

Study of mutual influence of hydrogen bonds in complicated complexes by low-temperature ^1H NMR spectroscopy*

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Abstract

^1H NMR spectra of various acid–base complexes of different stoichiometry at 100–120 K in freon mixtures have been obtained. The separate signals of non-equivalent OH-protons, involved in different H-bonds, have allowed us to consider the problem of the mutual influence of these bonds, using a correlation between the δ_{OH} chemical shift and the ΔH H-bond enthalpy. The mutual strengthening of H-bonds in complexes of the $\text{AH}\cdots\text{AH}\cdots\text{B}$ type and their weakening in $\text{AH}\cdots\text{B}\cdots\text{HA}$ complexes have been found, the value of the effect being about 10–30%

INTRODUCTION

The question of the mutual influence of several H-bonds in complicated complexes has been intensively discussed, (see, for example, the latest reviews [1–4]). Quantum chemical calculations, carried out for dimers, trimers and more complicated self-associates of simple molecules like HHal , H_2O , HCN and others, have shown that in the linear $\cdots\text{XH}\cdots\text{XH}\cdots\text{XH}\cdots$ associates the H-bond energies are higher than in the dimers due to mutual polarization of the bonds (the cooperative effect) [5–9]. This effect increases with the chain length, gradually reaching saturation. Similar results have been obtained when calculating the associations of more complex molecules (alcohols, amines and amides). An inverse effect has been predicted for branched complexes where two or more H-bonds are formed by one proton acceptor group (e.g. $\text{XH}\cdots\underset{\text{H}}{\text{X}}\cdots\text{HX}$).

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*Dedicated to Professor N.D. Sokolov on the occasion of his 80th birthday.

Here the mutual polarization weakens the H-bonds (anti-cooperative effect [9–11]). The origin of these effects is believed to be mainly electrostatic.

In many papers it has been shown that the interaction between the H-bonds also causes measurable changes in some physical properties which depend on H-bond strength, i.e. frequencies of vibrational bands of both proton donor and acceptor molecules, integral intensities of these bands and chemical shifts in NMR spectra. A change of internuclear distances in the complexes has been predicted, too.

Experimental data concerning the energies of individual H-bonds in complicated complexes are not numerous, because of difficulties of quantitative treatment of systems with multiple equilibria. Some IR, MS and ion cyclotron resonance data show that theoretical predictions of the effect of the mutual influence of H-bonds are qualitatively confirmed [12–16].

Experimentally obtained structural, thermodynamic and spectral characteristics of complicated complexes, which may give some indirect information about the cooperative effect in H-bonding, are much more readily available. Of most interest is IR spectroscopy of the complexes trapped in low-temperature matrices of inert gases [17,18]. Extreme narrowing of vibrational bands under these conditions results in high resolution and allows very small spectral shifts, originating from small variations in H-bond strengths, to be registered.

^1H NMR spectroscopy, while being very sensitive to H-bonding and having very high resolution, has hardly been used for studying the cooperativity effect in complicated complexes. The general difficulty in this application of NMR is the existence of fast (at room temperature) exchange processes, which average out the signals of protons involved in H-bonds. However, in refs 19–24 it was found that at temperatures as low as 100–150 K, the processes are usually slow enough for the signals of structurally non-equivalent active (OH- or NH-) protons of the complexes to be observed separately. Their fine spin-spin structure can often be revealed, giving useful additional information about the complexes. It is to be emphasized that the chemical shifts of the active protons, measured under the conditions of hindered exchange, do not depend on concentrations of complexes and impurities. The merits of low-temperature NMR in studying short-lived complexes outweigh considerably its disadvantages, the main one of which is the necessity of using special solvents (freon mixtures) and special techniques for preparing samples [19].

Earlier results [23,24] demonstrate the opportunity of direct investigation of the cooperativity effect in complexes with several H-bonds, using the linear correlation [25] between the δ_{AH} chemical shift of a proton, involved in H-bonding, and the ΔH enthalpy of the H-bond. When measuring all δ_{AH} values for the 1:1 and 2:1 complexes, one can, in principle, determine the energies of all the H-bonds and thus evaluate the effect.

