

# Conformations of, and NHO hydrogen bond in, piperidine-1-valeric acid and its dihydrate

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Received (in Cambridge, UK) 1st March 1999, Accepted 30th June 1999

Effects of hydration on hydrogen bonding and conformation of the amino acid, piperidine-1-valeric acid (PIPVAL), have been studied by X-rays, FTIR and quantum chemical calculations. PIPVAL forms anhydrous and dihydrate crystals. In PIPVAL·2H<sub>2</sub>O two zwitterionic molecules are linked by a pair of identical N<sup>+</sup>–H···O hydrogen bonds of 2.684(4) Å into a cyclic centrosymmetric dimer. The dimers form a network of hydrogen bonds with water molecules. The conformation of anhydrous PIPVAL was studied by semiempirical and *ab initio* calculations. Two cyclic dimers were derived by the PM3 method (neutral and zwitterionic, with the former being 50 kcal mol<sup>–1</sup> more stable) and only the neutral one at the SAM1 and HF levels. The solid state FTIR spectra of the anhydrous and dihydrate crystals are considerably different. The spectrum of PIPVAL·2H<sub>2</sub>O reflects the N<sup>+</sup>–H···O hydrogen bond determined by X-rays. The broad and intense absorption in the 1600–400 cm<sup>–1</sup> region resulting from the much shorter hydrogen bond N<sup>+</sup>–H···O of about 2.5 Å is observed in the anhydrous acid. This comparison clearly illustrates the specific features of amino acids associating with water, present in all living organisms.

## Introduction

From a structural point of view, amino acids can be considered as bifunctional compounds. It is well established that the neutral form, H<sub>2</sub>N–(CH<sub>2</sub>)<sub>n</sub>CHR–COOH, is the most stable structure for an isolated amino acid molecule,<sup>1–10</sup> that is to say, in the gas phase, however they have a zwitterionic structure, H<sub>3</sub>N<sup>+</sup>–(CH<sub>2</sub>)<sub>n</sub>CHR–COO<sup>–</sup>, in the solid state<sup>11</sup> and in polar media.<sup>12–18</sup> Biological systems are usually associated with aqueous solutions, where solute–solvent interactions significantly influence the energy, structure and vibrations of these molecules.<sup>19,20</sup> In amino-substituted carboxylic acids the N···O distance, their structures and conformations depend on both the number of the N–H···O hydrogen bonds and the number of the CH<sub>2</sub> groups between the nitrogen atom and the COO group.<sup>21–25</sup>

As part of a general study on the structure and conformation of zwitterionic compounds<sup>26</sup> and particularly on the role of hydrogen bonding and the attractive Coulombic interactions between the oppositely charged groups in controlling their structure, we report here our investigation on the structures of piperidine-1-valeric acid (PIPVAL) and its dihydrate (PIPVAL·2H<sub>2</sub>O).

So far theoretical calculations have been used successfully to analyse the relative energies and geometries of the conformers of single molecules of a fairly large number of amino acids. In this paper we extended calculations to two molecules forming dimers.

## Experimental

Piperidine-1-valeric acid dihydrate (PIPVAL·2H<sub>2</sub>O) was prepared from its hydrobromide (for preparation see ref. 27) by adding K<sub>2</sub>CO<sub>3</sub> in a small amount of water. After water evaporation *in vacuo*, the acid was extracted with chloroform. The extract was dried over Na<sub>2</sub>SO<sub>4</sub>, solvent evaporated and the residue was recrystallized from acetonitrile, PIPVAL·2H<sub>2</sub>O, mp 63–65 °C. The anhydrous acid was obtained after storing at 50 °C for 24 hours, PIPVAL, mp 81–83 °C.

