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Leonid N. Markovsky[ab]; Vitaly I. Kalchenko[ab]; Myroslav A. Vysotskya[ab]; Vladimir V. Pirozhenko[ab]; Yurij A. Simonov[bc]; Alexander A. Dvorkin[bc]; Alexander V. Iatsenko[bc]; Janusz Lipkowski[bc]
[a] Institute of Organic Chemistry of the National Ukrainian Academy of Sciences, Kiev-94, Ukraine [b] Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland [c] Institute of Applied Physics of the Moldova Academy of Sciences, Kishinev, Moldova

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Synthesis and Structure of Hexa(Diethoxyphosphoryloxy)calix[6]arene

LEONID N. MARKOVSKY[a]*, VITALY I. KALCHENKO[a], MYROSLAV A. VYSOTSKY[a], VLADIMIR V. PIROZHENKO[a], YURIJ A. SIMONOV[b], ALEXANDER A. DVORKIN[b], ALEXANDER V. IATSENKO[b], and JANUSZ LIPKOWSKI[b]

[a]*Institute of Organic Chemistry of the National Ukrainian Academy of Sciences, Murmanskaya str., 5, Kiev-94, 253660, Ukraine;* [b]*Institute of Applied Physics of the Moldova Academy of Sciences, Kishinev, 277028, Moldova; Institute of Physical Chemistry of the Polish Academy of Sciences, 01224, Warsaw, Poland*

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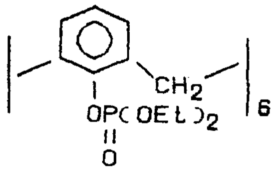
Hexapodand **1**, which contains six phosphoryl groups at the lower rim of the macrocycle, was synthesized by the reaction of calix[6]arene with diethylchlorophosphate and sodium hydride. The structure is confirmed by X-ray studies: $C_{66}H_{90}O_{24}P_6$, *Pbca*, a = 14.867 (4), b = 18.577 (4), c = 26.510(6), D_c = 1.265g/cm^3, Z = **4**, and *R* = 0.063 for the 4600 observed reflections. The molecule **1** exists in a centrosymmetrical *flattened 1,2,3-alternate* conformation, in which diametrically opposed benzene rings are parallel. Four phosphoryl groups are oriented away from the cycle, two other groups are self-included in the macrocycle cavity.

INTRODUCTION

Phosphoryl groups exhibiting outstanding cationo- and protonoaffinity are widely used for the optimization of chemical, physico-chemical and binding properties of macrocyclic "host"-molecules.[1–7] Of the phosphorus containing macrocycles, crown-ethers as well as their nitrogen analogues have been studied in detail.[1] The influence of phosphorus-containing substitutents on the properties of calixarenes (obtained by condensation of para-substituted phenols with formaldehyde[2,3]) and calix[4]resorcinarenes (synthesized from resorcinol and various aldehydes[2]) are less investigated.[4]

In this article we report the synthesis, X-ray analysis and ^{1}H NMR data of 37,38,39,40,41,42-hexa(diethoxyphosphoryloxy)calix[6]arene, **1**, which has a hexapodand structure with six phosphoryl groups at the lower rim of macrocycle.



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*Corresponding author.

EXPERIMENTAL SECTION

^1H and ^{31}P NMR spectra (at 200 and 81.026 MHz, respectively) were obtained on a Bruker WP-200 instrument with tetramethylsilane and 85% H_3PO_4 as internal and external standards, respectively. Synthesis of 37,38,39,40,41,42-hexa(diethoxyphosphoryloxy)calix[6]arene **1**.[1]

