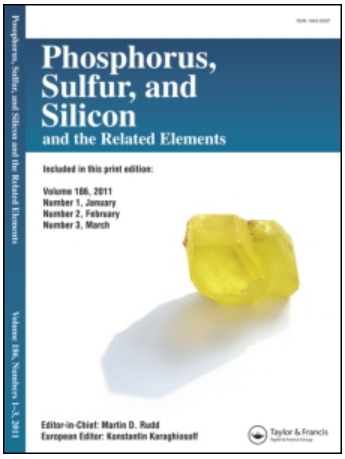

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF LONG CHAIN ALKYL AMMONIUM HEXATHIODIPHOSPHATE (IV): CHARACTERIZATION OF THE DIHYDROGENO-HEXATHIODIPHOSPHATE ANION $H_2P_2S^2_6$

H. Perez[a]
[a] C.E.A./C.E.-Saclay, Service de Chimie Moléculaire, Gif Sur Yvette, Cedex, France

To cite this Article Perez, H.(1993) 'SYNTHESIS OF LONG CHAIN ALKYL AMMONIUM HEXATHIODIPHOSPHATE (IV): CHARACTERIZATION OF THE DIHYDROGENO-HEXATHIODIPHOSPHATE ANION $H_2P_2S^2_6$', Phosphorus, Sulfur, and Silicon and the Related Elements, 79: 1, 7 — 12
To link to this Article: DOI: 10.1080/10426509308034392
URL: http://dx.doi.org/10.1080/10426509308034392

Phosphorus, Sulfur, and Silicon, 1993, Vol. 79, pp. 7–12
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF LONG CHAIN ALKYL AMMONIUM HEXATHIODIPHOSPHATE (IV): CHARACTERIZATION OF THE DIHYDROGENO-HEXATHIODIPHOSPHATE ANION $H_2P_2S_6^{2-}$

H. PEREZ

C.E.A./C.E.-Saclay, Service de Chimie Moléculaire, 91191 Gif Sur Yvette Cedex, France

(Received December 10, 1992; in final form February 16, 1993)

This paper describes the synthesis and characterization of the following two compounds: $(C_{18}H_{37}N^+H_3)_4$, $P_2S_6^{4-}$ and $(C_{22}H_{45}N^+(CH_3)_3)_2$, $H_2P_2S_6^{2-}$. The first compound is a "new classical salt" containing the hexathiodiphosphate (IV) anion whereas the second compound is absolutely new because it contains the $H_2P_2S_6^{2-}$ anion. The existence of this anion was supposed but it has not been isolated and characterized so far. In the present case, the characterization of $H_2P_2S_6^{2-}$ was ascertained by ^{31}P NMR studies. The stabilization of this moiety is explained in terms of steric effects.

Key words: Hexathiodiphosphate (IV); amphiphilic ammonium salt; ^{31}P NMR; heteronuclear decoupling; steric effects.

I. INTRODUCTION

Our attempts at synthesizing $M_2P_2S_6$ (M^{2+}, $P_2S_6^{4-}$) compounds to be inserted in Langmuir-Blodgett films[1,2] have lead us to the synthesis of long chain alkyl (amphiphilic) ammonium hexathiodiphosphates (IV), which were expected to exist as $(R^+)_4$, $P_2S_6^{4-}$. We have tried to synthesize such compounds using two different long chain alkyl ammonium cations: $C_{18}H_{37}N^+H_3$ and $C_{22}H_{45}N^+(CH_3)_3$ (the two products obtained from these cations have been respectively named (**I**) and (**II**)).

