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High-performance Liquid Chromatography Study of the Nitration Course of Tetrabutoxycalix[4]arene at the Upper Rim: Determination of the Optimum Conditions for the Preparation of 5,11,17-Trinitro-25,26,27,28-tetrabutoxycalix[4]arene

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A selective nitration of calix[4]arene at the upper rim in one pot process was described by monitoring the time dependence of the distribution of products by high-performance liquid chromatography (HPLC). The discrimination of five nitrated products was accomplished by molecular symmetry considerations and ^{1}H NMR analysis. As a result, unusual 5,11,17-trinitrocalix[4]arene (**2d**) was obtained in 57% isolated yield. 5,11-Dinitro-calix[4]arene (**2b**) and 5,11,17-trinitrocalix[4]arene (**2d**) with tetranitrocalix[4]arene **2e** were further characterized by crystal X-ray diffraction analysis. Furthermore, as an example of potential application, trinitrocalix[4]arene **2d** could be converted to triaminocalix[4]arene **3d** conveniently.

Keywords calix[4]arene, selective nitration, high-performance liquid chromatography

Introduction

Calix[4]arene is one of the most important supramolecular building blocks because of its capability of being readily modified both at the *para* positions of the aromatic rings (the upper or wide rim) and at the phenolic hydroxyls (the lower or small rim), and the functionalized calix[4]arenes can complex cations and neutral molecules.[1] Introduction of nitro groups at the upper rim of calixarene is a potent approach to realize modification of calixarene, as the *para*-nitro groups can be easily reduced to amino groups. The resulting species are important starting materials for model synthesis of complex compounds[2] and molecular receptors using calix[4]arene as a platform.[3]

Several procedures for the introduction of nitro groups at the upper rim have been established: direct nitration of free *para* positions,[4] ipso-substitution of the *tert*-butyl groups,[4e,5] replacement of *p*-sulfonate moieties,[6] or nitroso compounds.[4b] The selective introduction of one or two nitro groups at the upper rim has also been realized by a stepwise synthesis.[7] Calix[4]arenes having one or two nitro groups at the upper rim have been prepared in relatively low yields.[4e,8] Moreover, few reports concern the trinitrocalix[4]arene, in which the reaction conditions involve as long as 3 d to yield 5,11,17-trinitro-25,26,27,28-tetrapentyloxycalix[4]arene[9] in 41% yield. To our surprise, different reaction conditions for selective nitration reaction on calix[4]arene can be found in the literature.[4-6] But so far there is no paper about the systematic and optimized synthetic approach of nitration of calix[4]arene. Herein, a selective nitration course at the upper rim of tetrabutoxycalix[4]arene in one pot process is described, monitoring the reaction by HPLC, from which the optimum conditions for the preparation of 5,11,17-trinitro-25,26,27,28-tetrabutoxycalix[4]arene, which was hardly isolated before,[4a] can be determined. It is desirable to mention that our study here is the time dependent, because other parameters, such as temperature and stoichiometry, have been optimized. A detailed study of the nitration course by HPLC shows that 3 d reaction time for synthesis of the trinitrocalix[4]arene[9] is not necessary, and the trinitro derivative can be obtained in 124 min and 57% yield in our conditions.

Experimental

Materials and measurements

All reactions were performed in open atmosphere unless noted. The commercially available reagents and solvents were used without further purification unless otherwise noted. Column chromatography was per-

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formed with silica gel (200—300 mesh). All yields were given as isolated ones. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer. Chemical shifts (δ) are reported downfield from tetramethylsilane. Coupling constants (J values) are reported in Hz. IR and ESI-MS data were measured on a Bruker Vector 22 as KBr pellets and a Finnigan Mat TSQ 7000 instruments, respectively. Microanalyses were obtained on a Perkin-Elmer 240 instrument, and melting points were determined with a digital electrothermal apparatus without further correction. X-ray diffractions were carried out on a Bruker Smart Apex CCD diffractometer. HPLC was performed on an Agilent Technologies 1200 Series instrument. The standard pure samples for HPLC analysis of 25,26,27,28-tetrabutoxy calix[4]arene (**1**),[10] nitrocalix[4]arenes **2a—2c** and **2e**[4a] were prepared according to literature procedures.

