Selective ipso-nitration of *tert*-butylcalix[4]arene 1,3-diethers: X-ray structure of an unexpected side product

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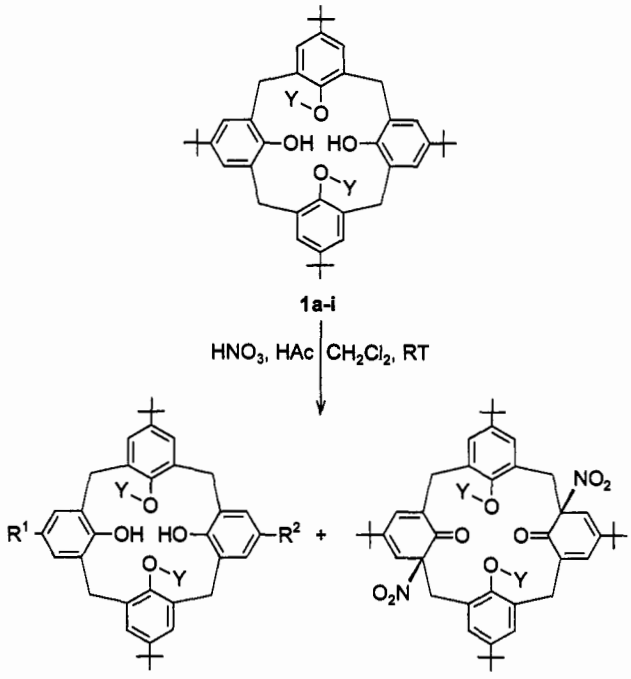
1,3-Diether derivatives of *tert*-butylcalix[4]arene can be selectively nitrated at the *para*-position of the phenolic units. In this way calix[4]arenes bearing *tert*-butyl and nitro groups at the upper rim in alternating sequence are easily available in yields up to 75%. Ipso-attack may also occur *ortho* to the phenolic hydroxy group leading in a side reaction to macrocyclic compounds with two 6-nitrocyclohexa-2,4-dienone units. Both types of structures were established by single crystal X-ray analysis.

Introduction

The selective functionalization of calixarenes is a topic of current interest and has led to these macrocyclic molecules being available as building blocks for the construction of larger molecules or molecular assemblies. Although numerous selectively functionalized calix[4]arenes bearing various substituents at the upper or lower rim have been described,[1,2] and although recent trends allow selective derivatives of calix[6]-,[3] calix[8]-[4] and to a lesser extent, calix[5]-arenes to be prepared,[5] simple and reliable procedures are often still lacking for calix[4]arenes. Selective substitutions at the upper rim mostly start with calixarenes selectively substituted at the lower rim, using the different reactivities of the phenol and phenol ether (or ester) units in electrophilic substitutions. Calix[4]arenes, selectively substituted by nitro groups have been mainly prepared by nitration of 1,3-diether derivatives.[6] To our knowledge, selective ipso-nitration of partial ethers has only been described for two diethers of *tert*-butylcalix[4]arene,[7] with low to reasonable yields of 24 and 46%. However, in a very recent paper the ipso-nitration of partial ethers of *tert*-butyl calix[6]arene has been decribed in better yields.[8] Since various tetra- or penta-nitro calix[4]- or calix[5]-arene ethers are easily available on a larger scale in excellent yields,[9] we wondered if simple conditions could also be found for the selective introduction of nitro groups by ipso-nitration.



Results and discussion

Synthesis

1,3-Diether derivatives of calix[4]arenes **1**, with a *syn*-arrangement of the alkoxy groups are easily available in high yield.[1,2] By a more or less systematic variation of the reaction conditions we have developed a procedure to convert them easily into dinitro derivatives **2**.

To a methylene dichloride solution of the 1,3-diether derivatives **1** was added with vigorous stirring at room temperature an excess of a mixture of concentrated nitric acid and glacial acetic acid (in the case of **1h** only concentrated nitric acid was used). After a relatively short reaction time (a few seconds to some minutes) the reaction mixture was quenched with water and the desired products **2** could be isolated by precipitation with methanol (ethanol in case of **2h**). Following this method the ipso-nitration products could be obtained in yields up to 75% with the exception of **2h** (32%) and **2i** (34%). In the latter case this is probably due to partial cleavage of the benzyl ether structures. The symmetrical (C_{2v}) structure of **2** is easily deduced from its ^{1}H NMR spectra, showing one singlet for *tert*-butyl-, one pair of doublets for $ArCH_2Ar$-, two singlets for ArH- and one singlet for OH-protons. A single set of signals was also observed for the alkoxy residue R. While this would, in principle, also be compatible with a structure in which the phenol ether units are nitrated, the lowfield signal (*e.g.* 9.39 ppm for **2e** in $CDCl_3$) for the OH protons suggested the presence of *p*-nitrophenol units rather than *p*-*tert*-butylphenol units. This was unambiguously established by a bathochromic shift of the long wavelength UV/vis absorption band under alkaline conditions due to the formation of *p*-nitrophenolate units. We further established the structure of calixarenes of type **2** by a single-crystal X-ray analysis of **2e** as shown in Fig. 1.

