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LETTERS TO THE EDITOR

Phosphacyclophanes Derived from Anthracene-2,6-diol

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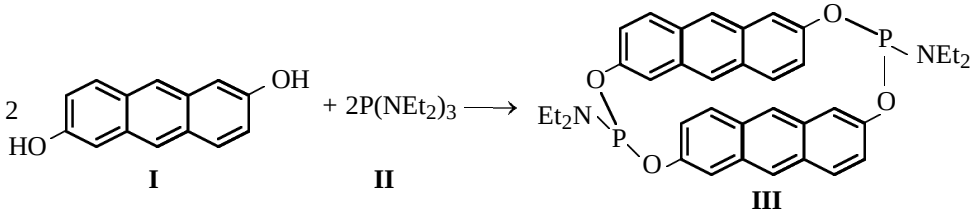
Previously we synthesized a series of phosphacyclophanes on the basis of benzene-, biphenyl-, and naphthalenediols [1]. This new type of cavity systems is of particular interest that is associated with the ability of phosphorus to form a wide range of functional groups, as well as by the possibility to make use of the "square" factor characteristic of the starting aromatic systems.

Proceeding with these works, we synthesized first representatives of phosphocyclophanes on the basis of anthracene-2,6-diol. There are scarce data in the literature on phosphorylation of anthracene and its derivatives [2], which is probably explained by the fact that the starting compounds are hardly available and extremely unstable. We suggested to approach anthracene-2,6-diol via a combination of two known procedures [3] and thus could much improve its yield.

To prepare a phosphacyclane comprising anthracene residues, we reacted equimolar amounts of anthracene-2,6-diol and hexaethylphosphorous triamide.

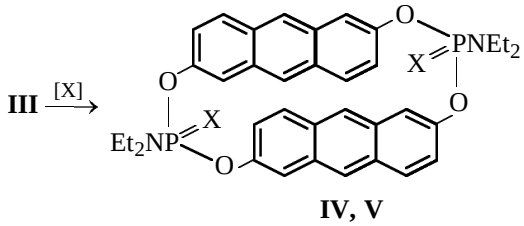


I **II** **III**

The reaction was performed in acetonitrile at room temperature. Cyclobis(phosphoramidite) **III** separated from the reaction solution as an oily material. It was dried in a vacuum to give a powder (mp 301–303°C). The spectrum of the product contained one singlet signal, implying a symmetrical structure. The ^{1}H NMR spectrum showed signals of all proton groups with expected integral intensities. The dimeric structure of the product was confirmed by its macular weight.

Computed steric energies showed that compound **III**, like related compounds derived from 1,4-hydroquinone and naphthalene-1,5-diol we obtained previously [1], can exist as a completely (**A**) or partially (**B**) eclipsed conformer (E_{ster} 5.26 and 1.6 eV, respectively). We consider structure **B** the most probable.

Compound **III** readily and in mild conditions is oxidized and sulfurized.



IV, V

X = O (**IV**), S (**V**).

Thus, we have demonstrated the possibility of synthesis and existence of phosphocyclophanes containing anthracene residues.

3,7-(Diethylamino)-1,5(2,6)-dianthracena-2,4,6,8-tetraoxa-3,7-diphosphacyclooctaphane (III). Hexaethylphosphorous triamide, 0.5 g, was added to 0.42 g of anthracene-2,6-diol in 30 ml of acetonitrile, and

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the mixture was stirred for 5 h at room temperature. After 1 day, the solution over the oily material that separated was decanted, the residue was washed with acetonitrile and dried in a vacuum for 3 h (1 mm Hg, 50°C). After drying, an amorphous yellowish brown powder. Yield 0.65 g (52%), mp 301–303°C, R_f 0.82 (benzene–dioxane, 3 : 1), 0.74 (benzene–dioxane, 5 : 1). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 1.15 m (12H, CH_3, $^3J_{HH}$ 7.02), 3.4 m (8H, NCH_2, $^3J_{PH}$ 10.0), 7.29 d (4H, $C^{3,7}$Hm $^3J_{HH}$ 8.8), 7.59 s (4H, $C^{1,5}$H), 7.91 d (4H, $C^{4,8}$H, $^3J_{HH}$ 9.1), 8.26 s (4H, C9,10H). ^{31}P NMR spectrum: δ_P 141 ppm. Found, %: C 69.48; H 5.87; P 9.71; *M* 655 (cryoscopy). $C_{36}H_{36}N_2O_4P_2$. Calculated, %: C 69.45; H 5.83; P 9.95; *M* 622.6.

3,7-(Diethylamino)-1,5(2,6)-dianthracena-2,4,6,8-tetraoxa-3(λ^5,λ^7)-diphosphacyclooctaphane 3,7-dioxide (IV). Yield 81%, decomp. point 240°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.09 m (12H, CH_3), 3.32 m (8H, NCH_2, $^3J_{PH}$ 11.3), 7.28 d (4H, $C^{3,7}$H, $^3J_{HH}$ 8.5), 7.39 s (4H, $C^{1,5}$H), 7.88 d (4H, $C^{4,8}$H, $^3J_{HH}$ 9.2), 8.32 s (4H, $C^{9,10}$H). ^{31}P NMR spectrum: δ_P 1.0 ppm.

3,7-(Diethylamino)-1,5(2,6)-dianthracena-2,4,6,8-tetraoxa-3(λ^5,λ^7)-diphosphacyclooctaphane 3,7-disulfide (V). Yield 42%, decomp. point 260°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.21 m (12H, CH_3), 3.56 m (8H, NCH_2, $^3J_{PH}$ 14.0), 7.84 d (4H, $C^{3,7}$H, $^3J_{HH}$ 8.6), 7.92 s (4H, $C^{1,5}$H), 7.97 d (4H, $C^{4,8}$H, $^3J_{HH}$ 9.2), 8.34 s (4H, $C^{9,10}$H). ^{31}P NMR spectrum: δ_P 67 ppm.

The ^{1}H NMR spectra were recorded on a Bruker WH-250 spectrometer (250 MHz). The ^{31}P NMR spectra were obtained in CH_2Cl_2 on a Bruker WP-80SY spectrometer (32.4 MHz) relative to 85% H_3PO_4.

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