Journal of Inclusion Phenomena and Macrocyclic Chemistry (2005) 52: 85–91
DOI 10.1007/s10847-004-5235-6

Synthesis and Solid-State Conformation of a Calix[8]arene 1,5-Diquinone Derivative

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(Received: 26 July 2004; in final form: 22 October 2004)

Key words: calix[8]arenes, calixquinones, chair-like conformation, inclusion complex, X-ray crystal structure

Abstract

The first example of a calix[8]quinone derivative, hexamethoxy-*p-tert*-butylcalix[8]-1,5-diquinone **5**, has been synthesized from *p-tert*-butylcalix[8]arene **1** by exploiting a protection-deprotection procedure. The structure of the **5**·toluene inclusion compound has been determined by a single crystal X-ray diffraction study. The calix[8]arene molecule possesses a crystallographic inversion centre and assumes a 'pseudo-chair-like' conformation, with two opposite 3/4-cone moieties, which resembles the previously reported *chair-like* conformation of *p-tert*-butylcalix[8]arene. The 4 toluene molecules per unit cell occupy interstitial voids and are released in the temperature range of 30–160 °C.

Introduction

Calix[*n*]quinones [1] are a class of calix[*n*]arene derivatives in which one or more aromatic rings have been oxidized to *p*-benzoquinone moieties. This conversion is usually obtained by direct oxidation of calixarene phenol rings with strong oxidizing agents such as $Tl(OCOCF_3)_3$ [2], ClO_2 [2, 3], $Tl(NO_3)_3{\cdot}3H_2O$ [4] and $NaBO_3{\cdot}4H_2O$ [5], but multistep syntheses have also been reported [6].

These derivatives are of particular interest because the redox-active 1,4-benzoquinone moieties [7] can be associated to diverse recognition sites to give systems electrochemically responsive to the presence of the guest [8]. In this way, calixquinone-based chemical sensors have been synthesized by Beer and coworkers for the selective recognition of K^+ [9], Rb^+, or Cs^+ [10], while Tuntulani and coworkers have built an analogous sensor for Na^+ [11]. An additional interest for calixquinones is related to their synthetic utility [12], mainly as the most obvious precursors of calixhydroquinones [1, 2], which have recently shown remarkable potentialities in the field of crystal engineering and nanotechnology [13].

The molecular structure of several calix[4]quinones has been determined by X-ray crystallography [6, 14], which has shown a certain preference for the relative *anti* orientation of freely rotating quinone rings. Examples of calix[5]- and -[6]quinones have also been reported and, in particular, the X-ray structure of calix[6]hexaquinone revealed an 'up-down-out-down-up-out' conformation of the macrocycle [2].

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As regards the larger calix[*n*]quinones, to the best of our knowledge, no examples of derivatives and no crystal structures had been reported for $n > 6$ and, consequently, no information is currently available concerning their conformational preferences. Only very recently we have reported, in a preliminary communication [15], the first example of a calix[8]quinone, **5**, obtained by exploiting the selective functionalization of the 1,5-aromatic rings of *p-tert*-butylcalix[8]arene **1**. Here we report full experimental data on the synthesis and characterization of 1,5-calix[8]diquinone **5** and its solid state conformation determined by X-ray crystallography.

Experimental

General comments

ESI(+) MS measurements were performed on a BIO-Q triple quadrupole mass spectrometer (MICROMASS) equipped with an electrospray ion source, using a mixture of H_2O/CH_3CN (1:1) and 5% HCOOH as solvent. The infrared spectrum was obtained on a Vector Bruker 22 spectrometer. Flash chromatography was performed using silica gel (Kieselgel-60, 0.040–0.063 mm, Merck). All chemicals were reagent grade and were used without further purification. *p-tert*-Butylcalix[8]arene (**1**) was prepared according to a literature procedure [16]. All NMR spectra were recorded at 400 (^{1}H) and 100 (^{13}C) MHz on a Bruker Avance-400 spectrometer. Chemical shifts are reported relative to the residual solvent peak ($CHCl_3$: $\delta = 7.26$, $CHCl_2CHCl_2$: $\delta = 6.00$, $CDCl_3$: $\delta = 77.2$, $CDCl_2CDCl_2$: $\delta = 73.8$). Reactions

were monitored by TLC on Merck silica gel plate (0.25 mm) and visualized by UV light and sprying with H_2SO_4–$Ce(SO_4)_2$.

