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Sterically Oriented Synthesis and Structure of New Perphosphorylated Resorcinarenes

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Abstract—Tetraarylresorcinarenes in a *chair* conformation of C_{2h} symmetry were synthesized by sterically oriented condensation of aromatic aldehydes with resorcinol and 2-methylresorcinol. By further phosphorylation of resorcinarenes with phosphorous amides perphosphorylated derivatives were obtained with *rctt* configuration of substituents at internuclear methylidene bridges. Structure of these compounds was proved using NMR spectroscopy and X-ray diffraction analysis.

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Resorcinarene is a convenient matrix for designing sophisticated macrocyclic systems of various architecture [1]. On this basis have been obtained cavitands and carcerands [2] including the phosphorus-containing ones [3, 4], coordination compounds [4, 5], and polyfunctional derivatives with different position of functional groups with respect to the macrocycle cavity [1]. These compounds are interesting as sensor systems, selective receptors of cations and neutral molecules, and as polymetallic catalysts [1, 5–8]. Therefore oriented synthesis of macrocyclic polyfunctional resorcinarene derivatves with a predetermined steric organization is an important challenge.

All the octaphosphorylated resorcinarenes prepared earlier had *rccc* configuration of R substituents at the internuclear methylidene bridges. The derivatives with aliphatic R are in a *boat* conformation [9–11] (Fig. 1, A), the conformation of derivatives with R=Ph exerts change due to the *repulsion* of sterically contiguous four phenyl groups in axial orientation, becoming intermediate between *boat* and *saddle* [11] (Fig. 1b).

Aiming at building up octaphosphorylated derivatives of a *chair* conformation and *rctt* configuration of substituent R (Fig. 1c) we performed in the present work a phosphorylation of resorcinarenes (**Ia–Id)** with bulky naphthyl substituents at methylidene bridges (**Ia**–**Ic**) or possessing phenyl substituents at internuclear bridges and methyl groups in the *ortho* positions of benzene rings in the macrocyclic frame (**Id**). As phosphorylating agents we used 2-diethylamido-5,5-dimethyl-1,3,2-dioxaphosphorinane and phosphorous hexamethyltriamide.

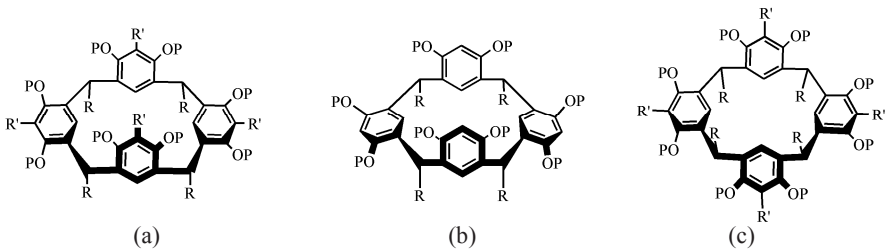
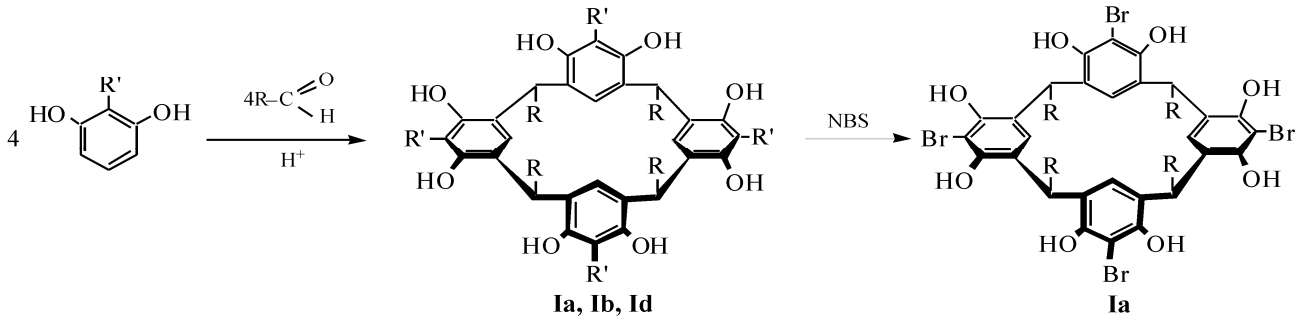


Fig. 1. Conformations of perphosphorylated resorcinarenes.



R = $C_{10}H_7$, R′ = H (**Ia**); R = $C_{10}H_7$, R′ = CH_3 (**Ib**); R = $C_{10}H_7$, R′=Br (**Ic**); R = Ph, R′ = CH_3 (**Id**).

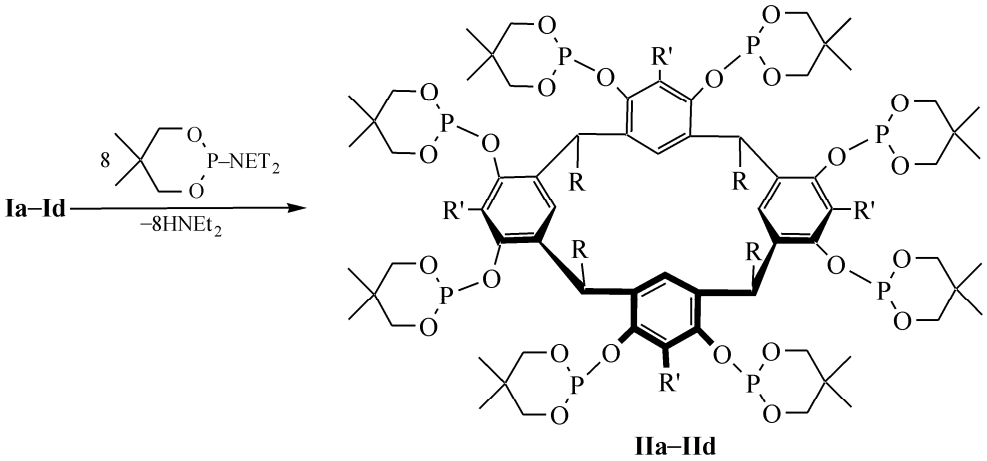
Tetraarylresorcinarenes **Ia, Ib**, and **Id** were prepared by acid-catalyzed condensation of resorcinols with the corresponding aldehydes, *ortho*-bromo-derivative **Ic** was obtained by reaction of resorcinarene **Ia** with NBS (*N*-bromosuccinimide) [1].