Sodium hydride (67 mmol) was added to solution of calix[6]arene (2 mmol) in 85 mL mixture THF-DMFA (10:1) under a dry argon atmosphere. After 1.5 h stirring diethylchlorophosphate (67 mmol) was added. The resultant mixture was refluxed for 2 h and water (5 mL) was added after cooling. The solid product was separated and washed with THF (10 mL). The liquids were combined and evaporated under reducing pressure. The residue was column chromatographed on silica gel (acetone) and recrystallized from ethyl acetate. Colorless crystals, yield 75%. Mp 156–157°C. ^1HNMR ($(CD_3)_2CO$): 1.05 (t, J = 6.8 Hz, 36H, CH_3), 3.98 (m, 24H, OCH_2), 4.26 (s, 12H, Ar-CH_2-Ar), 6.75 (m, 18H, C_6H_3) ppm; ($(CD_3)_2CO$, −68°C): 0.90 (t, J = 6.8 Hz, 12H, CH_3), 1.0–1.3 and 1.41 (br s and t, J = 6.8 Hz, 24H, CH_3), 3.83 (m, 8H, OCH_2), 3.98 and 4.88 (d, J = 16.8 Hz, 8H, Ar-CH_2-Ar), 4.21 (s, 4H, Ar-CH_2-Ar), 4.37 (m, 16H, OCH_2), 6.08 (d, J = 7.4 Hz, 4H, C_6H_3), 6.90 (t, J = 7.4 Hz, 2H, C_6H_3), 7.0–7.3 and 7.46 (br s and s, 12H, C_6H_3) ppm. ^{31}PNMR: −5.3 ppm. *Anal.* Calcd. for $C_{66}H_{90}O_{24}P_6$: C, 54.50; H, 6.24; P, 12.78%. Found: C, 54.49; H, 6.21; P 12.85%.

Structure Determination

Single crystals of hexaphosphorylated calix[6]arene **1** were recrystallized from tetrahydrofuran solution and used for X-ray analysis. Preliminary cell parameters were obtained on a CAD-4 diffractometer using MoK_α-radiation.

Refinement of the cell parameters was accomplished by using least squares techniques (Table I). The intensity data were collected at room temperature in the $3 < \theta < 23°$. Two standard reflection were monitored at regular (1 h) intervals without significant variations in intensity. The intensities were corrected for Lorentz and polarization effect but not for absorption. All calculations were performed by using the SHELXXTL system of programs run on an IBM personal computer.

TABLE I Crystal and experimental data

Chemical formula	$C_{66}H_{90}O_{24}P_{66}$
M.W.	1453.3
Space group	*Pbca*
a(Å)	14.867(4)
b(Å)	18.577(4)
c(Å)	26.510(6)
V(Å^3)	7630(1)
Z	4
Dc (g cm^{-3})	1.265
Specimen dimensions (mm)	0.25 × 0.3 × 0.4
μ(cm^{-1})	2.18
Radiation	MoK_α
Scan mode	$\omega - \theta/2\theta$
Θmax (deg)	23
No. measured refl.	4600
No. refining refl.	3029
$R(hkl)$	0.063
$R\omega[\omega = \sigma^{-2}(I)]$	0.067

The structure was solved by direct methods, and was refined by using full matrix least-squares techniques. Refinement of the non-hydrogen atoms was performed with anisotropic temperature factors while the hydrogen atoms were included in structure factor calculations at calculated positions and not refined. The final agreement factor and experimental data are listed in Table I, atomic fractional coordinate in Table II, and bond lengths and bond angles in Table III.

RESULTS AND DISCUSSION

In accordance with the X-ray structural analysis data (Fig. 1) the molecule of hexaphosphorylated calix[6]arene **1** synthesized by the reaction of calix[6]arene with diethylchlorophosphate

