NMR and X-ray crystallographic studies of unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl calix[4]arene bisphosphites with a large "through-space" P–P coupling†

Pathik Maji, Setharampattu S. Krishnamurthy* and Munirathinam Nethaji

Received (in Gainesville, FL, USA) 24th February 2009, Accepted 7th May 2010
First published as an Advance Article on the web 4th June 2010
DOI: 10.1039/b903771c

Three 25,26-bridged *para-tert*-butyl-calix[4]arene phosphites, **1–3**, have been synthesized by linking two proximal phenolic oxygen atoms of *para-tert*-butyl-calix[4]arene to a P(OR) [R = 2,6-Bu^t_2-4-Me-C_6H_2 (**1**), 2,6-Pr^i_2-C_6H_3 (**2**) or 2,4-Bu^t_2-C_6H_3 (**3**)] moiety. NMR spectroscopic data and X-ray crystallographic studies (**1** and **2** only) show that the calixarene framework in **1** adopts a cone conformation, whereas in **2** and **3** it assumes a partial cone conformation. Unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites **5–7** have been synthesized by the reaction of 25,26-bridged *para-tert*-butyl-calix[4]arene phosphite **1** with (R′O)PCl_2 [R′ = 2,4-Bu^t_2-C_6H_3 (**5**), 2,6-Pr^i_2-C_6H_3 (**6**) or (1*R*,2*S*,5*R*)-(−)menthyl (**7**)]. NMR investigations (homonuclear ^{31}P COSY) revealed an unprecedented "through-space" phosphorus–phosphorus coupling of 223–244 Hz for these unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites. The molecular structure of unsymmetrical 25,26;27,28-bridged bisphosphite **5** was determined by X-ray crystallography; the two phosphorus atoms are in close proximity and the P···P distance (3.543(2) Å) is less than the sum of their van der Walls radii.

1. Introduction

Functionalization of calix[4]arenes by incorporating soft donor phosphorus atom(s) and the transition metal chemistry of such "phospha-calixarenes" have been the subject of numerous investigations during the last twenty years.[1] Calix[4]arene phosphites can be divided into three main categories (A, B and C in Fig. 1), depending on whether one, two or three phenolic oxygen atoms at the lower rim are connected to a single phosphorus atom. Among these, by far the most widely investigated are those belonging to type A.[2–4] 25,26;27,28-Dibridged calix[4]arene bisphosphites of type B-2, in which each of the adjacent pairs of phenolic oxygen atoms at the lower rim are bonded to a phosphorus atom, were first reported by Paciello *et al.*[5] and Mahalakshmi *et al.*[6] Paciello *et al.* have shown that bisphosphites of type B-2 are good catalysts for rhodium-catalyzed hydroformylation reactions.[5] Mahalakshmi's work involved the synthesis of a calix[4]arene bisphosphite, in which two P(OC_6H_2-2,6-Bu^t_2-4-Me) groups were anchored at the lower rim, and its $PdCl_2$ complex, which underwent cyclometallation upon heating with the loss of a *tert*-butyl group.[6] There are no reports of 25,26-bridged calix[4]arene phosphites of type B-1. A 25,26,27-bridged calix[4]arene phosphite of type C, in which phosphorus(III) is connected to three phenolic oxygen atoms at the lower rim, was first reported by Lattman and co-workers.[7] Subsequently, several derivatives of this phosphite and their metal complexes have been reported.[8] The chemistry of calix[4]arene phosphates of types A, B and C has been reviewed by Gloede.[9]

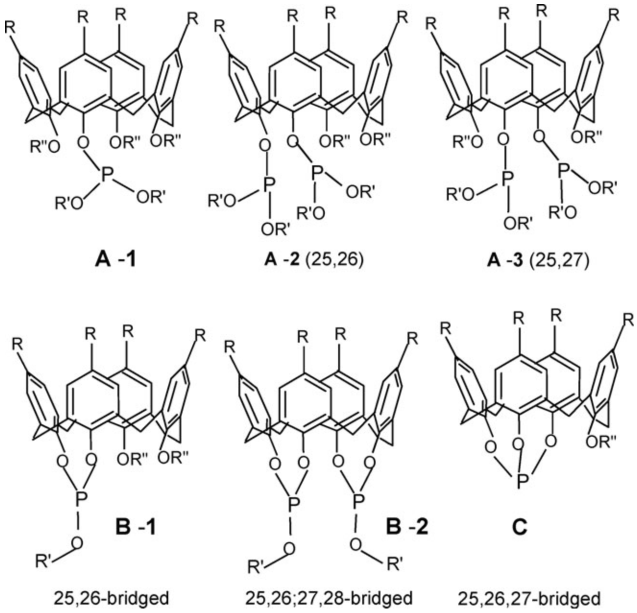


Fig. 1 Different types of calix[4]arene phosphites. For each type, various conformations are possible; here only the cone conformations are shown.

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012Karnataka, India. E-mail: sskrish@ipc.iisc.ernet.in; Fax: +91 80 2360 0683; Tel: +91 80 2293 2401

† Electronic supplementary information (ESI) available: Further experimental details and data. CCDC 695456, 695457 and 695459 contain the supplementary crystallographic data for 25,26-bridged phosphites **1**, **2** and unsymmetrical 25,26;27,28-dibridged bisphosphite **5**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b903771c

As a part of our research program on calix[4]arene phosphites and their transition metal chemistry,[6,10,11] we report here the synthesis and characterization of three 25,26-bridged *para-tert*-butyl-calix[4]arene phosphites by linking two proximal oxygen atoms of a calix[4]arene framework to a P(OR) moiety. We also report the synthesis of unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites. The structures of these calix[4]arene mono- and bisphosphites have been elucidated by NMR and X-ray crystallographic studies.

