Bulgarian Chemical Communications, Volume 40, Number 4 (pp. 456–463) 2008

Solid-state IR-LD spectroscopy of L-tryptophan-containing dipeptides L-tryptophyl-L-methionine (*H-Trp-Met-OH*), L-methionyl-L-tryptophan (*H-Met-Trp-OH*) and glycyl-L-tryptophan dihydrate (*H-Gly-Trp-OH.2H$_2$O*)

B. B. Koleva

St. Kliment Ohridsky Sofia University, Faculty of Chemistry, 1, J. Bourchier, Blv., 1164 Sofia, Bulgaria

Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

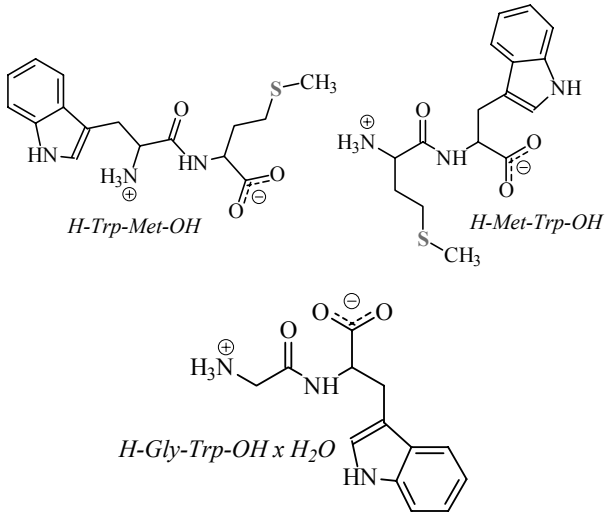
Received January 2, 2008, Revised January 11, 2008

IR-spectroscopic and structural elucidation of *L*-tryptophan-containing dipeptides L-tryptophyl-L-methionine (*H-Trp-Met-OH*), L-methionyl-L-tryptophan (*H-Met-Trp-OH*) and glycyl-L-tryptophan dihydrate (*H-Gly-Trp-OH.2H$_2$O*) by means of solid-state linear dichroic IR- (IR-LD) spectroscopy of orientated colloid suspensions in nematic host is performed. A correlation structure-spectroscopic property of the latter compound is done, comparing IR-LD and known single crystal X-ray diffraction data. Quantum chemical *ab initio* and DFT calculations of *H-Trp-Met-OH*/H_2O and *H-Met-Trp-OH*/H_2O systems support is made in addition to the IR-LD spectroscopic analysis.

Key words: L-tryptophyl-L-methionine (*H-Trp-Met-OH*), L-methionyl-L-tryptophan (*H-Met-Trp-OH*), glycyl-L-tryptophan dehydrate, solid-state linear polarized IR spectroscopy, quantum chemical calculations.

INTRODUCTION

Tryptophan-containing peptides are intensively studied during the last years, due to their possibility to recognize and cleave DNA at apurinic sites [1]. On the other side the aromatic interactions in tryptophan-containing peptides have been also studied [2]. A series of small peptides has been structurally investigated by single crystal X-ray diffraction [2]. As a part of systematic spectroscopic and structural elucidation of small peptides, their salts and metal complexes have been studied [3–15] by means of solid-state IR-LD spectroscopy of orientated colloids in nematic mesophase [16–19], herein included $_L$-tryptophane containing dipeptides as L-tryptophyl-L-methionine (*H-Trp-Met-OH*) and L-methionyl-$_L$-tryptophan (*H-Met-Trp-OH*) (Scheme 1). The conclusions about the structures of the above stated dipeptides are supported by the additionally performed IR-LD characterization of glycyl-L-tryptophan dihydrate (*H-Gly-Trp-OH.2H$_2$O*), shown in Scheme 1. The crystal structure of *H-Gly-Trp-OH.2H$_2$O* has been determined by single crystal X-ray diffraction [20], thus allowing a comparison between spectroscopic and structural data, *i.e.* correlation between structure-optical properties.



Scheme 1. Chemical diagram of dipeptides *H-Trp-Met-OH*, *H-Met-Trp-OH* and *H-Gly-Trp-OH.2H$_2$O*.

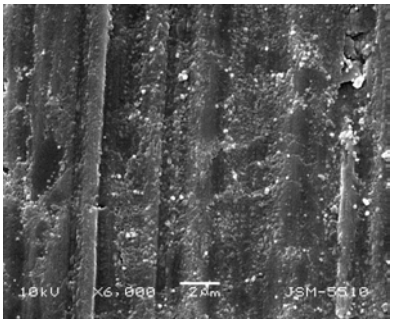
EXPERIMENTAL

Both peptides are "Bachem" (Switzerland) products. The *H-Gly-Trp-OH.2H$_2$O* is obtained by the procedure described in [20]. The purity of the studied compound was proved by mass spectrometry (ESI) and ^{1}H-NMR.

