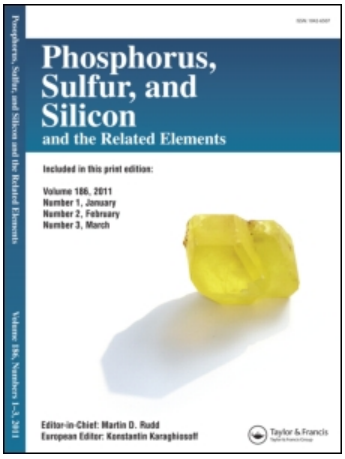

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A NOVEL ROUTE TO AN AMINOPHOSPHONIC ACID BY THERMOLYSIS OF A POLY(URETHANE PHOSPHONATE). THE BETAIN FORM OF 3-ETHYL-2-HYDROXY-2-OXO-1,4,2-OXAZA-PHOSPHORINANE. STRUCTURE AND PROPERTIES

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A NOVEL ROUTE TO AN AMINOPHOSPHONIC ACID BY THERMOLYSIS OF A POLY(URETHANE PHOSPHONATE). THE BETAIN FORM OF 3-ETHYL-2-HYDROXY-2-OXO-1,4,2-OXAZA-PHOSPHORINANE. STRUCTURE AND PROPERTIES

KOLIO TROEV[a], GERHARD HÄGELE[b*], KAY KREIDLER[b], RALF OLSCHNER[b], CLAUDIA VERWEY[b] and DAVID M. ROUNDHILL[c]

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(Received 24 November, 1998)

A poly(urethane phosphonate) was obtained via transesterification of phosphonic acid diesters with hydroxyalkyl carbamate based on propylene carbonate and 2-aminoethanol. Thermolysis of the poly(urethane phosphonate) yielded the betain form of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane. The structure of this novel cyclic aminophosphonic acid monoalkylester was established by $^{13}C\{^1H\}$-, ^{31}P- and $^{31}P\{^1H\}$-NMR-spectra supported by Molecular Modeling (MOPAC93 with AM1 and PM3). Stability-and dissociation constants were determined for the protolytic equilibrium (H_2L^+, HL, L^-) involving the betain of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane.

Keywords: phosphonic acid diesters; poly(urethane phosphonate); thermolysis; 1,4,2-oxazaphosphorinane; NMR; molecular modeling; stability constants; dissociation constants

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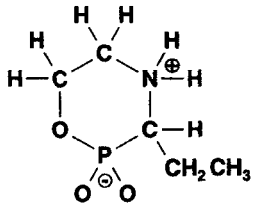
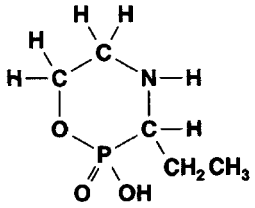
INTRODUCTION

The betain form **1** of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2** represents a cyclic α-aminoalkylphosphonic acid monoalkylester which is a derivative of the open chain α-aminopropane phosphonic acid **3.**



1



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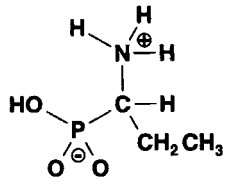
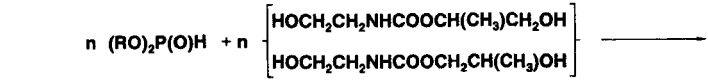
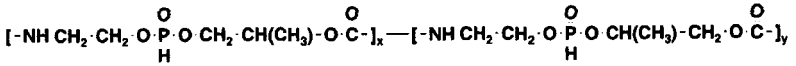


3

3 is a practically relevant member of the wide range of aminophosphonic acids, which are of considerable interest due to biological properties[1] and chelating abilities[2] towards various metal ions. Only a few references exist in the open literature which are devoted to the synthesis,[3] the structure[4] and applications[5] of the parent 1,4,2-oxazaphosphorinane system.

