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Experimental and calculated ^1H , ^{13}C and ^{31}P NMR spectra of (hydroxypyridin-3-yl-methyl)phosphonic acid

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Abstract

(Hydroxypyridin-3-yl-methyl)phosphonic acid named also 3-pyridylmethyl(hydroxy)-phosphonic acid, MC5, is biologically active compound and exhibits metal binding ability attributable to the presence of the phosphonic group and the pyridine nitrogen. Its proton NMR data have been previously reported, only. Thus, in this work we offer interpretation of ^1H , ^{13}C and ^{31}P NMR spectra of this compound dissolved in D_2O in the pH range between 1.5 and 9.0. Additionally, to support our interpretation of the obtained data, we calculated NMR spectra of all expected forms that are the result of consecutive deprotonation of MC5. Theoretical calculations of the NMR spectra as well as structural parameters of the compounds (cation, zwitteranion, and two anions) were performed at the B3PW91 level with the 6-311G** and 6-311++G** basis sets.

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1. Introduction

Heterocyclic phosphonates, phosphonic acids and their amino derivatives have been a subject of growing interest for the last two decades. They can be used as neuroactive agents since they can act either as agonists of neuronal receptors or exhibit antagonist activity depending upon their structures. Thus, the position of the phosphonic has considerable impact

on biological activity of these classes of compounds. However, in contrast to many heterocyclic aminophosphonic acids and their salts or coordination complexes, phosphonic compounds do not undergo the hydrolysis of the C–P bond [1–6].

(Hydroxypyridin-3-yl-methyl)phosphonic acid, named also 3-pyridylmethyl(hydroxy)-phosphonic acid (MC5), is one of the abovementioned compounds that exhibits some potential neuroactivity. Additionally, MC5 can also bind metal ions owing to the presence of phosphonic group as well as a lone electron pair localized on the pyridine nitrogen [1].

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To our best knowledge, ^1H and ^{31}P NMR spectra of MC5 performed in D_2O solution were previously reported only without detailed interpretation [7]. It has to be noted that chemical shifts of MC5 can be strongly dependent upon pH (pD) of the solution due to labile protons existing in the structure of the ligand. This ligand contains two dissociable protons within the measurable pH range (2.0–12.0). On the other hand, one more deprotonation has been postulated at pH below 2.0. Based on these data we propose four forms that result from consecutive deprotonations of MC5. Their chemical structures and atom numbering are shown in Fig. 1.

In this work we present detailed interpretation of experimental ^1H , ^{13}C and ^{31}P NMR spectra of MC5 dissolved in D_2O in the pD range of 1.5–9.0. The increase of pD was accomplished by adding dropwise of NaOD. The decrease of pD, if it was necessary, was reached by using D_2SO_4 . Assignment of observed carbon chemical shifts was based on quantum chemical calculation at the B3PW91/6-311G** and B3PW91/6-311++G** level followed geometry

optimization done by using the same method with abovementioned basis sets.

2. Experimental

2.1. Compound

The compound abbreviated as MC5 was synthesized as described earlier [7,8]. Briefly, a solution of proper pyridyl aldehyde, diethyl phosphonate and triethylamine in benzene was kept for 24 h at room temperature. Then, liquid phase was evaporated to give the crude hydroxyphosphonate as yellowish oil. After several hours just synthesized ester solidified, was recrystallized from a mixture of hexane and diethyl ether and then dissolved in 20% hydrochloric acid and refluxed by 6 h. After evaporation of solvent hydroxyphosphonic acid was obtained as glass-like solid. The obtained crude product was recrystallized from aqueous methanol to give white, lustrous crystals.