The IR-spectra were measured on a THERMO NICOLET 6700 FTIR-spectrometer (4000–400 cm^{-1}, 1 cm^{-1} resolution, 200 scans) equipped with a Specac wire-grid polarizer. The non-polarized solid-state IR spectra were recorded using KBr disk

* E-mail: BKoleva@chem.uni-sofia.bg

technique. The orientated samples were obtained as a colloid suspension in a nematic host (ZLI 1695, Merck), using the method described in [16–19]. The application of colloid suspensions in nematic liquid crystal host allows IR-spectroscopic and structural elucidation of embedded solid particles, which was demonstrated in series of papers dealing with characterization of inorganic compounds and glasses [21], organic and coordination compounds (see Refs. 3–19). It has been found out [19] that a partial orientation (15–20%) of suspended particles (Scheme 2), adequate for the recording of reasonable linearly polarized IR-spectra is achieved, when 5 ± 1% by weight of the given solid compound, with particle size within the limits 0.3–0.9 μm, is mixed with a nematic liquid crystal substance (ZLI 1695, ZLI 1538 or MLC 6815) suitable for IR spectroscopy and the obtained slightly viscous suspension is phase pressed between two KBr-plates. They are roughened in one direction prior to use with fine sandpaper (C800) (size 5 μm). The KBr-plates and pressed suspension are moved repeatedly with 3 μm/s for 100 times. The optimal cell thickness is 100 μm. The validation of this orientation solid-state method in regard to accuracy and precision, the influence of the liquid crystal medium on peak positions and integral absorbances of the guest molecule bands have been represented [17,18]. The reological model, the nature and balance of the forces in the nematic liquid crystal suspension system, the mathematical model, and morphology of the suspended particles are discussed [19].



Scheme 2. Electron microscopic data of the colloid suspension in nematic host.

The interpretation of the non-polarized and polarized infrared spectra includes determination of the position (ν_i) and integral absorbances (A_i) for each i-peak by deconvolution and curve fitting at a 50:50% ratio of Lorentzian to Gaussian peak functions. Usually χ^2 factor varies within 0.00013–0.00008 (in our case 1.2×10^{-5}–2.3×10^{-4}) and 2000 iterations [17, 18]. The mean values of two treatments were compared by the Student *t*-test. The experimental IR-spectral patterns were acquired and processed by means of the GRAMS/AI 7.01 IR spectroscopy (Thermo Galactic, USA) and the STATISTICA for Windows 5.0 (StatSoft, Inc., Tulsa, OK, USA) program packages.

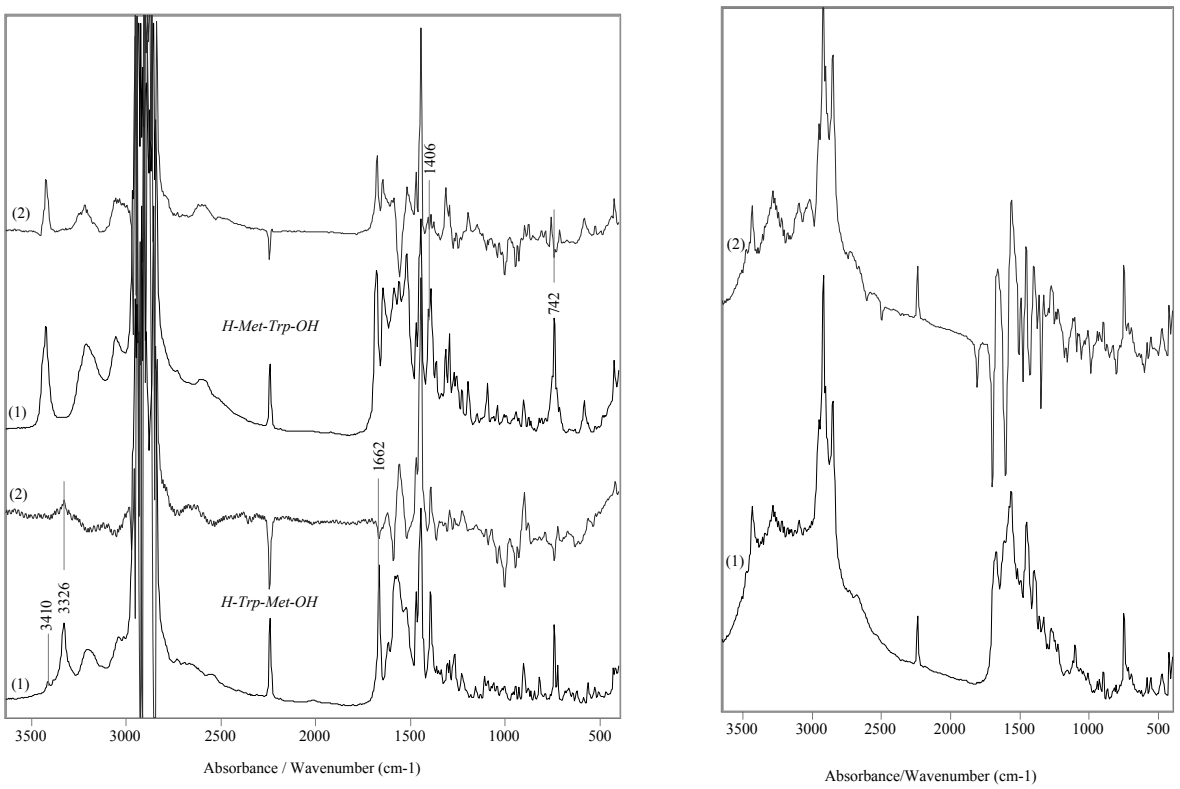
Spectroscopic and structural results by orientation technique presented here were obtained using the known "reducing-difference procedure" designated as "stepwise reduction" for polarized IR-spectra interpretation. This method was initially suggested by Thulstrup and Eggers for the interpretation of polarized UV-spectra [22]. The procedure involves consecutive elimination of the spectral bands of a given polarization by subtracting the perpendicular spectrum multiplied by a coefficient from the parallel one. This procedure was extended by Spanget-Larsen [23] and by Korte and Lampen [24] to include samples orientated in stretched polyethylene and in nematic solution, respectively. A systematic analysis of this approach and its application to IR-band assignment according to their symmetry appurtenance was developed by Jordanov and co-workers [25–28] for polarized IR-LD spectra in nematic liquid crystal solution. The method consists of subtraction of the perpendicular spectrum, ($IR_\perp$, resulting from a 90° angle between the polarized light beam electric vector and the orientation of the sample) from the parallel one ($IR_{||}$) obtained with a co-linear mutual orientation. The recorded *difference* ($IR_{||}$-$IR_\perp$) spectrum divides the corresponding parallel ($A_{||}$) and perpendicular ($A_\perp$) integrated absorbencies of each band into positive values originating from transition moments, which form average angles with the orientation direction (**n**) between 0° and 54.7° (magic angle), and negative ones corresponding to transition moments between 54.7° and 90°. In the *reducing-difference procedure*, the perpendicular spectrum multiplied by the parameter ***c***, is subtracted from the parallel one and ***c*** is varied until at least one band or a set of bands is eliminated. The simultaneous disappearance of these bands in the obtained *reduced* IR-LD spectrum ($IR_{||}$-$\boldsymbol{c}IR_\perp$) indicates co-linearity of the corresponding transition moments, thus yielding information regarding the mutual disposition of the molecular fragments.