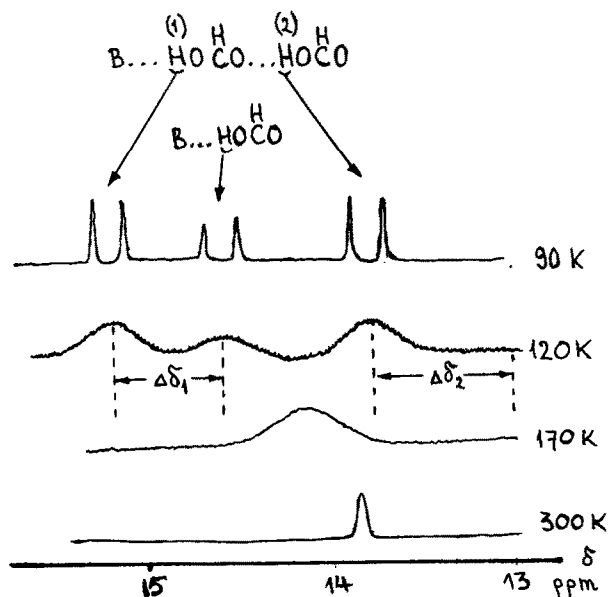


Fig. 1. ^1H NMR spectra (60 MHz) of a solution containing 0.08 M HCOOH and 0.05 M HMPT at 90 (top), 120, 170 and 300 K, in a mixture of CDF_3 and CDF_2Cl .

Taking into account that the δ_{AH}^0 value for a free AH molecule is, as a rule, unknown (especially at temperatures as low as 100–150 K), it is reasonable to limit oneself to a differential form of the correlation: $\Delta(\Delta H) = 1.1\Delta\delta_{\text{AH}}$ for evaluating the absolute change in the strength of one H-bond on formation of another.

The carboxylic acids RCOOH and pentafluorophenol $\text{C}_6\text{F}_5\text{OH}$ were taken as convenient model AH molecules for this study. These two types of molecules, while having rather strong proton donor ability, differ markedly in their ability to self-associate. This allows us to observe different kinds of complicated complexes formed by these molecules.

RESULTS AND DISCUSSION

Complexes of the AH...AH...B type

Such complexes are often formed in systems containing carboxylic acids and strong proton acceptors with no active protons. Figure 1 shows the transformation of the ^1H NMR spectrum of a solution containing formic acid and hexamethylphosphoramide (HMPT), as the temperature is lowered. At 300 K all the OH-protons give one averaged signal, which is gradually shifted downfield, broadened and finally split into three components. Cooling below 130 K results in doublet splitting of all the three

signals revealed due to spin–spin coupling with the formic CH-proton ($J_{\text{HH}} = 12.1$ Hz). Two of the three signals (δ 15.2 and 13.8 ppm) are of equal integral intensity (independent of the concentration ratio). With increasing concentration of HMPT both of these signals decrease and finally disappear; only the δ 14.6 ppm signal remains at a 1.5-fold HMPT excess. Therefore, the δ 14.6 ppm signal must be attributed to the equimolecular 1:1 complex, and the two others to the asymmetrical 2:1 complex: $\text{HCOOH}(2) \cdots \text{OCHOH}(1) \cdots \text{O}=\text{P}$. The attribution of the OH(1) and OH(2) signals was performed by virtue of the nuclear Overhauser effect (NOE) on the ^{31}P nucleus. As OH(1) is situated near the phosphoryl group, the saturation of its signal (δ 15.2) causes a marked enhancement of the ^{31}P signal ($\eta = 0.26$), while the saturation on the frequency corresponding to OH(2) (δ 13.8 ppm) has practically no effect.

Thus, the polarization of one H-bond ($\text{OH} \cdots \text{O}=\text{P}$) by another ($\text{OH} \cdots \text{O}=\text{C}$) gives rise to its strengthening, which is manifested by the downfield shift of the OH(1) signal ($\Delta\delta = 0.6$ ppm). The analogous change in the strength of the second H-bond is difficult to evaluate, since the ^1H NMR spectrum of the open dimer $\text{HCOOH} \cdots \text{OCHOH}$ is unknown. The value $\delta_{\text{OH}(1)}$ may be compared with the chemical shift of the cyclic dimer only ($\delta_{\text{OH}} = 13.0$ ppm [21]). It is clear that the signal of the open dimer should be shifted upfield compared with that of the cyclic one, and the real effect would be higher than $\Delta\delta = 0.8$ ppm.