1,5-Bridged calix[8]arene ***2***

To a solution of **1** (0.5 g, 0.385 mmol) in DMF (75 mL) was added Cs_2CO_3 (1 g, 3.08 mmol) under stirring. The mixture was kept under stirring at 90 °C (internal temperature) until it darkened, then a solution of 1,3-bis(bromomethyl)benzene (0.75 mmol) in DMF (4 mL) was added dropwise over 30 min. The reaction was stirred at 70 °C (internal temperature) for 36 h. After concentration under vacuum, the mixture was partitioned between CH_2Cl_2 (40 mL) and 1N HCl (50 mL). The organic phase was washed with water (3 × 30 mL) and dried over Na_2SO_4. Solvent evaporation under vacuum afforded a solid residue which was washed with ethanol. The crude product (0.431 g, 80%) was sufficiently pure, not requiring chromatography for its use in subsequent synthetic manipulations. An analytically pure sample of **2** was obtained by chromatography (SiO_2, dichloromethane/diethyl ether, 98/2, *v*/*v*): m.p. > 300 °C dec; ESI(+) MS *m*/*z* 1399 (MH^+); ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$, 393 K) δ: 1.21, 1.33, 1.35 [s, $C(CH_3)_3$, 18H, 36H, 18H], 3.79 (s, $ArCH_2Ar$, 8H), 4.09 (s, $ArCH_2Ar$, 8H), 5.53 (s, OCH_2, 4H), 7.09–7.32 (overlapped, ArH, 18H), 7.62 (s, ArH, 2H), 8.40 (bs, OH, 4H), 8.74 (bs, OH, 2H); ^{13}C NMR (100 MHz, $CDCl_2CDCl_2$, 353 K) δ: 30.0 [s, $C(CH_3)_3$], 31.2 [s, $C(CH_3)_3$], 31.4 [s, $C(CH_3)_3$], 31.4 (t, $ArCH_2Ar$, 8C), 32.4 [s, $C(CH_3)_3$], 33.7 [s, $C(CH_3)_3$], 34.1 [s, $C(CH_3)_3$], 77.4 (t, OCH_2), 125.6 (d, $C_{Ar}H$), 125.7 (d, $C_{Ar}H$), 126.1 (d, $C_{Ar}H$), 126.5 (d, $C_{Ar}H$), 126.8 (s, $C_{Ar}CH_2$), 127.0 (d, $C_{Ar}H$, 8C), 127.2 (s, $C_{Ar}CH_2$), 128.5 (s, $C_{Ar}CH_2$), 128.6 (d, $C_{Ar}H$), 132.9 (s, $C_{Ar}CH_2$, 8C), 137.5 [s, $C_{Ar}C(CH_3)_3$], 143.3 [s, $C_{Ar}C(CH_3)_3$], 143.8 [s, $C_{Ar}C(CH_3)_3$], 148.0 (s, $C_{Ar}O$), 148.5 (s, $C_{Ar}O$), 150.4 (s, $C_{Ar}O$). *Anal*. *Calcd* for $C_{96}H_{118}O_8$: C, 82.36; H, 8.50. *Found:* C, 82.45; H, 8.42.

Hexamethylated 1,5-bridged calix[8]arene ***3***

A suspension of **2** (1 g, 0.7 mmol) in acetone (80 mL), was added of Cs_2CO_3 (15 g, 42 mmol). The mixture was stirred at the reflux temperature for 30 min. and then methyl iodide (70 mmol, 4.35 mL) was added. The reaction mixture was stirred for 24 h under reflux. The solution was concentrated to dryness and the residue was partitioned between 1 N HCl (50 mL) and CH_2Cl_2 (50 mL). The organic phase was washed with water (3 × 30 mL) and dried over Na_2SO_4. Solvent evaporation under vacuum afforded a crude product that was subjected to flash chromatography on silica gel (dichloromethane/diethyl ether, 99/1, *v*/*v*), to give **3** (0.8 g, 74%): m.p. > 350 °C dec; ESI(+) MS *m*/*z* 1483 (MH^+); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 1.08, 1.15, 1.25 [s, $C(CH_3)_3$, 36H, 18H, 18H], 2.92 (s, OCH_3, 6H), 3.42 (s, OCH_3, 12H), 3.93 (s, OCH_2, 4H), 3.96 (s, $ArCH_2Ar$, 8H), 3.98 (s, $ArCH_2Ar$, 8H), 6.60 (bt, ArH, 1H), 6.71 and 7.02 (AB, ArH, J = 2.0 Hz, 8H), 6.90 (bd, ArH, 2H) 7.06–7.09 (overlapped, ArH, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 30.2 (t, $ArCH_2Ar$), 30.5 (t, $ArCH_2Ar$), 31.3 [s, $C(CH_3)_3$, 24C], 34.2 [s, $C(CH_3)_3$, 8C], 59.9 (q, OCH_3), 60.4 (q, OCH_3), 74.6 (t, OCH_2), 120.6 (d, $C_{Ar}H$), 123.8 (d, $C_{Ar}H$), 124.5 (d, $C_{Ar}H$), 125.2 (d, $C_{Ar}H$), 126.4 (d, $C_{Ar}H$), 127.1 (d, $C_{Ar}H$), 128.8 (d, $C_{Ar}H$), 123.2 (s, $C_{Ar}CH_2$), 133.2 (s, $C_{Ar}CH_2$), 133.7 (s, $C_{Ar}CH_2$), 133.8 (s, $C_{Ar}CH_2$), 137.6 (s, *m*-Xyl-$C_{Ar}CH_2O$), 145.7 [s, $C_{Ar}C(CH_3)_3$, 6C], 146.6 [s, $C_{Ar}C(CH_3)_3$], 153.9 (s, $C_{Ar}O$), 154.2 (s, $C_{Ar}O$), 154.7 (s, $C_{Ar}O$). *Anal*. *Calcd* for $C_{102}H_{130}O_8$: C, 82.55; H, 8.83. *Found:* C, 82.47; H, 8.91.

