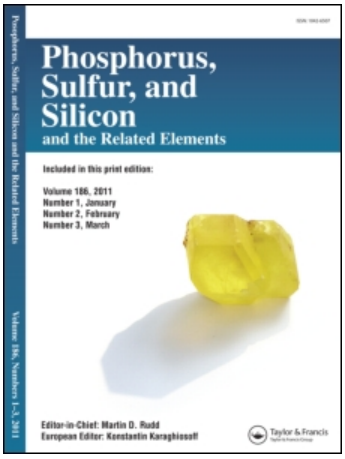

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TETRAPROPYLPHOSPHOCAVITANDS: SYNTHESIS, STRUCTURE, AND PROPERTIES

Vera I. Maslennikova[a]; Elena V. Shkarina[a]; Larisa K. Vasyanina[a]; Konstantin A. Lysenko[a]; Tatyana K. Sinicina[a]; Roman V. Merkulov[a]; Eduard E. Nifantyev[a]
[a] Moscow Pedagogical State University, Moscow, Russia

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TETRAPROPYLPHOSPHOCAVITANDS: SYNTHESIS, STRUCTURE, AND PROPERTIES

VERA I. MASLENNIKOVA, ELENA V. SHKARINA, LARISA K. VASYANINA, KONSTANTIN A. LYSENKO, TATYANA K. SINICINA, ROMAN V. MERKULOV and EDUARD E. NIFANTYEV

Moscow Pedagogical State University, per. Nesvizhskii, Moscow, 119021, Russia

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Cyclophosphorylation of tetrapropylcalyxresorcin[4]arene by phosphorous amides gave P(III)-phosphocavitands, modification of which resulted in a series of P(V)-phosphocavitands with different substituents at phosphorus atoms. The first alkylation of amidophosphocavitands has been performed.

Keywords: calyxresorcin[4]arenes; phosphorous amides; cyclophosphorylation; cavitands; oxidation; alkylation

INTRODUCTION

Phosphocavitands are two-rim molecules constructed by forming additional phosphorus-containing cycles around a calyxresorcinarene base. Two main problems were to be solved in their synthesis. The first problem was the selection of suitable phosphorylating agents. Chlorides of phosphorus acids[1–3] and phosphorous amides[4,5] were used for creating phosphocavitands. In both cases the effective stereoselective phosphorylation was noticed, but the conformations of products were different.

The second task concerned the regulation of conformational relationships in the process of calixarene phosphorylation. It was noted that the hydrocarbon radicals at the methylene bridges play a significant part in the fixation of the crown conformation required for cyclophosphorylation. It

was also found that a phenyl radical is less favourable than alkyl ones. The butyl homologue should be noted among calixarenes with alkyl radicals. This compound is available, convenient to use, and readily phosphorylated[5].

In this connection, it was expedient to examine the suitability of calyxresorcin[4]arenes with other alkyl radicals for phosphocavitand synthesis. The present work was launched in this direction. Our goal was to study the cyclophosphorylation of calyxresorcin[4]arenes with propyl radicals at the interphenyl bridges, to reveal the peculiarities of this reaction, and to synthesise a new group of phosphocavitands. In addition, we intended to examine new transformation types of phosphocavitands under study.

RESULTS AND DISCUSSION

The interaction of tetrapropyloctol **1** with phosphite triamides and phosphite diamidoester (Scheme 1) was conducted in dioxane at 20°C under the strict ratio octol : amide = 1 : 4. The reaction proceeded stereoselectivly. Predominant stereoisomers **2a-c** were obtained in high yields (67–90%). Their identities and symmetries were supported by ^{1}H and ^{31}P NMR spectroscopy (Table I). A narrow signal was present in the ^{31}P NMR spectra, and ^{1}H NMR spectra displayed a signal set for each type of protons, as was observed only for cavitands of C_{4v} symmetry[6] (in this case, the similar arrangement of substituents with respect to the cavity for all four phosphorus atoms).

In order to obtain the exact molecular structures, single-crystal X-ray diffraction analysis was undertaken. The X-ray structure of **2b** with the atomic numbering schemes is presented in Fig. 1; the atomic coordinates and the bond lengths and bond angles are given inTables II and III, respectively.

The X-ray diffraction analysis revealed that phosphocavitand **2b** cocrystallizes with one molecule of solvent dioxane.

The geometric parameters of **2b** are similar to those of a previously studied amidophosphocavitand with butyl radicals in the calixarene matrix[5].

The molecule of **2b** adopts a bowl form with hydrophobic n-propyl substituents on the bottom (the C(5), C(12), C(19), and C(26) atoms) and hydrophilic $P(O_2)NEt_2$ substituents above the top (the C(2), C(9), C(16), and C(23) atoms).

