Novel Condensed Thionated Bis(phosphonic) Acid Salts with a Rigid Naphthalene-1,8-diyl Backbone

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New salts of thionated (naphthalene-1,8-diyl)bis(phosphonic) acid monoanhydrides $[PPh_4^+]_2[C_{10}H_6PS_2(\mu\text{-}S)PS_2^{2-}]$ (**2**) and $[K^+]_2[C_{10}H_6PS_2(\mu\text{-}S)POS^{2-}]\cdot H_2O$ (**3**) both containing the C_3P_2S ring, were prepared in high yields by the reaction of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (**1**) with NaHS and PPh_4Cl, or KOH, respectively, in water. The derivative **3**, containing a P=O terminal bond as well as P–S–P bridge, undergoes, in acid conditions, a rearrangement reaction leading to the O,S-symmetrically substituted derivative $[K^+]_2[C_{10}H_6PS_2(\mu\text{-}O)PS_2^{2-}]$ (**4**) containing a C_3P_2O heterocycle. Dipotassium salt 4 was converted into the bis(tetraphenylphosphonium) salt **5** by the treating with PPh_4Cl. Hydrolysis of $[PyH^+][C_{10}H_6P(S)(NHMe)(\mu\text{-}S)PS_2^{2-}]$ (**15**) led to $[CH_3NH_3^+][PyH^+][C_{10}H_6POS(\mu\text{-}O)POS^{2-}]\cdot 1.5$ Py (**6**). New compounds were characterised by $^{31}P\{^1H\}$-, ^1H- and $^{13}C\{^1H\}$-NMR, FT-IR, ES-MS and in the cases **2**–**6** by X-ray structure determination. The $^{31}P\{^1H\}$-NMR spectra of these mixed O,S-derivatives are briefly discussed.

Introduction

Phosphonic acids and their esters form the largest group of compounds containing P−C linkages. Esters of thionated phosphonic acids have been extensively studied because of their use as oil additives and in pesticide chemistry.[1] 2,4-dialkyl(aryl)-1,3,2,4-dithiadiphosphetane 2,4-disulfides $(RPS_2)_2$, especially that with R = C_6H_4OMe (An), well-known as Lawesson reagent (LR), are commonly used for their preparation. In some cases they are converted into intermediates − alkali metal salts of dithio- and trithiophosphonic acids or their monoesters. These salts are either isolated as pure compounds[2][3] or without isolation from the reaction mixture they are directly alkylated to diesters.[4,5,6,7]

As a continuation of our interest in the chemistry of 2,4-(naphthalene-1,8-diyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **1** we studied its reactions with potassium hydroxide and sodium hydrogen sulfide, leading to salts of the composition described above. Because of the presence of a rigid organyl backbone in **1**, which fixes its phosphorus atoms in the sterically strained 1,8-positions of the naphthalene ring, we obtained condensed products − bis(phosphonates), containing a P−X−P bridge built into six-membered C_3P_2X (X = S or O) heterocycles.

Several examples of thionated bis(phosphonates) have been reported. In the form of their alkali metal salts RP(S)(OM)(μ-S)P(S)(OM)R they were obtained from $(RPS_2)_2$, where R = alkenyl with long chain, by mild alkalic hydrolysis by potassium and sodium hydroxide.[3] Partially thionated diesters RP(S)(OR′)(μ-S)P(S)(OR′)R were obtained in low yield by the reaction of $(RPS_2)_2$ with primary and secondary alcohols at higher temperatures,[5][8] particularly in boiling xylene. The more sulfur rich diester AnP(S)(SEt)(μ-S)P(S)(OEt)An was obtained in good yield by the reactions of LR with 1,1,1-triethoxyethane, tri- and tetraethoxymethane.[9][10] The fully thionated bis(phosphonate) diester AnP(S)(SPh)(μ-S)P(S)(SPh)An was obtained in low yield by the action of thiophenol on LR.[5] In these systems the ease of sulfur loss occurring on contact of thionated phosphonates with water requires the work to be performed with the exclusion of water.[2][7] However the substantially lower reactivity of **1** compared to common dithiadiphosphetane disulfides $(RPS_2)_2$ allowed us to prepare salts of perthionated as well as partially dethionated phosphonic acids in water.

Results and Discussion

The bis(tetraphenylphosphonium) salt of bis(trithiophosphonic acid) monoanhydride **2** was prepared in a good yield by the action of excess NaHS on **1** and consequent treatment of the resulting disodium salt (without its isolation from reaction mixture) with PPh_4Cl (Scheme 1). $^{31}P\{^1H\}$-NMR of the reaction mixture after the first step showed a singlet at δ = 69.0 ppm, belonging to the disodium salt $[Na^+]_2[C_{10}H_6PS_2(\mu\text{-}S)PS_2^{2-}]$. When a stoichiometric amount or only a small molar excess of NaHS was used, the larger amount of the side product, the anion of **3**, was observed by $^{31}P\{^1H\}$-NMR. Reaction of the disodium salt with PPh_4Cl afforded pure **2**, which is insoluble in many common solvents. Its slight solubility in CD_3CN/[D₆]DMSO allowed us to measure its $^{31}P\{^1H\}$- and ^1H-NMR spectra, however the concentration of such saturated solution was too low to obtain a good quality $^{13}C\{^1H\}$-NMR spectrum.

