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The weakening of the intramolecular hydrogen bond NH···O in complexes of ortho-substituted anilines with proton acceptors*

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Abstract

The IR spectra of *ortho*-nitroaniline and methyl anthranilate and their complexes with protonacceptors B have been studied in the region of the stretching vibrations of the NH_2, ND_2 and NHD groups. Weakening of the intramolecular hydrogen bond NH···O under the influence of the intermolecular bond NH···B has been found to occur. The cooperativity effect increases with the strength of the inter- and intramolecular hydrogen bonds. A method of estimating the intramolecular hydrogen-bond enthalpy in ortho-substituted anilines has been proposed, based on the assumption of the equality of two hydrogen-bond enthalpies in the complex with the symmetrically perturbed amino group. The equivalence of inter- and intramolecular perturbations were determined by the coincidence of *cis*- and *trans*-NH (and/or ND) frequencies of the NHD group.

INTRODUCTION

The mutual influence of hydrogen bonds in complexes with two or more such bonds, i.e. the problem of energetic non-additivity of complex molecular aggregates with hydrogen bonds, has been studied theoretically and experimentally in many works (see, for example, the recent publications refs. 1–14, and references cited therein). In most cases the cooperative strengthening of hydrogen bonds in chain or cyclic multimers, where each molecule forms two bonds as a donor and as an acceptor of a proton, has been considered. In complexes formed by the AH_n group (water, primary amines, ammonia, etc.) with two proton acceptor molecules, a mutual weakening of the hydrogen bonds (anticooperativity or negative cooper-

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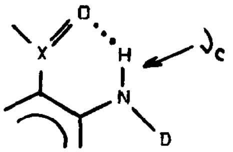
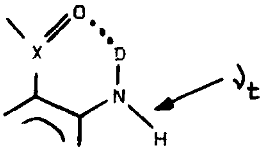
*Dedicated to Professor W.A.P. Luck.

ativity) has been observed [14–22]. A similar weakening has been found for complexes in which a proton-accepting group possessing more than one lone pair is linked with two or more proton-donor molecules [22–26]. All these effects can be explained qualitatively by the polarization of a molecule in the complex, resulting in a change in the proton-donating or proton-accepting ability of the molecule forming the second hydrogen bond.

Convenient subjects for the study of non-additivity are binary complexes with an intermolecular hydrogen bond AH···B, in which the proton-donating group of the molecule AH is involved simultaneously in an intramolecular hydrogen bond, as in salicylic acid or in some ortho-substituted anilines. The spectral study of such systems does not involve difficulties in identifying bands belonging to complexes of different compositions. The strengthening of the intramolecular hydrogen bond OH···OH has been effectively demonstrated by studying the IR spectra of 1,4-butanediol complexes with proton acceptors [5]. It was shown that the low-frequency shift of the νOH band, due to intramolecular bonding, increases with strengthening of the intermolecular bond OH···B in complexes of the type OH···OH···B. The same behaviour has been observed for complexes RCOOH···B formed by salicylic acid and N-substituted anthranilic acids with proton acceptors; with an increase of the proton accepting ability of B, the low-frequency shift of the νAH band in the IR spectrum and the low-field shift of the δAH signal in the ^{1}H NMR spectrum increases, showing the strengthening of the intramolecular hydrogen bond AH···O=C under the influence of the acceptor B [20,21].

In this work, a study of the anticooperativity of the two bonds formed by the NH_2 group as a proton donor was attempted, using the compounds with the intramolecular hydrogen bond NH···O, namely methyl anthranilate (I) and *ortho*-nitroaniline (II). These compounds can act as proton donors on account of the NH group not taking part in the intramolecular hydrogen bond; by studying the complexes of I and II with various proton acceptors, one can hope to detect a weakening of the intramolecular interaction when the intermolecular bond strength increases. The results of ref. 16 indicate the prospects for this study. However, in this case the direct estimate of non-additivity in terms of energy meets with failure, in contrast to the complexes of primary amines with acceptors, where it is possible to obtain the experimental values of equilibrium constants and enthalpies of 1 : 1 and 1 : 2 complexes [17,18]. The feature of ortho-substituted anilines with intramolecular hydrogen bonding is the symmetry of the potential curve of internal rotation of the NH_2 group; hence the concept of the intramolecular hydrogen-bond energy needs a special definition, based on a priori assumptions. The existence of such a bond is proved by vibrational and NMR spectra [16,27,28] and by X-ray crystallography [29]; as a quantitative measure of its strength, one can use the shift δνNH (or ND) in the IR spectrum of the semideuterated amino group [16,30–32]. The vibrations of the NH and ND bands in the DNH group are almost independent and the frequencies νNH (or νND) of the groups in cis and trans positions with respect to proton-accepting ortho-substituents differ, due to the participation of the cis group in the intramolecular hydrogen bond.