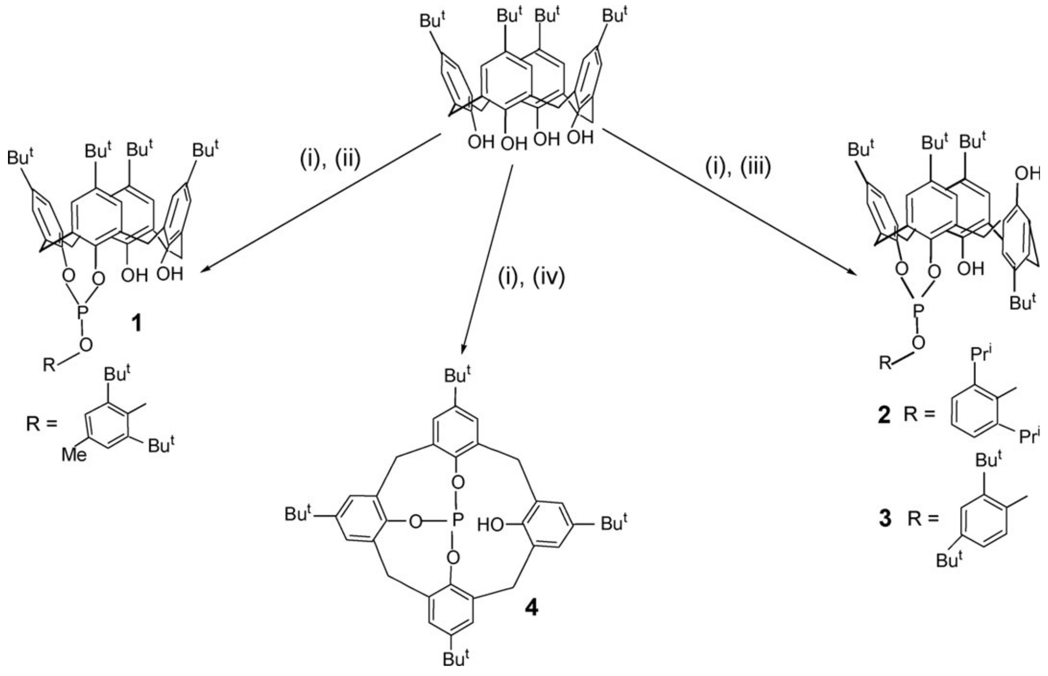
2. Results and discussion

2.1 The synthesis of 25,26-bridged and 25,26,27-bridged calix[4]arene monophosphites and their NMR spectra

25,26-Bridged *para-tert*-butyl calix[4]arene phosphites **1–3** were synthesized in moderate yields by the 1 : 1 stoichiometric reaction of the sodium salt of *para-tert*-butyl-calix[4]arene with phosphorodichloridites ($ROPCl_2$; R = 2,6-Bu^t_2-4-Me-C_6H_2, 2,4-Bu^t_2-C_6H_3 or 2,6-Pr^i_2-C_6H_3), as shown in Scheme 1. When the temperature of the reaction mixture was raised to 95 °C, the major product was the 25,26,27-bridged *para-tert*-butyl-calix[4]arene phosphite **4** in all the reactions. Phosphite **4** is formed by cleavage of the P–OR bond with the concomitant loss of phenol. Compound **4** was previously synthesized by Lattman's[7] and Pringle's research groups[8a] by a different method. The yields of the isolated products are low because of irreversible adsorption or decomposition during the chromatographic separation process. These monophosphite ligands are quite stable under an inert atmosphere for several months. They are moisture sensitive and easily oxidized by exposure to air and are moderately stable in dry methanol for a few days.

The ^{31}P NMR chemical shifts for 25,26-bridged and 25,26,27-bridged *para-tert*-butyl calix[4]arene phosphites **1–4** are shown in Table 1. The ^{31}P NMR chemical shift of 25,26-bridged *para-tert*-butyl calix[4]arene phosphite **1** lies upfield to that of the corresponding 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphite,[6] but the chemical shifts for the 25,26-bridged *para-tert*-butyl calix[4]arene phosphites **2** and **3** lie downfield to those of the corresponding 25,26;27,28-dibridged bisphosphites.[5,11]

The ^{1}H NMR spectra of 25,26-bridged *para-tert*-butyl calix[4]arene phosphites **1–3** show two different peaks in the *tert*-butyl region with a relative intensity of 1 : 1. The ^{1}H NMR spectrum of **1** shows one AX and two AB patterns of relative intensity 2H : 4H : 2H for the methylene protons of the calixarene framework. From the range of chemical shifts spanned by the CH_2 resonances (δ 3.35–4.99) and our previous results,[6,10c] we tentatively assign a cone conformation for **1** in solution. The cone conformation in the solid state is revealed by X-ray crystallography (see below). The ^{1}H NMR spectrum of 25,26-bridged *para-tert*-butyl calix[4]arene phosphites **2** and **3** shows three distinct AB quartets of relative intensity 2H : 4H : 2H for the methylene protons of the calixarene framework. The range of chemical shifts (δ 3.39–4.79) is less than that observed for **1**. Also, the difference in chemical shift of the pair of nuclei of one of the AB quartets is very small (δ 0.1–0.3), indicating that both **2** and **3** adopt a different conformation compared to that of **1** in solution. An X-ray crystallographic study of **2** revealed a partial cone conformation in the solid state (see below). If this conformation were to be retained in solution, the ^{1}H NMR spectrum of **2** and **3** should show four AB quartets. The observation of only three AB quartets implies that the ArOH groups undergo fast flipping through the cone conformation.



Scheme 1 Synthesis of 25,26-bridged and 25,26,27-bridged *para-tert*-butyl calix[4]arene phosphites **1–4**: (i) NaH, toluene, 85 °C, 3 h; (ii) $ROPCl_2$, 70 °C, 2 h; (iii) $ROPCl_2$, 70 °C, 1.5 h; (iv) $ROPCl_2$, 95 °C, 4 h.

Table 1 The ^{31}P ^{1}{H}NMR[a] data for 25,26-bridged calix[4]arene phosphites **1–3**, 25,26,27-bridged phosphite **4** and unsymmetrical 25,26;27,28-dibridged bisphosphites **5–7**[a]

				δ		
Monophosphite	δ	δ^b	Unsymmetrical bisphosphite	P_A	P_B	$^nJ_{P\text{–}P}$/Hz
1	118.2	123.8	**5**	123.2 (d)	116.1 (d)	243.1
2	119.8	115.6	**6**	123.6 (d)	119.3 (d)	236.7
3	120.5	119.8	**7**	126.6 (d)	124.8 (d)	223.8
4	113.2	—	—	—	—	—

[a] Recorded in $CDCl_3$ at 25 °C and at 161.9 MHz; δ in ppm. [b] Chemical shift for symmetrical bisphosphites of respective 25,26-bridged phosphites.

The ^{1}H and ^{31}P NMR data for the 25,26,27-bridged *para-tert*-butyl-calix[4]arene phosphite **4** agree well with those reported previously.[7] The ^{31}P NMR chemical shift of phosphite **4** lies upfield compared to the chemical shifts of 25,26-bridged phosphites **1–3** (see Table 1). The IR spectra of 25,26-bridged and 25,26,27-bridged *para-tert*-butyl-calix[4]arene phosphites **1–4** display strong absorption bands at 3510–3520 cm^{-1}, typical of the presence of hydroxyl groups.

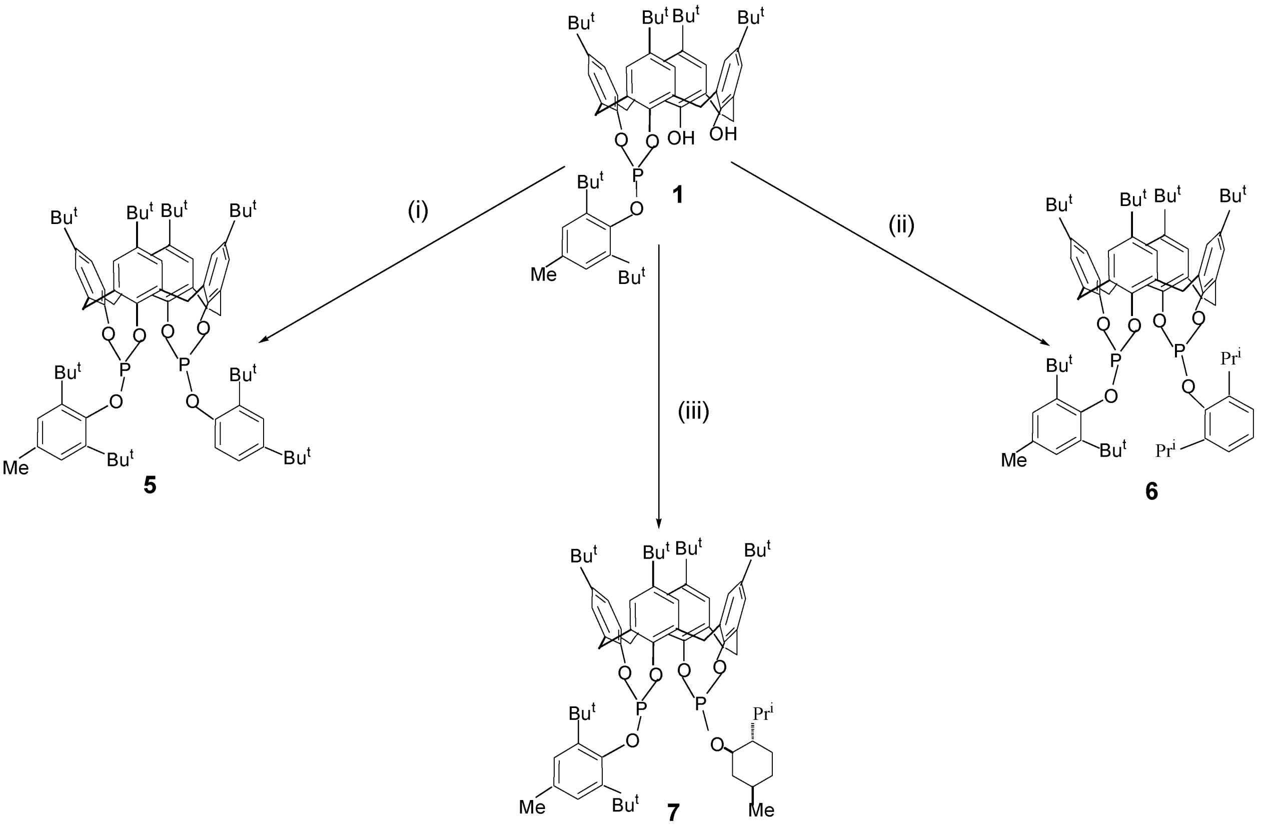
2.2 The synthesis of unsymmetrical 25,26;27,28-dibridged calix[4]arene bisphosphites and their NMR spectra

