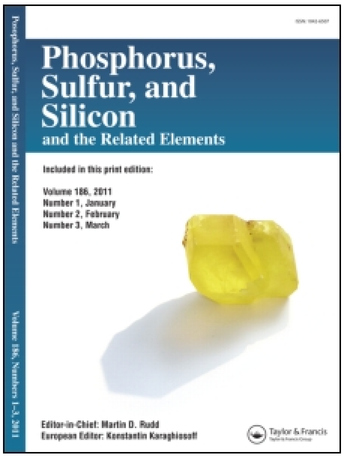

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND PHYSIOLOGICAL ACTIVITIES OF NEW ACYCLIC AMINOPHOSPHONATES

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To cite this Article Wieczorek, J. S. , Gancarz, R. , Bielecki, K. , Grzyś, E. and Sarapuk, J.(2000) 'SYNTHESIS AND PHYSIOLOGICAL ACTIVITIES OF NEW ACYCLIC AMINOPHOSPHONATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 166: 1, 111 — 123

To link to this Article: DOI: 10.1080/10426500008076535

URL: http://dx.doi.org/10.1080/10426500008076535

Phosphorus, Sulfur and Silicon, 2000, Vol. 166, pp. 111-123
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SYNTHESIS AND PHYSIOLOGICAL ACTIVITIES OF NEW ACYCLIC AMINOPHOSPHONATES

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(Received June 20, 2000)

The dependence of biological activity of 37 newly synthesized acyclic aminomethanephosphonic acid derivatives on their structure was studied. It was found that the phytotoxicity of the compounds studied depended on their hydrophobic parameters, and in a smaller extent on the electronic parameters of the substituents on nitrogen and phosphorus atoms. No phytotoxicity dependence on the steric parameters of compounds was found. Tested organism was *Spirodela oligorrhiza* and the parameter studied was the concentration of compounds causing 50 % growth inhibition (EC_{50}). The test had preliminary character and permitted to eliminate the less promising compounds out of further studies.

Keywords: Aminophosphonates; Synthesis; Physiological activity

INTRODUCTION

a-Aminophosphonates, i.e. derivatives of aminomethanephosphonic acid compounds of general structure:

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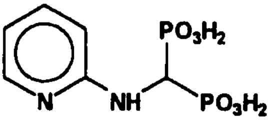
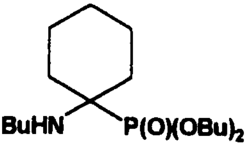
were described in the literature for the first time in 1943 by Pikl[1]. Very soon after Chavane predicted their existence in nature. His findings were written in papers after his death in 1947–1949[2–6].

The discovery of glyphosate[7] (N-phosphonomethylglycine) in 1971, and the finding that aromatic aminoacid synthesis in plant is affected by this compound[8], was a milestone in rational design of herbicides and initiated a synthesis of thousands of glyphosate derivatives, homologues and analogues[9] of the following structure:

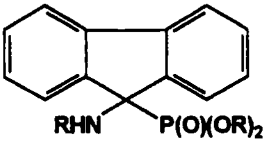
Next a new class of herbicides was first synthesized in Japan in 1979. They are derivatives of aminomethylenebisphosphonic acids[10–11] of general formula as follows:



Although some attempts were undertaken to define their mechanism of action[11–13] it still remains not resolved. The same conclusion applies to Trakephon (N-n-butylaminocyclohexane phosphonic acid dibutyl ester), a representative of another class of aminophosphonic herbicides which was found to exhibit herbicidal activity and the mechanism of in activity is to be determined yet[14]



Next an interesting class of plant growth regulators[15–28]are the aminophosphonic acid derivatives of fluorene of general structure:



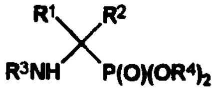
We have been studying this class of compounds since 1974. Some of the compounds we have synthesized happen to be highly active biologically; an activity comparable to the known herbicide gluphoshate. In conclusion of our recent paper on that topic[28] we stated that the biological activity of the tested compounds strongly correlates with their lipophilic character and is almost independent on their steric or electronic factors. In this aspect they resemble Trakephon. So, one can assume that probably their action is connected with the disruption of the function of plant membranes.[29–30]

We also know from our previous studies that derivatives of 1-amino-1-methylethanephosphonic acid, exhibit some herbicidal activity.[1] Physiological activity of a series of related compounds is routinely examined to define the structural requirements of target receptors. Thus in trying to understand better the mode of action of this class of compounds we have synthesized 37 acyclic derivatives of aminomethanephosphonic acid, and determined the influence of the structural variations of substitution at nitrogen, carbon and phosphorus on their herbicidal activity. In our future experiments we plan to study their effect on the plant membrane. Some of the tested compounds were found to exhibit strong herbicidal activity. In some cases their effect was similar to that observed for the popular herbicide glyphosate as well as Trakephon.

MATERIALS AND METHODS

The compounds were synthesized by standard method, described by us previously. Heating the carbonyl compound with the corresponding amine yielded an imine which was used without purification in the next step. After addition of dialkyl phosphite to the imine the reaction mixture was heated for several hours at elevated temperature. The final product was isolated and purified by column chromatography. All experimental data are given in the experimental part.

