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Combined matrix isolation IR spectroscopic and ab initio quantum chemical study of the molecular structure of aminomethylphosphinic acid

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Abstract

The molecular structure of 1-methylaminophosphinic acid (AMPA) was investigated with the matrix isolation IR spectroscopy and ab initio calculations performed with RHF, MP2, MP3, MP4(DQ), MP4(SDQ) and MP4(SDTQ) methods. Three pseudopotential basis sets designed as CEP-31G were used in the calculations: Basis Set I-CEP-31G with the d-functions on phosphorus; Basis Set II-CEP-31G with the d-functions on all heavy atoms; Basis Set III-CEP-31G with the d-functions on all heavy atoms and p-functions on hydrogens. Four stable molecular and four stable zwitterion conformers of aminophosphinic acid were found via ab initio calculations. According to the calculations, molecular conformers are always more stable than the zwitterion conformers, irrespective of the basis set size and level of theory. This result is in good agreement with matrix IR spectrum of the AMPA. The presence of the bands of OH stretching and NH_2 bending vibrations and the absence of the bands of POO^- and NH_3^+ vibrations are the evidence of molecular structure of AMPA in the isolated state. An increased number of vibrational bands is found in the IR spectrum. It is explained by the high conformation lability of AMPA molecules which is related to very low barrier of rotation about C–P bond. The IR spectrum is actually determined by multiple sites of AMPA molecule packed in the Ar crystal, which considerably increases the number of bands in the IR spectrum.

Keywords: Aminomethylphosphinic acid; Matrix isolation IR spectroscopy; Ab initio calculations

1. Introduction

Aminophosphinic acids are structurally similar to aminocarboxylic acids. The interest in the structures of aminophosphinic and aminophosphonic acids is because of the biological role of their derivatives. Phosphino- and phosphonopeptides have been described as protease inhibitors [1–3]. Aminoalkylphosphinic acids are inhibitors of the angiotensine converting enzyme [4], HIV protease [5], glutamine synthease [6]. It is known that intermolecular interactions considerably influence the structure of aminocarboxylic acids. They assume the zwitterion form in the condensed state (crystals, solutions in polar solvents) [7–11], while isolated amino acids are neutral [12–18]. Recent experimental [15–22] and

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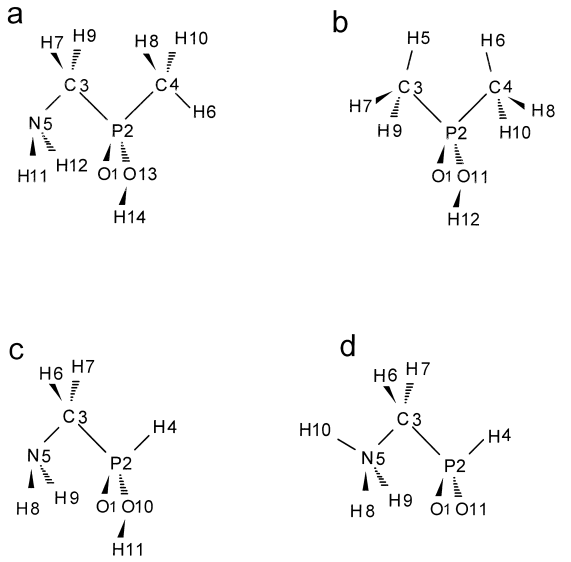

Fig. 1. Labelling convention used in tables to refer to the geometrical parameters of (a) aminomethylphosphinic acid, molecular form; (b) dimethylphosphinic acid; (c) aminophosphinic acid, molecular form; (d) aminophosphinic acid, zwitterion form.

theoretical [23–28] studies show that isolated amino acid molecules exist as various rotamers whose structural and spectral characteristics as well as relative stability are determined. The data for neutral aminocarboxylic acids are of special importance since these forms precisely correspond to the amino acid fragments in peptide chains. The replacing of carbon atom by phosphorous in peptide chains significantly changes the biological activity of the peptides. This determines the great interest in the investigations of molecular structure of aminomethylphosphinic acid which are their main component. According to the X-ray investigations in the solid state the phospho analogues of amino acids are in the zwitterion from [29]. This is supported by the IR spectroscopic results on 1-aminoalkylphosphinic acid crystals [30]. The structure of isolated aminoalkylphosphinic and phosphonic acids however, is not clear yet. Their thermal instability hampers gas-phase studies. The present study is aimed to fill this gap and to derive information about the molecular structure of isolated aminophosphinic acids.

Recently the IR spectroscopic method was applied to study the molecular structure of some amino acids isolated in noble gas matrices [14,19–22]. In this work we employ this experimental technique along with theoretical ab initio calculations to solve the problem of molecular structure of 1-aminomethylphosphinic acid, the phospho analogue of the simplest amino acid – glycine.

