Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **19:** 237–256, 1994.

Preparation, Structure and Stereodynamics of Phosphorus-Bridged Calixarenes*

OLEG ALEKSIUK, FLAVIO GRYNSZPAN and SILVIO E. BIALI**
Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

(Received: 30 October 1993; in final form: 3 March 1994)

Abstract. The pyrolysis of several dialkylphosphate ester derivatives of calix[4]arenes yielded the same phosphorus bridged compound **7**. Under the pyrolytic conditions the phosphate groups may be cleaved or intermolecularly transferred. X-ray crystallography of the bridged calixarenes **7** and **8** shows that they exist in a chiral 'flattened cone' (fc) conformation. The bridged calixarenes undergo in solution a dynamic process with a barrier of about 10.1 kcal mol^{-1} for **7** and **8** and 13.1 kcal mol^{-1} for **10**, respectively. The dynamic processes result in enantiomerization of the systems. Pyrolysis of partially phosphorylated calix[6]arenes resulted in the formation of two products (**11** and **12**), each consisting of two subunits of three proximal rings bridged by a phosphate group. The rotational barriers for **11** and **12** are 14.4 and 8.8 kcal mol^{-1}, indicating that the bridged calix[6]arene system **12** is appreciably more flexible than **11**.

Key words: Calixarenes, preparation, conformation, dynamics.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82169 (51 pages)

1. Introduction

One attractive feature of the calixarenes is their ability to host small molecules in their molecular cavities [1]. The systems may in principle exist in a large number of conformations. The conformational preferences of a calix[4]arene are usually discussed in terms of four ideal conformations: 'cone', 'partial cone', '1,2-alternate' and '1,3-alternate'. These conformations are interconvertible by rotation of the phenolic rings [1]. The parent *p-tert*-butylcalix[4]arene (**1**) exists in solution in a 'cone' conformation which undergoes a cone to cone inversion process with a barrier (in $CDCl_3$) of 15.9 kcal mol^{-1} [2]. For larger calixarenes, the number of possible ideal conformations increases [1, 3].

One possible approach to improve the binding capabilities of the calixarenes is to freeze them in a conformation with a well defined cavity suitable for hosting small molecules [4]. For calix[4]arenes this can be achieved by replacement of the hydroxylic protons by a bulky group. Since for a calix[4]arene the interconversion

* This paper is dedicated to the commemorative issue on the 50th anniversary of calixarenes.
** Author for correspondence.

between the ideal conformations requires the passage of the OH groups through the ring cavity, the bulky group raises the barrier of ring inversion and freezes the calixarene in a given geometry. By this approach conformationally stable calix[4]arenes at the laboratory timescale were isolated [5]. However, for the larger calixarenes the replacement of the hydroxylic protons by a bulky group is not a sufficient condition to ensure rigidity, since the interconversion between the conformers may take place by the passage of the extraannular part of the phenyl rings (e.g., the *p-tert*-butyl group) through the ring annulus [6].

A second approach to achieving conformational rigidity is to introduce 'bridges' into the calixarene, i.e., to link covalently two or more points of the skeleton by a single atom or a chain of atoms. This severely restricts the possible motion of the calixarene skeleton and may freeze the calixarene in a given conformation. Calixarenes have been bridged at the extraannular positions (*para* to the OH) by an alkane chain [7], or at the intraannular positions, by connecting the oxygens by a chain of atoms [8] or by a single metal atom [9]. Several groups have recently reported the preparation of calixarenes bridged by nonmetallic atoms (phosphorus [10], silicon [11], and carbon [12]). In this paper we describe the preparation, conformations and dynamic processes of *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[6]arene multiply bridged by trivalent or pentavalent phosphorus atoms [13, 14].

2. Experimental

All NMR spectra were obtained with a Bruker AMX 400 spectrometer. Melting points were determined on a Mel-Temp II apparatus and are uncorrected. The pyrolysis was conducted in a Büchi GKR–51 oven. LDA was purchased from Aldrich. Dry tetrahydrofuran was freshly distilled from Na/benzophenone.

X-RAY CRYSTAL STRUCTURE ANALYSIS

Data were measured on an ENRAF-NONIUS CAD-4 and a PW1100/20 Philips Four-Circle computer controlled diffractometers. CuK_α ($\lambda = 1.54178$ Å) or MoK_α ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. Intensities were corrected for Lorentz, polarization and absorption effects. All nonhydrogen atoms were found by using the results of the SHELXS-86 direct method analysis. After several cycles of refinements the positions of the hydrogen atoms were calculated and added to the refinement process.

Crystal data for **7**. $C_{44}H_{52}O_7P_2 \cdot 1.5\ CH_3CN$, space group $Pbca$, a: 20.272(4) Å, b: 33.099(3) Å, c: 14.184(1) Å; V: 9517(1) Å^3, Z: 8, ρ_{calc}: 1.14 g cm^{-3}, μ(CuK_α): 11.97 cm^{-1}, No. of unique reflections: 6599, No. of reflections with $I \geq 2\sigma_I$: 2666, R: 0.081, R_w: 0.099.

Crystal data for **8**. $C_{44}H_{52}P_2Cl_2$, space group $C2/c$. a: 9.182(2) Å, b: 26.625(3) Å,

c: 17.782(3) Å; β: 90.93(2)°, V: 4347(1) Å^3, Z: 4, ρ_{calc}: 1.19 g cm^{-3}, μ(MoK_α): 2.58 cm^{-1}, No. of unique reflections: 2834, No. of reflections with $I \geq 2\sigma_I$: 2325, R: 0.032, R_w: 0.045.

Calix[4]arene Monospirodienone Bis(diisopropyl phosphate ester)

A solution of 150 mg (0.23 mmol) **3** in 5 mL dry THF was cooled to −78°C, and under an argon atmosphere 0.5 mL of a 1.5 M solution (1 mmol) of LDA was slowly added. After 20 min 0.17 mL (1 mmol) of ClPO(Oi-Pr)$_2$ [26] were added and the mixture stirred for 1 h. The mixture was brought to room temperature and the solvent evaporated. The residue was dissolved in CH_2Cl_2 and washed with water. After evaporation of the CH_2Cl_2 the residue was chromatographed (silica, eluent 20 : 1 $CHCl_3$: MeOH) yielding 0.124 g (55%) of a yellow crystalline compound, mp 126–131°C (d).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.64 (d, J = 6.1 Hz, 3H, Me), 0.78 (d, J = 6 Hz, 3H, Me), 0.86 (d, J = 6.1 Hz, 3H, Me), 1.04 (d, J = 6.1 Hz, 3H, Me), 1.05 (s, 9H, t-Bu), 1.13 (overlapping d, 12H, Me), 1.19 (s, 9H, t-Bu), 1.30 (s, 9H, t-Bu), 1.32 (s, 9H, t-Bu), 2.85 (d, J = 13.2 Hz, 1H, CH_2), 2.95 (d, J = 15.5 Hz, 1H, CH_2), 3.27 (d, J = 13.9 Hz, 1H, CH_2), 3.53 (d, J = 15.5 Hz, 1H, CH_2), 4.04 (d, J = 13.9 Hz, 1H, CH_2), 4.30 (s, 2H, CH_2), 4.48 (m, 2H, C*H*Me$_2$), 4.58 (m, 2H, C*H*Me$_2$), 4.63 (d, J = 12.9 Hz, 1H, CH_2), 5.75 (d, J = 2.3 Hz, 1H), 6.78 (d, J = 2 Hz, 1H), 6.96 (d, J = 1.4 Hz, 1H), 6.99 (d, J = 2.3 Hz, 1H), 7.09 (d, J = 2.3 Hz, 1H), 7.14 (d, J = 2.2 Hz, 1H), 7.17 (d, 1H), 7.36 (d, J = 2.3 Hz, 1H). CI MS (isobutane) m/z 975.3 (MH$^+$).

Pyrolysis of the Mono(diisopropyl phosphate ester) Derivative of **3**

0.28 g of the phosphate ester were heated under vacuum to 240°C for 10 min. The product consisted of 35% **7** and 42% **1**.

