Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 743–750

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

L-Tryptophan L-tryptophanium chloride

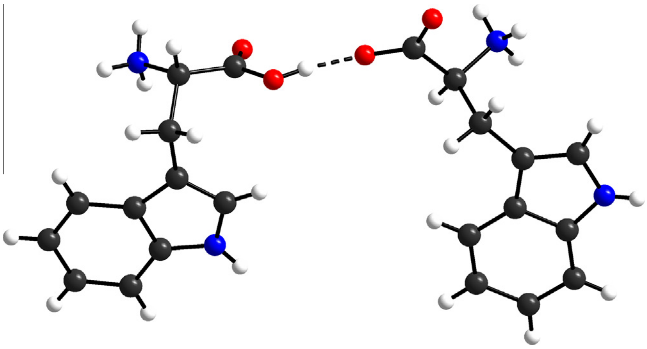
V.V. Ghazaryan [a], M. Fleck [b], A.M. Petrosyan [a,*]

[a] *Institute of Applied Problems of Physics, NAS of Armenia, 25 Nersessyan Str., 0014 Yerevan, Armenia*
[b] *Institute of Mineralogy and Crystallography, University of Vienna, Althanstr. 14, A-1090 Vienna, Austria*

HIGHLIGHTS

- Single crystal of 2L-Trp·HCl was obtained for the first time.
- Crystal and molecular structure of 2L-Trp·HCl has been determined.
- The existence of dimeric (L-Trp···L-TrpH) cation is established.
- IR and Raman spectra of 2L-Trp·HCl were studied and compared with spectra of previously known L-Trp·HCl.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form 14 September 2014
Accepted 19 September 2014
Available online 30 September 2014

Keywords:
L-Tryptophan L-tryptophanium chloride
Structure
Dimeric cation
Vibrational spectra

ABSTRACT

L-Tryptophan L-tryptophanium chloride is a new salt with ($A\cdots A^+$) type dimeric cation. It crystallizes in the monoclinic system (space group $P2_1$, $Z = 2$). The asymmetric unit contains one zwitterionic L-tryptophan molecule, one L-tryptophanium cation and one chloride anion. The dimeric cation is formed by a O—H···O hydrogen bond with the O···O distance equal to 2.5556(18) Å. The infrared and Raman spectra of the crystal are studied and compared with the spectra of L-tryptophanium chloride.

Introduction

Reactions of amino acids with inorganic and organic acids result in various type of compounds: simple salts with definite cations and anions, mixed salts with different anions and/or cations, salts with dimeric cations and adducts without forming of salts [1]. Three type dimeric cations are known: $A\cdots A^+$, $A^+\cdots A^+$ and $A^+\cdots A^{2+}$, where A, A^+, A^{2+} are amino acids in zwitterionic state, singly and doubly charged cations respectively. The $A\cdots A^+$ type dimeric cation can form all amino acids except amino acids capable to form doubly charged cation (e.g. lysine, ornithine, histidine and arginine), while these amino acids can form the $A^+\cdots A^{2+}$ type cation. These two type dimeric cations can form short and strong hydrogen bonds, while the $A^+\cdots A^+$ type dimeric cation is formed mainly by β-alanine and is formed by relatively long hydrogen bonds due to additional repulsion between positively charged cations. The largest number of salts is known for $A\cdots A^+$ type dimeric cation. For some amino acids large number of salts with $A\cdots A^+$ type dimeric cation is known. For some others only one salt is known and there are amino acids for which such salts were not obtained to date.

---

* Corresponding author. Tel.: +374 10 241106; fax: +374 10 281861.
E-mail addresses: aram.m.petrosyan@gmail.com, apetros@iapp.sci.am (A.M. Petrosyan).

http://dx.doi.org/10.1016/j.saa.2014.09.090

The largest amino acid L-tryptophan may be considered as an L-alanine molecules, in which one hydrogen atom of the methyl group is substituted by an indolyl group. For L-tryptophan some simple salts were obtained and structurally characterized. Takigawa et al. [2] obtained chloride and bromide of L-tryptophanium, determined their structures and showed that chloride and bromide are isostructural. In addition, they obtained one more salt with 2L-Trp·HBr·0.5H_2O composition according to chemical analysis and determined its symmetry and unit cell parameters without structure determination, however. The structure of L-tryptophanium bromide was determined also in [3] and more accurately in [4] at 100 K. The authors of [5] obtained crystals of L-tryptophanium picrate, while in [6,7] crystals of L-tryptophanium phosphite and L-tryptophanium hydrogen selenite were obtained and their crystal structures were determined. Bakke and Mostad [8] determined the structure of *DL*-tryptophan and also obtained *D*-tryptophanium hydrogen oxalate, when they tried to obtain *DL*-tryptophanium hydrogen oxalate. The first and during long time the only structurally characterized salt with L-tryptophan L-tryptophanium dimeric cation was the salt (L-Trp···L-Trp$^+$)($HgCl_3$)$^-$ obtained by Book et al. [9]. In our paper [10] we reported a reinvestigation of the structure of L-tryptophanium picrate, where we showed that there is a L-tryptophan L-tryptophanium dimeric cation in its structure. Inspired by this result, we supposed that the salt 2L-Trp·HBr·0.5H_2O also may be formed by this mechanism and contain L-tryptophan L-tryptophanium dimeric cations, so we decided to return to study the L-Trp + HCl + H_2O and L-Trp + HBr + H_2O systems. Our research showed that in addition to L-Trp·HCl, L-Trp·HBr and 2L-Trp·HBr·0.5H_2O at least two more salts, namely, 2L-Trp·HCl and 2L-Trp·HBr exist in these systems and we optimized the conditions of L-Trp·HCl and L-Trp·HBr. Based on spectroscopic data we supposed that they contain L-tryptophan L-tryptophanium dimeric cations. Recently we could obtain the salt 2L-Trp·HCl in form of single crystal and determined its crystal and molecular structure.

In the present paper we report the structure and vibrational spectra of 2L-Trp·HCl and compare with structure and vibrational spectra of L-Trp·HCl.