Recently we have shown that a poly(urethane phosphonate) may be obtained via transesterification of dialkylphosphonate with hydroxyalkyl carbamate[6] based on propylene carbonate and 2-aminoethanol as described by **eq. 1**





poly(urethane phosphonate)

At temperatures higher than 160 °C this poly(urethane phosphonate) undergoes a thermal decomposition yielding a polymer (which will not be

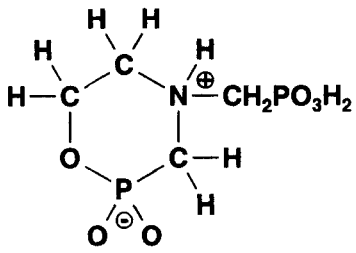
discussed here) and the betain form **1** of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane **2**[7] as shown in **eq. 2:**

Poly(urethane phosphonate) $\xrightarrow[-\,CO_2]{}$ **Polymer + 1**

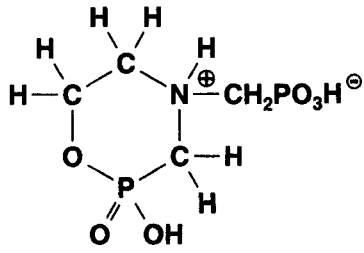
Here we establish unequivocally the structure of this cyclic betain **1** by NMR and Molecular Modeling. Corresponding stability and dissociation constants of the cationic acid $H_2L^+$are reported as well.

Obviously the routes following eqs. **1** and **2** represent a novel synthesis for pure 1,4,2-oxazaphosphorinane derivatives leading to the biorelevant class of α-substituted α-amino-alkanephosphonic acids.

Previous attempts to synthesize 1,4,2-oxazaphosphorinane derivatives via Mannich type reactions lead to complex reaction mixtures.[3e, 4d] From ethanolamine, formaldehyde and phosphorous acid a cyclic bisphosphonic acid was obtained unequivocally having the betain structure **3a** as shown by X-ray diffraction studies[4f] and not **3b.**



3a



3b

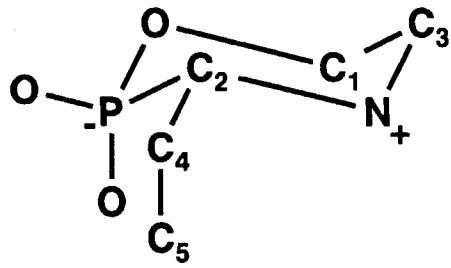
NMR-STUDIES

In the initial phase of our project the structure and purity of the reaction product **1** was derived by NMR methods.

$^{31}P\{^1H\}$-NMR: The D_2O-aqueous solution of **1** gives rise to a neat singlet in $^{31}P\{^1H\}$-NMR situated at δP 9.908 ppm, a value which comes

close to the typical chemical shift of 12.34 ppm[8] for the betain form **3** of α-aminopropane phosphonic acid.

$^{13}C\{^1H\}$- and ^{13}C-NMR: Further evidence is gained by $^{13}C\{^1H\}$- and ^{13}C-NMR: Five individual carbon resonances are identified using a spin labeling given in **Scheme 1** and by data shown in **Table I.**



SCHEME 1 Spin-labeling for ^{13}C-NMR

TABLE I Chemical shifts δ_C [ppm] and coupling constants $^nJ_{PC}$ and $^1J_{CH}$ [Hz] of a 5 % solution of **1** in D_2O. Ref: $(CH_3)_3Si\text{-}CD_2\text{-}CD_2\text{-}COONa$. a) 125.721 MHz Düsseldorf University. b) 100.577 MHz, Tulane University. The spin assignment was checked by DEPT spectra

C_i	$^{13}C\{^1H\}$ *a)*	$^{13}C\{^1H\}$ *a)*		^{13}C *b)*
i	δ_C	$^nJ_{PC}$	n	$^1J_{CH}$
1	65.855	5.4	2	148.1
2	58.857	135.8	1	136.9
3	47.471	3.4	3	144.3
4	24.267	2.3	2	129.5
5	12.900	6.9	3	125.8

^1H- and $^1H\{^{31}P\}$-NMR: The final confirmation of constitution and hints towards the conformation of **1** was derived from ^1H- and $^1H\{^{31}P\}$-NMR studies. The 500 MHz ^1H-NMR of **1** is shown in **Figure 1** below.

The total spectrum is iterated efficiently using the fragmentation concept of WIN-DAISY[9]: two fragments are formed from the total system.

