Nitration of thiacalix[4]arene using nitrosium nitrate complexes: synthesis and characterization of tetranitro-, tetraamino-, and tetra(4-pyridylimino)tetrahydroxythiacalix[4]arene

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The chemistry of the family of thiacalixarenes remains poorly documented although the potentiality of these molecules for complexing reactions or optical applications has been demonstrated. The reaction and the mechanism of the nitration of tetrahydroxythiacalixarene are reported in this paper. The synthesis and structural characterization of 5,11,17,23-tetranitro-25,26,27,28-tetrahydroxythiacalix[4]arene, as well as its reduction to tetraaminotetrahydroxythiacalix[4]arene and the formation of tetra(4-pyridylimino)tetrahydroxythiacalix[4]arene are discussed in this article.

In the scope of supramolecular chemistry calixarenes are among the most studied macrocycles.[1] Easily prepared from *p*-alkylphenol and formaldehyde under basic or acidic conditions, they present complexing properties for neutral or ionic species.[2] Calix[4]arenes were also reported for use in second-order nonlinear optical applications.[3] In thiacalix[4]arenes, which are metacyclophanes very similar to calixarenes, the original methylene bridges between the phenolic units of calixarene are substituted by sulfur.[4] These macrocycles are also interesting species for any kind of complexation,[5] and their nonlinear optical activity was recently investigated.[6] Nevertheless, the chemistry of thiacalixarenes is much less developed than the chemistry of calixarenes, probably due to the later discovery of the former.

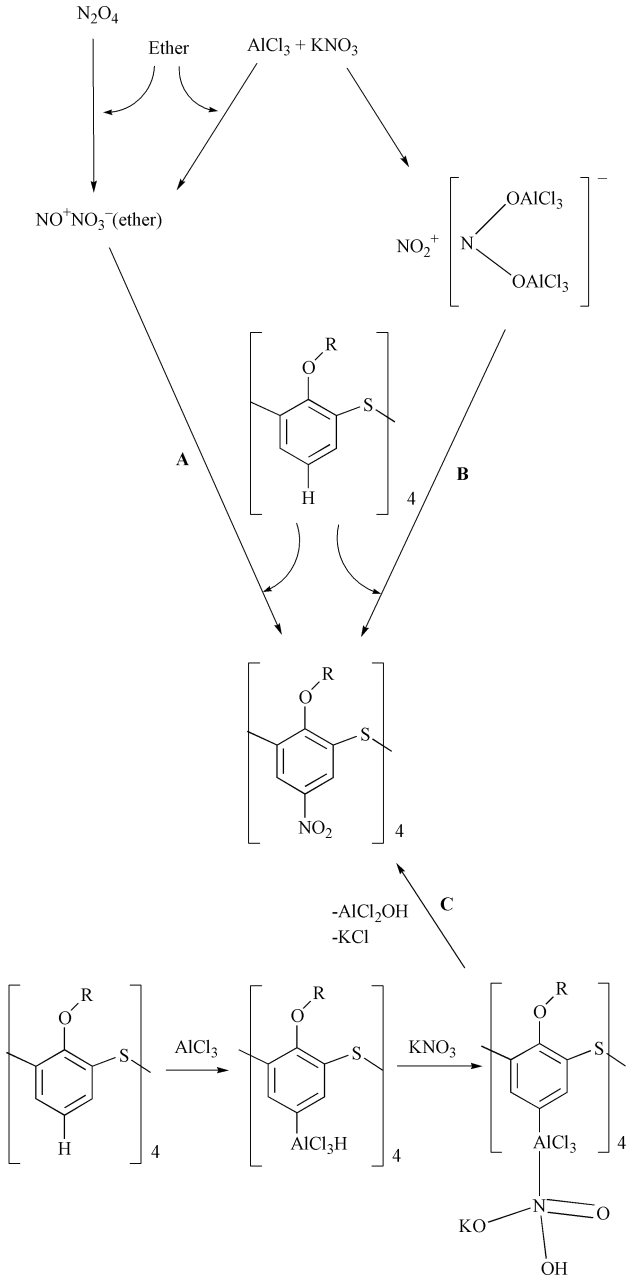
p-Nitrothiacalixarenes are important intermediates to the family of aminothiacalixarenes and thus the nitration reaction is an important step to the functionalization of these species. A recent review reported the different methods for the nitration of organic derivatives and in particular calixarenes.[7] Surprisingly, nothing has been reported on the nitration of thiacalixarenes while many articles have dealt with the nitration of calixarenes. Shinkai and co-workers described the nitration of calix[4]arene (21% yield) using concentrated sulfuric and nitric acids, followed by difficult purifications.[8] Reinhoudt and more recently Kumar and co-workers used *ipso*-nitration reactions on calixarenes.[9] Huang *et al*. reported nitration of calixarenes using potassium nitrate and aluminium chloride as nitrating agent, in acetonitrile.[10] In fact, this last reaction is quite controversial and it has been mentioned that it systematically failed when using only KNO_3 and $AlCl_3$ reagents.[1]

