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X-ray and NMR investigation of 25,27-dihydroxy-26,28-bis(diethoxyphosphoryloxy)-*tert*-butylcalix[4]arene in the *1,2-alternate* conformation

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ABSTRACT: The crystal structure of 25,27-dihydroxy-26,28-bis(diethoxyphosphoryloxy)-*tert*-butylcalix[4]arene (1) (hexane solvate, 1:1) was determined by x-ray crystallography. The crystal data are $P2_1/n$, $a = 12.652(1)$ Å, $b = 12.564(2)$ Å, $c = 18.781(4)$ Å, $\beta = 105.56(1)°$, $V = 2876.0(8)$ Å^3, $Z = 2$. In this complex the molecule adopts a *1,2-alternate* conformation. Both the calixarene and hexane molecules are centrosymmetric. The phenol units in the asymmetric part of the calix are inclined with respect to the main macrocyclic plane by 115.46(6)° and 128.01(7)° for the phosphorylated and the non-phosphorylated ring, respectively. Self-inclusion of the ethyl chains in the half-cavities is observed. One intramolecular O—H…O and several intermolecular C—H…O hydrogen bonds are present. In the ^{1}H NMR spectrum one average AX spin system for methylene bridge protons can be interpreted as fast (on the NMR time-scale) interconversion of non-phosphorylated phenol fragments. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: calixarenes; complexes; conformation; crystal structure; ^{1}H NMR; ^{13}C NMR

INTRODUCTION

Calix[4]arenes, owing to the bowl-like architecture of their molecular cavity, are widely used as receptors in the construction of various supramolecular complexes.[1] Their ability to form supramolecular complexes depends on both the nature and the number of binding centres, located at the upper and lower rim of the macrocycle, and as on the conformation of their skeleton. The latter can be described as *cone* (all benzene rings directed upwards with respect to the main macrocyclic plane), *partial cone* (three rings directed upwards and one downwards), *1,2-alternate* (two neighbouring rings oriented upwards and two others downwards) or *1,3-alternate* (two opposite rings pointing upwards and two others downwards).[1a]

Calix[4]arenes distally substituted at the lower rim of the macrocycle and existing in stereochemically rigid *cone* conformations are the most readily available and thoroughly studied derivatives among those synthesized up to now. These compounds have been used as building platforms for the synthesis of highly selective receptors for calcium,[2] potassium[3] and caesium cations[4] and for anions of carbonic acids[5] and halogens.[6] On their basis bifunctional receptors have been designed which are capable of the simultaneous selective binding of a sodium cation and dihydrophosphate[7a] or halide anions.[7b] At the same time, distally substituted calix[4]arenes having an *anti* orientation of functionalized benzene rings are rare and less investigated compounds. Up to now only a few examples with alkoxy[8,9] (**2–4**), benzoyloxy[10] (**5**), dimethylaminothiocarbonyloxy[11] (**6**) and dimethylaminocarbonylthio[11] (**7**) groups at the lower rim have been reported in the literature (see Table 2). Recently, 25,27-dihydroxy-26,28-bis(diethoxyphosphoryloxy)-*tert*-butylcalix[4]arene (**1**) having a similar conformational nature was also isolated.[12] This conformer was obtained as a collateral product in the synthesis of the distal diphosphate existing in the *cone* conformation by the reaction of tetrahydroxycalixarene with diethyl chlorophosphate and triethylamine.[12]

In this paper, we discuss the structure **1** both in solution (NMR method) and in the crystalline state (X-ray diffraction). Considering the stereochemical flexibility of *anti* distally substituted calix[4]arenes,[9,11] an understanding of their structure and stereodynamic properties would be of interest from the viewpoint of the design of allosteric receptors, whose spatial arrangement of binding centres changes under the influence of external factors.

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EXPERIMENTAL

NMR spectra. ^{1}H and ^{13}C NMR spectra were recorded on Gemini VXR-200 and Varian XL-300 spectrometers at 200 and 75.5 MHz, respectively, in $CDCl_3$ solution at room temperature. Chemical shifts are reported as δ values in ppm relative to TMS ($\delta = 0.0$) as an internal standard.