We also obtained other crystals which formed readily from the mother liquor (CH_2Cl_2–MeOH) of **2e**. Surprisingly, these

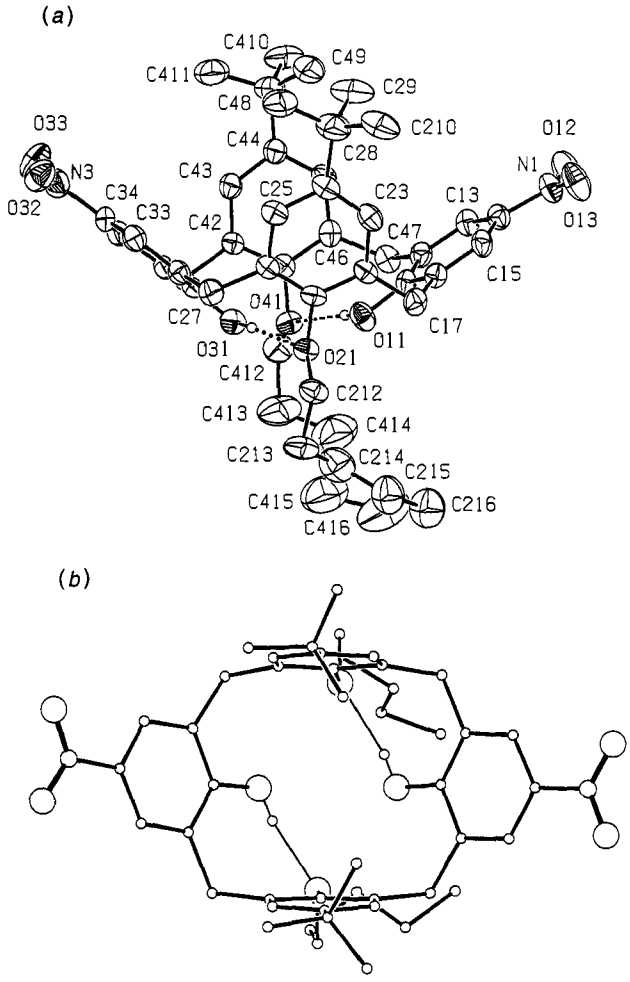


Fig. 1 (*a*) A view of molecule **2e** with numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Only the hydroxyl H atoms are shown and in each case only one of the two possible disordered orientations of the *tert*-butyl groups and side chain is shown. (*b*) A 'top-view' of **2e** with atoms shown as spheres of an arbitrary size.

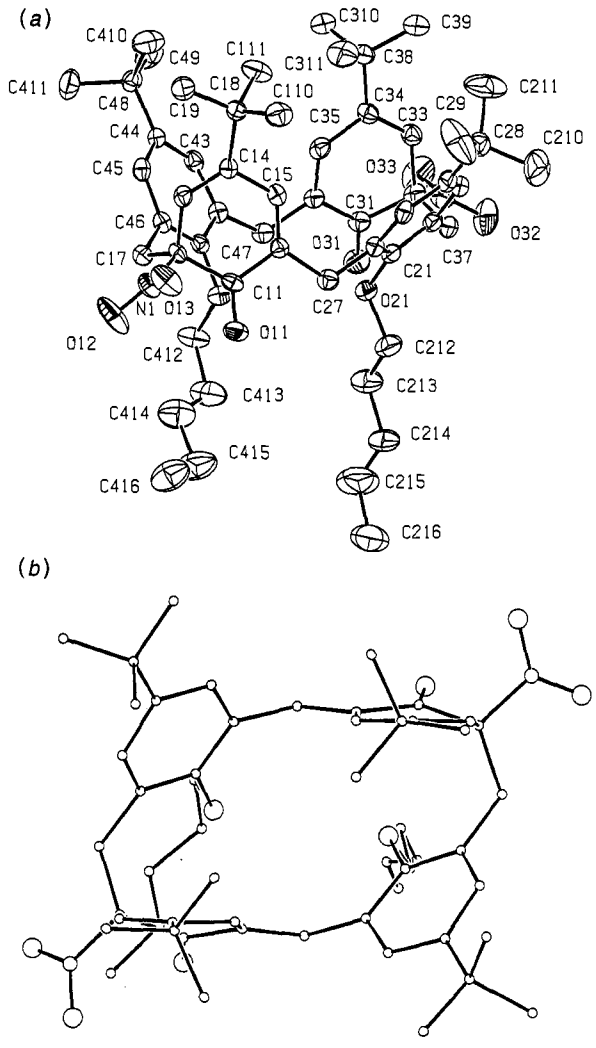


Fig. 2 (*a*) A view of molecule **3e** with numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Only one of the two possible disordered orientations of the *tert*-butyl groups is shown. (*b*) A 'top-view' of **3e** with atoms shown as spheres of an arbitrary size.