2. Experimental

The cryostat used for matrix isolation IR spectroscopy is described in detail elsewhere [31]. The updated SPECORD IR 75 grating spectrometer (Carl Zeiss, Jena) was sealed and blown through with dry nitrogen during the experiment to exclude the influence of atmospheric H_2O and CO_2 vapour. The samples were prepared by simultaneous deposition of the substance and the matrix gas onto a cooled optic CsI substrate. The substrate temperature was maintained at 17 K during matrix deposition to obtain samples with optimal scattering. To prevent matrix overheating in the spectrometer beam the samples were cooled down to 12 K when the spectra were recorded. The matrix gas was 99.99% Ar.

The measurements of IR spectra were carried out for 1-aminomethylphosphinic acid (AMPA) (Fig. 1a) and for a model compound – dimethylphosphinic acid (DMPA) (Fig. 1b). The substances were evaporated from the Knudsen cell at 53°C (DMPA) and 254°C (AMPA). The molar ratio compound : Ar in the samples was controlled by means of a low temperature quartz microbalance and was 1 : 1000 and 1 : 400 for DMPA and AMPA, respectively. The accuracy of the microbalance was 3%. The relatively higher AMPA concentration was taken to provide a more reliable record of low-intensity bands in the spectrum. Spectra were registered in the range 4000–400 cm^{-1} with a resolution of 3 cm^{-1} in the range 4000–2500 cm^{-1} and 1 cm^{-1} in the range 2500–400 cm^{-1}.

3. Calculations

Ab initio quantum chemical calculations were carried out with the GAUSSIAN 90 program package [32] to optimize geometries of the zwitterion and molecular conformers of aminophosphinic asid (Figs. 1c,d). The calculations were carried out with pseudopotential basis sets designed as CEP-31G [33]: Basis Set I-CEP-31G with the d-functions on

Table 1
Internal coordinates of the dimethylphosphinic acid (DMPA) and aminomethylphosphinic acid (AMPA)[a]

DMPA	AMPA
Stretching modes	
S1 = Δr P2–O1	S1 = Δr P2–O1
S2 = Δr P2–C3	S2 = Δr P2–C3
S3 = Δr P2–C4	S3 = Δr P2–C4
S4 = Δr C3–H5	S4 = Δr C3–N5
S5 = Δr C4–H6	S5 = Δr C4–H6
S6 = Δr C3–H7	S6 = Δr C3–H7
S7 = Δr C4–H8	S7 = Δr C4–H8
S8 = Δr C3–H9	S8 = Δr C3–H9
S9 = Δr C4–H10	S9 = Δr C4–H10
S10 = Δr P2–O11	S10 = Δr N5–H11
S11 = Δr O11–H12	S11 = Δr N5–H12
	S12 = Δr P2–O13
	S13 = Δr O13–H14
Bending modes	
S12 = $\Delta\beta$ O1–P2–C3	S14 = $\Delta\beta$ O1–P2–C3
S13 = $\Delta\beta$ O1–P2–C4	S15 = $\Delta\beta$ O1–P2–C4
S14 = $\Delta\beta$ P2–C3–H5	S16 = $\Delta\beta$ P2–C3–H5
S15 = $\Delta\beta$ P2–C4–H6	S17 = $\Delta\beta$ P2–C4–H6
S16 = $\Delta\beta$ P2–C3–H7	S18 = $\Delta\beta$ P2–C3–H7
S17 = $\Delta\beta$ P2–C4–H8	S19 = $\Delta\beta$ P2–C4–H8
S18 = $\Delta\beta$ P2–C3–H9	S20 = $\Delta\beta$ P2–C3–H9
S19 = $\Delta\beta$ P2–C4–H10	S21 = $\Delta\beta$ P2–C4–H10
S20 = $\Delta\beta$ H5–C3–H7	S22 = $\Delta\beta$ N5–C3–H7
S21 = $\Delta\beta$ H6–C4–H8	S23 = $\Delta\beta$ H6–C4–H8
S22 = $\Delta\beta$ H5–C3–H9	S24 = $\Delta\beta$ N5–C3–H9
S23 = $\Delta\beta$ H6–C4–H10	S25 = $\Delta\beta$ H6–C4–H10
S24 = $\Delta\beta$ H7–C3–H9	S26 = $\Delta\beta$ H7–C3–H9
S25 = $\Delta\beta$ H8–C4–H10	S27 = $\Delta\beta$ H8–C4–H10
S26 = $\Delta\beta$ C3–P2–C4	S28 = $\Delta\beta$ C3–P2–C4
S27 = $\Delta\beta$ O1–P2–O11	S29 = $\Delta\beta$ C3–N5–H11
S28 = $\Delta\beta$ O11–P2–C3	S30 = $\Delta\beta$ C3–N5–H12
S29 = $\Delta\beta$ O11–P2–C4	S31 = $\Delta\beta$ H11–N5–H12
S30 = $\Delta\beta$ P2–O11–H12	S32 = $\Delta\beta$ O1–P2–O13
	S33 = $\Delta\beta$ O13–P2–C3
	S34 = $\Delta\beta$ O13–P2–C4
	S35 = $\Delta\beta$ P2–O13–H14
Torsion modes	
S31 = $\Delta\tau$ O1–P2–C3–H9	S36 = $\Delta\tau$ O1–P2–C3–N5
S32 = $\Delta\tau$ O1–P2–C4–H10	S37 = $\Delta\tau$ O1–P2–C4–H6
S33 = $\Delta\tau$ O1–P2–O11–H12	S38 = $\Delta\tau$ O1–P2–O13–H14
	S39 = $\Delta\tau$ P2–C3–N5–H11