*Crystal structure determination for **1**.* The crystal structure of 25,27-dihydroxy-26,28-bis(diethoxyphosphoryloxy)-*tert*-butylcalix[4]arene (**1**) (hexane solvate, 1:1) was established by x-ray crystallography. Colourless crystals of **1** were obtained from a hexane solution. A single crystal was isolated and sealed in a glass capillary tube with the mother liquor. A preliminary search and data collection were performed on an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated Cu K_α radiation at room temperature (the first procedure was also carried out at 173 K). Reflections were recorded using the $\omega - 2\theta$ scan technique. The unit cell parameters were derived by a least-squares fit of the angles of 25 accurately centred reflections ($14.50° < \theta < 33.03°$ at room temperature and $24.35° < \theta < 27.04°$ at 173 K). Three standard reflections were monitored every hour. No decay was observed during the data collection. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by direct methods[13] and refined by full-matrix least-squares calculations[14] on F^2. The asymmetric unit contained one half of the calixarene and one half of the hexane molecule, their symmetrical equivalents being generated by a centre of symmetry. All non-hydrogen atoms were refined anisotropically. The hydroxyl hydrogen atom was found from a difference Fourier map and was refined isotropically. All other hydrogens were introduced in their idealized positions (C—H distances fixed at 0.97 and 0.96 Å for CH_2 and CH_3, respectively) and refined. Their isotropic thermal parameters were set to 1.3 (for CH and CH_2) or 1.5 (for CH_3) times U_{eq} of their parent C atom. Only hydrogen atoms of the ethoxy groups were subjected to a riding model refinement. The refinement converged at agreement factor $R1 = 0.0578$ [$I > 2\sigma$ (I)]. Full experimental details and crystal data are given in Table 1.

RESULTS AND DISCUSSION

NMR spectra

Cone, partial cone, 1,2-alternate and *1,3-alternate* conformations of calix[4]arenes show characteristic sets of signals in ^{1}H and ^{13}C NMR spectra, and in most cases can be reliably identified by these methods.[1,15]

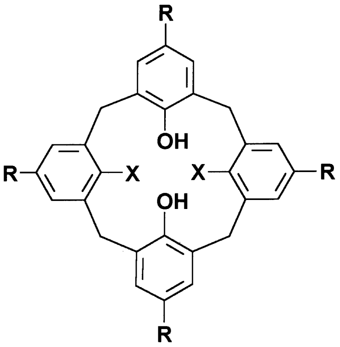
Table 1. Crystal data and structure refinement for **1** at room temperature, and at 173 K

Room temperature:	
Empirical formula	$C_{58}H_{88}O_{10}P_2$
Formula weight	1007.22
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 12.652(1)$ Å $b = 12.564(2)$ Å $c = 18.781(4)$ Å $\beta = 105.56(1)°$
Volume	2876.0(8) Å^3
Z	2
D_{calc}	1.163 gcm^{-3}
Absorption coefficient	1.118 mm^{-1}
$F(000)$	1092
Crystal size	0.28 × 0.35 × 0.40 mm
θ range for data collection	3.79 – 79.96°
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 0$, $0 \le l \le 23$
Reflections collected	6550
Independent reflections	6066 [R(int) = 0.0303]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5951 / 0 / 420
Goodness-of-fit on F^2	1.076
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0578$, $wR2 = 0.1468$
R indices (all data)	$R1 = 0.0685$, $wR2 = 0.1938$
Extinction coefficient	0.0145(6)
Largest diff. peak and hole	0.417 and −0.399 eÅ^{-3}
At 173 K:	
Unit cell dimensions	$a = 12.572(6)$ Å $b = 12.465(5)$ Å $c = 18.802(6)$ Å $\beta = 106.34(3)°$
Volume	2827(2) Å^3