Low solubility of tetranaphthylresorcinarene **Ia** in common solvents prevented registration of its ^{1}H NMR spectrum [12]. In contrast to **Ia**, *orto*-substituted resorcinarenes **Ib–Id** were well soluble in polar organic solvents, and application of ^{1}H NMR spectroscopy for elucidation of their structures was possible.

The ^{1}H spectra of compounds **Ib–Id** (Fig. 2a) contain two distinct singlets of benzene *meta* protons (H^3) and of *ortho* methyl groups indicating the C_2 symmetry of the molecules [13, 14].

Averaging of signals of the protons H^3 и H^5 in the vertical and planar fragments of macrocyclic frame inherent to the *rccc* stereoisomer of tetraphenyl analog **Ie** with unsubstituted *ortho* positions of benzene rings (Fig. 2b) at 25°C was not observed in samples **Ib–Id** even at heating to 150°C showing the lack of intercoversion typical of resorcinarenes in a *boat* conformation [13, 14].

The combination of all these facts allows a conclusion that resorcinarenes **Ia–Id** are individual stereoisomers in a *chair* conformation.



R = $C_{10}H_7$, R′ = H (**Ia, IIa**); R = $C_{10}H_7$, R′ = Me (**Ib, IIb**); R = $C_{10}H_7$, R′ = H (**Ic, IIc**); R = Ph, R′ = Me (**Id, IId**).

The octaphosphorylation of resorcinarenes **Ia–Id** with 2-amido-1,3,2-dioxaphosphorinane was carried out with excess phosphorylating agent (**I** : phosphorinane = 1 : 10) in dioxane or acetonitrile.

In dioxane at 95–100°C the reaction time was 18 to 65 h depending on the resorcinarene used. In acetonitrile the reaction was carried out at 75–80°C, but the time and efficiency of the process for compounds **Ia–Ic** did not substantially changed. With resorcinarene **Id** the use of acetonitrile in addition to the mentioned reduction in the reaction temperature decreased the reaction duration to 15 h and by 24% increased the yield of the targeted compound. Regardless the used solvent, the perphosphorylated resorcinarenes **IIa–IId**

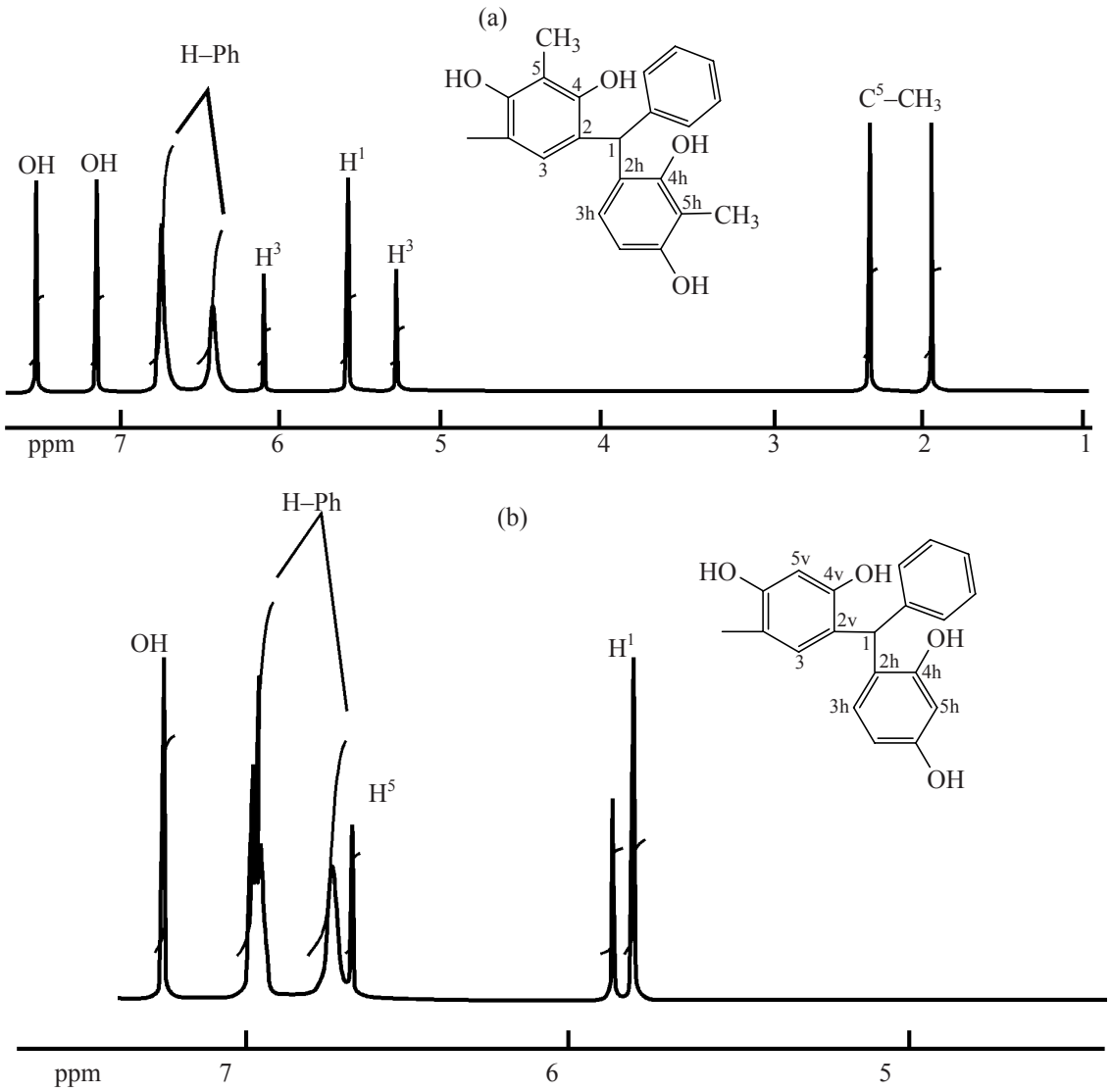


Fig. 2. ^{1}H NMR spectra of resorcinarenes (a) **Id** and (b) **Ie** (DMSO, 25°C).

spontaneously precipitated from the reaction mixture and were isolated as individual isomers in 67–79% yield.