*5,11,17,23-Tetra-tert-butyl-25,26-dihydroxy-27,28-bis(diisopropoxy-phosphonoxy) Calix[4]arene (***2d***)*

10 mg of the phosphate ester were refluxed for 15 min in 1.5 mL EtOH in the presence of 2 drops 48% HBr. After evaporation of the EtOH, the product was recrystallized from hexane, yielding 8.5 mg (85%) **2d**, mp 83–87°C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.75 (d, J = 6.2 Hz, 12H, CH*Me*$_2$), 0.99 (d, J = 6.2 Hz, 6H, CH*Me*$_2$), 1.04 (d, J = 6.1 Hz, 6H, CH*Me*$_2$), 1.20 (s, 18H, t-Bu), 1.28 (s, 18H, t-Bu), 3.58 (d, J = 14.9 Hz, 2H, CH_2), 3.64 (s, 2H, CH_2), 4.41 (m, 6H, CH_2 + C*H*Me$_2$), 4.48 (d, J = 15.0 Hz, 2H, CH_2), 6.98 (d, J = 2.3 Hz, 2H, Ar—H), 7.02 (d, J = 2.3 Hz, 2H, Ar—H), 7.15 (d, J = 2.5 Hz, 2H, Ar—H), 7.41 (d, J = 2.4 Hz, 2H, Ar—H). ^{13}C-NMR (100 MHz $CDCl_3$, RT) δ 22.77, 22.81, 22.87, 23.31, 23.36, 23.39, 23.45, 23.67, 29.68, 31.45, 31.54, 31.71, 33.87, 34.25, 35.40,

37.73, 73.11, 125.05, 125.32, 126.84, 127.12, 127.76, 128.93, 132.32 (d), 132.80 (d), 142.89, 144.71 (d), 147.51, 148.65.

5,11,17,23,29-Penta-tert-butyl-31,32,33,34,35-penta(diisopropoxyphosphonoxy) Calix[5]arene (**5**)

2.0 g of **4** (2.47 mmol), 0.3 g tetrabutyl ammonium bromide, and 10 mL diisopropylchlorophosphate were dissolved in 100 mL CH_2Cl_2 and 113 g of a solution of aqueous NaOH (50%) was slowly added. The mixture was refluxed and stirred for 6 h. After carefully adding 400 mL water, the phases were separated and the organic phase was washed with water and dried ($CaCl_2$). After evaporation of the organic solvent the residue was triturated with cold petroleum ether, yielding, after filtration, 2.94 g (73%) **5**, mp 225–230°C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 45H, t-Bu), 1.21 (d, 15H, J = 6.1 Hz, CH*Me*$_2$), 1.33 (d, 15H, J = 6.1Hz, CH*Me*$_2$), 3.47 (d, 5H, J = 15.3 Hz, CH_2), 4.71 (m, 20H, CH_2 and OC*H*Me$_2$), 6.94 (s, 10H, Ar—H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.63 (d, $^3J_{P\_C}$ = 5.6 Hz, OCHMe*Me*), 23.82 (d, $^3J_{P\_C}$ = 4.4 Hz, CH*Me*Me), 30.41, 31.35 (C*Me*$_3$), 34.00, 73.22 (d, $^2J_{P\_C}$ = 5.9 Hz, O*C*HMeMe), 125.79, 133.26 (d, J_{P_C} = 3 Hz), 143.52, 146.06. CI MS (isobutane) 1632.3 (MH^+).

Preparation of **7** *by Pyrolysis. General Procedure*

0.39 g of phosphorylated calixarene were heated to 230°C under vacuum for 35 min. During the heating period the compound first melted and then solidified and a liquid distilled. The compound was chromatographed (eluent: $CHCl_3$) yielding the product, mp 375–376.5°C. The yields obtained from the pyrolysis of the phosphorus-containing calixarenes were 32% (**2b**), 38% (**2c**), 72% (**2d**).

^{1}H-NMR, (400 MHz, RT, $CDCl_3$) δ 1.18 (s, 36H, t-Bu), 3.42 (d, 2H, J = 13.7 Hz, CH_2), 3.61 (d, 2H, J = 15.6 Hz, CH_2), 4.48 (d, 2H, J = 13.6 Hz, CH_2), 4.55 (d, 2H, J = 15.5 Hz, CH_2), 6.99 (d, 2H, J = 2.1 Hz, Ar—H), 7.05 (d, J = 2.1 H_3, 2H, Ar—H). ^{1}H-NMR (400 MHz, 203 K, CD_2Cl_2) δ 1.03 (s, 18H, t-Bu), 1.20 (s, 18H, t-Bu), 3.48 (d, J = 13.8 Hz, 2H, CH_2), 3.68 (d, 2H, J = 15.6 Hz, CH_2), 4.37 (d, 2H, J = 13.5 Hz, CH_2), 4.43 (d, 2H, J = 15.5 Hz, CH_2), 7.00 (s, 2H, Ar—H), 7.04 (s, 2H, Ar—H), 7.14 (s, 2H, Ar—H), 7.32 (s, 2H, Ar—H). ^{13}C-NMR (100 MHz, RT, $CDCl_3$) δ 31.19, 31.67, 34.27, 34.71, 125.91, 126.53, 128.44, 130.89 (t), 146.39 (t), 148.67. ^{31}P-NMR δ -24.11. FAB MS: (sample dissolved in MeOH) m/z 785.9 [M-H+MeOH]$^-$, (sample dissolved in EtOH) m/z 799.8 [M-H+EtOH]$^-$.

5,11,17,23-Tetra-tert-butyl-μ-25,26-chlorophosphite-μ-27,28-chlorophosphite Calix[4]arene (**8**)

A mixture of 0.25 g **1**, 1 mL Et_3N and 8 mL PCl_3 were refluxed under a nitrogen atmosphere for 20 min. The mixture was poured into ice, and the white precipitate

that resulted was filtered and washed with water yielding 0.28 g **8** (93%), mp 164–166°C (decompose).

^{1}H-NMR (400 MHz, 200 K, CD_2Cl_2) δ 0.83 (s, 18H, t-Bu), 1.09 (s, 18H, t-Bu), 3.31 (d, 2H, J = 13.6 Hz, CH_2), 3.38 (d, 2H, J = 15.1 Hz, CH_2), 4.22 (d, 2H, J = 13.5 Hz, CH_2), 4.66 (d, 2H, J = 15.0 Hz, CH_2), 6.72 (s, 2H, Ar—H), 6.78 (s, 2H, Ar—H), 6.90 (s, 2H, Ar—H), 7.20 (s, 2H, Ar—H), ^{1}H-NMR (400 MHz, RT, $CDCl_3$) δ 1.09 (s, 36H, t-Bu), 3.37 (d, 2H, J = 15.0 Hz, CH_2), 3.40 (d, 2H, J = 14.9 Hz, CH_2), 4.43 (d, 2H, J = 14.9 Hz, CH_2), 4.80 (d, 2H, J = 14.8 Hz, CH_2), 6.81 (s, 4H, Ar—H), 6.86 (s, 4H, Ar—H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 31.09, 31.26, 34.04, 38.62, 124.99, 126.72, 130.71, 132.24, 146.92 (t, J = 7 Hz) 147.07. ^{31}P-NMR (161.99 MHz, $CDCl_3$) δ 149.2 ppm. CI MS (isobutane): m/z 723.2.

*5,11,17,23-Tetra-tert-butyl-25-hydroxy-26-dichlorophosphate-μ-27,28-chlorophosphate Calix[4]arene (**9**)*

A solution of 2 mL $POCl_3$ in 20 mL $CHCl_3$ was added under a nitrogen atmosphere to a refluxing solution of 2 g **1** and 5 mL Et_3N dissolved in 150 mL $CHCl_3$. After reflux for 3 h the solution was washed with brine, dried ($CaCl_2$) and evaporated. The residue was triturated with 50 mL hot hexane and filtered, yielding 0.79 g (30%) of **9** as a white powder, mp 297–298°C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 9H), 1.18 (s, 9H), 1.34 (s, 9H), 1.36 (s, 9H), 3.49 (d, J = 12.8 Hz, 1H), 3.56 (d, J = 15.8 Hz, 1H), 3.76 (d, J = 15.6 Hz, 1H), 3.78 (s, 1H, OH), 3.93 (d, J = 15.6 Hz, 1H), 4.07 (d, J = 15.5 Hz, 1H), 4.18 (d, J = 14.2 Hz, 1H), 4.31 (d, J = 15.1 Hz, 1H), 4.64 (d, J = 15.7 Hz, 1H), 6.43 (br, 1H), 6.96 (d, J = 2.5 Hz, 1H), 7.06 (br, 1H), 7.14 (d, J = 2.2 Hz, 1H), 7.17 (d, J = 2.2 Hz, 1H), 7.26 (m, 1H), 7.30 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.84, 31.17, 31.42, 31.67, 32.17, 33.91, 34.02, 34.17, 34.40, 35.73, 37.27, 37.50, 125.44, 125.90 (d), 126.64 (d), 126.96 (d), 127.19, 127.44, 127.76, 128.21, 128.23, 128.33 (d), 130.01 (d), 130.17 (d), 132.10 (d), 132.52 (d), 142.40, 144.02 (d), 146.22 (d), 148.25 (d), 148.58 (d), 148.80 (d), 149.10, 151.77. ^{31}P-NMR δ 0.6, 3.2 ppm. MS (CI) m/z 845.2 (MH^+) *Microanalysis: Calcd.* for $C_{44}H_{53}O_6Cl_3P_2$ C: 62.45, H: 6.31, Cl: 12.57; *Found*: C: 62.74, H: 6.51, Cl: 12.96.