The ^{1}H NMR spectrum of the calix[4]arene diphosphate **1** displays two signals for *tert*-butyl groups (δ 1.25, 1.27 ppm), one triplet (δ 0.83 ppm) and one multiplet (δ 3.66 ppm) for ethoxy groups, one singlet (δ 5.00 ppm) for hydroxyl protons, two singlets (δ 7.08, 7.18 ppm) for protons of benzene rings and two doublets (δ 3.57, 4.40 ppm, $J = 13$ Hz) of an AB spin system caused by resonance of non-equivalent protons $ArCH_2Ar$ located in axial and equatorial positions with respect to the main macrocyclic plane (Table 2). Similar pairs of doublets are also present in the spectra of the other distally *anti*-substituted calix[4]arenes **2–6** described in the literature (Table 2). Whereas the differences in the chemical shifts of axial and equatorial protons ($\Delta\delta$) are in the range 0.12–0.49 ppm (Table 2) for **2–7,** for **1** $\Delta\delta = 0.84$ ppm. This value is very close to that for 25,27-dihydroxy-26,28-BIS(diethoxyphosphoryloxy)-*tert*-butylcalix[4]arene in the *cone* conformation ($\Delta\delta = 0.99$ ppm).[12]

The observed two doublets for methylene protons could be explained by the existence of diphosphate **1** in a conformation unusual for calix[4]arenes in which phenolic units are parallel to the main plane of the

Table 2. ^{1}H and ^{13}C NMR spectral data for distally *anti*-substituted calix[4]arenes



Compound	R	X	^{1}H NMR, δ (ppm): ArCH$_2$Ar H$_{eq}$	H$_{ax}$	^{1}H NMR, $\Delta\delta$(ppm)	^{13}C NMR, δ(ppm): ArCH$_2$Ar	Ref.
1	*t*-Bu	$OP(O)(OEt)_2$	3.57	4.41	0.84	34.9	12
2	H	OPr-*n*	3.79	3.99	0.20	34.7	9
3	*t*-Bu	OEt	3.74	3.95	0.21	-[a]	8b
4	*t*-Bu	OPr-*n*	3.74	3.96	0.22	-[a]	8a
5	H	OC(O)Ph	3.80	3.92	0.12	34.6	10
6	*t*-Bu	$OC(S)NMe_2$	3.99	3.63	0.36	-[b]	11
7	*t*-Bu	$SC(O)NMe_2$	4.27	3.78	0.49	-[c]	11

[a] For this compound the ^{13}C NMR spectrum has not been recorded.
[b] The signals of this carbon have not been assigned among the others caused by two *C*-CH$_3$: 34.38, 33.97, 34.25.
[c] The signals of this carbon have not been assigned among the others caused by *C*-CH$_3$: 34.24, 33.83.

macrocycle, while phosphorylated fragments are oriented upwards and downwards from this plane {*flattened partial cone* conformation, which is rare for calix[4]arene derivatives[16] [Figure 1(a)]}, as suggested by Groenen *et al.*[8b] and Iwamoto *et al.*[8a] for **3** and **4.** At the same time another interpretation of two doublets for the *anti* isomer of 25,27-dihydroxy- 26,28-dipropoxycalix[4]arene (**2**) was offered by van Loon.[9] In the case of stereochemical flexibility of the macrocyclic skeleton, the two doublets can result from fast (on the NMR time-scale) interconversion of phenolic rings of two *1,2-alternate* conformations, resulting in one average pair of doublets for two non-equivalent methylene links [Figure 1(b)]. The *1,2-alternate* conformation of **2** was confirmed by x-ray crystallography.[9]

We had attempted to investigate dynamics of **1** by ^{1}H NMR spectroscopy, but it failed. The spectrum did not undergo appreciable changes in the temperature range -60 to $+30\,°$C (CDCl$_3$), which suggests either the *flattened partial cone* conformation or fast interconversion of the *1,2-alternate* conformation.[12]

The well known test[15] for *syn* and *anti* orientations of neighbouring aromatic fragments of calix[4]arenes based on chemical shifts of signals for methylene bridge carbons in ^{13}C NMR spectra did not prove useful in this particular case. The shift of the signals for methylene bridge carbons of **1** is 34.9 ppm, which is intermediate between δ 31 ppm for a *syn* and δ 37 ppm for an *anti* orientation of benzene rings and is very close to those found for other distally *anti*-substituted calix[4]arenes (Table 2).