$$\delta\nu_{NH} = \nu_t - \nu_c$$

RESULTS AND DISCUSSION

The IR spectra in the νNH and νND regions have been obtained for compounds **I** and **II** and their deuterated forms in various solvents. Figures 1 and 2 show some of the spectra in the νND region. Besides the bands ν_c and ν_t of the DNH group, the bands of the ND_2 group are seen in these spectra. The low-frequency band of the ND_2 group has a complex structure because of Fermi-resonance with combination modes [19,33]. The frequencies ν_c, ν_t of the DNH group and their differences δνNH, δνND, as well as the frequencies of the NH_2 and ND_2 groups, are given in Tables 1 and 2. The results are close to those of Bellamy and Pace [16], obtained under similar conditions.

A comparison of the δν values in the spectra of **I** and **II** (64 and 31 cm^{-1}, respectively, for NH, and 43 and 17 cm^{-1}, respectively, for ND vibrations in CCl_4 solution) shows that the strength of the intramolecular interaction NH···O in **I** is higher than that in **II**. The formation by the trans group NH (or ND) of an intermolecular hydrogen bond with a proton acceptor results in a decrease in the corresponding frequency ν_t; both frequencies of the NH_2 (and ND_2) group vibrations decrease in the complex as well. With the strengthening of the intermolecular bond in a series of proton acceptors, the ν_t frequency approaches ν_c and becomes equal to it; the ν(D)NH (and ν(H)ND) band becomes a singlet. The equivalency of the two NH bonds in the NH_2 group in this complex provides evidence of the same perturbation by intra- and intermolecular interaction. For **I**, the frequencies ν_t and ν_c become indistinguishable in complexes with ethyl acetate and acetonitrile; the proton-donating power for intermolecular bonding of **II** is higher, but intramolecular interaction is weaker than in **I**, and the ν_t and ν_c frequencies coincide in its complexes with butyl chloride, chlorobenzene and toluene.

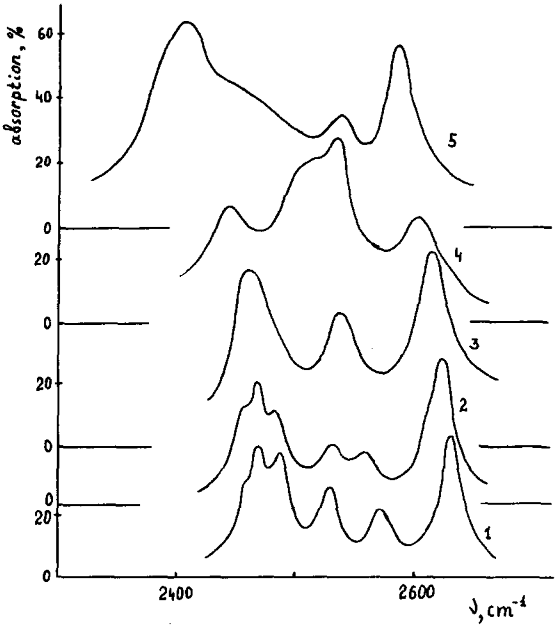


Fig. 1. IR spectra of partially deuterated methyl anthranilate solutions in (1) CCl_4, (2) toluene, (3) acetonitrile, (4) tetrahydrofuran and (5) a 20% solution of hexamethylphosphoramide in CCl_4. Concentration of methyl anthranilate, (mol l^{-1}): (1) 0.1, (2) 0.27, (3) 0.39, (4) 0.62, and (5) 0.32.