TABLE II Fractional Atomic Coordinates (x 10^4)

	x/a	y/b	z/c	B_{eq}
P1	5555(1)	1459(1)	5380(1)	4.40(4)
P2	5765(2)	4215(1)	6419(1)	6.94(4)
P3	4683(1)	6887(1)	7108(1)	4.70(4)
O11	5564(3)	2302(2)	5323(2)	3.8(1)
O12	6193(4)	1341(3)	5843(2)	6.8(1)
O13	6166(3)	1229(2)	4931(2)	5.5(1)
O14	4678(3)	1129(3)	5403(2)	6.1(1)
O21	4788(3)	4158(3)	6193(2)	4.5(1)
O22	6237(5)	4720(4)	6011(3)	13.0(3)
O23	6123(4)	3442(4)	6366(3)	10.5(2)
O24	5857(4)	4518(4)	6914(3)	10.3(2)
O31	4811(3)	6448(2)	6597(2)	3.8(1)
O32	5254(4)	6488(3)	7499(2)	8.1(2)
O33	5153(4)	7607(3)	6963(2)	6.1(1)
O34	3761(4)	6951(3)	7291(2)	7.0(1)
C11	4817(4)	2670(3)	5120(2)	3.6(1)
C12	4790(5)	2825(4)	4613(2)	4.0(1)
C13	4034(5)	3187(5)	4434(3)	5.5(2)
C14	3360(5)	3386(5)	4746(3)	6.0(2)
C15	3414(5)	3249(4)	5264(3)	4.9(2)
C16	4154(5)	2891(3)	5458(2)	3.9(1)
C17	4231(5)	2719(4)	6016(3)	4.3(2)
C21	4016(4)	3917(3)	6453(2)	3.6(1)
C22	3724(4)	3227(3)	6362(2)	3.6(1)
C23	2944(5)	3004(4)	6601(3)	4.8(2)
C24	2485(5)	3454(4)	6910(3)	5.2(2)
C25	2787(5)	4144(4)	6986(3)	4.8(2)
C26	3556(5)	4398(4)	6754(2)	3.8(1)
C27	3854(5)	5176(4)	6817(3)	4.1(2)
C31	4070(4)	6290(3)	6286(2)	3.3(1)
C32	3589(4)	5663(3)	6386(2)	3.5(1)
C33	2855(5)	5536(4)	6085(3)	4.2(2)
C34	2600(5)	6000(4)	5707(3)	5.3(2)
C35	3127(5)	6594(4)	5603(3)	4.5(2)
C36	3890(5)	6749(3)	5886(2)	3.7(1)
C37	4452(5)	7382(4)	5752(2)	4.3(2)
C121	5909(9)	1175(8)	6334(4)	12.2(4)
C122	6620(10)	768(7)	6591(4)	15.7(5)
C131	6133(6)	525(4)	4705(3)	6.6(2)
C132	5753(8)	572(5)	4205(4)	9.0(3)
C221	6300(10)	4500(10)	5487(5)	20.5(6)
C222	5310(10)	4910(10)	5146(7)	10.1(7)
C222*	7490(30)	4450(30)	5610(10)	31.0(20)
C231	6965(8)	3211(8)	6643(6)	16.0(5)
C232	7520(10)	2910(10)	6322(7)	20.7(6)
C321	6169(6)	6314(7)	7408(4)	10.9(4)
C322	6518(8)	6017(7)	7887(5)	12.4(4)
C331	5225(7)	8192(5)	7319(3)	7.7(2)
C332	5287(8)	8867(5)	7045(4)	9.0(3)

*Atoms C222 and C222# are disordered statistically over two positions.

TABLE III Bond Distanses (Å) and Bond Angles (°)