Since the NMR data did not provide the unequivocal answer to the conformational problem, x-ray diffraction analysis was performed to determine the crystal structure of **1.**

Crystal structure of 1

X-ray diffraction analysis confirmed the *1,2-alternate* conformation of **1** (hexane solvate) (Figure 2). In this complex the calixarene molecule proved to be centrosymmetric, and hence holds the opposite aryl rings parallel to each other. The inclinations of the phenol units in the asymmetric part of the molecule (Figure 3) with respect to the reference plane (defined by the C atoms in the methylene bridges) are 115.46(6)° for the phosphorylated and 128.01(7)° for the non-phosphorylated ring. The dihedral angle between the neighbouring rings is 71.63(7)°. In this conformation the ethyl chains take up the half-cavities formed by the upper and lower part of the molecule. We observed a similar self-inclusion of the alkyl chains in the resorcinol-derived calixarene.[17] The phosphorus atom shows almost tetrahedral geometry (Table 3). (Full experimental details, atomic coordinates, bond lengths and angles and thermal parameters are deposited as supplementary material.) Angles involving the P=O bond are larger than tetrahedral [112.4(1)–

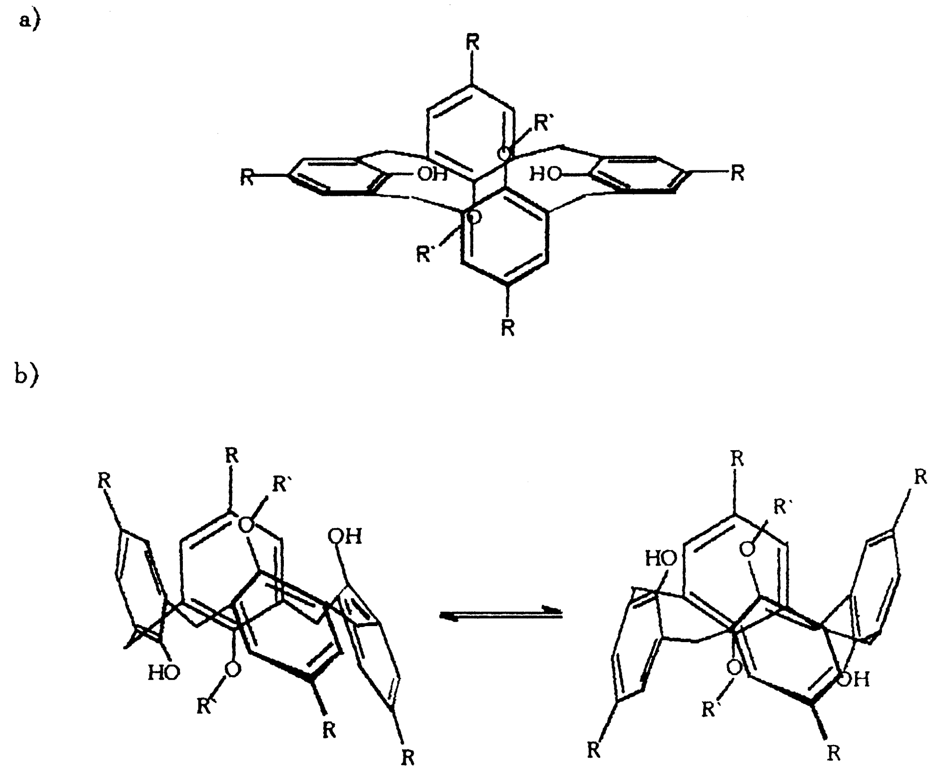


Figure 1. (a) *Flattened partial cone* conformation and (b) topomerization of two *1,2-alternate* conformations as possible explanations of average one AX spin system for methylene bridge protons of distally *anti*-substituted calix[4]arenes

117.01(9)°], while those based on two single P—O bonds are smaller, being in the range 100.94(9) – 107.9(1)°. All bond lengths in the PO_4 fragment are comparable to those in the literature.[18,19] There is also a small difference in the lengths of the chemically equivalent esterified P—O bonds.