*5,11,17,23-Tetra-tert-butyl-μ-25,26-chlorophosphate-μ-27,28-chlorophosphate Calix[4]arene (**10**)*

A mixture of 1 g **1**, 5 mL Et_3N and 1 mL $POCl_3$ in 80 mL xylene was heated to 85°C for 30 min. The sample was concentrated by distilling about 30 mL of solvent at atmospheric pressure. The solution was washed with water and evaporated. The resulting solid was treated with 50 mL hot MeCN and filtered yielding 0.12 g **10** as a white powder (10%), decomposing without melting at 365–380°C.

^{1}H-NMR (400 MHz, RT, $CDCl_3$) δ 1.09 (broad, 36H, t-Bu), 3.51 (d, J = 14.8 Hz, 2H, CH_2), 3.54 (d, J = 16.2 Hz, 2H, CH_2), 4.51 (d, J = 14.8 Hz, 2H, CH_2), 5.06 (d, J = 16.1 Hz, 2H, CH_2), 6.79 (br, 8H, Ar—H). ^{1}H-NMR (400 MHz, 245 K, $CDCl_3$)

δ 0.77 (s, 18H, t-Bu), 1.36 (s, 18H, t-Bu), 3.51 (d, J = 14.8 Hz, 2H, CH_2), 3.56 (d, J = 16.4 Hz, 2H, CH_2), 4.44 (d, J = 14.8 Hz, 2H, CH_2), 4.93 (d, J = 16.2 Hz, 2H, CH_2), 6.11 (s, 2H, Ar—H), 6.45 (s, 2H, Ar—H), 7.10 (s, 2H, Ar—H), 7.27 (s, 2H, Ar—H). ^{13}C-NMR ($CDCl_3$, RT) δ 29.85, 31.26, 34.08, 37.85, 125.5 (br), 128.12, 130.27, 147.1 (d), 147.65. ^{31}P-NMR δ 1.0 ppm. MS (CI) m/z 809.3 (MH^+).

*5,11,17,23,29,35-Hexa-tert-butyl-μ-37,38,39-phosphate-μ-40,41,42-phosphate Calix[4]arene (**11** and **12**)*

1.25 g of the product obtained by the partial phosphorylation of **6** [20] was heated at 330°C under vacuum. The residue was recrystallized from MeCN. The first batch of crystals collected (6.4%) was **12**, mp > 450°C, the second fraction corresponded to **11** (47.4%) mp > 440°C.

11. ^{1}H-NMR (400 MHz, RT, $CDCl_3$) δ 1.13 (br, 36H, t-Bu), 1.27 (s, 18H, t-Bu), 3.66 (d, J = 14.1 Hz, 4H, CH_2), 3.93 (d, J = 17.8 Hz, 2H, CH_2), 4.62 (d, J = 17.8 Hz, 2H, CH_2), 4.72 (d, J = 14.2 Hz, 4H, CH_2), 6.77 (s, 4H, Ar—H), 7.13 (br, 4H, Ar—H), 7.24 (br, 4H, Ar—H). ^{31}P-NMR δ -22.35 ppm. MS *Calcd.* for $C_{66}H_{78}P_2O_8$ 1060.5; *Found*: 1060.

12 ^{1}H-NMR (400 MHz, RT, $CDCl_3$) δ 1.21 (s, 36H, t-Bu), 1.28 (s, 18H, t-Bu), 3.71 (d, J = 14 Hz, 4H, CH_2), 4.29 (s, 4H, CH_2), 4.69 (d, J = 14.1 Hz, 4H, CH_2), 6.82 (s, 4H, Ar—H), 7.22 (d, J = 2.2 Hz, 4H, Ar—H), 7.28 (s, 4H, Ar—H). ^{31}P-NMR δ -22.27 ppm. MS (CI) m/z 1061 (MH^+).

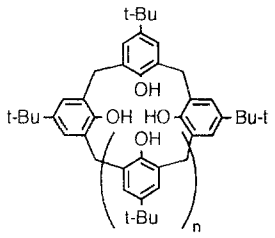
3. Results and Discussion

3.1. Preparation of Calixarene Phosphate Ester Derivatives

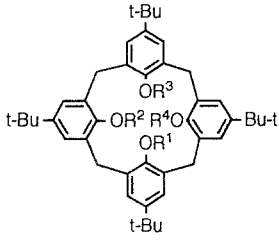
For the preparation of multiply phosphorus bridged systems, we studied the pyrolytic behavior of calixarene dialkyl phosphate ester derivatives. These compounds are useful intermediates for the OH-depletion of the calixarenes [15, 16] and for the preparation of aminocalixarenes [17]. These esters can be prepared by treatment of the calixarenes with a dialkyl chlorophosphate in the presence of base [18]. In the case of **1**, under mild conditions, the distal (i.e, 1,3-) bis(diethyl phosphate ester) derivative is obtained (**2a**) while under more drastic conditions (CH_2Cl_2/aq NaOH, phase transfer catalysis) the tetraphosphate **2b** is formed [15a]. Calixarene mono diisopropyl phosphate ester and 1,2-bis(diisopropyl phosphate ester) derivatives (**2c** and **2d**) were prepared by mono- or dideprotonation by LDA of the monospirodienone derivative **3** followed by treatment with the corresponding dialkyl chlorophosphate [15e, 17b]. Aromatization of the spirodienone products was achieved by heating or by their treatment with HBr yielding the dialkylphosphate esters derivatives **2c** and **2d** [15e, 17b].

p-tert-Butylcalix[5]arene [19] (**4**) was phosphorylated by its treatment with $ClPO(Oi\text{-}Pr)_2$ in the presence of base, yielding the pentaphosphate **5**. The compound displays a single *tert*-butyl signal, one pair of doublets for the methy-

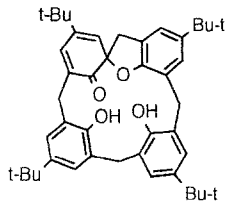
lene groups, and a single aromatic signal, indicating that at the NMR timescale the molecule exists in a symmetric cone-like conformation. The two methyl groups within a given isopropyl groups are symmetry nonequivalent and should be diastereotopic. Indeed, two doublets and two signals are observed for the isopropyl methyls of **5** in the ^{1}H- and ^{13}C-NMR spectrum, respectively.



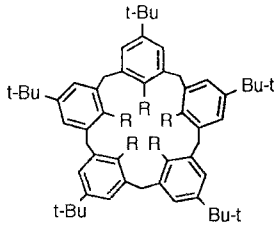
1 n=1
4 n=2
6 n=3



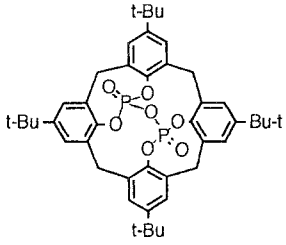
2a R^1=R^3=H, R^2=R^4=PO(OEt)$_2$
2b R^1=R^2=R^3=R^4= PO(OEt)$_2$
2c R^1=R^2=R^3=H, R^4=PO(OPr-i)$_2$
2d R^1=R^2=H, R^3=R^4=PO(OPr-i)$_2$



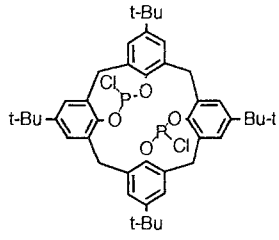
3



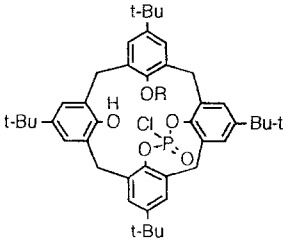
5 R = OPO(OPr-i)$_2$



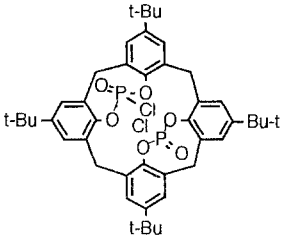
7



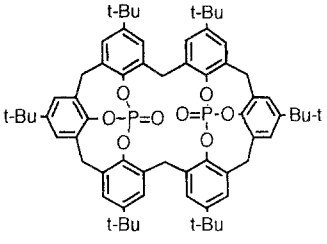
8



9 R = $POCl_2$



10



11 syn
12 anti

The partial phosphorylation of *p-tert*-butylcalix[6]arene (**6**) was first reported by Markovsky *et al.* [20] and recently studied by three groups [21]. We carried out the partial phosphorylation of **6** according to the literature procedure [20] and used the isolated product for the pyrolytic studies.