General procedure for the nitration of calix[4]arene 1, and the distribution of products monitored by HPLC

To a solution of *n*-tetrabutoxycalix[4]arene (**1**, 1.0 g, 1.5 mmol) and acetic acid (10 mL) in CH_2Cl_2 (100 mL) was added 65% nitric acid (15 mL, 217 mmol) over 4 min, and the resulting mixture stirred at 30 ℃. During the course of the reaction, 0.1 mL aliquots were transferred to water (3 mL) at regular intervals, and then extracted with CH_2Cl_2 (3 mL). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography using ethyl acetate as eluent to give a yellow solid, which was analyzed by HPLC (Agilent Eclipse XDB-C18, 100% MeCN, UV 205 nm, flow rate 1.0 mL/min. t_{2e}=4.8 min, t_{2d}=7.7 min, t_{2c}=11.9 min, t_{2b}=14.2 min, t_{2a}=24.8 min and t_1=41.8 min corresponding to the pure **1** and **2a—2e** respectively) to give the comparative percents of the components.

Synthesis of 5,11,17-trinitro-25,26,27,28-tetrabutoxycalix[4]arene (2d)

To a solution of *n*-tetrabutoxycalix[4]arene (**1**, 5.0 g, 7.5 mmol) and acetic acid (50 mL) in CH_2Cl_2 (500 mL) was added 65% nitric acid (75 mL, 1.1 mol) over 20 min, and the resulting mixture was stirred at 30 ℃. After 124 min, water (500 mL) was added and the mixture stirred for 10 min to quench the reaction. The organic layer was separated and washed with H_2O, Na_2CO_3 (5%), H_2O and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was recrystallized from CH_2Cl_2/MeOH to yield 3.35 g of a yellow solid. Yield 57%, m.p. 139—141 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.97—1.04 (m, 12H, CH_3), 1.31—1.44 (m, 4H, CH_2), 1.46—1.54 (m, 4H, CH_2), 1.80—1.89 (m, 8H, CH_2), 3.31 (d, J=14.4 Hz, 2H, $ArCH_2Ar$), 3.36 (d, J=14.4 Hz, 2H, $ArCH_2Ar$), 3.80 (t, J=6.9 Hz, 2H, $ArOCH_2$), 3.91 (t, J=6.9 Hz, 2H, $ArOCH_2$), 3.96—4.16 (m, 4H, $ArOCH_2$), 4.46 (d, J=14.4 Hz, 2H, $ArCH_2Ar$), 4.51 (d, J=14.4 Hz, 2H, $ArCH_2Ar$), 6.36 (s, 3H, ArH), 7.24 (s, 2H, O_2NArH), 7.79—7.82 (m, 4H, O_2NArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.9, 19.1, 19.3, 19.4, 31.0, 31.1, 32.2, 32.3, 75.3, 75.7, 122.7, 123.6, 123.7, 124.7, 128.4, 132.9, 134.9, 135.8, 137.5, 142.5, 142.8, 155.8, 161.3, 162.7; IR (KBr) v: 2959, 2932, 2872, 1585, 1520, 1456, 1345, 1298, 1262, 1208, 1094, 1025, 973, 898, 795, 769, 746 cm^{-1}; ESI-MS m/z (%): 806 ($[M+Na]^+$, 18), 1590 ($[2M+Na]^+$, 100). Anal. calcd for $C_{44}H_{53}N_3O_{10}$•0.5H_2O: C 66.65, H 6.86, N 5.30; found C 66.32, H 6.62, N 5.45.

General procedure for the preparation of aminocalix[4]arenes 3a—3e

Hydrazine hydrate (5.4 mL, 110 mmol) was added to a suspension of nitrocalix[4]arene **2** (1 mmol) and a catalytic amount of Raney nickel in methanol (50 mL). The mixture was refluxed for 4 h. After cooling to room temperature, the mixture was filtered. Then the filtrate was evaporated and the crude product was washed with water twice to afford pure aminocalix[4]arene **3** (>99% yield).