TABLE I Synthesized acyclic aminophosphonates and the values of their effective concentrations causing 50% inhibition of growth of Spirodela oligorrhiza (EC_{50})



Comp. No.	EC_{50}	R^1	R^2	R^3	R^4
1	>1.0E-4	CH_3	CH_3	n-C_4H_9	C_2H_5
2	>1.0E-4	CH_3	CH_3	n-C_4H_9	CH_3
3	>1.0E-4	CH_3	CH_3	n-C_4H_9	i-C_3H_7
4	>1.0E-4	CH_3	C_2H_5	n-C_4H_9	C_2H_5
5	>1.0E-4	CH_3	CH_3	n-C_4H_9	n-C_4H_9
6	7.9E-5	CH_3	C_2H_5	n-C_4H_9	n-C_4H_9
7	>1.0E-4	CH_3	C_2H_5	n-C_4H_9	i-C_3H_7
8	>1.0E-4	CH_3	C_2H_5	n-C_4H_9	CH_3
9	6.6E-5	CH_3	n-C_4H_9	n-C_4H_9	n-C_4H_9
10	6.9E-5	C_2H_5	C_2H_5	n-C_4H_9	n-C_4H_9
11	6.4E-5	n-C_3H_7	n-C_3H_7	n-C_4H_9	n-C_4H_9
12	6.1E-5	CH_3	n-C_3H_7	n-C_4H_9	n-C_4H_9
13	>1.0E-4	CH_3	n-C_4H_9	C_6H_{11}	C_2H_5
14	9.3E-5	C_2H_5	n-C_4H_9	n-C_4H_9	i-C_3H_7
15	1.2E-4	CH_3	n-C_5H_{11}	n-C_4H_9	CH_3
16	>1.0E-4	CH_3	CH_3	n-C_4H_9	C_6H_{11}
17	>1.0E-4	n-C_4H_9	n-C_4H_9	n-C_4H_9	C_2H_5
18	>1.0E-4	CH_3	n-C_5H_{11}	n-C_4H_9	C_2H_5
19	1.0E-4	CH_3	n-C_3H_7	Furyl	n-C_4H_9
20	5.8E-6	CH_3	n-C_4H_9	n-C_3H_7	n-C_4H_9
21	5.9E-5	CH_3	n-C_4H_9	i-C_4H_9	n-C_4H_9
22	2.5E-6	CH_3	n-C_4H_9	n-C_8H_{17}	n-C_4H_9
23	4.2E-6	CH_3	n-C_4H_9	n-C_6H_{13}	n-C_4H_9
24	6.5E-5	CH_3	n-C_5H_{11}	n-C_4H_9	n-C_4H_9
25	1.0E-5	CH_3	n-C_4H_9	n-$C_{14}H_{29}$	n-C_4H_9
26	8.6E-5	CH_3	n-C_4H_9	n-$C_{10}H_{21}$	n-C_4H_9
27	8.0E-6	CH_3	CH_3	n-$C_{10}H_{21}$	n-C_4H_9
28	1.0E-7	CH_3	CH_3	n-C_8H_{17}	n-C_4H_9
29	8.6E-7	CH_3	C_2H_5	n-C_8H_{17}	n-C_4H_9
30	1.8E-6	CH_3	n-C_5H_{11}	n-C_8H_{17}	n-C_4H_9
31	8.5E-6	CH_3	CH_3	n-C_8H_{17}	i-C_3H_7
32	6.6E-6	CH_3	i-C_4H_9	n-C_8H_{17}	i-C_3H_7
33	6.5E-5	CH_3	CH_3	n-$C_{14}H_{29}$	n-C_4H_9
34	4.8E-5	CH_3	n-C_4H_9	n-$C_{10}H_{21}$	i-C_3H_7
35	8.8E-6	CH_3	CH_3	n-$C_{10}H_{21}$	i-C_3H_7
36	>1.0E-4	CH_3	t-C_4H_9	n-$C_{10}H_{21}$	n-C_4H_9
37	>1.0E-4	CH_3	n-C_4H_9	n-C_5H_{11}	n-C_4H_9

Studies on physiological activity of the investigated compounds were done on *Spirodela oligorrhiza* (Knypl *et al.*, 1976; Skrabka and Jaskulska, 1987). Two equal fronds were placed in Erlenmayer flask containing modified Hoagland's solution (Czerwiński *et al.*, 1982). The plants were cultivated under constant illumination 120 μE m^{-2} s^{-1} at 25°C. After 8 days the dry weight of the plants was determined. Biomass data was expressed as percent control response. Calculation of the effective concentrations resulting in 50% growth inhibition (EC_{50}) compared to controls were calculated using non-linear regression (VanEwijk and Hoekstra, 1993). All synthesized compounds had the general structure given in Table I.

RESULTS AND DISCUSSION

The values of concentrations of studied aminophosphonates inhibiting growth of *Spirodela roligorhiza* to 50% changed between 10^{-4} and 10^{-7} M. These last values of EC_{50}, evidencing a very high physiological activity, were obtained for compounds with two butyl groups on the phosphorus atom and long enough alkyl chains on nitrogen and carbon atoms (for example, see compounds nos 23, 28, 29 or 31 in Tab. 1). Obvious conclusion is that the more hydrophobic the compound is the better is its phytotoxicity. Contrary, compounds of diminished hydrophobicity (for instance see compounds nos 1–5 or 17–19) exhibited decreased phytotoxic activity. This conclusion points to the lipid phase of biological membranes as a place where the interaction of the compound studied takes place.

It also agrees with the results of studies on the interaction of biologically active quaternary ammonium salts (quats) with model lipid and biological membranes[33–35], where the efficacy of that interaction was found to be directly connected with lipophilic properties of quats.

EXPERIMENTAL

All NMR spectra were taken on a Bruker Avance DRX 300 MHz instrument operating at 300.13 MHz (^1H) and 121.499 (^{31}P). IR spectra and elemental analysis were performed at the Institute of Organic Chemistry, Biochemistry and Biotechnology.

IMINE SYNTHESIS

Method a)

Carbonyl compound and corresponding amine were mixed in a molar ratio of 1:1.1 and dry potasium carbonate added. After 1 hr the product was filtered and the residue was evaporated on a warm water bath under reduced pressure. In all cases the product was pure enough for analysis and was used for aminophosphonate synthesis without further purification.