[a] is the angle between bonds, τ is the torsion angle.

phosphorus; Basis Set II-CEP-31G with the d-functions on all heavy atoms; Basis set III-CEP-31G with the d-functions on all heavy atoms and p-functions on hydrogens. The geometries of all zwitterion and molecular conformers were fully optimized at the HF and MP2 levels with Basis Set II. Additionally the energies of most stable conformers were calculated at the MP3, MP4(DQ), MP4(SDQ) and MP4(SDTQ) levels of theory.

The semiempirical AM1 method [34] was used to calculate the potential energy surface of AMPA employing the MOPAC6 program package [35]. Point-by-point optimisation was performed for two torsional angles N–C–P=O and O=P–O–H corresponding to the rotation about the single bonds C–P and P–O with a 10 step within 0°–360° for each torsion angle.

Normal coordinate analysis with the spectroscopic program package [36] was performed for the most stable molecular conformer of AMPA as well for the model compound DMPA to interpret their matrix IR spectra. The DMPA molecule has C_s symmetry. Its normal vibrations were grouped into 17 vibrations belonging to A' species (symmetrical) and 13 vibrations belonging to A'' species (asymmetrical). The AMPA molecule has C_1 symmetry. All vibrations of AMPA and DMPA are IR active. The alterations of the bond lengths, the bond angles and the torsion angles were used as internal vibrational coordinates. They are listed in Table 1. The total number of coordinates for the molecules is larger than the number of degrees of freedom, owing to appearance of the redundant coordinates, which were excluded as it was described in Ref. [36].

4. Results and discussion

4.1. Relative energies and structure of conformers

The AMPA molecules are structurally flexible because of possible internal rotation about single bonds. For glycine, the carbonic analogue of AMPA, numerous sophisticated non-empirical calculations [23–28] predict a great number of conformers, three of them were observed experimentally more recently [20,21]. Since sets of conformers may be expected both for molecular and zwitterion forms of AMPA, our first step was to find them using quantum chemical calculations.

Stable conformers were searched for the molecular (Fig. 1c) and zwitterion (Fig. 1d) forms of aminophosphinic acid. The geometries of starting structures

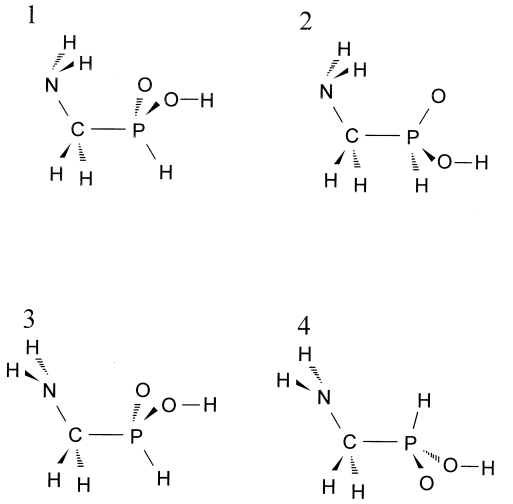

Fig. 2. Calculated structure of molecular (neutral) conformers of aminophosphinic acid.

formed due to rotations about the single P–C and C–N bonds were optimized at the HF and MP2 levels with Bases Set II. At both levels four minima of molecular form (Fig. 2) and four minima of zwitterion form (Fig. 3) were found. The predicted geometry parameters of the molecular and zwitterion conformers are given in Tables 2 and 3, respectively and the relative energies of the conformers are given in Table 4.

Molecular conformer IV with *trans* position of the amino protons with respect to phosphorous atom is predicted to be the most stable. Next in stability is conformer I with weak intramolecular H-bonds N–H···O. The energy difference between the conformers is 0.81 kcal/mol at the HF level and 0.58 kcal/mol at the MP2 level. The small energy difference is an important feature of molecular conformers, which permits us to expect the presence of low energy conformers in the isolated state (in the gas phase or an inert matrix).