5-Amino-25,26,27,28-tetrabutoxycalix[4]arene (**3a**): Grey solid; m.p. 102—104 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.98 (t, J=7.5 Hz, 12H, CH_3), 1.40—1.47 (m, 8H, CH_2), 1.84—1.90 (m, 8H, CH_2), 3.03 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 3.14 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 3.77—3.91 (m, 8H, $ArOCH_2$), 4.37 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 4.45 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 5.98 (s, 2H, ArH) , 6.53—6.66 (m, 9H, ArH).

5,11-Diamino-25,26,27,28-tetrabutoxycalix[4]arene (**3b**): Grey solid; m.p. 172—175 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.98 (t, J=6.9 Hz, 12H, CH_3), 1.35—1.48 (m, 8H, CH_2), 1.80—1.92 (m, 8H, CH_2), 2.91 (d, J=13.2 Hz, 1H, $ArCH_2Ar$), 3.03 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 3.04 (br s, 4H, NH_2), 3.15 (d, J=13.2 Hz, 1H, $ArCH_2Ar$), 3.78 (t, J=7.2 Hz, 4H, $ArOCH_2$), 3.86 (t, J=7.2 Hz, 4H, $ArOCH_2$), 4.29 (d, J=13.2 Hz, 1H, $ArCH_2Ar$), 4.37 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 4.45 (d, J=13.2 Hz, 1H, $ArCH_2Ar$), 5.98 (s, 2H, ArH), 6.02 (s, 2H, ArH), 6.62—6.65 (m, 6H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1, 19.4, 31.1, 32.2, 32.3, 74.8, 115.4, 121.5, 128.0, 128.1, 135.2, 135.6, 140.2, 149.9, 156.8; IR (KBr) v: 3439, 3345, 2958, 2928, 2868, 1612, 1463, 1381, 1288, 1213, 1125, 1083, 1032, 961, 856, 764 cm^{-1}; ESI-MS m/z (%): 679 ($[M+1]^+$, 27), 701 ($[M+Na]^+$, 78), 1358 ($[2M+1]^+$, 100). Anal. calcd for $C_{44}H_{58}N_2O_4$: C 77.84, H 8.61, N 4.13; found C 77.68, H 8.72, N 4.43.

5,17-Diamino-25,26,27,28-tetrabutoxycalix[4]arene (**3c**): Grey solid; m.p. 188—190 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.95—1.00 (m, 12H, CH_3), 1.35—1.50 (m, 8H, CH_2), 1.80—1.91 (m, 8H, CH_2), 3.03 (d, J=13.2 Hz, 6H, $ArCH_2Ar+NH_2$), 3.77 (t, J=7.2 Hz, 4H, $ArOCH_2$), 3.88 (t, J=7.5 Hz, 4H, $ArOCH_2$), 4.38 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 5.92 (s, 4H, ArH), 6.60—6.74 (m, 6H, ArH).

5,11,17-Triamino-25,26,27,28-tetrabutoxycalix[4]-arene (**3d**): Grey solid; m.p. 154—156 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.93—1.00 (m, 12H, CH_3), 1.30—1.54 (m, 8H, CH_2), 1.77—1.87 (m, 8H, CH_2),

2.91 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 3.04 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 3.16 (br s, 6H, NH_2), 3.72 (t, J=7.2 Hz, 4H, $ArOCH_2$), 3.81 (t, J=7.5 Hz, 2H, $ArOCH_2$), 3.90 (t, J=7.5 Hz, 2H, $ArOCH_2$), 4.29 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 4.38 (d, J=13.2 Hz, 2H, $ArCH_2Ar$), 5.89—6.19 (m, 6H, ArH), 6.72—6.84 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1, 19.3, 19.4, 31.1, 32.3, 74.8, 115.5, 115.9, 121.5, 128.2, 135.5, 135.9, 139.9, 140.2, 150.1, 157.0; IR (KBr) v: 3421, 3357, 2958, 2930, 2871, 1607, 1541, 1467, 1380, 1305, 1284, 1214, 1160, 1131, 1069, 1034, 1003, 985, 964, 910, 851, 804, 763, 731, 714 cm^{-1}; ESI-MS m/z (%): 694 ($[M+1]^+$, 56), 716 ($[M+Na]^+$, 100), 1387 ($[2M+1]^+$, 62). Anal. calcd for $C_{44}H_{59}N_3O_4 \cdot H_2O$: C 74.23, H 8.64, N 5.90; found C 74.52, H 8.91, N 5.68.