Achiral and chiral unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites **5–7** were synthesized by the reaction of achiral 25,26-bridged *para-tert*-butyl-calix[4]-arene phosphite **1** with 2,4-di-*tert*-butyl-phenyl, 2,6-diiso-propyl-phenyl or (1*S*,2*R*,5*S*)-(−)-menthyl phosphorodichloridites, respectively, as shown in Scheme 2. Achiral 25,26-bridged *para-tert*-butyl-calix[4]arene phosphite **1** was used as the starting material for the synthesis of unsymmetrical 25,26;27,28-di-bridged *para-tert*-butyl-calix[4]arene bisphosphites **5–7** because the other two proximal hydroxyl groups are on the same side of the calixarene core. Bisphosphites of the type **5–7** could not be synthesized by starting from 25,26-bridged phosphites **2** or **3** because the two remaining hydroxyl groups are in a *trans* orientation.

The ^{31}P NMR spectra of the unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites **5–7** display two doublets (AB pattern) (see the ESI, Fig. S1†). The ^{31}P NMR chemical shifts are shown in Table 1. The chemical shifts of the two phosphorus nuclei (P_A and P_B) are tentatively assigned by comparing them to the ^{31}P NMR chemical shifts of the corresponding symmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites[5,6,10c,11] and 25,26-bridged *para-tert*-butyl-calix[4]arene phosphites **1–3**. A high temperature ^{31}P NMR experiment (toluene-d_8, 90 °C) indicated no change in the spectral pattern, and we conclude that 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites **5–7** are conformationally rigid. The cone conformation of **5** in the solid state was confirmed by X-ray crystallography (see below). The ^{1}H NMR spectra of achiral unsymmetrical bisphosphites **5** and **6** show six doublets in the intensity ratio 1 : 1 : 2 : 1 : 1 : 2 (three doublets in the upfield region overlap for bisphosphite **5**) for the methylene protons of the calixarene framework, as would be expected for a cone conformation.[5,6,10c] Chiral unsymmetrical bisphosphite **7** would be expected to show eight doublets (intensity ratio 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1) because the chirality of the substituent attached to the phosphorus renders all the methylene protons non-equivalent. Actually, four doublets are observed in the downfield region (4.52–5.15 ppm) that arise from the equatorial protons oriented away from the calix[4]arene cavity, whereas one doublet and three overlapping doublets (3.24–3.85 ppm) are observed for the axial methylene protons oriented towards the calix[4]arene cavity.

A remarkable feature of the ^{31}P NMR spectra of unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites **5–7** is the observation of a very large (223–244 Hz) phosphorus–phosphorus coupling (see Table 1). The existence of a large coupling between the two magnetically non-equivalent phosphorus nuclei could be established by 2D-homonuclear ^{31}P COSY measurements. The homonuclear ^{31}P COSY NMR spectrum of **5** is shown in the ESI (Fig. S2).† The magnitude of the observed large phosphorus–phosphorus coupling for the unsymmetrical bisphosphites varies in the order **5** > **6** > **7** (see Table 1). Only limited data are available for long range phosphorus–phosphorus coupling constants. A $^7J_{P\text{–}P'}$ of 4.8 Hz was observed for *ZZ*-$Ph_2PCH_2C(t\text{-}Bu){=}N{-}N{=}C(t\text{-}Bu)\text{-}CH_2PPh_2$.[12] A $^7J_{P\text{–}P'}$ of 22.0 Hz has been reported for a 1,1″-biferrocene derivative bearing –CHMe(PPh_2) and –CHMe{P(C_6H_4Me-4)$_2$}groups.[13] Pastor *et al.* have observed $^7J_{P\text{–}P'}$ and $^8J_{P\text{–}P'}$ values of 30.3 and 30.6 Hz, respectively, for sterically-congested biaryl bisoxazaphospholidines and $^8J_{P\text{–}P'}$ values of 27.5 and 72.8 Hz for sterically-congested bisphosphites.[14–16] A nine bond P–P coupling of 10.2 Hz has been observed for a bis(diphenylphosphino)-β-cyclodextrin derivative.[17] More recently, Matt and co-workers have reported a phosphorus–phosphorus coupling of 8.0 Hz for a pendent calix[4]arene diphosphine with a ten bond P···P separation.[18] Large P–P coupling constants have been reported for 1,8-di(phosphinyl)naphthalene ($J_{P\text{–}P'}$ = 221.6 Hz),[19a,b] 1,8-bis(diphenylphosphino)naphthalene (199 Hz)[19c,d] and 1-bis(dimethylamino)phosphinyl-8-[(dimethylamino)(methoxy)-phosphinyl]naphthalene (246 Hz).[20] To date, there has been no report of large phosphorus–phosphorus coupling constants for 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites such as the ones observed in this study.

Regarding the origin of the large P–P coupling observed for 25,26;27,28-dibridged *para-tert*-butyl calix[4]arene bisphosphites **5–7**, the contribution from a "through-space" interaction would be predominant as the contribution from the "through-bond" interaction should be small or negligible, as even for a conjugated system, such as the one in 2,6-bis(diethoxylphosphinoyl-methyl)naphthalene, a $^9J_{P\text{–}P'}$ of only 4.0 Hz has been reported.[21] The large coupling arises because of through-space spin–spin interactions mediated by the lone pairs of electrons residing on



Scheme 2 Synthesis of unsymmetrical achiral and chiral 25,26;27,28-dibridged calix[4]arene bisphosphites **5–7**: (i) 2,4-di-*tert*-butyl-phenyl-phosphorodichloridite, THF, Et_3N, 25 °C, 14 h; (ii) 2,6-diiso-propyl-phenyl-phosphorodichloridite, THF, Et_3N, 25 °C, 12 h; (iii) (1*R*,2*S*,5*R*)-(−) menthyl-phosphorodichloridites, THF, Et_3N, 25 °C, 6 h.

the two phosphorus atoms. This lone pair overlap theory was originally developed by Mallory *et al.* for through-space ^{19}F–^{19}F couplings in organic compounds.[22] Recently, this model has been extended to through-space ^{31}P–^{31}P couplings in a ferrocenyl tetraphosphine ligand and its metal complexes.[23] Evidently, the two phosphorus atoms of unsymmetrical 25,26;27,28-dibridged calix[4]arene bisphosphites **5–7** are brought into close proximity because of the cone conformation (see section 3 below, dealing with the crystallographic studies).