P1-O11	1.576(4)	P1-O12	1.566(6)
P1-O13	1.558(5)	P1-O14	1.422(5)
P2-O21	1.576(5)	P2-O22	1.595(9)
P2-O23	1.538(7)	P2-O24	1.434(8)
P3-O31	1.593(5)	P3-O32	1.531(6)
P3-O33	1.556(5)	P3-O34	1.460(6)
O11-C11	1.410(8)	O12-C121	1.402(12)
O13-C131	1.439(9)	O21-C21	1.412(8)
O22-C221	1.45(2)	O23-C231	1.51(2)
O31-C31	1.406(7)	O32-C321	1.42(1)
O33-C331	1.44(1)	C11-C12	1.377(9)
C11-C16	1.392(9)	C12-C13	1.39(1)
C12-C37	1.53(1)	C13-C14	1.35(1)
C14-C15	1.40(1)	C15-O16	1.39(1)
C16-C17	1.519(9)	C17-C22	1.517(9)
C21-C22	1.375(9)	C21-C26	1.379(9)
C22-C23	1.38(1)	C23-C24	1.36(1)
C24-C25	1.37(1)	C25-C26	1.38(1)
C26-C27	1.520(9)	C27-C32	1.509(9)
C31-C32	1.392(9)	C31-C36	1.387(9)
C32-C33	1.373(9)	C33-C34	1.38(1)
C34-C35	1.38(1)	C35-C36	1.39(1)
C36-C37	1.487(9)	C121-C122	1.47(2)
C131-C132	1.44 (1)	C221-C222	1.89(3)
C221-C222	1.80(4)	C231-C232	1.31(2)
C321-C322	1.48(2)	C331-C332	1.45(1)
benzene ring number			
	1	2	3
01-P-02	102.1(3)	100.8(94)	105.1(3)
01-P-03	101.2(3)	102.8(3)	100.2(3)
01-P-04	115.8(3)	117.6(3)	115.9(3)
02-P-03	102.0(3)	109.5(4)	109.6(3)
02-P-04	117.1(3)	110.4(5)	109.5(3)
03-P-04	116.3(3)	114.7(5)	115.7(3)
P-01-C1	120.7(4)	125.7(4)	120.7(4)
P-02-C21	125.2(7)	120.7(9)	121.8(6)
P-03-C31	123.15(5)	120.4(7)	121.2(5)
01-C1-C2	119.8(6)	117.7(5)	117.7(5)
01-C1-C6	117.1(5)	118.8(6)	118.1(5)
C2-C1-C6	123.1(6)	123.3(6)	124.0(6)
C1-C2-C3	117.2(6)	117.6(6)	116.2(6)
C2-C3-C4	121.5(7)	120.9(7)	122.3(7)
C3-C4-C5	120.6(7)	119.9(7)	119.5(7)
C4-C5-C6	119.9(7)	121.7(7)	121.2(6)
C1-C6-C5	117.7(6)	116.5(6)	116.4(6)
C1-C6-C7	120.7(6)	122.3(6)	124.0(6)
C5-C6-C7	121.5(6)	121.2(6)	119.6(6)
O2-C21-C22	109.0(1)	107.0(1)	109.0(1)
O3-C31-C32	109.9(7)	106.0(9)	109.1(7)
C11-C12-C37	122.9(6)		
C16-C17-C22	144.6(6)		
C17-C22-C23	120.4(6)		
C27-C32-C31	120.8(6)		
O22-C221-C222*	84.0(1)		
C13-C12-C37	119.9(6)		
C17-C22-C21	122.0(6)		
C-26-C27-C32	114.3(6)		
C27-C32-C33	123.0(6)		

*statistically disordered atoms.

and sodium hydride, exists in a centrosymmetrical *flattened 1,2,3-alternate* conformation, in which one pair of diametrically opposite ben-