TABLE I ^{1}H and ^{31}P spectra parameters of phosphorylated cavitands ($CDCl_3$)

Comp.	$\delta\ ^{31}P$, *ppm.*	$\delta\ ^{1}H$, *ppm. (J, Hz)*				
		Hm	*Ho*	*CH* ($^{3}J_{HH}$)	*Pr*	*X*($^{3}J_{PH}$), *R*($^{2}J_{PH}$)
2a	141.1, s	7.20, s	6.58, s	4.68, t (8.0)	2.20, 1.41, 1.02	2.85,d (10.5), NCH_3
2b	142.6, s	7.13, s	6.51, s	4.62, t (8.0)	2,19, 1.73, 0.99	3.27, m (10.6), NCH_2; 1.18, t, CH_3
2c	131.1, s	7.18, s	6.65, s	4.63, t (7.7)	2.20, 1.38, 1.00	4.97, m (9,1), OCH, 1.40, d, CH_3
3a	66.7, s	7.03, s	6.59, s	4.57, t (8.5)	2.23, 1.40, 1.02	3.44, m (14.5), NCH_2; 1.21, t, CH_3
3b	57.4, s	7.16, s	6.64, s	4.63, t (7.7)	2.23, 1.50, 1.04	5.08, m (9.5), OCH, 1.45, d, CH_3
4	73.6*	7.11, s	6.58, t**	4.54, t (7.7)	2.23, 1.39, 1,02	2.96, d (12.8), NCH_3
5a	-1.2, s	7.10, s	6.74, s	4.54, t (7.7)	2.21, 1.34, 0.97	2.82, d (12.5), NCH_3
5b	-0.2, s	7.24, s	6.76, s	4.65, t (7.7)	2.46, 1.38, 0.99	3.31, m (13.7), NCH_2; 1.21, t, CH_3
5c	-14.9, s	7.19, s	6.87, s	4.63, t (7.7)	2.29, 1.38, 1.02	4.97, m (7.4), OCH, 1.46, d, CH_3
6a	58.3, s	8.31, s	7.47, s	4.40, t (7.8)	2.44, 1.51, 1.05	3.54, m (12.8), NCH_2; 1.34, t, CH_3 ; 3.41, d (14.9), PCH_3
6b	59.6, s	8.34, s	7.51, s	4.32, t (8.5)	2.99, 1.31, 1.00	3.52, m (12.8), NCH_2; 1,31, t,CH_3; 4.01, m (14.9), PCH_2; 1.03, t, CH_3

*$^{1}J_{PSe}$ 994 Hz
**$^{4}J_{PH}$ 2.1 Hz

TABLE II Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 2b

Atom	*x*	*y*	*z*	*U*	*Atom*	*x*	*y*	*z*	*U*
P(1)	-2417(1)	3195(1)	4453(1)	27(1)	C(24)	-923(2)	3487(2)	3760(2)	22(1)
P(2)	-4406(1)	-1326(1)	2918(1)	27(1)	C(25)	-252(2)	2830(2)	3773(2)	21(1)
P(3)	-4426(1)	-1111(1)	-538(1)	29(1)	C(26)	77(2)	2536(2)	3098(2)	21(1)
P(4)	-2358(1)	3344(1)	962(1)	32(1)	C(27)	-201(2)	2886(2)	2438(2)	22(1)
O(1)	-1271(2)	3830(1)	4426(1)	25(1)	C(28)	110(2)	2461(2)	4499(2)	20(1)
O(2)	-1800(2)	2530(1)	4981(1)	26(1)	C(29)	-3579(3)	4240(3)	5249(3)	59(1)
O(3)	-3272(2)	-853(1)	3821(1)	28(1)	C(30)	-4623(4)	3670(5)	4519(4)	81(2)
O(4)	-3869(2)	-2094(1)	2373(1)	27(1)	C(31)	-1530(3)	4570(2)	6015(2)	38(1)
O(5)	-3913(2)	-1982(1)	-257(1)	28(1)	C(32)	-1517(4)	4333(3)	6774(2)	46(1)
O(6)	-3352(2)	-681(1)	-783(1)	31(1)	C(33)	-4644(3)	-2837(2)	3451(2)	39(1)
O(7)	-1774(2)	2680(1)	390(1)	30(1)	C(34)	-5126(5)	-3819(3)	2799(4)	75(1)
O(8)	-1179(2)	3939(1)	1828(1)	28(1)	C(35)	-6301(3)	-2106(2)	3069(2)	39(1)
N(1)	-2526(2)	4008(2)	5239(2)	33(1)	C(36)	-6470(4)	-1866(3)	3880(3)	54(1)
N(2)	-5117(2)	-2107(2)	3166(2)	29(1)	C(37)	-5097(3)	-2437(2)	-2111(2)	36(1)
N(3)	-5349(2)	-1744(2)	-1488(1)	31(1)	C(38)	-5495(4)	-3454(2)	-2182(3)	48(1)
N(4)	-2464(2)	4178(2)	532(2)	41(1)	C(39)	-6482(3)	-1537(2)	-1742(2)	36(1)
C(1)	-1704(2)	1640(2)	4545(2)	22(1)	C(40)	-6576(4)	-813(3)	-2173(3)	55(1)
C(2)	-2541(2)	841(2)	4373(2)	25(1)	C(41)	-3500(4)	4535(3)	410(3)	57(1)
C(3)	-2441(2)	-50(2)	3966(2)	24(1)	C(42)	-3333(6)	5472(5)	1072(5)	106(2)
C(4)	-1519(2)	-171(2)	3730(2)	22(1)	C(43)	-1515(4)	4713(3)	434(3)	68(1)