Experimental

Synthesis and crystal growth

As initial reagents we used L-tryptophan (reagent grade, ⩾98%, TLC) purchased from “Sigma–Aldrich” Chem. Co. and hydrochloric acid (“chemically pure” grade, 32%) from “Reakhim” Co. Both 2L-Trp·HCl and L-Trp·HCl compounds have incongruent solubility. They have been obtained at room temperature by evaporation of aqueous solutions containing non-stoichiometric ratios of solved components: L-tryptophan and hydrochloric acid. From 2:1 M-ratio first L-tryptophan is formed. From 1.7:1 and 1.5:1 M-ratios 2L-Trp·HCl in form of needle crystals were obtained with negligible admixture of L-tryptophan. At equimolar ratio of L-tryptophan and HCl first the 2L-Trp·HCl crystal is formed without admixture of L-tryptophan. The needle-shaped crystals of L-Trp·HCl were obtained at 1:1.5 M-ratio. We also tried to obtain the chloride analog 2L-Trp·HCl·0.5H_2O of known compound 2L-Trp·HBr·0.5H_2O [2]. At 0 °C, however, anhydrous 2L-Trp·HCl was formed.

Crystal structure determination

Suitable single crystals of 2L-Trp·HCl were manually selected and checked for irregularities under the microscope. A well-developed crystal with the approximate size of 0.1 × 0.08 × 0.08 mm^3 was and mounted on a glass needle with laboratory grease. Single-crystal X-ray intensity data of 2L-Trp·HCl were obtained by a measurement on a Bruker APEX II diffractometer, equipped with a graphite monochromator and using Mo Kα (λ = 0.71073 Å) radiation. The structure was solved using direct methods; subsequent difference Fourier syntheses and least-square refinements yielded the positions of the remaining atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters, hydrogen atoms with isotropic displacement parameters. The hydrogen atoms were treated as riding on their parent atoms, except for the hydrogen atoms of the oxygen and nitrogen atoms. All calculations were performed using the Bruker instrument software and the SHELX97 program package [11–13].

The crystallographic data as well as details of the measurement are listed in Table 1. Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033), citing the title of this paper and the CCDC No. 1017250.

Vibrational spectra

Attenuated total reflection Fourier-transform infrared spectra (FTIR ATR) were registered by a Nicolet 5700 spectrometer (ZnSe prizm, Happ–Genzel apodization, ATR distortion is corrected, number of scans 32, resolution 4 cm^{-1}). Part of the IR spectrum in the region 500–400 cm^{-1} was taken from FTIR spectra registered with Nujol mull (4000–400 cm^{-1}, number of scans 32, resolution 2 cm^{-1}).

Fourier-transform Raman spectra were registered by a NXR FT-Raman Module of a Nicolet 5700 spectrometer at room temperature with resolution 4 cm^{-1}. Number of scans and laser power at the sample for L-tryptophanium chloride (I) were 256 and 0.29 W, while for L-tryptophan L-tryptophanium chloride (II) were: 512 and 0.45 W.

Table 1
Crystal data and details of the refinement for L-tryptophan L-tryptophanium chloride.

Formula	$C_{22}H_{25}ClN_4O_4$
M_r	444.91
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	13.284(3)
b (Å)	5.5844(11)
c (Å)	14.691(3)
α (°)	90.00
β (°)	99.46(3)
γ (°)	90.00
V (Å^3), Z	1075.0(4), 2
D_{calc} (gcm^{-3})	1.374
μ(Mo Kα) (cm^{-1})	0.210
F(000)	468
T (K)	296(2)
hkl range	−19/19, −8/8, −21/21
Reflections measured	7335
Reflections unique	7335
Data with ($F_o > 4\sigma(F_o)$)	5858
R_{int}	0.0000
Parameters refined	293
Flack parameter [14]	−0.04(4)
$R(F)$[a] (for $F_o > 4\sigma(F_o)$)	0.0377
$wR(F^2)$[a] (all reflections)	0.0930
Weighting parameters a, b	0.052/0.013
$\Delta\rho_{fin}$ (max/min) (e Å^{-3})	0.179/−0.252

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$, $P = (F_o^2 + 2F_c^2)/3$.

Results and discussion

Molecular and crystal structure of L*-tryptophan* L*-tryptophanium chloride*

The salt 2L-Trp·HCl crystallizes in the monoclinic system (space group $P2_1$, details in Table 1). The unit cell contains one asymmetric formula unit (Fig. 1) comprising one L-tryptophanium moiety, one zwitterionic L-tryptophan molecule and one chloride anion. Selected bond lengths and valence angles are shown in Table 2. Bond lengths of carboxyl and carboxylate groups are typical for these groups. The bond lengths of the carboxyl group C1A=O2A (1.2032(18) Å) and C1A—O1A (1.3134(18) Å) are in good agreement with respective data (1.204(3) Å and 1.316(3) Å) of L-tryptophanium cation in the structure of L-tryptophanium bromide [4], which are more accurate than that of [2,3]. Hydrogen bond parameters are shown in Table 3. L-Tryptophanium moiety and zwitterionic L-tryptophan are bonded with O1A—H1A···O2B hydrogen bond with O···O distance equal to 2.5556(18) Å thus forming dimeric cation. The bond length C1B—O2B (1.2473(18) Å) is slightly longer than C1B—O1B (1.245(2) Å) probably due to the formed hydrogen bond. The O···O distance (2.5556(18) Å) being short should be considered, however, as relatively long among O···O known distances of A···A$^+$ type dimeric cations. The shortest O···O contact (2.381(12) Å) was found in the structure of 2L-Ala·HBr, while the longest O···O distance was found in the structures of 2Gly·HBr (2.562(3) Å) and 2L-Val·$HClO_4$·H_2O (2.562(4) Å) (see [1] and references therein). The majority of hydrogen bonds fall in the 2.42–2.48 Å interval (*ca.* 71%) with typical value of 2.45 ± 0.01 Å [1]. In the structure of (L-Trp···L-Trp$^+$)$HgCl_3^-$ the O···O (2.41(2) Å) distance was found [9], while in the structure of L-tryptophan···L-tryptophanium picrate picric acid the O···O distance makes 2.470(6) Å [10]. So, one of three known O···O distances of L-tryptophan···L-tryptophanium cations is among the relatively short contacts, the second is among the most frequent distances, and the O···O distance of the present structure is among the relatively long distances.

The L-tryptophanium moiety in addition to mentioned O—H···O hydrogen bond forms also hydrogen bonds by the N(1A)H_3^+ group. The N(1A)H_3^+ group forms one weak hydrogen bond with O2B oxygen atom of symmetry-related zwitterionic L-tryptophan moiety and two hydrogen bonds with chloride ion (Table 3). The N2A—H group of indole group does not form any usual hydrogen bonds. The N(1B)H_3^+ group of L-tryptophan moiety forms one hydrogen bond with chloride ion and two hydrogen bonds with O1B oxygen atoms of two nearest symmetry-related molecules (Table 3). In contrast to the L-tryptophanium moiety here the N2B—H group of indole group also forms hydrogen bond with chloride ion. Thus, chloride ion forms four hydrogen bonds of N—H···Cl type.