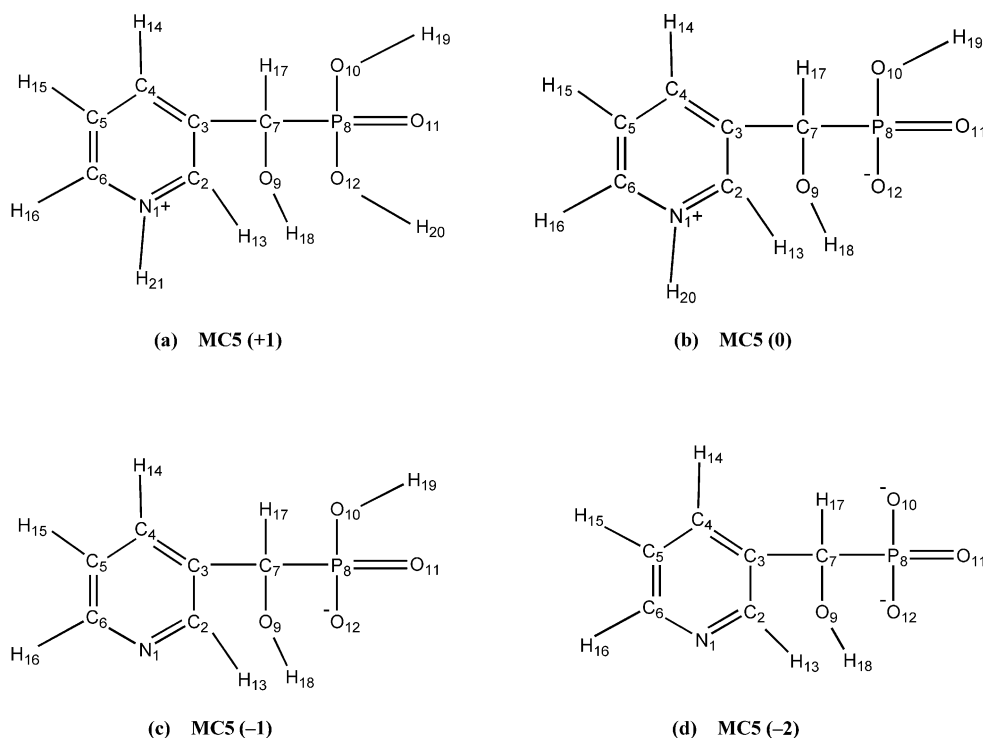


Fig. 1. Structures of MC5 connected with consecutive deprotonations: (a) the cation (+1); (b) the zwitterion (0) ('neutral' form); (c) the anion (-1); (d) the dianion (-2).

2.2. Spectral measurements

All NMR spectra were measured on a Bruker AMX 500 MHz spectrometer. For NMR experiments, MC5 was dissolved in D₂O, transferred to a standard NMR capillary and measured at room temperature. The ¹H NMR spectra were measured with DSS (sodium salt of 3-(trimethylsilyl)-1-propanesulphonic acid) as an external standard and with resonance frequency of 500.1 MHz. ¹³C NMR spectra were recorded with proton coupling and decoupling with dioxan as an external standard and resonance frequency of 125.8 MHz. ³¹P NMR spectra were recorded with 85% H₃PO₄ external standard with the 202.5 MHz resonance frequency.

2.3. Calculations

Calculations were carried out at density functional theory level (DFT) using B3PW91 [9,10] functional implemented in GAUSSIAN '98 program [11] at the Academic Computer Centre 'Cyfronet' in Kraków. B3PW91 functional is a hybrid method consisting of Becke's [10] three-parameter function as a linear combination of: (1) local density approximation, (2) Becke's gradient correlation [12] and (3) Hartree–Fock exchange energy based on Kohn–Sham orbitals [13]. Additionally, Perdew–Wang 91 [14,15] gradient-corrected correlation, called also non-local, functional was used. Calculations of geometry optimization and magnetic properties were carried out at the B3PW91 level with the 6-311G** and the 6-311++G** basis sets.

Calculated shielding values for each atom in molecule were shifted relatively from a frequency of standard compounds: tetramethylsilane (TMS) for hydrogen and carbon atoms and orthophosphorus acid (H₃PO₄) for phosphorus atom. In order to compare theoretical values with experimental results, we also computed the absolute shielding constants for TMS and H₃PO₄ using the same set of quantum chemical calculations.

Calculations of MC5 were performed for all four structures existing in different pH as the result of consecutive deprotonations of the ligand (Fig. 1).

