3250 3290	3437	227	~3425	~3250	−175	2370	2570	200	2530	2435	−95

form NHD of (I, II) change similarly to those of compounds (Ia, IIa) [1]. The ν_t frequencies of the NH and ND bonds in the NHD group involved in intermolecular hydrogen bond NH···B decrease as the proton-acceptor power of B weakens. The change in ν_t ($\Delta\nu_t$) in going from solution in CCl_4 to the complex with the strongest examined proton-acceptor, hexamethylphosphortriamide, is 300 and 230 cm^{-1} (NH bands) and 220 and 140 cm^{-1} (ND bands) for compounds (I, II), respectively. Hence, compound (I) is a stronger donor of a proton in intermolecular H bonding compared with (II), and compound (Ia) is a stronger proton donor as compared with (IIa). Naturally, this fact can be explained by the different electron-acceptor properties of the NO_2 and $COOCH_3$ groups (σ^0 0.82 and 0.46, respectively [5]). The values of $\Delta\nu_t$ for complexes of (I, II) are greater than those for for complexes of nonfluorinated analogs (Ia, IIa) with the same proton acceptors. Thus, with complexes with hexamethylphosphoric triamide, the values of $\Delta\nu_t$ for the NH and ND bands of (Ia) are 230 and 170 cm^{-1}; the corresponding values for (IIa) are 180 and 115 cm^{-1} [1]. Introduction of fluorine atoms into the benzene ring is known [6] to increase the acidity of anilines. For instance, the acidity of pentafluoroaniline is 8.2 p*K* units higher than that of aniline, in keeping with growing proton-donor power of the NH group upon fluorination of the ring. The presence of a fluorine atom in the *ortho* position with respect to the amino group creates steric hindrance for intermolecular H bonding, which results in strong distortion of the intermolecular potential in the vicinity of the proton-donor NH group [7], and, as follows from data in [8–10], the *ortho*-fluorine atom is capable of forming a weak intramolecular H bond, acting as proton acceptor. Therefore in a complex with an acceptor, the bond angle in the amino group can change, and the entire group adopts a different configuration due to rotation about the C—N bond through an angle that ensures optimal interaction with the acceptor [9].

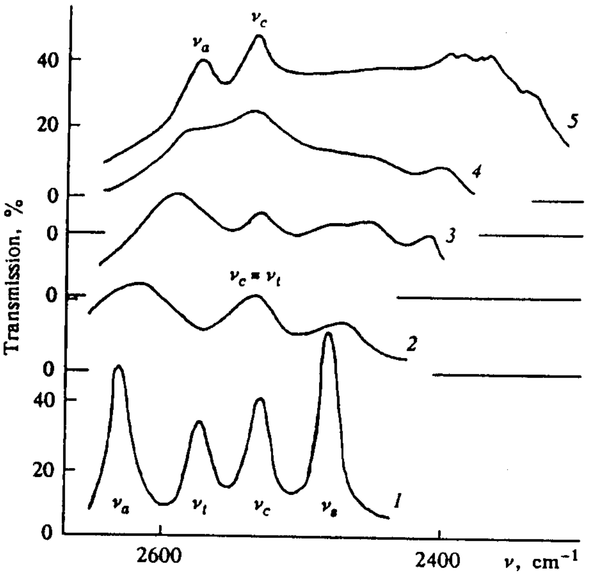

Fig. 1. IR spectra of solutions of partially deuterated compound (II) in CCl_4 (*1*), acetonitrile (*2*), tetrahydro furan (*3*), 6.0 M DMSO in CCl_4 (*4*), and 3.2 M hexa methylphosphoric triamide in CCl_4 (*5*). Concentration of (II), M: 0.1 (*1–4*), 0.2 (*5*).