Method b)

For low reacting carbonyl compounds a mixture of carbonyl compound with a 2–3 fold excess of butylamine and a catalytic amount of aluminium chloride was refluxed for a period of 2–3 hrs. Reaction was monitored by taking the IR spectra. When the reaction was completed the mixture was dissolved in dry ethyl ether, dried over potasium carbonate, filtered and evaporated from a hot water bath under reduced pressure. The obtained imine was used without further purification.

AMINOPHOSPHONATE SYNTHESIS

A mixture of imine and diethyl phosphite was heated at 70°C until the imine disappeared (by TLC method). It takes about 2–5 hrs. Then the mixture was dissolved in dry acetone to which the acetone solution of anhydrous oxalic acid was added and the mixture was kept at low temperatures. The oxalate was filtered off, and aqueous ammonia was added followed by extraction of the free aminophosphonate with ether or chloroform. After drying over potasium carbonate the solvent was removed and the residue was crystallized. In the cases of noncrystalline aminophosphonates they were used without further purifications or their oxalates were crystallized before converting them to the free aminophosphonates.

1. $C_{11}H_{26}NO_3P$; Diethyl ester of 1-methyl-1-N-(n-butylamino) ethanephosphonic acid; mp. 137–140°C, yield 78 %; ^{1}H-NMR ($CDCl_3$), 4.15–4.05 (m, 4H, $C\underline{H}_2$-O); 2.66 (t^*d, 2H, $C\underline{H}_2$-N, J_{HH}=7.1 Hz, 1 Hz); 1.5–1.3 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_2$-N); 1.28 (t, 6H, O-$CH_2$-$C\underline{H}_3$, 6.9 Hz); 1.25

(d, 6H, $C\underline{H}_3CCH_3$, J_{HP}=17.4 Hz); 0.86 (t, 3H, $C\underline{H}_3CH_2CH_2CH_2$-N, J_{HH}=7.1 Hz)

2. $C_9H_{22}NO_3P$; Dimethyl ester of 1-methyl-1N-(n-butylamino) ethanephosphonic acid; mp. 116–122°C, yield 78,%; ^{1}H-NMR ($CDCl_3$): 3.73 (d, 6H, $C\underline{H}_3$-O, J_{HP}=10.2 Hz); 2.63 (t, 2H, $C\underline{H}_2$-N, J_{HH}=6.9 Hz); 1.3–1.5 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_2$-N); 1.25 (d, 6H, $C\underline{H}_3$-C, J_{HP}=16 Hz); 0.85 (t, 3H, $C\underline{H}_3CH_2CH_2CH_2$-N, J_{HH}=7 Hz)

3. $C_{13}H_{30}NO_3P$; Diisopropyl ester 1-methyl-1-N-(butylamino) ethanephosphonic acid; mp. 132–133°C; yield 96,36%; ^{1}H-NMR ($CDCl_3$): 4.83–4.7 (m, 2H, $C\underline{H}$-O); 3.12 (t, 2H, $C\underline{H}_2$-N, J_{HP}=7.7 Hz); 1.35 (d, 6H, $C\underline{H}_3CH$-O, J_{HH}=6.0 Hz); 1.42–1.28 (m, 2H, $CH_3C\underline{H}_2CH_2CH_2$-N); 0,86 (t, 3H, $C\underline{H}_3CH_2CH_2CH_2$-N, J_{HH}=7.3 Hz)

4. $C_{12}H_{28}NO_3P$; Diethyl ester 1-methyl-1N-(n-butylamino) propanephosphonic acid; mp. 117–118°C; yield 80 %; ^{1}H-NMR($CDCl_3$): 4.11–4.04 (m, 4H, $C\underline{H}_2$-O), 2.7–2.55 (m, 2H, $C\underline{H}_2$-N), 1.73–1.58 (m, 2H, $CH_3C\underline{H}_2$-C), 1.5–1.3 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_2$-N), 1.28 (t, 6H, $C\underline{H}_3CH_2$-O, J_{HH}=7.1 Hz); 1.21 (d, 3H, $C\underline{H}_3$-C, J_{HP}=16 Hz), 0.87 (t, 3H, $C\underline{H}_3CH_2$-C, J_{HH}=7.1 Hz)

5. $C_{15}H_{34}NO_3P$; Dibutyl ester of 1-methyl-1-N (n- butylamino) ethanephosphonic acid; mp. 113–116°C; yield: 69%; ^{1}H-NMR: 4.29–4.13 (m, 4H, O-$C\underline{H}_2$); 3.12 (t, 2H, NH-$C\underline{H}_2$ J_{HH}=7.1Hz); 1.69–1.55 (m, 6H, O-$CH_2C\underline{H}_2$, NH-$CH_2C\underline{H}_2$); 1.5–1.37 (d, 6H, O-$CH_2CH_2C\underline{H}_2$, NH-$CH_2CH_2C\underline{H}_2$, J_{HP}=15.3 Hz); 1.35–1.32 (m, 6H, C-$C\underline{H}_3$); 0.88–0.84 (t, 9H, NH-$(CH_2)_3C\underline{H}_3$, $O(CH_2)_3C\underline{H}_3$)

6. $C_{16}H_{36}NO_3P$; Dibutyl ester of 1-methyl-1-N-(n-butylamino) propanephosphonic acid; mp. 124–126°C; yield 69.87%; ^{1}H-NMR ($CDCl_3$): 4.07–3.92 (m, 4H, $C\underline{H}_2$-O), 2.71–2.55 (m, 2H, CH_2-N), 1.79–1.60 (m, 2H, $C\underline{H}_2$-N), 1.79–1.60 (m, 2H, $C\underline{H}_2$-C), 1.62 (q, 4H, $C\underline{H}_2CH_2$-O, J_{HP}=7.5 Hz), 1.45–1.25 (m, 8H, $C\underline{H}_2CH_2CH_2$-O, $C\underline{H}_2C\underline{H}_2CH_2$-N), 1.24 (d, 3H, $C\underline{H}_3$-C, J_{HP}=16 Hz), 0.96–0.88 (m, 12H, $C\underline{H}_3CH_2$-C, $C\underline{H}_3CH_2CH_2CH_2$-O, $C\underline{H}_3CH_2CH_2CH_2$-N)