In dimeric cation zwitterionic L-tryptophan molecule and L-tryptophanium moiety have different conformations. Disposition of amino and carboxyl groups are determined by N1C2C3C4 (χ^1) and C1C2C3C4 ($\chi^{1,2}$) [15]. For L-tryptophanium moiety these values make 63.63°(χ^1) and (−58.31°)($\chi^{1,2}$), that is, have *gauche* disposition, while in case of zwitterionic moiety these values are (−58.76°)(χ^1) and (−179.00°)($\chi^{1,2}$), that is, carboxylate group has *trans* disposition. This conformation is similar to one in the structure of (L-Trp···L-Trp$^+$)$HgCl_3^-$, where for L-tryptophanium moiety these values make 65.98°(χ^1) and (−54.28°)($\chi^{1,2}$), while for zwitterionic moiety these values make (−76.33°)(χ^1) and

Table 2
Selected bond lengths (Å) and angles (°) in L-tryptophan L-tryptophanium chloride.

C1A—O1A	1.3134(18)	C1B—O1B	1.245(2)
C1A—O2A	1.2032(18)	C1B—O2B	1.2473(18)
C1A—C2A	1.5148(19)	C1B—C2B	1.527(2)
C2A—N1A	1.4882(18)	C2B—N1B	1.4896(18)
C2A—C3A	1.5372(19)	C2B—C3B	1.528(2)
C3A—C4A	1.498(2)	C3B—C4B	1.489(2)
C4A—C5A	1.370(2)	C4B—C5B	1.368(2)
C4A—C7A	1.439(2)	C4B—C7B	1.438(2)
C5A—N2A	1.374(2)	C5B—N2B	1.360(2)
N2A—C6A	1.363(2)	N2B—C6B	1.369(2)
C6A—C11A	1.400(2)	C6B—C11B	1.393(2)
C6A—C7A	1.416(2)	C6B—C7B	1.412(2)
C7A—C8A	1.402(2)	C7B—C8B	1.404(2)
C8A—C9A	1.382(2)	C8B—C9B	1.378(3)
C9A—C10A	1.401(3)	C9B—C10B	1.402(3)
C10A—C11A	1.375(3)	C10B—C11B	1.375(3)
O2A—C1A—O1A	124.74(14)	O2B—C1B—O1B	126.28(15)
O2A—C1A—C2A	123.34(13)	O2B—C1B—C2B	116.45(15)
O1A—C1A—C2A	111.90(12)	O1B—C1B—C2B	117.25(13)
N1A—C2A—C1A	107.76(11)	N1B—C2B—C1B	109.87(11)
N1A—C2A—C3A	111.35(11)	N1B—C2B—C3B	111.37(12)
C1A—C2A—C3A	113.70(11)	C1B—C2B—C3B	107.22(12)
C4A—C3A—C2A	115.32(12)	C4B—C3B—C2B	117.43(13)
C5A—C4A—C7A	106.08(13)	C5B—C4B—C7B	105.84(14)
C5A—C4A—C3A	127.28(14)	C5B—C4B—C3B	126.16(15)
C7A—C4A—C3A	126.60(13)	C7B—C4B—C3A	127.78(14)
C4A—C5A—N2A	110.03(14)	C4B—C5B—N2A	110.51(14)
C6A—N2A—C5A	109.39(13)	C6B—N2B—C5A	109.29(14)
N2A—C6A—C11A	130.43(14)	N2B—C6B—C11B	130.69(15)
N2A—C6A—C7A	107.47(13)	N2B—C6B—C7B	107.28(13)
C11A—C6A—C7A	122.10(14)	C11B—C6B—C7B	122.03(15)
C8A—C7A—C6A	118.85(13)	C8B—C7B—C6B	118.61(14)
C8A—C7A—C4A	134.13(14)	C8B—C7B—C4B	134.33(15)
C6A—C7A—C4A	107.02(13)	C6B—C7B—C4B	107.06(13)
C9A—C8A—C7A	118.72(15)	C9B—C8B—C7B	119.20(16)
C8A—C9A—C10A	121.54(16)	C8B—C9B—C10B	121.07(16)
C11A—C10A—C9A	121.25(16)	C11B—C10B—C9B	121.15(16)
C10A—C11A—C6A	117.54(15)	C10B—C11B—C6B	117.92(16)

Table 3
Hydrogen bonds parameters for L-tryptophan L-tryptophanium chloride (in Å and °).

D—H···A	D—H	H···A	D···A	<DHA
O1A—H1A···O2B^{i}	0.87(3)	1.69(3)	2.5556(18)	171(3)
N1A—H11A···O2B^{ii}	0.89	2.23	2.9959(19)	144
N1A—H12A···Cl1	0.89	2.33	3.1910(14)	164
N1A—H13A···Cl1^{i}	0.89	2.40	3.2588(15)	161
N1B—H11B···Cl1^{ii}	0.89	2.30	3.1682(16)	166
N1B—H12B···O1B^{i}	0.89	1.89	2.7410(18)	158
N1B—H13B···O1B^{iii}	0.89	2.13	2.9621(17)	155
N2B—H21B···Cl1^{iv}	0.81(2)	2.62(2)	3.2762(17)	139.1(19)

Symmetry code: (i) *x*, *y* − 1/2, −*z*; (ii) −*x* + 1, *y* − 1/2, −*z* + 1; (iii) −*x* + 1, *y* − 3/2, −*z* + 2; (iv) *x* − 1, *y* − 3/2, −*z*.

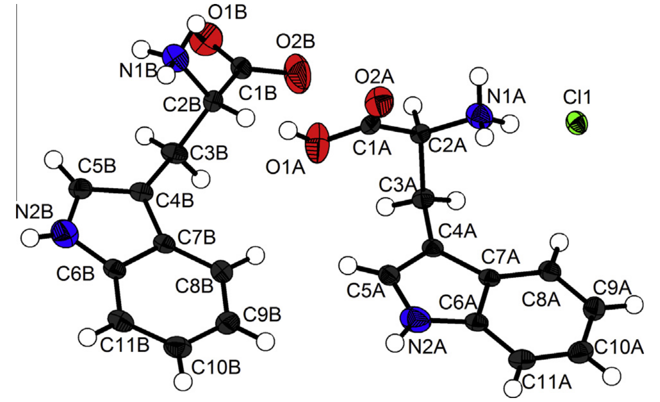


Fig. 1. Molecular structure of L-tryptophan L-tryptophanium chloride. Note that molecule A is in cation form, molecule B is a zwitterion, the charge is counterbalanced by the chloride anion.

