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Spectral manifestations of non-additivity of hydrogen bonds in complexes of substituted anthranilic acids[1]

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Abstract

In IR spectra of complexes of *N*-methyl- and *N*-phenylanthranilic acids with acceptors of the RCOOH $\cdots$ B type, the νNH band of the group taking part in the intramolecular hydrogen bond NH $\cdots$ O=C shifts to lower frequencies with an increase of the proton accepting ability of B. The intermolecular hydrogen bond of the C=O $\cdots$ HX type of methyl esters of these acids with proton donors results in a decrease of the νNH frequency. The strengthening (weakening) of the intramolecular bond is caused by a shift of electron density towards (from) the proton accepting site under the influence of the external proton acceptor (donor). The whole effect of the cooperative and anticooperative influence of the intermolecular hydrogen bond on the intramolecular hydrogen bond reaches 100–130 cm^{-1}.

1. Introduction

Studying the mutual influence of hydrogen bonds it is convenient to use compounds whose functional groups take part in intramolecular hydrogen bonds and can simultaneously form intermolecular bonds as proton donors or acceptors. The efficacy of such an approach was demonstrated by Kleeberg, Luck and co-workers using the example of diols in refs. 1–3. It allows the study of the diverse types of complex, both with mutual strengthening and weakening of hydrogen bonds; here it is possible to vary independently the strength of the intramolecular bonds on account of substituent groups, and the strength of intermolecular bonds on account of the choice of molecule partners. It gives the possibility not only of estimating qualitatively the magnitude of second order effects in spectroscopy and the energetics of hydrogen bonds, but also of ascertaining their quantitative properties. In refs. 4–8 the results of the spectral studies of complexes of ortho-substituted aromatic compounds with proton acceptors are described, which show the wide potential of this method.

2. Results and discussion

In the present work the influence of the intermolecular hydrogen bond RCOOH $\cdots$ B on the intramolecular bond NH $\cdots$ O=C in complexes of *N*-methyl- (MAA) and *N*-phenylanthranilic acid (PAA) with various proton acceptors has been studied by IR spectra in CCl_4 and $CHCl_3$ solutions.

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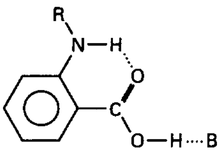


I

$R{=}CH_3$ MAA
C_6H_5 PAA

The strength of the intermolecular interactions in complexes has been estimated by the shift of the νNH band. At room temperature in a 0.01–0.001 M solution, MAA exists mainly in the form of cyclic dimers; the monomer–dimer equilibrium shifts to monomers on heating or on strong dilution of the solution. The position of the equilibrium can be monitored using the νC=O bands of the monomer at 1706 cm^{-1} and the dimer at 1666 cm^{-1} (Fig. 1), and also the νOH band of monomers at 3547 cm^{-1}. In the presence of a proton acceptor the intensity of the bands of monomers and dimers decreases and new bands belonging to the complex of type **I** appear. Varying the concentration of acceptor the dimerization can be suppressed almost completely, as has been seen from the νCO bands. In the spectrum of the solution of MAA in acetonitrile the frequency of the νCO band is reduced by 11 cm^{-1} in comparison with the monomer, the structural band νOH of dimers in the region 2500–3300 cm^{-1} disappears and the band νOH of complexes of the acid with acetonitrile appears at 3270 cm^{-1}; $\Delta\nu_{1/2} \approx$ 200 cm^{-1}. The νNH frequency of the group forming the intramolecular hydrogen bond in complexes with acetonitrile is practically the same as in monomers. In complexes with a stronger proton acceptor, methyl ethyl ketone, the νNH frequency is reduced by 10 cm^{-1} in comparison with monomers (Table 1). With the growth of proton accepting ability of a partner the shift $\Delta\nu$NH increases and reaches in complexes with hexametapol, $(Me_2N)_3PO$, 26 cm^{-1} and with tributylamine (CCl_4 solution) 38 cm^{-1}. When passing from CCl_4 to $CHCl_3$ solutions the shifts $\Delta\nu$C=O and $\Delta\nu$NH of complexes of MAA with tributylamine strongly increase and become close to the corresponding shifts in complexes with dibutylamine (the spectra of complexes of MAA with dibutylamine in $CHCl_3$ and in CCl_4 are virtually identical). It might be suggested that in CCl_4 solution the complex of MAA with a tertiary amine still has a molecular structure, the more polar medium of $CHCl_3$ stabilizing the ionic structure with proton transfer. But the complex with a secondary amine already in CCl_4 is an ionic pair, since the frequencies in the carbonyl region of 1623 cm^{-1} (tributylamine, $CHCl_3$) and 1620 cm^{-1} (dibutylamine) are typical for the $\nu_a CO_2^-$ carboxylate anion.