crystals proved to be the bis(6-nitrocyclohexa-2,4-dienone) derivative **3e** as shown in Fig. 2. Subsequent mass spectrometry and NMR studies of **3e** were, of course, entirely in accord with the X-ray structure; the ^{1}H NMR spectrum shows two singlets for *tert*-butyl groups (0.83 and 1.21 ppm), two pairs of doublets for methylene protons (3.27/4.16 and 3.26/3.83 ppm with geminal coupling, 19 and 12.5 Hz), a pair of doublets for the protons in the cyclohexadienone units (5.95/6.05 ppm, 1.8 Hz) and in the aromatic units (6.86/6.96 ppm, 2.2 Hz). The *O*-alkyl groups appear as a single set of signals while no signals for OH groups are found. A spectroscopically identical compound **3d** was also isolated reproducibly in similar yields from the mother liquor of **2d** and the formation of analogous compounds **3** was shown by TLC in other cases. Compounds of type **3** are obviously formed by ipso-attack of the nitrating agent (most likely the NO_2^+-cation) at the bridges and subsequent stabilisation by deprotonation of the hydroxy groups. There is no indication of the formation of other stereo- or regio-isomers. Obviously the structure of the macro ring, which is conformationally restricted also by the *syn*-position of the two alkoxy groups favours the regio- and stereo-chemical outcome of the reaction. It seems reasonable to assume that the NO_2^+ cation approaches the diether in its cone-conformation from outside the cavity. Inspection of molecular models suggests a more strained situation for the only alternative possibility under this assumption, the C_s symmetric regioisomer with the nitro groups pointing in the same direction. Such a compound was never detected in the reaction mixture although, for instance, the mononitro compound **4d** could be isolated in 2% yield.

It was not yet possible to show the chirality of compound **3** in solution, *e.g.* by splitting of peaks in the ^{1}H NMR spectrum in the presence of Pirkles reagent. Attempts to reduce the nitro groups (or the whole cyclohexadiene system) by hydrogenation have also been unsuccessful. Instead, the original diether **1** which obviously easily forms whenever the keto groups are protonated, was completely recovered. Thus, after addition of trifluoroacetic acid to a solution of **3** in $CDCl_3$ the ^{1}H NMR spectrum shows mainly the presence of **1**. Therefore, chromatographic isolation of **3** on silica gel was also impossible and, consequently chromatographic separation of the enantiomers seems at least difficult.

X-Ray structure analyses

Details of crystal data, structure solution and refinement details for **2e** and **3e** are concisely summarized in Table 1. For **2e** there was disorder of the *tert*-butyl methyl carbon atoms and C(215) in the pentyl chain; in **3e** there was disorder of the *tert*-butyl methyl carbon atoms at C(24). This was adequately allowed for in the refinement process with SHELXL93. Molecular dimensions for both **2e** and **3e** are in accord with expected values. Both compounds pack such as to give only normal van der Waals contacts between molecules. Full crystallographic data (coordinates, thermal parameters, dimensions, structure factors) have been deposited with the Cambridge Crystallo-

Table 1 Summary of crystal data, data collection, structure solution and refinement

	2e	**3e**
(a) Crystal Data		
Empirical formula	$C_{46}H_{58}N_2O_8$	$C_{54}H_{74}N_2O_8$
Molar mass	766.9	879.2
Colour, habit	Colourless, block	Pale yellow, block
Crystal size (mm)	0.42 × 0.29 × 0.28	0.41 × 0.27 × 0.22
Crystal system	Triclinic	Monoclinic
a/Å	12.208(2)	11.5677(15)
b/Å	12.424(2)	18.0871(15)
c/Å	15.175(2)	24.201(2)
α/°	92.528(10)	90
β/°	90.816(10)	90.544(12)
γ/°	101.789(12)	90
V/Å^3	2250.2(5)	5063.3(8)
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
$F(000)$	824	1904
d_{calc}/g cm^{-3}	1.132	1.153
μ/mm^{-1}	0.077	0.076
(b) Data acquisition[a]		
Temp (K)	294(1)	294(1)
Unit-cell reflections (θ-range°)	25 (8.2 14.9)	25 (8.5 17.3)
Max. θ (°) for reflections	24.9	26.9
hkl Range of reflections	−14 14; 0 14; −18 17	−14 14; 0 23; 0 30
Variation in 3 standard reflections	3.9%	1.6%
Reflections measured	7871	11 274
Unique reflections	7871	11 025
R_{int}	—	0.009
Reflections with $I > 2\sigma(I)$	2214	3496
(c) Structure Solution and Refinement		
Refinement on	F^2	F^2
Solution method	Direct methods	Direct methods
H-Atom treatment	Riding	Riding
No. of variables in L.S.	507	590
Weights: k in $w = 1/(\sigma^2F_o^2 + k)$ $[P = (F_o^2 + 2F_c^2)/3]$	$(0.0956P)^2$	$(0.0739P)^2$
R, R_w, *gof*	0.078, 0.221, 0.89	0.066, 0.177, 0.84
Density range in final Δ-map (e Å^{-3})	−0.317, 0.259	−0.270, 0.298
Final shift/error ratio	0.003	0.000