3. X-Ray crystallographic studies

The solid-state structures of 25,26-bridged *para-tert*-butyl-calix[4]arene phosphites **1** and **2** and unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphite **5** were determined by single crystal X-ray diffraction analysis. The ORTEP plots of the molecular structures of 25,26-bridged *para-tert*-butyl-calix[4]arene phosphites **1** and **2** are shown in Fig. 2 and Fig. 3, respectively. Selected bond lengths and angles are given in Table 2. The calix[4]arene framework in phosphite **1** adopts a cone conformation (up–up–up–up), whereas phosphite **2** shows a partial cone conformation (up–up–up–down) for the calixarene core. Phosphite **1** has crystallographically imposed mirror symmetry and the molecule is inherently chiral.[24,25] The unit cell contains four molecules and there is an inversion centre. The molecular assembly thus consists of a pair of enantiomers and the crystal is racemic. The difference in conformation assumed by the calix[4]arene core in phosphites **1** and **2** arises from the different steric bulk of the alkyl groups at the *ortho* positions of the phenyl substituent. The NMR data indicate that the conformation observed in the solid state of calix[4]arene phosphites **1** and **2** are retained in solution.

We attempted to determine the structure of 25,26,27-bridged *para-tert*-butyl-calix[4]arene phosphite **4** by X-ray crystallography. The poor quality of the crystals resulted in high *R*-factors and the structure is not of a publishable quality. Nevertheless, from the gross connectivities, we can infer that the calix[4]arene backbone adopts an "up–out–down–out" conformation,[11] which is in between the conformation of the corresponding *para-H*-calix[4]arene phosphate (up–up–out–down) reported by Khasnis *et al.*[8e] and the *para-tert*-butyl-calix[4]-arene phosphite derivative, in which the free hydroxyl group was substituted by a $-OCH_2C_6H_5$ group (up–up–out–up), reported by Parlevliet *et al.*[8c]

The conformation of the calix[4]arene backbone of phosphites **1** and **2** can be defined in terms of torsion angles or dihedral angles. The torsion angles are listed in Table 3 and Table 4 for phosphites **1** and **2**, respectively. An examination of the torsion angles show the sequence of signs for ϕ and χ to be $+ -, + -, + -, + -$ for phosphite **1** and $+ -, + -, + +, - -$ for phosphite **2**, as expected for cone and partial cone conformations, respectively. For phosphite **1**, the torsion angles differ significantly from the ideal cone conformation.[26]

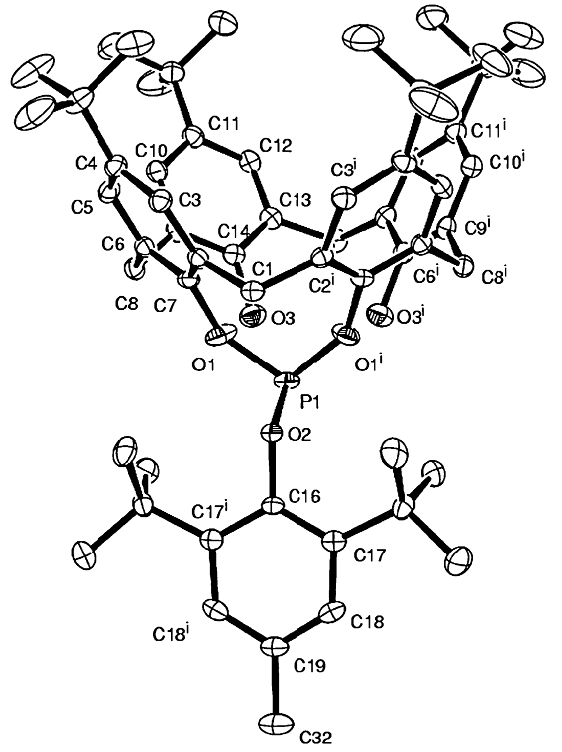


Fig. 2 An ORTEP plot of *para-tert*-butyl-calix[4]arene phosphite **1**. Thermal ellipsoids are drawn at the 50% probability level. The lattice-held water molecule and hydrogen atoms are omitted for clarity.

Table 2 Selected structural parameters for calix[4]arene phosphites **1** and **2**, and unsymmetrical bisphosphite **5** (distances in Å, angles in °)

	1^a	2	5^b
Bond distance			
P(1)–O(1)	1.622(3)	1.652(4)	1.637(4)
P(1)–O(2)	1.655(3)	1.607(4)	1.619(4)
P(1)–O(3)		1.640(4)	1.649(4)
P(2)–O(4)			1.634(4)
P(2)–O(5)			1.621(4)
P(2)–O(6)			1.641(4)
Bond angle			
O(1)–P(1)–O(2)	101.2(1)	102.0(2)	98.7(2)
O(1)–P(1)–O(3)	104.9(2)	98.5(2)	100.7(2)
O(2)–P(1)–O(3)		100.6(2)	103.6(2)
O(4)–P(2)–O(5)			100.2(2)
O(4)–P(2)–O(6)			103.5(2)
O(5)–P(2)–O(6)			97.5(2)

[a] O(1)–P(1)–O(3) = O(1)–P(1)–O(1)′. [b] P(1)···P(2) = 3.543(2) Å.

Table 3 Torsion angles to define the calixarene conformation in phosphite **1**

Torsion angle	ϕ (°)	Torsion angle	χ (°)
C6–C8–C9–C10	80.5(4)	C5–C6–C8–C9	−83.1(4)
C3–C2–C1–C2′	92.2(5)	C3′–C2′–C1–C2	−92.2(5)
C5′–C6′–C8′–C9′	83.1(5)	C6′–C8′–C9′–C10′	−80.5(4)
C12–C13–C15–C13′	87.6(5)	C12′–C13′–C15–C13	−87.6(5)

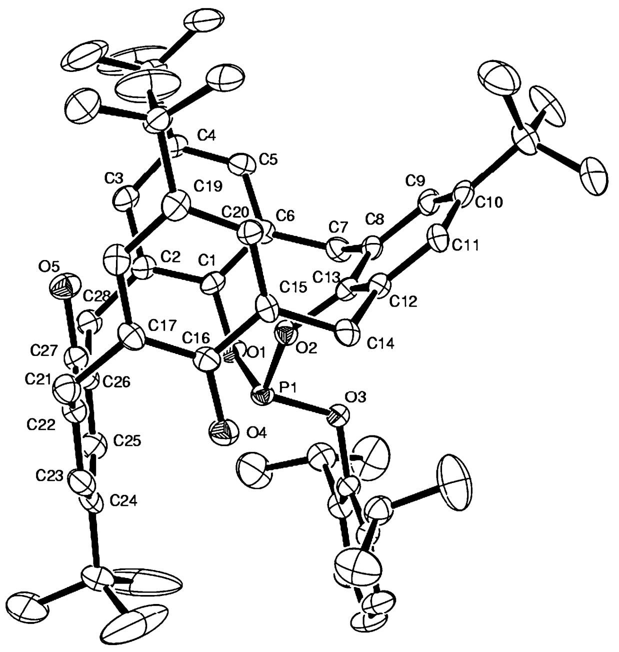


Fig. 3 An ORTEP plot of *para-tert*-butyl-calix[4]arene phosphite **2**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 4 Torsion angles to define the calixarene conformation in phosphite **2**

Torsion angle	ϕ (°)	Torsion angle	χ (°)
C5–C6–C7–C8′	84.4(6)	C6–C7–C8–C9	−120.8(5)
C11–C12–C14–C15	112.3(5)	C20–C15–C14–C12	−55.0(6)
C22–C21–C17–C18	113.8(6)	C17–C21–C22–C23	120.8(6)
C25–C26–C28–C2	−121.8(6)	C3–C2–C28–C26	−126.1(6)

The dihedral angles of the calix[4]arene aryl rings (A, B, C and D) with plane X of the four methylene carbon atoms of phosphites **1** and **2** are listed in Table 5. The observed dihedral angle (88.5°) between the plane of the methylene carbon atoms (X) and the plane of the aryl ring (D) (which contains the hydroxyl group) for phosphite **2** indicates an inverted orientation of this phenyl ring compared with the other three phenyl rings (A, B and C), thus confirming the partial cone conformation.