The compounds obtained are crystalline substances with a high melting point. The data of elemental analysis of phosphoresorcinarenes **IIa–IId** and molecular weights measured by MALDI method for compounds **IIb** and **IId** are consistent with the calculated values. Two singlet signals in the ^{31}P NMR spectra of phosphoresorcinarenes **IIa–IId** equal in intensity and close in chemical shifts point to nonequivalence of phosphorus atoms in the molecules.

The pattern observed in ^{1}H NMR spectra of compounds **IIa–IId** (Fig. 3a) is analogous to that observed in ^{1}H NMR spectrum of the earlier studied [11] *rccc* phosphoresorcinarene **IIe** (R = Ph, R' = H) that has the conformation intermediate between the *boat* and the *saddle* (Fig. 3b): two singlets of H^3 protons, two triplets of H^5 protons (**IIa**) or two singlets of H^9 protons of the *ortho*-methyl groups (**IIb**, **IId**), four singlets of methyl protons (H^8) and twice four multiplets of axial and equatorial methylene (H^6) protons of phosphorinane rings. But in ^{1}H NMR spectra of compounds **IIa–IId** (Fig. 3a) a sharp upfield shift occurs [δ = 5.24 (**IIa**), 5.07 (**IIb**), 5.24 (**IIc**), 5.11 (**IId**) ppm] of H^{3h} protons of planar benzene rings due to the shielding effect of aryl groups R indicating change in configuration as compared with **IIe** [δ (H^{3h}) = 6.34 ppm].

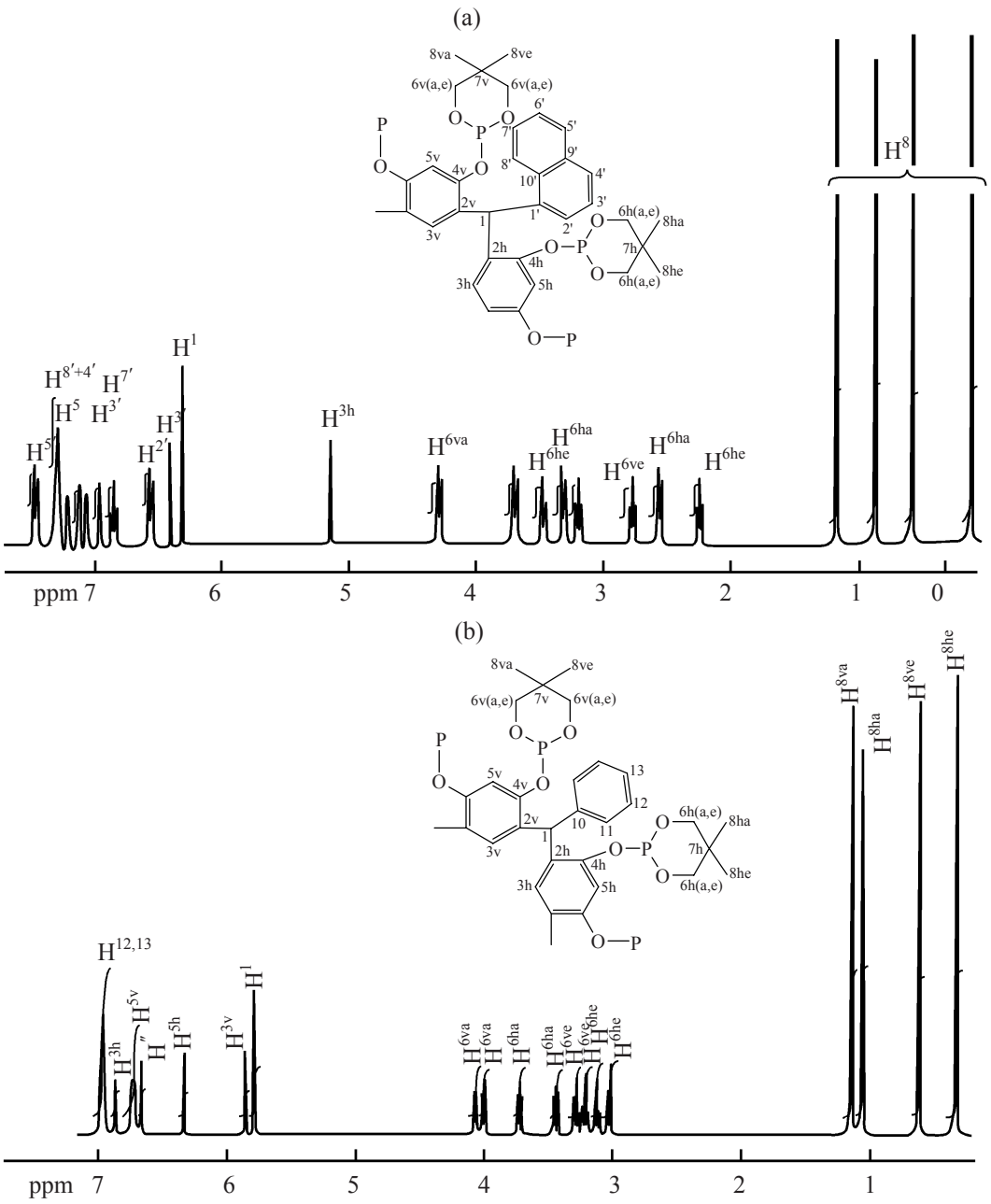
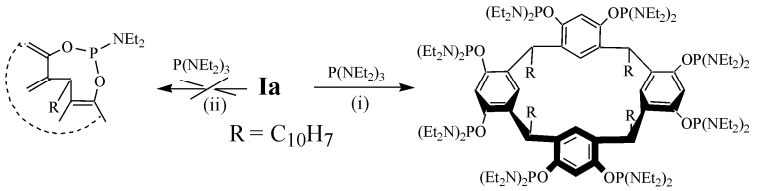


Fig. 3. ^{1}H NMR spectra of phosphoresorcinarenes (a) **IIa** and (b) **IIe** ($CDCl_3$, 25°C).