II. EXPERIMENTAL

The reactions are metatheses:

$$4R^+, X^- + Na_4P_2S_6 \rightarrow (R^+)_4, P_2S_6^{4-} + 4NaX$$

The experimental conditions for the synthesis of (**I**) and (**II**) are identical. We have used a diphasic system because of the large difference in the chemical nature of the reactants. The aqueous phase contains the $P_2S_6^{4-}$ anions (provided by the salt $Na_4P_2S_6$, $6H_2O$ and synthesized according to the method described by Falius).[3] The organic phase (80% $CHCl_3$–20% EtOH) contains the long chain alkyl ammonium salts (two fold excess) which are: $(C_{18}H_{37}N^+H_3)$, NO_3^- (for (**I**)) and $C_{22}H_{45}N^+(CH_3)_3$, Br^- (for (**II**)). The two phases (previously degassed) were vigorously stirred for one hour. For the $(C_{18}H_{37}N^+H_3)$, NO_3^- a complete precipitation of (**I**) occurs during the reaction whereas for the $C_{22}H_{45}N^+(CH_3)_3$, Br^-, the product (**II**) precipitates completely when cooling down the organic phase.

Supposing $((R+)_4, P_2S_6^{4-})$ as the products, the yields are 100% with $(C_{18}H_{37}N^+H_3)$, NO_3^- (product (**I**)) and 10.5% with $(C_{22}H_{45}N^+(CH_3)_3, Br^-$ (product (**II**)). The latter can recrystallize easily in $CHCl_3$, whereas (**I**) is completely insoluble in usual solvents and cannot be purified in this way. Therefore, we have pulverized and washed the precipitate (**I**) (3 hours) with a diphasic system similar to that used for the synthesis.

III. RESULTS AND CHARACTERIZATIONS

We have used IR spectroscopy, ^{31}P and ^1H NMR and elemental analysis as characterization techniques.

1°) Product (**I**) obtained using $(C_{18}H_{37}N^+H_3)$, NO_3^-.

We have recorded the infrared spectrum of (**I**) (not shown) and attributed the absorptions peaks as listed below:

—aliphatic chain: 2913 cm^{-1}, 2850 cm^{-1}, 1466 cm^{-1}, 720 cm^{-1}.
—N^+H_3 group: 1577 cm^{-1}, 1484 cm^{-1}.
—$P_2S_6^{4-}$ anion: 590 cm^{-1}, 575 cm^{-1}, 439 cm^{-1}.

Referring to the literature data,[4,5,6] the absorption peak located at 590 cm^{-1} (and 575 cm^{-1}) can be assigned to PS_3 groups ($\nu_d PS_3$). The attribution of the peak located at 439 cm^{-1} has been controversely discussed, some authors indicate that it is a related to the νP—P vibration[6] whereas others[5] assign it to the PS_3 groups ($\nu_s PS_3$).

Since compound (**I**) is insoluble, its ^{31}P NMR spectrum (not shown) has been performed in the solid state at the magic angle spinning, with a Bruker spectrometer working at 40 Mhz. The spectrum exhibits a unique unstructured line at 108.4 ppm (referring to H_3PO_4) which is characteristic of the $P_2S_6^{4-}$ species.[3]

The elemental analysis has confirmed that the product (**I**) is a classical ammonium salt of the hexathiodiphosphate (IV) anion $P_2S_6^{4-}$: $(C_{18}H_{37}N^+H_3)_4, P_2S_6^{4-}$.

2°) Product (**II**) obtained using $C_{22}H_{45}N^+(CH_3)_3, Br^-$.

The IR spectrum of (**II**) is shown in Figure 1. In addition to the absorptions of the aliphatic chains, the absorption peaks caused by the vibrations of C—N^+ bonds appeared in the range of 900–1000 cm^{-1}. In the 400–700 cm^{-1} region, several bands were observed which cannot be assigned either to $C_{22}H_{45}N^+(CH_3)_3, Br^-$ or to $P_2S_6^{4-}$ anion. The peak values are: 673 cm^{-1}, 654 cm^{-1}; 644 cm^{-1}; 604 cm^{-1}; 542 cm^{-1}; 484 cm^{-1}.

The ^{31}P NMR spectrum of (**II**) (not shown) has been recorded in $CDCl_3$ solution at 318°K to improve the signal/noise ratio. H_3PO_4 was used as reference and the spectra was recorded with a Bruker spectrometer working at 200 MHz.