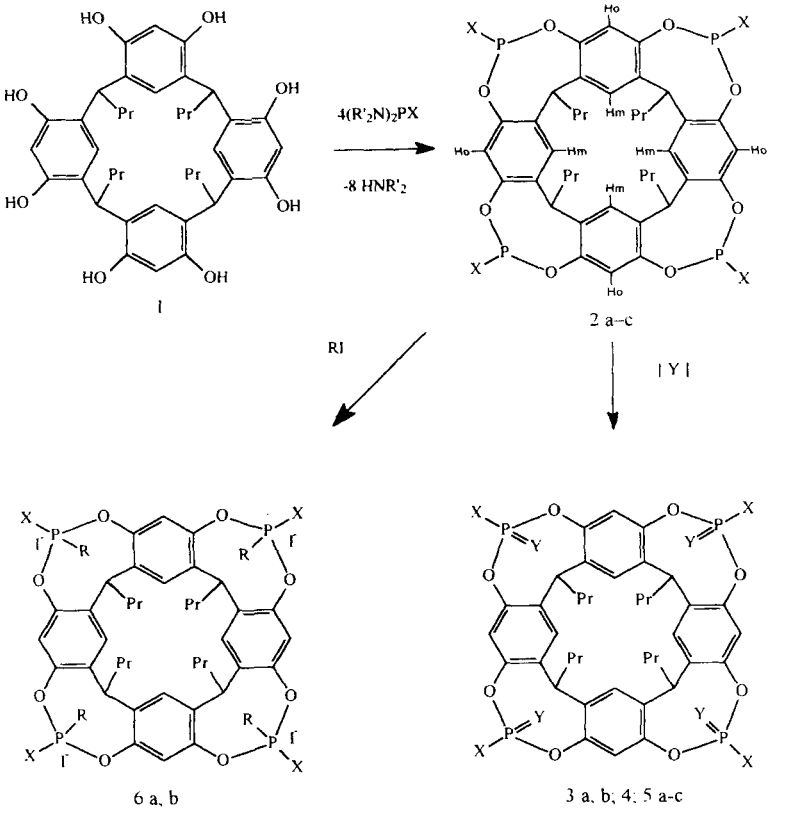
Atom	*x*	*y*	*z*	*U*	*Atom*	*x*	*y*	*z*	*U*
C(5)	-703(2)	650(2)	3917(2)	22(1)	C(44)	-1797(8)	4808(6)	-401(5)	111(2)
C(6)	-769(2)	1562(2)	4322(2)	22(1)	C(45)	1337(2)	2344(2)	4741(2)	26(1)
C(7)	-1472(2)	-1161(2)	3242(2)	23(1)	C(46)	2224(3)	3260(2)	4965(2)	32(1)
C(8)	-3284(2)	-1806(2)	1917(2)	24(1)	C(47)	2260(3)	4088(2)	5679(2)	48(1)
C(9)	-3874(3)	-2001(2)	1075(2)	26(1)	C(48)	-264(3)	-1316(2)	3448(2)	27(1)
C(9)	-3874(3)	-2001(2)	1075(2)	26(1)	C(49)	-211(S)	-2309(2)	2970(2)	37(1)
C(10)	-3300(2)	-1761(2)	597(2)	24(1)	C(50)	-883(4)	-3114(2)	3097(2)	46(1)
C(11)	-2139(2)	-1316(2)	961(2)	22(1)	C(51)	-294(3)	-1207(2)	715(2)	28(1)
C(12)	-1586(2)	-1124(2)	1812(2)	22(1)	C(52)	-257(3)	-2241(2)	622(2)	35(1)
C(13)	-2121(2)	-1369(2)	2311(2)	24(1)	C(53)	861(4)	-2344(3)	1170(3)	48(1)
C(14)	-1512(2)	-1065(2)	430(2)	24(1)	C(54)	1345(2)	2323(2)	1947(2)	27(1)
C(15)	-2488(2)	85(2)	-166(2)	26(1)	C(55)	2317(3)	3216(2)	2431(2)	36(1)
C(16)	-2552(3)	998(2)	-172(2)	29(1)	C(56)	2508(4)	3779(3)	1894(3)	54(1)
C(17)	-1700(2)	1774(2)	429(2)	25(1)	O(1S)	2006(3)	540(2)	3043(2)	79(1)
C(18)	-771(2)	1666(2)	1030(2)	22(1)	O(2S)	4333(2)	617(2)	3825(2)	76(1)
C(19)	-726(2)	741(2)	1015(2)	22(1)	C(1S)	2697(4)	343(3)	2567(3)	74(1)
C(20)	-1567(2)	-61(2)	421(2)	23(1)	C(2S)	3908(5)	852(4)	3082(4)	78(1)
C(21)	157(2)	2527(2)	1702(2)	22(1)	C(3S)	3637(4)	819(4)	4285(3)	70(1)
C(22)	-867(2)	3547(2)	2461(2)	23(1)	C(4S)	2444(4)	298(3)	3770(3)	64(1)
C(23)	-1223(2)	3854(2)	3120(2)	23(1)					