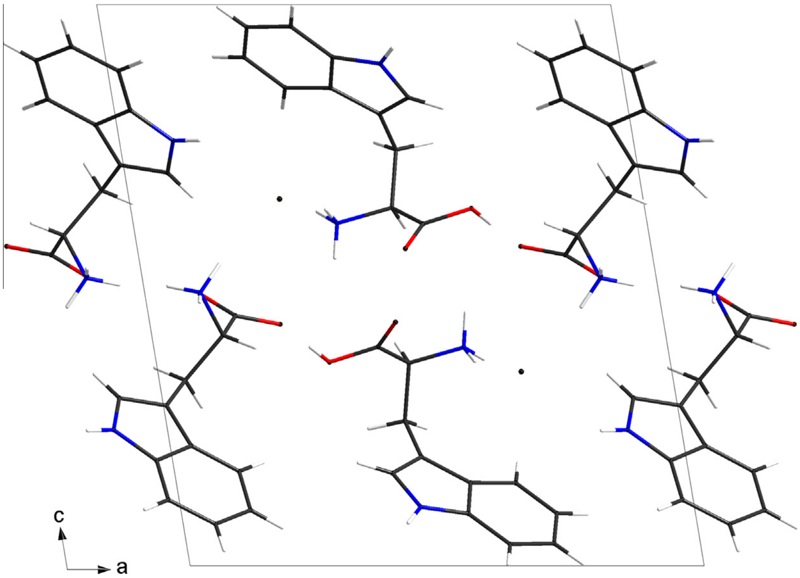


Fig. 2. Packing diagram of L-tryptophan L-tryptophanium chloride, viewed along [010].

167.10°)($\chi^{1,2}$) [9]. In the structure of L-tryptophan···L-tryptophanium picrate picric acid conformations are different. For the L-tryptophanium moiety the NH_3^+ group has *gauche* disposition (−72.15°)(χ^1), the carboxyl group *trans* disposition (168.50°) ($\chi^{1,2}$), while in the case of the zwitterionic moiety the situation is opposite: (172.62°)(χ^1) and (69.07°)($\chi^{1,2}$) [10]. In the case of L-tryptophanium chloride these values are equal to (−62.72°)(χ^1) and (57.85°)($\chi^{1,2}$) [2].

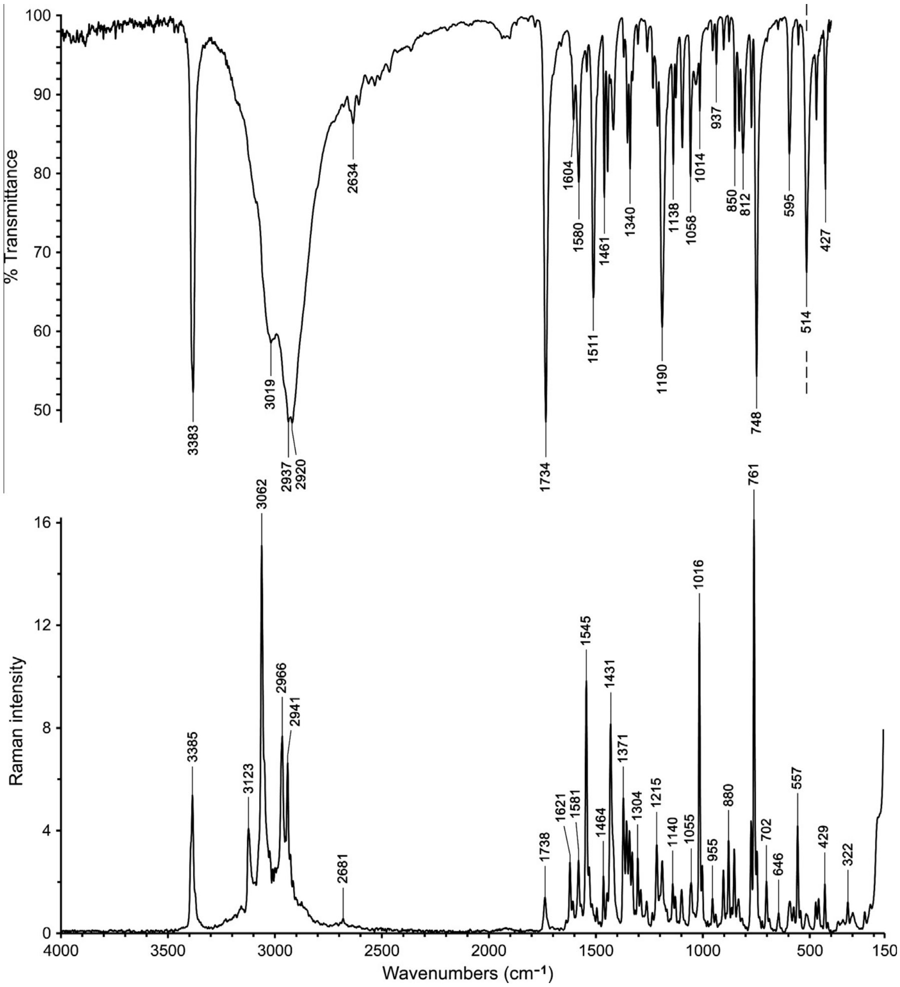


Fig. 3. Infrared and Raman spectra of L-tryptophanium chloride.