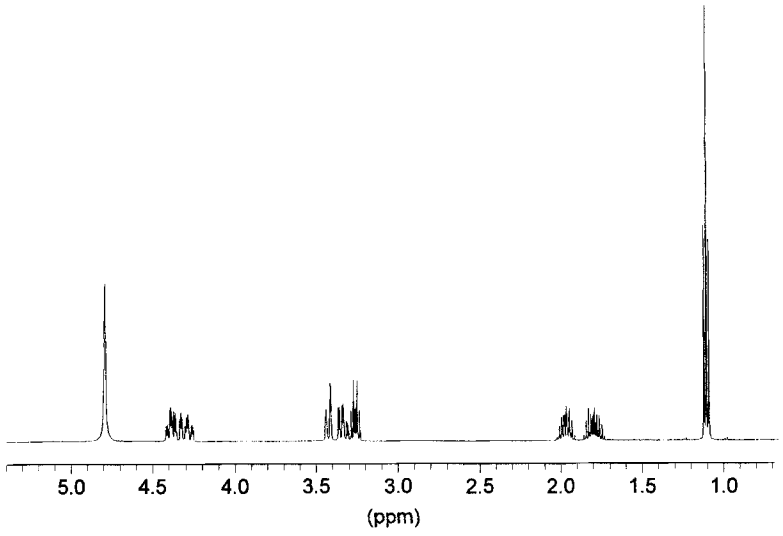
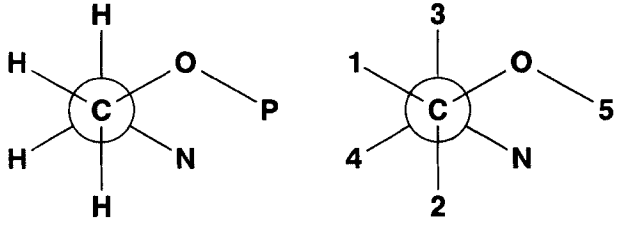


FIGURE 1 Total 500 MHz NMR-spectrum from a 2 % solution of the betain form of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane in D_2O. Singlet at 4.8 ppm: NH_2^+ / D_2O. For other multiplets see text below

Fragment 1 (P-O-CH_2-CH_2) and fragment 2 (P-CH-CH_2-CH_3) are well separated and iterated individually. The fragmentation principle speeds up NMR-calculations for those 7-spin- and 5-spin-sub-systems avoiding the more laborious total 11 spin-problem.

Results from fragment 1:

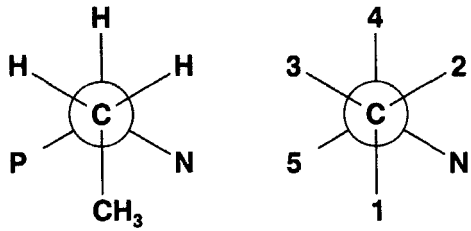


SCHEME 2 Spin labeling for ^{1}H-NMR: Fragment 1 : the P-O-CH_2-CH_2-N unit

TABLE II Results from fragment 1 (P-O-CH_2-CH_2-N unit) by iteration with WIN-DAISY. Chemical shifts δ_i [ppm], coupling constants $^nJ_{ik}$ [Hz], specific spectral half widths HWB_i of protons H_i [Hz]. n.i.: not iterated

Parameter	Type	Results	Error
δ_1	δ_H	4.296	
δ_2	δ_H	4.386	
δ_3	δ_H	3.336	
δ_4	δ_H	3.422	
δ_5	δ_P	9.908	
υ_2	υ_H	2148.77	±0.005
υ_2	υ_H	2193.53	±0.004
υ_3	υ_H	1668.23	±0.005
υ_4	υ_H	1711.39	±0.005
υ_5	υ_P	2005.97	n. i.
J_{12}	$^2J_{HH}$	-13.21	±0.007
J_{13}	$^3J_{HH}$	3.51	±0.006
J_{14}	$^3J_{HH}$	1.97	±0.007
J_{15}	$^4J_{PH}$	20.11	±0.010
J_{23}	$^3J_{HH}$	11.89	±0.006
J_{24}	$^3J_{HH}$	2.16	±0.006
J_{25}	$^4J_{PH}$	4.34	±0.008
J_{34}	$^2J_{HH}$	-13.84	±0.008
J_{35}	$^3J_{PH}$	0.71	±0.011
J_{45}	$^3J_{PH}$	1.48	±0.008
HWB_1	H_1	1.16	±0.008
HWB_2	H_2	1.05	±0.008
HWB_3	H_3	1.17	±0.012
HWB_4	H_4	1.15	±0.012

Results from fragment 2:



SCHEME 3 Spin labeling for ^{1}H-NMR: Fragment 2: the P-CH-CH_2-CH_3 unit

TABLE III Results from fragment 2 (P-CH-CH_2-CH_3 unit) by iteration with WIN-DAISY. Chemical shifts δ_i [ppm], coupling constants $^nJ_{ik}$ [Hz], specific spectral half widths HWB_i of protons H_i [Hz]. n.i.: not iterated