The spectra of solutions containing formic acid and other strong proton acceptors are quite similar, except for the values of the chemical shifts. This means that in all cases the 2:1 complex has the asymmetrical structure $\text{AH} \cdots \text{AH} \cdots \text{B}$. The spin–spin coupling proves that a possible proton transfer does not occur. (In ref. 26 it was shown that addition of the second molecule of a stronger acid, CF_3COOH , to the 1:1 molecular complex $\text{CF}_3\text{COOH-HMPT}$ results in the following proton transfer: $\text{AH} \cdots \text{B} + \text{AH} \rightarrow \text{AH} \cdots \text{A}^- \cdots \text{HB}^+$). In Table 1 the chemical shifts δ_{OH} , $\delta_{\text{OH}(1)}$ and $\delta_{\text{OH}(2)}$ are listed, as well as the values $\Delta(\Delta H_1)$ and $\Delta(\Delta H_2)$ of the H-bond energy change due to the cooperative effect (evaluated using the linear correlation). One can see that the interaction between two H-bonds leads to their mutual strengthening, with the absolute value of the effect increasing with rising proton-acceptor ability of B. This is illustrated in Fig. 2. The relative values of the effect, $\Delta(\Delta H)/\Delta H$, are not presented in the Table because of the lack of a reliable chemical shift, δ_{OH}^0 , for the free HCOOH molecule at 120 K. Taking this shift to be within the region 6–8 ppm, we can conclude that the enthalpies of the 1:1 complexes, presented in Table 1, vary within the range 7–12 kcal mol $^{-1}$. Addition of the second HCOOH molecule increases this value by 10–15%. However, the addition of B to the open dimer gives rise to an effect which depends on the basicity of B. For the strongest proton acceptor ($\text{C}_5\text{H}_5\text{N}$) the OH(2) $\cdots \text{O}$ bond energy is nearly

TABLE 1

Chemical shifts (ppm; TMS as internal standard) of OH-protons, for different complexes (1:1 and 2:1) of HCOOH with proton acceptors B at 100 K (60 MHz)

B	$\delta_{1:1}$	$\delta_{2:1}^{(1)}$	$\delta_{2:1}^{(2)}$	$\Delta(\Delta H)^{(1)}$ (kcal mol ⁻¹)	$\Delta(\Delta H)^{(2)}$ (kcal mol ⁻¹)
(CH ₃) ₂ SO	13.7	14.6	13.1	1.0	0.1
[(CH ₃) ₂ N] ₂ CO	14.4	15.2	13.6	0.9	0.6
[(CH ₃) ₂ N] ₃ PO	14.6	15.2	13.8	0.7	0.9
(C ₄ H ₉) ₃ PO	15.2	16.7	14.3	1.7	1.5
C ₅ H ₅ NO	17.8	19.0	16.9	1.3	4.3
C ₅ H ₅ N	18.7	20.1	18.0	1.6	5.6
HCOO ⁻ (with (C ₄ H ₉) ₄ N ⁺)	-	-	20.2	-	8.1

doubled. The chemical shift $\delta_{\text{OH}(2)}$ in such complexes approaches the limiting value $\delta = 20.2$, characteristic of a symmetrical H-bond in the bis-formate ion coupled with the tetrabutylammonium cation.

For the systems (AH + B) listed in Table 1 we have not succeeded in finding complexes with more complicated ratios than 2:1. Later the ionic 3:1 complexes of formic acid with trimethylamine will be described.