With a considerable excess of proton acceptor there exists the possibility of formation of the complex to account for the NH group after the breaking of the intramolecular hydrogen bond. However the immediate participation of the NH group in the hydrogen bond NH···B should result in a much larger low-frequency shift of the νNH band than has been observed under the conditions of our experiments (Table 1). Hence the shifts obtained, $\Delta\nu$NH, characterize the

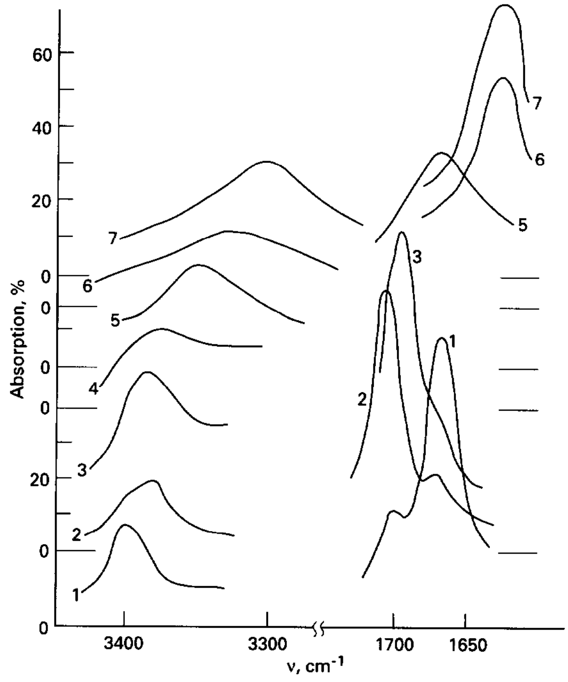


Fig. 1. IR spectra of solutions of *N*-methylanthranilic acid in CCl_4 (1,2), CH_3CN (3), CCl_4 in the presence of methyl ethyl ketone (4), tributylamine (5), dibutylamine (7), $CHCl_3$ in the presence of dibutylamine (6). Concentrations, mol l^{-1}: acid 0.002 (1,5,6,7), 0.0006 (2), 0.1 (3,4); acceptors 0.9 (4), 0.1 (5,6,7). Temperature, °C: 25 (1,3–7), 72 (2).

Table 1
Frequencies of the IR bands of *N*-methylanthranilic (MAA) and *N*-phenylanthranilic (PAA) acids and their complexes with proton acceptors (cm^{-1}; CCl_4 solutions)

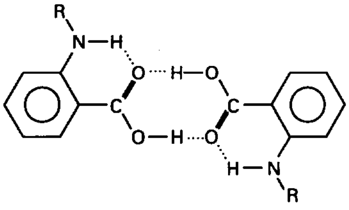
Proton acceptor	MAA			PAA		
	νNH	$\Delta\nu$NH	νCO	νNH	$\Delta\nu$NH	νCO
– (Dimers)	3396	−13	1666	3344	−10	1667
Acid monomers	3383	0	1706	3334	0	1707
Acetonitrile	3383	0	1695	3320	14	1694
Methyl ethyl ketone	3373	10	–	3310	24	–
Diethyl ether	3371	12	1689	3309	25	1691
Tetrahydrofuran	3370	13	1688	3306	28	1689
Dimethylsulfoxide	3368	15	1676	3303	31	1678
Tetramethylurea	3365	18	–	3300	34	–
Hexamethapol	3357	26	1675	3294	40	1678
Tributylamine	3345	38	1665	3260	74	1662
Tributylamine[a]	3323	60	1623	3240	94	1625
Dibutylamine	3302	81	1620	3230	104	1630