5,11,17,23-Tetramino-25,26,27,28-tetrabutoxycalix-[4]arene (**3e**): Grey solid; m.p. 221—223 ℃; ^1H NMR ($CDCl_3$, 300 MHz) δ: 0.96 (t, J=7.2 Hz, 12H, CH_3), 1.34—1.46 (m, 8H, CH_2), 1.78—1.88 (m, 8H, CH_2), 2.92 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 3.01 (br s, 8H, NH_2), 3.76 (t, J=7.5 Hz, 8H, $ArOCH_2$), 4.31 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 6.07 (s, 8H, ArH).

Results and discussion

Alkylated calix[4]arene has usually been used in the direct nitration of free *para* positions and in the replacement of *tert*-butyl groups via ipso aromatic nitration, as alkylation can avoid oxidation of the phenolic hydroxyl groups by nitric acid to form quinones.[8a] However, it is not easy to control the selective nitration of 25,26,27,28-tetrabutoxycalix[4]arene (**1**) at the upper rim in a one pot process to form pure nitrocalix[4]arenes **2a—2e** respectively. Normally, five species **2a—2e** (Scheme 1) might be formed when **1** was directly nitrated by a mixture of 65% nitric acid with acetic acid. All the reaction conditions including the reaction time, amount of acid, and temperature could affect the nitration process of calix[4]arene. Moreover, careful control of the temperature is a vital factor for the nitration of calix[4]arene: high temperatures can enhance the oxidation product, and low temperatures can decrease the reaction speed or even not trigger the reaction. Here, the reaction was performed at 30 ℃.

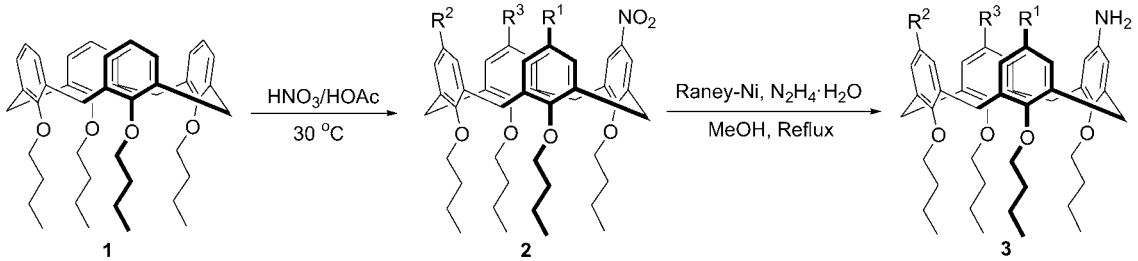
Calix[4]arene **1** (1.0 g, 1.5 mmol) was nitrated by a mixture of 65% nitric acid (15 mL, 217 mmol) and acetic acid (10 mL) in dichloromethane (100 mL) at 30 ℃. The change of the distribution of products during the reaction was detected by HPLC. As shown in Figure 1, the substrate **1** disappeared after 45 min reaction, and the products **2a—2d** were formed in the highest yield at 25, 35, 38 and 124 min, and then disappeared at 50, 75, 242 and 1200 min, respectively. After 1200 min, **2e** was the unique nitrated product. This experiment shows the course of product alternation from **2a** to **2e**, which allows us to select the optimal nitration time for a given product. Table 1 clearly shows the time and amount of each nitrated product at its maximum concentration, which clearly confirms that **2a—2e** can be prepared in their optimal yield provided that the reaction is stopped at 25, 35, 38, 124 and 1200 min, respectively. It seems that the nitration reaction is much faster than what could be expected on the basis of earlier studies.[4a,9,10] As a

Table 1 Distribution of products detected by HPLC during the nitration of calix[4]arene **1** to show the maximal concentrations observed for a given compound

Time/min	Distribution of product/%					
	1	**2a**	**2b**	**2c**	**2d**	**2e**
0	100[a]	0	0	0	0	0
25	45	38[a]	2	10	5	0
35	8	9	11[a]	50	22	0
38	4	5	10	54[a]	27	0
124	0	0	0	9	81[a]	0
1200	0	0	0	0	0	100[a]

[a] The numbers represent the maximal concentrations observed for a given compound.