[a] Data collection on an Enraf-Nonius CAD4 diffractometer with graphite monochromatised Mo-Kα radiation (λ 0.710 67 Å). [b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.*, 1989, **22**, 384–389) for initial refinement with observed data on F, and with SHELXL-93 (G. M. Sheldrick, 1993) for final refinement with all data on F^2.

graphic Data Centre.† These data are also available in Crystallographic Information File (CIF) format as Supplementary Data and from the authors.

The conformation found for molecule **2e** is similar to that found for many calix[4]arenes,[10] with two aromatic rings in opposition almost parallel and two almost normal (Fig. 1). This conformation is such that it is not possible to have any solvent molecule enclathrated within the calix cup. Thus rings C(21)–C(26) and C(41)–C(46) (bearing the pentyl ether functions) form a dihedral angle of 13.5(3)°; the value for the C(11)–C(16) and C(31)–C(36) dihedral angle is 106.9(2)°. The interplanar angles which the plane of the bridging methylene carbon atoms [C(17), C(27), C(37), C(47)] make with planes of rings C(n1)–C(n6) (n = 1 to 4) are 145.3(2), 101.1(1), 141.6(2), 92.4(2)° respectively. This calix[4]arene conformation is largely determined by the presence of two intramolecular O–H···O hydrogen bonds between phenolic hydroxy groups and proximal ether O atoms; the hydroxy H atoms were clearly visible in difference maps and the O···O H-bond distances are O(11)···O(41) 2.838(5) Å and O(31)···O(21) 2.744(5) Å. The other non-bonded adjacent O···O distances are O(11)···O(21) 3.030(5) and O(31)···O(41) 3.133(5) Å.

† See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/13.

Isomer **3e** has approximate molecular but not crystallographic C_2 symmetry and is found in a distorted cone conformation (Fig. 2). The presence of an approximate two-fold axis (which implies that both asymmetric carbons have the same configuration) is also in accord with the ^{1}H NMR spectrum. The conformation found for molecule **3e** (Fig. 2) although a distorted cone is quite different from that found for **2e** (Fig. 1). Here the rings C(21)–C(26) and C(41)–C(46) (bearing the pentyl ether functions) form a dihedral angle of 72.5(1)°, while the corresponding value for the C(11)–C(16) and C(31)–C(36) dihedral angle is 9.5(1)°. The interplanar angles which the plane of the bridging methylene carbon atoms [C(17), C(27), C(37), C(47)] makes with the planes of rings C(n1)–C(n6) (n = 1 to 4) are 91.5(1), 129.5(1), 98.0(1) and 123(1)° respectively. Thus, the rings bearing the pentyl ether functions are almost normal in **3e** in contrast to those in **2e** where they are almost parallel. This shape is a result of deformation of the calix[4]arene brought about by the non-planarity of two systems each of which contains an sp^3 hybridized carbon atom. Thus, the oxygen atoms [O(11)–O(41)] form a distorted quadrangle with O···O···O angles of 46.0, 131.3, 47.2 and 135.4° and O···O separations of 3.16 [O(1)–O(2)], 5.00 [O(2)–O(3)], 3.20 [O(3)–O(4)] and 5.08 [O(4)–O(1)] Å. Therefore, the alkoxy groups are not in opposition and the phenol ether units can make larger angles with the bridging methylene atom plane. As in **2e**, this conformation is such that

it is not possible to have any solvent molecule enclathrated within the calix cup.

As expected, the carbon atoms of the individual dienone rings in **3e** are not co-planar. Each dienone ring is in a half-chair conformation, with C(11) and C(12) above and below the plane of C(13)–C(16) and C(31) and C(32) above and below the plane of C(33)–C(36). The carbonyl groups [C(11)=O(1), C(31)=O(3)] are bent outwards [torsion angles O(11)–C(11)–C(16)–N(1) −33.7(4)°, O(31)–C(31)–C(36)–N(3) −40.0(4)°]. Although an inward orientation of the C=O groups would lead to a larger O–C–C–N torsion angle and to a less strained macro ring, the repulsion between ether and carbonyl oxygens obviously favours the conformation found in the crystal. The shortest adjacent O···O intramolecular contacts are O(11)···O(41) 3.197(3) Å and O(31)···O(41) 3.162(3) Å. Larger O–C–C–N torsion angles would have had the effect of reducing these distances to unacceptable values. The O(11)···O(21) and O(31)···O(41) intramolecular distances are much longer [4.998 and 5.080(3) Å, respectively].