In our attempts to prepare *p*-nitrothiacalix[4]arene, all these mentioned reactions were investigated and failed, even when changing the conditions (solvent, temperature, reaction time). This paper reports a new procedure, which was used for the nitration of thiacalixarenes, the reduction to *p*-aminothiacalixarenes and the synthesis of tetra(4-pyridylimino)tetrahydroxythiacalix[4]arene, as well as their characterization.

Results and discussion

Synthesis and characterization of 1

The nitration reactions by the classical methods,[7–9] as mentioned above, were performed on tetrahydroxythiacalix[4]arene but no nitrated species could be evidenced. The reaction described by Huang *et al*.[10] with $KNO_3/AlCl_3$ failed in most organic solvents (THF, acetonitrile, toluene, *etc*.) but surprisingly worked in the presence of di-, tri- or tetraglyme and allowed easy preparation and isolation of 5,11,17,23-tetranitro-25,26,27,28-tetrahydroxythiacalix[4]arene (**1**) in a good yield. These observations demonstrate the tremendous influence of the solvent on this reaction. It was found during these attempts that only the presence of an ether (even in trace amounts) showing complexing capabilities could induce a reaction. It was previously mentioned in the literature that a complex between nitrosium nitrate, $NO^+NO_3^-$, which is stable below 180 K, and 18-crown-6 ether was isolated at room temperature in the absence of moist air[11] and could be used for the nitration of phenol, for example.[12] Considering the literature, three mechanisms are possible to explain the nitration of the thiacalixarene (Scheme 1).[12–14] These reaction processes were investigated in our laboratory. The complex between nitrosium nitrate and the ether was prepared by reaction at low temperature of N_2O_4 and 18-crown-6, and isolated following the procedure described by Savoie and co-workers.[11] It was then reacted in the proper stoichiometry with tetrahydroxythiacalix[4]arene in chloroform. 5,11,17,23-Tetranitro-25,26,27,28-tetrahydroxythiacalix[4]arene (**1**) precipitated instantaneously and could be isolated in good yield by filtration. It is important to note that the same reaction occurred while using



Scheme 1 Procedures for the nitration of thiacalix[4]arene.[12–14]

di-, tri- or tetraglyme as the complexing reagent. In fact, the $NO^+NO_3^-$ ionic species responsible for the nitration is unstable at room temperature where the stable forms are the molecular entities NO_2 and N_2O_4. If the medium contains a complexing ether, the ionic species can be stabilized enough to induce a reaction on the macrocycles. This reaction worked regardless of the source of N_2O_4. The nitration reaction in the presence of KNO_3–$AlCl_3$–ether can thus be explained by the *in situ* formation of N_2O_4 ($KNO_3 + AlCl_3$) and then $NO^+NO_3^-$ (ether) stable species, which cannot be obtained in the absence of stabilizing agent. According to these observations mechanism A (Scheme 1) seems to be the more probable one, since no reaction was observed in the absence of ether.

5,11,17,23-Tetranitro-25,26,27,28-tetrahydroxythiacalix[4]-arene (**1**) was characterized by FT-IR, ^1H and ^{13}C NMR, mass spectroscopy and single crystal X-ray diffraction analysis. The ^1H NMR spectrum of **1**, prepared from tetrahydroxythiacalix[4]arene and the mixture $AlCl_3$–KNO_3 in the presence of tetraglyme (method I), displays only one singlet at 8.44 ppm corresponding to the two aromatic protons of the thiacalixarene, which indicates that the substitution with the nitro group takes place in the para position. A multiplet at 3.55–3.31 ppm shows that **1** is solvated by the tetraglyme. The presence of four nitro groups connected to the thiacalixarene is confirmed by mass spectral data, which exhibits only the parent molecular ion. **1** was also prepared from tetrahydroxythiacalix[4]arene and the nitrosium nitrate complex (method II). Single crystals were grown in DMSO and structure analysis was performed.