7. $C_{14}H_{32}NO_3P$; Diisopropyl ester of 1-methyl-1-N-(n-butylamino) propanephosphonic acid; mp.91–97°C; yield 66%; ^{1}H-NMR: 4.85–4.75 (m, 2H, $C\underline{H}_2$-N), 3.13 (t·d, 2H, $C\underline{H}$-O, J_{HH}=7 Hz, J_{HH}=7.2 Hz), 2.05–1.85 (m, 2H, $C\underline{H}_2CH_2$-N), 1.65–1.55 (m, 2H, $C\underline{H}_2CH_2CH_2$-N), 1.50 (d, 3H, $C\underline{H}_3$-C, J_{HP}=18.3 Hz), 1.41–1.29 (m, 2H, $CH_3C\underline{H}_2$-C), 1.36 (d, 6H, $C\underline{H}_3CH$-O, J_{HH}=6Hz), 1.00 (t, 3H,$C\underline{H}_3CH_2CH_2CH_2$-N, J_{HH}=7.4 Hz), 0,86 (t, 3H, $C\underline{H}_3CH_2$-C, J_{HH}= 7.3 Hz)

8. $C_{11}H_{24}NO_3P$; Dimethyl ester of 1-methyl-1-N-(n-butylamino) propanephosphonic acid; mp. 95–99°C; yield 55%, ^{1}H-NMR ($CDCl_3$): 3.77 (d, 6H, $C\underline{H}_3$-O, J_{HP}=10.2 Hz), 2.7–2.6 (m, 2H, $C\underline{H}_2$-N), 1.78–1.56 (m, 2H, $C\underline{H}_2$-C), 1.4–1.2 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_2$-N, 1.23 (d, 3H, $C\underline{H}_3$-C, J_{HP}=16.2 Hz), 0.9–0.8 (m, 6H, $C\underline{H}_3CH_2$-C, $C\underline{H}_3CH_2CH_2CH_2$-N)

9. $C_{18}H_{40}NO_3P$; Dibutyl ester of 1-methyl-1-N-(n-butylamineo) pentanephosphonic acid; mp. 95–101°C; yield 53%; ^{1}H-NMR ($CDCl_3$): 4.12–3.97 (m, 4H, $C\underline{H}_2$-O), 2.73–2.59 (m, 2H, $C\underline{H}_2$-N), 1.73–1.60 (m, 6H, $C\underline{H}_2CH_2$-O, $C\underline{H}_2$-C), 1.47–1.27 (m, 12H, $C\underline{H}_2C\underline{H}_2CH_2$-C, $C\underline{H}_2CH_2CH_2$-O, $C\underline{H}_2CH_2CH_2$-N), 1.24 (d, 3H, CH_3-C, J_{HP}=16.1 Hz), 0.97–0,88 (m, 12H, $C\underline{H}_3CH_2CH_2CH_2$-C, $C\underline{H}_3C\underline{H}_2CH_2CH_2$-O, $C\underline{H}_3CH_2CH_2CH_2$-N)

10. $C_{17}H_{38}NO_3P$; Dibutyl ester of 1-ethyl-1-N-(n-butylamino) propanephosphonic acid; mp. 99–102°C; yield 36%; ^{1}H-NMR ($CDCl_3$): 4.11–4.02 (m, 4H, $OC\underline{H}_2$); 2.68 (t, 2H, $NC\underline{H}_2$, J_{HH}=6.5 Hz); 1.71–1.62 (m, 8H, $OCH_2C\underline{H}_2$, C-$C\underline{H}_2$); 1.44–1.34 (m, 8H, $OCH_2CH_2C\underline{H}_2$, $NCH_2C\underline{H}_2C\underline{H}_2$); 0.98–0.89 (m, 15 H, C-$CH_2C\underline{H}_3$, $NCH_2CH_2CH_2C\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$)

11.$C_{19}H_{42}NO_3P$; Dibutyl ester of 1-n-propyl-1-N -(n-butylamino) butanephosphonic acid; mp. 138–141°C; yield 76%; ^{1}H-NMR ($CDCl_3$): 4.08–4.01 (m, 4H, $OC\underline{H}_2$); 2.66 (t, 2H, $NC\underline{H}_2$, J_{HH}=6.3 Hz); 1.66–1.59 (m, 8H, C-$C\underline{H}_2$, $OCH_2C\underline{H}_2$); 1.44–1.36 (m, 12H, C-$CH_2C\underline{H}_2$, $NCH_2C\underline{H}_2C\underline{H}_2$, $OCH_2CH_2C\underline{H}_2$); 0.94–0.91 (m, 15H, C-$CH_2CH_2C\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$, $NCH_2CH_2CH_2C\underline{H}_3$)

12. $C_{17}H_{38}NO_3P$; Dibutyl ester of 1 – methyl –1-N-(n-butylamino) butanephosphonic acid; mp. 68 – 71°C; yield 58%; ^{1}H-NMR ($CDCl_3$): 4.02–3.97 (m, 4H, O-$C\underline{H}_2$); 2.8–2.6 (m, 2H, N-$C\underline{H}_2$); 1.62–1.54 (m, 6H, O-$CH_2C\underline{H}_2$, C-$C\underline{H}_2$); 1.37–1.23 (m, 10H, O-$CH_2CH_2C\underline{H}_2$, N-$CH_2C\underline{H}_2C\underline{H}_2$, C-$CH_2C\underline{H}_2$); 1.20 (d, 3H, C-$C\underline{H}_3$, J_{HP}= 16.2 Hz); 0.90–0.83 (m, 12H, O-$CH_2CH_2CH_2C\underline{H}_3$, N-$CH_2CH_2CH_2C\underline{H}_3$, C-$CH_2CH_2C\underline{H}_3$)