The spectrum of (**II**) exhibits a unique triplet centered at 104.7 ppm. The lateral lines are separated from the center by 6.7 Hz and 6.8 Hz. As in the case of the IR spectrum, the ^{31}P NMR spectrum of (**II**) does not correspond to the $P_2S_6^{4-}$ anion (as described previously, it shows a single ^{31}P NMR line).

The lack of other lines in the spectrum indicates that the structured peak centered at 104.7 ppm, is not a result from a homonuclear coupling between the phosphorus

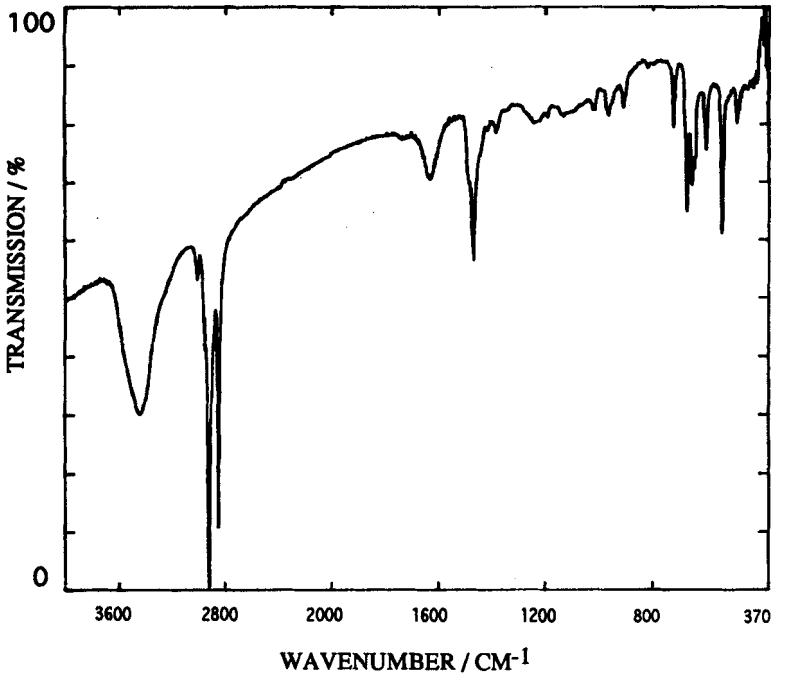

FIGURE 1 Transmission IR spectrum of product (II) between 370 and 4000 cm^{-1} (KBr pellet).

atoms. Consequently, we tried to find evidences of a heteronuclear coupling phenomenon. The ^{33}S (s = 3/2) cannot be responsible for such a coupling since it has weak isotopic abundance. Therefore, we have looked for a heteronuclear coupling between phosphorus and hydrogen atoms and we have recorded the ^{1}H NMR spectrum of (II) (shown in Figure 2).

In addition to the lines due to the organic cation, the spectrum shows a structure centered at 4.22 ppm, which looks like a triplet with a coupling constant of 6.7 Hz (because of the large number of hydrogen atoms in the compound we cannot define accurately the number of involved hydrogen atoms). We have verified by decoupling experiments that the protons appearing at 4.22 ppm are coupled with phosphorus atoms.

The elemental analysis of (II) confirmed that this product is obviously not $(C_{22}H_{45}N^{+}(CH_3)_3)_4$, $P_2S_6^{4-}$ and indicates the presence of oxygen which was not expected. (Calc: C, 69.52; H, 12.51; N, 3.24; P, 3.59; S, 11.12; O, 0. Found: C, 61.15; H, 10.74; N, 2.77; P, 6.61; S, 17.22; O, 1.73.)

IV. DISCUSSION

Regarding the product (I), the results are unambiguous and consistent with those expected. The synthesis leads to the formation of a "classical salt" containing the species $P_2S_6^{4-}$ which offers little interest towards a detailed discussion.