1,5-Dihydroxy-hexamethoxy calix[8]arene ***4***

A solution of **3** (0.8 g) in CH_2Cl_2 (80 mL) was added of Pd/C (0.12 g, 15%) and stirred for 1 h under H_2 at 25 °C. After filtration of the catalyst, the solvent was evaporated to give **4** (0.7 g, 90%): m.p. > 320 °C dec; ESI(+) MS *m*/*z* 1381 (MH^+); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 1.05, 1.15, 1.22 [s, $C(CH_3)_3$, 36H, 18H, 18H], 3.26 (s, OCH_3 , 6H), 3.62 (s, OCH_3, 12H), 3.91 (s, $ArCH_2Ar$, 8H), 3.98 (s, $ArCH_2Ar$, 8H), 6.88 and 6.93 (AB, ArH, J = 2.1 Hz, 8H), 6.95 (s, ArH, 4H), 7.01 (s, ArH, 4H), 7.45 (s, OH, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 29.9 (t, $ArCH_2Ar$, 8C), 31.1 [s, $C(CH_3)_3$], 31.3 [s, $C(CH_3)_3$], 31.5 [s, $C(CH_3)_3$], 33.9 [s, $C(CH_3)_3$], 34.0 [s, $C(CH_3)_3$], 34.1 [s, $C(CH_3)_3$], 60.3 (q, OCH_3), 61.2 (q, OCH_3), 125.4 (d, $C_{Ar}H$, 8C), 125.8 (d, $C_{Ar}H$, 8C), 126.7 (s, $C_{Ar}CH_2$), 132.6 (s, $C_{Ar}CH_2$), 132.8 (s, $C_{Ar}CH_2$), 132.9 (s, $C_{Ar}CH_2$), 142.1 [s, $C_{Ar}C(CH_3)_3$], 145.8 [s, $C_{Ar}C(CH_3)_3$], 146.5 [s, $C_{Ar}C(CH_3)_3$], 150.0 (s, $C_{Ar}O$), 152.9 (s, $C_{Ar}O$), 154.2 (s, $C_{Ar}O$). *Anal*. *Calcd* for $C_{94}H_{124}O_8$: C, 81.69; H, 9.04. *Found:* C, 81.60; H, 9.12.

1,5-Calix[8]diquinone ***5***

A solution of **4** (0.7 g, 0.5 mmol) and $Tl(OOCCF_3)_3$ (5.4 g, 10 mmol) in TFA (100 mL) was stirred for 12 h in the dark, at room temperature. The mixture was dried under vacuum and partitioned between CH_2Cl_2 (10 mL) and 1 N HCl (10 mL). The organic phase was washed with water (2 × 10 mL) and dried over Na_2SO_4. The crude product, obtained after solvent evaporation under vacuum, was subjected to flash chromatography on silica gel (dichloromethane/diethyl ether, 99/1, *v*/*v*) to give diquinone **5** (0.18 g, 28%,); m.p. > 250 °C dec; IR (KBr) ν_{max} 1610, 1649, 1654 cm^{-1}; ESI(+) MS *m*/*z* 1297 (MH^+); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 1.08, 1.20 [s, $C(CH_3)_3$, 18H, 36H], 3.46 (s, OCH_3, 6H), 3.48 (s, OCH_3, 12H), 3.75 (s, $ArCH_2Ar$, 8H), 4.00 (s, $ArCH_2Ar$, 8H), 5.96 (s, Quin-H, 4H), 6.83 (s, ArH, 4H), 6.99 and 7.05 (AB, ArH, J = 2.0 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ: 29.6 (t, $ArCH_2Ar$), 30.0 (t, $ArCH_2Ar$), 31.3 [s, $C(CH_3)_3$, 18C], 34.0 [s, $C(CH_3)_3$], 34.1 [s, $C(CH_3)_3$], 60.3 (q, OCH_3), 60.8 (q, OCH_3), 125.5 (d, $C_{Ar}H$), 126.2 (d, $C_{Ar}H$), 127.4 (d, $C_{Ar}H$), 129.2 (s, $C_{Quin}H$), 132.6 (s, $C_{Ar}CH_2$), 132.8 (s, $C_{Ar}CH_2$), 133.6

(s, $C_{Ar}CH_2$), 146.8 (s, $C_{Quin}CH_2$), 146.1 [s, $C_{Ar}C(CH_3)_3$], 148.8 [s, $C_{Ar}C(CH_3)_3$], 153.9 (s, $C_{Ar}O$), 154.4 (s, $C_{Ar}O$), 187.3 (s, C=O, 4C). *Anal. Calcd* for $C_{86}H_{104}O_{10}$: C, 79.59; H, 8.08. *Found:* C, 79.50; H, 8.12.