X-Ray diffraction analysis was carried out using a KUMA-4 diffractometer equipped with a graphite monochromator, the

**Table 1** Crystal data and structure refinement for C<sub>5</sub>H<sub>10</sub>N(CH<sub>2</sub>)<sub>4</sub>–COOH·2H<sub>2</sub>O

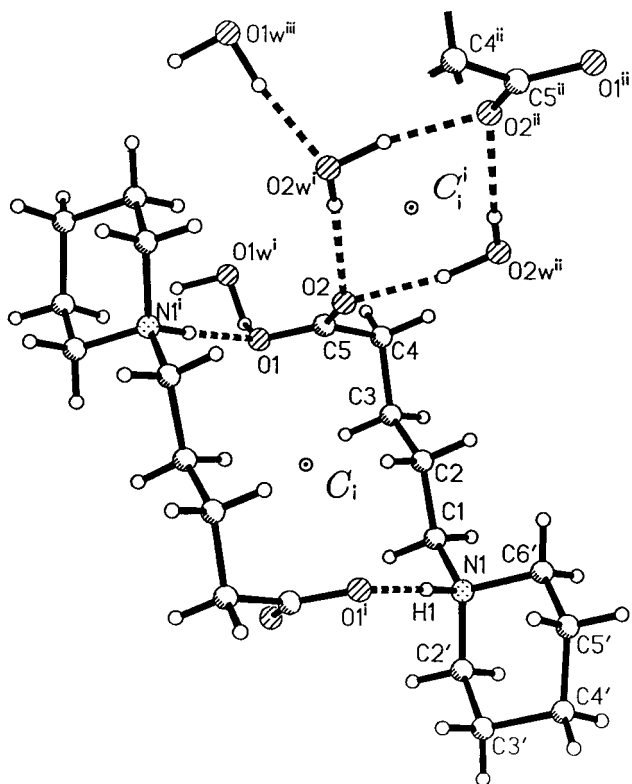
Empirical formula	C <sub>10</sub> H <sub>19</sub> NO <sub>2</sub> ·2H <sub>2</sub> O
Formula weight	221.30
Temperature	293(2) K
Crystal system	orthorhombic
Space group	<i>Pbca</i>
Unit cell dimensions	<i>a</i> = 16.008(3) Å <i>b</i> = 15.932(3) Å <i>c</i> = 9.647(2) Å
Volume	2460.4(8) Å <sup>3</sup>
<i>Z</i>	8
Absorption coefficient	0.749 mm <sup>–1</sup>
Reflections collected	1865
Independent reflections	1864 [ <i>R</i> (int) = 0.0027]
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.100
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> = 0.0612, <i>wR</i> = 0.1973

ω – 2θ scan mode was applied. The structure was solved by direct methods<sup>28</sup> and refined with SHELXL-93.<sup>29</sup> The crystal data and details concerning data collection and structure refinement are given in Table 1. Fig. 1 shows a structural fragment of the dimer and atom numbering.<sup>†</sup>

The FTIR spectra were measured in Nujol and Fluorolube at 2 cm<sup>–1</sup> resolution using a Bruker IFS 113v spectrometer, which was evacuated to avoid water and CO<sub>2</sub> absorptions. Each spectrum consists of 250 scans at 31 °C.

Structures and energies were calculated by the PM3<sup>30</sup> and SAM1<sup>31</sup> semiempirical methods, as implemented in the AMPAC program package.<sup>32</sup> In all cases, the PRECISE keyword was used and full geometry optimization was carried out without any symmetry restriction. The X-ray geometry without water molecules was used as an input file. The *ab initio* calculations were performed with the GAUSSIAN94 program package.<sup>33</sup> The *ab initio* Hartree–Fock (HF) level of theory was employed with the 6-31G(d,p) basis set. Both PM3 geometries were used as an input file.

<sup>†</sup> CCDC reference number 188/173. See <http://www.rsc.org/suppdata/p2/1999/1967> for crystallographic files in .cif format.