By the action of small excess of KOH on **1** (molar ratio 2.3:1) we obtained the potassium salt of the unsymmetrically O,S-substituted naphthalene-1,8-diyl bis(phosphonic)

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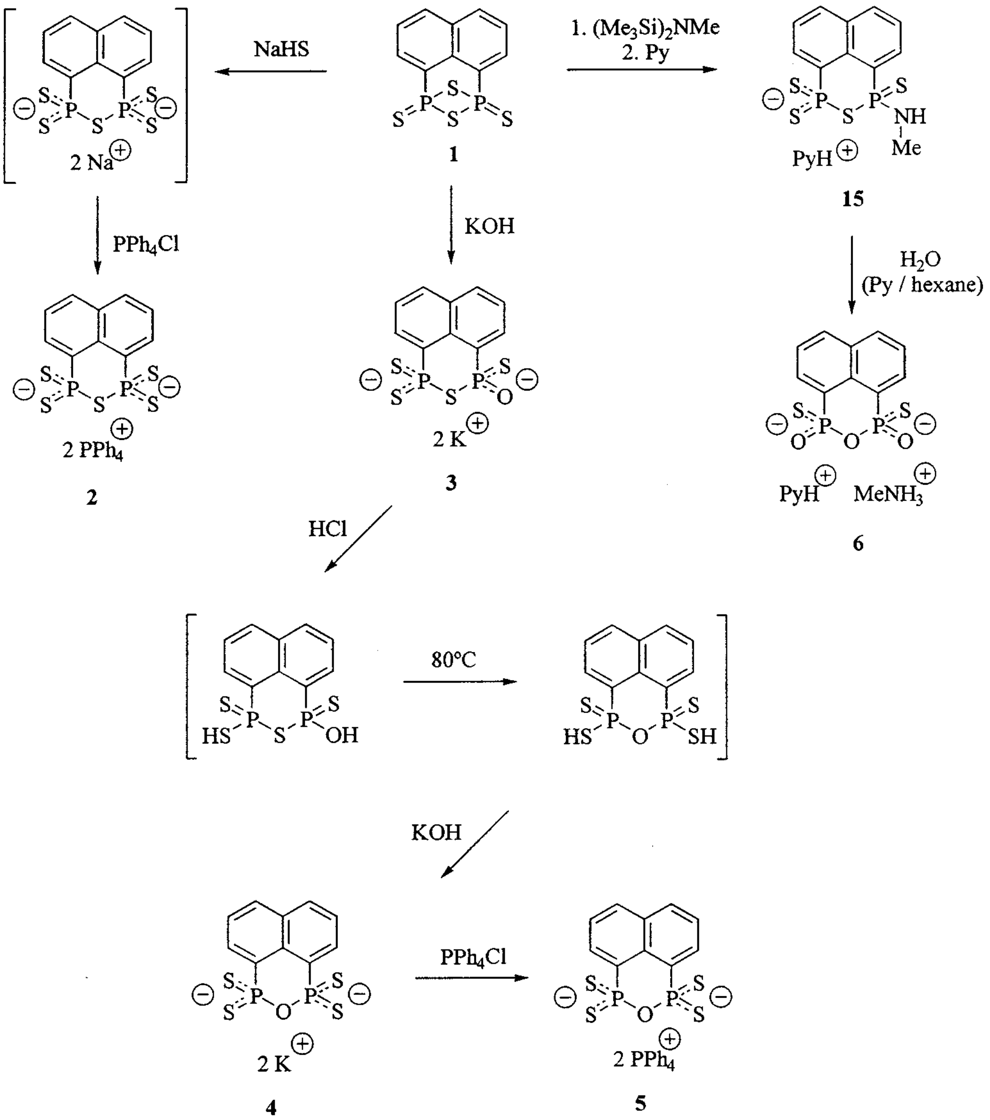
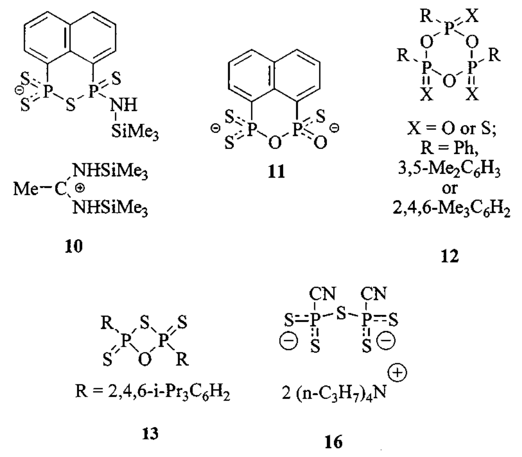


Scheme 1

acid, **3** (Scheme 1). The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed an AX system with δ 69.2 and 58.6 ppm. The magnitude of $J(PP) = 11.6$ Hz indicates that a P−S−P bridge is preserved in the product.[11][12] Both the ^1H and $^{13}C\{^1H\}$-NMR spectra showed unsymmetrical substitution of the naphthalene ring, whilst in the IR a very strong band at 1112 cm^{-1} corresponding to ν(P=O) was found. The position of this band in the lower frequency range for a P=O bouble bond valence vibration is due to the lowered bond order given by delocalisation of the negative charge between more terminal atoms. All these facts are in accord with the structure of **3** shown in Scheme 1, which was confirmed by X-ray structure determination (Figure 2). Signals in the ^1H and $^{13}C\{^1H\}$-NMR spectrum of **3** were assigned by analogy with **10**, where unambiguous assignment was performed by both 1D- and 2D-NMR.[11] Recrystallization of the crude product from non dried ethanol/methanol mixture afforded hygroscopic material, which after six hours of drying *in vacuo* was identified by elemental analysis as **3**, monohydrate, whilst 2.5 molecules of water per naphthalene entity were found in the crystal structure of **3** by X-ray structure determination. On attempts to convert the potassium salt **3** to its tetraphenylphosphonium relative by the reaction of **3** with PPh_4Cl a mixture of the desired product together with reorganised product **5** was obtained.