The orientations and conformations of the alkyl ether chains in both **2e** and **3e** are dictated to a large extent by crystal packing forces. In both compounds, the alkyl chains are essentially parallel with the C–C–C–C torsion angles close to gauche and *anti* values with the exception of C(212)–C(213)–C(214)–C(215) [91(1)° in **2e**, −132(1)° in **3e**].

Conclusion

Selective ipso-nitration of the *tert*-butyl phenol units in calix[4]arene 1,3-ethers is possible in a preparatively simple way by reaction with concentrated nitric acid. Yields of the easily available pure compounds are superior to the two examples described before. Ipso attack occurs also at the methylene bridges, but obviously the *tert*-butyl cation is a better 'leaving group', than a benzyl cation, a fact which is also reflected and frequently used in the easy de-(or trans-)-butylation of *tert*-butyl calix[4]arenes.[1,2] Thus, instead of a cleavage of the macro ring, the formation of 6-nitrocyclohexa-2,4-dienone units occurs. Under the nitration conditions this might well be a reversible process, which explains the good yield for the desired nitration products.

Experimental

Mps were determined with a Büchi melting point apparatus or with a MEL TEMP 2 capillary melting point apparatus and are uncorrected. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker AC200; ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AM400 Spectrometer. *J* Values are given in Hz. FD mass spectra were recorded with a Finningan MAT 90 (5 kV/10 mA/min) spectrometer. FT-IR spectra were recorded with a Nicolet 5DXC FT-IR spectrometer. Solvents were used in technical quality and distilled before use. All acids were used in p.a. quality as purchased by MERCK. Elemental analysis were performed at the microchemical laboratory, University of Mainz. The compounds **1a–i** were prepared according to the literature.[1,2,9]

General procedure for the preparation of 25,27-dialkyloxy-11,23-di-*tert*-butyl-26,28-dihydroxy-5,17-dinitrocalix[4]arenes 2a–i

To a vigorously stirred solution of compound **1** (2 mmol) in CH_2Cl_2 (50 ml) was added a mixture of concentrated nitric acid (6 ml, 62 mmol) and glacial acetic acid (6 ml). The colour of the reaction mixture immediately turned to dark purple or black. Over a period of time (a few seconds to some minutes) the colour of the mixture changed to yellow at which point it was diluted with water. The organic layer was washed several times with water, dried (Na_2SO_4), concentrated under reduced pressure and diluted with MeOH to precipitate **2**. The products thus obtained were always pure enough for subsequent reactions. If necessary for analytical purpose they could be purified by reprecipitation or recrystallisation (CH_2Cl_2–MeOH).

Compounds **3d** and **3e** were obtained as yellow crystals by slow evaporation of the solvent from the mother liquor of **2d** and **2e**.

11,23-Di-*tert*-butyl-26,28-dihydroxy-25,27-dimethoxy-5,17-dinitrocalix[4]arene 2a. A yellow solid (69%), mp > 350 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3200, 2960, 1515, 1332 and 1276; δ_H(200 MHz; $CDCl_3$) 0.99 [18 H, s, $C(CH_3)_3$], 3.49 (4 H, d, *J* 13.4, $ArCH_2Ar$, *eq*), 3.99 (6 H, s, OCH_3), 4.27 (4 H, d, *J* 13.4, $ArCH_2Ar$, *ax*), 6.87 (4 H, s, ArH), 8.06 (4 H, s, ArH) and 8.77 (2 H, s, OH); *m*/*z* (FD) 654.8 (M^+; 100%) (Found: C, 69.7; H, 6.4; N, 4.05. $C_{38}H_{42}N_2O_8$ requires C, 69.7; H, 6.5; N, 4.3%).

11,23-Di-*tert*-butyl-26,28-dihydroxy-5,17-dinitro-25,27-dipropoxycalix[4]arene 2b. A pale yellow solid (66%), mp > 320 °C (decomp.); δ_H(200 MHz; $CDCl_3$) 1.06 [18 H, s, $C(CH_3)_3$], 1.29 (6 H, t, *J* 7.4, CH_2CH_3), 2.12–2.01 (4 H, m, CH_2CH_3), 3.47 (4 H, d, *J* 13.2, $ArCH_2Ar$, *eq*), 3.98 (4 H, t, *J* 6.4, OCH_2), 4.28 (4 H, d, *J* 13.2, $ArCH_2Ar$, *ax*), 6.96 (4 H, s, ArH), 8.03 (4 H, s, ArH) and 9.47 (2 H, s, OH); *m*/*z* (FD) 710.9 (M^+; 100%) (Found: C, 70.75; H, 7.3; N, 4.1. $C_{42}H_{50}N_2O_8$ requires C, 71.0; H, 7.1; N, 3.9%).