A perspective view of the molecular structure of unsymmetrical 25,26;27,28-dibridged bisphosphite **5** is shown in Fig. 4. The calixarene framework adopts a cone conformation. The dihedral angles and torsion angles are listed in Table 5 and Table 6, respectively. These values indicate that the cone conformation in **5** is more flattened than in phosphite **1**. The important finding from the crystallographic studies is that the non-bonded P···P distance is 3.543(2), which is less than the sum of the van der Waals radii of the two phosphorus atoms (3.67 Å). Apparently, this rigid structure is retained in solution, providing a through-space pathway for the large P···P coupling.

4. Conclusions

The present study describes the synthesis of the first 25,26-bridged calix[4]arene monophosphites, in which two neighbouring phenoxy rings are linked by a P(OR) unit. These monophosphites can adopt different conformations, depending on

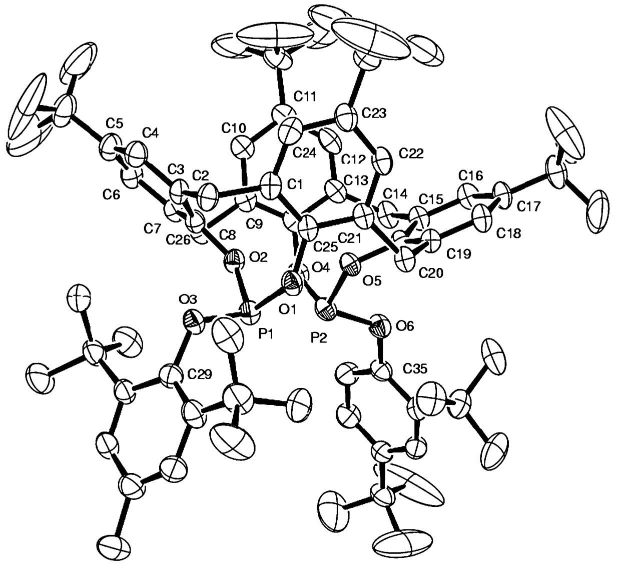


Fig. 4 An ORTEP plot of unsymmetrical *para-tert*-butyl-calix[4]-arene bisphosphite **5**. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 5 Dihedral angles between the planes[a] of the aryl rings of the calix[4]arene framework and the mean plane (X) defined by the methylene carbon atoms in phosphites **1** and **2**, and unsymmetrical bisphosphite **5**

Plane–plane	**1**	**2**	**5**
A–X	61.5(1)	27.4(2)	33.8(1)
B–X	59.1(1)	74.4(2)	85.0(1)
C–X	61.5(1)	81.4(1)	37.4(1)
D–X	59.1(1)	88.5(2)	82.6(1)

[a] A, B, C and D are the planes of the aromatic rings defined by C9–C14, C2–C8, C9–C14 and C2–C8 for phosphite **1**, C8–C13, C1–C6, C22–C27 and C15–C20 for phosphite **2** and (C28, C15–C19), (C27, C9–C13), (C26, C3–C7) and (C1, C21–C25) for unsymmetrical bisphosphite **5**, respectively.

Table 6 Torsion angles to define the calixarene conformation in unsymmetrical bisphosphite **5**

Torsion angle	ϕ (°)	Torsion angle	χ (°)
C24–C1–C2–C3	88.7(5)	C1–C2–C3–C4	−121.6(5)
C6–C7–C8–C9	94.3(5)	C7–C8–C9–C10	−49.9(5)
C12–C13–C14–C15	85.4(5)	C13–C14–C15–C16	−124.8(5)
C18–C19–C20–C21	100.0(5)	C19–C20–C21–C22	−53.6(5)

the steric bulk of the OR group. The isolation of these monophosphites has enabled us to develop a strategy to synthesize unsymmetrical 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites. Unusually large through-space P–P coupling constants (223–244 Hz) were observed for the unsymmetrical bisphosphites because of the close proximity of the two phosphorus atoms, held together in a rigid calixarene framework.

5. Experimental section

The general experimental procedures, and details of the spectroscopic and other physical measurements, are as described in our previous publications.[10] (1*R*,2*S*,5*R*)-(−)-Menthyl phosphorodichloridite was synthesized by a literature procedure.[27] The syntheses of the other phosphorodichloridites ($ROPCl_2$; R = 2,6-Bu^t_2-4-Me-C_6H_2, 2,4-Bu^t_2-C_6H_3 and 2,6-Pr^i_2-C_6H_3) are given in the ESI.†

Synthesis of achiral 25,26-bridged *para-tert*-butyl-calix[4]arene phosphite 1

Sodium hydride (60% dispersion in oil) (0.320 g, 8.0×10^{-3} mol) was added to a stirred suspension of *para-tert*-butyl-calix[4]-arene (2.46 g, 3.8×10^{-3} mol) in toluene (80 cm^3) and the mixture heated under reflux for 3 h at 85 °C. The suspension was cooled to 0 °C and 2,6-di-*tert*-butyl-4-methyl-phenyl phosphorodichloridite (1.24 g, 3.8×10^{-3} mol) added dropwise in toluene (10 cm^3). The reaction mixture was heated under reflux at 70 °C for 2 h. During this time, the thick insoluble suspension gradually dissolved to give a pale yellow solution and a white precipitate. The precipitate was filtered off, the solvent evaporated from the filtrate and the residue subjected to column chromatographic separation over silica gel using petroleum ether and EtOAc (200 : 4 v/v) to afford 25,26-bridged *para-tert*-butyl-calix[4]arene 2,6-di-*tert*-butyl-4-methyl-phenyl phosphite **1**. Phosphite **1** was crystallized from dichloromethane : methanol (1 : 2) to obtain colorless crystals. Yield: 0.82 g (24%); m.p. = 282–289 °C. Anal. calc. for $C_{59}H_{77}O_5P\cdot H_2O$ (mol. wt.: 915.19): C, 77.4; H, 8.7. Found: C, 77.8; H, 8.4%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.08 (s, 18H, Bu^t), 1.25 (s, 18H, Bu^t), 1.35 (s, 18H, Bu^t), 2.29 (s, 3H, Me), 3.35 (d, H, H_{b1}, J = 14.0 Hz), 3.44 (d, 2H, H_{b2}, J = 14.0 Hz), 3.73 (d, H, H_{b3}, J = 14.4 Hz), 3.92 (d, H, H_{a3}, J = 14.8 Hz), 4.29 (d, 2H, H_{a2}, J = 14.0 Hz), 4.99 (d, H, H_{a1}, J = 14.0 Hz), 5.15 (s, 2H, OH), 6.88 (s), 6.97 (s) (4H, calixarene aromatic protons), 7.03 (s, H, Ar), 7.05 (s, H, Ar), 7.10 (s), 7.15 (s) (4H, calixarene aromatic protons).