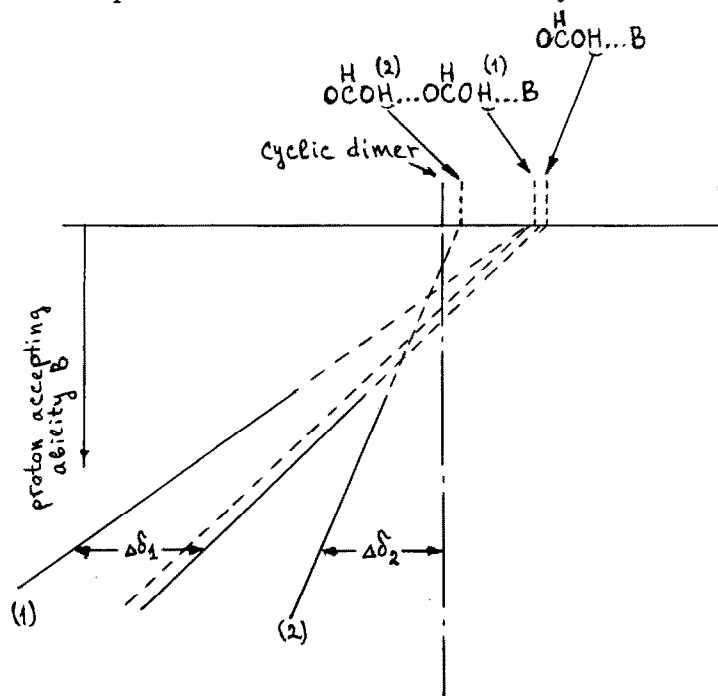


Fig. 2. A schematic diagram, showing changes in chemical shifts for an AH...AH...B complex with increasing proton-acceptor ability of B.

Complexes of the $AH \cdots B \cdots HA$ type

The low-temperature 1H NMR spectra of systems containing proton acceptors with an $X=O$ active group and an excess of pentafluorophenol (PFP) differ qualitatively from those described above. Let us consider at first the case of symmetrically substituted X-oxides like HMPT (C_{3v}) or tetramethylurea (C_{2v}). Except for a signal belonging to the 1:1 complex (which is the only OH-signal for the stoichiometric 1:1 composition of the solute), only one more signal, shifted upfield, can be observed. Relative integral intensities of the two signals (e.g. 1:1, if a 1.5-fold excess of PFP is taken) show that the high-field signal has to be referred to equivalent protons of a 2:1 complex having, most probably, the structure $AH \cdots B \cdots HA$. In this formula two equivalent lone pairs of the oxygen atom are capable of forming two H-bonds with the PFP molecules. The two H-bonds, when competing with one another, become weaker than in the 1:1 complex.

PFP, as mentioned above, has a very poor self-association ability. Thus, even at 100 K and concentrations as high as 10^{-2} M, its solution in CHF_2Cl contains mainly monomeric molecules (as seen from IR spectra). The following speculation may be a possible explanation. Strong acidity of PFP is accounted for by the inductive effect of the perfluoroaromatic ring, which lowers the electron density on the sole proton-acceptor oxygen atom. On the contrary, the main cause of the acidity of carboxylic acids is the conjugation between $C=O$ and $OH-$ groups, which results in the electron density on the carbonyl group being high enough to induce its high proton-acceptor ability and, therefore, the stability of self-associates and complicated complexes such as $RCOOH \cdots OC(R)OH \cdots B$. For the PFP molecule, the branched structure $AH \cdots B \cdots HA$ proves to be more favourable energetically.

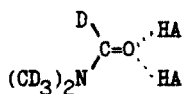
The δ_{OH} chemical shifts of a range of such 2:1 complexes are given in Table 2 (where some data from ref. 23 are also included). In this case the correlation between δ_{OH} and ΔH may be used for determining not only $\Delta(\Delta H)$, but ΔH also. In the symmetrical $AH \cdots B \cdots HA$ complexes of PFP the value of the anti-cooperative effect is 10-20%. Moreover, it increases distinctly with increasing ΔH .

Rather more complicated are the 1H NMR spectra of systems containing PFP and proton acceptors with an asymmetrically substituted $X=O$ group, like dimethylformamide (DMFA) (Fig. 3). Below 150 K in the spectrum two OH-signals are observed, belonging to the 1:1 and 2:1 complexes as in the previous case. The upfield signal is, however, split into a doublet with a distance between the components of about 0.3 ppm. This implies that the two H-bonds in the 2:1 complex are slightly non-equivalent due to asymmetry of the carbonyl group:

TABLE 2

Chemical shifts (ppm; TMS as internal standard) of OH-protons, for different complexes (1:1 and 2:1) of pentafluorophenol (PFP) with proton acceptors B at 100 K (60 MHz)

B	$\delta_{1:1}$	$\delta_{2:1}$	$\Delta(\Delta H)$ (kcal mol ⁻¹)
H ₂ CO	11.3	10.0	-1.3
(CH ₃) ₂ SO	14.8	13.6	-1.3
[(CH ₃) ₂ N] ₂ CO	15.1	13.9	-1.3
[(CH ₃) ₂ N] ₃ PO	16.9	15.1	-2.0
(C ₄ H ₉) ₃ PO	17.0	15.4	-1.8
C ₅ H ₅ NO	18.6	16.3	-2.6