The optimization of the structures of the peptides in the systems peptide/H_2O was carried out by *DFT* calculations (B3LYP) at 6-31+G** basis set using the Gaussian 98 and Dalton 2.0 program packages [29, 30]. The visualization of the output files is done by ChemCraft 5.0 [31]. The methodology for exploring the conformational energy landscape described in [32, 33] was used in our case too. The scheme first creates all possible conformers by rotating around the flexible bonds according to a set

of suitable step sizes and then employs a hierarchy of increasingly more accurate electronic structure methods. For every structure the stationary points found on the molecule potential energy hyper-surfaces were characterized using standard analytical harmonic vibrational analysis. The absence of imaginary frequencies, as well as of negative eigenvalues of the second-derivative matrix, confirmed that the stationary points correspond to minima of the potential energy hyper-surfaces. The calculations of vibrational frequencies and infrared intensities were checked to establish which kind of performed calculations agrees best with the experimental data.

RESULTS AND DISCUSSION

The non-polarized IR-spectra of the dipeptides are depicted in Figs. 1.1A and 1.1B. The IR-characteristic band assignment is listed in Table 1. The NH stretching vibration (ν_{NH}) is observed within 3326–3446 cm^{-1} range. The indole stretching $\nu_{NH(In)}$, usually observed as a strong band [8, 9, 15, 34–36] is obtained within 3409–3424 cm^{-1}. In all cases the asymmetric and symmetric stretching vibrations of NH_3^+ group (ν^{as}_{NH3+} and ν^{s}_{NH3+}) are observed as a broad band within wide 3200–2000 cm^{-1} ranges with highest frequency sub maxima about 3200 cm^{-1}. The IR-spectroscopic region 1800–1450 cm^{-1} is characterized with overlapping absorption bands of bending NH_3^+, Amide I ($\nu_{C=O}$), ν^{as}_{COO-}, δ_{NH} (Amide II) and indole in-plane (i.p.) vibrations (Table 1). In 800–400 cm^{-1} region are described and assigned to the out-of-plane (o.p.) bending vibrations of indole ring, bending vibrations of COO–-group and Amide IV-VI vibrations. The last ones are observed usually within the regions γ_{NH} (Amide V) 735 ± 60 cm^{-1}, $\delta_{C=O}$ (Amide IV) 695 ± 75 cm^{-1} and $\gamma_{C=O}$ (Amide VI) 600 ± 70 cm^{-1}, respectively [37]. Usually the indole o.p. mode about 740 cm^{-1} is characterized by strongest intensity within the discussed IR-spectroscopic region [8, 9, 15, 34–36]. Other characteristic IR-bands of latter structural fragment correlated well with the data for previously studied tryptophan containing peptides [8, 9, 15] and of L-tryptophan [34–36]. The IR-spectroscopic patterns are preliminaryly deconvoluted and curve fitted with a view to determine the band positions and integral absorbances. As reference procedure a second derivative analysis is also applied. The IR-characteristic bands of COO–-fragment are assigned as well by an independent way, studying the IR-characteristics of corresponding protonated forms of the peptides.