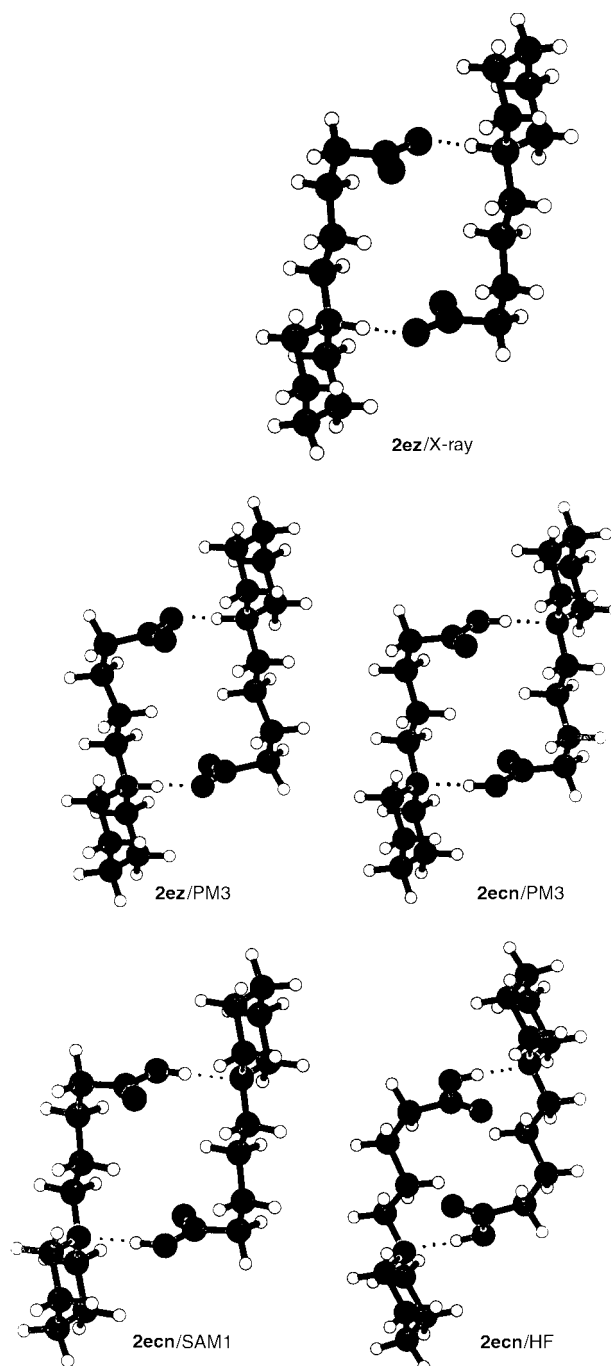


**Fig. 1** Structural fragment of piperidine-1-valeric acid dihydrate, PIPVAL·2H<sub>2</sub>O, showing the centrosymmetric dimer of zwitterions formed by a pair of NH...O hydrogen bonds, selected hydrogen-bonded water molecules, and a fragment of a zwitterion hydrogen-bonded with the dimer *via* two water molecules. The centres of symmetry at 0.5 0.5 0.5 and 0.5 0.5 are indicated by centred circles and denoted by C<sub>i</sub><sup>I</sup> and C<sub>i</sub><sup>II</sup>, respectively. The symmetry codes are: (I) 1 - x, 1 - y, 1 - z, and (II) 1 - x, -y, 1 - z.

