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# IR SPECTROSCOPY OF 2,3-POLYMETHYLENE-3,4-DIHYDROQUINAZOLINES AND THEIR COMPLEXES

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*We have investigated the IR spectra in the region of stretching vibration of $N^+$-H and OH groups of the hydrochlorides of 2,3-trimethylene-3,4-dihydroquinazoline (deoxypeganine, DOP), 2,3-tetramethylene-3,4-dihydroquinazoline (tetrazoline), and 2,3-pentamethylene-3,4-dihydroquinazoline (pentazoline) and peganol and peganine and the corresponding complexes with $ZnCl_2$, $CoCl_2$, and $MnCl_2$. The appearance of two additional absorption bands in the 3100-3300 $cm^{-1}$ region in the complexes investigated as compared with the corresponding hydrochlorides witnesses the formation of interionic hydrogen bonds between the quinazoline cation and the $(MeCl_4)^{2-}$ anion.*

With the aim of studying the mechanism of complex-formation, we have investigated the IR spectra in the region of the stretching vibrations of OH and $N^+$-H groups, $\nu$OH and $\nu N^+$-H (2000-3500 $cm^{-1}$), of the hydrochlorides of deoxypeganine (1), tetrazoline (2), pentazoline (3), peganine (4), and peganol (5); the results obtained are presented in Table 1.

Analysis of the spectral characteristics given in Table 1 showed the presence in the spectra of hydrochlorides (1)-(3) of an intense absorption band in the 3400-3500 $cm^{-1}$ region, which corresponds to the formation of an intermolecular hydrogen bond (interHB) between the $N_1{}^+$-H cation and the OH group of hydrate water ($N_1{}^+H\cdots OH$).

The high-frequency maxima at 3070 and 3090 $cm^{-1}$ observed in the IR spectra of peganine ($R_2$ = OH), peganol ($R_1$ = OH), and 4-hydroxy-9-$OCH_3$-peganine can be explained by the formation of an intramolecular hydrogen bond (intraHB)

TABLE 1. Characteristic IR Frequencies of 2,3-Polymethylene-3,4-dihydroquinazolines and the Corresponding Complexes with $ZnCl_2$, $CoCl_2$, and $MnCl_2$ in the 2700-3500 $cm^{-1}$ Region

| Compound | $\nu N^+$-H...Cl, $cm^{-1}$ | $\nu N^+$-H...OH, $cm^{-1}$ |
|---|---|---|
| 2 | 2825–2955 | 3409 |
| 3 | 2883–2989 | 3448 |
| 4 | 2766–2941 | 3480*, 3333 |
| 5 | 2771–3026 | 3435*, 3226 |
| 6 | 2747–2894 | 3123 |
| 7 | 3177, 3230 | – |
| 8 | 3130, 3245 | – |
| 9 | 3128, 3240 | – |
| 10 | 3158, 3247 | – |
| 11 | 3145, 3255 | – |
| 12 | 3130, 3250 | – |
| 13 | 3100, 3300 | – |
| 14 | 3275, 3250 | – |
| 15 | 3180, 3230 | – |
| 16 | 3135, 3235 | |

*3435, 3480 — H-bond with the OH group of hydrate water.

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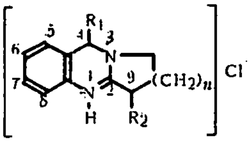
between the unshared electron pair of the nitrogen atom and the hydroxy group (N···HO; ΔH = 4-7 kcal/mole) [1]. The appearance in the spectra of the corresponding chlorides (4)-(6) of an intense absorption band in the 3100-3300 $cm^{-1}$ region suggests a partial breakdown of the N···HO intraHBs and the participation of some part of the molecules in the formation of $NH^+\cdots OH$ and $NH^+\cdots OCH_3$ interHBs.

The complex pattern of absorption in the $\nu N^+$-H region of the IR spectra of the complexes obtained (7)-(16) must be mentioned — a large number of narrow intense absorption bands (Fig. 1).



1-16

1) $n$ = 1; 2,3-trimethylene-3,4-dihydroquinazoline (deoxypeganine, DOP) hydrochloride
2) $n$ = 2; 2,3-tetramethylene-3,4-dihydroquinazoline (tetrazoline) hydrochloride
3) $n$ = 3; 2,3-pentamethylene-3,4-dihydroquinazoline (pentazoline) hydrochloride
4) $n = 1$, $R_1 = H_2$, $R_2$ = OH, peganine hydrochloride
5) $n = 1$, $R_1$ = OH, $R_2 = H_2$, peganol hydrochloride
6) $n$ = 1, 4-hydroxy-9-$OCH_3$-peganine hydrochloride
7) complex of DOP with $ZnCl_2$
8) complex of DOP with $MnCl_2$
9) complex of tetrazoline with $ZnCl_2$
10) complex of pentazoline with $ZnCl_2$
11) complex of pentazoline with $CoCl_2$
12) complex of peganine with $ZnCl_2$
13) complex of peganol with $ZnCl_2$
14) complex of peganol with $CoCl_2$
15) complex of peganol with $MnCl_2$
16) complex of 4-hydroxy-9-$OCH_3$-peganine with $ZnCl_2$