Scheme 1 Nitration and reduction of calix[4]arene **1**



a: $R^1 = R^2 = R^3 = H$
b: $R^1 = NO_2$, $R^2 = R^3 = H$
c: $R^1 = R^3 = H$, $R^2 = NO_2$
d: $R^1 = R^2 = NO_2$, $R^3 = H$
e: $R^1 = R^2 = R^3 = NO_2$

a: $R^1 = R^2 = R^3 = H$
b: $R^1 = NH_2$, $R^2 = R^3 = H$
c: $R^1 = R^3 = H$, $R^2 = NH_2$
d: $R^1 = R^2 = NH_2$, $R^3 = H$
e: $R^1 = R^2 = R^3 = NH_2$

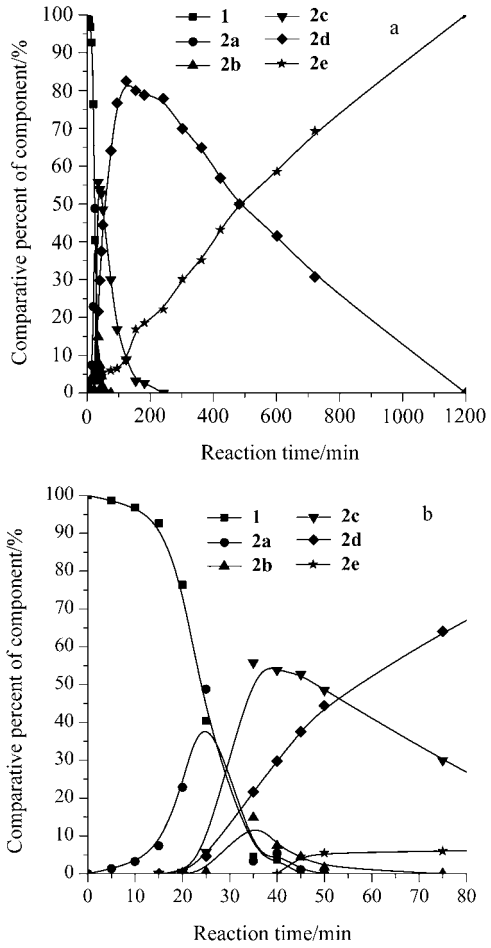


Figure 1 Distribution of products detected by HPLC during the nitration of calix[4]arene **1** between 0 and 1200 min.

result, 5,11,17-trinitro-25,26,27,28-tetrabutoxycalix[4]-arene **2d**, which was hardly isolated before, could be obtained in 57% isolated yield after the reaction was quenched with water at 124 min. It seems that the 3 day reaction time for synthesis of the trinitrocalix[4]arene[9] is not necessary in our condition. Furthermore, when the reaction was quenched at 35 min, the comparative percent of product **2b** was only 11% while those of **1**, **2a**, **2c** and **2d** were 8%, 9%, 50% and 22% respectively, which indicates that **2c** is the main product followed by **2d** but not **2b** at this time. It indicates that the nitration process does not proceed by stepwise introduction of the nitro groups.

The selectively nitrated products can be easily differentiated by ^{1}H NMR spectroscopy, since the numbers of residual aryl protons are different according to each product except for the two dinitrocalix[4]arenes (**2b** and **2c**), which have the same numbers of protons and nitro groups. In order to further distinguish them, the patterns of the methylene protons are very useful as they reflect the symmetry properties of the compounds. They appear as a pair of doublets with geminal coupling for C_{4v}- and C_{2v}-symmetrical compounds **2e** and **2c**, while two pairs of doublets are seen for the C_s-symmetrical compounds **2a** and **2d**, and three pairs of doublets for **2b**.[9] As illustrated in Figure 2, the symmetry of 5,17-dinitrocalix[4]-arene (**2c**) is C_{2v} because it possesses two symmetry planes (σ mirror) as well as a C_2 symmetric axis, while the symmetry of 5,11-dinitrocalix[4]arene (**2b**) which has only one σ mirror, is reduced to C_s. This difference is definitely shown by their ^{1}H NMR spectra (Figure 3) using the protons of the bridging methylene (4× *exo*-ArC**H**HAr and 4×*endo*-ArCH**H**Ar) as probes. In **2c**, the four *endo*-H and the four *exo*-H are in the same chemical environment respectively, and appear as a pair of equal doublets,[1b,11] while three pairs of doublets with a ratio 1∶2∶1 in each group are found in **2b**. Furthermore, the symmetries of **2a** and **2d** are both C_s (only one σ mirror), which means that two pairs of doublets will be observed, while **2e** shows a pair of equal doublets because its symmetry is C_{4v} (four σ mirrors and a C_4 symmetric axis).