3. Results and discussion

3.1. Interpretation of ¹H, ¹³C and ³¹P NMR spectra of MC5

Measured proton, carbon and phosphorus chemical shifts were compared with those predicted theoretically. The computed absolute shielding value of TMS and H₃PO₄ reference compounds are presented in Table 1. The observed chemical shifts of ¹³C NMR together with calculated data and proposed assignments are listed in Table 2. Interpretation of carbon spectrum of MC5 is based partly on coupling constants J(PC₇) listed in Table 3.

As expected, the proton decoupled ¹³C NMR spectrum consists of six resonance signals. Thus far, ¹³C NMR data of MC5 have not been reported in the literature. In the spectrum (not shown) there are five singlets and one doublet that indicates coupling of the carbon atom with a phosphorus nuclei. This doublet is observed at 68.31 ppm for a 'neutral' form (zwitterion) at pD 3.0 and has to be attributed to the aliphatic carbon C₇ that is adjacent to P₈. This assignment is additionally supported by the strong interaction between these two. Their coupling constant ¹J(PC₇) is equal 150.80 Hz at pD 3.0. The single resonance signals are attributed to five pyridine carbons. A single resonance at 141.12 ppm in the proton decoupled NMR spectrum appears also as a singlet in the proton coupled spectrum (Table 2). That is why this signal is attributed to a pyridine quaternary carbon, C₃. Its chemical shift is higher than a 'parent' carbon in pyridine. This down field shift is a result of the presence of substituent group at this position and can be explained by inductive and mesomeric effects. The other four peaks that appear as singlets in the proton decoupled ¹³C NMR spectrum are observed as doublets in the proton coupled ¹³C NMR spectrum. The chemical shifts and their values of coupling

Table 1
Calculated shielding constant of the references (in ppm)

Method	TMS		H ₃ PO ₄
	C	H	P
B3PW91/6-311G**	187.60	31.90	322.75
B3PW91/6-311++G**	187.20	31.86	325.80

Table 2
Experimental and calculated ^{13}C chemical shifts (in ppm) as a function of pD

Assignment	Cation (+1)		Neutral form (0)							Anion (-1)			Anion (-2)										
	Exp. pD	Cal.	Exp. pD							Cal.		Exp. pD			Cal.								
	1.5		2.0	2.5	3.0	3.5	4.0	4.5	5.0			5.5	6.0	6.5			7.0	7.5	8.0	9.0			
C ₂ ; (s;d) ^a	138.55	142.16 ^b ; 142.65 ^c	138.97	138.94	138.96	139.28	139.53	140.15	142.10	146.09 ^b ; 146.30 ^c	143.82	145.10	146.27	153.80 ^b ; 156.16 ^c	147.04	146.94	147.11	147.12	153.55 ^b ; 155.21 ^c				
C ₃ ; (s;s) ^a	140.42	148.88 ^b ; 148.75 ^c	141.09	141.09	141.12	141.02	140.99	140.42	139.36	160.90 ^b ; 161.04 ^c	138.28	137.66	137.51	147.67 ^b ; 147.39 ^c	137.77	137.72	137.77	137.83	163.80 ^b ; 164.36 ^c				
C ₄ ; (s;d) ^a	144.41	156.28 ^b ; 157.03 ^c	144.81	144.70	144.68	144.48	144.35	143.42	142.59	139.85 ^b ; 147.25 ^c	139.55	138.25	137.28	139.27 ^b ; 144.82 ^c	136.53	136.15	135.93	135.93	130.14 ^b ; 134.75 ^c				
C ₅ ; (s;d) ^a	126.41	134.73 ^b ; 134.95 ^c	126.80	126.73	126.72	126.71	126.72	126.33	125.74	127.63 ^b ; 128.28 ^c	125.06	124.64	124.32	124.57 ^b ; 125.40 ^c	124.07	123.77	123.66	123.63	122.77 ^b ; 124.10 ^c				
C ₆ ; (s;d) ^a	139.29	142.42 ^b ; 143.04 ^c	139.63	139.61	139.59	139.93	140.18	140.74	141.51	131.16 ^b ; 131.66 ^c	144.22	145.40	146.27	147.78 ^b ; 150.70 ^c	146.82	146.61	146.66	146.67	135.44 ^b ; 138.75 ^c				
C ₇ ; (d;dxd)	68.19	71.96 ^b ; 73.28 ^c	68.79	68.79	68.31	68.97	68.98	69.03	69.42	74.16 ^b ; 75.37 ^c	69.70	70.00	70.52	77.78 ^b ; 77.97 ^c	71.29	71.32	71.52	71.61	86.64 ^b ; 87.92 ^c				