It is particularly important to find out which form 7– molecular or zwitterion – of the aminophosphinic acid exists in the isolated state. The energy difference

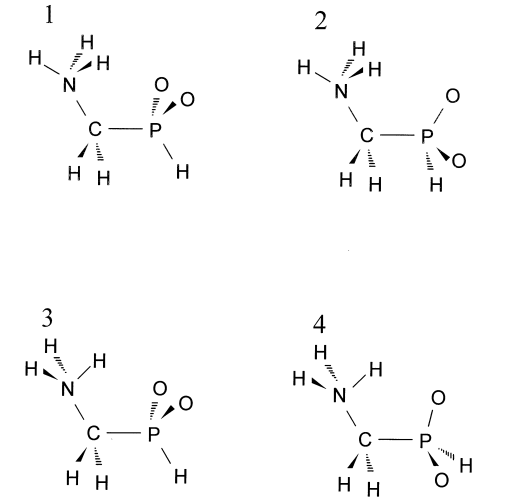

Fig. 3. Calculated structure of zwitterion conformers of aminophosphinic acid.

Table 2
Equilibrium geometries of molecular conformers of aminophosphinic asid (MP2/Basis set II)[a]

Parameter[b]	Conformer			
	I	II	III	IV
P2–H4	1.4125	1.4142	1.4073	1.4078
C3–P2	1.8382	1.8396	1.8356	1.8299
C3–N5	1.4620	1.4630	1.4673	1.4648
P2–O10	1.6223	1.6228	1.6138	1.6241
P2–O1	1.4823	1.4804	1.4812	1.4818
C3–H6	1.0899	1.0893	1.0943	1.0894
C3–H8	1.0896	1.0883	1.0888	1.0937
N5–H8	1.0064	1.0053	1.0058	1.0057
N5–H9	1.0059	1.0058	1.0061	1.0059
O10–H11	0.9546	0.9546	0.9554	0.9545
C3–P2–H4	105.69	104.20	106.28	104.58
N5–C3–P2	114.00	115.29	106.83	109.56
C3–P2–O10	102.61	102.65	103.10	102.39
C3–P2–O1	116.23	117.72	112.50	116.66
P2–C3–H6	107.19	107.04	108.84	106.20
P2–C3–H6	108.64	107.34	108.26	107.79
C3–N5–H8	110.50	111.30	110.77	110.40
C3–N5–H9	110.68	112.47	109.70	110.61
P2–O10–H11	110.62	110.61	111.31	110.17
N5–C3–P2–H4	181.26	−49.20	186.60	−50.96
H6–C3–P2–H4	59.99	73.62	62.07	67.15
H7–C3–P2–H4	−56.00	171.55	−55.77	177.48
H8–N5–C3–P2	124.05	113.85	173.52	169.34
H9–N5–C3–P2	116.84	124.60	67.67	71.65
H11–O10–P2–O4	18.63	16.69	50.14	13.90
H4–P2–O10	103.14	101.99	99.10	102.99
H4–P2–O1	114.48	114.58	116.39	115.28
O10–P2–O1	113.10	113.79	115.98	113.24
H6–C3–H7	107.60	107.20	108.57	107.85
H8–N5–H9	107.62	108.16	107.74	107.62

[a] Atom numbers are given on Fig. 1c. The conformers are depicted in Fig. 2.
[b] Bond lengths are in Å and bond angles in degrees.

Table 3
Equilibrium geometries of zwitterion conformers of aminophosphinic acid (MP2/Basis set II)[a]

Parameter[b]	Conformer I	II	III	IV
PH	1.4128	1.4433	1.4141	1.4475
CP	1.8949	1.9190	1.8948	1.9229
CN	1.5229	1.5349	1.5424	1.5443
PO	1.5024	1.4886	1.4995	1.4872
CH	1.0853	1.0844	1.0843	1.0829
NH_9	1.0101	1.0116	1.0193	1.0171
NH_{10}	1.0188	1.0130	1.0095	1.0108
CPH	103.98	95.66	102.80	95.68
NCP	97.90	108.21	100.44	107.45
CPO	101.33	105.48	101.82	105.70
PCH	115.26	112.13	114.94	111.30
CNH_9	115.04	113.26	108.98	108.77
CNH_{10}	107.09	109.86	112.00	112.42
OPCH	116.82	111.15	116.83	111.12
HCPH	66.25	116.94	65.42	117.76
H_9NCP	123.16	121.32	118.64	119.04
HPO	112.45	108.64	112.63	108.56
OPO	122.09	128.00	121.72	127.81
H_8NH_9	110.45	108.36	107.36	107.59
H_9NH_{10}	106.30	106.93	108.92	107.83

[a] Atom numbers are given on Fig. 1d. The conformers are depicted on Fig. 3.
[b] Bond lengths are in Å and bond angles in degrees.

between the most stable zwitterion conformer IV (Fig. 3) and two molecular conformers I and IV (Fig. 2) were calculated at the HF and MP2 levels using three different basis sets so that basis size effect on the energy difference could be revealed. The single point calculation at the MP3, MP4(DQ), MP4(SDQ), MP4(SDTQ) levels of theory were carried out to

Table 4
Relative energies (kcal/mol) of molecular and zwitterion conformers of aminophosphinic asid (Basis set II)

Method	Conformer I	II	III	IV
	Molecular form[a]			
SCF	0.809	1.563	4.374	0.
MP2	0.579	1.173	4.424	0.
	Zwitterion form[b]			
SCF	0.	16.395	5.324	18.647
MP2	0.	17.435	6.189	19.061

[a] With respect to conformer IV.
[b] With respect to conformer I.

