

Brief Communications

Synthesis and photophysical properties of 2,3,4,5-tetraphenyl-1-*n*-octyl-1-monophosphole*

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A new method for the preparation of 2,3,4,5-tetraphenyl-1-octyl-1-monophosphole was developed. It was shown that the reaction of *n*-octyl chloride with a mixture of sodium 1,2,3-tri- and 1-monophospholides obtained by refluxing sodium polyphosphides with diphenylacetylene resulted in the formation of exclusively 1-*n*-octyl-1-monophosphole. The photophysical properties of 1-*n*-octyl-1-monophosphole were studied by electron absorption and emission spectroscopy. According to the Raman spectroscopy data, the phenyl moieties of this molecule are efficiently conjugated with the diene system of the heterocycle leading to the appearance of the corresponding absorption and emission bands in the visible spectral range.

Key words: phosphorus heterocycles, phosphole, luminescence, conjugation effects, Raman spectroscopy.

Phospholes and their derivatives are of significant interest as building blocks for π -conjugated materials^{1–4} applied in molecular electronics for manufacturing light-

emitting diodes (LED), thin-film transistors, and photovoltaic cells.^{5–8} The oxidation and sulfonation of the phosphorus atom in monophospholes or complexation with transition metals induce the shift of the absorption and emission bands, which enables tuning the properties of the material.^{9,10} The use of phospholes as various sen-

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systems is of special interest.^{11–14} In addition, phospholes are attractive as labile π -acceptor mono- and bidentate ligands for the construction of catalysts for organic reactions.^{4,15}

Many methods for the synthesis of various monophospholes have been proposed so far.⁴ Their main drawbacks are the multistep character of synthesis and the use of toxic phosphorus(III) chloride and organometallic compounds. Therefore, the development of procedures for the preparation of organophosphorus compounds in less steps using directly elemental phosphorus P_4 is a challenging problem. The development of white phosphorus activation methods^{16,17} facilitated the emergence of new approaches to the synthesis of phospholide anions,^{18–21} and the alkylation of these anions results in the formation of diverse phospholes.^{4,22}

We have previously shown²³ that the reaction of a mixture of sodium polyphosphides consisting predominantly of NaP_5 and Na_3P_7 with diphenylacetylene affords sodium 4,5-diphenyl-1,2,3-triphospholide (**1**) and sodium 2,3,4,5-tetraphenylmonophospholide (**2**). Sodium and white phosphorus in a molar ratio of 2 : 1 were used to prepare a mixture of sodium polyphosphides. The purpose of this work is to study the reactivity of a mixture of sodium phospholides in the alkylation reactions aimed at synthesizing new mono- and triphospholes.

Results and Discussion

We found that sodium 1,2,3-triphospholide (**1**) and sodium 1-monophospholide (**2**) demonstrate different reactivities toward alkyl chlorides. For example, compound **2** easily reacts with *n*-octyl chloride at room temperature, whereas compound **1** cannot be alkylated under the same conditions (Scheme 1). After the reaction mixture containing a mixture of phospholides **1** and **2** was treated with

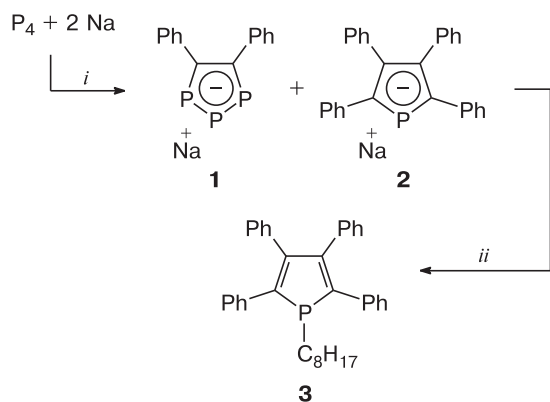
n-octyl chloride at ~ 20 °C, no changes in the AB_2 spin system of 1,2,3-triphospholide anion **1** are observed in the ^{31}P NMR spectrum, and the singlet at +100 ppm characteristic of 2,3,4,5-tetraphenylmonophospholide anion **2** shifts to +20 ppm characteristic of monophospholes.²⁴ The target compound 2,3,4,5-tetraphenyl-1-*n*-octyl-1-monophosphole (**3**) was completely separated from triphospholide anion **1** by extraction with petroleum ether. After the solvent was removed, the product was obtained as a yellow powder in a yield of 26%. The structure of compound **3** was proved by NMR spectroscopy, and the composition was confirmed by mass spectrometry and elemental analysis.