X-ray crystallography

p-tert-Butylcalix[8]arene-1,5-diquinone **5** was crystallized by vapor diffusion of methanol into a toluene solution. A single crystal suitable for X-ray diffraction measurements was mounted on a glass fiber. All diffraction measurements were performed using a Rigaku AFC7S diffractometer with graphite monochromated MoK_α radiation. During the data collection the intensity of the standards decreased by 34.9%, to account for this effect a decay correction was applied considering a 5° polynomial function. Crystallographic data and refinement details are reported in Table 1.

The crystallographic asymmetric unit consists of half *p-tert*-butylcalix[8]arene-1,5-diquinone molecule plus a toluene molecule. The structure was solved by direct methods using SIR92 [17] and refined on F^2 using SHELXL97 [18]. The toluene molecule showed to be disordered and was refined as a rigid group. Two *tert*-butyl groups (C36-C39 and C40-C44) resulted to be disordered and were refined by rigid group constraints assuming two opposite conformations rotated by 60° to each other.

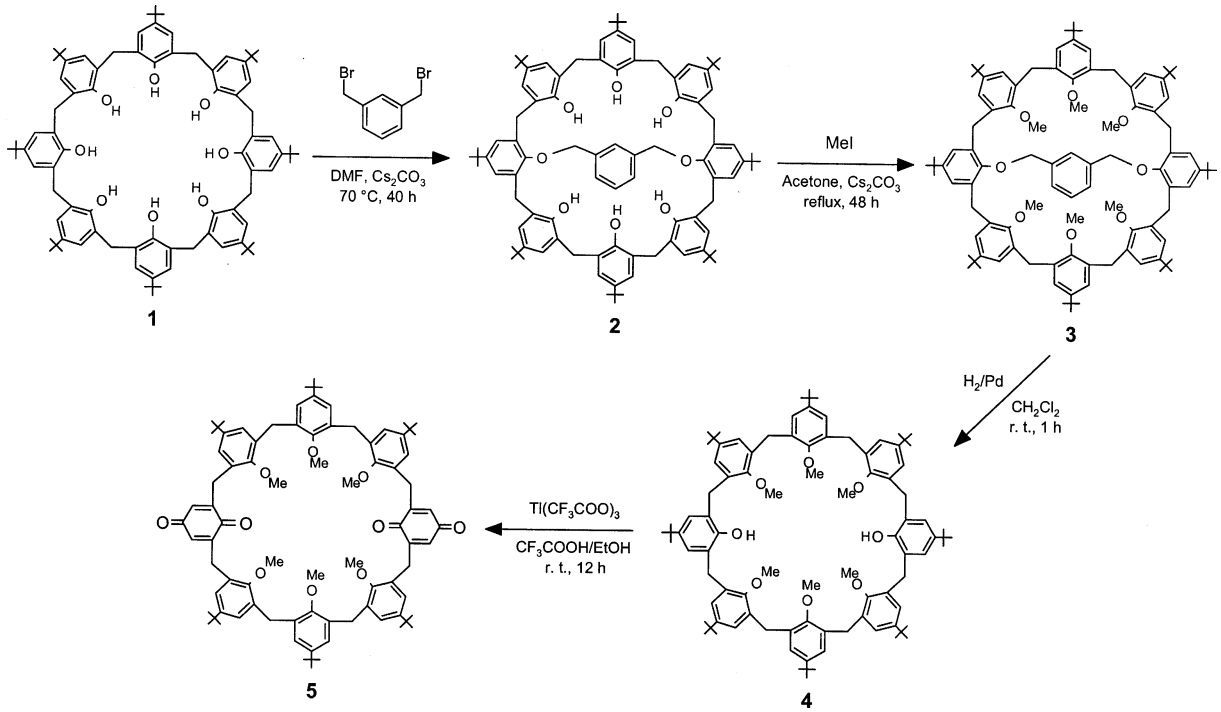
Since the number of observed reflections is low, isotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were positioned geometrically and refined using a riding model, the methyl group hydrogen atoms were assumed to be disordered over two sites rotated 60° to each other.

Table 1. Crystallographic data and refinement details for compound **5**

Chemical formula (a.u.)	$C_{43}O_5H_{52} \cdot C_7H_8$
Formula weight (a.u.)	741.02
Crystal size (mm)	$0.5 \times 0.2 \times 0.1$
Crystal colour, Habit	Gold, plate
Wavelenght (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimension	$a = 11.494(7)$ Å
	$b = 10.046(5)$ Å
	$c = 39.02(2)$ Å
	$\beta = 92.62(5)°$
Cell volume (Å^3)	4501(4)
Z	2
Crystallographic density (g/cm^3)	1.093
Absorption coefficient MoK_α (mm^{-1})	0.069
F(0,0,0)	1600
Θ range for data collection	2.02 – 22.51°
Range of *h, k, l*	$0 \le h \le 12$
	$0 \le k \le 10$
	$-42 \le l \le 41$
Reflections collected	6227
Indipendent reflections	5874 ($R_{int} = 0.042$)
No. of parameters	184
Final R indices ($I > 2\sigma_i$)	$R_1 = 0.1273, wR_2 = 0.3698$
R indices (all data)	$R_1 = 0.2723, wR_2 = 0.4416$
Goodness of fit	1.32

Packing bond length calculations were performed by means of the program PARST97 [19].