^a (Multiplicity in the proton decoupled ^{13}C NMR spectrum; multiplicity in the proton coupled ^{13}C NMR spectrum).

^b B3PW91/6-311G**.

^c B3PW91/6-311++G**.

Table 3
Experimental coupling constants $^1J(\text{PC}_7)$ (in Hz) as a function of pD

Assignment	Exp. pD															
	Cation (+1)		Neutral form (0)							Anion (-1)			Anion (-2)			
	1.5		2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	9.0
$^1J(\text{PC}_7)$	151.68		150.42	150.67	150.80	155.55	155.07	150.80	154.44	149.67	150.80	150.30	143.88	141.74	140.99	139.72

Table 4
Experimental and calculated ^1H chemical shifts (in ppm) as a function of pD

Assignment	Cation (+1)		Neutral form (0)					Anion (-1)		Anion (-2)								
	Exp. pD	Cal.	Exp. pD	Cal.	4.0	4.5	5.0	Exp. pD	Cal.	Exp. pD	Cal.							
H_{13} : (s) ^a	8.78	8.58 ^b ; 8.64 ^c	8.78	8.76	8.73	8.78	8.74	8.69	10.39 ^b ; 9.97 ^c	8.63	8.60	8.61	8.68 ^b ; 8.54 ^c	8.58	8.60	8.56	8.54	8.61 ^b ; 8.55 ^c
H_{16} : (d) ^a	8.68	8.49 ^b ; 8.52 ^c	8.68	8.70	8.66	8.63	8.68	8.57	7.59 ^b ; 7.60 ^c	8.50	8.47	8.48	8.25 ^b ; 8.34 ^c	8.44	8.46	8.41	8.39	7.21 ^b ; 7.41 ^c
H_{14} : (d) ^a	8.62	9.65 ^b ; 9.67 ^c	8.62	8.63	8.60	8.55	8.60	8.37	9.30 ^b ; 9.34 ^c	8.22	8.13	8.08	8.10 ^b ; 8.64 ^c	8.01	8.02	7.94	7.93	7.54 ^b ; 7.87 ^c
H_{15} : (dx/d) ^a	8.03	8.52 ^b ; 8.52 ^c	8.03	8.04	8.01	7.97	8.01	7.93	7.81	7.68	7.60	7.56	6.91 ^b ; 7.04 ^c	7.49	7.49	7.43	7.42	6.20 ^b ; 6.49 ^c
H_{17} : (s) ^a	5.14	5.35 ^b ; 5.55 ^c	5.13	5.13	5.09	5.06	5.12	5.07	5.03	4.96	4.93	4.87	4.49 ^b ; 4.88 ^c	?	?	?	?	4.36 ^b ; 4.53 ^c
H_{18} : (s) ^a	3.31	2.27 ^b ; 2.49 ^c	3.32	3.33	3.30	3.27	3.34	3.31	3.33	3.32	3.33	3.36	2.75 ^b ; 3.12 ^c	3.37	?	3.36	3.35	7.72 ^b ; 8.05 ^c

^a Multiplicity in the ^1H NMR spectrum).

^b B3PW91/6-311G**.

^c B3PW91/6-311++G**.

constants $^1J(\text{CH})$ resemble those of the pyridine ring [16–20]. Accordingly, a peak at lower field with the lowest coupling constant is assigned to C_4 . This MC5 signal is seen at 144.68 ppm with a coupling constant $J = 169.27$ Hz. The signals at 139.59 and 138.96 ppm characterized by coupling constants of $J = 192.29$ and $J = 193.29$ Hz, respectively, are attributed to α -carbons, i.e. C_6 and C_2 . In turn, resonance at 126.72 ppm with $J = 172.04$ Hz is assigned to β -carbon C_5 while that at 141.12 ppm is due to the second β -carbon, i.e. C_3 . [17,20].