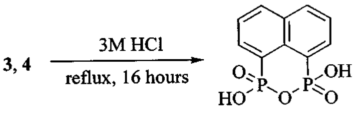
The potassium salt **3** is indefinitely stable in the solid state. However, when it is in the form of its conjugated acid, [obtained by the addition of diluted mineral acid (HCl) to the water solution of **3**], it undergoes a rearrangement reaction leading to O,S-symmetrically substituted acid, containing a P−O−P bridge (Scheme 1). Treatment of the crude mixture of the bis(phosphonic) acid and KCl with dry methanol allows the removal of a majority of KCl together with other methanol insoluble side products by filtration. Stripping off methanol, dissolving the resulting solid in water and titration with KOH afforded the potassium salt **4**. In its $^{31}P\{^1H\}$-NMR spectrum we found signals due to three distinct compounds. Besides the major signal of **4** (s, δ = 101.4) and minor signals of the starting material **3** (2 × d, δ = 69.2 and 58.6, ^2J(PP) = 11.6 Hz) other minor signals (2 × d, δ = 102.7 and 59.7, ^2J(P−O−P) = 47 Hz) were found, probably belonging to the dianion **11**. After another purification step (recrystallization from ethanol), pure **4** was obtained. Signals in the ^{1}H- and ^{13}C{^{1}H}-NMR spectrum of **4** were assigned on the basis of analogy with **10**.[11] The second order signals of carbons C1 and C9 (for numbering of atoms see Figure 4) represent AXX′ systems, where A is the carbon atom and X and X′ are phosphorus atoms. Magnitudes of their ^2J(PP), ^1J(PC) and ^3J(PC) coupling constants were obtained using the LAOCOON III simulation program.[13] The magnitude of ^2J(PP) = 51.2 Hz is comparable with the corresponding ^2J(PP) values found in thiotrimetaphosphonates **12**[14] (32−62 Hz) whilst it is substantially larger when compared with ^2J(PP) = 14.2 Hz in **13**[14] or with ^2J(PP) = 6.5 Hz in **1**.[15] In the IR spectrum of **4** no strong band was found in the 1100−1400 cm^{-1} region, which would be expected for ν(P=O) vibrations, whilst a very strong band, belonging to ν_{as}(P−O−P) was found at 825 cm^{-1}.



10 11 12 13 16

Figure 1. Structural formulas of compounds **10**, **11**, **12**, **13** and **16**

By the reaction of **1** with excess of ethylene glycol at 140°C a completely desulfurated compound **14** was obtained.[16] Compounds **3** or **4** respectively can be used for preparation of **14** as well. These desulfuration reactions were performed by prolonged boiling with 3 M HCl (Scheme 2). The identity of resulting products was confirmed by ^{31}P{^{1}H}-NMR and IR spectroscopy.



14

Scheme 2

To improve the solubility of the potassium salt **4** in organic solvents we converted it into the bis(tetraphenylphosphonium) salt **5** by the reaction of **4** with PPh$_4$Cl (Scheme 1). **5** shows good solubility in hot acetonitrile, whilst it is much less soluble at room temperature; this allowed very good yields when recrystalized from this solvent.

In our previous paper[17] we described the preparation of pyridinium salt **15** by the treatment of **1** with bis(trimethylsilyl)methylamine and pyridine (Py). An attempt to recrystallize **15** by diffussion of hexane into its pyridine solution led to hydrolysis with formation of **6** (Scheme 1). The product, obtained in the form of several crystals, was identified by X-ray structure analysis, but the small amount available only allowed further characterization by ^{31}P{^{1}H}- and ^{1}H-NMR. The latter showed 1:1.2 ratio of naphthalene and pyridine hydrogens, whilst in the crystal ratio 1:2.5 was found by X-ray structure analysis, the lower ratio found in solution is due to partial evaporation of solvated Py from crystals. The integral of the broad signal at 3.4 ppm, belonging to MeNH$_3^+$ and PyH$^+$ hydrogens was lower than the expected value from its comparison with integral value of CH$_3$ hydrogens of methylamine, probably due to their fast chemical exchange.

Discussion of ^{31}P{^{1}H}-NMR Spectra

When comparing ^{31}P-NMR shifts in dianionic O,S-mixed derivatives of (naphthalene-1,8-diyl)bis(phosphonic) acid, the following conclusions can be drawn:[2,3,10,11] In such systems it is common, that substitution of an O atom by a S atom leads to the lower field shift. This rule is obeyed very well when a series of compounds containing oxygen as a bridging atom between both phosphorus atoms is taken into account, compounds **5** (δ = 100 ppm), **6** (δ = 59 ppm) and **14** (δ = 7 ppm) contain moieties C−P(μ-O)S$_2$, C−P-(μ-O)OS and C−P(μ-O)O$_2$, respectively. A second group, for which the above rule applies as well, is formed by compounds containing sulfur as a bridging atom between both phosphorus atoms. Members of this group are compounds **2** (δ = 73 ppm, C−P(μ-S)S$_2$ moiety) and **3** (δ = 69 ppm, C−P(μ-S)S$_2$ moiety; 59 ppm C−P(μ-S)OS moiety), the missing member is a compound containing a C−P(μ-S)O$_2$ moiety, no example of this type has been described yet. The above rule obviously does not apply, when comparing compounds with C−P(μ-S)S$_2$ moiety (**2**, δ = 73 ppm) with C−P(μ-O)S$_2$ moiety (**5**, δ = 100 ppm), thus both groups with different P-X−P bridging atoms should be judged separately.

Discussion of X-ray Structure Analysis

X-ray structures of compounds **2**−**6** were measured, see Figure 2−6 and Tables 1−6. The naphthalene part and the phosphorus atoms lie very close to the mean plane fitted to these atoms in case of the anion of **2** [P(1) 0.05 Å above and P(9) 0.13 Å below the mean plane] and **6** both P(1) and P(9) lie 0.08 and 0.01 Å, respectively, above the mean plane], whilst in **3**, **4** and **5** the distortion is more significant and phosphorus atoms in each anion lie above and below the mean plane in distances between 0.31 and 0.44 Å.

The C_3P_2X (X = S or O) rings are hinged, the C_3P_2 and P_2X planes in anions of **2** and **3** (where X = S) are inclined by 52 and 48°, respectively. In **4** and **5** (where X = O) these angles are 32 and 36°, in **6** (X = O) the corresponding value of 50° was found.

The nonbonding P···P distances as well as internal P−S−P angles in **2** and **3** are very similar [3.31 and 3.27 Å; 103.31(7) and 101.5(1)°], substitution of sulfur bridging atom by oxygen led to shortening of P···P distances in **4** and **5** to 2.97 and 2.99 Å, the internal P−O−P angles are enlarged to 131°. The most compact P_2 environment is in **6**, where the Pψree dots aboveP distance 2.89 Å and corresponding internal P−O−P angle 125.2(1) is found.