TABLE III Bond lengths (Å) and angles (degrees) in the structure

Bond lengths					
P(1)-N(1)	1.649(2)	C(1)-C(6)	1.393(4)	C(23)-C(24)	1.380(4)
P(1)-O(1)	1.671(2)	C(2)-C(3)	1.381(4)	C(24)-C(25)	1.391(4)
P(1)-O(2)	1.665(2)	C(3)-C(4)	1.398(4)	C(25)-C(26)	1.392(4)
P(2)-N(2)	1.646(2)	C(4)-C(5)	1.393(4)	C(25)-C(28)	1.520(3)
P(2)-PO(3)	1.667(2)	C(4)-C(7)	1.523(4)	C(26)-C(27)	1.391(4)
P(2)-O(4)	1.669(2)	C(5)-C(6)	1.390(4)	C(28)-C(45)	1.534(4)
P(3)-N(3)	1.639(2)	C(6)-C(28)	1.528(4)	C(29)-C(30)	1.470(6)
P(3)-O(5)	1.669(2)	C(7)-C(13)	1.520(4)	C(31)-C(32)	1.502(5)
P(3)-O(6)	1.688(2)	C(7)-C(48)	1.533(4)	C(33)-C(34)	1.503(6)
P(4)-N(4)	1.649(3)	C(8)-C(9)	1.373(4)	C(35)-C(36)	1.497(5)
P(4)-O(7)	1.656(2)	C(8)-C(13)	1.395(4)	C(37)-C(38)	1.509(5)
P(4)-O(8)	1.680(2)	C(9)-C(10)	1.393(4)	C(39)-C(40)	1.502(5)
O(1)-C(24)	1.403(3)	C(10)-C(11)	1.394(4)	C(41)-C(42)	1.506(7)
O(2)-C(1)	1.394(3)	C(11)-C(12)	1.382(4)	C(43)-C(44)	1.478(7)
O(3)-C(3)	1.406(3)	C(11)-C(14)	1.530(4)	C(45)-C(46)	1.530(4)
O(4)-C(8)	1.398(3)	C(12)-C(13)	1.394(4)	C(46)-C(47)	1.502(5)
O(5)-C(10)	1.391(3)	C(14)-C(20)	1.524(4)	C(48)-C(49)	1.528(4)
O(6)-C(15)	1.389(3)	C(14)-C(51)	1.535(4)	C(49)-C(50)	1.513(5)
O(7)-C(17)	1.401(3)	C(15)-C(20)	1.389(4)	C(51)-C(52)	1.529(4)
O(8)-C(22)	1.396(3)	C(15)-C(16)	1.391(4)	C(52)-C(53)	1.501(5)
N(1)-C(29)	1.441(4)	C(16)-C(17)	1.381(4)	C(54)-C(55)	1.522(4)
N(1)-C(31)	1.475(4)	C(17)-C(18)	1.382(4)	C(55)-C(56)	1.511(5)
N(2)-C(33)	1.457(4)	C(18)-C(19)	1.396(4)	O(1S)-C(4S)	1.412(6)
N(2)-C(35)	1.470(4)	C(18)-C(21)	1.526(4)	O(1S)-C(1S)	1.427(6)
N(3)-C(37)	1.456(4)	C(19)-C(20)	1.393(4)	O(2S)-C(3S)	1.411(5)
N(3)-C(39)	1.472(4)	C(21)-C(27)	1.524(4)	O(2S)-C(2S)	1.430(6)
N(4)-C(41)	1.468(5)	C(21)-C(54)	1.535(4)	C(1S)-C(2S)	1.483(7)
N(4)-C(43)	1.460(5)	C(22)-C(23)	1.391(4)	C(3S)-C(4S)	1.469(6)
C(1)-C(2)	1.391(4)	C(22)-C(27)	1.391(4)		
Bond Angles					
C(17)-O(7)-P(4)	119.6(2)	C(11)-C(12)-C(13)	123.6(3)	N(1)-C(2)-C(30)	116.5(4)
N(1)-P(1)-O(2)	98.1(1)	C(3)-C(4)-C(7)	120.2(2)	C(18)-C(21)-C(54)	112.6(2)
N(1)-P(1)-O(1)	97.7(1)	C(6)-C(5)-C(4)	123.2(3)	C(23)-C(22)-C(27)	121.5(2)
O(2)-P(1)-O(1)	99.8(1)	C(5)-C(6)-C(1)	117.2(2)	C(23)-C(22)-O(8)	117.7(2)
N(2)-P(2)-O(3)	98.6(1)	C(5)-C(6)-C(28)	122.9(2)	C(27)-C(22)-O(8)	120.7(2)