The ^1H NMR experimental and calculated chemical shifts of MC5 in D_2O in the pD range of 1.5–9.0 are listed in Table 4. The integration of all peaks appearing in the spectrum arises from five protons that have to be attributed to hydrogens of the pyridine ring: H_{13} , H_{14} , H_{15} , H_{16} and aliphatic H_{17} . As expected, both protons from phosphonic group are exchanged by deuterium atoms and are not seen in the spectrum. Surprisingly, only weak resonance at ~ 3 ppm, that the most probably arises from proton H_{18} , indicates that even at these conditions this proton from alcoholic group may be replaced by deuterium atom. Assignment of the peak at 5.09 ppm for ‘neutral’ form (zwitterion) at pD 3.0 is trivial since it corresponds to the only aliphatic proton H_{17} . The singlet at 8.76 ppm we assign to H_{13} whereas the doublet of doublets at 8.01 ppm to H_{15} . The other two doublets observed at 8.60 and 8.66 ppm are due to H_{14} and H_{16} , respectively. This assignment is in good agreement with that found Refs. [1,21,22].

Obviously, the ^{31}P NMR spectrum of MC5 show only one signal at 14.01 ppm at pD 3.0 that is readily assigned to P_8 .

3.2. ^1H , ^{13}C and ^{31}P NMR chemical shifts of MC5 as a function of pD

Potentiometric measurements of MC5 indicate three pK_a constants resulting from consecutive deprotonations of the ligand (Fig. 1) [1,2]. In the measurable pD range two protons dissociate from the pyridine nitrogen and the phosphonic group ($\text{pK}_{a2} = 5.13$ and $\text{pK}_{a3} = 6.93$, respectively (Fig. 1(b)–(d))). However, one more deprotonation is postulated at low pH, i.e. below 2. This very acidic proton lives the phosphonic group [1,2]. In this paragraph we present experimental data of ^{13}C ,

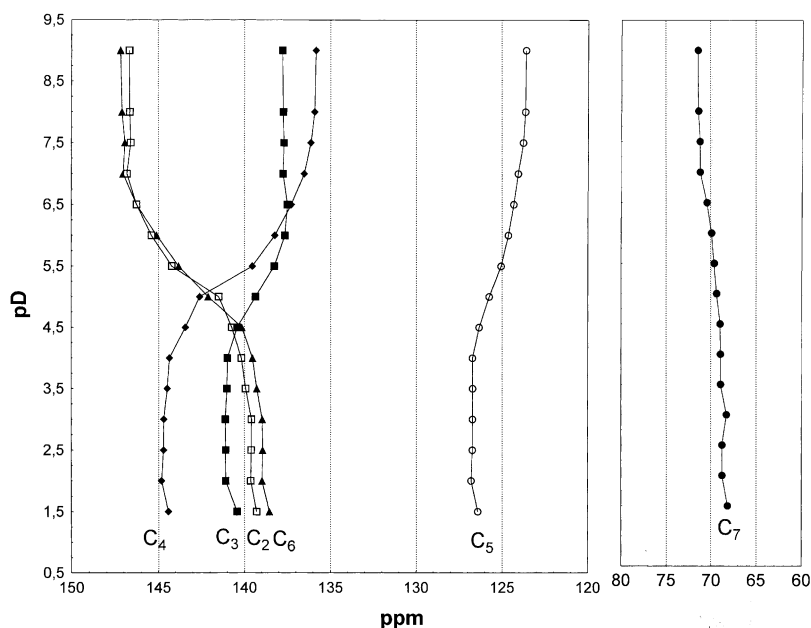


Fig. 2. Experimental ^{13}C chemical shifts as a function of pD.

^1H and ^{31}P NMR of MC5 in D_2O solution in the pD range of 1.5–9.0. Theoretical calculations were performed for all possible structures presented in Fig. 1.