[a] $CHCl_3$ solution.

increase of the strength of the intramolecular hydrogen bond NH···O=C owing to the redistribution of electronic density in the carboxylic group and an increase of the proton accepting ability of the carbonyl oxygen atom resulting from the influence of the intermolecular bond COOH···B. The shift, $\Delta\nu$NH, and consequently the magnitude of the cooperative effect increases with the growth of energy of the complex in the row of proton acceptors (Table 1), and reaches the largest values in ionic pairs with amines, where the intramolecular hydrogen bond is strengthened to the greatest degree in consequence of the appearance of the negative charge on the oxygen atom of the anion of the acid. Similar measurements carried out with PAA show that the sequence of shifts, $\Delta\nu$NH, in the complexes with proton acceptors is the same as in complexes of MAA, but the magnitude of the shifts in complexes with the same acceptor is more for PAA than for MAA (Table 1).

Proton donating ability of these acids in intermolecular hydrogen bonds is approximately the same; the enthalpies of their complexes of type I with tetrahydrofuran and hexametapol obtained by the procedure described in ref. 9 are 6.5 and 8 kcal mol^{-1} for MAA and 6.3 and 7.0 kcal mol^{-1} for PAA respectively. However, the estimate of the strength of the intramolecular interaction NH···O=C in these compounds is a problem which is not simple and is not unequivocal. Nevertheless it can be supposed qualitatively, proceeding from the notions of the influence of substituent groups CH_3 and C_6H_5, that in PAA the proton donating power of the NH group is higher than in MAA and the intramolecular bond is stronger. This also follows from the large difference in the frequencies νNH of monomeric molecules, although νCO frequencies do not differ. If this is really the case, the larger magnitude of the cooperative effect in complexes with intermolecular bonds of PAA in comparison with MAA corroborates the conclusion, drawn in refs. 5 and 6 by studying aniline derivatives, that the cooperative effect increases with strengthening of inter- and intramolecular hydrogen bonds.

In the cyclic dimers of MAA and PAA (**II**) each carboxylic group forms two hydrogen bonds; the bond formed by the proton donating OH group



II

results in a strengthening of the intramolecular bond NH···O=C, as in complex **I**. However, the influence of this intermolecular bond, acting through the chain H–O–C=O, on the proton accepting ability of oxygen, is weaker than the influence of the second intermolecular bond, formed by the carbonyl oxygen, which also takes part directly in the intramolecular bond as the proton acceptor. Thus in the dimer the sign of the cooperativity is determined by the influence of the intermolecular hydrogen bond with the carbonyl oxygen; this bond reduces the electron density of the lone pair taking part in the intramolecular bond and thus weakens this bond [10]. The second intermolecular bond somewhat diminishes this influence. Indeed, the frequencies νNH are lower in the spectra of the monomer than in those of the dimers (Table 1).

The similar weakening of the intramolecular interaction NH···O=C resulting from the participation of the second lone pair of the carbonylic oxygen in an intermolecular hydrogen bond has been observed in the complexes of methyl esters of MAA and PAA with proton donors HX (**III**). In the IR spectrum of the methyl ester of MAA in CCl_4 solution the νCO and νNH bands lie at 1690 and 3386 cm^{-1}: the spectrum does not depend on the concentration of the solute or on the temperature. On passing to solution in $CDCl_3$ the νC=O frequency decreases by 7 cm^{-1} and νNH increases by 8 cm^{-1} (Fig. 2, Table 2). The principal cause of these changes is the formation of the intermolecular hydrogen bond C=O···D–C with solvent molecules. In the presence of stronger OH proton donors in the CCl_4 solution of the ester the νCO and νNH bands of free molecules weaken and new bands of complex **III** appear. In the region νNH the wide band νOH···O of the hydroxy group of proton donor ROH in complex **III** is observed, its frequency for donors used being 3470 (CF_3CH_2OH), 3420 (C_6H_5OH), and 3300 cm^{-1} (C_6F_5OH), the intensity of the νOH band of the free donor molecules at higher frequencies diminishing. The identification of the νNH band of the complex, lying on the wing of a broad band