13. $C_{17}H_{38}NO_3P$; Diethyl ester of 1-methyl-1-N-(cyclohexylamino) propanephosphonic acid; oil; yield – 35%; ^{1}H-NMR: 3.94–4.03 (m, 4H, $OC\underline{H}_2$); 2.51–2.62 (m, 2H, $NC\underline{H}_2$); 1.48–1.62 (m, 6H, $OC\underline{H}_2CH_2$, C-$C\underline{H}_2$); 1.20–1.40 (m, 10 H, C-$CH_2C\underline{H}_2C\underline{H}_2$, $NCH_2C\underline{H}_2$, $OCH_2CH_2C\underline{H}_2$); 1.17 (d, 3H, C-$C\underline{H}_3$, J_{HP}=16,1 Hz); 0.87 (t, 9H, $OCH_2CH_2CH_2C\underline{H}_3$, $NCH_2CH_2C\underline{H}_3$, J=7.3 Hz); 0.84 (t, 3H, C-$CH_2CH_2CH_2C\underline{H}_3$, J=7.1 Hz)

14. $C_{16}H_{36}NO_3P$; Diisopropyl ester of 1-methyl-1-N-(n-butylamino) pentanephosphonic acid; oil; Yield 41%; ^{1}H-NMR ($CDCl_3$): 4.66 – 4.79 (m, 2H, O-C$\underline{H}$); 2.60 – 2.80 (m, 2H, N-C$\underline{H}_2$); 1.75 – 1.27 (m, 10 H, C-$CH_2CH_2CH_2$, N-CH$_2$C$\underline{H}_2$CH$_2$); 1.33 (d, 12H O-CHC$\underline{H}_3$ J_{HH}=6.1); 1.24 (d, 3H, C-C$\underline{H}_3$ J_{HP} = 16 Hz); 0.92 (t, 3H, C-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$ J_{HH}=6.7 Hz); 0.91 (t, 3H, N-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, J_{HH}=7.1 Hz)

15. $C_{12}H_{28}NO_3P$; Dimethyl ester of 1-N-(n-butylamino) hexanephosphonic acid; oil; yield 90%; ^{1}H-NMR (CDCl): 3.80 (d, 3H, O-C$\underline{H}_3$, J_{HP}=10.3 Hz); 3.79 (d, 3H, O-C$\underline{H}_3$, J_{HP}=10.3 Hz); 2.6–2.75 (m, 2H, N-C$\underline{H}_2$), 1.55–1.85 (m, 2H, C-C$\underline{H}_2$); 1.5–1.3 (m, 8H, N-CH$_2$C$\underline{H}_2$C$\underline{H}_2$, C-CH$_2$C$\underline{H}_2$C$\underline{H}_2$); 1.28 (d, 3H, C-C$\underline{H}_3$, J_{HP}=16.3 Hz); 0.93 (t, 3H, N-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, J_{HH}=6.7 Hz); 0.92 (t, 3H, C-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$ J_{HH}=6.9 Hz)

16. $C_{19}H_{26}NO_3P$; Diphenyl ester of 1-methyl-1-N-(n-butylamino ethanephosphonic acid; mp. 185–187°C; yield: 50%; ^{1}H-NMR ($CDCl_3$): 7.30–6.90 (m, 10H, Ar-$\underline{H}$); 2.63 (t, 2H, N-C$\underline{H}_2$, J_{HP}=7.2 Hz); 1.80 (t^*t, 2H, N-CH$_2$C$\underline{H}_2$, J_{HH}=7.2 Hz, J_{HH}=7 Hz); 1.52 (d, 6H, C-C$\underline{H}_3$, J_{HP}=13.6 Hz); 1.16 (t^*q, 2H, N-CH$_2$CH$_2$C$\underline{H}_2$, J_{HH}=7.3 Hz, J_{HH}=7.3 Hz); 0.79 (t, 3H, N-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, J_{HH}=7.3 Hz);

17. $C_{17}H_{38}NO_3P$; Diethyl ester of 1-n-butylo-1N- (n-butylamino) pentanephosphonic acid; mp. 87–89.5°C, yield 47%; ^{1}H-NMR (oxalate D_2O): 4.3–4.15 (m, 4H, O-C$\underline{H}_2$); 3.11 (t, 2H, N-C$\underline{H}_2$, J_{HH}=7 Hz); 2.05–1.7 (m, 4H, C-C$\underline{H}_2$); 1.7–1.5 (m, 2H, N-CH$_2$C$\underline{H}_2$); 1.4–1.2 (m, 16H, O-CH$_2$C$\underline{H}_3$, C-CH$_2$C$\underline{H}_2$C$\underline{H}_2$, N-CH$_2$CH$_2$C$\underline{H}_2$); 0.85 (bs, 9H, C-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$, N-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$)