In complexes with stronger acceptors, the bands ν(D)NH and ν(H)ND split into doublets and the splitting increases in the series of acceptors. The sign of the $\delta\nu$ value changes, the intermolecular hydrogen bond becomes stronger than the intramolecular bond and the frequency ν_t becomes less than the frequency ν_c.

Comparing the low-frequency shifts of the ν_t band for **I** and **II** in complexes with the same acceptors, one can see that in all cases the shift $\Delta\nu_t$ for **II** is greater than for **I**, i.e. **II** is the stronger proton donor in the intermolecular hydrogen bond. For a quantitative comparison of the proton donating ability of **I** and **II**, the enthalpies of their complexes with a common acceptor, hexamethylphosphoramide, have been measured. The νNH bands of free anilines and of complexes in CCl_4 solutions containing various amounts of acceptor have been separated graphically, and the intensity of the bands 3380 and 3404 cm^{-1} of **I** and **II**, respectively, have been used for determining the concentration of the free molecules [A]. Concentrations of complexes [AB] and of free hexamethylphosphoramide molecules [B] have been calculated using balanced equations. The equilibrium constant $K = [AB]/[A][B]$ has been found at four temperatures in the range 25–72° C and the enthalpies ΔH of the complexes have been obtained by the

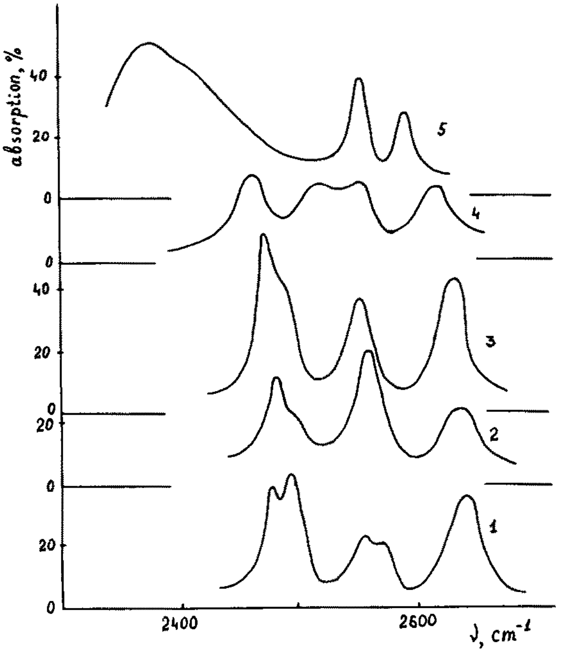


Fig. 2. IR spectra of partially deuterated *ortho*-nitroaniline solutions in (1) CCl_4, (2) ethyltrifluoroacetate, (3) toluene, (4) acetonitrile and (5) a 19% solution of hexamethylphosphoramide in CCl_4. Concentration of *ortho*-nitroaniline, (mol l^{-1}): (1) 0.1, (2) 0.3, (3) 0.48, (4) 0.2 and (5) 0.32.

van't Hoff law. The $-\Delta H$ values are 3.1 and 5.4 kcal mol^{-1} and $K = 6.2$ and 54 l mol^{-1} (at 25°C) for the anilines **I** and **II**, respectively.

In the series of complexes, the frequency ν_c increases with strengthening of the intermolecular hydrogen bond. This can be interpreted as a result of the intramolecular hydrogen bond weakening under the influence of the intermolecular bond, as a consequence of an electron density shift in the NH_2 group towards the cis bond. It can be seen from Tables 1 and 2 that the increase of ν_t in complexes with the same acceptor is larger for **I** than for **II**, i.e. the influence of the intermolecular hydrogen bond on the intramolecular bond is stronger for a compound with a stronger intramolecular bond. A similar situation was observed by Kleeberg and Luck [1] for cooperative effects in complexes with intermolecular hydrogen bonds and coordination compounds.