## Results and discussion

### X-Ray structure analysis

Each PIPVAL molecule is in the zwitterionic form typical for most amino acids in the solid state. The independent molecules are linked by two identical N(1)<sup>+</sup>H...O(1) = 2.684(4) Å hydrogen bonds to form hydrogen bonded cyclic dimers (Fig. 1). The adjacent dimers are bridged by water molecules. Two such units are further linked by a pair of centre-of-symmetry related water molecules O(2w<sup>I</sup>) and O(2w<sup>II</sup>), each forming two hydrogen bonds to the carboxy oxygen atoms O(2) and O(2<sup>II</sup>) related by the same symmetry centre C<sub>i</sub><sup>I</sup> (see Fig. 1). Each oxygen atom of the carboxylate group is involved in two hydrogen bonds. The bond length, valency angles and selected torsion angles are listed in Tables 2 and 3, respectively. Structures most appropriate for comparison with PIPVAL are 3-(*N*-pyrrolidiny)propanoic acid hemihydrate,<sup>24</sup> *N,N*-diethyl-β-alanine,<sup>34</sup> 1,4-piperazine-γ,γ'-dibutyric acid<sup>35</sup> and ω-phthalimidovaleric acid.<sup>25</sup> Whereas the first three acids are zwitterionic and form chains *via* N<sup>+</sup>-H...O hydrogen bonds, the last acid is not zwitterionic and generates carboxylic acid dimers, a familiar motif observed for such functional groups. In PIPVAL·2H<sub>2</sub>O the N<sup>+</sup>-H...O(1) hydrogen bond is longer than that in 3-(*N*-pyrrolidiny)propanoic acid, *N,N*-diethyl-β-alanine and 1,4-piperazine-γ,γ'-dibutyric acid, because the O(1) atom accepts two protons, which caused the observed elongation.<sup>36</sup> The geometry of the COO group in PIPVAL slightly differs from the mean values of amino acids:<sup>11</sup> the C(5)-O(2) bond is longer by *ca.* 0.02 Å and the O(2)-C(5)-O(1) angle is smaller by *ca.* 2°. This may be due to different hydrogen bond lengths: the O(2) atom is engaged in longer hydrogen bonds, of 2.791(5) and 2.864(5) Å, than the O(1) atom, 2.684(4) and 2.857(4) Å.



**Fig. 2** Structures of piperidine-1-valeric acid dimers as determined by X-ray and calculated by PM3, SAM1 and HF level of theory.

### PM3, SAM1 and HF calculations

As mentioned in the Introduction, the zwitterionic form of amino acids does not exist in the gas phase. *N,N*-dimethylglycine was analysed by high level *ab initio* calculations and five neutral conformers, one global and four local minima, were found. In the case of PIPVAL, both PM3 and B3LYP methods predict three stable conformers, one folded with an intramolecular N...HO hydrogen bond (**1ft**) and two extended (**1ec** and **1et**) without hydrogen bonds.<sup>27</sup> In this paper we carried out the PM3, SAM1 and HF calculations for cyclic dimers of anhydrous PIPVAL. Starting from the X-ray geometry without water molecules, two stable conformers, neutral and zwitterionic, were derived in the case of the PM3 calculations and only one neutral at the SAM1 and HF level (Fig. 2). The conformer formed by the molecular form (**2ecn**) is *ca.* 50 kcal mol<sup>-1</sup> more stable than that formed by zwitterions (**2ecz**). The