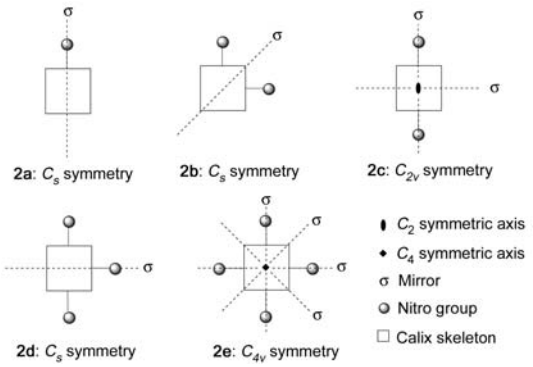


Figure 2 Symmetry of the nitrocalix[4]arenes **2a**—**2e**.

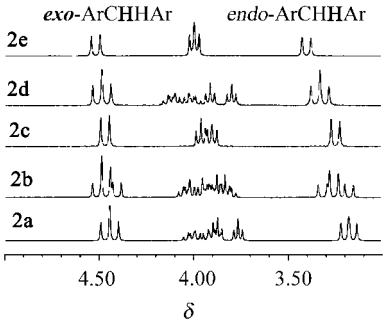


Figure 3 ^{1}H NMR patterns of the methylene protons of nitrocalix[4]arenes **2a**—**2e** ($CDCl_3$, 300 MHz).

In order to further confirm the substitution pattern of **2b**, its structure was characterized by X-ray crystallography.[12] High-quality single crystals of 5,11-dinitro-25,26,27,28-tetrabutoxycalix[4]arene (**2b**) suitable for X-ray crystallography were obtained by slow evaporation of its MeOH/CH_2Cl_2 (V∶V=10∶1) solution. The X-ray structure of **2b** (Figure 4) definitely shows that the two nitro groups were added onto the adjacent phenyl of the calix[4]arene and that the cone conformation was preserved by the four butoxy groups.

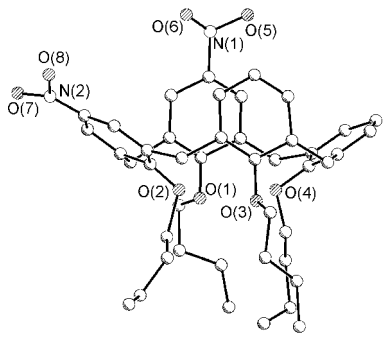


Figure 4 X-ray structure of **2b** (hydrogen atoms were omitted for clarity).

It is interesting to note that mixed crystals of **2d** and **2e** were obtained from the mother liquid by slow evaporation of its MeOH/CH_2Cl_2 (V ∶ V=10 ∶ 1) solution during the course of recrystallization of impure trinitrocalix[4]arene **2d**. The X-ray structure (Figure 5)[13] shows that compounds **2d** and tetranitrocalix[4]arene **2e** crystallize in the space group *P*-1 as three independent nitrocalix[4]arene **A**, **B** and **C**, and that all of them adopt a distorted cone conformation. Although **A** and **B** have the same molecular formula for **2d**, the distance of two opposite nitro groups in **A** [N(1)—N(3)] is 3.533 Å, whereas it is 12.559 Å in **B** [N(4)—N(6)].