11,23-Di-*tert*-butyl-26,28-dihydroxy-25,27-diisopropoxy-5,17-dinitrocalix[4]arene 2c. A pale yellow solid (70%), mp > 342 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3243, 2971, 1516, 1334 and 1105; δ_H(200 MHz; $CDCl_3$) 1.11 [18 H, s, $C(CH_3)_3$], 1.55 (12 H, d, *J* 6.1, $CHCH_3$), 3.45 (4 H, d, *J* 13.1, $ArCH_2Ar$, *eq*), 4.34 (4 H, d, *J* 13.1, $ArCH_2Ar$, *ax*), 4.45–4.26 (2 H, m, $CHCH_3$), 7.02 (4 H, s, ArH), 7.99 (4 H, s, ArH) and 9.53 (2 H, s, OH); δ_C(50 MHz; $CDCl_3$) 159.5, 148.2, 147.8, 139.8, 132.1, 128.8 (ArC), 126.1, 124.2 (ArCH), 79.3 ($ArCH_2Ar$), 34.2 (OCH_2), 32.0 [$C(CH_3)_3$], 31.1 [$C(CH_3)_3$] and 21.9 (CH_3); *m*/*z* (FD) 710.8 (M^+; 100%) (Found: C, 70.8; H, 7.1; N, 3.9. $C_{42}H_{50}N_2O_8$ requires C, 71.0; H, 7.1; N, 3.9%).

11,23-Di-*tert*-butyl-25,27-dibutoxy-26,28-dihydroxy-5,17-dinitrocalix[4]arene 2d. A pale white solid (68%), mp > 318 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3280, 2962, 1514, 1473, 1335 and 1259; δ_H(200 MHz; $CDCl_3$) 1.05 [18 H, s, $C(CH_3)_3$], 1.09 (6 H, t, *J* 7.4, CH_2CH_3), 1.83–1.64 (4 H, m, CH_2CH_3), 2.05 (4 H, p, *J* 6.7, OCH_2CH_2), 3.48 (4 H, d, *J* 13.2, $ArCH_2Ar$, *eq*), 4.02 (4 H, t, *J* 6.5, OCH_2), 4.27 (4 H, d, *J* 13.2, $ArCH_2Ar$, *ax*), 6.96 (4 H, s, ArH), 8.03 (4 H, s, ArH) and 9.43 (2 H, s, OH); *m*/*z* (FD) 739.0 (M^+; 100%) (Found: C, 71.3; H, 7.5; N, 3.7. $C_{44}H_{54}N_2O_8$ requires C, 71.5; H, 7.4; N, 3.8%).

Cyclohexadienone derivative 3d. Yellow crystals (8%), mp 182–183 °C (decomp); δ_H(200 MHz; $CDCl_3$) 0.85 [18 H, s, $C(CH_3)_3$], 0.99 (6 H, t, *J* 7.2, CH_2CH_3), 1.23 [18 H, s, $C(CH_3)_3$], 1.51–1.31 (4 H, m, CH_2CH_3), 1.95–1.79 (4 H, m, OCH_2CH_2), 3.28 (2 H, d, *J* 12.1, $ArCH_2Ar$), 3.31 (2 H, d, *J* 18.9, CH_2Ar), 3.57–3.44 (2 H, m, OCH_2), 3.89–3.81 (2 H, m, OCH_2), 3.87 (2 H, d, *J* 12.5, $ArCH_2Ar$), 4.19 (2 H, d, *J* 19.4, CH_2Ar), 5.96 (2 H, d, *J* 1.1), 6.09 (2 H, s br), 6.88 (2 H, d, *J* 2.3, ArH) and 6.98 (2 H, d, *J* 1.9, ArH); *m*/*z* (FD) 851.5 (M^+; 0.7%) (Found: C, 73.6; H, 8.1; N, 3.15. $C_{52}H_{70}N_2O_8$ requires C, 73.4; H, 8.3; N, 3.3%).