As expected, the bond lengths of exocyclic substituents of phosphorus atoms reflect delocalisation of the negative charge in the $P(X_{exo})_2$ groups (X_{exo} = S, O). When comparing $P-S_{exo}$ distances in **2**, **3**, **4**, **5** and **6** [range 1.945(2)−1.990(2) Å] with endocyclic $P-S_{endo}$ distances in **2** and **3** [range 2.102(3)−2.116(2) Å], the difference is substantial due to their different bond order. Similarly, the $P-O_{exo}$ distances in **3** and **6** [range 1.505(2)−1.521(5) Å] are substantially shorter than $P-O_{endo}$ distances in **4**, **5** and **6** [range 1.623(2)−1.650(4) Å], however they are significantly longer than conventional P=O double bond as found for example in phosphoric acid triesters (average value 1.45 Å).[18]

In the structure of the anion in **2** (Figure 2, Table 1 and 2) there is surprisingly no mirror plane along the S(19)C(5)C(10) plane, sulfur atoms S(1) and S(9) lie in substantially different distances from the mean plane fitted to naphthalene part and phosphorus atoms (1.40 and 0.95 Å). The steric effect of the naphthalene backbone results in a short P···P distance 3.31 Å in **2**, compare to P···P distance 3.50 Å in **16**,[19] where phosphorus atoms are not bridged by any organic substituent.

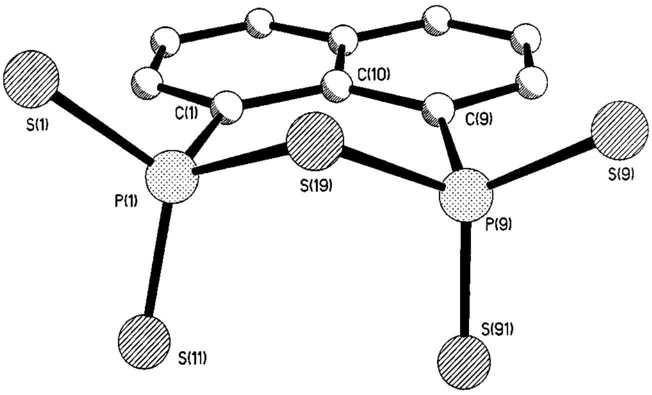


Figure 2. Molecular diagram of **2**

Table 2. Selected bond lengths (Å) and angles (°) in compound **2**

P(1)−S(19)	2.116(2)	P(9)−S(19)	2.108(2)
P(1)−S(1)	1.985(2)	P(1)−S(11)	1.968(2)
P(9)−S(9)	1.990(2)	P(9)−S(91)	1.955(2)
P(1)−C(1)	1.831(4)	P(9)−C(9)	1.841(5)
P(1)−S(19)−P(9)	103.31(7)		
S(1)−P(1)−S(11)	117.97(8)	S(9)−P(9)−S(91)	117.31(9)
S(1)−P(1)−S(19)	100.59(7)	S(11)−P(1)−S(19)	116.06(8)
S(9)−P(9)−S(19)	102.88(8)	S(91)−P(9)−S(19)	114.67(8)
C(1)−P(1)−S(1)	110.3(2)	C(1)−P(1)−S(11)	107.7(1)
C(9)−P(9)−S(9)	110.8(2)	C(9)−P(9)−S(91)	108.3(2)
C(1)−P(1)−S(19)	103.3(2)	C(9)−P(9)−S(19)	101.7(2)

In the structure of the anion in **3** (Figure 3, Table 1 and 3) the K^+ cations interact with all the sulfur atoms [including S(19)] with K···S distances in the range 3.24−3.75 Å, oxygen atom O(1) interacts with K···O distances in the range 2.76−3.02 Å. The water solvate molecules (2.5 molecule per naphthalene entity) coordinate to the K^+ centres.

Table 1. Details of the data collections and refinements for compounds **2**, **3**, **4**, **5** and **6**

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{58}H_{46}P_4S_5$	$C_{10}H_{11}K_2O_{3.5}P_2S_4$	$C_{10}H_6K_2OP_2S_4$	$C_{59}H_{47.5}N_{0.5}OP_4S_4$	$C_{23.5}H_{25.5}N_{3.5}O_3P_2S_2$
Formula weight	1027.13	455.57	410.53	1031.60	531.03
Colour	Yellow	Yellow	Yellow	Yellow	Colourless
Size/mm^{-3}	0.15 × 0.15 × 0.15	0.10 × 0.10 × 0.10	0.04 × 0.10 × 0.20	0.08 × 0.10 × 0.10	0.10 × 0.10 × 0.20
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	17.2282(5)	16.434(2)	7.2326(7)	13.8150(8)	8.8369(2)
b/Å	13.8956(3)	8.6746(8)	9.4191(9)	14.1522(8)	17.9208(4)
c/Å	23.1746(7)	24.862(2)	12.847(1)	15.5028(9)	17.2366(4)
α/°	90	90	102.356(2)	69.892(1)	90
β/°	110.853(1)	90.092(2)	98.509(2)	78.794(1)	101.473(1)
γ/°	90	90	108.969(2)	77.088(2)	90
Space group	$P2_1/a$	$C2/c$	P1bar	P1bar	$P2_1/n$
Z	4	8	2	2	4
d/gcm^{-3}	1.316	1.707	1.735	1.245	1.319
μ/mm^{-1}	0.385	1.193	1.323	0.328	0.349
Refl. Measured	22154	7619	4000	13531	11558
Refl. Independent (R_{int})	7443 (0.0913)	2562 (0.1095)	2233 (0.0344)	7706 (0.2332)	3828 (0.0347)
Final R [$I > 2\sigma(I)$]	$R^1 = 0.0535$, $wR^2 = 0.0907$	$R^1 = 0.0581$, $wR^2 = 0.1256$	$R^1 = 0.0337$, $wR^2 = 0.0690$	$R^1 = 0.0663$, $wR^2 = 0.1431$	$R^1 = 0.0400$, $wR^2 = 0.0961$
Goodness-of-fit on F^2	0.996	0.938	1.050	0.496	0.935
Largest difference peak and hole/eÅ^{-3}	0.370 and −0.265	1.423 and −0.763	0.466 and −0.254	0.530 and −0.645	0.271 and −0.206