According to available data,⁴ monophospholide anions are more reactive toward alkyl halides, whereas 1,2-diphospholides and 1,2,3-triphospholides react only with primary alkyl bromides or secondary alkyl iodides.²⁵ Indeed, we found that the alkylation of phospholides **1** and **2** occurred when alkyl bromides and alkyl iodides were used. The proposed synthetic method allows one to obtain systems with different functional groups at the phosphorus atom providing a number of advantages. For example, the elongation of the alkyl chain in the case of compound **3** contributes to the improvement of film morphology on mixing with a polymer matrix and/or the enhancement of solubility in organic solvents. The method proposed also makes it possible to attach chiral moieties to the phosphorus atom, which in combination with the luminescence properties enables the use of monophospholes in luminescent chiral recognition.^{26,27}

The experimental electronic absorption and photoluminescence spectra of a solution of compound **3** in dichloromethane are presented in Fig. 1, *a*. It is seen that the long-wavelength maximum of the electronic absorption (λ_{max}) lies at ~ 370 nm (3.35 eV), the next maximum is observed at 323 nm (3.84 eV), whereas the maximum in the fluorescence spectrum (λ_{em}) is located at 473 nm (2.62 eV). Thus, the Stokes shift observed in this case reaches the value of about 103 nm (0.73 eV). The location of the absorption and emission maxima in the visible range of the electromagnetic spectrum is indicative of an extended π -conjugated bond system, which has already been established for related systems.^{23,28–35} This is also evidenced by the most intense peaks attributed to the symmetric stretching vibrations of the phenyl moieties (1000 and 1600 cm^{-1}) in the Raman spectrum of compound **3** (see Fig. 1, *b*). It is known that the intensity of these lines is an indicator of efficient conjugation involving aromatic groups.^{36–40}

In conclusion, we showed that the reaction of a mixture of sodium 4,5-diphenyl-1,2,3-triphospholide (**1**) and sodium 2,3,4,5-tetraphenylmonophospholide (**2**) with *n*-octyl chloride affords exclusively 2,3,4,5-tetraphenyl-1-*n*-octyl-1-monophosphole (**3**), whereas 1,2,3-triphospholide anions do not undergo alkylation. All observed

Scheme 1



Reagents and reaction conditions: *i.* (1) diglyme, 160 °C, (2) Ph—≡—Ph; *ii.* *n*-C₈H₁₇Cl, THF, 0 °C, - P₃C₂Ph₂Na.

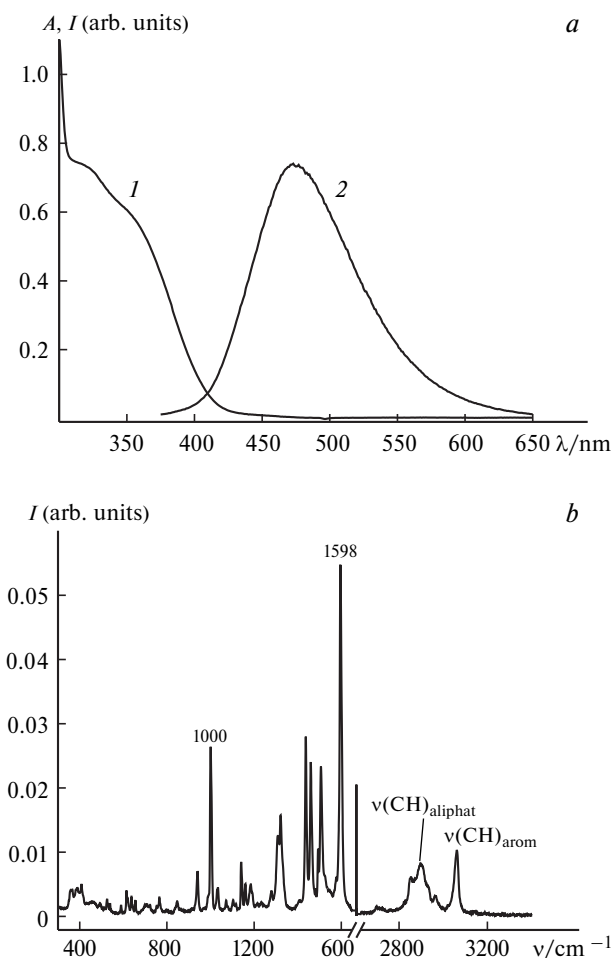


Fig. 1. Experimental (a) electronic absorption (I) and fluorescence spectra (2) of a solution of compound **3** in CH_2Cl_2 ($C \approx 10^{-4} \text{ mol L}^{-1}$, $\sim 20^\circ \text{C}$); (b) Raman spectrum of compound **3**.

spectral properties of the electronic and vibrational spectra attest to the efficient conjugation between the diene system of the heterocycle and aromatic moieties at the carbon atoms in compound **3**, whereas the luminescent response in the visible range of the electromagnetic radiation suggests that this system is promising for organic electronics and sensorics.