The chemical shift of ^{13}C as a function of pD is shown in Fig. 2 and collected in Table 2. As seen the chemical shifts of carbons C_2 and C_6 increase with the increase of pD, whereas the resonances of

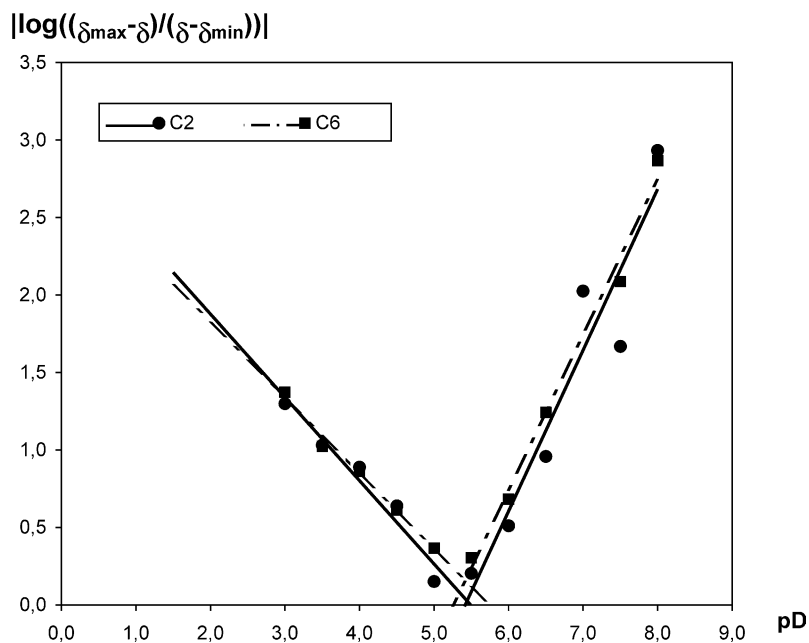


Fig. 3. Experimental dependence of $|\log((\delta_{\max} - \delta)/(\delta - \delta_{\min}))|$ on pD, according to Henderson–Hasselbalch equation.

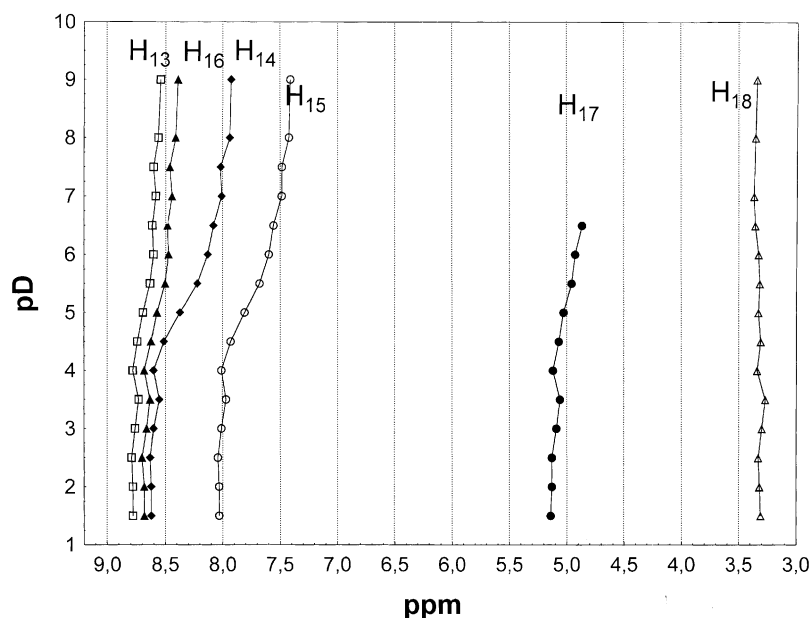


Fig. 4. Experimental ^1H chemical shifts as a function of pD.