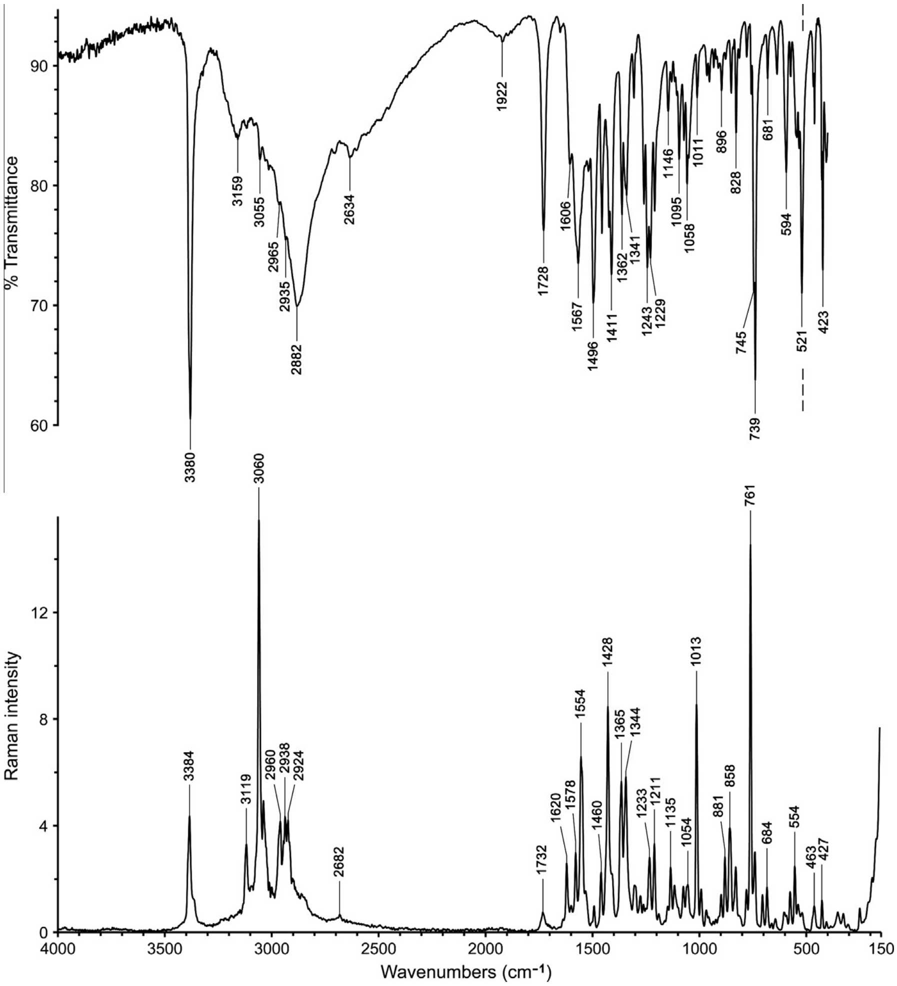


Fig. 4. Infrared and Raman spectra of L-tryptophan L-tryptophanium chloride.

In Fig. 2 a packing diagram of 2L-Trp·HCl is shown, viewed along [010]. The units are packed in a double layer-like pattern, with the amino and acid groups facing toward each other (in the middle of Fig. 2) and the indolyl groups facing outwards. The structure is polar; all amino acids molecule are inclined in the same direction (in Fig. 2, the indolyl groups are inclined toward the viewer, the amino and acid ends away from the viewer). The chloride anions are located in the voids of the structure (the discussion of the hydrogen bonding network is given above and further elaborated on in 'Infrared and Raman spectra').

Infrared and Raman spectra

For discussion of the 2L-Trp·HCl spectra we found useful to register and compare with the L-Trp·HCl spectra. In Figs. 3 and 4 the spectra of L-Trp·HCl (I) and 2L-Trp·HCl (II) are shown. Comparison with the spectrum of L-alaninium chloride (L-Ala·HCl) as well as with published spectra of indole and L-tryptophan is useful too. As it was shown in [1] the published spectra of L-Ala·HCl actually belong to L-alanine. So, in Fig. 5 we show also the IR and Raman spectra of L-Ala·HCl. Crystals of L-Ala·HCl were obtained similarly to L-Trp·HCl by evaporation from aqueous solution containing L-alanine and HCl in M-ratio 1:1.5. We expect to find in spectra of (I) and (II) the presence of characteristic bands of indole group, carboxyl group, protonated NH_3^+ group and CH, CH_2 groups, as well as reflection in the spectra of (II) the presence of O—H···O hydrogen bond of L-tryptophan L-tryptophanium dimer. The characteristic spectroscopic feature of indole group in the molecule of tryptophan is the stretching vibration of N—H group in high-frequency region (see e.g. [16,17]). It is easy to find it in Fig. 3 at 3383 cm^{-1} (IR) and 3385 cm^{-1} (R) and in Fig. 4 at 3380 cm^{-1} (IR) and 3384 cm^{-1} (R). Stretching vibrations of CH and CH_2 groups are better revealed in Raman spectrum. The lines at 3123 cm^{-1} (Fig. 3) and 3119 cm^{-1} (Fig. 4) we assign to stretching vibration of C—H bond of pyrrole ring. The lines at 3062 cm^{-1} (Fig. 3) and 3060 cm^{-1} (Fig. 4) we assign to C—H bonds of benzene ring, the lines at 2966 cm^{-1} and 2941 cm^{-1} (Fig. 3) and 3038, 2960, 2938, 2924 cm^{-1} (Fig. 4) to aliphatic CH and CH_2 groups. It may be noted that these lines are superimposed on broad bands in the region 3300–2500 cm^{-1}, which we assign to stretching vibrations of N—H bonds of NH_3^+ groups. In contrast to the Raman spectra, in the infrared spectra stretching vibrations of N—H bonds of NH_3^+ groups are revealed as strong absorption bands in 3300–2500 cm^{-1} (Fig. 3) and 3300–2100 cm^{-1} (Fig. 4) regions, while ν(CH) as weak peaks. In the structure of L-Trp·HCl the carboxyl group forms hydrogen bond with chloride anion O—H···Cl with O···Cl distance 3.04 Å and the NH_3^+ group forms three N—H···Cl hydrogen bonds with 3.17 Å, 3.19 Å and 3.24 Å distances. For these hydrogen bonds one may expect [18] ν(OH) and ν(NH) near 2900 cm^{-1}, 2950 cm^{-1}, 3000 cm^{-1} and 3100 cm^{-1} respectively, which well correspond to the peaks at 3019 cm^{-1}, 2937 cm^{-1} and 2920 cm^{-1} (Fig. 3). In the IR spectrum of 2L-Trp·HCl (Fig. 4) there is a broad absorption band with peak at 2882 cm^{-1}, which also we assign to ν(NH) of two NH_3^+ groups. This peak may be