A B

Fig. 1. Non-polarized IR (1) and difference IR-LD (2) spectra of *H-Trp-Met-OH*, *H-Met-Trp-OH* (A) and *H-Gly-Trp-OH.2H$_2$O* (B).

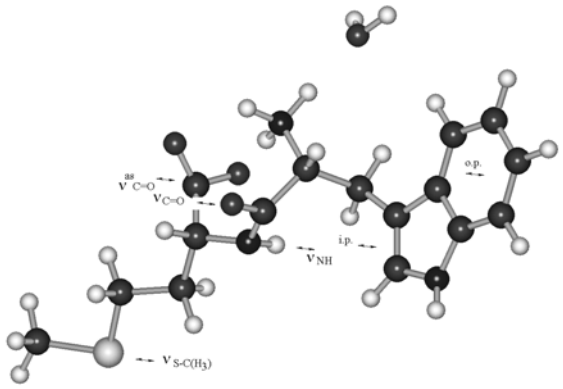
Table 1. IR-characteristic bands of L-tryptophyl-L-methionine (*H-Trp-Met-OH*), L-methionyl-L-tryptophan (*H-Met-Trp-OH*) and glycyl-L-tryptophan dihydrate (*H-Gly-Trp-OH.2H$_2$O*) in solid-state.

Assignment	*H-Trp-Met-OH* ν, cm^{-1}	*H-Met-Trp-OH* ν, cm^{-1}	*H-Gly-Trp-OH.2H$_2$O* ν, cm^{-1}
ν_{NH}	3326	3446	3430
$\nu_{NH(In)}$	3409	3424	3419
$\nu_{OH(H2O)}$	-	-	3280
ν^{as}_{NH3+}, ν^{s}_{NH3+} Sub. maximum	3190	3208	3210
δ_{NH3+}	1675	1685	1689
$\nu_{C=O}$ (Amide I)	1662	1675	1673
δ^{as}_{NH3+}	1623	1643	1617
Indole i.p.	1612, 1469, 1265	1615, 1465, 1265	1610, 1465, 1265
ν^{as}_{COO-}	1581	1615	1563
δ_{NH} (Amide II)	1521	1508	1540
ν^{s}_{COO-}	1396	1406	1395
ν_{C-N}/δ_{NH} (Amide III)	1257	1260	1255
ν_{N-C}	1000	1008	1010
Indole o.p.	738, 424	742, 420	750, 424
$\nu_{S-C(H3)}$	721	723	718
δ_{COO-}	684	661	696
ρ_{COO-}	505	484	468
γ_{NH} (Amide V)	651	665	474
$\delta_{C=O}$ (Amide IV)	580	640	576
$\gamma_{C=O}$ (Amide VI)	526	560	553

The assignment given in Table 1 is experimentally proved by the possibilities of the IR-LD spectroscopy of orientated colloid suspensions stated below. Moreover, for the dipeptides L-tryptophyl-L-methionine (*H-Trp-Met-OH*) and L-methionyl-L-tryptophan (*H-Met-Trp-OH*) crystallographic data are not available.

Similar to other peptide systems [3–15] a significant degree of macro-orientation of suspended particles is obtained [17–19], thus resulting in a reasonable interpretation of the polarized IR-spectra.

In the IR-spectrum *H-Trp-Met-OH* the $\nu_{NH(In)}$ stretching vibration typical for indole ring is low intensive band (Table 1), which can be explained with the participation of the NH_{In} group in intermolecular interactions in solid-state. The intensive band at 1662 cm^{-1} ($\nu_{C=O,}$ Amide I) stretching vibration and the corresponding ν_{NH} one are eliminated in difference IR-LD spectrum (Fig. 1A.2), indicating a co-linear orientation of the transition moments. The last result supposed a *trans*-configuration of the O=C–NH fragment. The low-intensive bands at 1675 cm^{-1} and 1623 cm^{-1} are assigned as δ^{as}_{NH3+} and δ^{s}_{NH3+}, while the intensive band at 1581 cm^{-1} – to ν^{as}_{COO-}. The discussed bands are overlapped with the low-intensive maxima in the 1600–1450 cm^{-1}, typical for in-plane vibrations of indole ring (Table 1). Only the band at 1469 cm^{-1} is well defined. Its elimination leads to a disappearance of the band at 721 cm^{-1}, typical for $\nu_{S-C(H3)}$ of L-methyonyl-side chain [6, 7, 10, 38–40]. This fact supposed a co-linear disposition of both transition moments (Scheme 3). The elimination of the intensive band at 740 cm^{-1} (out-of-plane mode of indole ring) with the band of ν^{as}_{COO-} (1581 cm^{-1}) at equal dichroic ratio also indicates a collinear orientation of the corresponding transition moments, which is realized in the frame of the proposed structure of *H-Trp-Met-OH*, shown in Scheme 3. The intensive band at 1396 cm^{-1} belongs to ν^{s}_{COO-}. The experimentally proposed structure of the dipeptide correlated well with the theoretically approximated model of the system dipeptide/water. A torsion angle of 179.3(6)^{o} of the O=C–NH group indicates a *transoide*-configuration of the fragment (see IR-LD spectroscopic analysis). On the other side the indole o.p. modes are co-linear to ν^{as}_{COO-} closing an angle of 3.2(6)^{o}. The corresponding value of 2.1(2)^{o} between the indole i.p. and $\nu_{S-C(H3)}$ transition moments also correlated well with the predicted structure (Scheme 3).