The quantity $\Delta\nu = \nu_t - \nu_c$ {the difference between the ν[NH(ND)] frequencies of the free groups, i.e., groups that interact with the solvent, and of those involved in intramolecular H bond} is used as a measure of the strength of the intramolecular H bond; it increases upon fluorination. The $\Delta\nu$ value for compound (II) is considerably greater than that for (I); the same is true of nonfluorinated compounds (Ia, IIa). This indicates that the intramolecular H bond in (II) is stronger. Obviously, the energy of the molecular orbital wholly contributed by the oxygen $2p_\pi$-AO in nitrobenzene [11] is lower than that for carbonyl compounds [12], and the amino group proton interacts with the $COOCH_3$ group more effectively than with NO_2. Due to formation of the intermolecular H bond NH···B $\Delta\nu$ decreases, and its value passes through zero and becomes negative for complexes in which the intramolecular H bond is weaker that intermolecular H bond. Comparison with compounds (Ia, IIa) shows that similar ν_c and ν_t frequencies are observed with complexes of (I, II) with the same acceptors. This provides an additional support for the fact that the strength of the intramolecular H bond changes only slightly upon fluorination of the benzene ring. We showed previously that, according to data of x-ray emission spectroscopy and MNDO calculations, the NO_2 [13] and C=O groups [14] in pentafluoronitrobenzene and methyl pentafluorobenzoate interact with the π system of the benzene ring through internal π and σ levels and that this interaction follows an exclusively inductive mechanism. A similar pattern is observed with nitrobenzene [15]. That is why introduction of fluorine atoms into the benzene ring should not appreciably affect the strength of the intramolecular H bond. The enthalpy of complexes for which $\delta\nu \approx 0$ can be taken as a measure of the strength of intramolecular H bond [1].

The ν_c[NH(ND)] frequency of the group involved in NH···Y intramolecular H bond slightly increases with increasing strength of the intermolecular H bond. For complexes with hexamethylphosphoric triamide, the difference $\Delta\nu_c$ (relative to a solution of the pure compound) is 4 cm^{-1} (2 cm^{-1} for ND) for compound (I) and 12 cm^{-1} (4 cm^{-1}) for compound (II). This indicates weakening of the intramolecular H bond due to the effect of external proton acceptor B (cf. [16—19]). The increase in ν_c for compound (II) is greater than that for compound (I) (CCl_4 solutions of complexes with similar proton acceptors). In the latter case the difference is within the experimental error. Complexes of (Ia) and (IIa) demonstrate a stronger effect of the intermolecular hydrogen bond on the intramolecular hydrogen bond. With complexes with hexamethylphosphoric triamide, $\Delta\nu_c$(NH) is 8 cm^{-1} (for ND, 3 cm^{-1} ND) for compound (Ia) and 19 cm^{-1} (12 cm^{-1}) for methyl ester (IIa). We presume that in compounds (I, II) transmission of the effect through the nitrogen atom is hindered because of the strong influence of the fluoroaryl moiety on the electron-density distribution in the CNH_2 group, which results in some "saturation" of the cooperative and anticooperative effects. This problem calls for further investigation.

To estimate the proton-donor power of compounds (I, II) we also determined the enthalpies of formation of their complexes with hexamethylphosphoric triamide. From the ν(NH) band intensities of the free molecules with the use of the balance equations we determined the equilibrium constants for formation of bimolecular complexes of (I) and (II) with hexamethylphosphoric triamide. Temperature dependences of the equilibrium constants in the range 25—72°C gave the enthalpies of complex formation for compounds (I) and (II) of 5.0 and 2.5 kcal/mole, respectively. These values are somewhat lower than those for compounds (Ia) and (IIa) (5.4 and 3.1 kcal/mole, respectively [1]), although the difference is within the experimental error. The equilibrium constant for complex formation increases upon fluorination of the benzene ring: 54 and 62 liter/mole for compounds (Ia) and (I) and 6.2 and 9.0 liter/mole for compounds (IIa) and (II) at 25°C.