Structure of tetranitrotetrahydroxythiacalix[4]arene (1)

Fig. 1, calculated with PLATON,[15] shows the crystal structure of **1** and the atom numbering scheme. The macrocycle possesses a center of symmetry and adopts a 1,2-alternate conformation. The usual cyclic intramolecular hydrogen bonds disappear but there are strong hydrogen bonds with the DMSO guest molecule: O14···O50: 2.707, O13···O50: 2.663 Å. This compound also shows interactions between the hydroxyl group and the sulfur bridges: O13···S7: 3.069, O14···S7: 3.076 Å. The two nitro groups are not equivalent: one is nearly coplanar with the aromatic ring [3.2(2)°] while the second makes an angle of 9.6(2)°. The packing shows

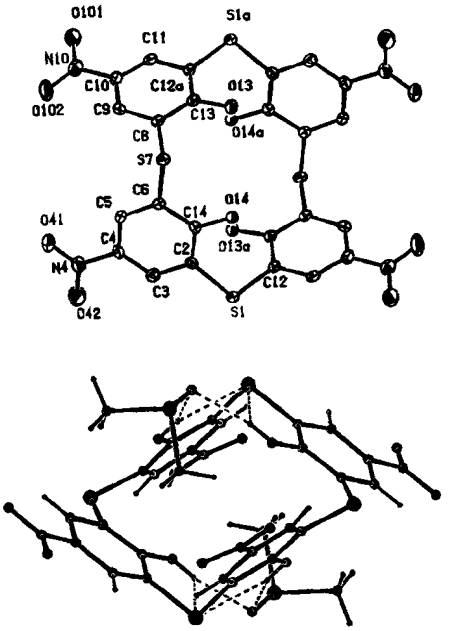


Fig. 1 ORTEP of 5,11,17,23-tetranitro-25,26,27,28-tetrahydroxythiacalix[4]arene (**1**) showing atomic numbering scheme and interactions with the solvent DMSO.

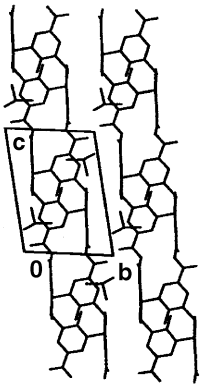


Fig. 2 View of the packing in the structure of **1**.

layers of calixarenes with the NO_2 groups facing each other (Fig. 2).

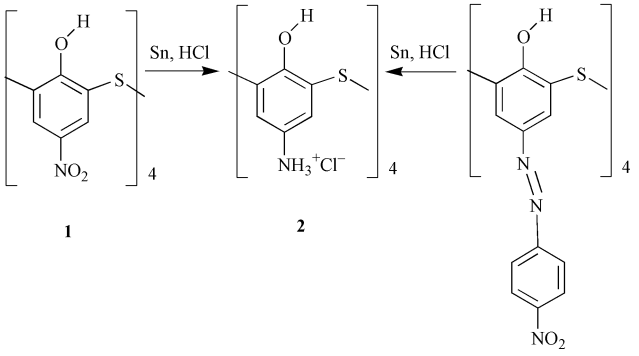
Reduction of tetranitrotetrahydroxythiacalix[4]arene and synthesis of tetra(4-pyridylimino)tetrahydroxythiacalix[4]arene

Reduction of the NO_2 groups was achieved by reacting compound **1** with metallic Sn in acidic (HCl) medium (Scheme 2). The reaction was instantaneous and 5,11,17,23-tetraamino-25,26,27,28-tetrahydroxythiacalix[4]arene hydrochloric salt (**2**) was obtained as a white powder in a good yield. The infrared spectra (Fig. 3) showed clearly the replacement of the NO_2 vibration bands (697 cm^{-1}) by $NH_3^+Cl^-$ ones (3131, 2834, 2575 cm^{-1}). This was confirmed by the mass spectrum showing the parent peak for the tetraamino species. Compound **2** was also easily prepared with a nearly quantitative yield (95%) by reacting *p*-tetrakis(4-nitrophenylazo)tetrahydroxythiacalix[4]-arene, which was previously reported,[6] with Sn in concentrated HCl (Scheme 2). This may be a convenient route for the synthesis of **2** if one considers the yield for the synthesis of the nitrophenylazo species, which was reported to be over 70%.