X-Ray diffraction investigation revealed that compound **IId** formed crystals including four dioxane molecules. In crystal two independent molecules of **IId** both have C_{2h} local symmetry within experimental error and are very similar in geometry. Both molecules are in the *chair* conformation. Two methylphenyl rings of the macrocyclic frame, C^1–C^6 and C^{1A}–C^{6A}, are located on different sides of the plane formed by two other benzene nuclei of the macrocycle, C^8–C^{13} and C^{8A}–C^{13A} (Fig. 4). The dihedral angle between the planes C^1–C^6 and C^9–C^{16} equals 74.3°. The phenyl substituents at methylidene bridges are orthogonal to the plane of C^1–C^6 ring.

The octaphosphorylation of resorcinarene **Ia** with phosphorous hexaethyltriamide was carried out in dioxane at 70–75°C at the reagents ratio **Ia :** triamide = 1 : 10.

Note that phosphorylation of *rccc* tetraphenylresorcinarene **Ie** with phosphorous hexaethyltriamide



under these conditions proceeded nonselectively: besides the octaphosphorylated derivatives (i), formation of cyclic compounds (ii) was observed [15]. With tetranaphthylresorcinarene (**Ia**) occurred regioselective process along pathway (i). In the ^{31}P NMR spectrum of reaction mixture no signals appeared in the region of 140 ppm typical of monoamide phosphocyclic tetraphenylresorcinarene derivatives [15], and signals of diamidophosphite acyclic fragments were registered in the region of 125 ppm.

Phosphoresorcinarene **III** crystals formed directly in the reaction mixture and were isolated in 47% yield. In the ^{31}P NMR spectrum of compound **III** there were two singlet signals at δ 125 and 127 ppm equal in intesity. In the ^{1}H NMR spectrum of **III** were observed 4 pairs of the signals of methyl and methylene protons of phosphamide groups, signals of the bridge CH-protons, and of aromatic protons. Like the spectra of compounds **IIa–IId**, that of **III** showed upfield shift (δ = 5.41 ppm) of the protons of the in-plane benzene rings (H^{3h}).

According to the data of X-ray diffraction analysis, phosphoresorcinarene **III** unlike compound **IId** formed crystals without solvate molecules. In the crystal compound **III** has C_{2h} local symmetry within experimental error and is present in a *chair* conformation. Two benzene nuclei of the macrocyclic frame, C^1–C^6 and C^{1A}–C^{6A}, are located on the opposite sides of the plane formed by two other benzene rings,

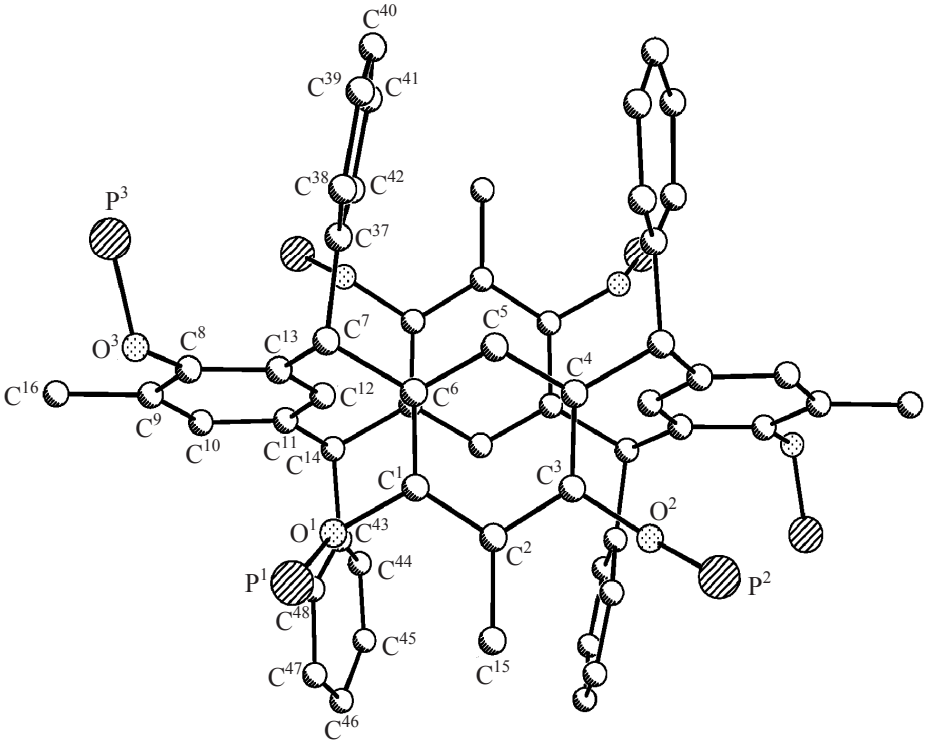


Fig. 4. General view of **IId** molecule. Phosphorinane rings are omitted.

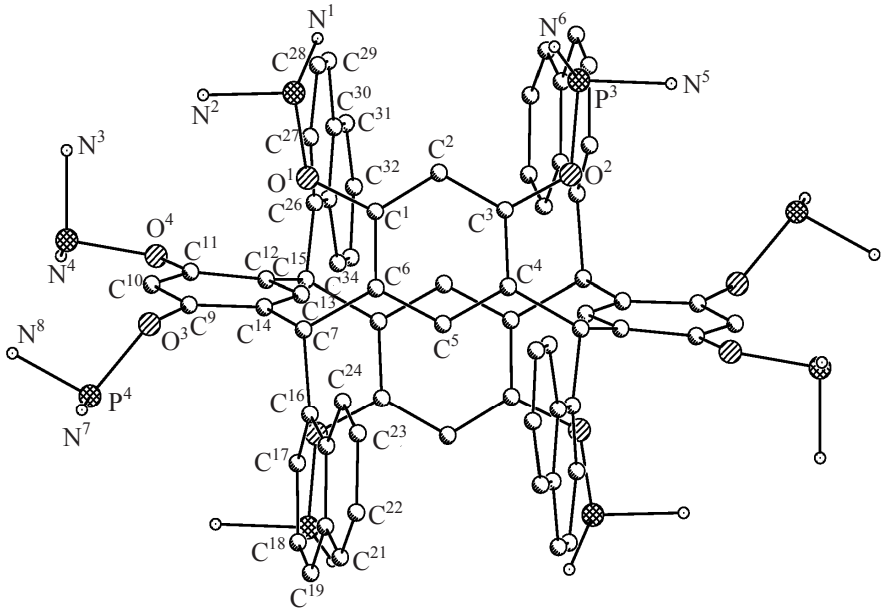


Fig. 5. General vie of molecule **III**. Ethyl groups are omitted.