The conformation of the calixarene is stabilized by an intramolecular O—H...O hydrogen bond between the

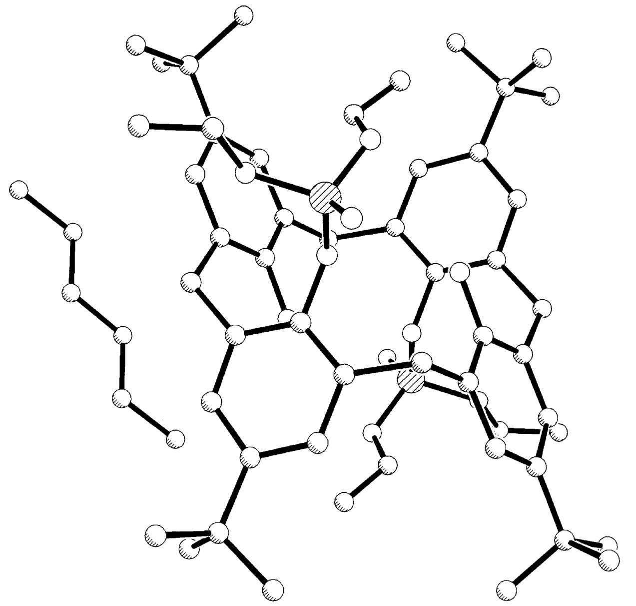


Figure 2. Overall view of compound **1** (hydrogen atoms omitted for clarity)

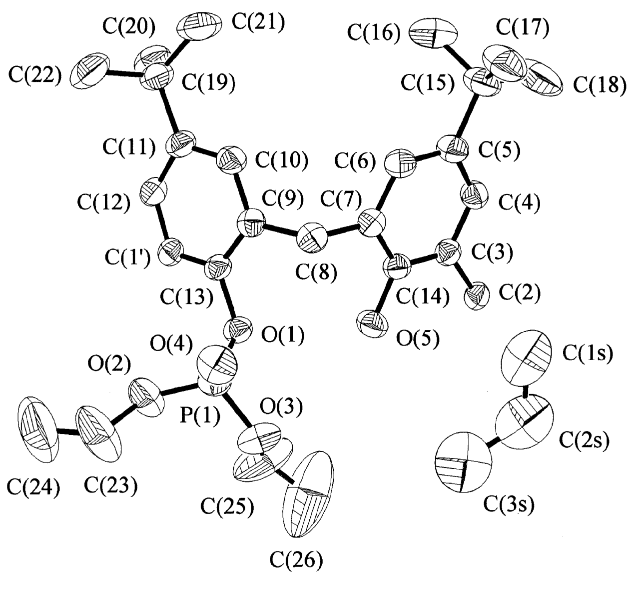


Figure 3. Labelling scheme of the asymmetric parts of the calixarene and hexane molecules. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity

Table 3. Bond lengths (Å) and angles (°) for **1** (for non-hydrogen atoms)[a]