The results are illustrated by the scheme shown in Fig. 3. A rough estimate of the anticooperativity effect can be made by taking the frequency shift $\Delta\nu_c$ as a measure of the change of intramolecular bond strength [5]. In the complex with the strongest acceptor used, hexamethylphosphoramide, the frequency ν_cNH of **I** increases by 19 cm^{-1}, so that the strength of

TABLE 1

The frequencies νNH and νND (in cm^{-1}) in the IR spectra of methyl anthranilate and its complexes with proton acceptors

Solvent	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	$\delta\nu$
Carbon tetrachloride	3380	3509	129	3416	3480	64	2466, 2484	2628	162	2527	2570	43
Butyl chloride	3380	3498	118	3419	3463	44	2467, 2485	2623	156	2530	2559	29
Toluene	3379	3494	115	3419	3456	37	2466, 2484	2631	155	2530	2555	25
Mesitylene	3377	3491	114	3420	3447	27	2455, 2465, 2483	2619	155	2530	2546	16
Ethyl acetate	3377	3484	107	3429		0	2455, 2470	2615	155	2536		0
Acetonitrile	3377	3484	107	3427		0	2455, 2465	2614	155	2536		0
Methyl ethyl ketone	3372	3478	106	3427		0	2452	2611	159	2534		0
Diethyl ether	3362	3471	109	3423	3390	−33	2448	2606	158	2532	2520	−12
Tetrahydrofuran	3354	3464	110	3424	3377	−47	2442	2600	158	2532	2515	−17
Tetramethylurea	3310, 3337	3458	120	3431	3346	−85	2431	2593	162	2538	2491	−47
Dimethylsulfoxide	3310, 3335	3458	130	3426	3348	−78	2431	2593	162	2534	2488	−46
Hexamethylphosphoramide	3185, 3213, 3244, 3300	3452	180	3435	3300	−135	2408	2586	178	2539	2455	−84

TABLE 2

The frequencies νNH and νND (in cm^{-1}) in the IR spectra of *ortho*-nitroaniline and its complexes with proton acceptors

Solvent	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	$\delta\nu$
Carbon tetrachloride	3404	3523	119	3450	3481	31	2477, 2494	2645	151	2555	2572	17
Ethyl trifluoroacetate	3402	3512	110	3459		0	2480, 2500	2636	156	2558		0
Butyl chloride	3397	3509	112	3454		0	2487, 2495	2634	147	2556		0
Chlorobenzene	3395	3509	114	3453		0	2476, 2490	2635	159	2555		0
Toluene	3393	3506	113	3451		0	2475, 2490	2631	156	2553		0
Mesitylene	3388	3502	114	3453	3437	−16	2473, 2490	2628	155	2555	2545	−10
Ethyl acetate	3370	3489	119	3455	3413	−42	2465	2619	154	2556	2523	−33
Acetonitrile	3375	3495	120	3453	3400	−53	2468	2622	154	2558	2525	−33
Methyl ethyl ketone	3190, 3364	3488	124	3458	3400	−58	2460	2617	157	2558	2516	−42
Acetophenone	3190, 3363	3484	121	3452	3390	−62	2460	2615	155	2556	2515	−41
Diethyl ether	3190, 3346	3484	138	3458	3380	−78	2415, 2445	2612	167	2558	2500	−58
Tetrahydrofuran	3195, 3335	3479	160	3457	3343	−114	2410, 2438	2606	180	2557	2490	−67
Tetramethylurea	3184, 3314	3472	200	3457	3290	−167	2400	2600	200	2558	2430	−128
Hexamethylphosphoramide	3168, 3287	3471	270	3458	3250	−210	2370	2595	225	2558	2400	−160

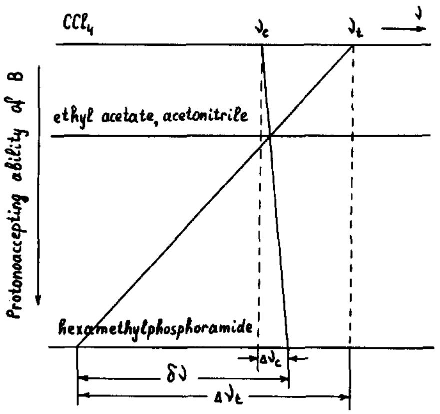


Fig. 3. The scheme of ν_c and ν_t frequencies of the NHD group of methyl anthranilate in complexes with proton acceptors B.

the intramolecular bond, which is estimated in CCl_4 solution to have the value $\delta\nu = 64\,cm^{-1}$, diminishes in the complex by about 30%. A comparison of the corresponding quantities in the νND region, 12 and 43 cm^{-1}, gives the same result. For the complex of **II** with hexamethylphosphoramide, the effect is less; the corresponding quantities for the NH bands are 8 and 31 cm^{-1}, and 3 and 17 cm^{-1} for the ND bands.