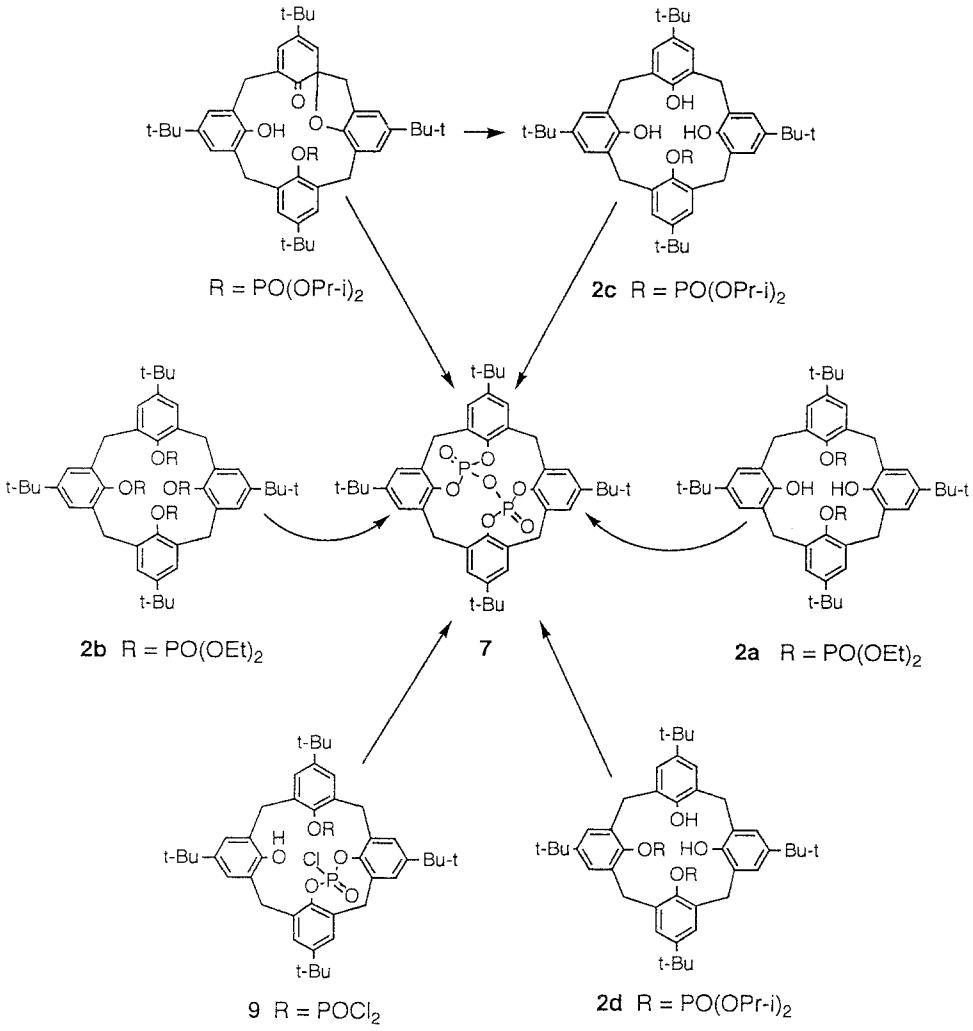
3.2. PREPARATION OF PHOSPHORUS BRIDGED CALIX[4]ARENES BY PYROLYSIS OR DERIVATIZATION

Vacuum pyrolysis of the phosphate ester derivatives was carried out by heating them above their melting point. Usually, the product solidified at the high temperature. Pyrolysis of the bis(diethyl phosphate ester) derivative **2a** (230°C) for 35 min yielded a main product of mp 375.5–376.5°C in 35% yield (Scheme 1) together with the formation of **1**. The product was characterized by its spectroscopic data and by X-ray crystallography as the pyrophosphate **7** (see below). The system contains two phosphorus bridges, each spanning over the oxygens of two proximal rings with an additional oxygen bridge connecting the two phosphorus atoms.

Since pyrolysis of the distal bis(dialkyl phosphate ester) derivative of **1** yielded the pyrophosphate **7**, it was of interest to examine also the pyrolytic behavior of other dialkyl phosphate ester derivatives of **1**. We examined first the pyrolysis of the tetraphosphate **2b**. The product obtained (Scheme 1) was pyrophosphate **7**, indicating that under the reaction conditions two phosphate groups were cleaved. Pyrolysis of the proximal diphosphate ester **2d** also gave **7**. We then examined the pyrolytic behavior of the mono(dialkyl phosphate ester) derivative **2c**. We expected that its pyrolysis will result in the formation of a phosphorus monobridged system, however, the product of the reaction (Scheme 1) was again pyrophosphate **7**, accompanied by **1**. Since the starting material has only a single phosphorus atom, while the product has two, obviously an intermolecular transfer of a phosphate ester group took place under the reaction conditions. Pyrolysis of the mono(diisopropyl phosphate ester) derivative of the spirodienone **3** resulted also in the formation of **7**. The spirodienone derivative has an interesting thermal behavior: at a lower temperature (170°C, 10 min), the spirodienone moiety is reduced to two phenol groups and **2c** is obtained, while at a higher temperature (240°C, 10 min) **7** is the product, most likely through the intermediacy of **2c**. Heating a mixture of **5** and **1** *in vacuo* for 15 min to 240°C resulted also in the exclusive formation of **7**, providing an additional evidence that under the reaction conditions intermolecular phosphate ester transfers take place. The pyrolytic studies are summarized in Scheme 1. It can be concluded that irrespectively of the starting calix[4]arene phosphate ester derivative, **7** is the bridged product formed. Its formation may involve fragmentation or intermolecular migrations of the phosphate groups. The multiple bridging present may account for the high stability of the compound.

The relatively facile formation of the phosphorus-bridged system led us to examine also the preparation by simple derivatization of **1** of systems with trivalent and pentavalent phosphorus bridges. Reaction of **1** with PCl_3 in the presence of base gave the bis P(III) bridged system **8**. In contrast with the kinetic stability of pyrophosphate **7**, this compound readily undergoes hydrolysis. For example, attempted recrystallization of **8** from MeOH regenerated **1**.

Reflux of a $CHCl_3$ solution of **1** and $POCl_3$ in the presence of Et_3N yielded the monobridged system **9**. Higher reaction temperatures (xylene, 85°C) yielded the



Scheme 1.

bis-bridged system **10**. It should be noted that in principle several isomers exist for **10** depending on the relative locations of the chlorines and terminal oxygen groups. Interestingly, the pyrolysis of **9** also afforded **7**.