Such a form of absorption is characteristic for $\nu N^+$-H vibrations perturbed by the formation of interHBs and is probably the consequence of an interaction of the same types of vibrations of $N^+$-H and C—H bonds and a possible resonance interaction [2, 3, 7]. The $\nu N^+$-H absorption in the spectra under discussion was therefore evaluated from the frequency of the maximum of the center of gravity of the enveloping constituent vibrational functions. In the IR spectra of the corresponding complexes (7)-(16) the $N^+$-H stretching vibrations were characterized mainly by two absorption bands at about 3100 and 3200 $cm^{-1}$. These bands permit the assumption of the presence in the complexes under study of nonequivalent interionic hydrogen bonds $N^+\text{-}H\cdots Cl^-$ [4-6]. This hypothesis was confirmed by the results of an x-ray analysis of the complex of deoxypeganine with $ZnCl_2$ [6].

It has been shown that in the complex 2[DOP $H^+](ZnCl_4)^{2-}$ the length of the $N^+\cdots Cl^-$ bond with one molecule is 3.13 Å and with the other it is 3.34 Å. Moreover, in the case of the complexes of unsubstituted 2,3-polymethylene-3,4-dihydroquinazolines that were investigated (7)-(11) we detected an appreciable displacement of $\nu N^+$-H into the high-frequency region of 3100-3300 $cm^{-1}$ relative to that of the hydrochlorides (2400-2700 $cm^{-1}$). This probably indicates a weakening of the hydrogen bonds of the extra-sphere protonated amine with the complex anion as compared with the amine salt [3, 6]. According to x-ray results, the length of the $N^+\cdots Cl^-$ bond in the complex of DOP with $ZnCl_2$ is 3.34 Å and in the corresponding hydrochloride it is 3.11 Å [6]. From this, it may be assumed that the displacement of the electron density of the chlorine atom in the complex anion $(MeCl_4)^{2-}$ towards the proton is considerably smaller than in the corresponding hydrochloride.

Thus, a comparison of the spectra of 2,3-polymethylene-3,4-dihydroquinazolines and of the complexes obtained with $ZnCl_2$, $CoCl_2$, and $MnCl_2$ showed the presence of two absorption bands in the 3100-3300 $cm^{-1}$ region. On the basis of the IR spectroscopy of complexes of $UO_2Cl_2$ with pyridine [7] and with triethylamine [3] and also an x-ray analysis of complexes of DOH with $ZnCl_2$ [6] and of peganine with $ZnCl_2$ [8] it may be concluded that these absorption bands witness the formation of interionic hydrogen bonds between the cation [quinazoline $H^+$] and the anion $(MeCl_4)^{2-}$.

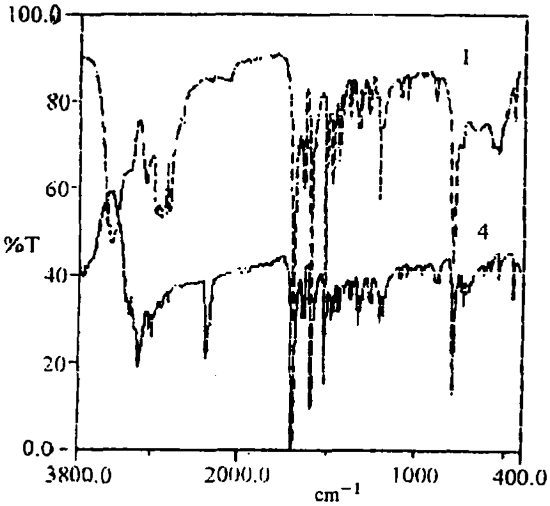
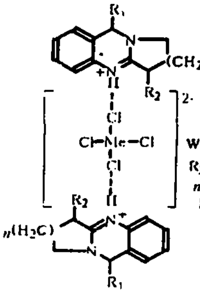


Fig. 1. IR spectra: *1*) DOP·HCl; *4*) complex of DOP with $ZnCl_2$.

The presence of two absorption bands characterizes different values of the energy of formation of the hydrogen bond, which, in all probability, is less strong in the complexes investigated than in the corresponding hydrochlorides. On the basis of what has been said, a schematic representation of the complexes investigated, with the exception of compounds (**12**)-(**16**), may be given in the following form:



where $R_1=H_2$; OH
$R_2=H$; OH; $OCH_3$
$n=1,2,3$
Me=Zn, Co, Mn

## EXPERIMENTAL

Spectra were recorded on a Perkin-Elmer model 2000 IR Fourier spectrometer (System 2000 FT-IR). Samples were prepared by molding into tablets with KBr. The resolution of the instrument was 4 cm$^{-1}$ and the rate of scanning 0.2 cm/sec.

The complex salts of deoxypeganine, peganine, peganol, tetramethylenequinazoline, and pentamethylenequinazoline, were obtained by the procedure described in [6].

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