The exchange of position of two HA molecules requires full breaking of at least one H-bond, which below 150 K would proceed slowly in the NMR time scale. Cooling of the solution to below 110 K leads to the splitting of the downfield signal, too. This appears to be related to the slowing down of the

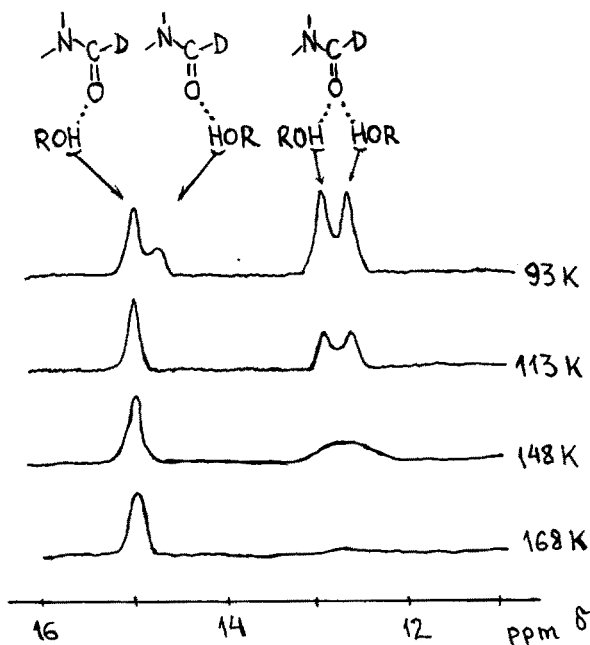


Fig. 3. ¹H NMR spectra (60 MHz) of a solution containing 0.08 M HCOOH and 0.06 M (CD₃)₂NCDO at 93 (top), 113, 148 and 168 K, in a mixture of CDF₃, CDF₂Cl and CDFCl₂.

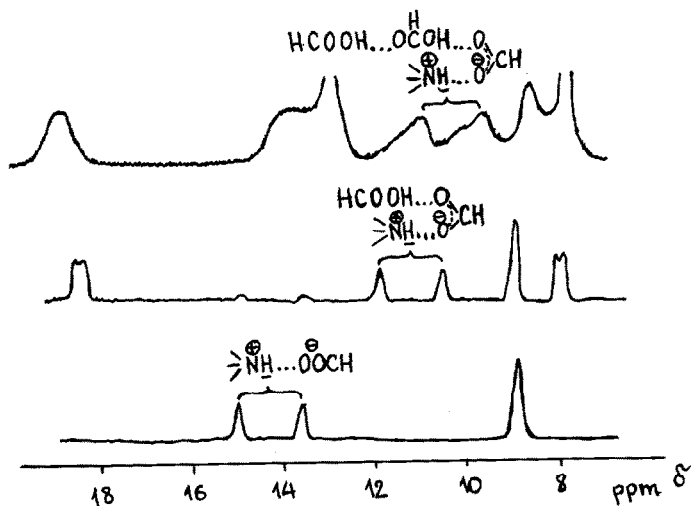


Fig. 4. ^1H NMR spectra (60 MHz) of solutions containing HCOOH and trimethylamine $(\text{CD}_3)_3^{15}\text{N}$ at 100 K and with concentrations 0.006 M plus 0.013 M (bottom), 0.01 M plus 0.006 M, and 0.100 M plus 0.006 M.

rearrangement of two stereoisomeric 1 : 1 complexes:



(A similar stereoisomerism for the complexes of HF with CH_3COOH and $\text{CH}_3\text{COOCH}_3$ was found [27] by means of IR spectra in an argon matrix at 4 K). If this rearrangement proceeded via full breaking of one H-bond followed by the formation of another, its rate would be determined by that of the breaking stage, i.e. the splitting would be observed at 150–140 K. Most probably, the reaction occurs as an intramolecular process such as internal rotation or inversion. The kinetics of such a process for a similar complex of formaldehyde was described in ref. 23.