C^9–C^{14} and C^{9A}–C^{14A} (Fig. 5). The dihedral angle between the planes C^1–C^6 and C^9–C^{14} equals 82.3°. Orientation of naphthyl groups with respect to the C^1-C^6 plane is slightly different: the dihedral angles are 73.5 and 94.7° for the naphthyl rings C^{16}–C^{24} and C^{26}–C^{33} respectively. Analysis of mutual orientation and of intramolecular contacts showed that naphthyl rings are not involved in stacking interaction.

Thus, steric orientation of the synthesis of perphosphorylated resorcinarenes is controlled in the step of cyclocondensation of aldehydes with resorcinols. The increase in steric hindrances of the R groups in aromatic aldehydes and R′ substituents in 2 position of the resorcinol leads to the formation of resorcinarenes in *chair* conformation with *rctt* configuration of the sub-stituents R at the internuclear methylidene bridges. Configuration of the macrocyclic frame in the perphosphorylated derivatives corresponds to that in the parent resorcinarenes.

EXPERIMENTAL

X-Ray diffraction investigation of compound IId and **III** was caried out on a Bruker SMART 1000 CCD and a Bruker SMART APEX II CCD diffractometers (Mo-K_α irradiation, graphite monochromator, ω-scanning) at 120 and 100 K, respectively. Integration was performed using program package SAINT, extinction was accounted for semiempirically through equivalent reflexes (the program SADABS) [18]. Structures were solved by the direct method and refined by means of full-matrix least-squares procedure on F^2 in anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated geometrically. Analysis of differential Fourier charts showed that in **IId** the phenyl substituents and phosphorinane ring are disordered. Besides, one of dioxane molecules in the independent part of **IId** cell is disordered completely. Inasmuch as this disordering cannot be described correctly, its contribution into scattering was excluded from the experimental data array on the basis of SQUEEZE procedure in PLATON984 program [19].

The disordered atoms were refined in the isotropic approximation. The principal crystallographic data and refinements for **IId** and **III** are listed in Table 1. All calculations were carried out with SHELXTL PLUS package [20].

The main crystallographic data were deposited into the Cambridge Database of Crystallographic Data (CCDC 654538 for **IId** and CCDC 654539 for **III**).

The ^{1}H and ^{13}C NMR spectra were registered on a spectrometer WM-200 with internal reference TMS. The ^{31}P NMR spectra were registered on a WP–80 instrument at operating frequency 32.4 MHz, external reference 85% H_3PO_4. The mass spectra were re-

Principal crystallographic data and parameters of refinement for compounds **IId** and **III**

Compound	**IId**	**III**
Formula	$C_{114}H_{160}O_{34}P_8$	$C_{132}H_{200}N_{16}O_8P_8$
M	2322.18	2386.84
T, K	120(2) K	100(2)
Crystal system	Triclynic	Triclynic
Space group	*P*-1	*P*-1
a (Å)	15.333 (2)	14.0111 (10)
b (Å)	17.744 (3)	15.3509 (12)
c (Å)	25.645 (4)	17.9208 (14)
α (°)	84.264 (4)	107.807 (2)
β (°)	74.311 (3)	104.330 (2)
γ (°)	64.417 (3)	104.321 (2)
V (Å^3)	6057.7 (16)	3330.5 (4)
Z (*Z*′)	2 (1)	1 (0.5)
F (000)	2472	1288
$d_{calc,}$ g cm^{-1}	1.273	1.190
μ, cm^{-1}	1.91	0.165
Scan type	ω	ω
2θ max (°)	50	55
Number of measured reflexions	40919	23658
Number of independent reflexions	20944 [0.0780]	14811 [0.0322]
Number of observed reflexions [$I > 2\sigma(I)$]	8850	8634
Number of parameters	1375	755
$R(F_{hkl})$: R_1	0.0989	0.0517
wR_2	0.1877	0.1290
GOF	0.908	0.973
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.696/–0.461	0.534/–0.343

gistered by MALDI-TOF method on a Bruker Ultra Flux instrument.

All the syntheses were carried out under argon atmosphere in dry oxygen-free solvents. Resorcinarene **Ia** was prepared along the procerdure in [11]. 2-Amido-1,3,2-dioxaphosphorinane was synthesized by procedure in [17].

Resorcinarene Ib. To a solution of 5 g (0.0403 mol) of 2-methylresorcinol and 5.8 g (0.04 mol) of 1-naphthalaldehyde in 50 ml of methanol was added dropwise 4.6 ml of concentrated hydrochloric acid. The reaction mixture was refluxed at stirring for 18 h, then it was quickly cooled in an ice bathe. The precipitate formed was filtered off and washed with 20 ml of CH_3OH/H_2O (10 : 5) mixture. The crude product was recrystallized from hot acetone. The crystals formed were filtered off and dried for 20 h at 95–100°C (1 mm Hg). Yield 53 %, mp 268–274°C (decomp.). ^{1}H NMR spectrum (200 MHz, $(CD_3)_2SO$, 30°C) δ, ppm 1.88 s (6H, CH_3), 2.21 s (6H, CH_3), 5.03 s (2H, H^{3h}), 6.29 s (2H, H^{3v}), 6.31 s (4H, H^1), 6.45 d (4H, $H^{2'}$, $^3J_{H,H}$ 6.4 Hz), 6.83 d.d (4H, $H^{7'}$, $^3J_{HH}$ 8.5 Hz), 6.85 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.3 Hz), 7.06 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.3 Hz), 7.28 d (4H, $H^{8'}$, $^3J_{HH}$ 8.5 Hz), 7.32 br.s (8H, OH), 7.36 d ($H^{4'}$, $^3J_{HH}$ 9.1 Hz), 7.46 d ($H^{5'}$, $^3J_{HH}$ 8.2 Hz). Mass spectrum, *m/z*: 1048 (100%) [M^+]. Found, %: C 82.47, H 5.43. $C_{72}H_{56}O_8$. Calculated, %: C 82.42, H 5.38.