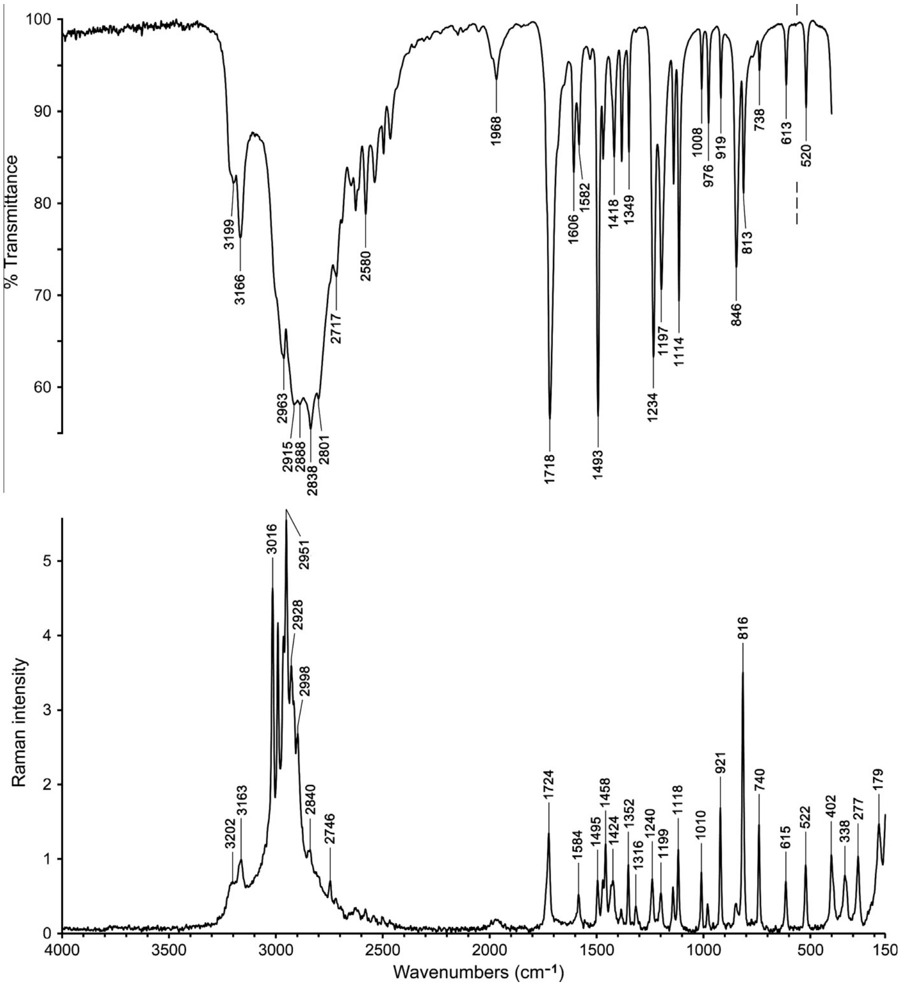


Fig. 5. Infrared and Raman spectra of L-Ala·HCl.

caused by ν(NH) of N1B—H12B···O1B with shortest N—H···O bond equal to 2.7410(18) Å. The peak at 3159 cm^{-1} we also assign to ν(NH) and not to ν(CH) because of absence of corresponding line in the Raman spectrum. The ν(NH) of all other N—H···O are expected in this region, while ν(OH) of O—H···O bond is expected at lower wavenumbers. The presence of COOH carboxyl group of L-tryptophanium cation in L-Trp·HCl is confirmed by presence of a strong absorption band at 1734 cm^{-1} and a line at 1738 cm^{-1} caused by ν(C=O) (Fig. 3). In the spectra of 2L-Trp·HCl these values are somewhat lower: 1728 cm^{-1} (IR) and 1732 cm^{-1} (R) (Fig. 4). The region 1700–400 cm^{-1} also contains modes caused by both the main alaninyl group and side indolyl group. The Raman-lines in the spectrum of 2L-Trp·HCl at 1620 cm^{-1}, 1578 cm^{-1} and 1554 cm^{-1} (Fig. 4) we assign to vibrations of indolyl group. One may assume that the line at 1620 cm^{-1} is caused by asymmetric stretching vibration of carboxylate group of zwitterionic L-tryptophan moiety. Indeed, the authors of [17] assigned the line at 1622 cm^{-1} to asymmetric stretching vibration of carboxylate group of zwitterionic L-tryptophan. However, we cannot agree with this assignment because this vibration is characteristic also for indole (see e.g. [19]). In addition, these three lines are present in the spectrum of L-Trp·HCl (Fig. 3) at 1621 cm^{-1}, 1581 cm^{-1} and 1545 cm^{-1} with similar intensities, where carboxylate COO^{-} group is absent. The lines at 1545 cm^{-1} and 1554 cm^{-1} (labeled as W3) are caused mainly by stretching vibration of C4—C5 bond of pyrrole ring (see Fig. 1) (see e.g. [20]. Two other lines are caused by stretching vibrations of benzene ring. The value of W3 correlates with torsion $\chi^{2,1}$ angle [21] (see also [20]): $\nu_{W3}(\mathrm{cm}^{-1}) = 1542 + 6.7(\cos 3|\chi^{2,1}| + 1)^{1/2}$, where $\chi^{2,1}$ is the C2C3C4C5 torsion angle (see Fig. 1). For L-Trp·HCl [2] this angle is equal to −77.96° and $\nu_{W3} = 1546$ cm^{-1}, which is in good agreement with observed (1545 cm^{-1}) value. In case of 2L-Trp·HCl the value of $\chi^{2,1}$ for zwitterionic moiety makes 101.89° and respective calculated value $\nu_{W3} = 1550$ cm^{-1}, while for L-tryptophanium moiety $\chi^{2,1} = 82.95°$ and respectively $\nu_{W3} = 1547$ cm^{-1}. However, in this case the observed value is equal to 1554 cm^{-1}. In the IR spectra the band at 1580 cm^{-1} (Fig. 3) and 1567 cm^{-1} (Fig. 4) may also be caused (or mainly be caused) by asymmetric deformation vibration of NH_3^+ groups, while rather strong bands at 1511 cm^{-1} (Fig. 3) and 1496 cm^{-1} (Fig. 4) we assign to symmetric deformation vibration of the same groups. It should be noted that in the IR spectrum of L-Ala·HCl (Fig. 5) there are similar peaks at 1606 cm^{-1} and 1582 cm^{-1}, which are caused probably by skeletal vibration of L-alaninium cation and asymmetric deformation vibration of NH_3^+ group, while the strong band at 1493 cm^{-1} may be assigned to symmetric deformation vibration of NH_3^+ group. Rather intensive Raman-lines at 1431 cm^{-1} (Fig. 3) and 1428 cm^{-1} (Fig. 4) are characteristic for deformation scissoring vibration of CH_2 group. The absorption band at 1411 cm^{-1} (Fig. 4) may be caused by symmetric stretching of COO^{-} carboxylate group. However, it should be noted that in the IR spectrum of L-Trp·HCl (Fig. 3) there is also a peak at 1418 cm^{-1} as well as in the spectra of L-Ala·HCl (Fig. 5) and indole [19]. There is an absorption band with peaks at 1362 cm^{-1} and 1341 cm^{-1} (Fig. 4) with respective Raman lines at 1365 cm^{-1} and

Table 4
Wavenumbers (in cm^{-1}) and assignment of peaks in IR and Raman spectra of L-tryptophanium chloride (I) and L-tryptophan L-tryptophanium chloride (II).