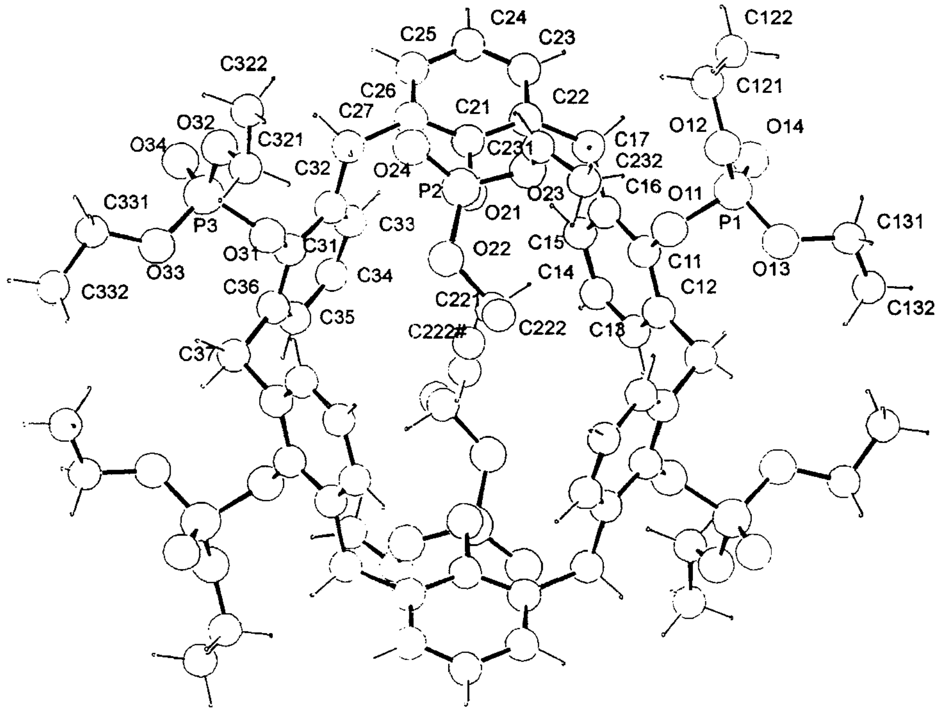

FIGURE 1 View of hexa(diethoxyphosphoryloxy)calix[6]arene, **1**, on the mean molecular plane and atoms numbering.

zene rings (2) are nearly parallel to the main plane of the macrocycle formed by the six methylene links and the other two (1, 3) pairs are oriented up and down. This structure can also be rationalized as (**uo**, u, d, do, d, u) conformation, as suggested by Gutsche.[5] The dihedral angles between neighbouring benzene rings are 84.7 (1 − 2), 72.9 (1 − 3) and 89.0° (2 − 3), and the dihedral angles with the main plane of the macrocycle are 61.7 (1), 38.7 (2) and 108.4° (3). In this conformation the four phosphoryl groups connected to benzene rings (1) and (3) are oriented away from the macrocycle, and the other two groups are inside the cavity.

The configuration of **1** is very similar to ones observed in the crystalline state for 37,38,39,40,41,42-hexa(2-methoxyethoxy)*tert*-butylcalix[6]arene[6a] and 37,38,39,40,41,42-hexa(ethoxycarbonylmethoxy)calix[6]arene.[6b]

The geometry of the phosphoryl groups of compound 1 is similar to that of ordinary phosphoryl compounds[P] The average bond distances (Table III) P-01, P-02 and P-03, P-04 are 1.582(6), 1.56(1) and 1.44(1) Å respectively. C-O and C-C bond lengths of the ethoxy groups (other than the disordered ones) are 1.443 and 1.548 Å. Bond angles at the phosphorus atoms are in the range 101–117°.

The packing of **1** is presented on Figure 2. Pseudospherical molecules are tightly packed by van der Waals interactions.

Unlike conformationaly rigid phosphorylated calix[4]arenes[4d,f,j,m] which adopt the *cone* conformation, molecule **1** is flexible. In solution, owing to free internal rotation of the aromatic rings around the Ar-C-Ar bonds, only a broad singlet for the methylene protons in ^{1}H NMR spectra (acetone-d$_6$) is observed at room temperature