Resorcinarene IIc. A mixture of 1 g (0.00107 mol) of resorcinarene **Ia** and 0.95 g (0.00535 mol) of *N*-bromosuccinimide in 20 ml of DMF was stirred in the dark for 24 h at cooling to 0°C. The reaction mixture was poured into 50 ml of water. The precipitate formed was filtered off and recrystallized from hot acetone. The crystals were filtered off and dried for 10 h at 95–100°C (1 mm Hg). Yield 88 %. mp 233–235°C (decomp.). ^{1}H NMR spectrum (200 MHz, $(CD_3)_2SO$, 30°C) δ, ppm 5.11 s (2H, H^{3h}), 6.28 s (2H, H^{3v}), 6.34 s (4H, H^1), 6.38 d (4H, $H^{2'}$, $^3J_{HH}$ 6.8 Hz), 6.84 d.d (4H, $H^{7'}$, $^3J_{HH}$ 8.0 Hz), 6.92 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.3 Hz), 7.08 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.0 Hz), 7.27 d (4H, $H^{8'}$, $^3J_{HH}$ 7.8 Hz), 7.33 d ($H^{4'}$, $^3J_{HH}$ 8.1 Hz), 7.46 d ($H^{5'}$, $^3J_{HH}$ 8.3 Hz), 8.1–8.3 br.s (8H, OH). Mass spectrum, *m/z*: 1308 (100%) [M^+]. Found, %: C 62.47, H 3.43. $C_{68}H_{44}Br_4O_8$. Calculated, %: C 62.41, H 3.39.

Resorcinarene Id. To a solution of 5 g (0.0403 mol) of 2-methylresorccinol and 14.3 g (0.04 mol) of benzaldehyde in 38 ml of 95% ethyl alcohol was added dropwise 9.4 ml of concentrated hydrochloric acid. The reaction mixture was stirred for 35 h. Precipitate separated was filtered off, suspended in 20 ml of ethyl alcohol and after shaking for 20 min it was filtered off. The operation was repeated twice. The precipitate was filtered off and dried for 20 h at 130–140°C (1 mm Hg). Yield 80 %, mp 293–294°C. ^{1}H NMR spectrum [200 MHz, $(CD_3)_2SO$, 30°C], δ, ppm: 1.93 s (6H, CH_3), 2.11 s (6H, CH_3), 5.37 s (2H, H^{3h}), 5.62 s (4H, H^1), 6.20 s (2H, H^{3v}), 6.67 m (8H, H^{Ph}), 6.87 m (12H, H^{Ph}), 7.02 s (4H, OH), 7.48 s (4H, OH). Found, %:C 78.80, H 5.11. $C_{52}H_{40}O_8$ Calculated, %: C 78.77, H 5.09.

Resorcinarene IIc. A mixture of 1 g (0.00107 mol) of resorcinarene **Ia** and 0.95 g (0.00535 mol) of N-bromosuccinimide in 20 ml of DMF was stirred in the dark for 24 h at cooling to 0°C. The reaction mixture was poured into 50 ml of water. The precipitate formed was filtered off and recrystallized from hot acetone. The crystals were filtered off and dried for 10 h at 95-100°C (1 mm Hg). Yield 88 %, mp

233–235°C (decomp.). ^{1}H NMR spectrum (200 MHz, $(CD_3)_2SO$, 30°C) δ, ppm 5.11 s (2H, H^{3h}), 6.28 s (2H, H^{3v}), 6.34 s (4H, H^1), 6.38 d (4H, $H^{2'}$, $^3J_{HH}$ 6.8 Hz), 6.84 d.d (4H, $H^{7'}$, $^3J_{HH}$ 8.0 Hz), 6.92 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.3 Hz), 7.08 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.0 Hz), 7.27 d (4H, $H^{8'}$, $^3J_{HH}$ 7.8 Hz), 7.33 d ($H^{4'}$, $^3J_{HH}$ 8.1 Hz), 7.46 d ($H^{5'}$, $^3J_{HH}$ 8.3 Hz), 8.1-8.3 br.s (8H, OH). Mass spectrum, *m/z*: 1308 (100%) [M^+]. Found, %: C 62.47, H 3.43. $C_{68}H_{44}Br_4O_8$. Calculated, %: C 62.41, H 3.39.

Resorcinarene Id. To a solution of 5 g (0.0403 mol) of 2-methylresorccinol and 14.3 g (0.04 mol) of benzaldehyde in 38 ml of 95% ethyl alcohol was added dropwise 9.4 ml of concentrated hydrochloric acid. The reaction mixture was stirred for 35 h. Precipitate separated was filtered off, suspended in 20 ml of ethyl alcohol and after shaking for 20 min it was filtered off. The operation was repeated twice. The precipitate was filtered off and dried for 20 h at 130–140°C (1 mm Hg). Yield 80 %, mp 293–294°C. ^{1}H NMR spectrum [200 MHz, $(CD_3)_2SO$, 30°C], δ, ppm: 1.93 s (6H, CH_3), 2.11 s (6H, CH_3), 5.37 s (2H, H^{3h}), 5.62 s (4H, H^1), 6.20 s (2H, H^{3v}), 6.67 m (8H, H^{Ph}), 6.87 m (12H, H^{Ph}), 7.02 s (4H, OH), 7.48 s (4H, OH). Found, %:C 78.80, H 5.11. $C_{52}H_{40}O_8$ Calculated, %: C 78.77, H 5.09.