I IR	I Raman	II IR	II Raman	Assignment
3383	3385	3380	3384;3363sh	ν(NH) Indole
		3159		ν(NH), NH_3^+
	3123	3117	3119	ν(CH) pyrrole
	3062	3076; 3055	3060	ν(CH) benzene
3019; 2937; 2920			3038	ν(NH), NH_3^+
	2966; 2941	3014; 2965; 2935	3038; 2960; 2938; 2924	ν(CH), CH, CH_2
	2880	2882	2861	ν(NH), NH_3^+
2634; 2608	2681	2711; 2634; 2605	2682	Combi
1938; 1903		1922		Combi
1734	1738	1728	1732	ν(C=O)
1663		1651		
1604	1621; 1607	1606	1620; 1600	BR str
1580	1581	1567	1578	$\delta_{as}(NH_3^+)$, BR str
1542	1545		1554	Indole stretch
	1531sh; 1518	1519		
1511	1495	1496	1493	$\delta_s(NH_3^+)$
1461; 1445	1464; 1447	1456	1460	
1418	1431	1422	1428	$\delta(CH_2)$
		1411	1408sh	$\nu_s(COO^-)$
1370; 1352; 1340	1371; 1356; 1343	1362; 1341	1365; 1344	
1328	1330			
1303	1304	1306	1303	δ(CH)
1260	1290; 1262	1259	1276; 1261	
1233; 1212; 1190	1236; 1215; 1190	1243; 1229; 1209	1233; 1211; 1190	
1138; 1126; 1096	1140; 1129; 1099	1146; 1130; 1115; 1095	1148; 1135; 1117	$\rho(NH_3^+)$, δ(NH), Indole
1058; 1032	1055	1072; 1058; 1050	1075; 1054	ν(C—N)
1014	1016	1011	1013	β(CH), Indole
954; 937	1002; 955; 940	987; 965; 953; 933; 921	991; 968	
902	904	912		
877	880	896; 877	898; 881	$\rho(CH_2)$
850; 830; 812	865; 853; 833; 817	851; 828; 813	858; 830	
773	774	778; 757	780	
748	761	745sh; 739	761	γ(CH), Indole
	747; 722		741	
700	702			
648	690; 646	681; 637	705; 684; 645	
595	593	594	604; 594	
553	575; 557; 543	573; 547; 534	576; 554; 538	
514	517	521	520	γ(NH), Indole
	472; 459; 429	467; 462; 428; 423	463; 427	
	416	407	406	
	367; 345; 322		353; 327	
	299; 243; 217		250; 192	

Combi – combination, overtone, sh – shoulder, s – symmetric, as – asymmetric, ν – stretching, δ – deformation, ω – wagging, τ – torsion, β – in-plane, γ – out of plane, ρ – rocking, BR – benzene ring.

1344 cm^{-1}. This is the region of wagging vibration of CH_2 group. Similar peaks are present in the spectra of L-Trp·HCl (Fig. 3) and L-Ala·HCl (Fig. 5). However, the spectra of indole also contain peaks in this region; hence they may be caused also by indolyl group. In the region of ν(C—OH) (*ca.* 1250 cm^{-1}) there is a band with peaks at 1259, 1243, 1229, 1209 cm^{-1} and Raman lines at 1233, 1211 cm^{-1} (Fig. 4). This is also the region of twisting vibration of CH_2 group and also deformation vibration of CH bonds of indolyl group. The absorption peak at 1146 cm^{-1} (Fig. 4) may be caused by rocking vibration of NH_3^+ group, however, there are vibrations of indole group also in this region. There are rather intensive Raman-lines at 1013 cm^{-1} and 761 cm^{-1} in the spectrum of 2L-Trp·HCl (Fig. 4) and similar lines in the spectrum of L-Trp·HCl at 1016 cm^{-1} and 761 cm^{-1} (Fig. 3). Respective absorption band of the line at 761 cm^{-1} is at 748 cm^{-1} (Fig. 3) and doublet with peaks at 745 cm^{-1} and 739 cm^{-1} (Fig. 4). Both bands are rather strong. These Raman-lines and absorption bands are caused by vibrations of indole group. They are present also in the spectra of L-tryptophan [16,17] and indole [19] and probably are caused by deformation of CH groups and ring breathing.

Let us now compare the two IR spectra in Figs. 3 and 4 entirely. One can note that absorption peaks in Fig. 4 are superimposed on additional absorption in the region 1700–800 cm^{-1}. We consider that this additional absorption is caused by ν(OH) of O—H···O hydrogen bond of dimeric cation. This absorption band is not strong enough. In addition, it is difficult to point out its center. Nevertheless, its position is somewhat shifted toward lower wavenumbers compared to that expected according to the curve of known correlation between ν(OH) and R(O···O) [22] (*ca.* 2000 cm^{-1}). However, it should be noted that there are not experimental results for R(O···O) value near 2.55 Å [22]. There are only two points for *ca.* 2.58 Å with ν(OH) values *ca.* 2000 cm^{-1} and 1800 cm^{-1}. Later reinvestigated or investigated a number of crystals with dimeric cations with O—H···O hydrogen bonds [1]. For example in the structures of 2Gly.HCl and 2Gly.HBr the O···O distances are close to this value: 2.552(5) Å [23] and 2.562(3) Å [1] respectively. The IR spectra of these crystals provided in [24,25] consist each two broad absorption bands: 3118–2241 cm^{-1} and *ca.* 2200–500 cm^{-1} centered at *ca.* 3000 cm^{-1} and *ca.* 1500 cm^{-1} for 2Gly.HCl [24] and 3116–2230 cm^{-1} and *ca.* 2200–550 cm^{-1} centered at *ca.* 3000 cm^{-1} and *ca.* 1500 cm^{-1} for 2Gly.HBr [25]. The authors of [24,25] assigned the bands at 3118–2241 cm^{-1} and 3116–2230 cm^{-1} to stretching vibrations of O—H and NH_3^+ groups. In our opinion these bands are caused by stretching vibration of NH_3^+ groups, while the bands centered at *ca.* 1500 cm^{-1} are caused by stretching vibration of O—H groups. More detailed study of the spectra of 2Gly·HCl was carried out in [26]. These authors assigned to ν(OH) the peak at 2026 cm^{-1}. The value R(O···O) = 2.55 Å falls into the region which separates the regions with weak and intermediate hydrogen bonds from the region with strong hydrogen bonds [22].

