

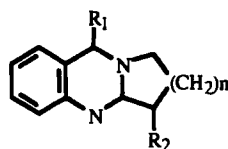
IR SPECTRA AND CRYSTAL STRUCTURE OF HYDROCHLORIDES AND COMPLEX SALTS OF 2,3-POLYMETHYLENE-3,4-DIHYDROQUINAZOLINES AND -4-QUINAZOLONES

B. Tashkhodzhaev, K. K. Turgunov,
and É. L. Kristallovich

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IR spectra are reconsidered on the basis of the results of x-ray structural analysis of the crystal structures of hydrochlorides and complex salts of 2,3-polymethylene-3,4-dihydroquinazolines and -4-quinazolones. It has been established that two absorption bands ($NL^+—H$) in the complex salts characterize different energies of formation of an H-bond, which is weaker than in the corresponding hydrochlorides. The nature of an absorption band in the $3400—3500\text{ cm}^{-1}$ region has been established from the XSA results.

Previously, in order to study the mechanism of complex-formation, we considered the IR spectra in the region ($\nu = 2000—3500\text{ cm}^{-1}$) of the stretching vibrations of the O—H and $N^+—H$ groups of hydrochlorides of 2,3-trimethylene-3,4-dihydroquinazoline (deoxypeganine — DOP), 2,3-tetramethylene-3,4-dihydroquinazoline (tetrazoline — TET), 2,3-pentamethylene-3,4-dihydroquinazoline (pentazoline — PEN), peganine (PGN), and peganol (PGL) and the corresponding complex salts with $ZnCl_2$, $MnCl_2$, and $CoCl_2$ [1]. In addition, the x-ray structural method was used to determine the crystal structures of the majority of the above-mentioned alkaloids in the form of hydrochlorides and complex salts and also of derivatives of 4-quinazolones. IR spectroscopy is considered to be extremely sensitive to intermolecular interactions [2], and the spectra of the substances under investigation were taken in the solid-phase state (by molding powders of the substance with KBr), while the XSA method permits the tracing of all types of intermolecular interactions realized in salts and complexes of 2,3-polymethylene-3,4-dihydroquinazolines and -4-quinazolones in the solid state. It appeared of interest to compare the results of IR spectroscopy with those of XSA.



- $n = 1, R_1 = R_2 = H_2$ — 2,3-trimethylene-3,4-dihydroquinazoline
- $n = 2, R_1 = R_2 = H_2$ — 2,3-tetramethylene-3,4-dihydroquinazoline
- $n = 3, R_1 = R_2 = H_2$ — 2,3-pentamethylene-3,4-dihydroquinazoline
- $n = 1, R_1 = H_2, R_2 = H, OH$ — peganine
- $n = 1, R_1 = H, OH, R_2 = H_2$ — peganol
- $n = 1, R_1 = O, R_2 = H_2$ — deoxyvasicinone
- $n = 3, R_1 = O, R_2 = H_2$ — pentazoline

In the IR spectra of the hydrochlorides and complex salts of 2,3-polymethylene-3,4-dihydroquinazolines, $N^+—H$ and O—H stretching vibrations appear in the form of a large number of narrow intense absorption bands. The characteristic frequencies in the $2100—3500\text{ cm}^{-1}$ region of the hydrochlorides and complex salts (1—20) are given in Table 1.

Earlier [1], in analyzing the IR spectral characteristics of the hydrochlorides of compounds (1—5) an intense absorption band in the $3400—3500\text{ cm}^{-1}$ region was assigned to intermolecular H-bonds with the OH groups of water of hydration. However, an analysis of the crystal structure of the salts of DOP (1) and of pentazoline (3) that we have investigated shows that this assignment is not correct.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (371) 120 64 75. Translated from *Khimiya Prirodnikh Soedinenii*, No. 3, pp. 364—367, May-June, 1999. Original article submitted December 23, 1998.