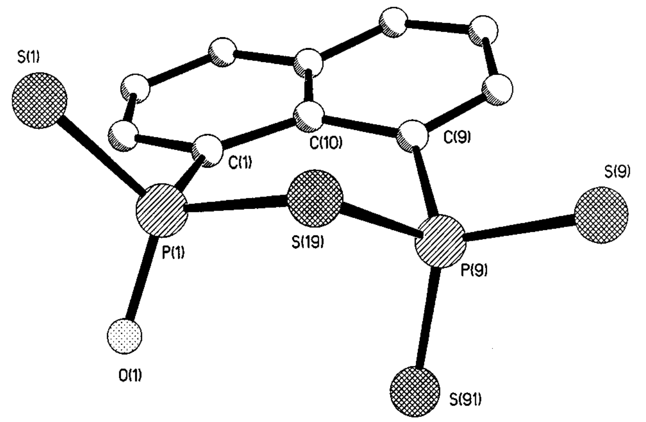


Figure 3. Molecular diagram of **3**

Table 3. Selected bond lengths (Å) and angles (°) in compound **3**

P(1)−S(19)	2.116(3)	P(9)−S(19)	2.102(3)
P(1)−S(1)	1.979(3)	P(1)−O(1)	1.521(5)
P(9)−S(9)	1.988(3)	P(9)−S(91)	1.984(3)
P(1)−C(1)	1.837(7)	P(9)−C(9)	1.814(7)
K(1)−S(1)	3.381(3)	K(2)−O(1)	3.018(6)
K(1)−O(1)	2.759(5)	K(1)−O(1)	2.956(5)
K(1)−S(9)	3.535(3)	K(2)−S(9)	3.746(4)
K(1)−S(91)	3.393(2)	K(1)−S(91)	3.576(3)
K(2)−S(91)	3.239(3)	K(2)−S(91)	3.355(3)
K(1)−S(19)	3.588(2)		
P(1)−S(19)−P(9)	101.48(11)		
S(1)−P(1)−O(1)	116.3(2)	S(9)−P(9)−S(91)	115.46(13)
S(1)−P(1)−S(19)	103.21(11)	O(1)−P(1)−S(19)	111.6(2)
S(9)−P(9)−S(19)	104.11(12)	S(91)−P(9)−S(19)	112.68(11)
C(1)−P(1)−S(1)	109.6(2)	C(1)−P(1)−O(1)	109.4(3)
C(9)−P(9)−S(9)	111.1(2)	C(9)−P(9)−S(91)	110.0(2)
C(1)−P(1)−S(19)	106.2(3)	C(9)−P(9)−S(19)	102.7(2)

Symmetry transformations used to generate equivalent atoms: #1: -x+2, y, -z+1; #2: −x+5/2, y+1/2, -z+1/2; #3: −x+5/2, y-1/2, -z+1/2

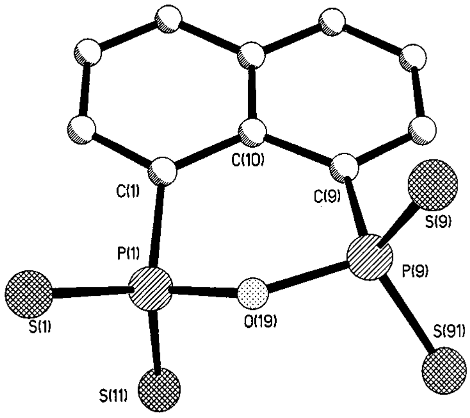


Figure 4. Molecular diagram of **4**

Table 4. Selected bond lengths (Å) and angles (°) in compound **4**

P(1)−O(19)	1.626(2)	P(9)−O(19)	1.638(3)
P(1)−S(1)	1.954(1)	P(1)−S(11)	1.983(1)
P(9)−S(9)	1.976(1)	P(9)−S(91)	1.962(2)
P(1)−C(1)	1.806(4)	P(9)−C(9)	1.811(4)
K(1)−S(1)	3.351(2)		
K(2)−S(1)	3.188(2)	K(2)−S(1)	3.182(2)
K(1)−S(11)	3.399(1)	K(1)−S(11)	3.430(1)
K(2)−S(11)	3.344(1)	K(2)−S(11)	3.355(1)
K(1)−S(9)	3.422(2)	K(2)−S(9)	3.241(2)
K(1)−S(91)	3.285(1)	K(1)−S(91)	3.389(2)
K(2)−S(91)	3.351(1)	K(1)−O(19)	2.829(2)
P(1)−O(19)−P(9)	131.0(2)		
S(1)−P(1)−S(11)	117.54(7)	S(9)−P(9)−S(91)	116.66(6)
S(1)−P(1)−O(19)	105.2(1)	S(11)−P(1)−O(19)	109.3(1)
S(9)−P(9)−O(19)	103.5(1)	S(91)−P(9)−O(19)	111.2(1)
C(1)−P(1)−S(1)	111.4(1)	C(1)−P(1)−S(11)	109.5(1)
C(9)−P(9)−S(9)	110.9(1)	C(9)−P(9)−S(91)	110.6(1)
C(1)−P(1)−O(19)	102.7(2)	C(9)−P(9)−O(19)	102.9(2)

Symmetry transformations used to generate equivalent atoms: #1: $x+1$, y, z; #2: $-x$, $-y$-1, $-z$; #3: $-x$, $-y$, -z; #4: $x+1$, $y+1$, z; #5: $x-1$, y, z; #6: $x-1$, $y-1$, z

Because of the close similarity of anionic parts in the structures of **4** (Figure 4, Table 1 and 4) and **5** (Table 1 and 5), only the former is discussed here. As well as in the structure of the anion of **2**, in the structure of anion of **4**, there is no mirror plane along the 0(19)C(5)C(10) plane, even when the substitution pattern is symmetric. Atoms in *trans* positions [e.g. S(1) and S(91)] are approximately in the same distance from the plane fitted to carbon and phosphorus atoms, thus when disregarding the O(19) atom (lying 0.37 Å above mean plane), the anion has approximate C_2 symmetry. The K^+ ions in **4** form close contacts with the sulfur atoms in the range 3.18−3.43 Å, and there is a K(1)···O(19) distance of 2.83Å.