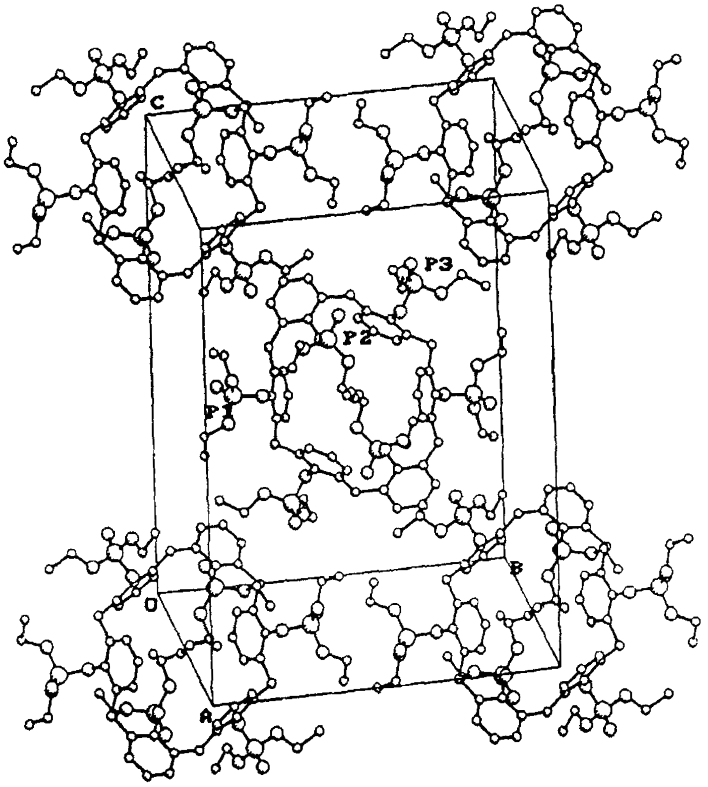

FIGURE 2 Packing of molecules **1** in the unite cell of crystal.

(Fig. 3a). Decreasing the temperature to −68°C leads to the following changes in the ^{1}HNMR spectrum (Fig. 3b). There is one pair of doublets (3.99 and 4.89 ppm) of an AB spin system for four methylene bridges and broad singlet (4.25 ppm) for the last two links in the spectrum. The splitting of the multiplets for the methylene groups of the diethoxyphosphoryl substituents (at 3.83 ppm for 8H and at 4.37 ppm for 16H) is also clearly shown in the spectrum. Broad signals are still observed in the regions 1.0–1.3 and 7.0–7.3 ppm due to some interconvertion process of the macrocyclic skeleton occuring at this temperature. We believe that these facts point to the existence of **1** in the flexible *flattened 1,2,3-alternate* conformation, in which two diethoxyphosphoryl groups (with δ CH_3 0.90 ppm and δ OCH_2 3.83 ppm) are self-included in the cavity.

Recently, the concept of *cone* conformation stabilization in hexasubstituted calix[6]arenes by self-inclusion of methyl or ethyl groups attached to the 1, 3 and 5 positions at the lower rim was described.[8] We may extend this concept to explain the energetic advantage of the *1,2,3-alternate* conformation in our and similar[6a,b] cases by self-inclusion of bulky substituents *attached to 1 and 4 positions* at the lower rim.

In conclusion, the hexaphosphorylated calix[6]arene synthesized by the reaction of calix[6]arene with diethylchlorophosphate and sodium hydride has been described. Its X-ray analysis and ^{1}H NMR spectra described in this paper show that this compound exists in the *flattened 1,2,3-alternate* conformation stabilized by self-inclusion of substituents attached to the *1 and 4* positions on the lower rim.