Parameter	*Type*	*Results*	*Error*
δ_1	δ_H	1.106	
δ_2	δ_H	1.795	
δ_3	δ_H	1.967	
δ_4	δ_H	3.258	
δ_5	δ_P	9.908	
υ_1	υ_H	552.88	±0.001
υ_2	υ_H	897.68	±0.004
υ_3	υ_H	983.84	±0.004
υ_4	υ_H	1629.39	±0.003
υ_5	υ_P	2005.97	n. i.
J_{12}	$^2J_{HH}$	7.56	±0.006
J_{13}	$^3J_{HH}$	7.56	±0.006
J_{14}	$^4J_{HH}$	0.00	±0.026
J_{15}	$^4J_{PH}$	-0.01	±0.032
J_{23}	$^2J_{HH}$	-14.18	±0.006
J_{24}	$^3J_{HH}$	7.33	±0.011
J_{25}	$^3J_{PH}$	18.47	±0.008
J_{34}	$^3J_{HH}$	7.67	±0.012
J_{35}	$^3J_{PH}$	9.32	±0.007
J_{45}	$^2J_{PH}$	-11.39	±0.006
HWB_1	H_1	0.98	±0.001
HWB_2	H_2	1.01	±0.009
HWB_3	H_3	1.06	±0.009
HWB_4	H_4	1.16	±0.007

Parameters obtained were used to simulate the 500 MHz NMR spectrum as shown in **Figures 2 to 4** below. The simple triplet structure for the methyl group H_1 in fragment 2 is omitted.

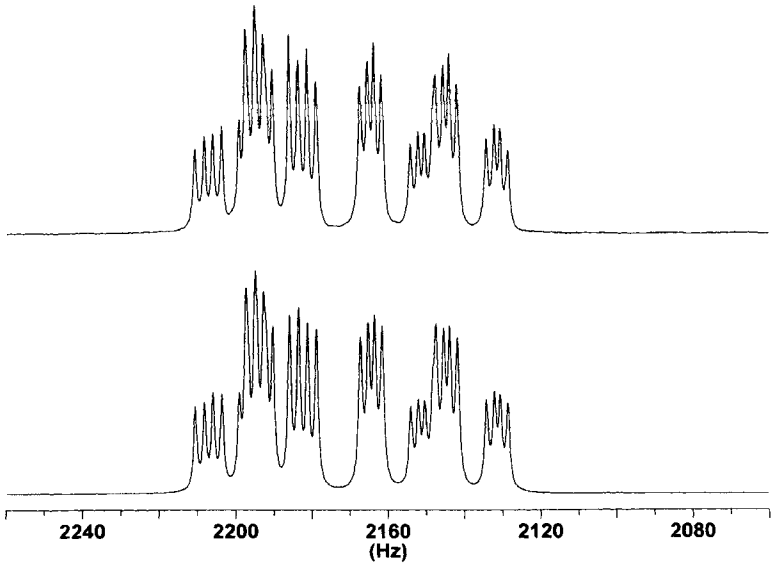


FIGURE 2 500 MHz NMR-spectrum from a 2 % solution of the betain form of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane in D_2O. Window from 2250 to 2060 Hz covering protons H_1 and H_2 from fragment 1 (P-O-CH_2-CH_2-N). Upper: experimental, lower: simulated

MOLECULAR MODELING

Simulations were performed using the semi empirical program MOPAC93[10] with parameter sets AM1[11] and PM3.[12] A standard continuum model[13] was applied taking into account the solvent H_2O. Geometries were optimized without and with fixed dihedral angles C-C-C-N.

While the ring system is more or less rigid the adjacent alkyl group gives rise to intramolecular flexibility. The formation enthalpy of the model system was calculated for the rotation around the C-C-C-N axis of the CH_3-CH_2-CH-NH_2 skeleton. The dihedral angle C-C-C-N was rotated in steps of 30°. Individual rotamers were calculated using the partial optimization technique: the C-C-C-N angle was kept fixed while the rest of the molecule was open to optimization by MOPAC93. Using the parameter set PM3 a minimum of formation enthalpy was found for a dihedral angle of 90° while the parameter set AM1 yielded a slightly smaller dihedral angle of 60° as shown in **Figure 5.**