Ionic complexes of the $\text{AH} \cdots \text{A}^- \cdots \text{HB}^+$ type

In ref. 24 the results of the low-temperature ^1H NMR study of the interaction between HCOOH and trimethylamine $(\text{CD}_3)_3^{15}\text{N}$ were reported. The spectra at different concentration ratios are given in Fig. 4. Large doublet splitting of the low-field signal in the 1 : 1 complex can originate only from ^1H – ^{15}N spin–spin coupling, which indicates ionic character of the complex $\text{A}^- \cdots \text{HB}^+$. Addition of the second HCOOH molecule results in two more doublets belonging to the OH and NH protons in a 2 : 1 complex, and addition of the third molecule in the appearance of three signals which may be connected with a 3 : 1 complex of the type $\text{AH} \cdots \text{AH} \cdots \text{A}^- \cdots \text{HB}^+$. In these systems the chemical shifts of OH-protons should be compared with those

in the open $\text{HCOOH} \cdots \text{OCHOH}$ dimer as well as in the “free” homoconjugated bis-formate anion. Practically, only the values for the cyclic dimer and for ionic pairs involving the bis-formate anion and tetra-alkylammonium cations are available. Figure 4 shows that in the $\text{AH} \cdots \text{A}^- \cdots \text{HB}^+$ complex the two H-bonds weaken one another, similar to the analogous effect in molecular $\text{AH} \cdots \text{B} \cdots \text{HA}$ complexes. The third AH molecule makes the $\text{AH} \cdots \text{A}^-$ H-bond stronger, while the interionic $\text{A}^- \cdots \text{HB}^+$ bond becomes a little weaker, which may be detected by a small upfield shift of the NH-signal. It should be emphasized that for the 3:1 complex of HCOOH with trimethylamine, any influence of the terminal acid molecule on the $\text{NH}^+ \cdots \text{O}^-$ bond strength, at a distance of seven bonds, is evident from the position of the δNH signal.

Similar results have been obtained for the ionic complexes of HCOOH with dimethylamine $(\text{CD}_3)_2^{15}\text{NH}$. In this case ^1H NMR spectra at low temperature demonstrate that addition of a HCOOH molecule to the 1:1 ionic pair, having a symmetric structure with two equivalent NH_2^+ protons, disturbs the symmetry. The spectrum is now characteristic of the ABX spin system ($X = ^{15}\text{N}$; $^2J_{\text{HH}} = 14 \text{ Hz}$); a small difference $\Delta\delta_{\text{NH}}$ indicates some difference in the corresponding H-bond energies.

Mutual influence of intramolecular and intermolecular H-bonds

As convenient models for studying the cooperativity effect in systems with intramolecular H-bonding, 2-hydroxy- and 2,6-dihydroxybenzoic acids have been chosen. In these molecules phenolic OH-groups are involved in H-bonding with the carboxylic CO group. In solutions containing such an acid and a proton acceptor B, intermolecular H-bonding occurs through the carboxylic OH-proton, with no breaking of the intramolecular H-bond. With rising proton acceptor ability of B, the signals of the two OH-protons undergo a downfield shift simultaneously, thus showing some strengthening of the intramolecular H-bond induced by increase of electron density on the C=O group [28]. The effect could be interpreted in terms of some charge transfer from B to the carboxylic group, but, it is possible that electrostatic mutual polarization of two H-bonds would be a sufficient explanation. In this case a quantum chemical calculation is needed.

Let us consider in detail the interaction of 2,6-dihydroxybenzoic acid with proton acceptors. Even the strongest oxygen proton acceptors B are not capable of breaking the intramolecular H-bond, and, therefore, in an excess of B the acid is found in solution as a complex with the carboxylic group forming the $\text{COOH} \cdots \text{B}$ intermolecular H-bond. Figure 5 represents the ^1H NMR spectrum of a freon solution, containing 2,6-dihydroxybenzoic acid and HMPT. As the signals of the COOH and OH protons can be averaged only by proton exchange, their splitting occurs at a temperature