18. $C_{15}H_{34}NO_3P$; Diethyl ester of 1-methyl-1-N-(n-butylamino) n-hexanephosphonic acid; mp. 99–103°C; yield 54%; ^{1}H-NMR ($CDCl_3$): 4,19–4.14 (m, 4H, O-C$\underline{H}_2$); 3.05–2.99 (m, 2H, N-C$\underline{H}_2$); 1.29–1.27 (m, 2H, C-CH$_2$C$\underline{H}_2$); 1.27–1.25 (d, 3H, C-C$\underline{H}_3$, J_{HP}=16,3Hz); 1.25–1.19 (m, 14H, C-CH$_2$CH$_2$C$\underline{H}_2$C$\underline{H}_2$, O-CH$_2$C$\underline{H}_3$, N-CH$_2$C$\underline{H}_2$C$\underline{H}_2$); 0.80–0.74 (m, 6H,C-CH$_2$CH$_2$CH$_2$CH$_2$C$\underline{H}_3$; N-CH$_2$CH$_2$CH$_2$C$\underline{H}_3$)

19. $C_{18}H_{34}NO_4P$; Dibutyl ester of 1-methyl-1-N-(furylmethylamino) butanephosphonic acid; oil; yield 55 %; ^{1}H-NMR: 7.33 (d^*d, 1H, ring O-C$\underline{H}$=, J_{HH}=3.2 Hz, J_{HH} =1.8 Hz); 6.29 (d^*d, 1H, ring O-CH=C$\underline{H}$); 6.15 (d, 1H, O-CH=CH-CH=, J_{HH} =3.2 Hz); 4.10 (t-t, 4H, O-C$\underline{H}_2$, J_{HP}=7.4 Hz); 3.92 (m, 2H, N-C$\underline{H}_2$, J_{HH}=13.7 Hz, J_{HH} =2.2 Hz); 1.77–1.55 (m, 6H, C-C$\underline{H}_2$, O-CH$_2$C$\underline{H}_2$); 1.30 (d, 3H, C-C$\underline{H}_3$, J_{HP}=16 Hz); 0.94 (t, 6H,

$O\text{-}CH_2CH_2CH_2C\underline{H}_3$, J_{HH}=7.4 Hz); 0.93 (t, 3H, $C\text{-}CH_2CH_2C\underline{H}_3$, J_{HH}=7. 1 Hz)

20. $C_{17}H_{38}NO_3P$; Dibutyl ester of 1-methyl 1-N-(propylamino) pentanephosphonic acid; oil; yield – 35%; ^{1}H-NMR: 3.94–4.03 (m, 4H, $OC\underline{H}_2$); 2.51–2.62 (m, 2H, $NC\underline{H}_2$); 1.48–1.62 (m, 6H, $OC\underline{H}_2CH_2$, $C\text{-}C\underline{H}_2$); 1.20–1.40 (m, 10H, $C\text{-}CH_2C\underline{H}_2CH_2$, $NCH_2C\underline{H}_2$, $OCH_2CH_2C\underline{H}_2$); 1.17 (d, 3H, $C\text{-}C\underline{H}_3$, J_{HP}=16,1 Hz); 0.87 (t, 9H, $OCH_2CH_2CH_2C\underline{H}_3$, $NCH_2CH_2C\underline{H}_3$, J_{HH}=7.3 Hz); 0.84 (t, 3H, $C\text{-}CH_2CH_2CH_2C\underline{H}_3$, J_{HH}=7.1 Hz)

21. $C_{18}H_{40}NO_3P$; Dibutyl ester of 1-methyl 1-N-(isobutylamino) n-pentanephosphonic acid; oil; yield: 25 %; ^{1}H-NMR: 3.95 – 4.03 (m,4H, $OC\underline{H}_2$); 2.36 – 2.43 (m, 2H, $NC\underline{H}_2$); 1.53 - 1.62 (m, 8H, $OCH_2C\underline{H}_2C\underline{H}_2$); 1.20 – 1.40 (m, 7H, $NCH_2C\underline{H}$ $(C\underline{H}_3)_2$; 1.18 (d, 3H, J_{HP} = 16.1 Hz, $CC\underline{H}_3$); 0.82 – 0.89 (m, 15H, $CCH_2C\mathit{H}_2C\underline{H}_2C\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$)

22. $C_{22}H_{48}NO_3P$; Dibutyl ester of 1-methyl 1-N (octylamino) n-pentanephosphonic acid; oil; yield: 25.90 %; 1H-NMR ($CDCl_3$): 3.93 (m, 4H, $OC\underline{H}_2$); 2.54 (m, 2H, $NC\underline{H}_2$); 1.52 (m, 7H, $CCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_3$); 1.32 – 1.10 (m, 22H, $NCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$, $CC\underline{H}_2$, $OCH_2C\underline{H}_2C\underline{H}_2$); 0.80 (m, 12H, $CC\underline{H}_3$, $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2C\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$)

23. $C_{20}H_{44}NO_3P$; Dibutyl ester of 1-methyl –1-N (n-heæylamino) pentanephosphonic acid; oil; yield: 85%; ^{1}H-NMR ($CDCl_3$): 4.18 –4.10 (m,4H, $OC\underline{H}_2$); 2.95 (m, 1H, $N\underline{H}$); 2.10 – 1.35 (m, 27H, $CC\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_3$, $OCH_2C\underline{H}_2C\underline{H}_2$, $NC\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 0.95 (m, 12H, $NCH_2CH_2CH_2CH_2CH_2C\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$, $CC\underline{H}_3$)

24. $C_{19}H_{42}NO_3P$; Dibutyl ester of 1-methyl-1N (n-butylamino) n-hexanephosphonic acid; oil, yield: 99%; ^{1}H-NMR: 2.71–2.61 (m, 2H, $NH\text{-}C\underline{H}_2$); 1.67–1.62 (m, 6H, $O\text{-}CH_2C\underline{H}_2$, $C\text{-}C\underline{H}_2$); 1.44–1.21 (m, 17H, $O\text{-}CH_2CH_2C\underline{H}_2$, $NH\text{-}CH_2C\underline{H}_2C\underline{H}_2$, $C\text{-}CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$, $C\text{-}C\underline{H}_3$); 0.96–0.87 (m, 12H, $O\text{-}CH_2CH_2CH_2C\underline{H}_3$, $C\text{-}CH_2CH_2CH_2CH_2C\underline{H}_3$, $NH\text{-}CH_2CH_2CH_2C\underline{H}_3$)