TABLE 1. Characteristic Frequencies of Hydrochlorides and Complex Salts of 2,3-Polymethylene-3,4-dihydroquinazolines and -4-quinazolones in the 2100—2500 cm^{-1} Region

Compound	$\nu(\text{N-H}), \text{cm}^{-1}$ $\text{N}^+-\text{H}\cdots\text{Cl}$	$\nu(\text{O-H}), \text{cm}^{-1}$	$\nu(\text{H}_2\text{O}), \text{cm}^{-1}$ $\text{O-H}\cdots\text{Cl}$
1. DOP hydrochloride	2776 — 2980	-	3430
2. TET hydrochloride	2825 — 2955	-	3409
3. PEN hydrochloride	2883 — 2989	-	3448
4. PGN hydrochloride	2766 — 2941	3333	3480
5. PGL hydrochloride	2771 — 3026	3226	3435
6. 4-Hydroxy-9-OCH ₃ -PGN hydrochloride	2747 — 2894	3123	-
7. Complex of DOP with ZnCl ₂	3177, 3230	-	-
8. Complex of DOP with MnCl ₂	3130, 3245	-	-
9. Complex of TET with ZnCl ₂	3128, 3240	-	-
10. Complex of PEN with ZnCl ₂	3158, 3247	-	-
11. Complex of DOP with CoCl ₂	3145, 3255	-	-
12. Complex of PGN with ZnCl ₂	3130, 3250	-	-
13. Complex of PGL with ZnCl ₂	3100, 3300	-	-
14. Complex of PGL with CoCl ₂	3175, 3250	-	-
15. Complex of PGL with MnCl ₂	3180, 3230	-	-
16. Complex of 4-hydroxy-9-OCH ₃ -PGN with ZnCl ₂	3135, 3235	-	-
17. DOV hydrochloride	2100 — 3250	-	-
18. Pentazolone hydrochloride	2134 — 3149	-	-
19. Complex of DOV with CoCl ₂	2392 — 3446	-	-
20. Complex of PEON with ZnCl ₂	2421 — 3485	-	-

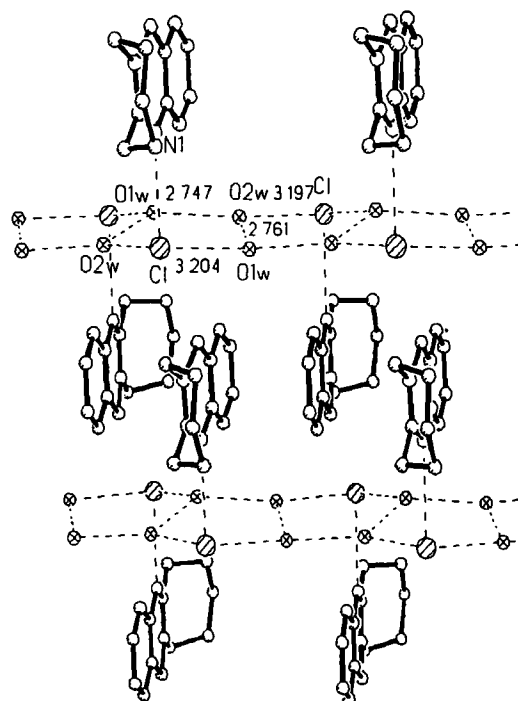


Fig. 1. Crystal packing of the complex $\text{PEN}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ (3).

TABLE 2. $N^+ \cdots Cl^-$ Distances (Å) in Salts and Complexes of 2,3-Polymethylene-3,4-dihydroquinazolines

Compound	$N1^+ \cdots H \cdots Cl^-$		N3...Cl
	cation A	cation B	
Complex salts			
$2(DOP+H^+) \cdot [ZnCl_4]^{2-}$	3.15	3.34; 3.43	
$2(DOV+H^+) \cdot [ZnCl_4]^{2-}$	3.05	3.13	
$2(DOV+H^+) \cdot [CoCl_4]^{2-}$	3.08	3.15	3.18
$2(PEN+H^+) \cdot [ZnCl_4]^{2-}$	3.15	3.20	
Hydrochlorides			
$DOP \cdot HCl \cdot 2H_2O$	3.11		
$DOV \cdot HCl$	3.01		3.29
$PEN \cdot HCl \cdot 2H_2O$	3.12		

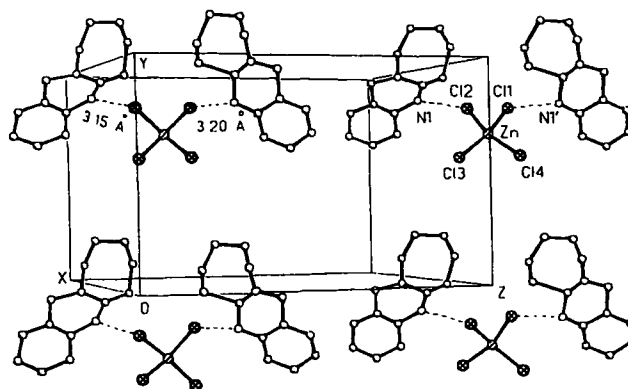


Fig. 2. Crystal packing of the complex $2(PEN+H^+) \cdot [ZnCl_4]^{2-}$ (10).