Scheme 3. Most stable conformer of the *H-Trp-Met-OH* peptide/water system with E_{rel} of 0.2 kJ/mol; Directions of the selected transition moments.

The difference IR-LD spectrum of *H-Met-Trp-OH* (Fig. 1A.2) is characterized by eliminated bands at 1406 cm^{-1} (ν^{s}_{COO-}) and 742 cm^{-1} (o.p. mode of indole ring), thus assuming a collinear orientation of their transition moments. In contrast to *H-Trp-Met-OH*, in this case the NH-stretching region is characterized by pairs of bands at 3446 cm^{-1} and 3424 cm^{-1} (ν_{NH} and $\nu_{NH(In)}$) stretching vibrations. The consequent eliminations of these bands result in a disappearance of the maxima at 1685 cm^{-1} (δ^{as}_{NH3+}) and 1675 cm^{-1} (Amide I) (Figs. 2.2 and 2.3). This result can be observed when the HN–C=O amide fragment possesses *cisoide*-configuration. The band at 723 cm^{-1} ($\nu_{S-C(H3)}$) is eliminated with the bands of ν_{NH}, proposing a co-linearity of these transition moments as well. The predicted geometry of the dipeptide is supported by the theoretical structure with E_{rel} of 0.7 kJ/mol, where a dihedral angle of 8.6(1)° of HN–C=O fragment is obtained. On the other side the transition moments of ν_{NH} and $\nu_{S-C(H3)}$ close an angle of 2.6(2)°, indicating their co-linearity. The calculated angle between the transition moments of $\nu_{NH(In)}$ and Amide I of 5.2(1)°, is in accordance with the obtained elimination of last two bands at different dichroic ratio (Figs. 2.2 and 2.3). In the frame of the optimized electronic structure of *H-Met-Trp-OH* the o.p. mode of indole and ν^{s}_{COO-} close an angle of 7.8(3)°. These data also support the experimentally proposed structure of the dipeptide. An experimental evidence of the *cisoide*-configuration of the amide fragment in this dipeptide follows from the obtained cyclic dipeptide in strongly acidic medium, in contrast to *H-Trp-Met-OH*, where a hydrochloride salt is obtained. Similar results have been observed in the case of other tryptophan-containing dipeptides, where the cyclic product has been characterized spectroscopically [20].