P(1)—O(4)	1.448(2)	O(4)—P(1)—O(3)	112.4(1)
P(1)—O(3)	1.553(2)	O(4)—P(1)—O(2)	115.0(1)
P(1)—O(2)	1.563(2)	O(3)—P(1)—O(2)	107.9(1)
P(1)—O(1)	1.587(2)	O(4)—P(1)—O(1)	117.01(9)
O(1)—C(13)	1.416(2)	O(3)—P(1)—O(1)	100.94(9)
O(2)—C(23)	1.438(4)	O(2)—P(1)—O(1)	102.18(9)
O(3)—C(25)	1.455(4)	C(13)—O(1)—P(1)	123.4(1)
O(5)—C(14)	1.369(2)	C(23)—O(2)—P(1)	120.4(2)
C(1′)—C(13)	1.388(3)	C(25)—O(3)—P(1)	121.8(2)
C(1′)—C(12)	1.388(3)	C(13)—C(1′)—C(12)	116.7(2)
C(1′)—C(2)#1	1.511(3)	C(13)—C(1′)—C(2)#1	124.0(2)
C(2)—C(1′)#1	1.511(3)	C(12)—C(1′)—C(2)#1	119.3(2)
C(2)—C(3)	1.518(3)	C(1′)#1—C(2)—C(3)	120.2(2)
C(3)—C(14)	1.389(3)	C(14)—C(3)—C(4)	118.2(2)
C(3)—C(4)	1.399(3)	C(14)—C(3)—C(2)	123.6(2)
C(4)—C(5)	1.394(3)	C(4)—C(3)—C(2)	118.1(2)
C(5)—C(6)	1.387(3)	C(5)—C(4)—C(3)	122.6(2)
C(5)—C(15)	1.536(3)	C(6)—C(5)—C(4)	117.1(2)
C(6)—C(7)	1.388(3)	C(6)—C(5)—C(15)	119.8(2)
C(7)—C(14)	1.404(3)	C(4)—C(5)—C(15)	123.1(2)
C(7)—C(8)	1.521(3)	C(5)—C(6)—C(7)	122.7(2)
C(8)—C(9)	1.518(3)	C(6)—C(7)—C(14)	118.5(2)
C(9)—C(13)	1.385(3)	C(6)—C(7)—C(8)	119.8(2)
C(9)—C(10)	1.395(3)	C(14)—C(7)—C(8)	121.7(2)
C(10)—C(11)	1.383(3)	C(9)—C(8)—C(7)	112.3(2)
C(11)—C(12)	1.398(3)	C(13)—C(9)—C(10)	117.8(2)
C(11)—C(19)	1.541(3)	C(13)—C(9)—C(8)	123.3(2)
C(15)—C(18)	1.523(4)	C(10)—C(9)—C(8)	118.8(2)
C(15)—C(16)	1.531(5)	C(11)—C(10)—C(9)	122.2(2)
C(15)—C(17)	1.537(4)	C(10)—C(11)—C(12)	117.2(2)
C(19)—C(21)	1.526(4)	C(10)—C(11)—C(19)	122.8(2)
C(19)—C(20)	1.530(4)	C(12)—C(11)—C(19)	120.0(2)
C(19)—C(22)	1.536(4)	C(1′)—C(12)—C(11)	123.2(2)
C(23)—C(24)	1.350(6)	C(9)—C(13)—C(1′)	122.8(2)
C(25)—C(26)	1.286(6)	C(9)—C(13)—O(1)	118.3(2)
C(1s)—C(1s)#2	1.49(1)	C(1′)—C(13)—O(1)	118.7(2)
C(1s)—C(2s)	1.512(8)	O(5)—C(14)—C(3)	117.5(2)
C(2s)—C(3s)	1.504(9)	O(5)—C(14)—C(7)	121.5(2)
		C(3)—C(14)—C(7)	120.9(2)
		C(18)—C(15)—C(16)	110.0(3)
		C(18)—C(15)—C(5)	111.9(2)
		C(16)—C(15)—C(5)	109.5(2)
		C(18)—C(15)—C(17)	109.0(3)
		C(16)—C(15)—C(17)	107.1(3)
		C(5)—C(15)—C(17)	109.2(2)
		C(21)—C(19)—C(20)	108.6(3)
		C(21)—C(19)—C(22)	109.5(3)
		C(20)—C(19)—C(22)	108.3(2)
		C(21)—C(19)—C(11)	111.5(2)
		C(20)—C(19)—C(11)	110.6(2)
		C(22)—C(19)—C(11)	108.1(2)
		C(24)—C(23)—O(2)	113.8(4)
		C(26)—C(25)—O(3)	116.7(4)
		C(1s)#2—C(1s)—C(2s)	115.7(5)
		C(3s)—C(2s)—C(1s)	114.8(5)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x+1$, $-y+1$, $-z$; #2, $-x+2$, $-y+1$, $-z$.

unsubstituted hydroxyl group and the O atom of the phosphorylated hydroxyl group (Table 4). Additionally, weaker intramolecular contacts, such as C8—H8A…O4 and C2—H2A…O2#1 (Table 4), are present. Taking into account the criteria given by Pedireddi and Desiraju,[20] these also may be classified as hydrogen bonds. We may expect that the spatial arrangement of the phosphoryloxy groups, where the P=O moieties are directed outwards, will favour the formation of the intermolecular hydrogen bonds. Indeed, having two donor and two acceptor groups, each molecule is engaged in four intermolecular hydrogen bonds (Figure 4), leading to a hydrogen-bonded

Table 4. Geometry of the intra- and intermolecular hydrogen bonds for **1** (distances in Å, angles in °)