Table 5
Difference in energy (kcal/mol) between the molecular and zwitterion conformers of aminophosphinic acid

Method	Zwitterion conformer I − Molecular conformer I		
	Basis set I	Basis set II	Basis set III
SCF	16.93	21.88	23.94
MP2	8.74	14.79	17.78
MP3	11.49		
MP4 (DQ)	10.87		
MP4 (SDQ)	9.81		
MP4 (SDTQ)	8.42		
	Zwitterion conformer I − Molecular conformer IV		
SCF		22.69	
MP2		15.37	
MP3		18.28	
MP4 (DQ)		18.03	
MP4 (SDQ)		17.07	
MP4 (SDTQ)		15.69	

predict the energy difference between zwitterion conformer I and molecular conformer I with Basis set I and between zwitterion conformer I and molecular conformer IV with Basis set II. These results are summarized in Table 5.

According to the calculations, molecular conformers I and IV are always more stable than the zwitterion conformers, irrespective of the basis size and level of theory. When the basis set is increased, the energy difference between the molecular and zwitterion conformers is larger both at the HF and MP2 levels. Energy correlation calculated at the Moller–Plesset level decreases the energy gap between both forms. We may thus expect that AMPA isolated in an argon matrix takes the molecular form.

4.2. IR spectra in Ar matrices

The 1700–400 cm^{-1} region of the IR spectra of DMPA and AMPA isolated in Ar matrices is shown in Fig. 4. Although these two molecules have similar structures, their spectra are appreciably different. The DMPA spectrum has narrow non-overlapping absorption bands, which are typical for the spectra of most compounds isolated in inert gas matrices. In the IR spectrum of AMPA the bands are considerably broadened, their half widths being up to several reciprocal

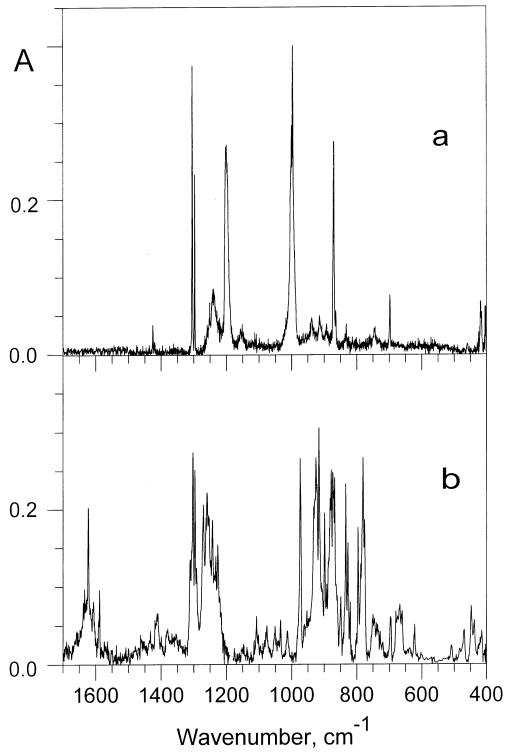

Fig. 4. Infrared spectra of monomeric dimethylphosphinic acid (a) and aminomethylphosphinic acid (b) isolated in Ar at 12 K (region 1700–400 cm^{-1}).

centimetres. Besides, a multiplet structure of bands is observed almost in all spectral regions. In result, the number of bands in the AMPA spectrum exceeds the number of internal coordinates of the molecule.

The increased number of bands in matrix IR spectra may be because of several reasons; self-association is one of them. At high enough concentration of a sample in a matrix the IR spectrum is actually a superposition of spectra of monomer, dimers and higher aggreggates spectra. However two factors allows us to exclude self-association as a reason for the increased number of bands in the AMPA spectrum. First, the spectrum was measured at relatively low concentration (1 : 400) at which, according to the OH stretching region (see Fig. 7) most molecules appear as monomers. Second, the spectral manifestations of selfassociation are different from those we observe in the AMPA spectrum. (see, for example Ref. [37]).