Bond lengths

N(2)-P(2)-O(4)	96.5(1)	C(1)-C(6)-C(28)	119.9(2)	C(24)-C(23)-C(22)	119.3(2)
O(3)-P(2)-O(4)	99.1(1)	C(13)-C(7)-C(4)	108.8(2)	C(23)-C(24)-C(25)	121.7(2)
N(3)-P(3)-O(5)	99.1(1)	C(13)-C(7)-C(48)	113.1(2)	C(23)-C(24)-O(1)	117.9(2)
N(3)-P(3)-O(6)	98.8(1)	C(4)-C(7)-C(48)	114.1(2)	C(25)-C(24)-O(1)	120.4(2)
O(5)-P(3)-O(6)	97.9(1)	C(9)-C(8)-C(13)	121.8(2)	C(24)-C(25)-C(26)	117.1(2)
N(4)-P(4)-O(7)	98.6(1)	C(9)-C(8)-O(4)	118.3(2)	C(24)-C(25)-C(28)	121.0(2)
N(4)-P(4)-O(8)	98.5(1)	C(13)-C(8)-O(4)	119.9(2)	C(26)-C(25)-C(28)	121.8(2)
O(7)-P(4)-O(8)	99.0(1)	C(8)-C(9)-C(10)	119.5(3)	C(27)-C(26)-C(25)	123.4(3)
C(24)-O(1)-P(1)	119.9(2)	O(5)-C(10)-C(9)	118.3(2)	C(22)-C(27)-C(26)	117.0(2)
C(1)-O(2)-P(1)	119.7(2)	O(5)-C(10)-C(11)	120.6(2)	C(22)-C(27)-C(21)	121.4(2)
C(3)-O(3)-P(2)	121.0(2)	C(9)-C(10)-C(11)	121.0(2)	C(26)-C(27)-C(21)	121.6(2)
C(8)-O(4)-P(2)	120.2(2)	C(12)-C(11)-C(10)	117.3(2)	C(25)-C(28)-C(6)	110.2(2)
C(10)-O(5)-P(3)	115.9(2)	C(12)-C(11)-C(14)	121.9(2)	C(25)-C(28)-C(45)	112.7(2)
C(15)-O(6)-P(3)	117.5(2)	C(10)-C(11)-C(14)	120.7(2)	C(6)-C(28)-C(45)	113.8(2)
C(22)-O(8)-P(4)	118.4(2)	C(12)-C(13)-C(8)	116.8(2)	N(1)-C(31)-C(32)	114.3(3)
C(29)-N(1)-C(31)	113.2(3)	C(12)-C(13)-C(7)	121.8(2)	N(2)-C(33)-C(34)	113.4(3)
C(29)-N(1)-P(1)	124.5(2)	C(8)-C(13)-C(7)	121.5(2)	N(2)-C(35)-C(36)	113.7(3)
C(31)-N(1)-P(1)	122.3(2)	C(20)-C(14)-C(11)	109.3(2)	N(3)-C(37)-C(38)	113.5(3)
C(33)-N(2)-C(35)	117.3(2)	C(20)-C(14)-C(51)	113.7(2)	N(3)-C(39)-C(40)	113.8(3)
C(33)-N(2)-P(2)	123.1(2)	C(11)-C(14)-C(51)	111.9(2)	N(4)-C(41)-C(42)	113.6(4)
C(35)-N(2)-P(2)	119.5(2)	C(20)-C(15)-O(6)	120.7(2)	N(4)-C(43)-C(44)	114.4(5)
C(37)-N(3)-C(39)	118.2(2)	C(20)-C(15)-C(16)	121.1(2)	C(46)-C(45)-C(28)	113.8(2)
C(37)-N(3)-P(3)	124.6(2)	O(6)-C(15)-C(16)	118.2(2)	C(47)-C(46)-C(45)	115.0(3)
C(39)-N(3)-P(3)	117.0(2)	C(17)-C(16)-C(15)	119.5(3)	C(49)-C(48)-C(7)	114.4(2)
C(43)-N(4)-C(41)	114.5(3)	C(50)-C(49)-C(48)	121.6(2)	C(16)-C(17)-C(18)	117.9(3)
C(43)-N(4)-P(4)	124.0(3)	C(16)-C(17)-O(7)	118.0(2)	C(52)-C(51)-C(14)	113.2(2)
C(41)-N(4)-P(4)	116.8(3)	C(18)-C(17)-O(7)	120.3(2)	C(53)-C(52)-C(51)	113.6(3)
C(2)-C(1)-C(6)	121.7(2)	C(17)-C(18)-C(19)	117.5(2)	C(55)-C(54)-C(21)	113.8(2)
C(2)-C(1)-O(2)	118.1(2)	C(17)-C(18)-C(21)	121.3(2)	C(56)-C(55)-C(54)	113.5(3)
C(6)-C(1)-O(2)	120.2(2)	C(19)-C(18)-C(21)	121.1(2)	C(4S)-O(1S)-C(1S)	109.1(3)
C(3)-C(2)-C(1)	119.0(3)	C(20)-C(19)-C(18)	122.8(3)	C(3S)-O(2S)-C(2S)	109.4(4)
C(2)-C(3)-C(4)	121.8(2)	C(15)-C(20)-C(19)	117.5(2)	O(1S)-C(1S)-C(2S)	110.9(4)
C(2)-C(3)-O(3)	118.4(2)	C(15)-C(20)-C(14)	120.7(2)	O(2S)-C(2S)-C(1S)	111.4(4)
C(4)-C(3)-O(3)	119.7(2)	C(19)-C(20)-C(14)	121.7(2)	O(2S)-C(3S)-C(4S)	110.8(4)
C(5)-C(4)-C(3)	117.0(2)	C(27)-C(21)-C(18)	108.7(2)	O(1S)-C(4S)-C(3S)	111.8(4)
C(5)-C(4)-C(7)	122.6(2)	C(27)-C(21)-C(54)	114.2(2)		