25. $C_{28}H_{60}NO_3P$; Dibutyl ester of 1-methyl-1N-(tetradecylamino) n-pentanephosphonic acid; oil; yield: 55%; ^{1}H- NMR: 0.89 (t, 3H, $CC\underline{H}_3$ J_{HP}= 7.1 Hz); 0.91 (t, 6H, J_{HH}=7.0,Hz, $N(CH_2)_{12}C\underline{H}_3$, $CCH_2CH_2CH_2C\underline{H}_3$); 1.19–1.68 (m, 46H, $OC\underline{H}_2C\underline{H}_2C\underline{H}_3$, $NC\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$, $CC\underline{H}_2C\underline{H}_2C\underline{H}_2$); 2.55–1.70 (m, 1H, $N\underline{H}$); 4.02 (t, 4H, $OC\underline{H}_2$ J_{HP} = 7.1Hz)

26. $C_{24}H_{52}NO_3P$; Dibutyl ester of 1-methyl-1-N-(decylamino) n-pentanephosphonic acid; oil; yield: 85%; 1H-NMR: 0.89 (t, 3H, $CC\underline{H}_3$, J_{HP}= 7.1 Hz); 0.93 (t, 6H, J_{HP} = 7.0 Hz $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C\underline{H}_3$, $CCH_2CH_2CH_2C\underline{H}_3$); 1.21–1.68 (m, 38H,NH-$(C\underline{H}_2)_9$, $CC\underline{H}_2C\underline{H}_2C\underline{H}_2$, $OCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_3$); 2.45–2.70 (m,1H,N$\underline{H}$); 4.06(t, 4H, $OC\underline{H}_2J_{HP}$=7.0 Hz)

27. $C_{21}H_{46}NO_3P$; Dibutyl ester of 1-methyl-1-N-(decylamino) ethanephosphonic acid; oil, yield: 52%; ^{1}H-NMR: 4.10–4.03 (m, 4H, O-$C\underline{H}_2$); 2.72–2.67 (t, 2H, NH-$C\underline{H}_2$); 1.7–1.61 (m, 4H, O-$CH_2C\underline{H}_2$); 1.47–1.37 (m, 6H, NH-$CH_2C\underline{H}_2$, O-$CH_2CH_2C\underline{H}_2$); 1.35–1.21 (m, 20H, NH-$CH_2CH_2(C\underline{H}_2)_7$, C-$C\underline{H}_3$); 0.97–0.86 (m, 9H, O-$CH_2CH_2CH_2C\underline{H}_3$)

28. $C_{19}H_{42}NO_3P$; Dibutyl ester of 1-methyl-1-N-(octylamino) ethanephosphonic acid; oil, yield: 86%; ^{1}H-NMR: 4.08–4.0 (m, 4H, O-$C\underline{H}_2$); 2.69–2.64 (t, 2H, NH-$C\underline{H}_2$); 1.67–1.58 (m, 4H, O-$CH_2C\underline{H}_2$); 1.44–1.35 (m, 6H, O-$CH_2CH_2C\underline{H}_2$, NH-$CH_2C\underline{H}_2$); 1.34–1.23 (m, 16H, NH-$CH_2CH_2(C\underline{H}_2)_5$, C-$C\underline{H}_3$); 0.94–0.89 (t, 6H, O-$CH_2CH_2CH_2C\underline{H}_3$); 0.87–0.83 (m, 3H, NH-$(CH_2)_7C\underline{H}_3$)

29. $C_{20}H_{44}NO_3P$; Dibutyl ester of 1-methyl-1-N-(octylamino) n-propanephosphonic acid; oil, yield: 91%; ^{1}H-NMR: 4.1–4.02 (m, 4H, O-$C\underline{H}_2$); 2.7–2.62 (m, 2H, NH-$C\underline{H}_2$); 1.69–1.6 (m, 6H, O-$CH_2C\underline{H}_2$, C-$C\underline{H}_2$); 1.47–1.35 (m, 6H, NH-$CH_2C\underline{H}_2$, O-$CH_2CH_2C\underline{H}_2$); 1.32–1.21 (m, 13H, NH-$CH_2CH_2(C\underline{H}_2)_5$, C-$C\underline{H}_3$); 0.97–0.86 (m, 12H, C-$CH_2C\underline{H}_3$, $NH(CH_2)_7C\underline{H}_3$, O-$CH_2CH_2CH_2C\underline{H}_3$)

30. $C_{23}H_{50}NO_3P$; Dibutyl ester of 1-methyl-1-N-(octylamino) n-hexanephosphonic acid; oil; yield: 51%; ^{1}H- NMR ($CDCl_3$): 4.06 (m, 4H, $OC\underline{H}_2$); 2.65 (m, 2H, $NC\underline{H}_2$); 1.63 (m,6H, $CC\underline{H}_2$, $OCH_2C\underline{H}_2$); 1.28 (m 25H, $OCH_2CH_2C\underline{H}_2$, $NCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$, $CCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_3$); 0.90 (m, 12H, $CC\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$, $OCH_2CH_2CH_2C\underline{H}_3$, $NCH_2CH_2CH_2CH_2CH_2CH_2CH_2C\underline{H}_3$)