The increased number of bands in the AMPA

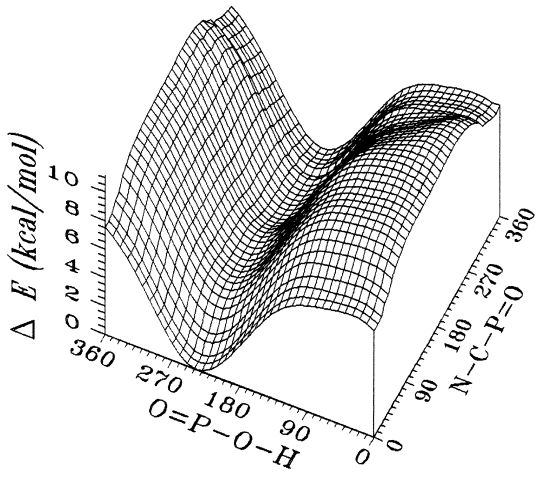

Fig. 5. Potential energy surface of aminomethylphosphinic acid. Three-dimensional plot.

spectrum may be because of multiple trapping site effect or owing to the presence of several AMPA conformers in the matrix. The latter is characteristic of flexible molecules and was earlier observed for aminocarboxylic acids [19–22]. A correct separation of the contributions arising from matrix and conformational splittings is hardly possible. When frozen in a matrix, molecule changes its structure as compared to the gas phase. The extent of the change is dependent, on the one hand, upon the matrix properties and, on other hand, upon the properties of the molecule itself, e.g., the shape of the potential energy surface near minima. An additional factor determing the general shape of the IR spectra of matrix isolated conformers may be complexes formed between molecule in question and inert gas atoms.

We have calculated the potential energy surface of AMPA (shown in Fig. 5) and found no distinct minimum. Instead, there was a gently sloping valley, which corresponds to a practically isoenergetic rotation of the phosphine group about the C–P bond. The cross-section of the potential energy surface with the torsion angle O=P–O–H fixed at 240° (the valley bottom) is shown in Fig. 6. We estimated the kT energy, being 1.05 kcal/mol at the evaporation temperature of the AMPA sample (254°C). The horizontal dashed line in Fig. 6 corresponds to this energy. As the torsion angle N–C–P=O changes within 240° → (360° = 0°) → 40°, the change in the relative

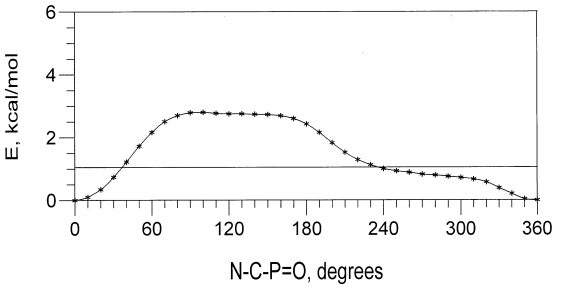

Fig. 6. Torsion potential of aminomethylphosphinic acid. The torsional angle N–C–P=O was varied, while O=P–O–H angle was fixed at 240°. Horizontal dashed line corresponds to the *kT* energy at evaporation temperature of the substance (254°C), being 1.05 kcal/mol.

energy does not exceed the *kT* energy. It means that all AMPA states with the torsion angle N–C–P=O within the above range are possible in the gas phase. If all these states were frozen in the matrix, the spectrum would have broad absorption bands. The bands in the IR spectrum of AMPA have actually a multiplet structure with a set of distinct narrow maxima. This indicates that the matrix fixes only a limited set of AMPA conformations with certain values of the torsion angle N–C–P=O. It means that the high flexibility permits the AMPA molecules to take the forms which ensures the most energy-adventageous packings in the Ar crystal and in the spectra each type of packing is represented by the appropriate maximum of each multiplet band.

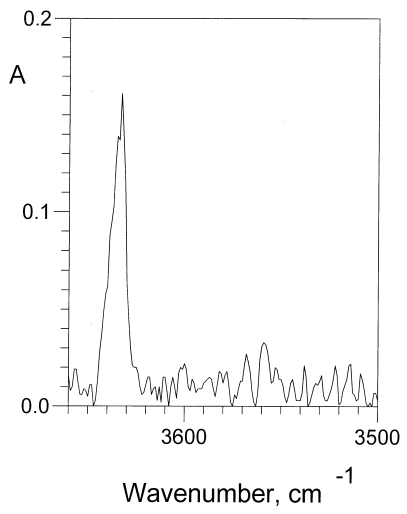

Fig. 7. OH stretching region of IR spectrum of aminomethylphosphinic acid (region 3660–3500 cm^{-1}).

The structure of AMPA molecules is also determined by weak intramolecular H-bonds N–H···O. as the torsion angle N–C–P=O changes, so does the mutual orientation of amino and phosphinic groups and the geometry of the H-bonds. It is clear that the IR spectrum should be very sensitive to the changing of intramolecular geometry. The spectral effects should be most pronounced for the bands corresponding to the vibrations of the groups involved in the intramolecular interaction: NH_2, P=O and P–O stretching and bending vibrations. In contrast, the bands representing the groups which are not involved in the intramolecular interactions (e.g., OH stretching and bending vibrations) should be insensitive to changes in the H–C–P=O torsion angle. These assumptions are well supported experimentally. The observed frequencies and intensities are given in Table 6 along with the results of the normal coordinate analysis.