CCDC 245735 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc



Scheme 1.

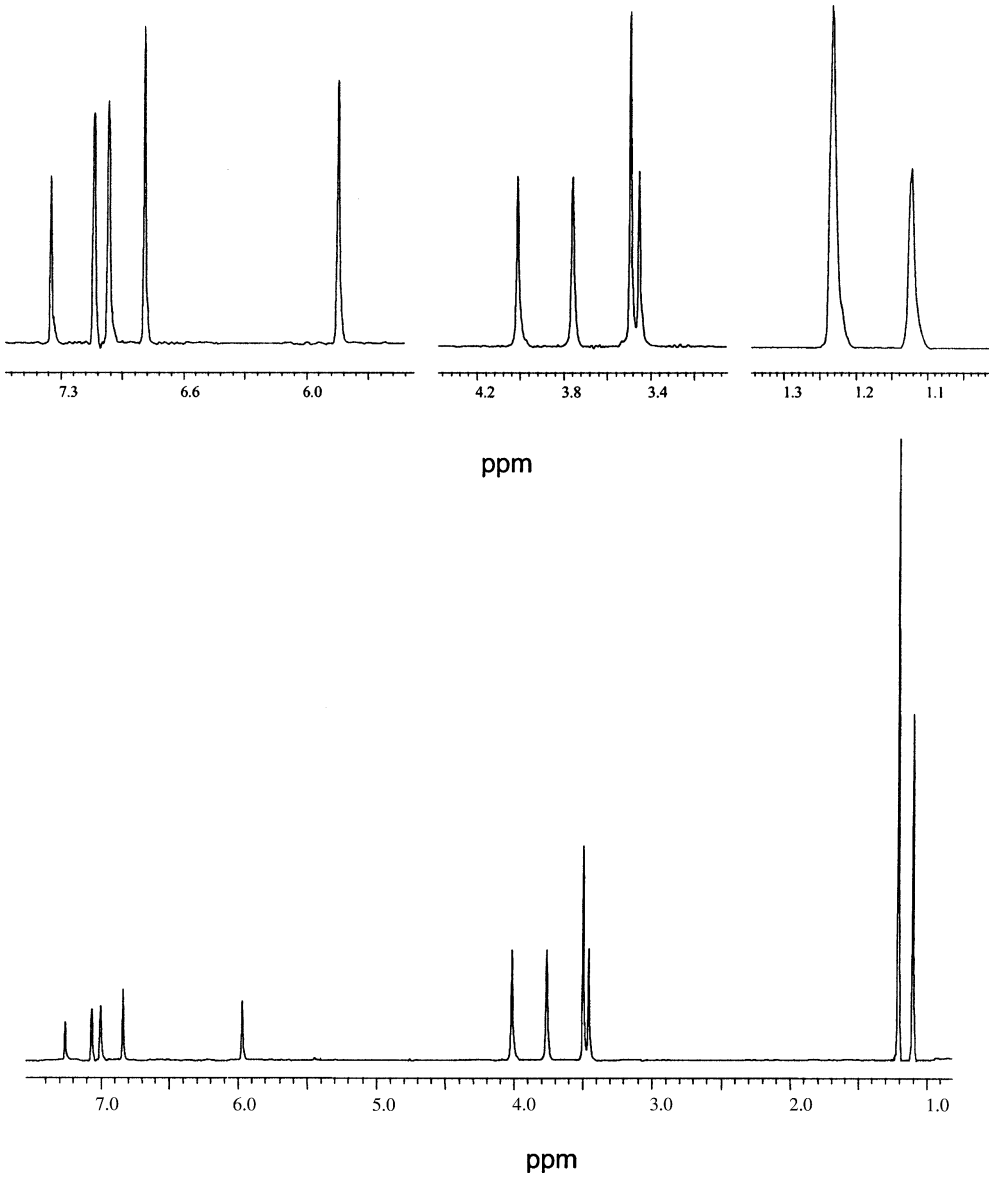


Figure 1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of 1,5-calix[8]diquinone **5**.

.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Thermal analyses

Thermo-gravimetric analyses (TGA) were run on a Pabisch Mettler TA4000 instrument under air flow at 5 °C/min up to 350 °C. Differential scanning calorimetry (DSC) measurements were run on a TA DSC 2920 instrument under air flow at 5 °C/min from 30 °C up to 350 °C.

