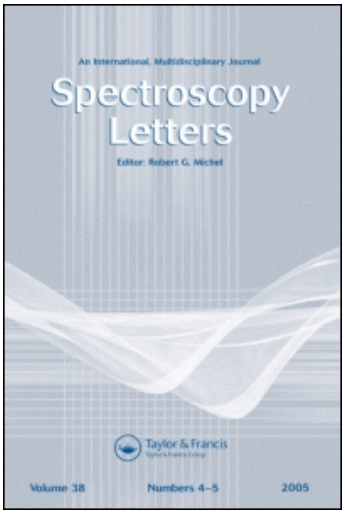


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# COMPLEXES OF A-H ACIDS WITH TRIETHYLAMINE: SPECIFICITIES OF SPECTROSCOPIC CHARACTERISTICS

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According to the donor-acceptor model of hydrogen bonding, the intermolecular bonds R-AH...$BR_1$ and $R\text{-}A^-...H^+BR_1$ are, in the main, of the same nature[1]. In this case, the charge transfer at acid-base interaction

$$R\text{-}AH + BR_1 \longleftrightarrow \underset{I}{R\text{-}AH...BR_1} \longleftrightarrow \underset{II}{R\text{-}A^-...H^+BR_1} \qquad (1)$$

causes the existence of H-complexes I and II and the majority of their properties. For one thing, this determines the significant changes in the intensity (A) stretching vibration $\nu$(AH) in the IR-spectra and in the proton chemical shift ($\delta_H$) in the PMR spectra. In view of this, the study of changes in the magnitudes of A and $\delta_H$, when the acid-base properties of the molecules interacting in the reaction (1) vary widely, presents significant interest. This allows not only to elucidate more fully the reasons causing changes in the values A

and $\delta_H$, but to establish their bonds with the structure of forming H-complexes and the enthalpy of their formation ($-\Delta H$), which for (1) changes from ~1 to 40 kcal/mole[2].

Recently, we reported[3,4] that the linear dependency

$$-\Delta H = 1.11\,\Delta\delta + 0.49 \qquad (2)$$

is observed between the magnitude $\Delta\delta = \delta_H - \delta_o - \delta_b$, where $\delta_o$ and $\delta_b$ are the monomer chemical shift and contribution due to the magnetic anisotropy of the molecule of base $BR_1$, respectively, and the enthalpy of the H-complex R-AH...$BR_1$.

In this case, the said dependency exists for different H-complexes up to the symmetric structure R-A...H...$BR_1$. In continuing to examine the characteristics $\delta_H$ and A in strong H-complexes, we this time report on changes in these values for $Et_3N$ H-complexes with acids of different strength, which allow the formation of structures I and II in a wide range of $-\Delta H$ changes, from ~2 to 30 kcal/mole. Rather characteristic specificities in the behavior of $\delta_H$, A and $\nu$ were observed. Thus, in the H-complexes II, their behavior is diametrically opposite to that in H-complexes I. The use of only $Et_3N$ as a base in (1) provides for the same $\delta_b$ contribution in the $\delta_H$ value observed.

PMR spectra were recorded on ZKR-60 and Bruker HX-90E instruments. Chemical shifts were counted from TMS in the $\delta$ scale. In order to avoid the influence of $H_2O$ on $\delta_H$, all acids and $Et_3N$ were thoroughly dried, and all subsequent operation were performed in a dry box. IR-spectra were recorded on UR-20

(Karl Zeiss, Jena) instrument with a logarithmic self-recorder. The IR-band frequencies were measured as the center of gravity ($\nu_0$) by numerical integration, and their intensities as the summary intensity of all components observed in the complex structure $\nu$(AH), the appearance of the said components in the range 3000-1000 $cm^{-1}$ for complexes I and II with $-\Delta H > 6$ kcal/mole having been caused by the Fermi resonance[4,5]. The measurement results for the magnitudes $\delta_H$, A and $\nu_0$ of the H-complexes studied are shown in Table 1.

Earlier it was shown[4,5] that acids №1–8 (see Table 1) with $Et_3N$ form H-complexes (1:1) with structure I. As is apparent from Table 1, the values $\delta_H$ and A in those complexes grow regularly, while the value $\nu_0$ decreases with increased values of $-\Delta H$. Further increase in acid strength (№9-14) leads to formation of H-complexes II (1:1)[5], this, in turn, causing an opposite tendency in the changes of the above values. Fig.1 and 2 show the general trend of $-\Delta H$-dependent changes in the said parameters for the complete reaction (1). Fig.1 shows that the straight line drawn through the points corresponding to H-complexes I does not correspond to the dotted line drawn in accord with (2). The discrepancy is ostensibly due to the unaccounted anisotropy of the $Et_3N$ molecule, and, as is apparent from the figure, $\delta_b = +1.3$ ppm. As is apparent from the figures, the maximum values for $\Delta\delta_{max.}$, $\Delta A^{1/2}_{max.}$ (points of intersections of lines) shall correspond to H-complexes with structures close to the symmetrical ($R\text{-}A\ldots H\ldots BR_1$), and would equal ~14 ppm and $\sim 5.5 \cdot 10^2$ $l^{1/2} mole^{-1/2} cm^{-1}$, respectively. In this case (for the symmet-