31. $C_{17}H_{38}NO_3P$; Diisopropyl ester 1-methyl-1-N-(octylamino) ethanephosphonic acid; oil, yield: 33%; ^{1}H-NMR: 4.73–4.67 (m, 2H, O-$C\underline{H}$); 2.72–2.68 (t, 2H, NH-$C\underline{H}_2$ J_{HH}=7.2Hz); 1.43–1.23 (m, 30H, C-$C\underline{H}_3$, O-$CH(C\underline{H}_3)_2$, NH-$CH_2(C\underline{H}_2)_6$); 0.89–0.85 (t, 3H, NH-$(CH_2)_7C\underline{H}_3$ J_{HH}=6,4Hz)

32. $C_{20}H_{44}NO_3P$; Diisopropyl ester 1-isobutyl-N-(octylamino) ethanephosphonic acid; oil; yield: 27 %; ^{1}H – NMR: 4.71 (m, 2H, $OC\underline{H}$); 2.70 (m, 4H, $CC\underline{H}_2$); 1.93 (m, 1H, $CC\underline{H}$); 1.65 – 1.25 (m, 27 H,

$OCH(C\underline{H}_3)_2$), $NCH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_3$) 0.95 (t, 6H, $CCH_2CH(C\underline{H}_3)_2$ J_{HP} = 7.1 Hz); 0.87 (t, 3H, $CC\underline{H}_3$ J_{HP} = 7,2Hz)

33. $C_{25}H_{54}NO_3P$; Dibutyl ester of 1-methyl-1N-(tetradecylamino) ethanephosphonic acid; oil, yield: 85 %; ^{1}H-NMR: 4.1–3.98 (m, 4H, $O\text{-}C\underline{H}_2$); 2.68–2.64 (t, 2H, $NH\text{-}C\underline{H}_2$); 1.64–1.59 (m, 4H, $O\text{-}CH_2C\underline{H}_2$); 1.44–1.31 (m, 8H, $O\text{-}CH_2CH_2C\underline{H}_2$. $NH\text{-}CH_2C\underline{H}_2C\underline{H}_2$); 1.28–1.22 (m, 26H, $NH\text{-}CH_2CH_2CH_2(C\underline{H}_2)_{10}$, $C\text{-}C\underline{H}_3$); 0.93–0.88 (m, 6H, $O\text{-}CH_2CH_2CH_2C\underline{H}_3$); 0.87–0.84 (m, 3H, $NH\text{-}(CH_2)_{13}C\underline{H}_3$)

34. $C_{22}H_{48}NO_3P$; Diisopropyl ester 1-methyl – 1-N-(n-decylamino) n-pentanephosphonic acid; oil, yield: 69%; ^{1}HNMR: 4.77–4.64 (m, 2H, $O\text{-}C\underline{H}$); 2.71–2.59 (m, 2H, $NH\text{-}C\underline{H}_2$); 1.53–1.18 (m, 37 H, $O\text{-}CHC\underline{H}_3$, $NH\text{-}CH_2(C\underline{H}_2)_8$, $C\text{-}C\underline{H}_3$, $C\text{-}C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 0.93–0.85 (m, 6H, $C\text{-}(CH_2)_3C\underline{H}_3$, $N(CH_2)_9C\underline{H}_3$)

35. $C_{19}H_{42}NO_3P$; Diisopropyl ester 1-methyl-1-N-(n-decylamino) ethanephosphonic acid; oil, yield: 65 %; ^{1}HNMR: 4.77–4.7 (m, 2H, $O\text{-}C\underline{H}$); 2.74–2.69 (t, 2H, $NH\text{-}C\underline{H}_2$); 1.46–1.22 (m, 34H, $NH\text{-}CH_2(C\underline{H}_2)_8$, $O\text{-}CH(C\underline{H}_3)_2$, $C\text{-}C\underline{H}_3$); 0.91–0.86 (t, 3H, $NH\text{-}(CH_2)_9C\underline{H}_3$ J_{HH}=7.2Hz)

36. $C_{24}H_{52}NO_3P$; Dibutyl ester of 1-t-butyl-1-N-(n-decylamino) ethanephosphonic acid; oil, yield: 50 %; ^{1}HNMR: 4.1–4.03 (m, 4H, $O\text{-}C\underline{H}_2$); 2.72–2.67 (t, 2H, $NH\text{-}C\underline{H}_2$ J_{HH}=7.2Hz); 1.68–1.61 (m, 4H, $O\text{-}CH_2C\underline{H}_2$); 1.47–1.09 (m, 32 H, $C\text{-}C\underline{H}_3$, $C\text{-}C(C\underline{H}_3)_3$, $O\text{-}CH_2CH_2C\underline{H}_2$, $NH\text{-}CH_2(C\underline{H}_2)_8$); 0.97–0.86 (m, 9H, $O\text{-}CH_2CH_2CH_2C\underline{H}_3$, $NH\text{-}(CH_2)_9C\underline{H}_3$);

37. $C_{19}H_{42}NO_3P$; Dibutyl ester of 1-methyl-1-N-(n-pentylamino) pentanephosphonic acid; oil, yield: 71.17%; ^{1}HNMR: 4.12–4.00 (m, 4H, $O\text{-}C\underline{H}_2$); 2.7–2.59 (m, 2H, $N\text{-}C\underline{H}_2$); 1.69–1.59 (m, 6H, $C\text{-}C\underline{H}_2$, $O\text{-}CH_2C\underline{H}_2$); 1.43–1.21 (m, 17H, $C\text{-}C\underline{H}_3$, $C\text{-}CH_2C\underline{H}_2C\underline{H}_2$, $NH\text{-}CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2$, $O\text{-}CH_2CH_2C\underline{H}_2$); 0.96–0.86 (m, 12H, $C\text{-}(CH_2)_3C\underline{H}_3$, $NH\text{-}(CH_2)_4C\underline{H}_3$, $O\text{-}(CH_2)_3C\underline{H}_3$)

Acknowledgements

This work was supported by the Polish Research Committee (KBN), grant no. 6 P04 G 050 17.

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