Compound **2** was reacted with pyridine-4-carboxyaldehyde in the presence of triethylamine (Scheme 3). Tetra(4-pyridylimino)tetrahydroxythiacalix[4]arene (**3**) was isolated and characterized. The ^1H NMR spectrum showed two doublets at 8.79 and 7.70 ppm attributed to the pyridyl groups (16H), one singlet at 8.06 ppm for the phenyl groups of the thiacalixarene (8H) and one singlet at 8.37 ppm for the imino group (4H).

Thermal analysis

Differential scanning calorimetry and thermogravimetric analysis experiments were performed in order to investigate the thermal stability of these compounds. Previous investigations on phenylazo substituted thiacalix[4]arenes have shown



Scheme 2 Synthesis of **2**.

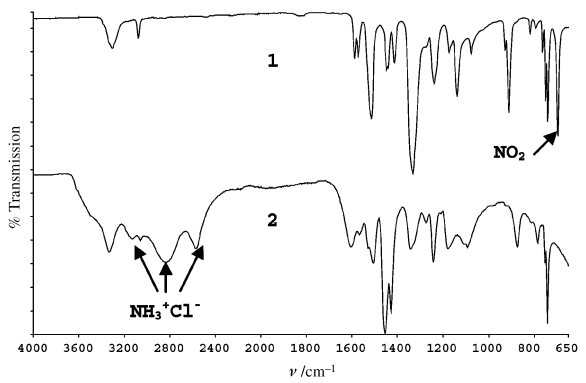
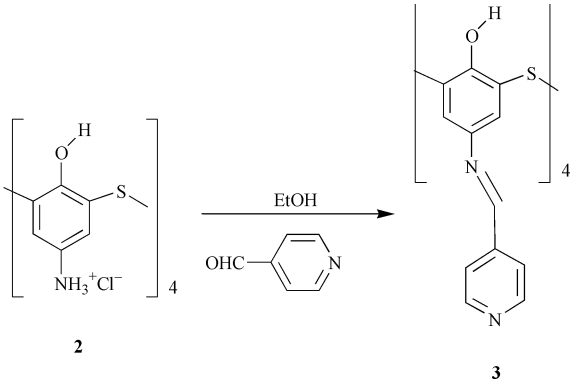


Fig. 3 FT-IR spectra for **1** and **2**.



Scheme 3 Synthesis of tetra(4-pyridylimino)tetrahydroxythiacalix[4]-arene (**3**).

decomposition temperatures as high as 320 °C.[6] In the case of the tetranitrotetrahydroxythiacalix[4]arene (**1**), a first loss of mass was observed at 130 °C corresponding to the elimination of the solvent, followed by a second reaction at 280 °C, which was attributed to the decomposition of the thiacalix[4]arene. For tetraaminotetrahydroxythiacalix[4]arene (**2**), decomposition of the macrocycle starts at lower temperatures, around 120 °C.

Experimental

General

All reactions were carried out with dry reagents and solvents. FT-IR spectra were recorded on a Nicolet Magna-IR560 spectrometer. ^1H and ^{13}C NMR spectroscopy were performed on a Brüker AM300 spectrometer, and mass spectra were collected on a MAT 95 XL Finnigan spectrometer. The characterization of the thermal behavior of these compounds was done by means of a Mettler Toledo TA 8000 equipment monitored by a Dell station and STAR 6.1 software. The thermal stability was studied using a Mettler Toledo TGA 851e thermobalance monitored by the same software as the DSC. Aluminium oxide crucibles were used in the temperature range 25–400 °C. All experiments were achieved under an atmosphere of argon with a heating rate of 5 °C min^{-1}.