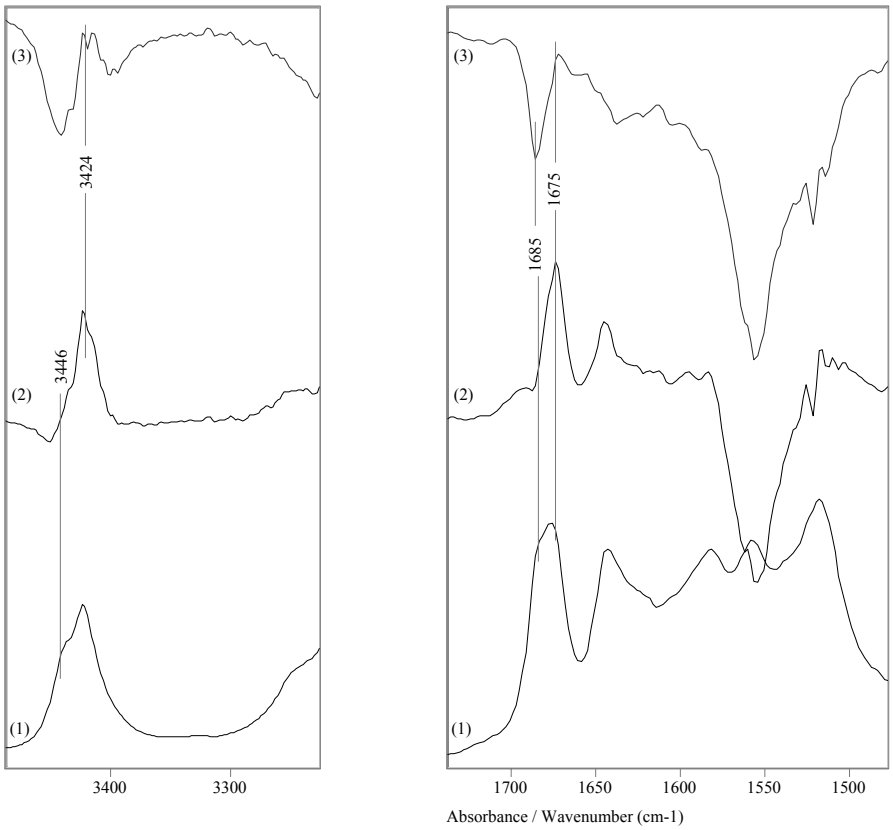
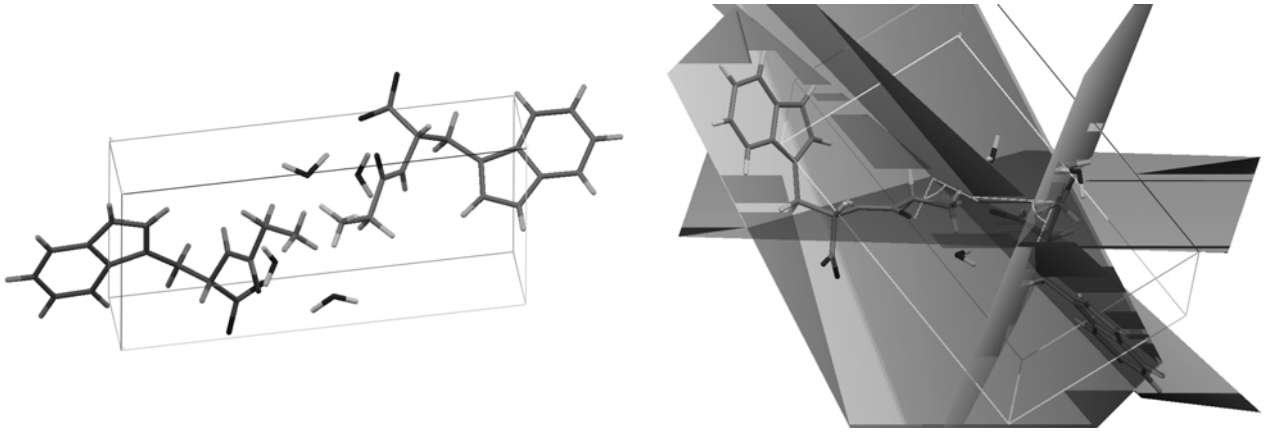


Fig. 2. Non-polarized IR (1) and reduced IR-LD spectra of *H-Met-Trp-OH* after elimination of the bands at 3446 cm^{-1} (2) and 3424 cm^{-1} (3).

The characterization of the dipeptide *H-Gly-Trp-OH.2H₂O* is carried out, comparing the IR-spectroscopic data and the known crystalline structure [20]. *H-Gly-Trp-OH.2H₂O* crystallizes in $P2_1$ space group and the unit cell contains two peptide molecules, perpendicularly orientated (Scheme 4). The amide HN–C=O fragment is flat *trans*-configurated with a dihedral angle of 177.4(9)° [20]. For this reason the elimination of the bands of ν_{NH} and $\nu_{C=O}$ (Amide I) at equal dichroic ratio is observed (Fig. 3A.2). The transition moments of indole o.p. modes of the two molecules close an angle of 64.6(4)°, while those of the amide fragment – 68.6(2)°, respectively (Scheme 4). It is valid for o.p. vibrations

of amide fragment. In all cases the consequent elimination of the bands at 750 cm^{-1} or 553 cm^{-1} leads to disappearance of the maxima at 424 cm^{-1} and 474 cm^{-1}, respectively. In all cases the observation of second peaks of the same symmetry class are observed. As for example the bands at 754 cm^{-1} and 750 cm^{-1} are eliminated at different dichroic ratio (Fig. 3B.2). The phenomenon has been described in a series of papers on the IR-band assignment, by means of the method represented here, describing the systems crystallizing in different space groups and containing non-equivalent molecules in the unit cell [10, 11].

Acknowledgements: *The author wishes to thank Prof. T. Kolev (Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences) for the possibility to use Gaussian 98 program and Prof. T. Spassov (St. Kliment Ohridski Sofia University) for the electron microscopic data.*



Scheme 4. Unit cell of *H-Gly-Trp-OH.2H₂O*.