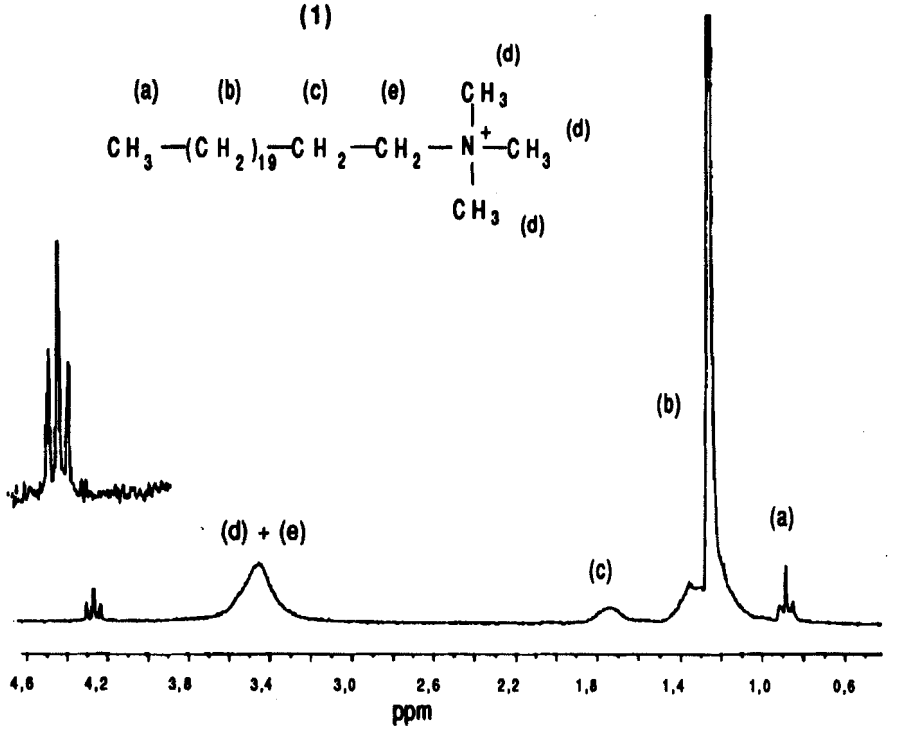

FIGURE 2 ^{1}H NMR spectrum of the product (**II**) between 0.6 and 4.6 ppm. TMS (Tetramethylsilan) was used as reference.

In contrast, the second synthesis is much more interesting. An overview of the results collected for (**II**) shows clearly that we have synthesized a new compound containing a species quite similar to the $P_2S_6^{4-}$ anions. The chemical shift of 104.7 ppm is comparable to the chemical shift recorded for compound (**I**), which contains the hexathiodiphosphate (IV) anion. Therefore, we have supposed the existence of a P—P bond in the anionic species associated with $C_{22}H_{45}N^+(CH_3)_3$. Consequently, the anion has two magnetically equivalent phosphorus atoms because its ^{31}P NMR spectrum exhibits a unique structure. In spite of the presence of oxygen in the elemental analysis of (**II**), we can exclude (symmetrical) species such as $P_2S_{6-n}O_n^{4-}$, because the corresponding values for the chemical shift are distinctly less than 100 ppm.[7]

For the ^1J P—H coupling constants we have found classical values of some hundreds Hertz in the literature.[8] This indicates clearly that there is no direct P—H linkage in compound (**II**). Since the magnetical equivalence of the two phosphorus atoms of the P—P bond, we can also deduce that hydrogen atoms are even in number and are symmetrically distributed around the P—P bond. Finally, if we suppose the anionic moiety associated with $C_{22}H_{45}N^+(CH_3)_3$ to be a protonated form of $P_2S_6^{4-}$ (the neutral and completely protonated species ($H_4P_2S_6$) was completely excluded), then the unique possible formula is in Figure 3.