Syntheses

5,11,17,23-Tetranitro-25,26,27,28-tetrahydroxythiacalix[4]-arene. *Method I.* Tetraethyleneglycoldimethyl ether (tetraglyme; 0.60 mL, 2.69 mmol) and KNO_3 (0.25 g, 2.47 mmol) were added to a suspension of tetrahydroxythiacalix[4]arene (0.20 g, 0.40 mmol) in CH_2Cl_2 (15 ml). The mixture was stirred for 15 min at room temperature. After cooling to 0 °C, $AlCl_3$ (0.30 g, 2.25 mmol) was added to the suspension. The mixture became orange and was refluxed for 22 h. The brown solution was hydrolyzed at room temperature by slow addition of water (20 mL). The aqueous layer was extracted by ethyl acetate (30 mL). The organic layer was washed with water (80 mL) until the pH was neutral, dried over Na_2SO_4 and concentrated. The product **1** (0.30 g, 67%) was obtained by precipitation with diethyl ether.

^1H NMR (300 MHz, CD_3CN, 25 °C): $\delta = 8.44$ (s, 2H, ArH), 3.55–3.31 (m, 22H, tetraglyme). ^{13}C NMR (300 MHz, CD_3CN, 25 °C): $\delta = 168.52$ (s, Ar*C*–OH), 138.58 (s, Ar*C*–NO_2), 133.98 (s, Ar–*C*H), 122.44 (s, Ar*C*–S–Ar). ES-MS (negative mode): m/z calcd $M = 676.58$, $[M - H]^- = 674.9$.

Method II. (a) Formation of the nitrosium nitrate complex. Decomposition of dried lead(II) nitrate at 600 °C under

nitrogen led to the formation of gaseous NO_2. The gas was cooled to −20 °C and bubbled in a solution of 18-crown-6 ether (1 g, 3.8 mmol) in chloroform (15 ml) at −20 °C. The reaction mixture was stirred for 1 h at low temperature and then allowed to warm up at room temperature. The solvent was then concentrated and diethyl ether was added (1 ml) in order to crystallize the complex at 0 °C (0.7 g, 45%).

(b) Nitration. The previously prepared complex (0.9 g, 2.16 mmol) was added to a solution of tetrahydroxythiacalix[4]-arene (0.21 g, 0.42 mmol) in chloroform (10 ml). The reaction medium was stirred for 12 h at room temperature and filtrated. The powder was then washed with several portions of ether (5 ml) and dichloromethane (5 ml) to isolate **1** (0.11 g, 38%).

5,11,17,23-Tetraamino-25,26,27,28-tetrahydroxythiacalix[4]-arene (2). *Method I.* 5,11,17,23-Tetranitro-25,26,27,28-tetrahydroxythiacalix[4]arene (0.5 g, 0.7 mmol) was suspended in concentrated HCl (20 mL). Tin was then added to the suspension (2 g, 17 mmol). The reaction medium was heated for 1 h, then the white suspension was cooled in an ice bath and filtered. The precipitate was washed with HCl, acetone and diethyl ether (0.47 g, 95%). ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 25 °C]: $\delta = 9.92$ (s, 4H, O*H*), 7.44 (s, 8H, Ar*H*). ^{13}C NMR (300 MHz, D_2O, 25 °C): $\delta = 158.59$ (s, Ar*C*–OH), 122.93 (s, Ar*C*–NH_2), 131.86 (s, Ar–*C*H), 122.38 (s, Ar*C*–S–Ar). ES-MS (positive mode): m/z calcd $M = 556.0$, $[M + H]^+ = 557.2$.

Method II. *p*-Tetrakis(4-nitrophenylazo)tetrahydroxythiacalix[4]arene was prepared following the procedure previously reported.[6] This thiacalixarene (0.17 g, 0.16 mmol) was suspended in 37% HCl (15 ml). Sn (0.5 g, 2.13 mmol) was then added and the suspension was refluxed for 1 h. The medium was cooled in an ice bath and filtered. The precipitate was washed with HCl, acetone and diethyl ether (0.1 g, 95%).

5,11,17,23-Tetra(4-pyridylimino)-25,26,27,28-tetrahydroxy-thiacalix[4]arene (3). 5,11,17,23-Tetraamino-25,26,27,28-tetrahydroxythiacalix[4]arene tetrachlorhydrate salt (0.1 g, 0.142 mmol) was suspended in ethanol (20 mL). After the suspension was degassed over N_2, Et_3N (0.2 mL, 1.435 mmol) and pyridine-4-carboxyaldehyde (0.07 mL, 0.73 mmol) were added. The yellow suspension was stirred for 24 h and evaporated to dryness. The orange powder (**3**) was then washed with several portions of water and diethyl ether (0.1 g, 77%).