11,23-Di-*tert*-butyl-26,28-dihydroxy-5,17-dinitro-25,27-dipentyloxycalix[4]arene 2e. A yellow solid (76%), mp 285–287 °C (decomp.); δ_H(200 MHz; $CDCl_3$) 0.99 (6 H, t, *J* 7.0, CH_2CH_3), 1.05 [18 H, s, $C(CH_3)_3$], 1.74–1.35 [8 H, m, $(CH_2)_2CH_3$], 2.07 (4 H, p, *J* 6.9, OCH_2CH_2), 3.45 (4 H, d, *J* 13.0, $ArCH_2Ar$, *eq*), 4.01 (8 H, t, *J* 7.0, OCH_2), 4.28 (4 H, d, *J* 13.0, $ArCH_2Ar$, *ax*), 6.95 (4 H, s, ArH), 8.03 (4 H, s, ArH) and 9.39 (2 H, s, OH); *m*/*z* (FD) 766.8 (M^+; 100%).

Cyclohexadienone derivative 3e. Yellow crystals (12%), mp 182 °C (decomp.); ν_{max}(KBr)/cm^{-1} 2963, 2871, 1686, 1558 and 1547; δ_H(400 MHz; $CDCl_3$) 0.826 [18 H, s, $C(CH_3)_3$], 0.92 (6 H,

t, J 7.2, CH_2CH_3), 1.206 [18 H, s, $C(CH_3)_3$], 1.407–1.194 [8 H, m, $(CH_2)_2CH_3$], 1.976–1.762 (4 H, m, OCH_2CH_2), 3.264 (2 H, d, J 12.5, $ArCH_2Ar$, *eq*), 3.274 (2 H, d, J 19.3, CH_2Ar, *eq*), 3.487–3.422 (2 H, m, OCH_2), 3.873–3.813 (2 H, m, OCH_2), 3.829 (2 H, d, J 12.6, $ArCH_2Ar$, *ax*), 4.159 (2 H, d, J 18.7, CH_2Ar, *ax*), 5.946 (2 H, d, J 1.8), 6.052 (2 H, d, J 1.5), 6.863 (2 H, d, J 2.3, ArH), 6.955 (2 H, d, J 2.2, ArH); δ_C(100 MHz; $CDCl_3$) 194.2 (CO), 155.4, 145.7, 144.9, 136.5 (ArC or C), 134.4, 129.2, 129.1 (ArCH or CH), 128.3, 125.9 (ArC or C), 122.8 (ArCH or CH), 96.7 ($ArCH_2$), 76.4 ($ArCH_2Ar$), 41.3, 34.1 (CH_2 or C), 31.5 [$C(CH_3)_3$], 29.5 (CH_2 or C), 28.7 [$C(CH_3)_3$], 27.8, 29.9, 22.6 (CH_2) and 14.1 (CH_3); *m/z* (FD) 879.3 (M^+; 0.3%) (Found: C, 73.5; H, 8.2; N, 3.1. $C_{54}H_{74}N_2O_8$ requires C, 73.7; H, 8.5; N, 3.2%).

11,23-Di-*tert*-butyl-25,27-dihexyloxy-26,28-dihydroxy-5,17-dinitrocalix[4]arene 2f. A white solid (67%), mp 229–231 °C; δ_H(200 MHz; $CDCl_3$) 0.94 (6 H, t, J 6.7, CH_2CH_3), 1.04 [18 H, s, $C(CH_3)_3$], 1.49–1.34 [8 H, m, $(CH_2)_2CH_3$], 1.73–1.59 [4 H, m, $O(CH_2)_2CH_2$], 2.06 (4 H, p, J 6.9, OCH_2CH_2), 3.46 (4 H, d, J 13.2, $ArCH_2Ar$, *eq*), 4.01 (4 H, t, J 6.7, OCH_2), 4.27 (4 H, d, J 13.2, $ArCH_2Ar$, *ax*), 6.95 (4 H, s, ArH), 8.03 (4 H, s, ArH) and 9.38 (2 H, s, OH); δ_C(100 MHz; $CDCl_3$) 159.5, 149.8, 148.4, 139.8, 131.2, 128.7 (ArC), 126.1, 124.3 (ArCH), 77.0 ($ArCH_2Ar$), 34.1 (OCH_2), 31.6, 31.5 (C_q and CH_2), 31.1 [$C(CH_3)_3$], 29.9, 25.5, 22.5 (CH_2) and 13.9 (CH_3); *m/z* (FD) 794.8 (M^+; 100%) (Found: C, 72.1; H, 8.4; N, 3.5. $C_{48}H_{62}N_2O_8$ requires C, 72.5; H, 7.9; N, 3.5%).

11,23-Di-*tert*-butyl-25,27-didecyloxy-26,28-dihydroxy-5,17-dinitrocalix[4]arene 2g. A white solid (64%), mp 148–149 °C; δ_H(200 MHz; $CDCl_3$) 0.86 (6 H, m br, CH_2CH_3), 1.06 [18 H, s, $C(CH_3)_3$], 1.76–1.18 [28 H, m br, $(CH_2)_7CH_3$], 2.05 (4 H, p, J 6.8, OCH_2CH_2), 3.46 (4 H, d, J 13.2, $ArCH_2Ar$, *eq*), 4.01 (4 H, t, J 6.6, OCH_2), 4.27 (4 H, d, J 13.0, $ArCH_2Ar$, *ax*), 6.95 (4 H, s, ArH), 8.02 (4 H, s, ArH) and 9.43 (2 H, s, OH); *m/z* (FD) 907.4 (M^+; 100%) (Found: C, 74.25; H, 8.5; N, 3.25. $C_{56}H_{78}N_2O_8$ requires C, 74.1; H, 8.7; N, 3.1%).