I

2 a–c

6 a, b

3 a, b; 4; 5 a-c

2. a. X=NMe_2; 3.a. X=NEt_2, Y=S; 5.a. X=NMe_2, Y=O; 6.a. X=NEt_2, R=Me;
b. X=NEt_2; b. X=OPr-i, Y=S; b. X=NEt_2, Y=O; b. X=NEt_2, R=Et
c. X=OPr-i; 4. X=NMe_2, Y=Se; c. X=OPr-i, Y=O;

SCHEME 1

The phosphorus atoms in **2b** are coordinated in a trigonal pyramid and deviate from the plane of substituents by 0.80 Å on the average. The phosphorus-containing eight-ring cycles have a chair-boot conformation (all NEt_2 groups at the phosphorus atoms are equatorial), and *n*-propyl substituents adopt a transoidal conformation. The top and bottom diameters of

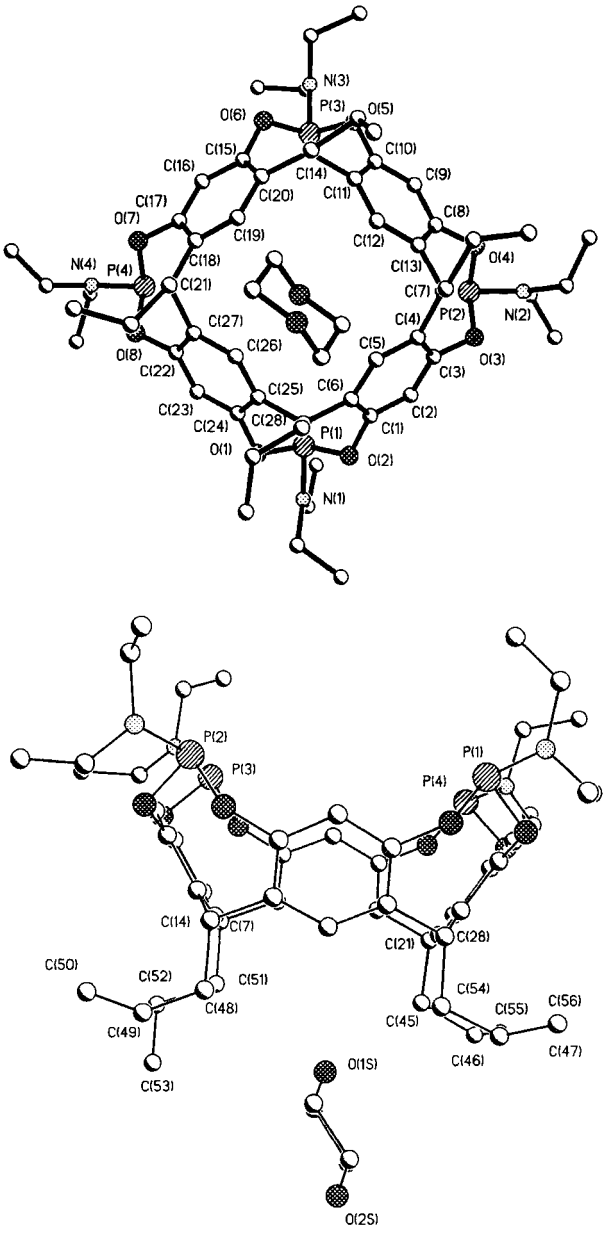


FIGURE 1 The general view of the molecular 2b and numbering scheme (a) and (b) show different views

phosphocavitand **2b** are 8.291(5) and 5.236(5) Å, respectively. The bowl declivity (the angle between the planes of phenyl rings and the bottom plane) is 56.4°. It should be noted that appreciable distortions are observed for the structure of **2b**, as in the case of its tetrabutyl analogue[5]. The distances between the opposite phosphorus atoms P(1)...P(3) and P(2)...P(4) are 8.775(3), 9.181(3) and 9.38(1), 8.62(1) Å, respectively. These distortions can be explained by the effect of crystalline packing and, mainly, of solvent molecules cocrystallising with phosphocavitands (CH_2Cl_2 for tetrabutylphosphocavitand and dioxane for **2b**). The average distance between the adjacent phosphorus atoms is 6.350(3) Å.