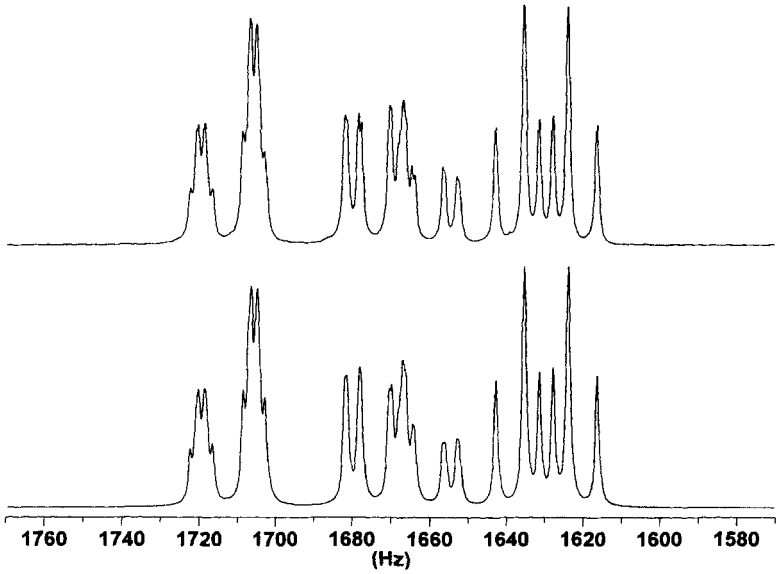


FIGURE 3 500 MHz NMR-spectrum from a 2 % solution of the betain form of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane in D_2O. Window from 1770 to 1570 Hz covering protons H_3 and H_4 from fragment 1 (P-O-CH_2-CH_2-N) and H_4 from fragment 2 (P-CH-CH_2-CH_3). Upper: experimental, lower: simulated

Full optimization of the molecule, which requires considerably more computing time than the faster partial optimization, changes the dihedral angle only slightly. With the parameter set PM3 the C-C-C-N dihedral angle is found to be 75°, while AM1 calculates 60°. According to our experiences the parameter set PM3 yields more realistical simulations for phosphorus containing organic compounds while AM1 suffices for usual CHNO-models.

Figure 6 shows the calculated minimum structure for full optimization with MOPAC93 using the PM3 parameters.

Clearly a situation having the dihedral angle of the P-C-C-CH_3 unit close to trans position is obtained. Data for the heat of formation of 13 specific rotamers for full optimization is calculated varying the dihedral angle C-C-C-N from 0° to 360° in 13 steps of 30°. Results are shown in **Table IV.** Table IV lists the relative enthalpies of rotamers related to the enthalpy of the most stable rotator defined to be zero.

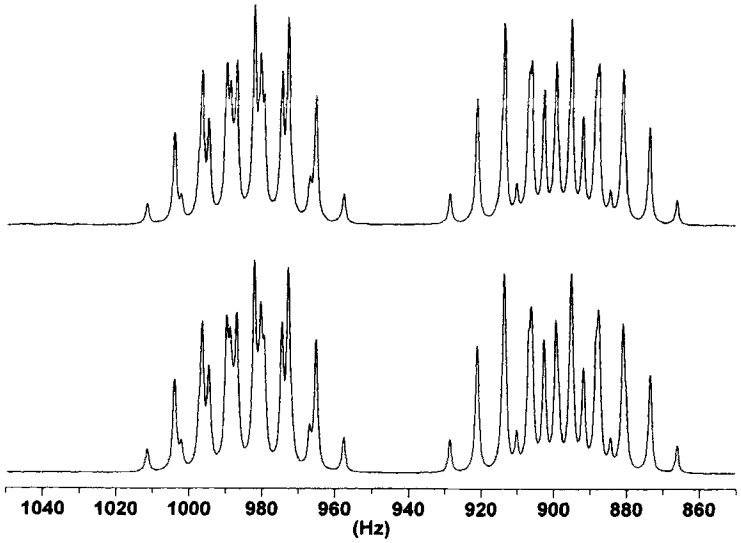


FIGURE 4 500 MHz NMR-spectrum from a 2 % solution of the betain form of 2-Hydroxy-2-oxo-3-ethyl-1,4,2-oxazaphosphorinane in D_2O. Window from 1050 to 850 Hz covering protons H_2 and H_3 from fragment 2 (P-CH-CH_2-CH_3). Upper: experimental, lower: simulated