The species $H_2P_2S_6^{2-}$ meets the criterion previously described and the resulting formula for the compound (**II**), $(C_{22}H_{45}N^+(CH_3)_3)_2$, $H_2P_2S_6^{2-}$, is in agreement with

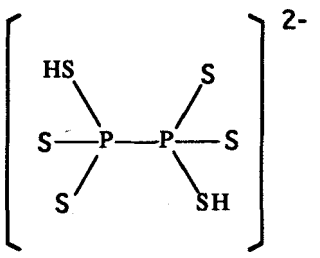

FIGURE 3 Formula proposed for the anionic species associated with the N-docosyl trimethyl ammonium cation.

the elemental analysis. (Calc: C, 60.48; H, 11.08; N, 2.82; P, 6.25; S, 19.35; O, 0. Found: C, 61.15; H, 10.74; N, 2.77; P, 6.61; S. 17.22; O, 1.73.)

The slight lack of sulfur can be related to the presence of oxygen. This is not very surprising since the compound (**II**) (as the compound (**I**)) emits a hydrogen sulfide odor which gives evidence of a slight chemical instability.

In order to explain the ^{31}P NMR of product (**II**) (and the structure centered at 4.22 ppm in the ^{1}H NMR spectrum) it has to be mentioned that the coupling constants ^{2}J P—H and ^{3}J P—H can have identical values. Such examples are known in the case of hydrogen-phosphorus coupling established through carbon-carbon linkage (in this case the coupling constants are found to be in the range between 10 Hz and 20 Hz).[9] Therefore, we suggest the following explanation for the NMR spectra of compound (**II**): the coupling structures result from the overlapping of two doublet lines caused by the couplings ^{2}J P—H and ^{3}J P—H, the values of which are quite identical. These doublet lines are not resolved and appear as triplet lines in which, obviously, the central peak has the double height compared with the neighbored lines.

V. CONCLUSION

We have synthesized two new compounds. The first one is a "classical" ammonium salt containing the $P_2S_6^{4-}$ anion. The second compound contains the anion $H_2P_2S_6^{2-}$ which has never been described and characterized so far. The stabilization of this protonated form of the $P_2S_6^{4-}$ anion can be explained in terms of steric effects: the large ammonium cation $C_{22}H_{45}N^{+}(CH_3)_3$ prevents the formation of $(C_{22}H_{45}N^{+}(CH_3)_3)_4$, $P_2S_6^{4-}$. In place of, it reacts with $H_2P_2S_6^{2-}$ which should exist in weak concentration in the aqueous solutions of $P_2S_6^{4-}$. The argument of steric effects is strengthened by the fact that the same phenomenon is observed with the diazabiclo 2,2,2 octane (DABCO) when it is quaternized with one long alkyl chain.

ACKNOWLEDGEMENTS

The author acknowledges the members of the NMR laboratory of the "Service de Chimie Moléculaire" (C.E.A./C.E. Saclay 91191 Gif sur Yvette Cedex) who made available all facilities for recording the NMR spectra.

REFERENCES

1. H. Perez, PhD Thesis, Paris XI (France), 1991.
2. H. Perez, A. Ruaudel-Teixier and M. Roulliay, Thin Solid Films, **210,** 410 (1992).
3. H. Falius, *Z. Anorg. Allg. Chem.*, **356,** 189 (1968).
4. H. Bürger and H. Falius, *Z. Anorg. Allg. Chem.*, **363,** 24 (1968).
5. R. Mercier, J. P. Malugani, B. Fahys, J. Douglade and G. Robert, *J. Solid State Chem.*, **43,** 151 (1982).
6. Y. Mathey, R. Clément, C. Sourisseau and G. Lucazeau, *Inorg. Chem.*, **19,** 2773 (1980).
7. H. Falius and W. Krause, *Z. Anorg. Allg. Chem.*, **477,** 21 (1981).
8. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, "P^{31} Nuclear Magnetic Resonance," Topics in phosphorus chemistry, (Interscience 1977), Vol. 5, Chap. 1, p. 51.
9. Gorenstein, D. G., "Phosphorus 31 NMR, principles and applications," (Academic Press, 1984) Chap. 2, p. 42.