3.3. Solid State Conformation of 7 and 8

Bridging two proximal rings by a single atom severely limits the possible conformations of the moiety. It was therefore of interest to determine the solid state conformation of the systems by X-ray crystallography. A single crystal of **7** suitable for X-ray crystallography was grown from a MeCN solution. The molecule crys-

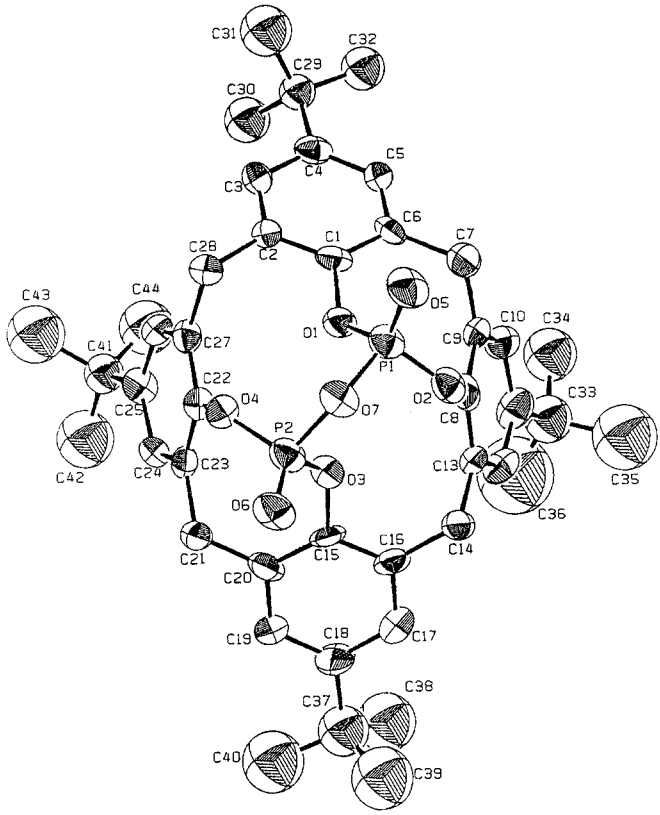


Fig. 1. Numbering scheme of the molecular structure of **7**. MeCN molecules are omitted.

tallizes with 1.5 molecules of MeCN. The numbering scheme and a stereoscopic view of the molecular structure are displayed in Figures 1 and 2. As shown in the figures, the two terminal P=O and the bridging P—O—P oxygen atoms (O(6), O(5) and O(7)), respectively) are pointing outside the molecular cavity. The dihedral angles between the plane of the rings and the mean plane defined by the four methylene carbons are 40° for the ring defined by the carbons C(1)—C(6), 66° for C(8)—C(13), 29° for C(15)—C(20), and 69° for C(22)—C(27). The conformation of the rings clearly departs from an ideal cone, with two nonvicinal rings being more twisted from the macrocyclic plane than the other two. This conformation sometimes called 'pinched' [22a] or 'boat' [22b] will be designated in the present paper as a 'flattened cone' (fc). For identification purposes the two rings with the larger torsional angle (C(8)—C(13) and C(22)—C(27)) will be dubbed 'twisted rings', whereas the rings with the smaller torsional angle will be dubbed 'coplanar rings'. Although the crystallographic conformation has strictly C_1 symmetry, for the bridged system this conformation should have ideally C_2 symmetry.

A single crystal of the bridged calixarene **8** was grown from hexane. The compound crystallizes in the $C2/c$ space group, with the center of the molecule located

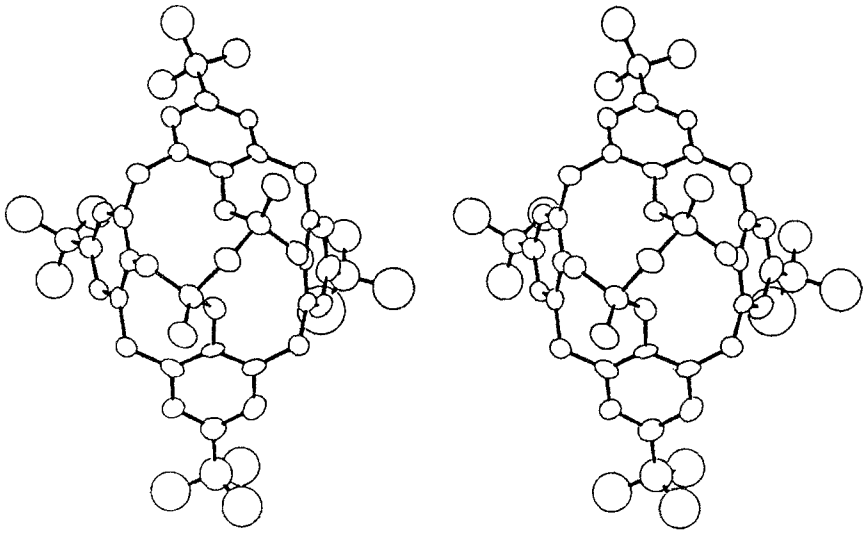


Fig. 2. Stereoscopic view of the crystal structure of **7**.

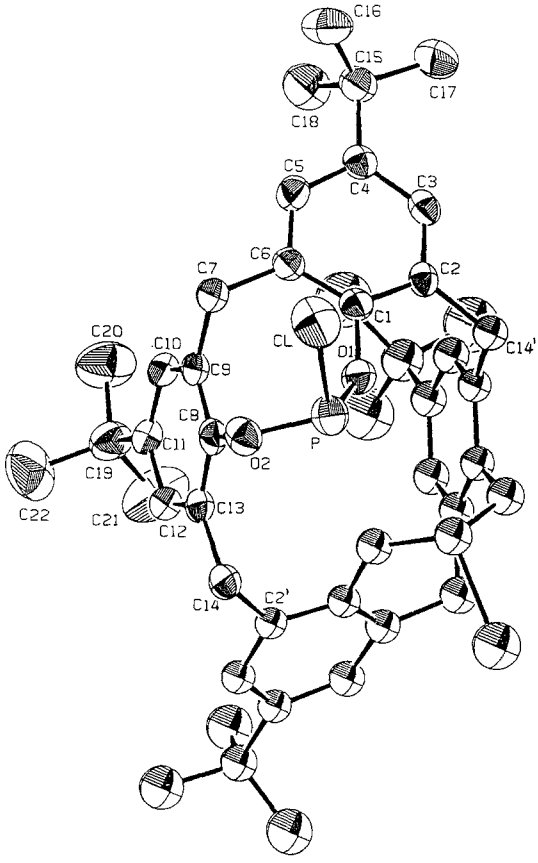


Fig. 3. Numbering scheme of the molecular structure of **8**.

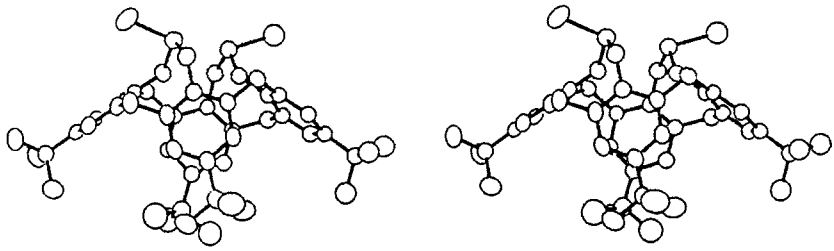


Fig. 4. Stereoscopic view of the crystal structure of **8**.

TABLE I. Selected bond distances and angles[a] for **8**.

Cl—P	2.095 (1)	P—O(1)	1.606(2)
P—O(2)	1.617(2)	O(1)C(1)	1.407(2)
O(2)C(8)	1.415(3)	Cl—P—O(1)	102.2(1)
Cl—P—O(2)	101.7(1)	O(1)—P—O(2)	102.8(1)
P—O(1)C(1)	135.2(2)	P—O(2)C(8)	124.2(1)
O(1)C(1)C(2)	115.5(2)	O(1)C(1)C(6)	121.8(2)
C(6)C(7)C(9)	112.4(2)	C(2′)C(14)C(13)	108.9(2)

[a]Bond length distances in Å, angles in degrees.

in the crystallographic C_2 axis. The compound also exists in a "fc" conformation very similar to that found for **7** but with exact C_2 symmetry. An ORTEP picture and a stereoscopic view of the structure are displayed in Figures 3 and 4. Selected bond lengths and angles are collected in Table I. The dihedral angles of the rings with the mean plane defined by the four methylenic carbons are 36° for C(1)—C(6) and 87° for C(8)—C(13). As shown in the figures, the two chlorine atoms are pointing away from the center of the molecule, while the two lone pairs at the phosphorus atoms are pointing to the C_2 axis. This feature makes the bridged calixarene **8** a potential bidentate ligand.

3.4. Room temperature NMR spectra of the double bridged calix[4]arenes

Since the main difference between compounds **7**, **8** and **10** is in the nature of the phosphorus bridges it was interesting to examine the ^{31}P-NMR of the compounds. The calixarenes **7**, **8** and **10** display ^{31}P–NMR signals at δ -22.3, 149.2 and 1.0 ppm, respectively. The chemical shift of the ^{31}P-signal of **8** is in agreement with the shift observed for other trivalent phosphorus compounds [23]. The monobridged calixarene **9** displays two ^{31}P-signals of δ 0.6 and 3.2 ppm. In the nonbridged diphosphate ester **2a** the phosphorus atoms resonate at -6.4 ppm.