The x-ray structural results for the hydrochlorides of (1) and (3) showed that the $N^+—H$ group in them forms an H-bond only with the Cl^- ion and does not participate in other intermolecular interactions (the distance from $N(1)H^+$ to the closest atom of the molecular environment in the crystal packing is greater than the sum of their van der Waals radii). The two molecules of water of crystallization participating in packing form a substructure thanks to H-bonds with the Cl^- anion.

Figure 1 gives, as an example, the packing of the molecules in complex (3), where the substructure formed through intermolecular H-bonds stands out clearly. It is possible that such a substructure with the participation of a water molecule and a Cl^- anion is also formed in complexes (2, 4, and 5), since it leads to the appearance in them of an intense absorption band in the $3400—3500\text{ cm}^{-1}$ region that is assigned to the stretching vibrations of an OH group [2]. It must be mentioned that in the crystal of (-)-peganine hydrochloride (structure established by German authors [5]) there are no molecules of hydrate water. However, according to its IR spectral frequencies, the packing of the racemate of peganine hydrochloride that we investigated was contain a molecule of water of crystallization.

An intense absorption band in the $3100—3300\text{ cm}^{-1}$ region in the case of hydrochlorides (4—6) probably relates to the alcoholic OH group that is present only in the cations of chlorides (4—6) and possibly takes part in intermolecular interactions.

In the IR spectra of the corresponding complexes (7—16), $N^+—H$ stretching vibrations are characterized mainly by two absorption bands at about 3100 and 3200 cm^{-1} . These bands are shifted appreciably in the high-frequency direction relative to those of the corresponding hydrochlorides (1—6) ($2700—3050\text{ cm}^{-1}$, see Table 1), which shows a weakening of the H-bonds of a protonated amine with a complex anion in comparison with a salt of the amine. In actual fact, according to the XSA results, the length of the $N^+ \cdots Cl^-$ bonds in the complexes $2(DOP+H^+) \cdot [ZnCl_4]^{2-}$ [6], $2(DOV+H^+) \cdot [ZnCl_4]^{2-}$,

$2(\text{DOV}+\text{H}^+)\cdot[\text{CoCl}_4]^{2-}$ [7], and $2(\text{PEG}+\text{H}^+)\cdot[\text{ZnCl}_4]^{2-}$ [8] amounts to 3.34 Å. In the corresponding hydrochlorides — $\text{DOP}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ [3], $\text{DOV}\cdot\text{HCl}$ [7], and $\text{PEN}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ [4], this distance ranges between 3.01 and 3.12 Å.

The two absorption bands of $\text{N}^+\cdots\text{H}$ stretching vibrations mentioned above show the presence in the complexes under study (7—16) of nonequivalent hydrogen bonds of the $\text{N}^+\cdots\text{H}\cdots\text{Cl}^-$ type, and this was confirmed by the XSA of the complexes $\text{DOP}\cdot\text{ZnCl}_2\cdot\text{HCl}$, $\text{PEN}\cdot\text{ZnCl}_2\cdot\text{HCl}$, $\text{DOV}\cdot\text{CoCl}_2\cdot\text{HCl}$, and $\text{DOV}\cdot\text{ZnCl}_2\cdot\text{HCl}$. Figure 2 gives as an example the packing of the molecules in the complex $\text{PEN}\cdot\text{ZnCl}_2\cdot\text{HCl}$. In the crystal, these complexes (independent part of the unit cell) are formed on the $2(\text{BASE}+\text{H}^+)\cdot[\text{MeCl}_4]^{2-}$ principle; i.e., there is one metal ion to two cations (A and B). Correspondingly, in the metallocomplexes investigated the $\text{N}^+\cdots\text{H}$ groups of cations A and B are linked to different Cl atoms of one and the same $[\text{MeCl}_4]^{2-}$ ion and have different lengths of the $\text{N}^+\cdots\text{Cl}^-$ bond. According to Table 2, in these complexes cations A (responsible for the 3100 cm^{-1} band) form stronger H-bonds than cations B (responsible for the 3200 cm^{-1} band).

Thus, the presence of two absorption bands characterizes different values of the energy of formation of an H-bond, which is less strong in complexes than in the corresponding hydrochlorides. Furthermore, the nature of the absorption band in the $3400\text{—}3500\text{ cm}^{-1}$ region has been determined from XSA results.

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