The presence of the bands of OH stretching (Fig. 7) and NH_2 bending vibrations and the absence of the bands of POO^- and NH_3^+ vibrations are the evidence of molecular structure of AMPA molecules that is in good agreement with the calculated relative energies of the molecular and zwitterion conformers of AMPA.

The singlet structure of the stretching vibration of OH group (Fig. 7) which is not involved in the intramolecular interactions, as well the multiplet structure of P=O stretching and NH_2 bending vibrations (Fig. 8 and Table 6) are in good agreement with the conclusion on the conformational lability of AMPA molecules.

5. Concluding remarks

The high conformation lability of AMPA molecules revealed in this study may be related to very low barrier of rotation about C–P bond and is responsible for the extraordinary appearance of the IR spectrum of the compound in question when it is isolated in Ar matrices. The observed multiplet structure of the matrix IR spectrum may be taken as a spectral criterion of the isoenergetic rotation in molecules. The possibility of rotation about the C–P bonds persists when AMPA derivatives are included in the

Table 6
Observed and calculated frequencies of DMPA and AMPA (Ar matrix, 12 K)[a]

Dimethylphosphinic acid					Aminomethylphosphinic acid				
Observed		Calculated			Observed		Calculated		
ω	I	ω	Assignment[b,c]		ω	I	ω	Assignment[b,c]	
		3641	OH str [99]	A'	3633	0.16	3642	OH str [99]	
					3451	0.07	3443	NH_2 str as [100]	
					3431	0.08			
					3338	0.07	3352	NH_2 str s [100]	
		2973	CH_3 str [100]	A"	2989	0.11	2979	CH_2 str [100]	
		2972	CH_3 str [100]	A'	2950	0.10	2972	CH_3 str [100]	
		2961	CH_3 str [100]	A"	2940	0.10	2960	CH_3 str [100]	
		2960	CH_3 str [100]	A'	2916	0.11	2913	CH_2 str [100]	
		2886	CH_3 str [100]	A"	2894	0.10	2887	CH_3 str [100]	
		2886	CH_3 str [100]	A'	2883	0.10			
					1638	0.08	1627	NH_2 bend [89]	
					1630	0.09			
					1623	0.17			
					1608	0.09			
					1589	0.09			
		1471	CH_3 bend [87]	A'	1461	0.05	1469	CH_3 bend [92]	
		1469	CH_3 bend [87]	A"					
1425	0.05	1430	CH_3 bend [91]	A'					
1421	0.03	1427	CH_3 bend [91]	A"	1412	0.07	1427	CH_3 bend [89]	
		1348	CH_3 bend [93]	A"	1381	0.05	1393	CH_2 bend [75]	
		1345	CH_3 bend [93]	A'	1354	0.05	1344	CH_3 bend [84]	
1305	0.37	1301	P=O str [65],		1312	0.13	1299	P=O str [61],	
1297	0.29		P-O str [21]	A'	1303	0.29		P-O str [19],	
					1297	0.25		NH_2 bend [14]	
					1292	0.12			

Table 6 (*continued*)

Dimethylphosphinic acid					Aminomethylphosphinic acid			
Observed		Calculated			Observed		Calculated	
ω	I	ω	Assignment[b,c]		ω	I	ω	Assignment[b,c]
					1271	0.20	1264	NH_2 bend [32],P=O str [23],
					1261	0.21		CH_2 bend [20],
1251	0.06	1237	CH_3 bend [65],		1255	sh		CH_3 bend [17]
			P-O str [18]	A'	1243	0.17	1242	OH bend [45], P-O str [29],
1200	0.27	1216	OH bend [48],P-O str [27],		1232	0.14		CH_2 bend [18]
			CH_3 bend [17]	A"	1226	0.16	1230	CH_3 bend [59],NH_2 bend [17]
1151	0.04	1148	CH bend [62],		1145	0.04	1138	CH_3 bend [37], C-N str [21],
			C-P str [17]	A'	1109	0.06		CH_2 bend [18], NH_2 bend 12]
		1146	CH bend [68],		1077	0.05		
			C-P str [16]	A"	1053	0.06	1043	CH_2 bend [61],
					1035	0.07		C-N str [11]
1000	0.30	1012	P-O str [35],		1015	0.06		
996	0.40		OH bend [21], P=O str [14],		974	0.28	987	P-O str [31], C-N str [29],
			CH_3 bend [14]	A'				OH bend [13]
					962	0.07		
					954	0.09		
938	0.04	927	CH_3 bend [37],CP-O bend [24],		926	0.31	938	C-N str [34], P-O str [28],
914	0.04		OH tor [11]	A"	916	0.30		NH bend [14]
892	0.03				900	0.20	885	C-P str [27], NH_2 bend [21],
					894	0.11		C-N str [21], P-O str [14]
					882	sh		
870	0.28	873	CH_3 bend [31],		880	0.24	864	CH bend [37],
864	0.05		OH tor [28],		874	0.29		C-N str [16],
			C-P str [17]	A"	869	0.26		OH tor [13]
832	0.04	847	C-P str [47],		849	0.08	842	C-P str [42],
813	0.03		P-O str [17], OH bend [16],					P-O str [23], OH bend [16]
			CP=O bend [14]	A'	835	0.22	818	C-N str [25],