C_3 , C_4 and C_5 show opposite trend. The strongest changes with the increase of pD are observed for γ -carbon C_4 . This effect is the most likely caused by mesomeric effect that results in decrease on electron density on γ -carbon. The chemical shift of carbon C_7 (aliphatic) is practically constant with the changes of pD. In general, these data agree with those presented for most substituted pyridines [17, 19]. Recently, similar behavior we have reported for pyridine-2-phosphono-4-carboxylic acid [23]. Discussed here changes in the chemical shifts correspond to changes of charge polarization and electric field effects on proper carbon atoms [18–20]. These experimental data and proposed assignments are fully supported by our calculations listed in Table 2. The trends of the chemical shifts of proper carbon atoms as a function of pD are well reproduced by the calculation despite of their larger values in comparison to experimental data. The chemical shifts are known to be very sensitive to the molecular geometry and even small variations in intermolecular distances can change them substantially [24–27]. Thus, calculations of the chemical shifts should be performed on the experimentally determined geometries. Obviously, such data are not available in our case that is why we had to perform

theoretical studies on series of possible structures and optimized their geometrical parameters. It has to be noted that the largest difference between calculated and experimental data are observed for carbon C_6 , especially in zwitterion and dinegative anion of MC5. It has to be also emphasized that obtained data do not depend upon basis sets used in calculations (6-311G** and 6-311++G**), except these for carbon C_4 . Thus, addition of the diffusion functions to basis set does not improve substantially

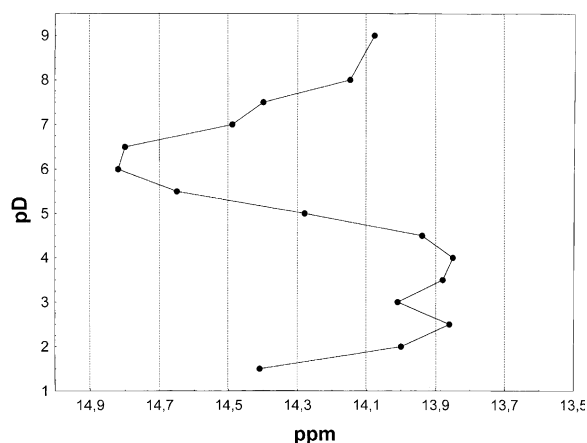


Fig. 5. Experimental ^{31}P chemical shifts as a function of pD.

Table 5
Experimental ³¹P chemical shifts (in ppm) as a function of pD

Assignment	Cation (+1)		Neutral form (0)		Anion (-1)		Anion (-2)												
	Exp. pD	Cal.	Exp. pD	Cal.	Exp. pD	Cal.	Exp. pD	Cal.											
	1.5		2.0	2.5	3.0	3.5	4.0	4.5	5.0										
P ₈	14.41	30.84 ^a , 34.83 ^b	14.00	13.86	14.01	13.88	13.85	13.94	14.28	23.69 ^a , 27.81 ^b	14.65	14.82	14.80	26.37 ^a , 33.98 ^b	14.49	14.40	14.15	14.08	40.93 ^a , 48.38 ^b

^a B3PW91/6-311G**.

^b B3PW91/6-311++G***.

the values of the chemical shifts but increases the time of calculations, only.

Fig. 3 shows dependence of $|\log((\delta_{\max} - \delta)/(\delta - \delta_{\min}))|$ versus pD obtained by titration of MC5 with NaOD. According to Henderson and Hasselbach this allows one to determine pK_a values of *N*-heterocyclic compounds [17]. Based on the chemical shifts of carbons C₂ and C₆, we determined pK_a values of pyridine as 5.44 and 5.42, respectively, that is in very good agreement with literature data [1,28].

Table 3 lists the experimental values of coupling constant ¹J(PC₇). As seen these values do not show monotonic dependence on pD as it was observed by us for pyridine-2-phosphono-4-carboxylic acid [23]. However, they indicate the changes of bond length of coupling atoms, i.e. P₈-C₇. It is clearly seen from the table that these values are gathered in four groups that represent discussed structures of MC5 presented in Fig. 1.