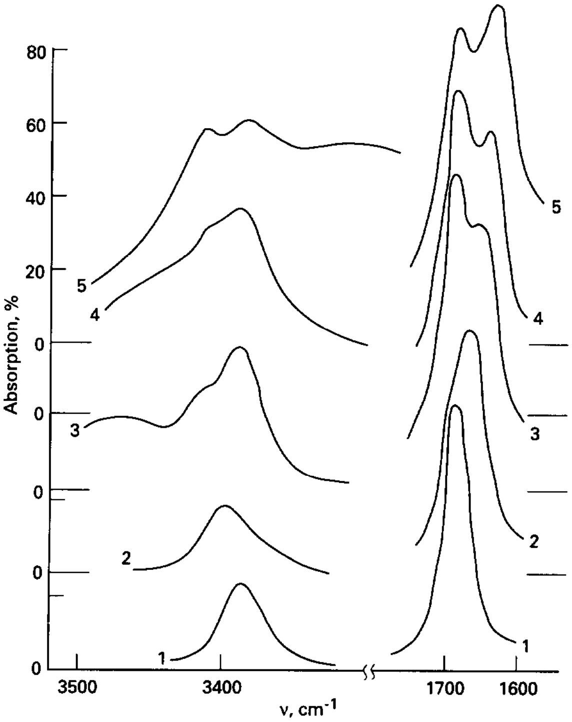
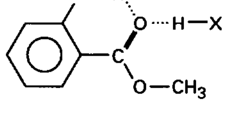


Fig. 2. IR spectra of the methyl ester of *N*-methylanthranilic acid in CCl_4 (1), $CDCl_3$ (2), solutions of CF_3CH_2OH (3), C_6H_5OH (4), C_6F_5OH (5) in CCl_4. Concentrations, mol l^{-1}: ester 0.06 (1,2), 0.15 (3–5); proton donors 0.4 (3), 0.3 (4,5).

Table 2

Frequencies νC=O and νNH in IR spectra of the methyl esters of *N*-methylanthranilic (MAA) and *N*-phenylanthranilic (PAA) acids and their complexes with proton donors (cm^{-1})

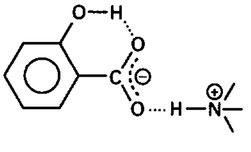
Proton donor	MAA methyl ester		PAA methyl ester	
	νNH	νCO	νNH	νCO
CCl_4	3386	1690	3328	1694
$CDCl_3$	3394	1683	3336	1684
CF_3CH_2OH	3415	1674	3365	1675
C_6H_5OH	3415	1670	3365	1672
C_6F_5OH	3417	1667	3367	1670

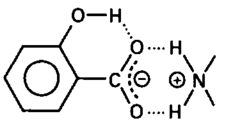


III R=CH_3
C_6H_5

νOH$\cdots$O near the νNH band of free molecules, could be performed by comparing the spectra in the νNH and νCO region at different concentrations of proton donor ROH. With the increase of proton donating ability of ROH the band νCO shifts to lower frequencies; unfortunately the precision of measurements of the νNH band position does not allow the confident determination of the tendency for change of this frequency for complexes of the ester of MAA with three OH donors. Analogous results have been obtained for the complexes of the methyl ester of PAA with proton donors (Table 2). With the strengthening of the intermolecular hydrogen bond the low-frequency shift of the νCO band increases; for the same proton donors the shifts are similar for both esters, but the increase of νNH frequency is considerably larger for the ester of PAA. On the basis as the arguments used for acids (the difference of the νNH frequencies, 58 cm^{-1}, of free ester molecules being greater than for monomers of acids, 49 cm^{-1}), it can be assumed that the greater influence of a given proton donor on the intramolecular bond in the ester of PAA than in the ester of MAA is caused by the greater strength of the interaction NH$\cdots$O=C in the former ester molecule.