In the structure of the anion in **6** (Figure 5, Table 1 and 6) the exocyclic substituents are in the *cis* position and the molecule possesses an approximate mirror plane along the O(19)C(5)C(10) plane, which is in contrast with *trans* geometry of **14**.[16] The NH protons in the $MeNH_3^+$ counterion are hydrogen-bonded to a solvated pyridine nitrogen atom [H(20a)···N(41) 1.94 Å, N(20)−H(20a)−N(41) 169°], to O(9) atom [H(20b)···O(9) 1.79 Å, N(20)−H(20b)−O(9) 175°] and to O(9′) atom in adjacent anion [H(20c)···O(9′) 1.95 Å, N(20)−H(20c)−O(9′) 167°]. The pyridinium NH proton strongly bonds to the anion O(1) atom [H(31)···O(1) 1.64 Å, N(31)−H(31)−O(1) 175°].

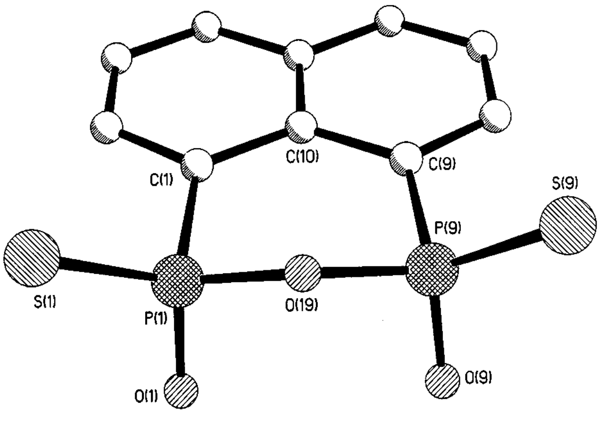


Figure 5. Molecular diagram of **6**

Table 5. Selected bond lengths (Å) and angles (°) in compound **5**

P(1)−O(19)	1.650(4)	P(9)−O(19)	1.631(4)
P(1)−S(1)	1.962(3)	P(1)−S(11)	1.972(3)
P(9)−S(9)	1.987(3)	P(9)−S(91)	1.960(3)
P(1)−C(1)	1.819(8)	P(9)−C(9)	1.824(7)
P(1)−O(19)−P(9)	131.3(2)		
S(1)−P(1)−S(11)	117.6(1)	S(9)−P(9)−S(91)	117.3(1)
S(1)−P(1)−O(19)	106.3(2)	S(11)−P(1)−O(19)	111.7(2)
S(9)−P(9)−O(19)	105.8(2)	S(91)−P(9)−O(19)	111.7(2)
C(1)−P(1)−S(1)	111.5(3)	C(1)−P(1)−S(11)	108.0(2)
C(9)−P(9)−S(9)	108.1(2)	C(9)−P(9)−S(91)	110.9(2)
C(1)−P(1)−O(19)	100.5(3)	C(9)−P(9)−O(19)	101.9(3)

Table 6. Selected bond lengths (Å) and angles (°) in compound **6**

P(1)−O(19)	1.623(2)	P(9)−O(19)	1.630(2)
P(1)−S(1)	1.945(1)	P(1)−O(1)	1.508(2)
P(9)−S(9)	1.946(1)	P(9)−O(9)	1.505(2)
P(1)−C(1)	1.808(3)	P(9)−C(9)	1.812(3)
P(1)−O(19)−P(9)	125.2(1)		
S(1)−P(1)−O(1)	116.73(9)	S(9)−P(9)−O(9)	117.71(9)
S(1)−P(1)−O(19)	109.34(8)	O(1)−P(1)−O(19)	107.8(1)
S(9)−P(9)−O(19)	107.93(8)	O(9)−P(9)−O(19)	108.2(1)
C(1)−P(1)−S(1)	112.2(1)	C(1)−P(1)−O(1)	108.0(1)
C(9)−P(9)−S(9)	112.4(1)	C(9)−P(9)−O(9)	107.4(1)
C(1)−P(1)−O(19)	101.5(1)	C(9)−P(9)−O(19)	102.0(1)

Conclusion

In this paper we have gained access to almost all possible permutations of O,S-substituted phosphorus environments in salts of (naphthalene-1,8-diyl)bis(phosphonic) acids. The only missing member in this group of environments of general formula C−P(μ-X)X$_2$, where X = either O, S, or their permutations, is the C−P(μ-S)O$_2$ moiety. All other members were characterised by ^{31}P{^{1}H}-NMR and by X-ray structure analysis either in this paper or elsewhere.[16] Current investigations are focusing on the preparation of other interesting main group derivatives of 1,8-bis(phosphorus) substituted naphthalenes

Experimental Section

General Remarks: 1 was prepared by the reaction of P$_4$S$_{10}$ with 1-bromonaphthalene[20][21] and recrystallized from dichloromethane, tetraphenylphosphonium chloride was obtained from Aldrich. Methanol was dried by boiling with CaH$_2$ and subsequent distillation under nitrogen. In vacuo refers to a pressure of 0.1 Torr at 20°C. NMR spectra were recorded on a Bruker DPX-400 spectrometer. For ^{1}H- and ^{13}C-NMR spectroscopy TMS or TSPSA [(4-trimethylsilyl)propane sulfonic acid Na salt, δ(^{1}H) = 0.015 ppm] were used as internal standards, for ^{31}P-NMR 85% H$_3$PO$_4$ was used as an external standard. IR spectra were recorded as a pellets with KBr on a Perkin−Elmer system 2000. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Microanalyses were carried out by the Departmental service.