The experimental chemical shifts of ¹H as a function of pD is reported in Fig. 4 and Table 4. All observed resonance from protons show generally insignificant decrease of the chemical shift with the increase of pD. Our calculations show fairly good agreement with experimental data especially for H₁₄, H₁₅, and H₁₇ (Table 4).

The behavior of the chemical shift of phosphorus nuclei is presented in Fig. 5 and Table 5. Theoretical calculations are consistent with the experimental dependence on pD. Unusual pattern of the observed shifts can be explained by the changes of the phosphorus atom charge. This can be easily correlated with changes in the coupling constant J(PC₇) discussed above.

Overall good agreement between experimental and theoretical data confirm that the suggested structures formed in different pD ranges shown in Fig. 1 and used in our calculations are correct. These data support the sequence of deprotonation of MC5, i.e. the first proton leaving the phosphonic group, the next pyridine nitrogen and then the phosphonic group.

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References

- [1] L. Chruściński, P. Młynarz, K. Malinowska, J. Ochocki, B. Boduszek, H. Kozłowski, *Inorg. Chem. Acta* (2000) 303.
- [2] B. Boduszek, M. Dyba, M. Jeżowska-Bojczuk, T. Kiss, H. Kozłowski, *J. Chem. Soc., Dalton Trans.* (1997) 973.
- [3] T. Kiss, M. Jeżowska-Bojczuk, H. Kozłowski, P. Kafarski, K. Antczak, *J. Chem. Soc., Dalton Trans.* (1991) 2275.
- [4] P. Kafarski, P. Mastalerz, *Beitr. Wirkst. Forsch.* 21 (1984) 1.
- [5] T.W. Stone, *Br. J. Pharmacol.* 81 (1984) 175.
- [6] M.N. Perkins, T.W. Stone, *Brain Res.* 259 (1983) 259.
- [7] B. Boduszek, *Tetrahedron* 52 (1996) 12483.
- [8] B. Boduszek, *Phosphorus Sulphur Silicon* 113 (1996) 209.
- [9] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1998) 785.
- [10] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. 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, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Revision A.1, GAUSSIAN 98, Gaussian Inc., Pittsburgh PA, 1998.
- [12] A.D. Becke, *J. Chem. Phys.* 88 (1998) 1053.
- [13] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) 1133.
- [14] J.P. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244.
- [15] B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc, Pittsburgh, 1993.
- [16] C.J. Pouchert, J. Behnke, *The Aldrich Library of ¹³C and ¹H NMR Spectra*, 1993.
- [17] E. Breitmaier, K.-H. Spohn, *Tetrahedron* 29 (1973) 1145.
- [18] J. Młochowski, *Chemia związków heterocyklicznych*, PWN, Warszawa, 1994.
- [19] H.-O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR spectroscopy*, Wiley, Chichester, 1988.
- [20] W. Zieliński, A. Rajca, *Metody Spektroskopowe i ich zastosowanie do identyfikacji związków organicznych*, WNT, Warszawa, 1995.
- [21] N.C. Singha, J. Anand, D.N. Sathyanarayana, *J. Mol. Struct.* 443 (1998) 1.
- [22] C.L. Broadhurst, W.F. Schmidt, J.B. Reves III, M.M. Polansky, K. Gautschi, R.A. Anderson, *J. Inorg. Biochem.* (1997) 121.
- [23] K. Chruszcz, M. Barańska, K. Czarniecki, B. Boduszek, L.M. Proniewicz, *J. Mol. Struct.* (2003) in press.
- [24] A.P. Mazurek, J.Cz. Dobrowolski, J. Sadlej, *J. Mol. Struct.* 436 (1997) 435.
- [25] C.J. Jameson, H.J. Osten, G.A. Webb, *Annu. Rep. NMR Spectrosc.* 17 (1986) 1.
- [26] D.B. Chesnut, D.W. Wright, *J. Comp. Chem.* 12 (1991) 54.
- [27] K. Jackowski, A. Leś, *J. Mol. Struct. (Theochem)* 331 (1995) 295.
- [28] J.R. Kincaid, L.M. Proniewicz, K. Bajdor, A. Bruha, K. Nakamoto, *Am. Chem. Soc.* 107 (1985) 6775.