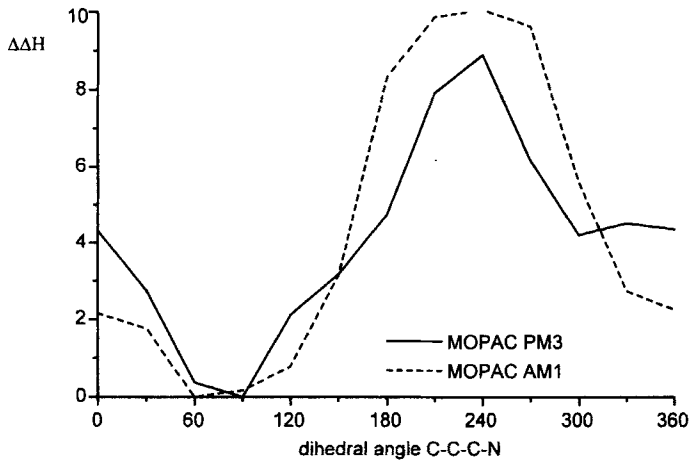


FIGURE 5 Relative potential energies ΔΔH [kcal/mol] as a function of the dihedral angle C-C-C-N, calculated by MOPAC93 using parameter sets PM3 and AM1

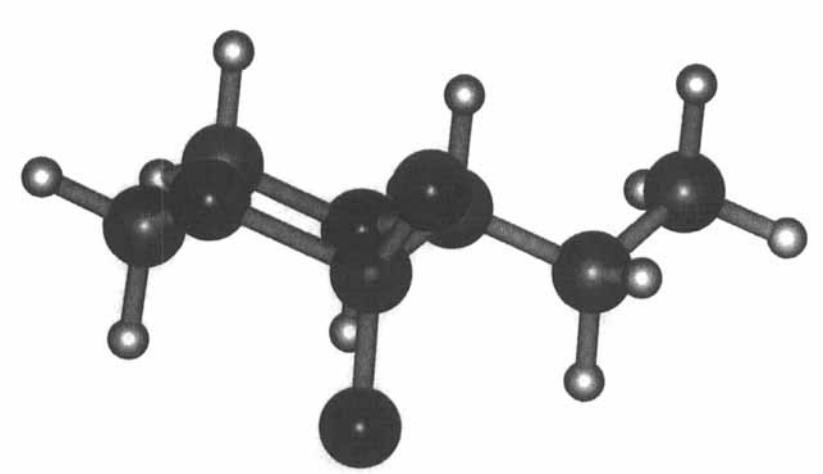


FIGURE 6 Fully optimized structure from MOPAC PM3, dihedral angle C-C-C-N = 75°

TABLE IV Full optimization with MOPAC93 (parameter sets AM1 and PM3). Listed are: a) the starting and final values for the dihedral angles C-C-C-N; b) the heat of formation (ΔH_F)[kcal/mol] and the differences in heat of formation ($\Delta\Delta H_F$) [kcal/mol] relative to the heat of formation of the most stable rotamer which is indicated by bold numbers

Starting angle	*MOPAC PM3*			*MOPAC AM1*		
	ΔH_F	$\Delta\Delta H_F$	*Final angle*	ΔH_F	$\Delta\Delta H_F$	*Final angle*
0	-207.41	0.18	75	-230.39	2.56	-22
30	-207.48	0.11	75	-232.87	0.08	60
60	-207.00	0.59	60	-232.89	0.06	60
90	-207.37	0.22	90	-232.86	0.09	60
120	-207.52	0.07	75	-232.87	0.08	60
150	-207.57	0.02	75	-232.95	**0.00**	60
180	-207.51	0.08	75	-232.92	0.03	59
210	-207.59	**0.00**	75	-222.78	10.17	-113
240	-203.38	4.21	-47	-222.98	9.97	-110
270	-203.29	4.30	-47	-230.46	2.49	-22
300	-203.33	4.26	-47	-230.47	2.48	-22
330	-203.16	4.43	-47	-230.50	2.45	-22
360	-207.39	0.20	75	-230.38	2.57	-22

Molecular dynamics[14] calculations obtained for T = 1000 K are consistent with these results as may be derived from **Figure 7 and Figure 8.**