^{1}H NMR (300 MHz, C_5D_5N, 25 °C): $\delta = 8.79$, 7.70 (d, 16H, Py*H*), 8.06 (s, 8H, Ar*H*), 8.37 (s, 4H, NC*H*). ^{13}C NMR (300 MHz, C_5D_5N, 25 °C): $\delta = 163.78$ (Ar*C*–OH), 155.17 (*C*=N), 150.97 (Py*C*–H), 143.76 (Ar*C*–N), 141.20 (Py*C*–CN), 135.04 (Ar*C*–S–Ar), 132.13 (Ar*C*–H), 122.48 (Py*C*–H). ES-MS (negative mode): m/z calcd M = 912.24, $[M - H]^- = 911$.

Table 1 Crystallographic data for 5,11,17,23-tetranitro-25,26,27,28-tetrahydroxythiacalix[4]arene

Formula	$C_{28}H_{24}N_4O_{14}S_6$
M	832.87
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.2988(17)
b/Å	9.1492(18)
c/Å	12.431(3)
α/°	93.27(3)
β/°	107.02(3)
γ/°	113.53(3)
U/Å^3	811.0(3)
Z	1
T/K	173(2)
μ/mm^{-1}	0.501
Measured reflections	5948
Unique reflections	3462
R_{int}	0.0680
Final R_1 [$I > 2\sigma(I)$]	0.0590
Final wR_2 [$I > 2\sigma(I)$]	0.1426
R_1 (all data)	0.1103
wR_2 (all data)	0.1722

Table 2 Selected bond lengths (Å), angles and torsion angles (°) for **1**

S(1)–C(12)#1	1.766(4)	S(7)–C(6)	1.783(4)
S(1)–C(2)	1.769(4)	S(7)–C(8)	1.785(5)
C(2)–C(3)	1.387(6)	C(8)–C(9)	1.388(6)
C(2)–C(14)	1.402(6)	C(8)–C(13)	1.398(6)
C(3)–C(4)	1.396(6)	C(9)–C(10)	1.386(6)
C(4)–C(5)	1.384(6)	C(10)–C(11)	1.370(6)
C(5)–C(6)	1.371(6)	C(11)–C(12)	1.381(6)
C(6)–C(14)	1.436(5)	C(12)–C(13)	1.421(6)
C(4)–N(4)	1.467(6)	C(10)–N(10)	1.459(6)
N(4)–O(41)	1.227(5)	N(10)–O(101)	1.222(5)
N(4)–O(42)	1.225(5)	N(10)–O(102)	1.235(5)
C(14)–O(14)	1.334(5)	C(13)–O(13)	1.349(5)
C(12)#1–S(1)–C(2)	107.18(19)	C(6)–S(7)–C(8)	101.0(2)
C(3)–C(2)–S(1)	116.6(3)	C(5)–C(6)–S(7)	120.6(3)
C(11)–C(12)–S(1)#1	117.5(3)	C(9)–C(8)–S(7)	120.3(3)
C(14)–C(2)–S(1)	122.9(3)	C(14)–C(6)–S(7)	119.5(3)
C(13)–C(12)–S(1)#1	122.7(3)	C(13)–C(8)–S(7)	119.4(3)
C(3)–C(2)–C(14)	120.4(4)	C(6)–C(5)–C(4)	119.4(4)
C(9)–C(8)–C(13)	120.2(4)	C(10)–C(11)–C(12)	120.0(4)
C(2)–C(3)–C(4)	118.8(4)	C(5)–C(6)–C(14)	119.9(4)
C(10)–C(9)–C(8)	119.0(4)	C(11)–C(12)–C(13)	119.4(4)
C(5)–C(4)–C(3)	122.3(4)	C(2)–C(14)–C(6)	119.1(4)
C(11)–C(10)–C(9)	121.9(4)	C(8)–C(13)–C(12)	119.3(4)
C(5)–C(4)–N(4)	119.6(4)	C(3)–C(4)–N(4)	118.1(4)
C(11)–C(10)–N(10)	119.5(4)	C(9)–C(10)–N(10)	118.5(4)
O(13)–C(13)–C(8)	124.5(4)	O(13)–C(13)–C(12)	116.3(4)
O(14)–C(14)–C(6)	123.3(4)	O(14)–C(14)–C(2)	117.6(3)
C(12)#1–S(1)–C(2)–C(3)	135.1(3)	S(7)–C(6)–C(14)–O(14)	0.2(6)
S(1)–C(2)–C(3)–C(4)	173.2(3)	C(3)–C(2)–C(14)–O(14)	179.9(4)
C(4)–C(5)–C(6)–S(7)	179.3(3)	C(2)–C(3)–C(4)–N(4)	178.4(4)
C(6)–S(7)–C(8)–C(9)	80.3(4)	N(10)–C(10)–C(11)–C(12)	−179.2(4)
S(7)–C(8)–C(9)–C(10)	180.0(3)	C(5)–C(4)–N(4)–O(41)	1.0(6)
S(7)–C(8)–C(13)–O(13)	−1.0(6)	C(11)–C(10)–N(10)–O(101)	−11.1(6)