The influence of the intermolecular hydrogen bond on the intramolecular bond OH$\cdots$O=C in complexes of ortho-hydroxy substituted aromatic acids is manifested in IR and NMR spectra in a similar manner [11, 12]. With the strengthening of the intermolecular COOH$\cdots$B bond the νOH band of the hydroxy group forming the intramolecular bond shifts to lower frequencies, and the proton signal of this group moves to a lower field. The maximum strengthening of intramolecular bonds was observed in complexes with aliphatic amines which have the structure of an ionic pair. In these complexes the carboxylate anion takes part as a proton acceptor in interionic hydrogen bonds with NH$^+$ and NH$_2^+$ groups of the cation in the corresponding salts of tertiary and secondary amines. These bonds perturb the electronic structure of the carboxylate group differently, and in salts with tertiary and secondary amines the magnitudes of the OH group perturbances are not the same. The spectral shifts $\Delta\nu$OH and $\Delta\delta$OH both increase when passing from tertiary to secondary amines. Therefore, when interacting with the R$_2$NH$_2^+$ cation, the electronic density is fixed to a greater extent on the anion oxygen which takes part in the intramolecular hydrogen bond. By analogy with structures proposed in ref. 12 for ionic pairs of tetrafluoroanthranilic acid with aliphatic amines, the following configuration for ionic pairs can be suggested.

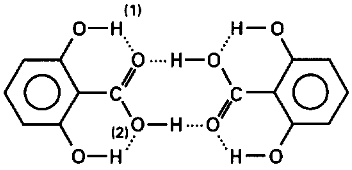




The maximum strength of an intramolecular bond is attained in the quaternary ammonium salts where the cation Alk$_4$N$^+$ virtually does not perturb the electronic structure of the anion at all: the proton accepting ability of the oxygen atom of the anion in the intramolecular hydrogen bond OH$\cdots$O$^-$ is not subjected to the competitive influence of proton donating centers of the cation and is realized in a most effective way.

As the cyclic dimer of the derivatives of salicylic and anthranilic acids is formed, the intramolecular hydrogen bond weakens compared with the monomeric molecule, in a similar way to the *N*-substituted anthranilic acids which were described earlier, and for the same reasons. A more complicated picture is observed in the IR spectra of 2,6-dihydroxybenzoic (γ-resorcylic) acid, since this molecule has two intramolecular bonds. Unlike the OH$\cdots$O=C bond, which weakens when passing from monomer to dimer, the weaker OH$\cdots$O< bond is strengthened; the 3497 cm^{-1} band of this hydroxy group shifts to 3480 cm^{-1} [12]. In this case the sign of cooperativity is governed by the dominant influence of the nearby intermolecular bond in dimer **IV**, since this bond is formed with an oxygen of the hydroxy group taking part in the intermolecular bond as a proton donor.

The farther apart second intermolecular bond in which the carboxylic oxygen is a proton acceptor weakens the effect of the former bond by only a



IV

small extent. In the anionic form of the acid clearly both intramolecular bonds become equivalent, although local interactions with the cation may somewhat disturb this equivalence.

In studies of the mutual influence of hydrogen bonds the magnitudes of spectral shifts can be used only as semi-quantitative characteristics of the perturbation and it is desirable to obtain more precise estimates in energy units. However, when dealing with the compounds with intramolecular hydrogen bonds it is necessary to keep in mind that the concept of the energy of the intramolecular bond is not always unambiguous and should be carefully defined. In certain cases it is possible to propose definite experimental approaches (see for example refs. 4 and 13). In other cases, for example *N*-substituted anthranilic acids and corresponding esters, the direct thermodynamic approach turns out to be invalid, and the indirect estimates have to suffice, for example, with spectral or structural parameters, while the theory of these notable issues remains to be investigated.

3. Acknowledgment

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