11,23-Di-*tert*-butyl-25,27-bis(ethoxycarbonylmethoxy)-26,28-dihydroxy-5,17-dinitrocalix[4]arene 2h. Concentrated nitric acid was used without glacial acetic acid in this case and the product was precipitated with ethanol as a white solid (32%), mp 216–217 °C (lit.,[7] 198–200 °C); ν_{max}(KBr)/cm^{-1} 3349, 2963, 1751, 1515, 1336 and 1203; δ_H(200 MHz; $CDCl_3$) 1.12 [18 H, s, $C(CH_3)_3$], 1.37 (6 H, t, J 7.2, CH_2CH_3), 3.48 (4 H, d, J 13.2, $ArCH_2Ar$, eq), 4.35 (4 H, q, J 7.2, OCH_2), 4.48 (4 H, d, J 13.3, $ArCH_2Ar$, *ax*), 4.81 [4 H, s, $(C{=}O)CH_2$], 7.03 (4 H, s, ArH), 7.97 (4 H, s, ArH) and 8.98 (2 H, s, OH); δ_C(50 MHz; $CDCl_3$) 169.3 (CO) 158.9, 150.5, 149.1, 140.1, 131.7, 128.9 (ArC), 126.6, 124.5 (ArCH), 72.2 ($ArCH_2Ar$), 61.9 (OCH_2CO), 34.3 (OCH_2), 31.8 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$] and 14.2 (CH_3); *m/z* (FD) 798.4 (M^+; 100%).

25,27-Dibenzyloxy-11,23-di-*tert*-butyl-26,28-dihydroxy-5,17-dinitro[4]arene 2i. A yellow solid (34%), mp > 305 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3343, 2962, 1517 and 1336; δ_H(200 MHz; $CDCl_3$) 1.01 [18 H, s, $C(CH_3)_3$], 3.42 (4 H, d, J 13.5, $ArCH_2Ar$, *eq*), 4.24 (4 H, d, J 13.4, $ArCH_2Ar$, *ax*), 5.06 (4 H, s, OCH_2), 6.89 (4 H, s, ArH), 7.43–7.39 (6 H, m, ArH), 7.60–7.55 (4 H, m, ArH), 8.03 (4 H, s, ArH) and 8.86 (2 H, s, OH); δ_C(50 MHz; $CDCl_3$) 159.4, 149.5, 148.7, 139.7, 135.9, 131.0, 128.8, 128.6, 128.4, 127.5 (ArC and ArCH), 126.2, 124.2 (ArCH), 78.5 ($ArCH_2Ar$), 34.1 (OCH_2), 31.4 [$C(CH_3)_3$] and 31.0 [$C(CH_3)_3$]; *m/z* (FD) 807.0 (M^+; 100%) (Found: C, 74.3; H, 6.2; N, 3.4. $C_{50}H_{50}N_2O_8$ requires C, 74.4; H, 6.25; N, 3.5%).

11,17,23-Tri-*tert*-butyl-25,27-dibutoxy-26,28-dihydroxy-5-nitrocalix[4]arene 4d. A white solid (2%), mp 158–159 °C; δ_H(200 MHz; $CDCl_3$) 1.05 [18 H, s, $C(CH_3)_3$], 0.99–1.11 (6 H, m, CH_2CH_3), 1.24 [9 H, s, $C(CH_3)_3$], 1.65–1.83 (4 H, m, CH_2CH_3), 2.03 (4 H, p, J 6.5, OCH_2CH_2), 3.34 (2 H, d, J 12.9, $ArCH_2Ar$, *eq*), 3.43 (2 H, d, J 13.3, $ArCH_2Ar$, *eq*), 3.91–4.09 (4 H, m, OCH_2), 4.28 (4 H, d, J 12.9, $ArCH_2Ar$, *ax*), 6.86 (2 H, d, J 2.3, ArH), 6.97 (4 H, d, J 2.3, ArH), 7.03 (2 H, s, ArH), 7.95 (1 H, s, OH), 8.02 (2 H, s, ArH) and 9.56 (1 H, s, OH); *m/z* (FD) 749.8 (M^+; 100%) (Found: C, 76.75; H, 8.7; N, 2.05. $C_{48}H_{63}NO_6$ requires C, 76.9; H, 8.5; N, 1.9%).

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