Crystallography

Parameters for data collection and refinement of **1** are summarized in Table 1; selected bond lengths and angles are listed in Table 2. Data were collected on a Kappa CCD Nonius diffractometer with Mo-Kα radiation ($\lambda = 0.71069$ Å). The crystal was mounted on a glass capillary and bathed in a cold nitrogen stream during the collection. The structure was solved by direct methods using SHELXS97.[16] The refinement was performed using full-matrix least-squares methods by SHELXL97.[17] Anisotropic thermal parameters were refined for non-hydrogen atoms.

CCDC reference number 182824. See http://www.rsc.org/suppdata/nj/b1/b110609k/ for crystallographic data in CIF or other electronic format.

References

1 (*a*) C. D. Gutsche, *Calixarenes Revisited*, The Royal Chemical Society, London, 1998; (*b*) *Calixarenes, a Versatile Class of Macrocyclic Compounds*, eds. J. Vicens and V. Böhmer, Kluwer, Dordrecht, 1991.
2 S. Shinkai, *Tetrahedron*, 1993, **49**, 8933.
3 (*a*) E. Kelderman, L. Derhaeg, G. Heesink, W. Verboom, J. Engbersen, N. van Hulst, A. Persoons and D. Reinhoudt, *Angew. Chem.*, 1992, **104**, 1107; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1075; (*b*) E. Kelderman, L. Derhaeg, W. Verboom, J. Engbersen, S. Harkema, A. Persoons and D. Reinhoudt, *Supramol. Chem.*, 1993, **2**, 183; (*c*) P. Kenis, E. Kerver, B. Snellink-Ruël, G. van Hummel, S. Harkema, M. Flipse, R. Woudenberg, J. Engbersen and D. Reinhoudt, *Eur. J. Org. Chem.*, 1998, 1089.
4 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971.
5 G. Mislin, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1345.
6 C. Desroches, S. Parola, F. Vocanson, N. Ehlinger, P. Miele, R. Lamartine, J. Bouix, A. Eriksson, M. Lindgren and C. Lopes, *J. Mater. Chem.*, 2001, **11**, 3014.
7 J. P. Adams and J. R. Paterson, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3695.
8 S. Shinkai, K. Araki, T. Tsubaki, T. Arimura and O. Manabe, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2297.
9 (*a*) W. Verboom, A. Durie, R. Egberink, Z. Asfari and D. Reinhoudt, *J. Org. Chem.*, 1992, **57**, 1313; (*b*) S. Kumar, N. D. Kurur, H. M. Chawla and R. Varadarajan, *Synth. Commun.*, 2001, **31**, 775.
10 W. Zhang, Y. Zheng and Z. Huang, *Synth. Commun.*, 1997, **27**, 3763.
11 S. Ricard, P. Audet and R. Savoie, *J. Mol. Struct.*, 1988, **178**, 135.
12 N. Iranpoor, H. Firouzabadi and R. Heydari, *Synth. Commun.*, 1999, **29**, 3295.
13 G. B. Bachman and C. M. Vogt, *J. Am. Chem. Soc.*, 1958, **80**, 2987.
14 A. V. Topchiev, *Nitration of Hydrocarbons and Other Organic Compounds*, Pergamon Press, New York, 1959.
15 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 1999.
16 G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
17 G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.