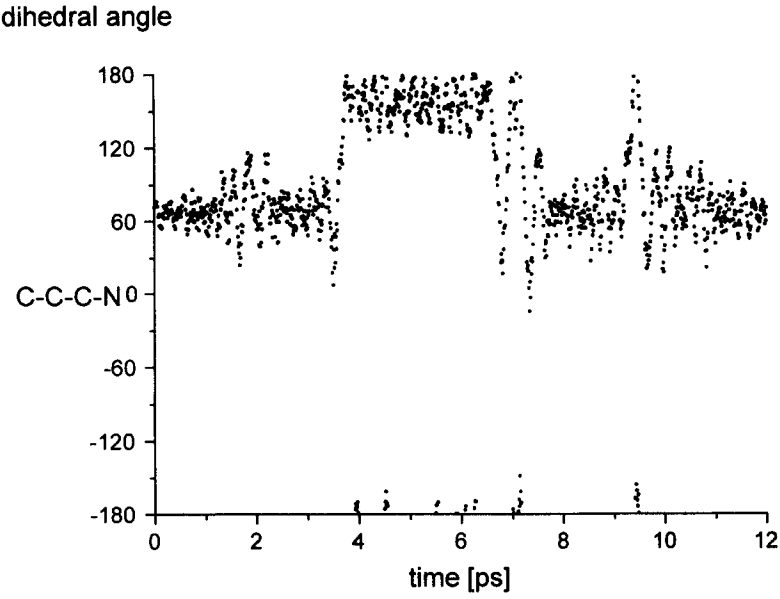


FIGURE 7 Molecular Dynamics calculated for T = 1000 K. Dihedral angle = C-C-C-N

The main population around C-C-C-N is close to 60° with frequent changes to 150° indicating a rotation around the dihedral angle of P-C-C-CH_3 from gauche to trans. Changes in the dihedral angle of O-C-C-N from +60° to −60° point towards ring inversion for the hypothetical temperature of T = 1000K.

ANALYTICAL STUDIES

To understand the acid-base behavior of **1,** the betain form of 3-ethyl-2-hydroxy-1,4,2-oxazaphosphorinane, stability and dissociation constants were determined via high precision volume-equidistant titration of **1** vs. 0.1 n NaOH. The titration status was monitored by glass electrode which was calibrated by blank titration (HCl/NaOH).

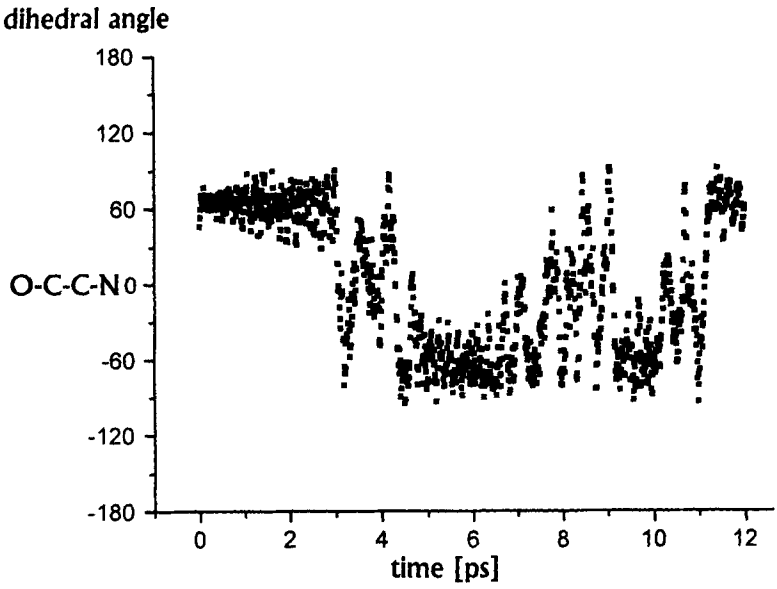


FIGURE 8 Molecular Dynamics calculated for T = 1000 K. Dihedral angle = O-C-C-N

The betain form of 3-ethyl-2-hydroxy-1,4,2-oxazaphosphorinane **1** behaves like the neutral HL form of a typical two-basic cationic acid of type H_2L^+ similar to monoesters of amino phosphonic acids. Stability constants were found as logβ_1 12.64 ± 0.03 and log β_2 19.88 ± 0.03 resp. Dissociation constants were calculated as pKs_1 7.24 ± 0.06 and pKs_2 12.64 ± 0.03 resp. The first dissociation takes place on the POH function, while the se- cond is governed by deprotonation of the NH_2^+ unit of the oxazaphosphorinane ring system **1.** These findings are consistent with data for the second and third dissociation steps from the parent compound, the open chain α-amino-propane phosphonic acid **2:** pKs_1 0.62; pKs_2 5.53; pKs_3 10.46 resp.[8] NMR.-controlled titrations[8] of this model system showed, that the deprotonation sequence follows a route given by: $CH_3CH_2CH(NH_3^+)PO_3H_2 \rightarrow CH_3\text{-}CH_2CH(NH_3^+)PO_3H^- \rightarrow CH_3CH_2CH(NH_3^+)PO_3^{2-} \rightarrow CH_3CH_2CH(NH_2)PO_3^{2-}$.