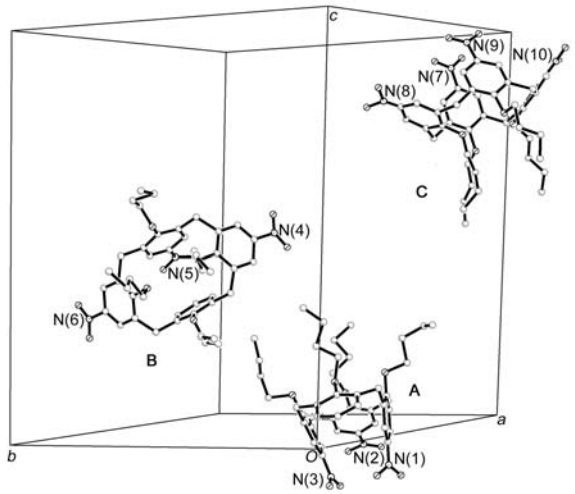


Figure 5 View of the unit cell of the X-ray crystal structure of trinitrocalix[4]arene **2d** (**A** and **B**) with tetranitrocalix[4]arene **2e** (**C**). Hydrogen atoms and solvent molecules are omitted for clarity.

Nitrocalix[4]arenes are often converted to aminocalix[4]arenes, which are important starting materials for molecular receptors based on calixarenes. The reactions use either Raney-Ni/NH_2NH_2,[5e,14] $SnCl_2$•$2H_2O$[8c,15] or H_2-Pd/C.[3] Herein, all nitrocalix[4]arenes **2** were conveniently and quantitatively reduced by Raney nickel and hydrazine hydrate in refluxing methanol to form the corresponding aminocalix[4]arenes **3** respectively (Scheme 1).

Conclusion

In conclusion, the study has determined in a clear cut manner what reaction time should be used in a selective nitration reaction of calix[4]arene at the upper rim in a one pot process to obtain a given substitution pattern by monitoring the distribution of products by HPLC. The distinction among the five nitrated products was established by ^{1}H NMR analysis, using molecular symmetry properties. As a result, unusual 5,11,17-trinitro-25,26,27,28-tetrabutoxycalix[4]arene **2d** was obtained in an acceptable yield (57%), and the structures of 5,11-dinitro-25,26,27,28-tetrabutoxycalix[4]arene **2b** and trinitrocalix[4]arene **2d** with tetranitrocalix[4]arene **2e** were further confirmed by single crystal X-ray diffraction analysis. This work has presented an efficient way to prepare various important nitrocalix[4]arenes in relatively high yield and short reaction time, which has led to substantial improvement of the literature conditions.

Achnowledgement

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12 X-ray crystal data for **2b**. CCDC 703837; empirical formula: $C_{44}H_{54}N_2O_8$; formula weight: 738.89; crystal color: yellow; crystal dimensions: 0.30 mm×0.26 mm×0.24 mm; crystal system: monoclinic; lattice parameter: a=17.573(3) Å, b=18.503(2) Å, c=25.893(4) Å; β=94.907(3)°; V=8388(2) Å^3; space group: $P21/c$; Z=8; D_c=1.170 g/cm^3; F_{000}=3168; diffractometer: Bruker Smart Apex CCD area detector; residuals: R_1=0.0958, wR_2=0.1079. CCDC 703837 contains the supplementary crystallographic data for **2b** has been deposited at the Cambridge Crystallographic Data Centre. Copies of available material can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; email: deposit@ccdc.cam.ac.uk].

13 X-ray crystal data for **2d** and **2e**. CCDC 710215; empirical formula: $C_{132}H_{162}N_{10}O_{34}$; formula weight: 2432.72; crystal color: yellow; crystal dimensions: 0.30 mm×0.26 mm ×0.24 mm; crystal system: triclinic; lattice parameter: a=16.979(11) Å, b=18.535(11) Å, c=23.93(2) Å; α=94.465(11)°, β=91.639(11)°, γ=115.571(8)°; V=6756(8) Å^3; space group: P-1; Z=2; D_c=1.196 g/cm^3; F_{000}=2592; diffractometer: Bruker Smart Apex CCD area detector; residuals: R_1=0.0531, wR_2=0.1146. CCDC 710215 contains the supplementary crystallographic data for **2d** and **2e** has been deposited at the Cambridge Crystallographic Data Centre. Copies of available material can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; email: deposit@ccdc.cam. ac. uk].

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