[PPh$_4$$^+$]$_2$[C$_{10}H_6PS_2$(*μ*-S)PS$_2$$^{2-}$] (2): **1** (200 mg, 0.63 mmol) was added to a solution of NaHS.H$_2$O (220 mg, 3.0 mmol) in water (5 cm^3) and refluxed with stirring until all the solid **1** dissolved (ca. 10 min). The resulting cloudy solution was filtered using a sintered glass funnel with a plug of celite. The filtrate was added with vigorous stirring to a solution of PPh$_4$Cl (472 mg, 1.26 mmol), the resulting yellow solid was filtered off, washed with water (5 × 20 cm^3) and dried in vacuo. The crude product was of sufficient purity, however for recrystalisation acetonitrile can be used. Crystals of **2** suitable for X-ray structure determination were obtained by slow cooling of its hot saturated solution in acetonitrile. Yield 531 mg (82%) before recrystalisation. − C$_{58}$H$_{46}$P$_4$S$_5$: calcd. C 67.8, H 4.5; found C 67.6, H 4.6. − M.p. 271−273°C (decomp.). − IR (cm^{-1}): ṽ = 690vs and 669vs [ν(P=S)]. − ^{31}P{^{1}H}-NMR (CD$_3$CN/[D$_6$]DMSO 3:1; for numbering of atoms see Figure 2): δ = 72.8 (s, anion), 29.1 (s, PPh$_4$$^+$). − ^{1}H-NMR (CD$_3$CN/[D$_6$]DMSO 3:1; for numbering of atoms see Figure 2): δ = 8.64 (2 H, m, 2-H and 8-H), 7.92 (8 H, m, PPh$_4$$^+$), 7.79−7.65 (34 H, m, 4-H, 6-H and PPh$_4$$^+$), 7.40 (2 H, m, 3-H and 7-H). − Mass spectrum (ES+): *m*/*z* 339 (PPh$_4$$^+$), 262 (PPh$_3$); (ES−): *m*/*z* 687 (anion + PPh$_4$$^+$), 349 (anion + H), 317 (anion − S), 253 (anion − 3S + H), 189 (C$_{10}$H$_6$P$_2$ + H), 174 (anion, z = 2).

[K$^+$]$_2$[C$_{10}$H$_6$PS$_2$(*μ*-S)POS^{2-}]·H$_2$O (3): 1 (500 mg, 1.58 mmol) was added to a solution of KOH (204 mg, 3.64 mmol) in water (5 cm^3) and refluxed with stirring for 1 hour. The resulting cloudy solution was filtered using a sintered glass funnel with a plug of celite and the filtrate was evaporated on a rotavapor. The resulting light yellow hygroscopic solid was recrystalised from mixture of ethanol/methanol (4:1) and dried in vacuo at room temperature. Crystals of **3** suitable for X-ray structure determination (in the form of hydrate with 2.5 molecule of water per naphthalene entity) were obtained by evaporation of its saturated solution in an ethanol/methanol mixture. Yield 489 mg (72%) of monohydrate. − C$_{10}$H$_6$K$_2$OP$_2$S$_4$·H$_2$O: calcd. C 28.0, H 1.9; found C 28.0, H 1.9. − Decomp. above 200°C. − IR (cm^{-1}): ṽ = 1112vs [ν(P=O)], 650vs [ν(P=S)]. − ^{31}P{^{1}H}-NMR (D$_2$O; for numbering of atoms see Figure 3): δ = 69.2 (d, P-2), 58.6 (d, P-1), ^2J(PP) = 11.6 Hz. − ^{1}H NMR (D$_2$O; for numbering of atoms see Figure 3): δ = 8.75 [1 H, ddd, ^3J(PH) = 20.8, ^3J(HH) = 7.3, ^4J(HH) = 1.4 Hz, 2-H or 8-H], 8.60 [1 H, ddd, ^3J(PH) = 18.9, ^3J(HH) = 7.3, ^4J(HH) = 1.4 Hz, 2-H or 8-H], 8.04 (2 H, m, 4-H and 6-H), 7.64 (2 H, m, 3-H and 7-H). − ^{13}C{^{1}H}-NMR (D$_2$O; for numbering of atoms see Figure 3): δ = 140.0 [dd, ^1J(PC) = 80.4, ^3J(PC) = 3.1 Hz, C-9], 137.6 [dd, ^1J(PC) = 106.5, ^3J(PC) = 3.9 Hz, C-1], 134.0 [t, ^3J(PC) = 10.6 Hz, C-5], 133.5 (m, C-4 or C-6), 133.3 (m, C-4 or C-6), 131.4 [d, ^2J(PC) = 11.6 Hz, C-8], 130.1 [d, ^2J(PC) = 14.0 Hz, C-2], 126.8 [t, ^2J(PC) = 8.9 Hz, C-10], 125.6 [d, ^3J(PC) = 12.2 Hz, C-3 or C-7], 125.4 [d, ^3J(PC) = 12.8 Hz, C-3 or C-7]. − Mass spectrum (ES+): *m*/*z* 449 (M + K), 317 (anion − O + H); (ES-): *m*/*z* 371 (anion + K), 333 (anion + H).

[K$^+$]$_2$[C$_{10}$H$_6$PS$_2$(*μ*-O)PS$_2$$^{2-}$] (4): To **3** (monohydrate, 500 mg, 1.17 mmol) 0.5M HCl (5 cm^3) was added, resulting solution was heated to 70°C for 1 hour and then filtered using a sintered glass funnel with a plug of celite. The filtrate was evaporated on a rotavapor and the resulting solid was dried in vacuo. The following purification process for crude product was used: To the solid dry methanol (10 cm^3) was added, the resulting suspension was well mixed, filtered and the filtrate was evaporated on a rotavapor. The solid was then dissolved in water (8 cm^3) and titrated by 1M KOH to pH 7. The resulting light yellow hygroscopic solid obtained after stripping off water was recrystalised from non-dried ethanol. Crystals of **4** suitable for X-ray structure determination were obtained by cooling of its hot saturated solution in ethanol. Yield 249 mg (52%). − C$_{10}$H$_6$K$_2$OP$_2$S$_4$: calcd. C 29.2, H 1.5; found C 28.8, H 1.5. − M.p. 310°C. − IR (cm^{-1}): ṽ = 825vs [ν$_{as}$(P−O−P)], 678s, 661vs [ν(P=S)]. − ^{31}P{^{1}H}-NMR (D$_2$O; for numbering of atoms see Figure 4): δ = 101.4 (s), ^2J(PP) = 51.2 Hz (calculated value).