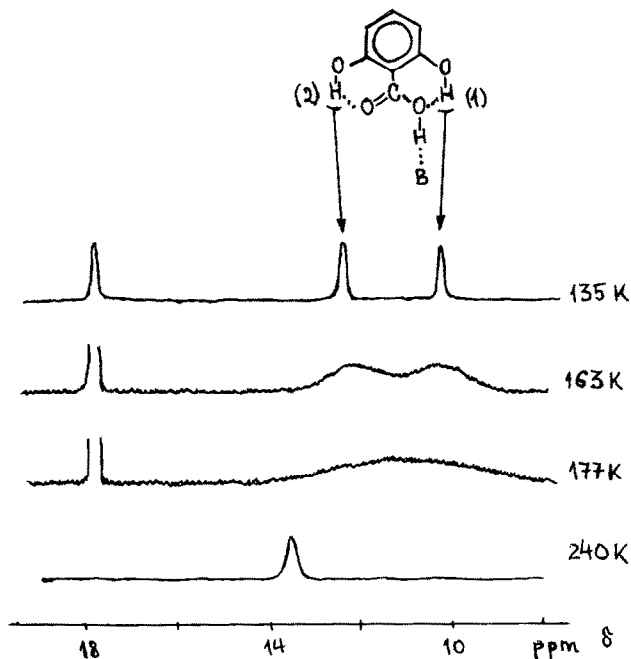
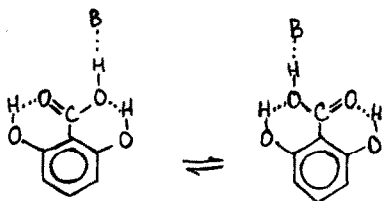


Fig. 5. ^1H NMR spectra (200 MHz) of a solution containing 2,6-dihydroxybenzoic acid (0.007 M) and HMPT (0.010 M) at 135 (top), 163, 177 and 240 K.

as high as 220 K. The splitting of the signals of two non-equivalent OH-groups, being connected with a slowing down of the internal rotation of the COOH group around a single C–C bond, occurs at 150–170 K (for complexes with weaker proton acceptors, such as acetonitrile, complete signal separation may be observed at 110–120 K).



In Table 3 the chemical shifts of COOH and two OH-signals for the complexes with different B molecules are listed. The high-field signal belongs undoubtedly to the OH-group, forming a weaker H-bond with the carboxylic OH-group, while the low-field one refers to the OH \cdots O=C H-bond. The position of the latter practically coincides with that for the corresponding complex of salicylic acid. It is seen that with increasing proton-acceptor ability of B, both the OH-signals are shifted downfield, which shows cooperative strengthening of both intramolecular H-bonds.

TABLE 3

Chemical shifts of carboxylic and two phenolic OH-protons in complexes of 2,6-dihydroxybenzoic acid with proton acceptors at 120 K (200 MHz)

B	δ_{COOH}	$\delta_{\text{OH}}^{(1)}$	$\delta_{\text{OH}}^{(2)}$
CD ₃ CN	12.35	7.58	11.40
(CD ₂) ₄ O	14.03	8.11	11.72
(CD ₃) ₂ SO	16.10	9.50	11.89
[(CD ₃) ₂ N] ₃ PO	17.84	10.22	12.31
C ₅ H ₅ NO	19.15	11.73	12.74
C ₅ D ₅ N	—	13.29	
(C ₄ H ₉) ₃ N	—	13.37	
(C ₄ H ₉) ₄ N ⁺	—	13.80	

The distance between the two OH-signals decreases; thus, an intermolecular H-bond affects more strongly a weaker intramolecular H-bond (see Fig. 6). This might be, however, a simple result of a fast-fading cooperativity effect with increasing distance between the interacting H-bonds.

For the complexes of 2,6-dihydroxybenzoic acid with pyridine and tributylamine, the separation of two OH-signals has not been observed down to a temperature as low as 90 K. These complexes are ionic pairs with the carboxylic proton transferred to the base, and the interionic H-bond slightly disturbing the symmetry of the CO₂⁻ group. Two intramolecular H-bonds should be slightly non-equivalent, although this is not seen from