Table 6 (*continued*)

Dimethylphosphinic acid					Aminomethylphosphinic acid			
Observed		Calculated			Observed		Calculated	
ω	I	ω	Assignment[b,c]		ω	I	ω	Assignment[b,c]
					828	0.15		NH_2 bend [25],
					821	0.08		C-P str [19]
					797	0.17	785	NH_2 bend [37],
					788	sh		C-P str [21]
					781	0.26		
					777	sh		
745	0.04	729	OH tor [84]	A"	750	0.08	732	OH tor [76],
					745	0.07		NH_2 bend [12]
					740	0.06		
					735	0.06		
					730	0.04		
					723	0.03		
698	0.07	679	C-P str [51], P-O str [13]	A'	696	0.06	682	C-P str [53],
					680	sh		P-O str [19],
					675	sh		NH_2 bend [10]
					670	0.08		
					663	sh		
					625	0.05		
					590	0.03		
					470	0.05	463	NCP bend [58]
419	0.06	423	O-P=O bend [33], CPC bend [21]	A'	447	0.07	438	O-P=O bend [37],
					439	0.07		NCP bend [15]
405	0.05	412	CPC bend [20], CP=O bend [18], CP-O bend [16]	A'	416	0.05	410	CP=O bend [26],CP-O bend [23], CPC bend [14]
							381	CPC bend [39], NCP bend [18]
		315	CP=O bend [41], OPO bend [25]	A"			316	CP=O bend [44], OPO bend [22]

Table 6 (*continued*)

Dimethylphosphinic acid				Aminomethylphosphinic acid			
Observed		Calculated		Observed		Calculated	
ω	I	ω	Assignment[b,c]	ω	I	ω	Assignment[b,c]
273			CP-O bend [37], CP=O bend [19]			281	CP-O bend [46], CP=O bend [13]
			A'				A'
179			CH tor [75]			167	CH tor [69]
			A"				A"
156			CH tor [79]			112	NCPO tor [41], CH tor [22]
			A'				A'

[a] Matrix ratio 1 : 1000 for DMPA and 1 : 400 for AMPA.
[b] str, stretching; bend, bending; tor, torsion.
[c] Potential energy distributions (> 10%) are given in square brackets.

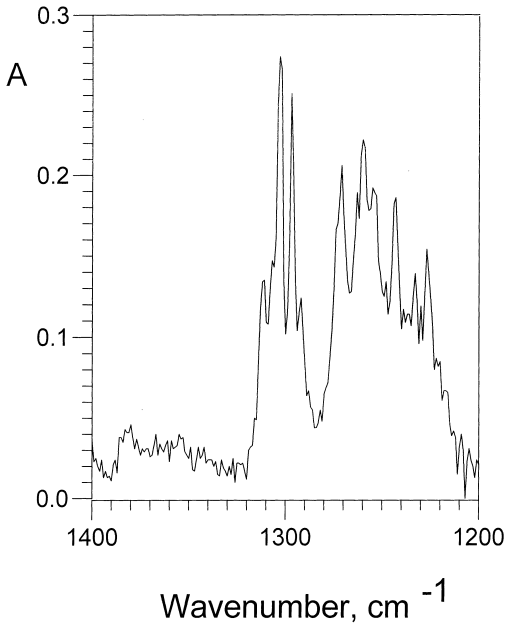

Fig. 8. P=O stretching and NH_2 bending region of IR spectrum of aminomethylphosphinic acid (region 1400–1200 cm^{-1}).

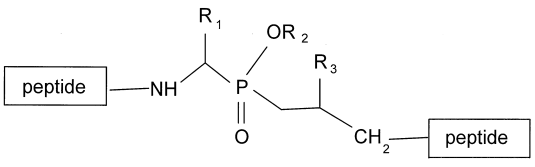

Fig. 9. Structure of phosphinopeptide.

peptide chain (the phosphinopeptide structure is schematically shown in Fig. 9).

This must increase the conformational mobility of the entire phosphopeptide and may cause high biological activity of this class of compounds. In contrast, the introduction of volume and/or polar substituents into the phosphinic fragment should change the barrier of rotation about the C–P bond and hence the phosphopeptide structure. It is possible that this modification would essentially affect the biological activity of the phosphopeptides and is a potential method of synthesizing new bioactive compounds.

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