Results and discussion

The synthesis of calix[8]arene 1,5-diquinone **5** relies on a convenient method of regioselective functionalisation at the upper rim of *p-tert*-butylcalix[8]arene **1** based on a protection-deprotection procedure [15]. The protection of the 1,5-positions of calix[8]arene **1** was obtained by intramolecular bridging with a short xylene spacer. In fact, 1,5-singly bridged calix[8]arene **2** was obtained in 80% yield by alkylation of *p-tert*-butylcalix[8]arene **1** with 1,3-bis(bromomethyl)benzene in the presence of Cs_2CO_3 as base, in non-dry DMF (Scheme 1). The crude product of reaction was sufficiently pure for the subsequent synthetic transformation. As pointed out previously, the high yield and the regiochemical outcome of this short-bite 1,5-bridging indicate that in the closure step the macrocycle adopts a conformation having the 1,5-positions very close to each other [20].

Compound **2** was hexamethylated to **3** (74%), which was deprotected by treatment with H_2/Pd to give adequately pure hexamethoxy-calix[8]arene-1,5-diol **4** in 90% yield (Scheme 1). Selective oxidation of 1,5-phenol rings of **4** with $Tl(OOCCF_3)_3$ afforded 1,5-calix[8]diquinone **5** in 28% yield, after column chromatography on silica gel.

Compounds **2–5** were mainly characterized by spectral analysis. Their molecular formulas were confirmed by the presence of the pseudo-molecular ion peak in the ESI(+) mass spectrum. The presence of sharp signals in their room-temperature ^{1}H and ^{13}C NMR spectra indicated an high conformational mobility of the macrocycle. Consequently, very simple spectral patterns were observed, which were indicative of the presence of two-orthogonal symmetry elements. Thus, for example, the ^{1}H NMR spectrum of 1,5-calix[8]diquinone **5** showed two *t*-Bu signals at 1.08 and 1.20 ppm (1:2), two $ArCH_2Ar$ singlets at 3.75 and 4.00 ppm (1:1), two methoxyl resonances at 3.46 and 3.48 ppm (2:1), and a single 4H quinone singlet at 5.96 ppm (Figure 1). The presence of the two equivalent quinone moieties was also proved by two accidentally isochronous ^{13}C NMR resonances at 187.3 ppm for the carbonyl groups.

Crystals of a 1:1 inclusion complex of **5** with toluene, suitable for X-ray analysis, were obtained by slow diffusion of methanol vapors into a toluene solution of it. In the X-ray structure (Figure 2a–b) the calix[8]arene molecule of **5** contains a crystallographic inversion centre and assumes a conformation that can be defined as a 'pseudo-chair-like' due to the resemblance with the previously reported *chair-like* conformation of *p-tert*-butylcalix[8]arene **1** [21]. In Figure 2c–d two views of the *chair-like* calix[8]arene molecule are shown for comparison with compound **5**. The similarity between the two conformations can be quantitatively evaluated by considering the rmsd value of 1.95 obtained by superimposition of non-H atoms of calixarene backbone (excluding all the *para* and O-substituents).

The differences between the two molecular structures can be estimated by the torsion angles around the methylene bridges (φ, χ), which are different for the absolute values and, more relevantly, for the signs. According to the convention suggested by Ugozzoli and Andreetti [22], the *chair-like* conformation is characterized by the following signs of the torsion angles − +, + −, + −, − +, + −, − +, − +, + − (see Table 2 for actual values). This determines a 3/4-cone geometry for