Synthesis of 25,26-bridged *para-tert*-butyl-calix[4]arene phosphites 2 and 3

25,26-Bridged *para-tert*-butyl-calix[4]arene phosphite **2** was synthesized as described above for monophosphite **1** by the reaction of *para-tert*-butyl-calix[4]arene (4.00 g, 6.2×10^{-3} mol) in toluene (120 cm^3) and NaH (60% dispersion in oil) (0.520 g, 13.0×10^{-3} mol) with (2,6-diiso-propyl-phenyl phosphorodichloridite (1.73 gm, 6.2×10^{-3} mol). Phosphite **2** was crystallized from dichloromethane : methanol (1 : 2) to obtain colorless crystals. Yield: 1.48 g (28%); m.p. = 272–279 °C. Anal. calc. for $C_{56}H_{71}O_5P$ (mol. wt.: 855.10): C, 78.6; H, 8.4. Found: C, 78.7; H, 8.3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.05 (s, 18H, Bu^t), 1.06 (s, 6H, methyl of isopropyl), 1.23 (s, 6H, methyl of isopropyl), 1.27 (s, 18H, Bu^t), 3.23 (m, 2H, methyne proton of isopropyl), 3.39 (d, H, H_{b1}, J = 12.8 Hz), 3.54 (d, 2H, H_{b2}, J = 12.6 Hz), [3.86 (AB quartet, H, H_{b3}, J = 14.4 Hz), 3.87 (AB quartet H, H_{a3}, J = 14.4 Hz], 4.25 (d, 2H, H_{a2}, J = 14.0 Hz), 4.79 (d, H, H_{a1}, J = 14.0 Hz), 4.72 (s, 2H, OH), 6.89 (s), 7.01 (s) (4H, calixarene aromatic protons), 7.05 (3H, m, Ar), 7.08 (s), 7.19 (s) (4H, calixarene aromatic protons).

para-tert-Butyl-calix[4]arene phosphite **3** was synthesized as described above for phosphite **2** by the reaction of *para-tert*-butyl-calix[4]arene (4 gm, 6.2×10^{-3} mol) in toluene (80 cm^3)

and NaH (60% dispersion in oil) (0.520 g, 13.0 × 10^{-3} mol) with 2,4-di-*tert*-butyl-phenyl phosphorodichloridite (1.72 g, 6.2 × 10^{-3} mol). Yield: 1.36 g (25%); m.p. = 276–281 °C. Anal. calc. for $C_{58}H_{75}O_5P$ (mol. wt.: 883.33): C, 78.8; H, 8.6. Found: C, 79.1; H, 8.4%. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.10 (s, 18H, Bu^t), 1.14 (s, 9H, Bu^t), 1.23 (s, 9H, Bu^t), 1.27 (s, 18H, Bu^t), 3.32 (d, H, H$_{b1}$, J = 14.4 Hz), 3.57 (d, 2H, H$_{b2}$, J = 14.4 Hz), [3.82 (AB quartet, H, H$_{b3}$, J = 15.2 Hz), 3.86 (AB quartet, H, H$_{a3}$, J = 14.8 Hz)], 4.28 (d, 2H, H$_{a2}$, J = 14.6 Hz), 4.52 (d, H, H$_{a1}$, J = 14.6 Hz), (the OH peaks were not resolved), 6.95 (s), 7.00 (s) (4H, calixarene aromatic protons), 7.05 (s), 7.09 (s, 3H, Ar), 7.16 (s), 7.24 (s) (4H, calixarene aromatic protons).

Synthesis of 25,26,27-bridged *para-tert*-butyl-calix[4]arene phosphite 4

Sodium hydride (60% dispersion in oil) (0.320 g, 8.0 × 10^{-3} mol) was added to a stirred suspension of *para-tert*-butyl-calix[4]-arene (2.5 gm, 3.8 × 10^{-3} mol) in toluene (80 cm^3). The reaction mixture was heated under reflux for 4 h at 85 °C. The suspension was cooled to 0 °C and 2,6-di-*tert*-butyl-4-methyl-phenyl phosphorodichloridite (1.24 gm, 3.8 × 10^{-3} mol) was added dropwise. The reaction mixture was heated under reflux at 95 °C for 4 h. During this time, the thick insoluble suspension gradually dissolved to give a pale yellow solution and a white precipitate. The precipitate was filtered off. The ^{31}P NMR spectrum of the reaction mixture showed the formation of two products; two singlets were observed at 113.1 and 118.2 ppm, corresponding to 25,26,27-bridged phosphite **4** and 25,26-bridged phosphite **1**, respectively. 25,26,27-Bridged phosphite **4** was the major product. The mixture was subjected to column chromatographic separation over silica gel using EtOAc and petroleum ether (200 : 4 v/v) to afford the less polar phosphite **4**. **4** was also obtained when *para-tert*-butyl-calix[4]arene was treated with 2,6-di-isopropyl-phenyl phosphorodichloridite or 2,4-di-*tert*-butyl-phenyl phosphorodichloridite in boiling toluene. Phosphite **4** was crystallized from dichloromethane : methanol (1 : 2) to obtain colorless crystals. Yield: 0.56 g (22%); m.p. = 308–314 °C. Anal. calc. for $C_{44}H_{53}O_4P$ (mol. wt.: 673.68): C, 78.4; H, 7.9. Found: C, 78.2; H, 7.6%. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.19 (s, 9H, Bu^t), 1.30 (s, 9H, Bu^t), 1.38 (s, 18H, Bu^t), 3.58 (d, 2H, H$_{b2}$, J = 14.8 Hz), 3.69 (d, 2H, H$_{a2}$, J = 16.8 Hz), 4.32 (d, 2H, H$_{b1}$, J = 16.8 Hz), 4.57 (d, 2H, H$_{a1}$, J = 14.8 Hz), (the OH peak was not resolved), 7.10 (s), 7.16 (s), 7.21 (s), 7.23 (s) (Ar, 8H, calixarene aromatic protons).

Synthesis of unsymmetrical and achiral 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphites 5 and 6

Triethylamine (1.52 g, 15 × 10^{-3} mol) was added to a stirred suspension of achiral 25,26-bridged *para-tert*-butyl-calix[4]-arene phosphite (**1**) (4.48 g, 5.0 × 10^{-3} mol) in 80 cm^3 THF and the reaction mixture stirred at room temperature for 15 min. The solution was cooled at 0 °C and 2,4-di-*tert*-butyl-phenyl phosphorodichloridite (1.55 g, 5.0 × 10^{-3} mol) was slowly added through a dropping funnel. The reaction mixture was stirred at room temperature for 8 h. During this time, a white precipitate was formed. The precipitate was filtered off and the filtrate evaporated to obtain a yellowish-white foamy solid. The mixture was then subjected to chromatographic separation using petroleum ether : EtOAc (200 : 1 v/v) to afford unsymmetrical and achiral 25,26;27,28-dibridged *para-tert*-butyl-calix[4]arene bisphosphite (**5**). Bisphosphite **5** was crystallized from dichloromethane : methanol (1 : 2) to obtain colorless crystals. Yield: 1.13 g (20%); m.p. = 182–186 °C. Anal. calc. for $C_{73}H_{96}O_6P_2$ (mol. wt.: 1131.44): C, 77.4; H, 8.5. Found: C, 77.5; H, 8.0%. ^{1}H NMR δ = 1.10 (s, 9H, Bu^t), 1.13 (s, 18H, Bu^t), 1.17 (s, 18H, Bu^t), 1.27 (s, 9H, Bu^t), 1.32 (s, 18H, Bu^t), 2.26 (s, 3H, Me), 3.35 (d, 3H, H$_{b3}$ and H$_{b2}$, J = 14.0 Hz), 3.40 (d, H, H$_{b1}$, J = 13.6 Hz), 4.64 (d, H, H$_{a2}$, J = 13.8 Hz), 4.75 (d, 2H, H$_{a3}$, J = 14.8 Hz), 5.14 (d, H, H$_{a1}$, J = 14.2 Hz), 6.79 (s), 6.83 (s), 6.92 (s), 6.96 (s), 7.10 (s), 7.12 (s), 7.30 (s) (13H, aromatic protons and calixarene protons).