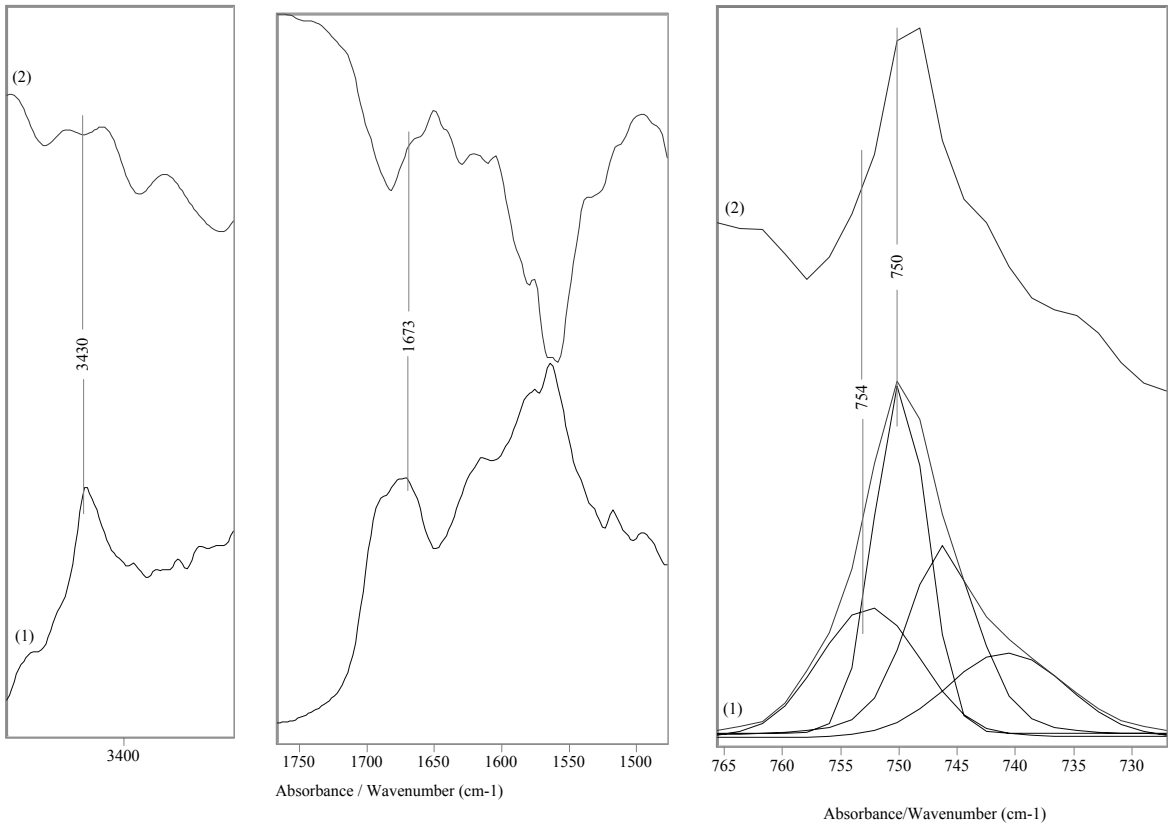


Fig. 3. A: Non-polarized IR (1) and reduced IR-LD (2) spectra of *H-Gly-Trp-OH.2H₂O* after the elimination of the band at 1673 cm^{-1}; B: Curve-fitted ($\chi^2 = 1.2\times10^{-5}$) IR (1) and reduced IR-LD (2) spectra of *H-Gly-Trp-OH.2H₂O* after the elimination of the band at 754 cm^{-1}.