Experimental

All works related to the preparation of the starting reagents and synthesis and isolation of products were carried out in an inert atmosphere using the standard Schlenk technique. All solvents were distilled over Na/benzophenone or P_2O_5 immediately before use. NMR spectra were recorded on a Bruker MSL-400 instrument (^1H , 400 MHz; ^{31}P , 121.7 MHz; ^{13}C , 100.6 MHz) using TMS as an internal standard for ^1H and ^{13}C NMR spectra and using 85% H_3PO_4 as an external standard for ^{31}P NMR spectra. For spectral measurements, 10–20% solutions in inert solvents (CDCl_3 , THF-d_8) were prepared. Elemental analysis was carried out on a EuroVector EA 3000 CHNS-O automated

analyzer. A mixture of sodium 4,5-diphenyl-1,2,3-triphospholide (**1**) and sodium 2,3,4,5-tetraphenylmonophospholide (**2**) was prepared using a previously described procedure.²³ Diphenylacetylene and *n*-octyl chloride were used as received.

Electronic and vibrational spectroscopy. The Raman spectra of samples of the studied compounds (powders in glass tubes filled in an inert atmosphere) were recorded on a Vertex-70 Fourier-transform spectrometer (Bruker) equipped with a Ram II module with an optical resolution of 2 cm^{-1} . A Nd:YAG laser with a wavelength of 1064 nm served as an excitation source. The exciting radiation power was varied from 100 to 250 mW. UV absorption spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer using a quartz cell (10 mm) at 20°C . The spectra were recorded with a scanning rate of 480 nm min^{-1} at the spectral slit width of 1 nm. All samples were prepared in dichloromethane at the concentration of $10^{-4} \text{ mol L}^{-1}$. Photoluminescence spectra of solutions were recorded at room temperature on a Cary Eclipse Fluorescence Spectrophotometer spectrofluorimeter (Varian) using a quartz cell (10 mm). The luminescence signal was excited in the absorption range of the substance ($\lambda_{\text{exc}} = 350 \text{ nm}$), and the concentration was selected from the calculation of the absorbance less than 0.1 at the wavelength of the exciting line to avoid the "internal filter" effect.

2,3,4,5-Tetraphenyl-1-*n*-octyl-1-monophosphole (3). A mixture of metallic sodium (0.32 g, 13.9 mmol), white phosphorus (0.86 g, 6.8 mmol), and catalytic quantities of dibenzo-18-crown-6 in diglyme (30 mL) was refluxed for 4 h. Then diphenylacetylene (1.23 g, 6.8 mmol) was added to the reaction mixture, which was refluxed for 3 h more. During reflux the reaction mixture turned dark red. After the indicated time, the solution was separated from the precipitate by filtration and concentrated to dryness. The dry residue was successively dissolved in THF (5 mL) and then precipitated adding petroleum ether (30 mL), and the procedure was repeated twice. A mixture of solvents was removed by simple decantation, and the precipitate was dried *in vacuo*. The obtained precipitate containing sodium 4,5-diphenyl-1,2,3-triphospholide (**1**) and sodium 2,3,4,5-tetraphenylmonophospholide (**2**) was dissolved in THF (20 mL) and cooled to 0°C . Then *n*-octyl chloride (1.7 mL, 10.2 mmol) was added. The reaction mixture was stirred for 12 h at $\sim 20^\circ \text{C}$. Then the solvent was evaporated, and the product was extracted with petroleum ether ($3 \times 40 \text{ mL}$). After the solvent was evaporated, a yellow powder of the product was obtained in a yield of 0.90 g (26%). M.p. = $117\text{--}118^\circ \text{C}$. ^{31}P NMR (C_6D_6), δ : 21.3 (s). ^1H NMR (CDCl_3), δ : 0.86 (t, 3 H, CH_3 , $^3J_{\text{HH}} = 7.0 \text{ Hz}$); 1.13–1.35 (m, 12 H, $(\text{CH}_2)_6$); 1.84–1.88 (m, 2 H, P-CH_2); 6.98–7.39 (m, 20 H, Ph). ^{13}C NMR (CDCl_3), δ : 14.1 (s, CH_3); 22.5, 24.6 (both s, CH_2); 26.8 (d, PCH_2 , $^1J_{\text{PC}} = 18.5 \text{ Hz}$); 28.8, 28.9, 30.4, 31.7 (all s, CH_2); 126.3 (s, *p*- C_{Ph}); 126.4 (s, *p*- C_{Ph}); 127.5 (s, *m*- C_{Ph}); 128.0 (s, *m*- C_{Ph}); 129.5 (s, *o*- C_{Ph}); 129.6 (s, *o*- C_{Ph}); 130.4 (m, *ipso*- C_{Ph}); 136.9 (d, $\text{C}=\underline{\text{C}}-\text{P}$, $^1J_{\text{CP}} = 17.2 \text{ Hz}$); 147.7 (d, $\underline{\text{C}}=\text{C}-\text{P}$, $^2J_{\text{CP}} = 10.6 \text{ Hz}$). MS (EI): 500 $[\text{M}]^+$. Calculated for $\text{C}_{36}\text{H}_{37}\text{P}$ (M 500) (%): C, 86.36; H, 7.45; P, 6.19. Found: C, 86.24; H, 7.62; P, 6.24.

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