Unsymmetrical achiral *para-tert*-butyl-calix[4] arene bisphosphite **6** was synthesized as described above for bisphosphite **5**. Bisphosphite **6** was crystallized from dichloromethane : methanol (1 : 2) to obtain colorless crystals. Yield: 1.02 g (18%); m.p. = 210–214 °C. Anal. calc. for $C_{71}H_{92}O_6P_2$ (mol. wt.: 1103.39): C, 77.2; H, 8.4. Found: C, 77.5, H, 8.3%. ^{1}H NMR δ = 1.03 (s, 6H, Pr^i), 1.05 (s, 6H, Pr^i), 1.12 (s, 18H, Bu^t), 1.13 (s, 18H, Bu^t), 1.29 (s, 18H, Bu^t), 2.25 (s, 3H, Me), 3.15 (m, 2H, methyne proton of isopropyl), 3.31 (d, 2H, H$_{b2}$, J = 14.6 Hz), 3.39 (d, H, H$_{b3}$, J = 14.4 Hz), 3.43 (d, H, H$_{b1}$, J = 11.8 Hz), 4.66 (d, 2H, H$_{a2}$, J = 13.6 Hz), 4.91 (d, H, H$_{a3}$, J = 16.2 Hz), 5.12 (d, H, H$_{a1}$, J = 14.2 Hz), 6.82 (s), 6.83 (s), 6.86 (s), 6.93 (s), 7.04 (s), 7.07 (s) (13H, aromatic protons and calixarene protons).

Synthesis of unsymmetrical and chiral 25,26;27,28-dibridged *para-tert*-butyl calix[4]arene bisphosphite 7

Chiral bisphosphite **7** was synthesized as described above for bisphosphite **5** by the reaction of achiral *para-tert*-butyl-calix[4]arene 25,26-bridged phosphite **1** (3.40 gm, 3.8 × 10^{-3} mol) with (1*R*,2*S*,5*R*)-(−)-menthyl phosphorodichloridite (0.98 gm, 3.8 × 10^{-3} mol) in 60 cm^3 THF in the presence of triethylamine (1.21 g, 12 × 10^{-3} mol) for 6 h. Yield: 0.99 gm (24%); m.p. = 173–177 °C; [α] = 90.2° (*c* 1.0, 25 °C, CHCl$_3$). Anal. calc. for $C_{69}H_{94}O_6P_2$ (mol. wt.: 1081.63): C, 76.6; H, 8.7. Found: C, 76.1 H, 8.6%. ^{1}H NMR δ = 0.55 (d, 3H), 0.57 (d, 3H), 0.82 (d, 3H), 0.87–1.42 (m, 9H, menthyl group + 54H, Bu^t), 2.31 (s, 3H, Me), 3.24 (d, H$_{b3}$ and Hb$_4$, J = 12.0 Hz), 3.26 (d, H$_{b2}$, J = 12.4 Hz), 3.38 (d, H$_{b1}$, J = 16.4 Hz), 3.98 (bs, H-methyne protons of the menthyl group), 4.52 (d, H$_{a4}$, J = 10.8 Hz), 4.62 (d, H$_{a3}$, J = 12.4 Hz), 4.68 (d, H$_{a2}$, J = 14.4 Hz), 5.15 (d, H$_{a1}$, J = 16.4 Hz), 6.66 (s), 6.69 (d), 6.82 (s), 6.88 (s), 6.98 (s), 7.16 (s) (10H, aromatic protons and calixarene protons).

X-Ray crystallography

X-Ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer. SMART[27] software was used for cell refinement and data acquisition, and SAINT[28] software was used for data reduction. An absorption correction was made on the intensity data using the SADABS[29] programme. All the structures were solved using SHELXS[30] and the WinGX graphical user interface. Least-square refinements were performed by the full-matrix method with SHELXL.[31]

Table 7 Crystal data for 25,26-bridged calix[4]arene phosphites **1** and **2**, and unsymmetrical 25,26;27,28-dibridged calix[4]arene bisphosphite **5**

Empirical formula	$C_{59}H_{79}O_6P$ (**1**·H_2O)	$C_{56}H_{71}O_5P$ (**2**)	$C_{73}H_{96}O_6P_2$ (**5**)
Formula weight	915.19	855.10	1131.44
Temperature/K	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$I2/m$	$P21/n$	$P\bar{1}$
Unit cell dimensions	a = 14.929(3) Å b = 21.378(3) Å c = 18.173(2) Å $\alpha = \gamma$ = 90° β = 108.9(1)°	a = 10.280(5) Å b = 27.784(5) Å c = 17.984(5) Å $\alpha = \gamma$ = 90° β = 91.060(5)°	a = 13.678(2) Å b = 16.739(2) Å c = 19.432(2) Å α = 71.800(2)° β = 78.874(2)° γ = 77.135(2)°
Volume/Å^3	5487.8(2)	5136.0(3)	4083.7(8)
Z	4	4	2
Density (calc.)/Mg m^{-3}	1.108	1.106	0.920
Absorption coefficient/mm^{-1}	0.097	0.098	0.094
F(000)	1984	1848	1224
Crystal size/mm	0.48 × 0.36 × 0.30	0.38 × 0.32 × 0.28	0.48 × 0.42 × 0.34
Theta range for data collection	1.52 to 24.99	1.35 to 25°	1.78 to 25°
Index ranges	$-18 \Leftarrow h \Leftarrow 18$ $-26 \Leftarrow h \Leftarrow 26$ $-21 \Leftarrow h \Leftarrow 22$	$-12 \Leftarrow h \Leftarrow 12$ $-33 \Leftarrow h \Leftarrow 33$ $-21 \Leftarrow h \Leftarrow 21$	$-16 \Leftarrow h \Leftarrow 16$ $-19 \Leftarrow h \Leftarrow 19$ $-23 \Leftarrow h \Leftarrow 21$
Reflections collected	21140	36813	29696
Independent reflections	5620 R_{int} = 0.0538	9034 R_{int} = 0.1786	14290 R_{int} = 0.0602
Completeness to θ (%)	100	99.8	99.4
Absorption correction	Empirical	Empirical	Empirical
Max. and min. transmission	0.9714 and 0.9549	0.9730 and 0.9636	0.9688 and 0.9564
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5620/0/330	9034/0/583	14290/6/732
Goodness-of-fit	1.277	0.851	0.763
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1067 wR_2 = 0.3228	R_1 = 0.1108 wR_2 = 0.2505	R_1 = 0.1151 wR_2 = 0.3161
R indices (all data)	R_1 = 0.1373 wR_2 = 0.3451	R_1 = 0.2604 wR_2 = 0.3289	R_1 = 0.2291 wR_2 = 0.3908
Largest differential peak and hole/e Å^{-3}	1.253 and −0.478	0.622 and −0.550	0.977 and −0.387
Absolute structure parameters	—	—	—

Details pertinent to the data collection, structure solution and refinement are summarized in Table 7. The oxygen atom of the solvent water molecule in compound **1** occupies a special position; both site occupancy factor and thermal parameters for this oxygen atom were refined alternately. The hydrogen atoms attached to this oxygen atom were neither located nor fixed. Some of the *tert*-butyl groups of compounds **2** and **5** were disordered and the hydrogen atoms of these disordered groups were neither located nor fixed. PLATON checks for **5** showed that there is a very large solvent accessible void (1079 Å^3) centered at (0, 0.5, 0). The PLATON/SQUEEZE routine was used to remove the contributions of any disordered solvent molecules. The CIF format output from PLATON (generated as platon.sqf) is appended to the CIF.

Acknowledgements

We thank the Department of Science and Technology, New Delhi, India for financial support and also for data collection using the CCD X-ray facility at IISc, Bangalore set up under the IRHPA program. S. S. K. thanks the Indian National Science Academy, New Delhi for a Senior Scientist position.