Phosphoresorcinarene IIa. A mixture of 0.1 g (0.105 mmol) of resorcinarene **Ia** and 0.215 g (1.05 mmol) of phosphorous neopentyleneamide in 1 ml of dioxane was heated for 65 h at 90–95°C. The precipitate formed was filtered off and washed with di-oxane. The product was dried for 10 h at 75–80°C (1 mm Hg). Yield 67 %, mp above 360°C. ^{31}P NMR spectrum (80 MHz, $CDC1_3$, 30°C), δ, ppm: 114.30, 115.40. ^{1}H NMR spectrum (200 MHz, $CDC1_3$, 30°C), δ, ppm: –0.40 s (12H, H^8), 0.54 s (12H, H^8), 0.85 s (12H, H^8), 1.22 s (12H, H^8), 2.38 d.d (4H, H^{6e}, $^2J_{HH}$ 10.7 Hz, $^3J_{PH}$ 11.0 Hz), 2.65 d.d (4H, H^{6a}, $^2J_{HH}$ 10.7 Hz, $^3J_{PH}$ 2.4 Hz), 2.78 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 11.3 Hz), 3.17 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 10.7 Hz), 3.31 d.d (4H, H^{6a}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 2.4 Hz), 3.37 d.d (4H, H^{6e} $^2J_{HH}$ 11.0 Hz, $^3J_{PH}$ 11.4 Hz), 3.75 d.d (4H, H^{6a}, $^2J_{HH}$ 11.0 Hz, $^3J_{PH}$ 11.4 Hz), 4.27 d.d (4H, H^{6a}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 2.7 Hz), 5.24 s (2H, H^{3h}), 6.38 s (4H, H^1), 6.45 s (2H, H^{3v}), 6.55 d (4H, $H^{2'}$, $^3J_{HH}$ 7.0 Hz), 6.88 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.7 Hz), 6.93 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.6 Hz), 7.01 t (2H, H^5, $^4J_{PH}$ 2.7 Hz), 7.04 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.6 Hz), 7.20 t (2H, H^5, $^4J_{PH}$ 2.1 Hz), 7.30 d (8H, $H^{4,8}$, $^3J_{HH}$ 8.4 Hz), 7.40 d (4H, $H^{5'}$ $^3J_{HH}$ 8.4 Hz). ^{13}C NMR spectrum (50 MHz, $CDC1_3$, 30°C): δ, ppm 21.06 s (C^8), 22.03 s (C^8), 22.30 s (C^8), 22.47 s (C^8), 31.69 s (C^7), 32.68 s (C^7), 39.69 s (C^1), 68.11 s (C^6), 68.94 s (C^6), 69.14 s (C^6), 69.73 s (C^6), 106.32 t (C^5, $^3J_{PC}$ 18.3 Hz), 108.46 t (C^5, $^3J_{PC}$ 15.7 Hz), 123.03 s ($C^{8'}$), 124.16 s ($C^{3'}$), 124.87 s ($C^{6'}$), 125.29 s ($C^{7'}$), 126.03 s ($C^{2'}$), 126.60 s ($C^{4'}$), 127.18 s (C^2), 127.58 s ($C^{5'}$), 128.09 s (C^2), 130.64 s ($C^{9'}$), 132.32 s ($C^{10'}$, C^3), 133.06 s (C^3), 137.75 s ($C^{1'}$), 149.01 s (C^4), 149.81 s (C^4). Found, %:C 63.30, H 5.95, P 12.11. $C_{108}H_{120}O_{24}P_8$ Calculated C 63.28, H 5.90, P 12.09.

Phosphoresorcinarene IIb was prepared similarly to compound **IIa** by reaction of 0.99 g (0.945 mmol) of **Ib** with 1.94 g (9.45 mmol) of phosphorous neopentyleneamide for 50 h. Yield 79 %, mp above 360° C. ^{31}P NMR spectrum (80 MHz, $CDC1_3$, 30°C), δ, ppm: 118.37, 120.21. ^{1}H NMR spectrum (200 MHz, $CDC1_3$, 30°C), δ, ppm: –0.41 s (12H, H^8), 0.49 s (12H, H^8), 0.83 s (12H, H^8), 1.22 s (12H, H^8), 2.14 m (4H, H^{6e}), 2.18 s (6H, H^9), 2.38 s (6H, H^9), 3.02 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 11.9 Hz), 3.19 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 11.6 Hz), 3.44 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 11.0 Hz), 3.78 d.d (8H, H^{6a}, $^2J_{HH}$ 11.00 Hz, $^3J_{PH}$ 2.2 Hz), 3.92 d.d (4H, H^{6a}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 2.2 Hz), 4.30 d.d (4H, H^{6a}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 2.2 Hz), 5.07 s (2H, H^{3h}), 6.10 s (2H, H^{3v}), 6.21 s (4H, H^1), 6.54 d (4H, $H^{2'}$, $^3J_{HH}$ 7.3 Hz), 6.84 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.6 Hz), 6.88 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.7 Hz), 7.04 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.3 Hz), 7.28 d (4H, $H^{8'}$, $^3J_{HH}$ 8.4 Hz), 7.34 d (4H, $H^{4'}$, $^3J_{HH}$ 8.4 Hz), 7.41 d (4H, $H^{5'}$, $^3J_{HH}$ 8.0 Hz). ^{13}C NMR spectrum (50 MHz, $CDC1_3$, 30°C), δ, ppm: 12.18 s (C^8), 13.09 s (C^9), 22.20 s (C^8), 22.40 s (C^8), 22.61 s (C^8), 32.18 s (C^7), 32.69 s (C^7), 42.57 s (C^1), 68.59 s (C^6), 69.23 s (C^6), 123.65 s ($C^{8'}$), 123.89 s ($C^{3'}$), 124.93 s ($C^{6',7'}$), 126.32 s ($C^{2,2'}$), 126.79 s ($C^{2,4'}$), 128.06 s ($C^{5'}$), 129.53 s (C^5), 130.24 s (C^5), 131.29 s ($C^{3,9'}$), 131.61 s ($C^{10'}$), 133.06 s (C^3), 138.21 s ($C^{1'}$), 148.98 s (C^4). Mass spectrum, *m/z*: 2106 (100%) [M^+]. Found, %: C 63.90, H 6.15, P 11.80. $C_{112}H_{128}O_{24}P_8$ Calculated C 63.87, H 6.13, P 11.77.

Phosphoresorcinarene IIc was prepared similarly to compound **IIa** by reaction of 0.07 g (0.05 mmol) of **Ic** with 0.11 g (0.5 mmol) of phosphorous neopentyleneamide for 18 h. Yield 75 %, mp above 360°C (decomp.). ^{31}P NMR spectrum (80 MHz, $CDC1_3$, 30°C): δ, ppm 118.37, 120.21. ^{1}H NMR spectrum (200 MHz, $CDC1_3$, 30°C): δ, ppm 0.41 s (12H, H^8), 0.52 s (12H, H^8), 0.82 s (12H, H^8), 1.22 s (12H, H^8), 2.02 d.d (4H, H^{6e}, $^2J_{HH}$ 11.2 Hz, $^3J_{PH}$ 9.5 Hz), 3.08 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 10.6 Hz), 3.31 d.d (4H, H^{6e}, $^2J_{HH}$ 11.0 Hz,