REFERENCES

1. 1. T. Behmoaras, J.-J. Toulmé, C. Hélène, *Nature*, **292**, 858 (1981).
2. 2. A. Sengupta, R. Mahalaksmhi, N. Shamala, P. Balaram, *J. Pept. Res*., **65**, 113 (2005).
3. 3. B. B. Ivanova, M. Mitewa, *J. Coord. Chem.,* **57**, 217 (2004).
4. 4. B. B. Ivanova, M. G. Arnaudov, *Prot. Pept. Lett.,* **13**, 889 (2006).
5. B. B. Ivanova, *J. Mol. Struct.,* **782**, 122 (2006).
6. B. B. Ivanova, M. G. Arnaudov, *Spectrochim. Acta*, **65A**, 56 (2006).
7. B. B. Ivanova, M. G. Arnaudov, St. Todorov, W. S. Sheldrick, H. Mayer-Figge, *Struct. Chem*., **17**, 49 (2006).
8. B. B. Ivanova, *Spectrochim. Acta,* **64A**, 931 (2006).
9. B. B. Ivanova, *Spectrochim. Acta. Part A,* (2007) in press. DOI: http://dx.doi.org/10.1016/ j.saa.2007.09.005.
10. B. B. Ivanova, T. Kolev, S. Y. Zareva, *Biopolymers,* **82**, 587 (2006).
11. B. B. Koleva, T. M. Kolev, M. Spiteller, *Biopolymers,* **83**, 498 (2006).
12. B. B. Ivanova, *J. Coord. Chem*., **58(7)**, 587 (2005).
13. T. Kolev. B. B. Ivanova, S. Y. Zareva, *J. Coord. Chem*., **60**, 109 (2007).
14. B. B. Koleva, Ts. Kolev, S. Y. Zareva, M. Spiteller, *J. Mol. Struct*., **831**, 165 (2007).
15. B. B. Koleva, Ts. Kolev, M. Spiteller, *Inorg. Chim. Acta,* **360**, 2224 (2007).
16. B. B. Ivanova, M. G. Arnaudov, P. R. Bontchev, *Spectrochim. Acta*, **60**, 855 (2004).
17. B. B. Ivanova, D. L. Tsalev, M. G. Arnaudov, *Talanta,* **69**, 822 (2006).
18. B. B. Ivanova, V. D. Simeonov, M. G. Arnaudov, D. L. Tsalev, *Spectrochim. Acta,* **67A**, 66 (2007).
19. B. B. Koleva, T. Kolev, V. Simeonov, T. Spassov, M. Spiteller, *Colloids Surf.* (2007) submitted.
20. T. J. Emge, A. Agrawal, J. P. Dalessio, G. Dukovic, J. A. Inghrim, K. Janjua, M. Macaluso, L. L. Robertson, T. J. Stiglic, Y. Volovik, M. M. Georgiadis, *Acta Crystallogr*., **C56**, e469 (2000).
21. Ts. Kolev, B. Koleva, B. Shivachev, *Inorg. Chim. Acta,* (2007) in press. doi:10.1016/j.ica.2007.10.030
22. E. W. Thulstrup, J. H. Eggers, *Chem. Phys. Lett*., **1**, 690 (1996).
23. J. Spanget-Larsen, *SPIE*, **1575**, 404 (1992).
24. E. H. Korte, P. Lampen, Private communications, 1988.
25. B. Jordanov, R. Nentchovska, B. Schrader, *J. Mol. Struct.,* **297**, 401 (1993).
26. B. Jordanov, B. Schrader, *J. Mol. Struct*., **347**, 389 (1995).
27. M. Belhakem, B. Jordanov, *J. Mol. Striuct*., **218**, 309 (1990).
28. M. Rogojerov, D. Kolev, B. Jordanov, *J. Mol. Striuct*., **349**, 447 (1995).
29. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, Ö. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komáromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, Gaussian, Inc., Pittsburgh, PA (1998).
30. "DALTON, a molecular electronic structure program, Release 2.0 (2005), http://www.kjemi.uio.no/ software/dalton/dalton.html "
31. G. A. Zhurko, D. A. Zhurko, ChemCraft: Tool for Treatment of Chemical Data, Lite version build 08 (2005).
32. D. Toroz, T. Van Mourik, *Molec. Phys*., **105**, 209 (2007).
33. D. Toroz, T. Van Mourik, *Molec. Phys*., **104**, 559 (2006).
34. X. Cao, G. Fischer, *J. Phys. Chem*. A **103**, 9995 (1999).
35. C. Snoek, R. T. Kroemer, M. R. Hockridgea, J. P. Simons, *Phys. Chem. Chem. Phys*., **3**, 1819 (2001).
36. B. C. Dian, A. Longarte, T. S. Zwiera, *J. Chem. Phys*., **118**, 6 (2003).
37. N. Roeges, A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures, J. Wiley, N.Y. (1993).
38. X. Cao, G. Fischer, *J. Phys. Chem*. A, **106**, 41 (2002).
39. D. T. Rosa, J. A. K.Bauer, M. J. Baldwin, *Inorg. Chem*., **40**, 1606 (2001).
40. B. B. Koleva, *Vibr. Spectrosc*., **44**, 30 (2007).

ТВЪРДОТЕЛНА ЛИНЕЙНО-ДИХРОИЧНА ИЧ СПЕКТРОСКОПИЯ НА L-ТРИПТОФАН-СЪДЪРЖАЩИ ДИПЕПТИДИ L-ТРИПТОФИЛ-L-МЕТИОНИН (*H-TRP-MET-OH*), L-МЕТИОНИЛ-L-ТРИПТОФАН (*H-MET-TRP-OH*) И ГЛИЦИЛ-L-ТРИПТОФАН ДИХИДРАТ (*H-GLY-TRP-OH*.2H_2O)

Б. Б. Колева

Софийски университет „Св. Климент Охридски“, Химически факултет, Катедра „Аналитична химия“, бул. „Дж. Баучер“ № 1, 1164 София

Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

Постъпила на 2 януари 2008 г., Преработена на 11 януари 2008 г.

(Резюме)

С помощта на линейно-дихроичния ИЧ-спектрален анализ на ориентирани проби в твърдо състояние като суспензии в нематичен течен кристал бе проведено ИЧ-спектрално и структурно охарактеризиране на L-триптофан-съдържащите дипептиди L-триптофил-L-метионин (*H-Trp-Met-OH*), L-метионил-L-триптофан (*H-Met-Trp-OH*) и глицил-L-триптофан дихидрат (*H-Gly-Trp-OH.2*H_2O). Зависимостта структура–спектрални свойства бе изследвана чрез сравнителен анализ на данните от ИЧ спектроскопия с тези, получени чрез рентгенова дифракция от монокристален образец на *H-Gly-Trp-OH.2*H_2O. В допълнение са представени резултати от квантово-химични пресмятания на *ab initio* и ТФП нива на теория за системите дипептид/H_2O.