The ^{1}H-NMR spectra of compounds **7**, **8** and **10** show a similar pattern of signals. Compounds **7** and **8** display (400 MHz, $CDCl_3$, RT) one *tert*-butyl signal, four doublets for the methylene protons and two doublets for the aromatic protons. The ^{13}C-NMR (100 MHz, $CDCl_3$, RT) is relatively simple with four aliphatic and six aromatic signals for each molecule. The ^{1}H- and ^{13}C-NMR spectra display fewer signals than those expected for a frozen "fc" conformation, and indicate that at room temperature the molecules are conformationally flexible on the NMR timescale. Notably, although the bridges limit the motions of the phenyl rings, they do not freeze completely their internal rotation.

Calixarene **10** displays in the ^{1}H-NMR (400 MHz, $CDCl_3$, RT) two extensive broad signals for the *tert*-butyl and aromatic protons, and two pairs of doublets for the methylene signals, indicating that a dynamic process is taking place on the NMR timescale. Upon raising the temperature the t-Bu and aromatic signals became sharper. As in the case of **7** and **8**, the fast exchange NMR spectrum is in agreement with a species of dynamic C_{2v} symmetry. Lowering the temperature resulted in separation of the broad signals into two signals each. Based on the slow exchange NMR it is reasonable to assume that the system exists also in a fc conformation of C_2 symmetry. However, we cannot conclude whether the two symmetry-related chlorine atoms are both facing each other or not. The monobridged system **9** displays four t-Bu signals, eight doublets for the methylene signals, an OH signal at δ 3.77 ppm, and eight signals for the aromatic protons, in agreement with a frozen conformation of C_1 symmetry.

3.5. DYNAMIC NMR SPECTRA OF DOUBLE BRIDGED CALIX[4]ARENES

Upon lowering the temperature of a CD_2Cl_2 solution of **7** and **8** the ^{1}H-NMR spectrum changed. The single *tert*-butyl signal separated into two signals and the two aromatic signals into two pairs of signals while the methylene doublets remained unchanged. The ^{1}H-NMR spectrum of **7** at different temperatures is shown in Figure 5. The slow exchange NMR spectra for both compounds are in agreement with a fc conformation of C_2 symmetry. Coalescence processes were observed for the two pairs of aromatic protons and for the *tert*-butyl groups. Exchange rates at the coalescence temperatures were calculated using the Gutowsky–Holm equation [24]. The coalescence data for the compounds are collected in Table II. As shown in the table, the barriers measured from the coalescence of the different groups (t-Bu or aromatic protons) are identical within experimental error, indicating that the same process is being monitored at different parts of the molecule. Interestingly, the dynamic processes of **7** and **8** have barriers (10.1 kcal mol^{-1}) which are identical within experimental error. This indicates that the presence of an additional oxygen atom in **7** which connects the two phosphorus bridges does not result in an increase in the rigidity of the molecule. The rotational barrier of **10** is larger (13.1 kcal mol^{-1}), the higher barrier being probably the result of the steric inter-

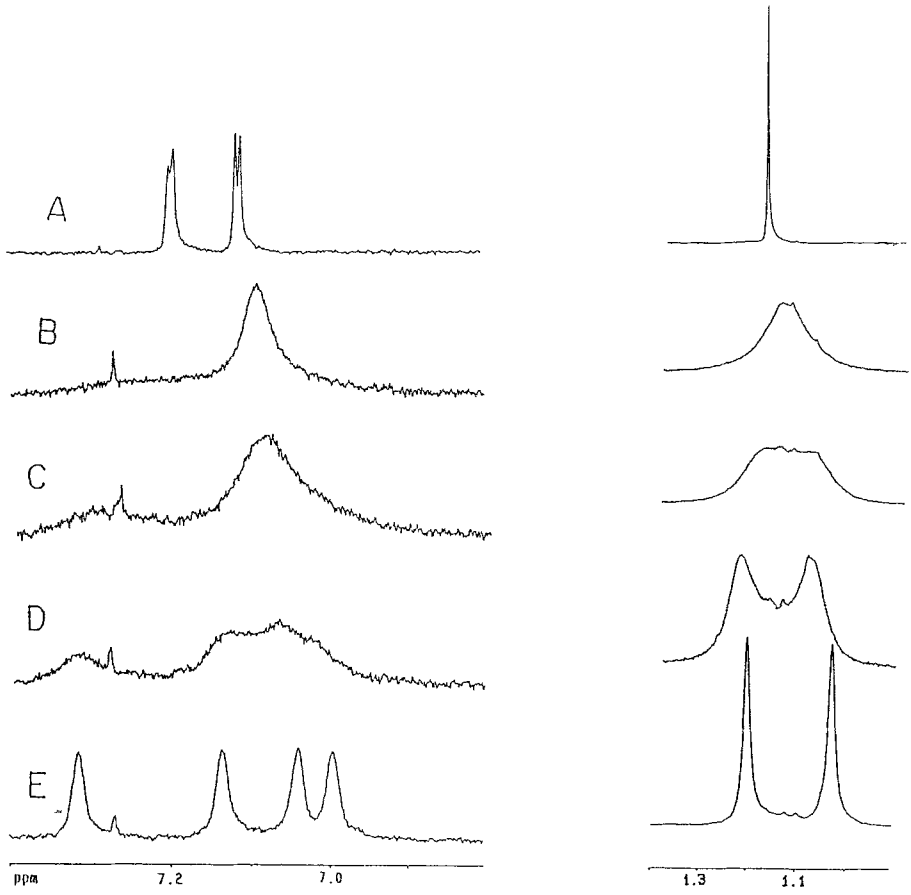


Fig. 5. 400 MHz ^{1}H-NMR spectrum of **7** at different temperatures. Left: aromatic region; right: *tert*-butyl region. A: 295 K, B: 217 K, C: 212 K, D: 209 K, E: 203 K.

ference in the transition state of the two groups in the bridges (Cl or O) which are facing each other.

The dynamic process which the systems **7**, **8** and **10** undergo *is not* a ring inversion process since, even under fast exchange conditions, the two methylene protons within a given methylene group remain diastereotopic. The process observed must involve the rotation of the rings and should exchange the coplanar and twisted rings but without involving their passage through the macrocyclic plane. A possible dynamic process which is in agreement with the observed data is depicted in Figure 6, according to which the process results in the enantiomerization of the system, and therefore the measured barriers represent their enantiomerization barriers. Inspection of Dreiding models shows that in the case of **7**, the rotation of the rings in a given Ar—O—P—O—Ar bridge is accompanied by ca. 120° rotations about the two O(P)—O bonds. As viewed from the phosphorus, both

TABLE II. Coalescence data for the phosphorus bridged calixarenes.

Compound	Probe	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_c^{\neq}$ (kcal mol^{-1})
7[a]	t-Bu	68.5	212	10.1
	Ar—H	56.1	209	10.1
	Ar—H	243.7	217	10.2
8[a]	t-Bu	104.3	217	10.2
10[b]	t-Bu	233.4	285	13.1
11[c]	CH_2	108.7	303	14.4
	CH_2	111.0	303	14.4
12[d]	Ar—H	35.5	180	8.8
	Ar—H	85.8	174	8.4
	CH_2	108.7	180	8.7
	CH_2	68.5	180	8.8

[a] In CD_2Cl_2.
[b] In $CDCl_3$.
[c] In toluene-d_8.
[d] In $CDCl_2F$.