− ^{1}H NMR (D_2O; for numbering of atoms see Figure 4): δ = 8.39 (2 H, m, 2-H and 8-H), 8.07 (2 H, m, 4-H and 6-H), 7.66 (2 H, m, 3-H and 7-H). − $^{13}C\{^1H\}$-NMR (D_2O; for numbering of atoms see Figure 4): δ = 137.8 [m, $^1J(PC)$ = 103.4, $^3J(PC)$ = 3.6 Hz, C-1 and C-9], 133.1 [t, $^3J(PC)$ = 9.9 Hz, C-5], 132.3 (s, C-4 and C-6), 131.3 (m, C-2 and C-8), 126.5 (m, C-3 and C-7), 125.7 [t, $^2J(PC)$ = 8.0 Hz, C-10]. − Mass spectrum (ES+): *m/z* 449 (M + K), 317 (anion − O + H); (ES-): *m/z* 371 (anion + K), 333 (anion + H), 317 (anion − O + H), 237 (anion − 3S + H), 205 (anion − 4S + H), 189 ($C_{10}H_6P_2$ + H), 166 (anion, z = 2).

$[PPh_4^+]_2[C_{10}H_6PS_2(\mu\text{-}O)PS_2^{2-}]\cdot 0.5\ CH_3CN$ (5): To a solution of PPh_4Cl (365 mg, 0.97 mmol) in water (10 cm^3) a solution of **4** (200 mg, 0.49 mmol) in water (10 cm^3) was added with vigorous stirring. The resulting yellow solid was filtered off, washed with water (5 × 20 cm^3), dried in vacuo and recrystalised from acetonitrile. Crystals of **5** suitable for X-ray structure determination were obtained by slow cooling of its hot saturated solution in acetonitrile. Yield 397 mg (79%) of acetonitrile hemisolvate. − $C_{58}H_{46}OP_4S_4.1/2CH_3CN$: calcd. C 68.7, H 4.6, N 0.7; found C 68.3, H 4.5, N 0.5. − Decomposes above 180°C. − IR (cm^{-1}): ṽ = 851 s [$\nu_{as}(P{-}O{-}P)$], 690 vs and 671 vs [$\nu(P{=}S)$]. − $^{31}P\{^1H\}$-NMR (CD_3CN, for numbering of atoms see Figure 4): δ = 100.3 (s, anion), 29.8 (s, PPh_4^+). − ^{1}H NMR (CD_3CN, for numbering of atoms see Figure 4): δ = 8.20 (2 H, m, 2-H and 8-H), 7.85 (8 H, m, PPh_4^+), 7.70−7.56 (34 H, m, 4-H, 6-H and PPh_4^+), 7.34 (2 H, m, 3-H and 7-H). − $^{13}C\{^1H\}$-NMR ([D$_6$]DMSO; for numbering of atoms see Figure 4): δ = 142.8 (m, C-1 and C-9), 135.4 (d, PPh_4^+), 134.8 (d, PPh_4^+), 131.9 [t, $^3J(PC)$ = 9.0 Hz, C5], 130.5 (d, PPh_4^+), 129.2 (t, C-2 and C-8), 128.2 (s, C-4 and C-6), 125.7 [t, $^2J(PC)$ = 7.4 Hz, C-10], 124.8 (t, C-3 and C-7), 117.6 (d, PPh_4^+). − Mass spectrum (ES+): *m/z* 339 (PPh_4^+), 262 (PPh_3); (ES−): *m/z* 671 (anion + PPh_4^+), 333 (anion + H), 237 (anion − 3S + H), 166 (anion, z = 2).

$[CH_3NH_3^+][PyH^+][C_{10}H_6POS(\mu\text{-}O)POS^{2-}]\cdot 1.5\ Py$ (6): A solution of **15** (20 mg) in pyridine/hexane was left in an open test tube at room temperature. After 5 days colourless crystals suitable for X-ray structure determination were formed. M.p. 102−104°C. Several crystals were examined by NMR. $^{31}P\{^1H\}$-NMR (D_2O): δ = 59.4 (s). − ^{1}H NMR (D_2O): δ = 8.60−7.58 (protons of naphthalene and pyridinium entity), 3.4 (br s, acid protons of $CH_3NH_3^+$ and PyH^+), 2.51 (s, CH_3).

$C_{10}H_6P(O)(OH)(\mu\text{-}O)P(O)(OH)]$ (14): To **3** (monohydrate, 500 mg, 1.17 mmol) 3M HCl (20 cm^3) was added, resulting solution was refluxed for 16 hours and then filtered using a sintered glass funnel with a plug of celite. The volume was reduced to 2 cm^3 on rotavapor and the solid **14** precipitated aftef cooling to 0°C was filtered off and dried in vacuo. Yield ca 65%. − $^{31}P\{^1H\}$-NMR (MeOH): δ = 7.1 (s). A similar procedure was applied when **4** was used as a starting material.

X-ray Crystallographic Study: Details of the data collections and refinements are summarised in Table 1. Data were collected at room temperature using graphite-monochromatized Mo-K_α (λ = 0.71073 Å) radiation on a Siemens SMART CCD diffractometer. Full hemisphere of data with 0.3° steps was collected. Sadabs corrections were applied. All of the non-hydrogen atoms were refined anisotropically, calculations employed the SHELXTL program system.[22] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 120586−120590, see http://www.ccdc.cam.ac.uk.

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