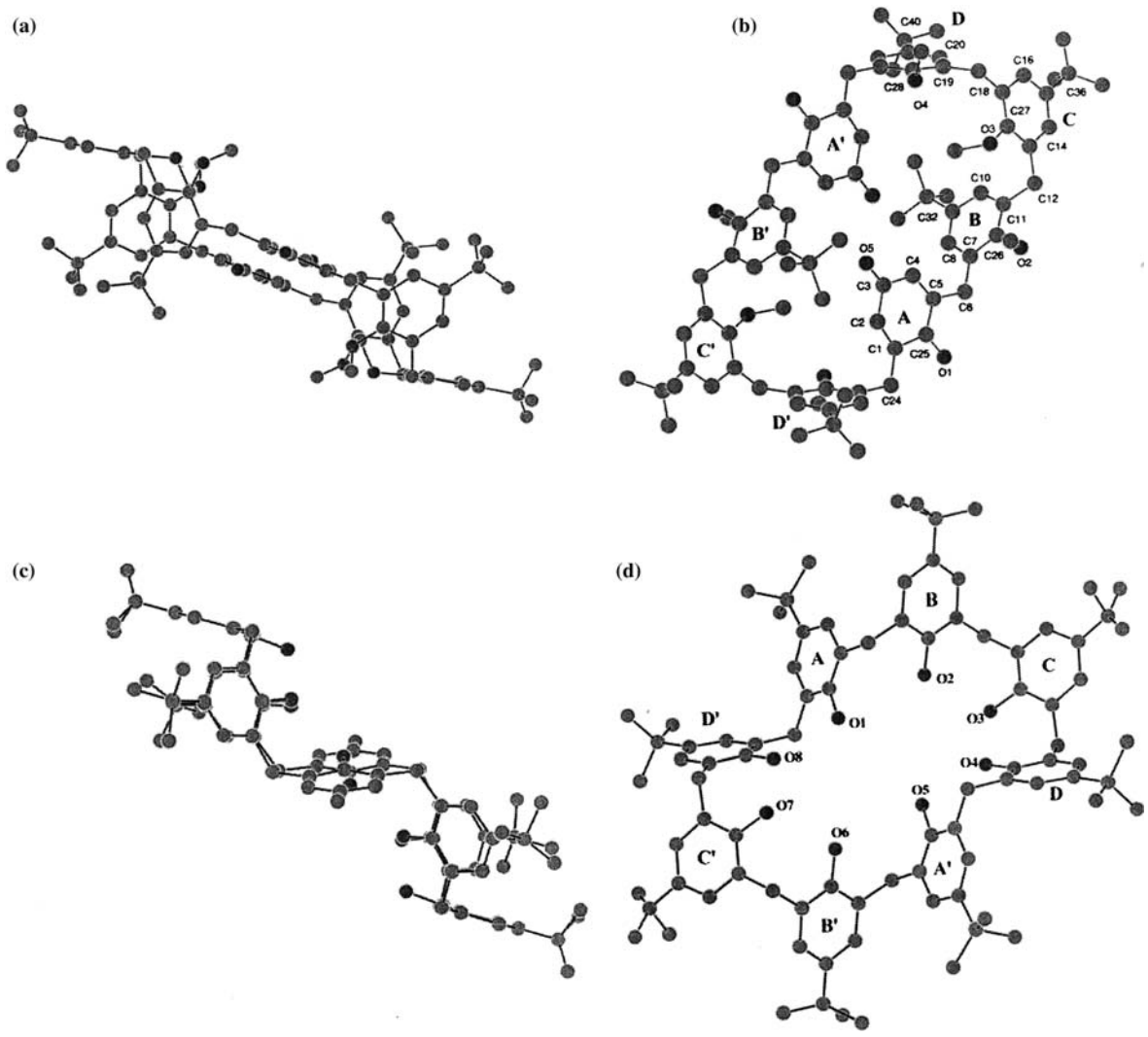


Figure 2. Comparison of X-ray molecular structures of 1,5-calix[8]diquinone **5** and *p-tert*-butylcalix[8]arene **1** [21]. Side- (a) and top-view with the numbering scheme (b) of the 'pseudo-chair-like' conformation of **5**. Side- (c) and top-view with the numbering scheme (d) of the 'chair-like' conformation of **1**. In (c) the methyl groups on the central rings have been omitted for clarity.

Table 2. Torsion angles around the $ArCH_2Ar$ bonds for compounds **5** and **1**[a]

	φ			χ	
	5	**1**		**5**	**1**
C(4)–C(5)-C(6)–C(7)	−14.7(13)	−76.9	C(5)–C(6)–C(7)–C(8)	−66.2 (11)	95.3
C(10)–C(11)–C(12)–C(13)	27.8(11)	95.7	C(11)–C(12)–C(13)–C(14)	−114.6 (9)	−79.1
C(16)–C(17)–C(18)–C(19)	88.1(10)	76.9	C(17)–C(18)–C(19)–C(20)	−47.0 (12)	−92.6
C(21)–C(22)–C(23)–C(24)	106.0(9)	−105.1	C(2)–C(1)–C(24)–C(23)	−6.6 (13)	59.3

[a]The indicated numbering refers only to compound 5.