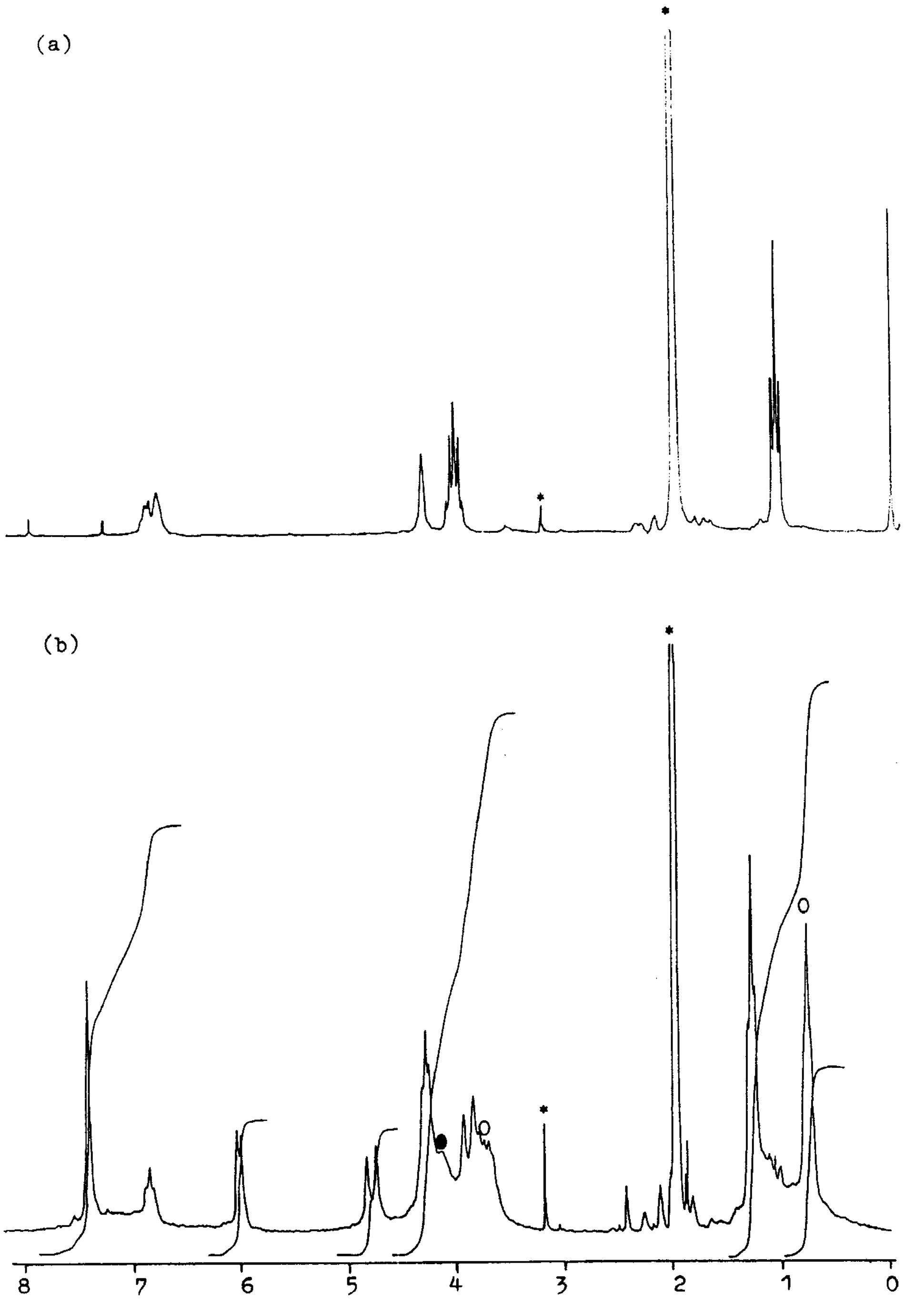

FIGURE 3 ^1H NMR spectra of **1** in a solution of $(CD_3)_2CO$ at different temperatures: (a) 20°C; (b) −68°C; the signals of self-included diethoxyphosphoryl groups, methylene bridges between *anti*-oriented benzene rings, and solvent are marked by a hollow circle (O), full circle (●) and asterisks (*), respectively. The integrated intensities in the region 4.50–8.0 ppm are enlarged two times.

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Endnotes

1. This compound is now commercially available from Acros Organics.