Table 1. Characteristics for H-complexes I and II of various A-H acids with $Et_3N$.

| № | Acids | $A \cdot 10^{-4}$ l.mole$^{-1}$cm$^{-2}$ | $\nu_0$ cm$^{-1}$ | $\delta_H$ ppm | $-\Delta H$ *) kcal/mole |
|---|---|---|---|---|---|
| 1. | $CHCl_3$ | - | - | 8.58[10] | 4.0[10] |
| 2. | t-BuOH | 7.0 | 3290 | 3.00 | 5.2[11] |
| 3. | $C_4H_4NH$ | 9.2 | 3100 | 10.64 | 5.9[10] |
| 4. | p-FPhOH | 15.5 | 2855 | 9.73[12] | 8.9[2] |
| 5. | PhOH in $CCl_4$ | 17.5 | 2600 | 10.45 | 9.1[2] |
| 6. | p-$NO_2$PhOH in $CH_2Cl_2$ | 21.0 | 2280 | 12.24 | 9.7[13] |
| 7. | $CH_3COOH$ | 25.0 | 1800 | 12.90 | 10.4 |
| 8. | $C_6H_5COOH$ in $CH_2Cl_2$ | 36.0 | 1480 | 15.25 | 13.0[13] |
| 9. | $CH_2ICOOH$ in $CH_2Cl_2$ | 24.5 | 1770 | 14.90 | 16.9[13](20.2) |
| 10. | $CH_2ClCOOH$ in $CH_2Cl_2$ | 23.0 | 1830 | 14.50 | 18.2[13](20,6) |
| 11. | $CHCl_2COOH$ in $CH_3CN$ | 16.0 | 2235 | 12.10 | 21.7[13](23.3) |
| 12. | $CCl_3COOH$ in $CH_3CN$ | 14.0 | 2390 | 10.80 | 25.6[13](24.7) |
| 13. | $CF_3COOH$ in $CH_3CN$ | 12.0 | 2400 | 10.45 | 26.0[13](25.1) |
| 14. | $HClO_4$ in $CDCl_3$ | 6.0 | 2975 | 7.40 | - (27.0) |

*) $-\Delta H$ in parenthesis calculated as $2 \cdot (-\Delta H_{sym}) - (1.11 \Delta\delta + 0.49)$.

rical H-complexes), the value of $-\Delta H_{sym.}$ for one H-bond would be ~16 kcal/mole. Similar values ($\delta_{max.}$ ~ 13-14 ppm) for symmetrical H-complexes $(Hal...H...Hal)^-Bu^n_4N^+$ in $CH_2Cl_2$ were obtained earlier[6]. For the symmetrical H-complex $(CF_3COO...H...OOCCF_3)^-Bu^n_4N^+$, $\delta_H$ was observed at 18.3 ppm[7], which also

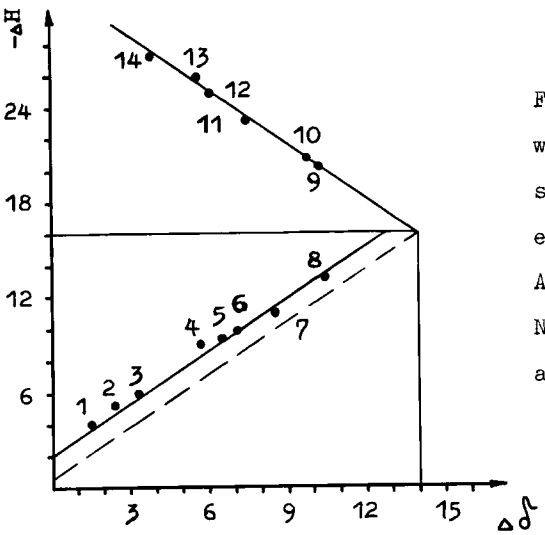


Fig.1. Relationship between changes in chemical shifts and H-bonding energies of H-complexes A-H acids with $Et_3N$. Numbering of H-complexes according to Table 1.