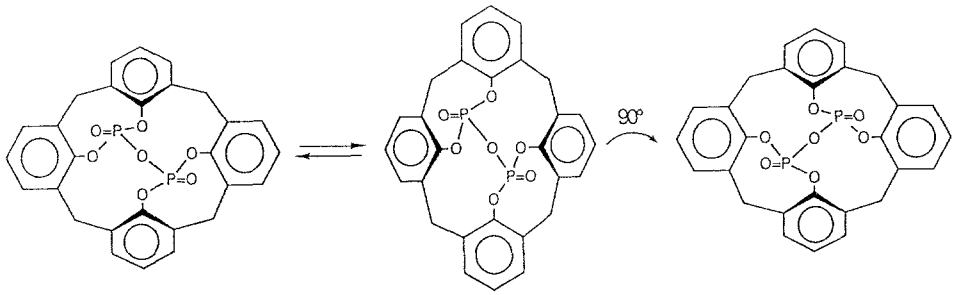


Fig. 6. Fc $\rightleftharpoons$ fc interconversion in **7**. The process results in an exchange of the twisted and coplanar rings. As is readily seen by 90° rigid body rotation of the central structure, the process results in enantiomerization.

rotations must occur in the same direction (clockwise or counterclockwise), the sense of rotation depending on the enantiomer undergoing the internal rotation. For example, for the enantiomer depicted in Figure 1, these rotations must be in a clockwise fashion. The experimental data do not allow us to decide whether the rotational process involves a single-step correlated rotation of the four rings or whether the rotation takes place through the intermediacy of a high energy form undetectable by NMR.

3.6. PYROLYSIS OF PARTIALLY PHOSPHORYLATED CALIX[6]ARENES

The multiple bridging of *p-tert*-butyl-calix[6]arene **6** is of special interest since, in contrast to **1**, the introduction of bulky groups in the intraannular positions is not sufficient for the elimination of the ring inversion process at the laboratory timescale [6]. Pyrolysis of the product obtained by the partial phosphorylation of **6** *in vacuo* at 330°C for 1.5 h resulted in the formation of a major product (**11**, 47%) and a minor product (**12**, 6.4%). Both compounds are high melting (mp > 440°C) and were characterized as multiple bridged calixarenes based on their mass spectral and spectroscopic properties. The phosphorus atoms of **11** and **12** resonate in the ^{31}P-NMR ($CDCl_3$, RT) at δ -20.35 and -20.38 ppm, respectively, indicating that both structures are closely related. Both compounds display in CI MS molecular peaks at m/z 1061 (MH^+), in agreement with structures of general formula $C_{66}H_{78}P_2O_8$. The observed molecular mass is in agreement with structures in which two P=O moieties span over three neighboring phenoxy groups.

3.7. STEREOCHEMISTRY OF THE MULTIPLY BRIDGED CALIX[6]ARENES

The attachment of three phenol groups to a phosphorus atom severely restricts the conformations possible for the system. In discussing the stereochemistry of the bridged derivatives of **6** two factors should be considered. Firstly, the bridging phosphate group may exist with the terminal P=O group oriented *endo* or *exo* to the molecular cavity. Secondly, the two subunits may exist with their cavities arranged in a *syn* or *anti* fashion.

The crystal structure of **11** was described in our preliminary communication [13]. The molecule adopts a conformation in which each of the two $OP(OAr)_3$ subunits exists in a 'flattened cone' conformation with one ring nearly coplanar to the reference plane and the two remaining rings twisted. The two P=O bonds are oriented in a parallel fashion and *exo* to the macrocyclic plane.

3.7.1. *NMR Spectra*

The ^{1}H-NMR spectrum of **11** (400 MHz, RT, $CDCl_3$) displays at room temperature both a sharp and a broad signal in the *tert*-butyl region, one pair of sharp doublets and one pair of somewhat broad doublets for the methylene groups, and one sharp singlet and two broad signals for the aromatic protons. The presence of some broad signals in the NMR suggests that the molecule is not rigid in the NMR timescale. The molecule displays under slow exchange conditions on the NMR timescale ($C_6D_5CD_3$, 250 K) three t-Bu signals and six methylenic doublets (Figure 7) in agreement with a frozen conformation of C_2 symmetry. The rotational barrier was calculated from the coalescence behavior of the signals in the methylenic region (Table II). Interestingly, whereas at a slow exchange six doublets are observed, four doublets are observed under fast exchange conditions.

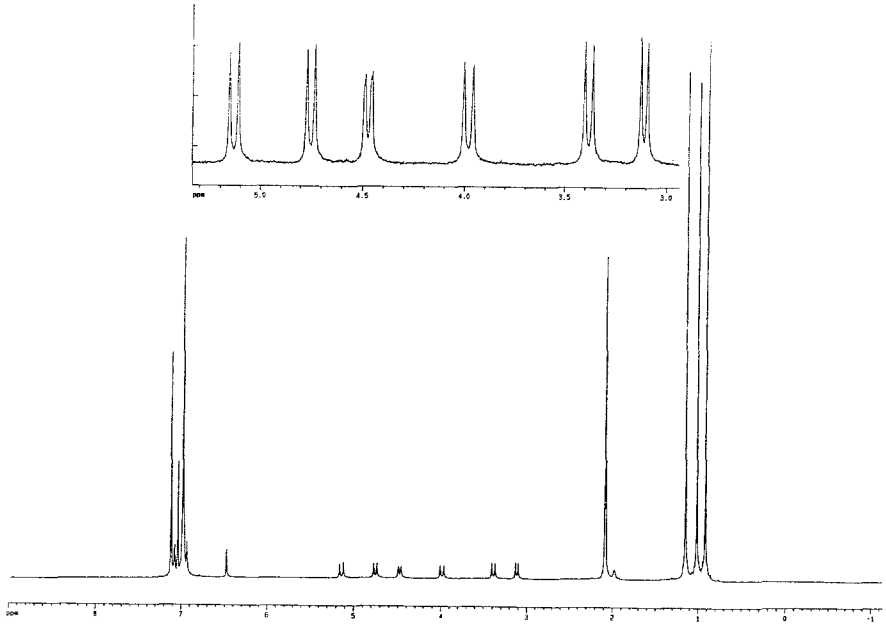


Fig. 7. Slow exchange ^{1}H-NMR spectrum (400 MHz, toluene-d_8, 250 K) of **11**. Top: expansion of the methylene region.

The ^{1}H-NMR spectrum of **12** (400 MHz, RT, $CDCl_3$) displays two *tert*-butyl signals in a 1 : 2 ratio, one pair of doublets and one singlet for the methylene protons and three aromatic signals. Lowering the temperature of a $CDCl_2F$ [25] solution of **12** resulted in decoalescence of the largest t-Bu signal, and of the aromatic protons. One of the methylene doublets decoalesced into two close-spaced doublets while the central singlet showed some broadening but no detectable decoalescence process. At slow exchange conditions the exchanging t-Bu signals were too close to determine an accurate coalescence temperature. Rates of exchange at the coalescence temperatures were derived from the coalescence behavior of the methylene and aromatic protons and a barrier of 8.6 ± 0.2 kcal mol^{-1} was calculated for the dynamic process followed by NMR. This barrier is significantly lower than the barrier of **11**.

3.7.2. *Dynamic Processes of* **11** *and* **12**

In the case of **11**, the protons within a methylene unit remain diastereotopic at the temperature range studied which rules out a ring inversion process. Assuming that the solution conformation is similar to the one present in the crystal, the dynamic process observed must exchange the coplanar ring with a nonvicinal twisted ring. This process, if present in both subunits, should result in enantiomerization of the system and should lead to mutual exchange of two pairs of methylene protons, as shown in Figure 8. The assignment of the dynamic process in **12** is difficult since we were unable to obtain crystals suitable for X-ray diffraction and therefore its solid

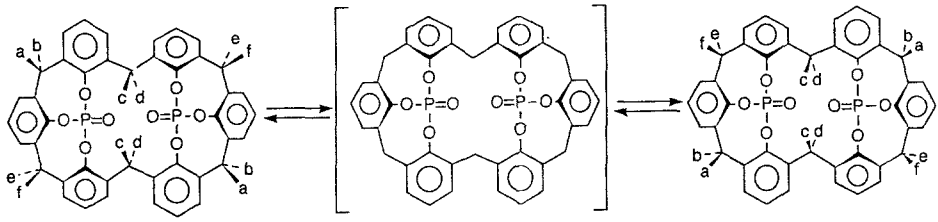


Fig. 8. The process of fc ⇌ fc interconversion **11**, leading to enantiomerization. The different methylene protons are denoted by letters (a–e). Homotopic sites are denoted by identical letters, enantiotopic sites are denoted by the same letter with a bar. As a result of the dynamic process the following exchanges take place: a ⇌ $\bar{f}$, e ⇌ $\bar{b}$, $\bar{a}$ ⇌ f and $\bar{e}$ ⇌ $\bar{b}$. Note that the two protons within a given methylene group do not mutually exchange.

state conformation is not known. The appearance of four methylenic protons as a singlet indicates that a C_2 axis passes through two methylene groups. Assuming that **12** is a stereoisomer of **11**, these methylenes must be the ones which connect the two $(ArO)_3PO$ subunits (the 'central' methylenes). The cavities of the two subunits must be oriented in an *anti* fashion. The appreciable lower barrier observed for **12** indicates than an analogous process to that observed for **11** is not taking place since in that case similar barriers should be observed. We therefore tentatively suggest that in **12** both P=O bonds are oriented *endo* to the cavities of the subunits. Inspection of space filling models indicates that in such arrangement, each subunit exists in a rigid cone-like conformation. The dynamic process observed does not involve changes in the torsional angles of the rings, but most likely involves partial rotations about the bonds linking the central methylenes to the two subunits. This is probably the reason why **12** has a lower rotational barrier than **11**.