As follows from data in Tables 1 and 2, in the series of complexes of semideuterated derivatives of (I, II), the ν_c and ν_t frequencies of the NH (ND) bonds in complexes of (I) become similar with weaker acceptors (ethyl trifluoroacetate, butyl chloride, toluene) than in the case of compound (II) (acetonitrile, methyl ethyl ketone). This fact qualitatively confirms the conclusion that the intramolecular hydrogen bond in (II) is stronger and provides the possibility of quantitatively estimating its energy. Let us assume that similar perturbations of the ν(NH) frequencies of the two NH bonds in the amino group have similar energies. Then, the enthalpy of a Y···HNH···B complex in which the NH bonds are equivalent can be taken as a measure of the strength of the intramolecular H bond. The enthalpy of the complex of compound (II) with methyl ethyl ketone was determined from the temperature dependence of the equilibrium constant, using the Vant-Hoff equation. We obtained a value of ΔH —2.1 kcal/mole. We failed to estimate the enthalpies of weaker complexes of (I) with toluene and butyl chloride because of the strong overlap of the bands of the free molecules and the complexes. Therefore, we used the correlation between the enthalpy and the gain in the ν(NH) intensity [20]. The enthalpies of the two complexes, thus determined, were —0.4 kcal/mole. To check this procedure we also determined the enthalpy of the complex of (II) with methyl ethyl ketone, which coincided with that calculated by the Vant-Hoff equation. Taking into account the anticooperative effect of hydrogen bonds in the complexes, the enthalpies of the intramolecular hydrogen bonds in the free molecules were estimated as 0.4 and 2.3 kcal/mole for compounds (I) and (II), respectively.

These findings confirm a weak trend of the intramolecular NH···O bond to enhance upon fluorination of the benzene ring. The value 0.3 kcal/mole obtained for a weak H bond in (I) is almost the same as that given in [1] for compound (Ia). For a stronger H bond in (II), the gain in the enthalpy relative to (IIa) (~1 kcal/mole) exceeds the experimental error. This led us to conclude that, in the first approximation, the opposite effects of fluorine atoms on the proton-donor power of the NH group and the proton-acceptor power of the *ortho* substituent compensate for each other. A somewhat stronger increase in the proton-donor power appears as a second-order effect. It would be of interest to analyze the effects of all factors that influence electron-density distribution in the vicinity of the interacting groups by quantum-chemical methods.

To conclude, note that the study of complexes of (I) with strong electron acceptors revealed the ability of molecule (I) to bind more than one molecule of the acceptor provided that the latter is present in considerable excess. This means that the energy liberated upon formation of the second intermolecular H bond by the amino group exceeds the loss in energy due to rupture of the intramolecular H bond and breakage of conjugation because of rotation of the amino group about the C—N bond. No such pattern is observed with systems containing compound (II), for the intramolecular hydrogen bond in (II) is higher, and the proton-donor power of the amino group is weaker than in compound (I). By the procedure reported in [18,19], we determined the equilibrium constant for addition of a second molecule of proton acceptor to the 1:1 complex at 25 and 72°C. We also estimated the enthalpy of this reaction in the system compound (I)—hexamethylphosphoric triamide in CCl_4 by the Vant-Hoff equation. The obtained values, K(25°C) 0.18 liter/mole and ΔH —1.0 kcal/mole, turned out to be considerably smaller than those for the 1:1 complex, which is attributable to the anticooperative effect and rotation of the amino group about the C—N bond. As follows from analysis of the ν_c and ν_t frequencies in the series of 1:1 complexes of (I) with proton acceptors, the first effect is insignificant. Therefore, the main reason for sharply reduced energy of addition of the second molecule of hexamethylphosphoric triamide to compound (I) is the energy loss due to rupture of the intramolecular NH···ON and the reduced proton-donor power of the amino group due to breakage of conjugation with the aromatic ring.

Experimental

The IR spectra were recorded on a UR-20 spectrophotometer. The solvents were purified and dried by common procedures. Compounds (I) and (II) were prepared as described in [21].

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