**Table 2** Bond lengths (Å) and angles (°) for piperidine-1-valeric acid dimer

	[C <sub>5</sub> H <sub>10</sub> N(CH <sub>2</sub> ) <sub>4</sub> <sup>+</sup> COOH·2H <sub>2</sub> O] <sub>2</sub>		[C <sub>5</sub> H <sub>10</sub> N(CH <sub>2</sub> ) <sub>4</sub> COOH] <sub>2</sub>		
	X-ray		HF/6-31G(d,p)	PM3	SAM1
	zwitterion <b>2ez</b> <sup>a</sup>		neutral <b>2ecn</b>	zwitterion <b>2ez</b>	neutral <b>2ecn</b>
O(1)–C(5)	1.263(5)		1.3173	1.2797	1.3422
O(2)–C(5)	1.241(5)		1.9142	1.2499	1.2223
C(5)–C(4)	1.517(6)		1.5096	1.5256	1.5119
C(1)–N(1)	1.486(5)		1.4634	1.5191	1.4974
C(1)–C(2)	1.522(6)		1.5285	1.5251	1.5259
C(2)–C(3)	1.520(6)		1.5315	1.5205	1.5201
C(3)–C(4)	1.518(6)		1.5358	1.5192	1.5206
N(1)–C(6')	1.503(5)		1.4658	1.5199	1.4975
N(1)–C(2')	1.505(5)		1.4626	1.5200	1.4980
N(1)–H(1)	1.05(4)		1.8935	1.0817	1.8083
O(1)–H(1)	1.624		0.9693	1.6353	0.9781
C(2')–C(3')	1.503(7)		1.5263	1.5211	1.5218
C(3')–C(4')	1.517(7)		1.5273	1.5210	1.5204
C(4')–C(5')	1.528(7)		1.5274	1.5206	1.5201
C(5')–C(6')	1.511(6)		1.5257	1.5230	1.5241
N(1)···O(1)	2.684(4)		2.8627	2.7165	2.7821
O(1)···O(1w <sup>i</sup> )	2.857(4)				
O(1w <sup>iii</sup> )···O(2w <sup>i</sup> )	2.841(4)				
O(2)···O(2w <sup>i</sup> )	2.864(5)				
O(2)···O(2w <sup>iii</sup> )	2.791(5)				
O(2)–C(5)–O(1)	123.7(4)	123.35		117.45	117.21
O(2)–C(5)–C(4)	120.6(4)	124.27		122.34	126.79
O(1)–C(5)–C(4)	115.8(3)	112.38		120.20	115.99
N(1)–C(1)–C(2)	113.1(3)	114.61		111.67	111.28
C(3)–C(2)–C(1)	111.5(3)	111.23		110.37	110.58
C(4)–C(3)–C(2)	112.2(3)	113.34		111.69	112.36
C(5)–C(4)–C(3)	112.5(3)	112.71		111.87	112.79
C(1)–N(1)–C(6')	113.0(3)	109.86		110.39	111.41
C(1)–N(1)–C(2')	111.8(3)	112.72		110.38	111.79
C(6')–N(1)–C(2')	109.2(3)	111.05		109.70	111.18
C(3')–C(2')–N(1)	110.7(3)	111.61		110.53	110.46
C(2')–C(3')–C(4')	111.8(4)	111.21		110.47	110.57
C(3')–C(4')–C(5')	110.1(3)	109.72		110.67	110.45
C(6')–C(5')–C(4')	111.9(4)	111.24		111.48	111.38
N(1)–C(6')–C(5')	110.5(3)	111.86		110.46	110.57
N(1)–H(1)–O(1)	171.1	178.78		177.87	173.35
					168.05

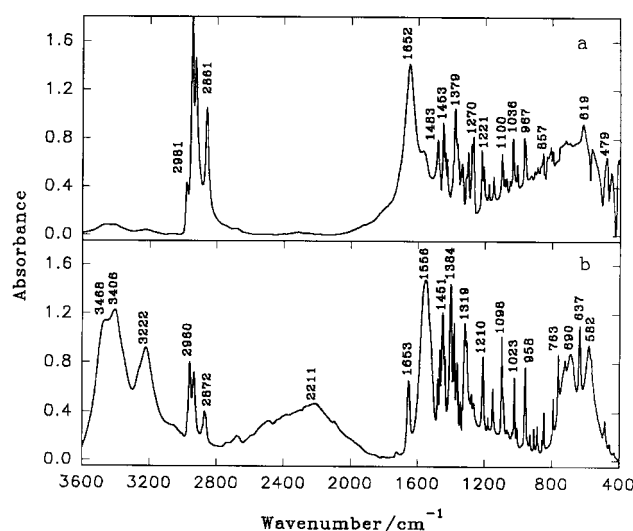
<sup>a</sup> For abbreviations see Table 4.

formation of a cyclic dimer by the neutral molecules, **2ecn**, lowers their energy by *ca.* 6.7 kcal mol<sup>−1</sup>. The calculated molecular energies, dipole moments and selected geometric parameters are summarised in Table 4. The calculated N···O distance is longer than that in the crystal. This is typical for semiempirical calculations, which predict longer hydrogen bonds. The calculated geometrical parameters along with the X-ray results for the zwitterion are listed in Table 2 and their agreement is satisfactory.