4. Conclusions

Multiply bridged calixarenes can be easily obtained by pyrolysis of calixarene (dialkyl phosphate ester) derivatives. The multiple bridging of the calix[4]- and calix[6]arenes raises the barrier for ring inversion, but it does not completely freeze all possible dynamic processes.

Acknowledgements

We thank Dr. Shmuel Cohen for the X-ray structural determinations and the Mass Spectrometry Center at the Technion, Haifa for the mass spectra determinations. This work was supported by the Israel Science Foundation, administered by The Israeli Academy of Sciences and Humanities.

References

1. For comprehensive reviews on calixarenes see: C. D. Gutsche: *Calixarenes*, Royal Society of Chemistry, Cambridge (1989); *Calixarenes: A Versatile Class of Macrocyclic Compounds*, J. Vicens and V. Böhmer (Eds.), Kluwer, Dordrecht (1991).
2. C. D. Gutsche and L. J. Bauer: *J. Am. Chem. Soc.* **107**, 6052 (1985).
3. See for example H. Taniguchi, E. Nomura, and T. Hinomoto: *Chem. Express* **7**, 853 (1992).
4. For a recent example of a conformationally rigid 18-crown-6 derivative see: G. Li and W. C. Still: *J. Am. Chem. Soc.* **115**, 3804 (1993).
5. K. Iwamoto, K. Araki, and S. Shinkai: *J. Org. Chem.* **56**, 4955 (1991). S. Shinkai, K. Fujimoto, T. Otsuka, and H. L. Ammon: *J. Org. Chem.* **57**, 1526 (1992). H. Iki, T. Kikuchi, and S. Shinkai: *J. Chem. Soc. Perkin Trans. 1*, 205 (1993).
6. H. Otsuka, K. Araki, and S. Shinkai: *Chem. Express* **8**, 479 (1993).
7. For examples of calixarenes bridged by a chain of atoms see: H. Goldmann, W. Vogt, E. Paulus, and V. Böhmer: *J. Am. Chem. Soc.* **110**, 6811 (1988). V. Böhmer and W. Vogt: *Pure Appl. Chem.* **65**, 403 (1993).
8. A. Arduini, A. Casnati, L. Dodi, A. Pochini, and R. Ungaro: *J. Chem. Soc., Chem. Commun.* 1597 (1990). V. Böhmer, G. Ferguson, J. F. Gallagher, A. J. Lough, M. A. McKervey, E. Madigan, M. B. Moran, J. Phillips, and G. Williams: *J. Chem. Soc., Perkin Trans. 1* 1521 (1993). Z. Asfari, J. Weiss, S. Pappalardo, and J. Vicens: *Pure Appl. Chem.* **65**, 585 (1993).
9. See for example G. D. Andreetti, G. Calestani, F. Ugozzoli, A. Arduini, E. Ghidini, A. Pochini, and R. Ungaro: *J. Incl. Phenom.* **5**, 123 (1987). F. Corrazza, C. Floriani, A. Chiesi-Villa, and C. Guastini: *J. Chem. Soc., Chem. Commun.* 1083 (1990).
10. D. V. Khasnis, M. Lattman, and C. D. Gutsche: *J. Am. Chem. Soc.* **112**, 9422 (1990). D. V. Khasnis, J. M. Burton, M. Lattman, and H. Zhang: *J. Chem. Soc., Chem. Commun.* 562 (1991). D. V. Khasnis, J. M. Burton, J. D. McNeil, H. Zhang, and M. Lattman: *Phosphorus, Sulfur and Silicon* **75**, 253 (1993).
11. X. Delaigue, M. W. Hosseini, A. De Cian, J. Fischer, E. Leize, S. Kieffer, and A. Van Dorsselaer: *Tetrahedron Lett.* **34**, 3285 (1993).
12. P. Neri, J. F. Ferguson, G. Gallagher, and S. Pappalardo: *Tetrahedron Lett.* **33**, 7403 (1992).
13. For a preliminary communication of the present work see: F. Grynszpan, O. Aleksiuk, and S. E. Biali: *J. Chem. Soc., Chem. Commun.* 13 (1993).
14. A double bridged calix[6]arene has been reported recently. See: J. K. Moran and D. M. Roundhill: *Phosphorus, Sulfur and Silicon* **71**, 7 (1992).
15. (a) Z. Goren and S. E. Biali: *J. Chem. Soc., Perkin Trans. 1* 1484 (1990). (b) F. Grynszpan, Z. Goren, and S. E. Biali: *J. Org. Chem.* **56**, 532 (1991). (c) Y. Ting, W. Verboom, L. C. Groenen, J.-D. van Loon, and D. N. Reinhoudt: *J. Chem. Soc., Chem. Commun.* 1432 (1990). (d) J. E. McMurry and J. C. Phelan: *Tetrahedron Lett.* **41**, 5655 (1991). (e) O. Aleksiuk, F. Grynszpan, and S. E. Biali: *J. Chem. Soc., Chem. Commun.* 11 (1993).
16. For recent work on intraannular phosphorus containing calixarenes see for example: C. Floriani, D. Jacoby, A. Chiesi-Villa, and C. Guastini: *Angew. Chem. Int. Ed. Engl.* **28**, 1376 (1989). J. K. Moran and D. M. Roundhill: *Inorg. Chem.* **31**, 4213 (1992). D. Jacoby, C. Floriani, A. Chiesi-Villa, and C. Rizzoli: *J. Chem. Soc., Dalton Trans.* 813 (1993). D. Matt, C. Loeber, J. Vicens, and Z. Asfari: *J. Chem. Soc., Chem. Commun.* 604 (1993). L. N. Markovsky, V. I. Kalchenko, D. M. Rudkevich, and A. N. Shivanyuk: *Mendeleev Commun.* 106 (1992). For extraannular phosphorus substituted systems see: I. Kalchenko, L. I. Atamas, V. V. Pirozhenico, L. N. Markovsky, *Zh. Obschs. Khim.* **62**, 2623 (1992).
17. (a) F. Ohseto, H. Murakami, K. Araki, and S. Shinkai: *Tetrahedron Lett.* **33**, 1217 (1992). (b) F. Grynszpan, O. Aleksiuk, and S. E. Biali, *J. Org. Chem.* **59**, 2070 (1994).
18. G. W. Kenner and N. R. Williams: *J. Chem. Soc.* 523 (1955).
19. D. R. Stewart and C. D. Gutsche: *Org. Prep. Proceed. Int.* **25**, 137 (1993).
20. L. N. Markovsky, V. I. Kalchenko, and N.A. Parhomenko: *Zh. Obshch. Khim.* **60**, 2811 (1990).
21. R. G. Janssen, W. Verboom, S. Harkema, G. J. van Hummel, D. N. Reinhoudt, A. Pochini, R. Ungaro, P. Prados, and J. de Mendoza: *J. Chem. Soc., Chem. Commun.* 506 (1993).
22. (a) M. Conner, V. Janout, and S. Regen: *J. Am. Chem. Soc.* **113**, 9670 (1991). (b) E. Dahan and S. E. Biali: *J. Org. Chem.* **56**, 7269 (1991).

23. J. C. Tebby: in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, J. G. Verkade and L.D. Quin (Eds.), Ch. 1, VCH, Deerfield Beach (1987).
24. H. S. Gutowsky and C. H. Holm: *J. Chem. Phys.* **25**, 1228 (1956).
25. J. S. Siegel and F. A. L. Anet: *J. Org. Chem.* **53**, 2629 (1988).
26. H. McCombrie, B. C. Saunders, and G. J. Stacey: *J. Chem. Soc.* 380 (1945).