Conclusions

L-Tryptophan L-tryptophanium chloride, a new salt with an (A···A$^+$) type dimeric cation, crystallizes in monoclinic system, with space group $P2_1$. The O···O distance in O—H···O hydrogen bond of dimeric cation makes 2.5556(18) Å. Being short this hydrogen bond is relatively long compared to other known salts with dimeric cation, particularly, compared to two previously known salts with (L-Trp···L-Trp$^+$) dimeric cations: (L-Trp···L-Trp$^+$)$HgCl_3$ (2.41(2) Å) [9] and (L-Trp···L-Trp$^+$) picrate picric acid (2.470(6) Å) [10]. Conformations of zwitterionic and cationic moieties in dimeric cation are different. Vibrational (IR and Raman) spectra of 2L-Trp.HCl were studied and compared with spectra of L-Trp.HCl (see Table 4) and L-Ala.HCl.

References

[1] M. Fleck, A.M. Petrosyan, Salts of Amino Acids: Crystallization, Structure and Properties, Springer, Dordrecht, 2014.

[2] T. Takigawa, T. Ashida, Y. Sasada, M. Kakudo, The crystal structures of L-tryptophan hydrochloride and hydrobromide, Bull. Chem. Soc. Jap. 39 (1966) 2369–2378.

[3] R. Ramachandra Ayyar, R. Chandrasekharan, Crystal structure of L-tryptophan hydrobromide, Curr. Sci. 36 (6) (1967) 141–143.

[4] K. Stewart, Redetermination of L-tryptophan hydrobromide, Acta Crystallogr. E 65 (2009) o1291–o1292.

[5] T. Ishida, H. Nagata, Y. In, M. Doi, M. Inoue, M.W. Extine, A. Wakahara, X-ray crystal structure of L-tryptophan-picric acid charge-transfer complex and comparison with *DL*-tryptophan-picric acid complex, Chem. Pharm. Bull. 41 (1993) 433–438.

[6] M. Ramos Silva, J.A. Paixão, A. Matos Beja, Crystal structure of L-tryptophanium phosphite ($C_{11}H_{13}N_2O_2$)[H_2PO_3], Z. Kristallogr. NCS 220 (2005) 487–488.

[7] J.A. Paixão, M. Ramos Silva, A. Matos Beja, E. Eusébio, Crystal structure and properties of L-tryptophanium hydrogen selenite, Polyhedron 25 (2006) 2021–2025.

[8] O. Bakke, A. Mostad, The structure and conformation of tryptophan in the crystal of the pure racemic compound and the hydrogen oxalate, Acta Chem. Scand. B34 (1980) 559–570.

[9] L. Book, A.J. Carty, C. Chieh, Five-coordinated halogenomercurate(II) complexes: crystal structures of bis(L-tryptophanium) trichloromercurate(II) and bis(D, L-homocysteine thiolactonium) tetrabromomercurate(II), Can. J. Chem. 59 (1981) 138–143.

[10] A.M. Petrosyan, M. Fleck, V.V. Ghazaryan, Reinvestigation of L-tryptophan picrate: establishment of the existence of the L-tryptophan L-tryptophanium dimeric cation, Spectrochim. Acta A 104 (2013) 486–491.

[11] NONIUS, Kappa CCD Program Package: COLLECT, DENZO, SCALEPACK, SORTAV, Nonius BV, Delft, The Netherlands, 1999.

[12] Z. Otwinowski, W. Minor, Processing of X-ray diffraction data collected in oscillation mode, Methods Enzymol. A 276 (1997) 307–326.

[13] G.M. Sheldrick, A short history of SHELX, Acta Crystallogr. A 64 (2008) 112–122.

[14] H.D. Flack, On enantiomorph-polarity estimation, Acta Crystallogr. A 39 (1983) 876–881.

[15] C.B. Hübschle, M. Messerschmidt, P. Luger, Crystal structure of DL-tryptophan at 173 K, Cryst. Res. Technol. 39 (2004) 274–278.

[16] X. Cao, G. Fischer, Infrared spectral, and conformational studies of zwitterionic L-tryptophan, J. Phys. Chem. A 103 (1999) 9995–10003.

[17] C.H. Chuang, Y-T. Chen, Raman scattering of L-tryptophan enhanced by surface plasmon of silver nanoparticles: vibrational assignment and structural determination, J. Raman Spectrosc. 40 (2009) 150–156.

[18] K. Nakamoto, M. Margoshes, R.E. Rundle, Stretching frequencies as a function of distances in hydrogen bonds, J. Amer. Chem. Soc. 77 (1955) 6480–6486.

[19] N. Sundaraganesan, H. Umamaheswari, B. Dominic Joshua, C. Meganathan, M. Ramalingam, Molecular structure and vibrational spectra of indole and 5-aminoindole by density functional theory and ab initio Hartree-Fock calculations, J. Mol. Struct.: THEOCHEM. 850 (2008) 84–93.

[20] L.J. Juszczak, R.Z.B. Desamero, Extension of the tryptophan $\chi^{2,1}$ dihedral angle-W3 band frequency relationship to a full rotation: correlation and caveats, Biochemistry 48 (2009) 2777–2787.

[21] H. Takeuchi, Raman spectral marker of tryptophan conformation: theoretical basis and extension to a wider range of torsional angle, J. Mol. Struct. 1023 (2012) 143–148.

[22] A. Novak, Vibrational spectroscopy of hydrogen bonded systems, Infrared and Raman Spectroscopy of Biological Molecules, vol. 43, NATO Advanced Study Institute Series, 1979, pp. 279–303.

[23] S. Natarajan, C. Muthukrishnan, S.A. Bahadur, R.K. Rajaram, S.S. Rajan, Reinvestigation of the crystal structure of diglycine hydrochloride, Z. Kristallogr. 198 (1992) 265–270.

[24] B. Narayana Moolya, S.M. Darmaprakash, Nonlinear optical diglycine hydrochloride: synthesis, crystal growth and structural characteristics, J. Crystal Growth 293 (1) (2006) 86–92.

[25] B. Narayana Moolya, S.M. Dharmapraksh, Growth and characterization of nonlinear optical diglycinehydrobromide single crystals, Mater. Lett. 61 (17) (2007) 3559–3562.

[26] Jan Baran, Austin J. Barnes, Henryk Ratajczak, The polarized IR and Raman spectra of the diglycine hydrochloride crystal, J. Mol. Struct. 1009 (2012) 55–68.