EXPERIMENTAL

Synthetic studies

A mixture of diethylphosphonate and hydroxyalkyl carbamate based on propylene carbonate and 2-aminoethanol, in molar ration 1:1 was heated at 150 °C for 3 h and after that at 160 °C for 4 h. The betain form of 3-ethyl-2-hydroxy-2-oxo-1,4,2-oxazaphosphorinane was separated with absolute methanol. The colorless product is insoluble in methanol but dissolves readily in water. It decomposes at 303 °C when heated.

NMR-studies

All spectra were recorded at 300 K on a Bruker DRX 500 spectrometer operating at 500 MHz for protons. D_2O was used as an internal lock; the sodium salt of 2,2,3,3,-tetradeutero-3-(trimethylsilyl)-propionic acid served as an internal reference for ^{1}H and ^{13}C. 85% phosphorus acid served as an external reference for ^{31}P. For ^{1}H NMR-spectra, the spectral width was set to 4000 Hz with 64K points leading to a digital resolution of ≤ 0.1 Hz per point and an acquisition time of 8.2 s. The spectral width for ^{13}C-NMR-spectra was chosen to 12500 Hz with 64K points resulting in a digital resolution of ≤ 0.2 Hz per point and an acquisition time of 2.6 s. ^{31}P NMR-spectra were recorded with 128K points with a spectral width of 15150 Hz and an acquisition time of 4.3 s leading to a digital resolution of ≤ 0.12 Hz per point. The FID was left unchanged for subsequent Fourier transformation. Iteration with WINDAISY[9]: By using intervals (spectral windows) the total of 64K spectral points was reduced effectively to 8454 points. Both fragments were iterated simultaneously. The total fit is characterized by the following parameters: Final sum of squares 3.431339. Number of spectral points 8454. Degrees of Freedom 8418. Standard Deviation of measurements 0.020190. R-Factor (%) 0.286052. Calculation time 4 min. 23 seconds computed on a Pentium-Pro-System operating with 200 MHz. We wish to point out the methodical progress made be introducing the fragmentation principle for larger spin systems.

Analytical studies

Apparatus and programs

PC-guided titration equipment consisting of: program system MINI_T4.01, developed in Düsseldorf,[15] IBM-compatible PC (286 type), pH-meter CG 841*, motor burette T 200*, temperature controlled titration vessel, Pt-resistance thermo sensor Pt 1000*, reference electrode B 3520* (Ag/AgCI) and glass electrode H 2680*. (*SCHOTT-GERÄTE GmbH, Hofheim a. Ts., Germany). Titration data were iterated using the program system ITERAX[16] developed in Düsseldorf.

Reagents

0.1 mol NaOH ("Fixanal"® Riedel-de-Haën), 0.1 mol HCl ("Fixanal"® Riedel-de-Haën), quartz-bi-dist. water. Calibration via Na_2CO_3 (Merck) and potassium hydrogenphthalate (Merck). Ionbuffer I = 0.5; 14.61 g NaCI/500 ml.

Blank titration

A mixture of 10 ml 0.10084 N HCl, 10 ml 0.5M NaCI (I = 0.5) and 30 ml quartz-bi-dist. H_2O, was titrated vs. 0.10109 N NaOH in equidistant steps (ΔV = 0.05 ml) until a maximum volume of titrator of 15 ml. Temperature: 25.0°C. The electrode parameters for the extended Nernst equation ($E = E_o - \sigma\, pH + j_H\, c_H + j_{OH}\, c_H / k_W$) were calculated using ITERAX[16]: E_o = 402.903 [mV], σ = 58.917 [mV], j_H = −84.113 [mV/mol], j_{OH} = 740.548 [mV/mol], pK_W = 13.78.

Stability and dissociation constants

ca. 50 mmol of **1**, 10 ml 0.5 M NaCl, 5 ml 0.10084 N HCl and 35 ml quartz-bi-dist. water were combined to make a starting volume of titrand of 50 ml. The titrator, 0.10109 N NaOH, was added in equidistant steps (ΔV = 0.05 ml) until a maximum volume of 18 ml. Temperature: 25.0°C. Stability constants were calculated via ITERAX.[16]. Results are given as averages from 3 experiments.

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