The results obtained provide an opportunity for the estimation of a value of the intermolecular bond-energy in ortho-substituted anilines. In a complex with a proton acceptor in which $\delta\nu = 0$, the perturbations of the NH_2 group due to the inter- and intramolecular bonds are equal, and the enthalpy of this complex can be assumed to be a measure of the intramolecular hydrogen-bond energy. Measurement of the enthalpy change in the reaction $A + B \rightleftharpoons AB$ is carried out spectroscopically by a conventional procedure, if the bands of the proton donor A and the complex AB are observed separately. Such experiments have been realized for the complex **I** with CH_3CN in which $\delta\nu \approx 0$. For determining [A], the concentration of free molecules **I**, the band $\nu NH = 3509\,cm^{-1}$ was used after its graphic separation from the band 3484 cm^{-1} of the complex. The measurements have been carried out at 25 and 72°C, and the enthalpy found by the van't Hoff law equals 1 $kcal\,mol^{-1}$. The low accuracy of this value, about 30–50%, is restricted by the uncertainty of the separation of strongly overlapping bands. An estimation of the equilibrium constants at two temperatures has also been made by an approximate method, using the centre of gravity of the two overlapping bands at 3509 and 3484 cm^{-1}, and taking into account their absorption coefficients. The result almost coincides with the previous one. Finally, the same value, about 1 $kcal\,mol^{-1}$, has been obtained from the empirical correlation between the enthalpy and the increase of the νAH band integrated intensity [34]. For the systems **II** with toluene and **II** with butyl chloride, where $\delta\nu \approx 0$, the band overlap is stronger and the separation cannot be carried out with an acceptable degree of reliability. Therefore, the enthalpy of these complexes has been determined only from the correlation [34]. The values for the two complexes differ insignificantly and are approximately equal to 0.35 and 0.3 kcal mol^{-1}, respectively.

Thus, the enthalpy of the intramolecular hydrogen bond NH···O defined by the proposed method has been found to be 1 kcal mol^{-1} for **I** and about 0.3 kcal mol^{-1} for **II**. For comparison, the enthalpies of complexes **I** with butyl chloride (0.2 kcal mol^{-1}), **I** with toluene (0.25 kcal mol^{-1}) and **II** with acetonitrile (1.5 kcal mol^{-1}) have been determined from correlation [34]. These data corroborate the conclusion that aniline **II** is a stronger proton donor in intermolecular hydrogen bonding than **I**. This can be attributed partially to the stronger anticooperativity effect in **I** due to the stronger intramolecular hydrogen bond.

It is important to emphasize that the enthalpy values obtained by the described method characterize the strength of the intramolecular hydrogen bond in the complexes of anilines **I** and **II** with proton acceptors, in which they are weakened on account of the influence of the acceptor. In order to obtain the intramolecular bond energy in a free molecule of ortho-substituted aniline, it is necessary to make a correction for the anticooperativity effect, which can be roughly estimated from a high-frequency shift $\Delta\nu_c$, using the ratio $\Delta\nu_c/\delta\nu$. For **I** in complex with acetonitrile, this weakening is 20% (11 and 64 cm^{-1} for frequencies ν(D)NH, 9 and 43 cm^{-1} for ν(H)ND); for **II** in complexes with butyl chloride and toluene it is about 10% (1–4 and 31 cm^{-1}, 1–2 and 17 cm^{-1}, respectively). In the gas phase, the enthalpies will increase by 10–20% compared with CCl_4 solution, so that, taking into account these corrections, the values of ΔH will increase by a maximum of 30–40%. These values are of the same order of magnitude as the values of the energies of the intermolecular hydrogen bond formed by aromatic amines with analogous proton acceptors [35], the latter being naturally defined by their origin. The considerable difference from the value of the intramolecular hydrogen bond enthalpy 3.2 kcal mol^{-1}, obtained chromatographically [36], is not a problem, since the authors [36] used dissolution heat differences of the ortho and para isomers of the given compound in a polar immovable phase, i.e. they defined the state without intramolecular hydrogen bonding in a different way, hence giving a different definition of the quantity sought.

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