The analysis of molecular packing revealed that the crystal structure of **2b** consists of discrete molecules with no abnormally close intermolecular contacts. The molecules in a crystal are head-to-tail arranged with a little shift. Solvent dioxane molecules are located between them, blocked by the propyl substituents of one cavitand and two NEt_2 groups of the next cavitand. Such a disposition of the dioxane molecule (Fig. 1b) can result in different conformations of the propyl groups, which in turn disturb the local C_{4v} symmetry of the molecule. The torsion angles C(7)C(48)C(49)C(50), C(14)C(51)C(52)C(53), C(21)C(54)C(55)C(56), and C(28)C(45)C(46)C(47) are −58.6, −158.5, −72.7, and 58.6°, respectively.

In order to obtain P(V)-phosphocavitands with different substituents at phosphorus atoms, amidophosphites **2a,b** and phosphite **2c** were introduced into reactions with oxidising and alkylating agents (Scheme 1).

Sulfur and selenium were stereospecifically added to cavitands **2a-c** to form an isomer with four axial sulfur (selenium) atoms and equatorial amido (**3a, 4**) or isopropoxy (**3b**) groups. This fact was confirmed by the identity of the spectral parameters of **3a,b** and **4** with those of previously studied thiophosphatocavitands, whose structure has been proved by the X-ray diffraction analysis[7,8].

The interaction between cavitands **2a-c** and oxygen-bearing agents was not so unambiguous. In this case, the stereoselectivity of the process was dependent on the oxidising agent. The oxidation of **2a-c** by ozone and oxygen (UV irradiation) resulted in isomeric phosphocavitands **5a-c** with different arrangement of substituents at phosphorus atoms with respect to the cavity, as evidenced by the ^{31}P NMR spectra of these compounds, where signals of phosphate groups with both axial (**5a-b**: −0.2, −1.2; **5c**: −14 ppm) and equatorial (**5a,b**: −14...−15, **5c**: −20 ppm) orientations of oxo

groups[2] were observed. At the same time, the use of iodozobenzene or the adduct of hydrogen peroxide with urea favoured the stereoregular process resulting in symmetric **5a-c** isomers with the axial orientation of all oxo groups. This fact was confirmed by the ^{1}H and ^{31}P NMR spectra of phosphocavitands **5a-c** (Table I). It should be noted that the adduct of hydrogen peroxide with urea is the most suitable oxidant, because the oxidation by-product is easily removed from the reaction mixture in this case.

Amidophosphite **2b** was alkylated in chloroform with a great excess of alkyl iodide. The reaction resulted in quasiphosphonic salts of cavitands **6a,b** as individual C_{4v}-symmetric stereoisomers in high yields (73–76%). The composition and the structure of **6a,b** were proved by the elemental analysis and ^{1}H and ^{31}P NMR spectroscopy (Table I).

Thus, calyxresorcin[4]arenes containing short alkyl radicals ($C_{3,4}$) are very suitable objects for the synthesis of a broad spectrum of phosphocavitands with different substituents at phosphorus atoms.

EXPERIMENTAL

All syntheses were conducted in dry deoxygenated solvents under argon. ^{1}H NMR spectra were recorded on a Bruker WM-200 spectrometer with TMS as an internal standard. ^{31}P NMR spectra (at 32.4 MHz, 85% H_3PO_4 as an external standard) were recorded on a Bruker WP-80 spectrometer.

Crystallographic data for **2b** $C_{60}H_{88}N_4O_{10}P_4$ were obtained at 193K using a four-cycle Syntex $P2_1$ diffractometer (monochromatised MoKα radiation, θ/2θ-scans, $2\theta < 60°$). The crystal of **2b** is monoclinic at 193K: $a = 12.815(4)$ Å, $b = 15.073(3)$ Å, $c = 18.009(7)$ Å, $\alpha = 106.39(3)°$, $\beta = 109.38(3)°$, $\gamma = 97.29(3)°$, $V = 3053(2)$ Å, $Z = 2$, space group P1, $\mu = 0.183$ mm^{-1}, $F(000) = 1232$, $d_{calc} = 1.250$ g.cm^{-3}. The total number of the measured reflections for the **2b** structure was 9414.

The structure of **2b** was solved by the direct method and refined by a full-matrix least squares on F^2 in the anisotropic-isotropic (H-atoms) approximation. All hydrogen atoms were located by the electron density difference synthesis and were included in the final refinement.

The results of the refinement for **2b** are: R1 = 0.0505 for the 7285 independent reflections with $I > 2\sigma(I)$ and wR2 = 0.1303 and GOF = 1.035 for all 8345 independent reflections, respectively. All calculations were per-

formed with an PC/AT computer using a SHELXTL programs package (ver. 5). The final atomic parameters for the **2b** structure are listed in Table II

Phosphitocavitands 2a-c

A solution of octol **1** (0.25 mmol) and corresponding amide (1 mmol) in dioxane was kept at 20°C for 5 (**2a**), 3 (**2b**), and 12 days (**2c**). The precipitate formed was filtered off, washed with hexane, and dried *in vacuo.*

Amidophosphitocavitand 2a (stereoisomer)

Yield 90%. M. p. 260–262°C. Anal. Calcd for $C_{48}H_{64}N_4O_8P_4$ (948.88): C, 60.75; H, 6.80; N, 5.90; P, 13.57. Found: C, 60.31; H, 6.90; N, 5.81; P, 13.40.