References

1 (*a*) C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93–161; (*b*) C. Jeunesse, D. Matt, M. R. Yaftian, M. Burgard and J. M. C. R. Harrowfield, *C. R. Acad. Sci., Ser. IIc: Chim.*, 1998, 479–502; (*c*) I. Neda, T. Kaukorat and R. Schmutzler, *Main Group Chem. News*, 1998, **6**, 4–29; (*d*) C. Jeunesse, D. Armspach and D. Matt, *Chem. Commun.*, 2005, 5603; (*e*) D. M. Homden and C. Redshaw, *Chem. Rev.*, 2008, **108**(12), 5086.

2 (*a*) C. Floriani, D. Jacoby, A. Chiesi-Villa and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1376; (*b*) J. K. Moran and D. M. Roundhill, *Inorg. Chem.*, 1992, **31**, 4213; (*c*) D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1993, 813; (*d*) W. Xu, R. J. Puddephatt, L. M. Muir, K. W. Muir and C. S. Frampton, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1994, **19**, 277; (*e*) I. Shevchenko, H. Zhang and M. Lattman, *Inorg. Chem.*, 1995, **34**, 5405; (*f*) M. Stolmàr, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.*, 1997, **36**, 1694.

3 (*a*) C. Loeber, D. Matt, P. Briard and D. Grandjean, *J. Chem. Soc., Dalton Trans.*, 1996, 513; (*b*) P. Faidherbe, C. Wieser-Jeunesis, D. Matt, A. Harriman, A. D. Cian and J. Fischer, *Eur. J. Inorg. Chem.*, 1998, 451; (*c*) C. Jeunesse, C. Dieleman, S. Steyer and D. Matt, *J. Chem. Soc., Dalton Trans.*, 2001, 881; (*d*) S. Steyer, C. Wieser-Jeunesse, J. Harrowfield and D. Matt, *Dalton Trans.*, 2005, 1301.

4 (*a*) B. R. Cameron, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Org. Chem.*, 1995, **60**, 2802; (*b*) C. Kunze, D. Selent, I. Neda, M. Freytag, P. G. Jones, R. Schmutzler, W. Baumann and A. Börner, *Z. Anorg. Allg. Chem.*, 2002, **628**, 779.

5 R. Paciello, L. Siggel and M. Roper, *Angew. Chem., Int. Ed.*, 1999, **38**, 1920.

6 L. Mahalakshmi, M. Nethaji and S. S. Krishnamurthy, *Curr. Sci.*, 2002, **83**(7), 870.

7 D. V. Khasnis, M. Lattman and C. D. Gutsche, *J. Am. Chem. Soc.*, 1990, **112**, 9422.

8 (*a*) C. J. Cobley, D. D. Ellis, A. G. Orpen and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 2000, 1101; (*b*) C. J. Cobley, D. D. Ellis, A. G. Orpen and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 2000, 1109; (*c*) F. J. Parlevliet, C. Kiener, J. Fraanje, K. Goubitz, M. Lutz, A. L. Spek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, 2000, 1113; (*d*) S. Steyer, C. Jeunesse, D. Matt, R. Walter and M. Wesolek, *J. Chem. Soc., Dalton Trans.*, 2002, 4264; (*e*) D. V. Khasnis, J. M. Burton, J. D. MeNeil, C. J. Santini, H. Zhang and M. Lattman, *Inorg. Chem.*, 1994, **33**, 2657.

9 J. Gloede, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1997, **127**, 97–111.

10 (*a*) A. Sarkar, M. Nethaji and S. S. Krishnamurthy, *Polyhedron*, 2007, **26**, 3904; (*b*) A. Sarkar, M. Nethaji and S. S. Krishnamurthy, *J. Organomet. Chem.*, 2008, **693**, 2097; (*c*) P. Maji, S. S. Krishnamurthy and M. Nethaji, *Polyhedron*, 2008, **27**(17), 3519; (*d*) A. Sarkar, S. S. Krishnamurthy and M. Nethaji, *Tetrahedron*, 2009, **65**, 374.

11 P. Maji, Phosphite ligands based on the calyx[4]arene scaffold and their palladium, platinum and rhodium complexes, *PhD Thesis*, Indian Institute of Science, Bangalore, India, 2005.

12 S. D. Perera, B. L. Shaw, M. Thornton-Pett and J. D. Vessey, *Inorg. Chim. Acta*, 1993, **207**, 175.

13 M. Sawamura, H. Hamashima, M. Sugawara, R. Kuwano and Y. Ito, *Organometallics*, 1995, **14**, 4549.

14 S. D. Pastor, J. L. Hyun, P. A. Odorisio and R. K. Rodebaugh, *J. Am. Chem. Soc.*, 1988, **110**, 6547.

15 S. D. Pastor, S. P. Shum, R. K. Rodebaugh, A. D. Debellis and F. H. Clarke, *Helv. Chim. Acta*, 1993, **76**, 900.

16 S. D. Pastor, S. P. Shum, A. D. DeBellis, L. P. Burke and R. K. Rodebaugh, *Inorg. Chem.*, 1996, **35**, 949.

17 Y. T. Wong, C. Yang, K.-C. Ying and G. Jia, *Organometallics*, 2002, **21**, 1782.

18 P. Kuhn, C. Jeunesse, D. Matt, J. Harrowfield and L. Ricard, *Dalton Trans.*, 2006, 3454.

19 (*a*) T. Costa and H. Schmidbaur, *Chem. Ber.*, 1982, **115**, 1374; (*b*) S. A. Reiter, S. D. Nogali, K. Karaghiosoff and H. Schmidbaur, *J. Am. Chem. Soc.*, 2004, **126**, 15833; (*c*) A. Karaçar, H. Thönnessen, P. G. Jones, R. Bartsch and R. Schmutzler, *Heteroat. Chem.*, 1997, **8**, 539; (*d*) R. D. Jackson, S. James, A. G. Orpen and P. G. Pringle, *J. Organomet. Chem.*, 1993, **458**, C3.

20 P. Kilian, A. M. Z. Slawin and J. D. Woollins, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2004, **179**, 999.

21 L. Ernst, *J. Chem. Soc., Chem. Commun.*, 1977, 375.

22 (*a*) F. B. Mallory, *J. Am. Chem. Soc.*, 1973, **95**, 7747; (*b*) F. B. Mallory, C. W. Mallory, K. E. Butler, M. B. Lewis, A. Q. Xia, E. D. Luzik, L. E. Fredenburgh, Jr., M. M. Ramanjulu, Q. N. Van, D. Francl, A. Freed, C. C. Wray, C. Hann, M. Nerz-Stormes, P. J. Carroll and L. E. Chirlian, *J. Am. Chem. Soc.*, 2000, **122**, 4108.

23 (*a*) J.-C. Hierso, A. Fihri, V. V. Ivanov, B. Hanquet, N. Pirio, B. Donnadieu, B. Rebiere, R. Amardeil and P. Meunier, *J. Am. Chem. Soc.*, 2004, **126**, 11077; (*b*) J.-C. Hierso, D. Evrard, D. Lucas, P. Richard, H. Cattey, B. Hanquet and P. Meunier, *J. Organomet. Chem.*, 2008, **693**, 574.

24 K. Iwamoto, H. Shimizu, K. Araki and S. Shinkai, *J. Am. Chem. Soc.*, 1993, **115**, 3997.

25 A. Ikeda and S. Shinkai, *Chem. Rev.*, 1997, **97**, 1713.

26 F. Ugozzoli and G. D. Andretti, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1992, **13**, 337.

27 J.-M. Brunel and G. Buono, *J. Org. Chem.*, 1993, **58**, 7313; *Bruker SMART, v. 6.028*, Bruker AXS Inc., Madison, WI, USA, 1998.

28 *Bruker SAINT, v. 6.02*, Bruker AXS Inc., Madison, WI, USA, 1998.

29 G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

30 G. M. Sheldrick, *SHELXS-97, Program for the solution of crystal structures*, University of Göttingen, Germany, 1997.

31 G. M. Sheldrick, *SHELXL-97, Program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.