As Fig. 2 shows, the optimised conformations are very similar to that determined by X-rays and are practically independent of the position of the H-bonded proton. In the zwitterionic conformers a significant amount of the positive charge on the nitrogen atom is delocalized to the adjacent carbon atoms. This causes the observed differences in the N–C bonds and C–N–C angles between the two forms (see Table 2).

### FTIR spectra

Fig. 3 compares the powder spectra of the PIPVAL and PIPVAL·2H<sub>2</sub>O. The most striking features of the PIPVAL·2H<sub>2</sub>O spectrum are two broad bands at *ca.* 3406 and 3222 cm<sup>−1</sup> due to water molecules, a broad band with a maximum at 2211 cm<sup>−1</sup> corresponding to hydrogen bonded NH, and an intense band at 1556 cm<sup>−1</sup> due to the ν<sub>as</sub>COO mode. The frequency of the ν(NH···O) band is typical for hydrogen bonds with an N···O distance between 2.6 and 2.7 Å. The spectrum of the

**Fig. 3** FTIR spectra in Nujol and Fluorolube of (a) PIPVAL and (b) PIPVAL·2H<sub>2</sub>O.

PIPVAL strongly differs from that of PIPVAL·2H<sub>2</sub>O: the broad absorption from the range of 2700–1900 cm<sup>−1</sup> moves to the 1800–400 cm<sup>−1</sup> region and its intensity is typical for a short-strong hydrogen bond (SSHB) with the N···O distance of *ca.* 2.5 Å. The intense band at *ca.* 1652 cm<sup>−1</sup> is typical for the

**Table 3** Selected torsion angles (°) in piperidine-1-valeric acid dimer and its dihydrate

	$[\text{C}_5\text{H}_{10}\text{N}(\text{CH}_2)_4\text{COOH}\cdot 2\text{H}_2\text{O}]_2$	$[\text{C}_5\text{H}_{10}\text{N}(\text{CH}_2)_4\text{COOH}]_2$			
	X-ray	HF/6-31G(d,p)	PM3	SAM1	
	zwitterion <b>2ez</b> <sup>a</sup>	neutral <b>2ecn</b>	zwitterion <b>2ez</b>	neutral <b>2ecn</b>	neutral <b>2ecn</b>
valeric acid chain					
N(1)–C(1)–C(2)–C(3)	–175.9(3)	–174.25	–171.50	176.43	175.45
C(1)–C(2)–C(3)–C(4)	–176.9(3)	179.52	–178.93	–173.42	173.66
O(2)–C(5)–C(4)–C(3)	110.8(4)	114.27	–120.45	118.45	–115.96
O(1)–C(5)–C(4)–C(3)	–68.8(4)	–65.44	59.45	–62.79	65.64
C(2)–C(3)–C(4)–C(5)	–62.9(5)	–66.42	65.81	–63.78	64.40
C(2)–C(1)–N(1)–C(6')	–66.1(4)	–66.78	63.28	–63.48	59.24
C(2)–C(1)–N(1)–C(2')	170.3(3)	168.80	–175.26	171.44	–171.16
C(1)–N(1)–C(2')–C(3')	–174.1(3)	178.0	–178.86	176.19	–176.40
C(1)–N(1)–C(6')–C(5')	175.3(3)	–176.63	–179.79	–177.21	176.24
piperidine ring					
C(6')–N(1)–C(2')–C(3')	60.2(4)	–58.24	59.27	–58.61	55.16
N(1)–C(2')–C(3')–C(4')	–57.8(5)	56.41	56.42	–55.60	–53.72
C(2')–C(3')–C(4')–C(5')	53.2(5)	–53.08	–55.28	54.95	57.53
C(3')–C(4')–C(5')–C(6')	–52.8(5)	52.72	–55.26	54.95	–50.75
C(2')–N(1)–C(6')–C(5')	–59.4(4)	57.99	–59.93	57.37	–54.26
C(4')–C(5')–C(6')–N(1)	56.8(4)	–55.74	56.42	–55.60	51.96