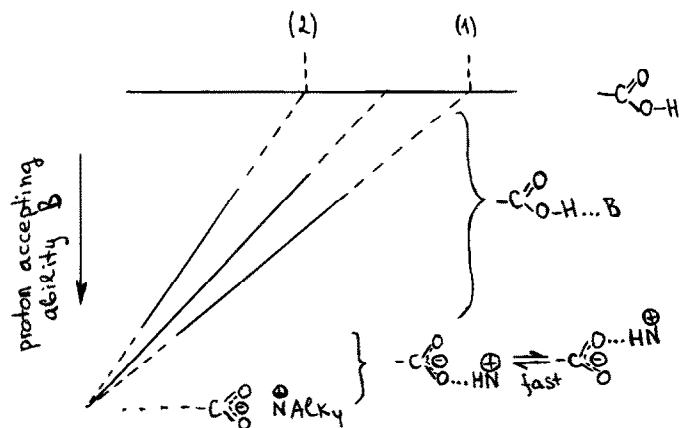
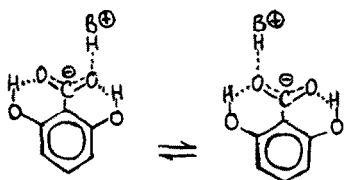


Fig. 6. A schematic diagram, showing chemical shifts of OH-protons in complexes of 2,6-dihydroxybenzoic acid depending on the proton-acceptor ability of B.

the spectra, perhaps because of the high rate of the averaging process:



In the limiting case of the ionic pair with the tetrabutylammonium cation, which hardly disturbs the anion symmetry, the signal of two equivalent OH-groups has a chemical shift as high as 13.8 ppm.

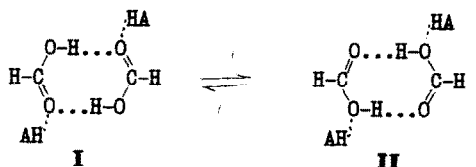
These data can demonstrate that the structure of the carboxylic group changes gradually from the least symmetrical O=C–OH in a free-acid molecule, through equalizing the bond orders to the fully symmetrical CO₂⁻ in a “free” anion. The difference in strengths of H-bonds formed by two different oxygen atoms can be used as an indicator of the asymmetry.

Complexes of cyclic dimers of carboxylic acids with proton donors

In ref. 29 the interaction between carboxylic acids and PFP, as a proton donor, was investigated. At low temperature these acids are nearly completely dimerized, which in the case of formic acid can be proved by the characteristic triplet structure of the proton signal (δ 13.1 ppm), caused by the fast intramolecular proton transfer:

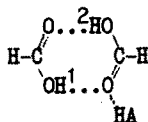


As can be seen from the vibrational spectra [29], addition of an excessive amount of PFP does not break the dimeric (HCOOH)₂ cycle. The OH-signal shifts 1.7 ppm upfield and transforms into a doublet. This may indicate formation of a symmetrical 1:1 complex of the dimer with two additional H-bonds, which weaken H-bonds in the cycle and make the proton transfer non-degenerate:



In this case the additional H-bonds are undoubtedly formed by the lone pairs of C=O groups (I); otherwise, as in II, H-bonds in the cycle would become stronger than in the “free” dimer. The structure I was confirmed [29] by a large low-frequency shift of the IR band, corresponding to the asymmetric stretching vibration of C=O bonds.

When an insufficient amount of PFP is taken, a complex with one PFP molecule is dominant in solution:



III

Two separate signals at $\delta = 11.3$ and 13.4 ppm, are observed in the spectrum, the first being attributed to the H(1) proton, involved in an H-bond, weakened as compared to that in the cyclic dimer by the anti-cooperative effect. The signal of the H(2) proton is shifted 0.3 ppm downfield compared with the dimer, which may point out some strengthening of the second H-bond due to the cooperative effect. The influence of PFP on the second H-bond is, of course, weaker, than on the first, because of different distances between the interacting groups.

A more considerable disturbance of the spectrum of $(\text{HCOOH})_2$ was described in ref. 30 for an asymmetrical complex of type III, where AH is a very strong proton donor, i.e. $\text{SbCl}_5 \cdot \text{HCOOH}$.

The results reported in this paper allow us to state that low-temperature ^1H NMR is a very suitable method for examining second-order effects in H-bonding. The high selectivity of the method (10^3 – 10^4 , if 10–15 ppm and 0.01–0.1 ppm are taken as a characteristic chemical shift interval and a typical linewidth of OH-signals at 100–120 K respectively) determines its qualitative possibilities. Measurement of relative integral intensities of the separate signals could provide thermodynamic values for equilibria between different H-bonded complexes using the Van't-Hoff equation. However, this requires a reliable system of thermostabilization of a sample in an NMR probehead for the temperature range 80–120 K.

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