Amidophosphitocavitand 2b (stereoisomer)

Yield 88%. M. p. 245–247°C. Anal. Calcd for $C_{56}H_{80}N_4O_8P_4$ (1061.08): C, 63.38; H, 7.60; N, 5.28; P, 11.68. Found: C, 63.01; H, 7.69; N, 5.27; P, 11.55.

Phosphitocavitand 2c (stereoisomer)

Yield 67%. M. p. 275–277°C. Anal. Calcd for $C_{52}H_{68}O_{12}P_4$ (1008.92): C, 61.87; H, 6.84; P, 12.27. Found: C, 61.40; H, 6.88; P, 12.03.

Thiophosphatocavitands 3a,b

A solution of the corresponding cavitand (0.13 mmol) and sulfur (0.52 mmol) in benzene (4 ml) was stirred at 60°C for 2.5 (**3a**) and 3.5 h (**3b**). Next, the solvent was partly evaporated, and the precipitate formed was filtered off and dried *in vacuo.*

Amidothiophosphatocavitand 3a (stereoisomer)

Yield 63%. M. p. 278–280°C. Anal. Calcd for $C_{56}H_{80}N_4O_8P_4S_4$ (1189.27): C, 56.56; H, 6.77; N, 4.71; P, 10.42; S, 10.79. Found: C, 56.48; H, 6.80; N, 4.69; P, 10.38; S, 10.70.

Thiophosphatocavitand 3b (stereoisomer)

Yield 58%. M. p. >350°C. Anal. Calcd for $C_{52}H_{68}O_{12}P_4S_4$ (1137.18): C, 54.92; H, 6.02; P, 10.89; S, 11.28. Found: C, 54.88; H, 6.07; P, 10.84; S, 11.27.

Amidoselenophosphatocavitand 4 (stereoisomer)

A solution of cavitand **2a** (0.13 mmol) and selenium (0.52 mmol) in a mixture of dioxane (9 ml) and chloroform (1 ml) was stirred at 90–100°C for 5.5 h. The solvents were removed; 2 ml of chloroform was added to the residue, and the excess of selenium was filtered off. Next, chloroform was evaporated; the product was washed with hexane and dried *in vacuo*. Yield 50%. M. p. >350°C. Anal. Calcd for $C_{48}H_{64}N_4O_8Se_4$ (1264.74): C, 45.58; H, 5.10; N, 4.43; P, 9.79. Found: C, 45.12; H, 5.12; N, 4.37; P, 9.30.

Phosphatocavitands 5a-c

A solution of cavitand **2** (0.06 mmol) and the adduct of hydrogen peroxide with urea $[H_2O_2(NH_2)_2CO]$ (0.24 mmol) in methylene chloride (2 ml) was stirred at 20°C for 3–4 h. The precipitate of $[H_2O_2(NH_2)_2CO]$ was filtered off; the solvent was partly evaporated; the residue was washed with water; methylene chloride was removed, and the product was dried *in vacuo*.

Amidophosphatocavitand 5a (stereoisomer)

Yield 59%. M. p. >350°C. Anal. Calcd for $C_{48}H_{64}N_4O_{12}P_4$ (1012.88): C, 56.92; H, 6.36; N, 5.53; P, 12.23. Found: C, 56.51; H, 6.42; N, 5.50; P, 12.17.

Amidophosphatocavitand 5b (stereoisomer)

Yield 39%. M. p. 324–326°C. Anal. Calcd for $C_{56}H_{80}N_4O_{12}P_4$ (1125.08): C, 59.78; H, 7.16; N, 4.98; P, 11.01. Found: C, 59.30; H, 7.26; N, 4.89; P, 10.93.

Posphatocavitand 5c (stereoisomer)

Yield 55%. M. p. 300–302°C. Anal. Calcd for $C_{52}H_{68}O_{16}P_4$ (1072.91): C, 58.21; H, 6.38; P, 11.55. Found: C, 58.17; H, 6.41; P, 11.53.

Quasiphosphonic salts of cavitands 6a,b

A solution of cavitand **2b** (0.05 mmol) and the corresponding alkyl bromide (3 mmol) in chloroform (1 ml) was kept for 7 days at 20°C (**6a**) or 7 h at 120°C (**6b**). Hexane (0.5 ml) was added to the reaction mixture; the precipitate formed was filtered off and dried *in vacuo*.

Quasiphosphonic salt 6a (stereoisomer)

Yield 73%. M. p. 325–330°C (decomp.). Anal. Calcd for $C_{60}H_{92}I_4N_4O_{16}P_4$ (1628.83): C, 44.23; H, 5.65; N, 3.44; P, 7.62. Found: C, 43.80; H, 5.29; N, 3.15; P, 7.27.

Quasiphosphonic salt 6b (stereoisomer)

Yield 76%. M. p. 330–335°C (decomp.) Anal. Calcd for $C_{64}H_{100}I_4N_4O_8P_4$ (1684.93): C, 45.60; H, 5.94; N, 3.33; P, 7.36. Found: C, 45.71; H, 5.85; N,3.29; P, 7.30.

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