	D...A	D—H	H...A	D—H...A
Intramolecular:				
O(5)—H(5)...O(1)	2.931(2)	0.76(3)	2.20(3)	162(3)
C(8)—H(8A)...O(4)	3.358(3)	0.97(3)	2.62(3)	133(2)
C(2)—H(2A)...O(2)#1	3.175(3)	0.95(3)	2.59(3)	120(2)
Intermolecular:				
C(6)—H(6)...O(4)#2	3.475(3)	0.98(3)	2.49(3)	178(2)
C(10)—H(10)...O(4)#2	3.663(3)	0.95(3)	2.74(3)	166(2)
C(16)—H(16A)...O(4)#2	3.912(5)	1.04(5)	2.95(5)	154(3)
C(17)—H(17A)...O(4)#2	3.866(5)	1.01(5)	2.90(5)	161(3)
C(21)—H(21A)...O(4)#2	3.564(4)	1.03(5)	2.90(5)	123(3)

[a] Symmetry transformations used to generate equivalent atoms: #1, −x+1, −y+1, −z; #2, −x+1.5, y+0.5, −z+0.5.

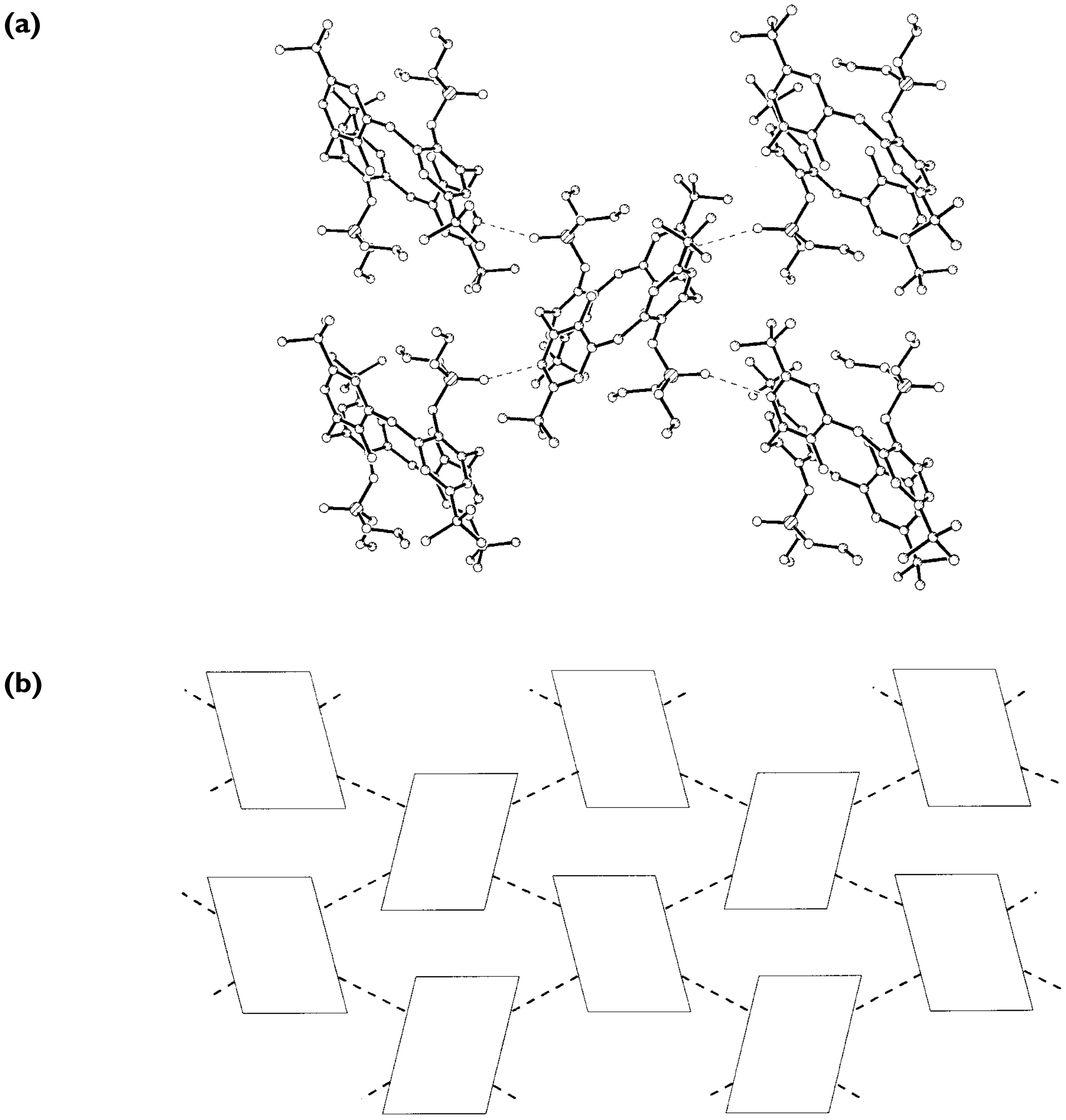


Figure 4. Intermolecular hydrogen bonding pattern of **1**: (a) the calixarene molecule and its closest surrounding; (b) schematic drawing of the infinite hydrogen-bonded layer of calixarene moieties. Intermolecular hydrogen bonds are indicated by dashed lines

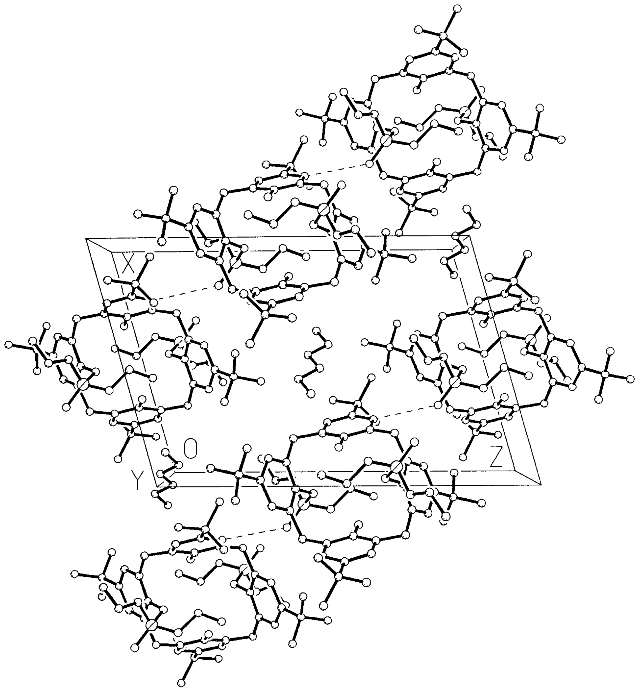


Figure 5. Packing diagram of **1** showing a layered arrangement of host molecules (projection along the *y*-axis). Intermolecular hydrogen bonds are indicated by dashed lines

layered structure [(layers parallel to (101)]. The intermolecular hydrogen bonds are of P=O…H—C type; the carbon atom belonging to a phenyl ring. As in the case of intramolecular hydrogen bonds, several weaker interactions may also be observed. These are listed in Table 4, but as they are much weaker are not marked in Figure 4. Although they satisfy norms set for C—H…O hydrogen bonds, especially the last three should be considered as contacts rather than bondings.

