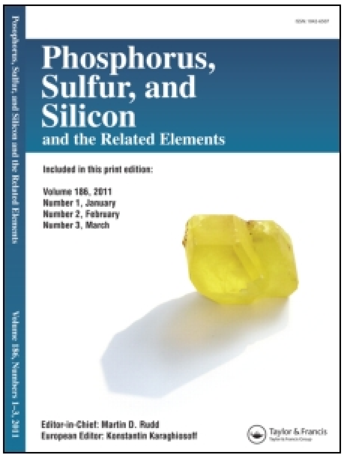

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Communication

QUININE-BASED DIOXAPHOSPHOLANE WITH *N*-DECYLQUINUCLIDINE FRAGMENT

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The ionic organophosphorus compound 2 with dioxaphospholane cycle, *N*-decylquininium bromide 1 derivative, was obtained for the first time. Its structures is discussed on the basis of ^{31}P and ^{13}C NMR IR, XPS, plasma desorption mass spectrometry and ultracentrifugation data.

Key words: *N*-decylquininium bromide, dioxaphospholane, 2-methoxy-[7-(N-decyl-5′-vinylquinuclidiniumyl-2′), 7-(6″-methoxy-quinolyl-4″)]-1,3,2-dioxaphospholane bromide, ultracentrifugation, alkaloid, quinine.

The phosphorylation of alkaloids by use of trivalent phosphorus acids amides is practically not known.[1] Some time ago an interesting reaction was reported between the 2-diethylamino-1,3,2-dioxaphospholane and quinine, leading to the formation of the polyfunctional ligand for coordination design.[2] In this work, a single-stage procedure is proposed for the synthesis (Scheme I) of a new ionic phosphite 2 on base of N-decylquininium bromide 1.

The product 2 is an orange-red substance which is readily soluble in CH_2Cl_2 and $CHCl_3$. The ^{31}P NMR spectrum of 2 in $CDCl_3$ contains a singlet with σp 136.0 ppm. The ^{13}C NMR spectrum of 2 shows the following signals ($CDCl_3$): $C_{6''}$ 157.6 ppm, $C_{2''}$ 147.2 ppm, $C_{4''}$ 146.6 ppm, $C_{8''a}$ 144.4 ppm, HC = 141.5 ppm, $C_{8''}$ 131.6 ppm, $C_{4''a}$ 126.1 ppm, $C_{3''}$ 121.4 ppm, $C_{7''}$ 118.9 ppm, $=CH_2$ 114.1 ppm, $C_{5''}$ 101.1 ppm, C_7 74.2 ppm (J_{c-p} 15Hz), $C_{4,5}$ 68.9 and 63.9 ppm (J_{c-p} 8.5Hz), $C_{2'}$ 60.0 ppm, $C_{6'}$ 56.8 ppm, H_3CO 55.5 ppm, $C_{7'}$ 42.5 ppm, $C_{5'}$ 39.6 ppm, $C_{4'}$ 27.5 ppm, $C_{8'}$ 26.8 ppm, $C_{3'}$ 22.4 ppm, N^+-$C_{10}H_{21}$ 66.2–12.0 ppm. These spectral data are in good agreement with the structure of the phosphite 2. The ionic nature of 2 was confirmed by X-ray photoelectron spectroscopy (Table I). Thus, the alkylation of the quinuclidine nitrogen atom (in compound 2) as well its protonation (in quinine x HCl) lead to a significant increase of the N1S binding energy in comparison with the starting quinine; the value of Br 3d binding energy in 2 is typical for anionic bromides.[3]

The plasma desorption mass spectrum of 2 contains only one signal of $[M-C_{10}H_{21}]^+$ species at m/z 494. Molecular mass measurement under milder conditions by ultracentrifugation in $CHCl_3$ at 25°C indicate the aggregative nature of phosphite 2 (Figure 1): 88% of dimeric form $[M_2]$ ($\tilde{M}z = 1250 \pm 3\%$) and 12% of decameric form