$^3J_{PH}$ 10.6 Hz), 3.46 d.d (4H, H^{6e}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 10.6 Hz), 3.71 d.d (8H, H^{6a}, $^2J_{HH}$ 11.00 Hz, $^3J_{PH}$ 2.2 Hz), 3.92 d.d (4H, H^{6a}, $^2J_{HH}$ 11.0 Hz, $^3J_{PH}$ 2.2 Hz), 4.43 d.d (4H, H^{6a}, $^2J_{HH}$ 10.2 Hz, $^3J_{PH}$ 2.2 Hz), 5.24 s (2H, H^{3h}), 6.14 s (2H, H^{3v}), 6.27 s (4H, H^1), 6.52 d (4H, $H^{2'}$, $^3J_{HH}$ 7.3 Hz), 6.87 d.d (4H, $H^{7'}$, $^3J_{HH}$ 7.8 Hz), 7.00 d.d (4H, $H^{3'}$, $^3J_{HH}$ 8.0 Hz), 7.07 d.d (4H, $H^{6'}$, $^3J_{HH}$ 8.3 Hz), 7.23 d (4H, $H^{8'}$, $^3J_{HH}$ 8.5 Hz), 7.38 d (4H, $H^{4'}$, $^3J_{HH}$ 7.4 Hz), 7.44 d (4H, $H^{5'}$, $^3J_{HH}$ 8.4 Hz). Found, %: C 53.90, H 5.15, P 10.80. $C_{112}H_{128}Br_4O_{24}P_8$ Calculated, %: C 54.84, H 4.94, P 10.48.

Phosphoresorcinarene IId. *a.* Prepared similarly to compound **IIa** by reaction of 0.1 g (0.118 mmol) of **Id** with 0.242 g (1.18 mmol) of phosphorous neopentyleneamide for 65 h. Yield 44 %.

b. A mixture of 0.09 g (0.106 mmol) of **Id** and 0.217 g (1.06 mmol) of phosphorous neopentyleneamide in 1 ml of acetonitrile was kept for 16 h at 75-80°C. The precipitate formed was filtered off, washed with 5 ml of acetonitrile, and dried for 8 h at 75-80°C (1 mm Hg). Yield 68 %, mp above 360°C. ^{31}P NMR spectrum (80 MHz, $CDC1_3$, 30°C), δ, ppm: 118.11, 120.12. ^{1}H NMR spectrum (200 MHz, $CDC1_3$, 30°C), δ, ppm: 0.40 s (12H, H^8), 0.70 s (12H, H^8), 1.16 s (12H, H^8), 1.17 s (12H, H^8), 2.21 s (6H, H^9), 2.29 s (6H, H^9), 3.15 d.d (4H, H^{6e}, $^2J_{HH}$ 10.1 Hz, $^3J_{PH}$ 10.2 Hz), 3.25 d.d (4H, H^{6e}, $^2J_{HH}$ 11.0 Hz, $^3J_{PH}$ 11.2 Hz), 3.29–3.34 m (8H, H^{6e}), 3.62 d.d (4H, H^{6a}, $^2J_{HH}$ 10.7 Hz, $^3J_{PH}$ 2.4 Hz), 4.15 d.d (4H, H^{6a}, $^2J_{HH}$ 10.4 Hz, $^3J_{PH}$ 2.1 Hz), 4.29 d.d (4H, H^{6a}, $^2J_{HH}$ 10.1 Hz, $^3J_{PH}$ 2.4 Hz), 4.42 d.d (4H, H^{6a}, $^2J_{HH}$ 10.7 Hz, $^3J_{PH}$ 2.7 Hz), 5.11 s (2H, H^{3h}), 5.63 s (4H, H^1), 5.97 s (2H, H^{3v}), 6.41 d (4H, H^{Ph}, $^3J_{HH}$ 7.3 Hz), 6.88–6.99 m (16H, H^{Ph}). Mass spectrum, *m/z*: 1905 (100%) [M^+]. Found, %:C 60.48, H 6.29, P 12.95. $C_{96}H_{120}O_{24}P_8$. Calculated C 60.50, H 6.35, P 13.00.

Phosphoresorcinarene III. A mixture of 0.12 g (0.12 mmol) of resorcinarene **Ia** and 0.30 g (1.2 mmol) of phosphorous hexaethyltriamide in 1 ml of dioxane was heated for 23 h at 70–75°C. The reaction mixture was evaporated to 1/3 of volume, the precipitate formed was filtered off, washed with cold dioxane and dried for 3 h at 70–75°C (1 mm Hg). Yield 47 %, mp 235°C (decomp.). ^{31}P NMR spectrum (80 MHz, $CDC1_3$, 30°C), δ, ppm: 125.14, 127.04. ^{1}H NMR spectrum (200 MHz, $CDC1_3$, 30°C), δ, ppm: 0.43 t (24H, NCH_2CH_3, $^3J_{HH}$ 6.9 Hz), 0.63 t (24H, NCH_2CH_3, $^3J_{HH}$ 7.3 Hz); 0.92 t (24H, NCH_2CH_3, $^3J_{HH}$ 6.9 Hz), 1.04 t (24H, NCH_2CH_3, $^3J_{HH}$ 7.0 Hz), 2.07–2 .31 m (16H, NCH_2CH_3), 2.41–2.71 m (16H, NCH_2CH_3), 2.89–3.07 m (16H, NCH_2CH_3), 3.07–3.26 m (16H, NCH_2CH_3), 5.41 s (2H, H^{3h}), 6.34 s (4H, H^1), 6.45 d (4H, $H^{2'}$, $^3J_{HH}$ 6.9 Hz), 6.57 s (2H, H^{3v}), 6.61–6.67 m (2H, H^5; 4H, $H^{7'}$), 6.75 d.d (4H, $H^{3'}$, $^3J_{HH}$ 7.7 Hz), 6.97 d.d (4H, $H^{6'}$, $^3J_{HH}$ 7.3 Hz), 7.11–7.17 m (8H, $H^{4',8'}$; 2H, H^5), 7.30 d (4H, $H^{5'}$, $^3J_{HH}$ 8.0 Hz). Found, %:C 66.45, H 8.48, N 9.42, P 10.41. $C_{132}H_{200}N_{16}O_8P_8$ Calculated, %: C 66.42, H 8.45, N 9.39, P 10.38.

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