The solvate of **1** with hexane is an *exo* complex, in which guest molecules are located between the H-bonded layers formed by the host (Fig. 5). Interestingly, they are stacked between the neighbouring calixarene molecules forming a non-bonded H–G–H–G pattern along the *x*-axis. The hexane molecule is almost parallel [13.2(4)°] to the non-phosphorylated phenyl ring of both neighbouring calixarene moieties. The closest distance between the molecules is for C(1s) and C(14) atoms, and equals 3.903(5)Å being significantly larger than their sum of van der Waals radii.

CONCLUSION

X-ray analysis of 25,27-dihydroxy-26,28-bis(diethoxyphosphoryloxy)-*tert*-butylcalix[4]arene (hexane solvate) demonstrated a *1,2-alternate* conformation in the crystalline state. This implies that observed in solution (^{1}H NMR), in the temperature range -60 to $+30$°C ($CDCl_3$), one average AX spin system of methylene bridge protons results from fast (on the NMR time-scale) interconversion of non-phosphorylated moieties. The behaviour of the ^{1}H NMR spectra of the distally *anti*-substituted calix[4]arenes **2–4**[8,9] is the same. In ^{13}C NMR spectra of all compounds of this kind, the shifts of the carbons of the methylene bridges are in the range 34.0–34.9 ppm, which can be used as a probe for the fast topomerization of distally *anti*-substituted calix[4]arenes.

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