<sup>a</sup> For abbreviations see Table 4.**Table 4** Heats of formation (kcal mol<sup>–1</sup>), dipole moments (Debye) and selected geometrical parameters for various conformations of piperidine-1-valeric acid and its dimer calculated by the PM3, SAM1 and HF methods<sup>a</sup>

	Method	$\Delta H$	$E$	$E_{\text{rel}}$	$\mu$	N⋯O	N⋯H	O⋯H	∠NHO	∠O=C–OH
monomer										
<b>1ft</b> * [27]	PM3	–122.1		1.2	6.23	2.785	1.818	0.971	173.9	–177.5
<b>1ft</b> [27]	B3LYP		–597.733918	0	6.45	2.706	1.706	1.008	171.4	–182.7
<b>1ec</b> [27]	PM3	–123.3		0	1.26	7.138	—	0.952	—	–0.1
<b>1ec</b> [27]	B3LYP		–597.753427	0.3	1.23	7.425	—	—	—	–0.08
<b>1et</b> [27]	PM3	–121.3		2	4.05	6.891	—	0.949	—	–178.9
<b>1et</b> [27]	B3LYP		–597.744179	6.1	3.52	7.488	—	—	—	–179.9
dimer										
<b>2ecn</b>	HF/6-31G**		–1187.973786		0.001	2.863	1.894	0.963	178.8	–1.0
<b>2ecn</b>	PM3	–253.3	50.1	0.003	2.782	1.635	0.978	177.9	–5.1	
<b>2ez</b>	PM3	–203.2		0	0.018	2.716	1.082	1.808	173.3	—
<b>2ecn</b>	SAM1	–218.0		0.133	2.851	1.869	0.996	168.4	4.3	
<b>2ez</b>	X-ray**					2.684(4)	1.06(4)	1.624	171.1	—

<sup>a</sup> Abbreviations: **e** — extended (*trans*-zig-zag) and **f** — folded (*gauche*) conformation on the N(CH<sub>2</sub>)<sub>4</sub>COOH moiety, respectively; **c** — *cis* and **t** — *trans* arrangement of the C=O/OH bonds, respectively; **1** — monomer and **2** — dimer, **n** — neutral, **z** — zwitterion; \*\* dihydrate.

$\nu_{\text{as}}\text{COO}^-$  mode of the carboxylate group engaged in a strong hydrogen bond. All these differences in absorption are consistent with the expected structural differences between PIPVAL and PIPVAL·2H<sub>2</sub>O, and agree well with the general rule that bonds involving single acceptors (N–H⋯O) are shorter than those with multiple acceptors (N–H⋯O(C)⋯HOH).<sup>36</sup>

## Conclusions

PIPVAL·2H<sub>2</sub>O forms cyclic dimers bonded by two N<sup>+</sup>–H⋯O<sup>–</sup> hydrogen bonds. The dimers are further connected by water molecules. For PIPVAL the PM3 method predicts two stable cyclic dimers, neutral and zwitterionic, while the SAM1 and HF reproduce only the neutral structures. According to the PM3 data the dimer formed by neutral molecules is 50.1 kcal mol<sup>–1</sup> more stable than that formed by zwitterionic acid. The conformations optimized by PM3, SAM1 and HF calculations are very similar to the X-ray one. The proton transfer from the COOH group to the nitrogen atom has a negligible effect on the dimer conformation. The broad and intense absorption in the 1600–400 cm<sup>–1</sup> region in the FTIR spectrum

of anhydrous PIPVAL indicates that an SSHB with N⋯O distance of *ca.* 2.5 Å is formed. In PIPVAL·2H<sub>2</sub>O both oxygen atoms of the carboxylate group are engaged in two hydrogen bonds and, in consequence, the NHO hydrogen bond is weaker and longer than that in PIPVAL. Dimerization plays an important role in the relative stability of amino acid conformers and further investigations are needed.

## Acknowledgements

This work was partly supported by the Polish State Committee of Scientific Research (KBN), grant 3T O9A 09414. The *ab initio* calculations were done at the Poznań Supercomputing and Network Centre.

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