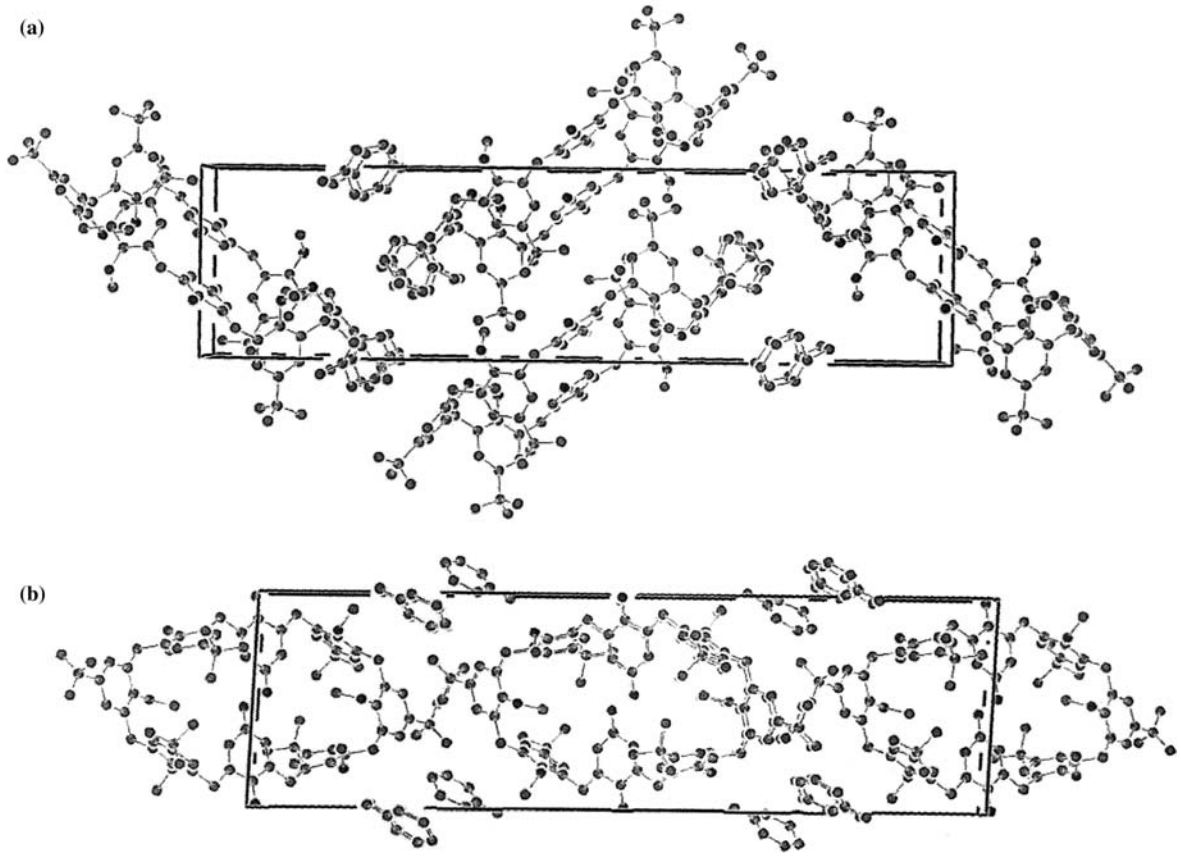


Figure 3. (a) Crystal packing of the toluene inclusion compound of 1,5-calix[8]diquinone **5** along the *a* axis; (b) along the *b* axis.

the rings B–C–D (and B′–C′–D′) stabilized by intramolecular H-bonds, so that the two opposite rings B/D (and B′/D′) appear almost superimposed to each other (Figure 2c).

The φ and χ values of the 'pseudo-chair-like' conformation of **5** are reported in Table 2: the sequence is − −, + −, + −, + −, + +, − +, − +, − + (indeed this last sign remains undetermined, being the torsion angle very close to zero and considering the esd). In the calix[8]arene diquinone molecule **5** the sequence of the signs determines a deformed 3/4-cone arrangement of the three lateral anisol B–C–D rings (and B′–C′–D′ rings) due to the absence of any stabilizing H-bond. Consequently, in the side-view (Figure 2a) the two opposite rings B/D (and B′/D′) appear significantly less symmetrical and even with different inclinations. In fact, ring B (and B′) possesses an inward inclination bringing its *tert*-butyl groups to self-fill the 3/4-cone cleft. The two symmetry related 3/4-cones are *anti* oriented, while the two quinone rings are on parallel planes (interplanar distance of 1.4 Å). The oxygens O(5) and O(5)* of the quinone rings point towards the centre of the macrocycle with a distance of 3.272(11) Å.

A packing diagram of the **5**·toluene inclusion compound is shown in Figure 3. The calix[8]arene molecules are stacked respectively along the *a* and *b* axes, displaying an overall herring bone arrangement. Each calixarene molecule is connected to two other ones through probable CH-π interactions [23] between *tert*-butyl H atoms and C aromatic ring [distance C38···centroid of C-ring 3.74(2) Å].

Four symmetry equivalent toluene molecules are included in the unit cell and are stacked along *a* axis.

The toluene molecule is disordered and interacts mainly with one methyl group of the disordered *tert*-butyl group [3.80(2), 3.86(2) and 3.88(2) Å].

As indicated in the experimental section, a decay of intensity of the standard reflections was observed during the data collection, which can be attributed to a slow loss of the clathrated toluene molecules. This was confirmed by TGA measurements, which indicated a 13% weight loss corresponding to the 4 toluene molecules of the unit cell. The release of toluene occurs in the temperature range of 30–160 °C. As it results from DSC measurements the compound starts to decompose at 257 °C.

Conclusions

The conformational propensities of the larger calix[*n*]arenes are yet relatively ill-defined because their higher conformational mobility is associated to a multitude of possible conformations. At this regard, X-ray analysis represents a valuable tool that can provide structural information often hardly attainable by alternative means (e.g. by NMR). In this respect, the results reported in this paper represent an interesting addition to the limited number of X-ray crystal structure of organic calix[8]arene derivatives currently available in the literature [24]. It is here demonstrated that the first example of a calix[8]quinone derivative, synthesized through a protection-deprotection procedure, adopts a 'pseudo-chair-like' conformation in the solid state. This structure is characterized by two opposite 3/4-cone moieties and resembles the *chair-like* conformation previously reported for *p-tert*-butylcalix[8]arene. In both instances results evident the propensity of the calix[8]-arene macrocycle to assume elongated shapes, which have to be taken into account in the design of new calix[8]arene-based hosts.

Acknowledgements

Financial support from the Italian MIUR (COFIN-2003, Supramolecular Devices Project) is gratefully acknowledged. Thanks are due to Dr. A. D'Amato (Dip. di Chimica, Università di Salerno) for ESI-MS measurements.

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