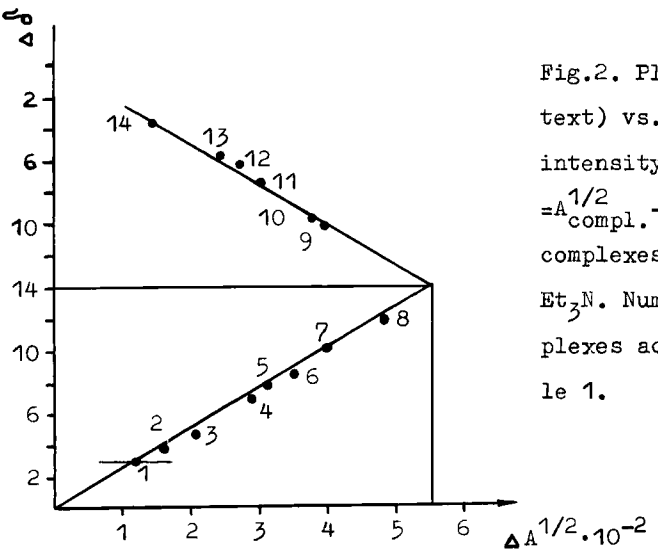


Fig.2. Plot of $\Delta\delta$ (see text) vs. increasing of intensity $\nu$(AH) ($\Delta A^{1/2} = A^{1/2}_{compl.} - A^{1/2}_{free}$) for H-complexes acids with $Et_3N$. Numbering of H-complexes according to Table 1.

gives $\Delta\delta_{max.} \sim 14$ ppm. We also studied carboxylic acids with $(CH_3)_3NO$ in $CH_2Cl_2$ solutions which, at excess $(CH_3)_3NO$, form symmetrical H-bonds $(NO...H...ON)^+RCO_2^-$ [5]. According to the data in Table 2, the value of $\Delta A^{1/2}$ is close to those of $\Delta A^{1/2}_{max.}$. Unfortunately, the $\delta_H$ values obtained (Table 2) do not allow to calculate the values of $\Delta\delta$, since $\delta_o$ for $(CH_3)_3NO^+H$ is unknown. However, judging from the constancy of $\delta_H$ in the H-complexes of all carboxylic acids, the value of $\delta_o$, compared with $\Delta\delta_{max.}$, shall probably not exceed ~3 ppm. It is noteworthy that, in comparing $\Delta\delta$ and $-\Delta H$, one should be very careful in his approach to H-complexes which allow the formation of symmetrical structures of the type $(AHA)^-$ and $(BHB)^+$. In this case, $\Delta\delta$ would not be subject to significant changes (see Table 2), whereas the heat of admixture would be redistributed between the H-bond and the ionic bond in the forming ions. Indeed, for fluorosulphonic acid that protonizes oxygen bases, slight changes for $\delta_H$ (~12-15 ppm) were observed, while $-\Delta H$ changes within the range of 14--30 kcal/mole[8].

According to Alexandrov and Sokolov[9], the following effects chiefly influence the proton screening magnitude at H-bond formation: 1) change in the polarity degree of bond A-H ($\delta_1$); 2) stretching of bond A-H ($\delta_2$); 3) formation of donor-acceptor bond H...B, leading to a shift in the center of gravity of the cloud of the unpaired B-atom electrons toward the H atom ($\delta_3$). Moreover, the contribution in $\delta_H$ of 1) and 2) is negative, and that of 3) is positive. The cha-

Table 2. Characteristics of symmetrical hydrogen bond $(Me_3NO...H...ONMe_3)^+$.

| № | Anion | $A \cdot 10^{-4}$ | $\nu_o$ | $\delta_H$ |
|---|---|---|---|---|
| 1. | $CH_3CH_2COO^-$ | 32.0 | $1150 \pm 50$ | 15.08 |
| 2. | $CH_2ClCOO^-$ | 33.0 | | 15.76 |
| 3. | $CHCl_2COO^-$ | 33.0 | | 15.35 |
| 4. | $CF_3COO^-$ | 32.0 | | 15.59 |

racter of dependency of $\Delta\delta$ on $-\Delta H$ for the H-complexes studied allows to evaluate the inputs in $\delta_H$ at different stages of proton movement from A to B in (1). As we can see from Fig.1 at proton movement to A...H...B $|\delta_1+\delta_2| > |\delta_3|$ ; at further proton movement to $A^-...H^+B$ $|\delta_3| > |\delta_1+\delta_2|$ . For the structure A...H...B, $|\delta_1+\delta_2| - |\delta_3|$ attains the maximum value of $\sim 14$ ppm. The above results show that a theoretical study of the screening character of the H-atom nucleus in strong H-complexes should essentially account the inputs in $\delta_H$ of all three of the above-mentioned effects.

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