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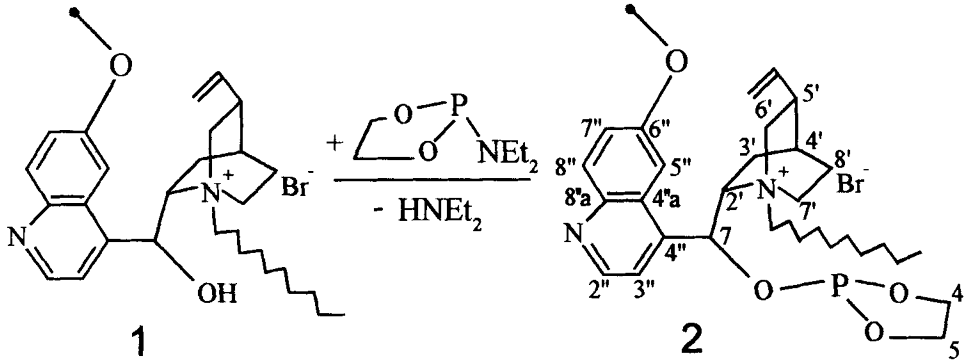
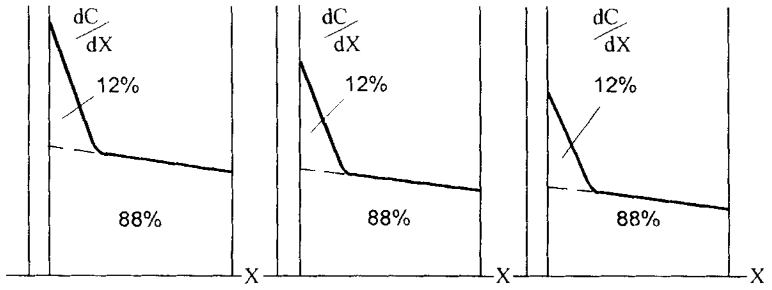


SCHEME I

TABLE I

XPS parameters of 2 and related compounds

	Binding energy, eV				
Compound	O1S	N1S quinuclidine	 quinoline	P2p	Cl 2p or Br 3d
Quinine	532.6	398.5	398.3	—	—
Quinine x HCl	532.3	401.1	398.1	—	197.0
2	532.6	401.3	398.5	132.6	68.3



C = 1.0 g/dl C = 0.8 g/dl C = 0.6 g/dl

FIGURE 1 Sedimentagrams of solutions of compound 2 in $CHCl_3$ for three different concentrations.

$[M]_6$ ($\bar{M}z = 6500 \pm 3\%$). The percentage of dimeric and decameric forms is not dependent on concentration. In our opinion this association is a result of the ionic nature of compound 2.

The possible application of phosphite 2 in coordination chemistry of Rh(I) and Pt(II) are currently under investigation.

EXPERIMENTAL

All manipulations were carried out under dry argon with carefully dried reactants and solvents. The starting *N*-decylquininium bromide (1) was prepared according to the published technique.[4]

The IR spectra were recorded on a Specord M-80 spectrometer using samples prepared as KBr pellets. NMR spectra were recorded at 81.0 and 50.1 MHz for ^{31}P and ^{13}C, respectively, on a Bruker AC-200 spectrometer. The X-ray photoelectron (XPS) spectra were measured on a MAC-2 Riber spectrometer calibrated against Ag lines at 901.5 and 367.9 eV, correction for the sample charging was performed at C1S = 284.6 eV, the accuracy of the line maximum determination was ±0.1 eV. Plasma desorption mass spectra were recorded on a MSVKh time-of-flight spectrometer with ionization by californium - 252 fission fragments. Sedimentation equilibrium of compound 2 in $CHCl_3$ at 25°C was studied using a MOM 3180 ultracentrifuge. The molecular weight was calculated by means of the following formula:

$$\bar{M}z = \frac{dC/dX}{c \cdot x} \times \frac{RT}{(1 - \bar{v}\rho_0)w^2} \quad \text{where } w = \frac{2\pi n}{60},$$

$\bar{v} = 0.786\ cm^3/g$ and $\rho_0'^{25} = 1.473\ g/cm^3$ (for $CHCl_3$), c = concentration (g/dl), x = the distance between the axis of revolution and points of gradienting curve, n-number of revolution of rotor per minute (40.000), The method of sedimentation equilibrium in thin layer (~3 mm) was employed.[5]

2-Methoxy-[7-(N-decyl-5′-vinylquinuclidiniumyl-2′), 7-(6″-methoxyquinolyl-4″)]- 1,3,2-dioxaphospholane bromide (2): an equimolar mixture of *N*-decylquininium bromide (10^{-3} mol) and 2-diethylamino-1,3,2-dioxaphospholane (10^{-3} mol) was heated to 130°C under vigorous stirring, cooled to 60°C and kept at this temperature under vacuum (3 mm Hg) until the evolution of $HNEt_2$ ceased. Orange-red solid material, 97% yield, m.p. 115–117°C; ν_{max}, cm^{-1} (KBr): 3090 (CH, vinyl), 2962 (CH_3, as), 2928 (CH_2, as), 2878(CH_3, s), 2855 (CH_2, s), 1638 (C=C, vinyl), 1620 (C=N), 1592 and 1508 (C=C, quinolyl), 1028 and 1018 (PO-C). Found: C, 60.4; H, 7.2; P4.7.$C_{32}H_{48}BrN_2O_4P$ calcd.: C, 60.5; H, 7.6; P4.9%.

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