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Isolation and X-Ray Crystal Structure of a Stable Calix[4]arene Monohemiketal

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Abstract. The formation of a stable calix[4]arene monohemiketal is described. X-ray crystallographic data provide conclusive evidence for the presence of a stabilizing hydrogen bond.

Key words: calix[4]arene, oxidation, hemiketal.

Supplementary Data. Lists of H-atom parameters and bond lengths and angles involving hydrogens have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 82159 (5 pp.).

1. Introduction

Calix[4]arenes have frequently been used as building blocks in supramolecular chemistry during the past ten years [1,2]. Functionalization at both the lower and the upper rim offers the opportunity for the synthesis of selective receptor molecules for ions and neutral molecules [3]. One of the possibilities for functionalization is the oxidation of calix[4]arenes to give calix[4]quinones [4–9]. Using ClO_2 or $Tl(OCOCF_3)_3$ as an oxidizing agent, the phenolic rings are effectively converted to 1,4-benzoquinone rings, even in the presence of *tert*-butyl groups. When the reaction is carried out on partially alkylated calix[4]arenes, only the phenolic rings are usually oxidized [3]. These bisquinones have recently been used for the synthesis of chiral calix[4]arenes via a 1,4-addition to the quinonoid system [4]. Biali and coworkers have shown that calix[4]monospirodienone can serve as a suitable intermediate for the conversion of a hydroxyl group in calix[4]arene to an amino group [10]. In this paper we report the synthesis of a calix[4]arene derivative (**1**), in which oxidation has taken place selectively on one of the alkylated rings, leading to a quinone mono*hemi*ketal. To the best of our knowledge, this type of hemiketal has never been observed before in calixarene chemistry.

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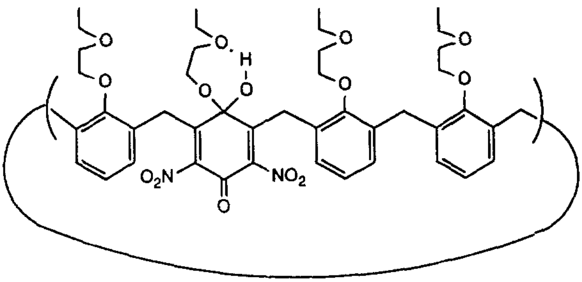

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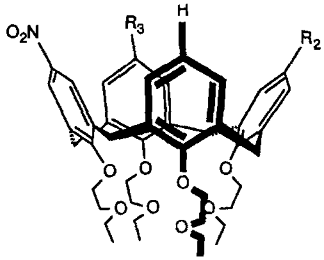


2 $R_1=R_2=H$
3 $R_1=H$, $R_2=NO_2$
4 $R_1=NO_2$, $R_2=H$

Fig. 1.

TABLE I. Crystallographic data.

Experimental	
Crystal data	
$C_{44}H_{54}N_2O_{14}$	$D_x = 1.311$ Mg m^{-3}
$M_r = 834.9$	Mo K_α radiation
monoclinic	$\lambda = 0.7107$ Å
$P2_1/n$	Cell parameters from 25 reflections
$a = 14.946(2)$ Å	$\theta = 7.0 - 15°$
$b = 12.681(2)$ Å	$\mu = 0.91$ cm^{-1}
$c = 23.304(3)$ Å	$T = 293(1)$K
$\beta = 106.65(2)°$	
$V = 4230$ Å	
$Z = 4$	
Data Collection	
Enraf-Nonius CAD4 single-crystal diffractometer	$\theta_{max} = 25.0°$
$\omega/2\theta$ scans	$h = -17 \rightarrow 17$
7424 measured reflections	$k = 0 \rightarrow 15$
3538 observed reflections	$l = 0 \rightarrow 27$
$[I > 3.0\sigma(\mathrm{I})]$	3 standard reflections, frequency 60 min. intensity decrease: 4.5%
Refinement	
Refinement on F_0	Most H-atoms treated as riding atoms
Final $R = 0.069$	Calculated weights
$wR = 0.080$	$w = 1/[\sigma^2(F)]$
$S = 2.34$	$(\Delta/\sigma)_{max} = 0.19$
3538 reflections	$\Delta\rho_{max} = 1.08$ e Å^{-3}
549 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}

2. Experimental

2.1. X-RAY STRUCTURE DETERMINATION

A small sample of **1** was recrystallized from MeOH and its crystal structure was determined by X-ray diffraction. The most important crystallographic data are collected in Table I. Data were collected in the $\omega/2\theta$ scan mode (scan width (ω): $1.10 + 0.34 \tan\theta$), using graphite monochromated MoK_α radiation. The intensity data were corrected for Lorentz and polarization effects and for long time scale variation. No absorption correction was applied. The structure was solved with MULTAN [11] and refined by full-matrix least-squares methods. Weights for each reflection in the refinement (on F) were $w = 4F_0^2/\sigma(F_0^2)$, $\sigma(F_0^2) = \sigma^2(I) + (pF_0^2)^2$; the value of the instability factor, p, was determined as 0.04. All calculations were done with SDP [12]. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography* [13]. Atomic parameters are given in Table II. Bond distances and angles are given in Table III. The atom numbering and structure determined are shown in Figure 2. The terminal atoms (O(314)...C(316)) of one of the ethoxyethyl side chains show rather large thermal motions indicating disorder. H-atoms (with the exception of the H-atoms of the disordered atoms) were placed in calculated positions and refined as riding atoms. The H-atom of O(217), the position of which is not determined by symmetry, was found from a difference Fourier synthesis. The position and thermal parameter (isotropic) of this atom were refined. All non H-atoms were refined with anisotropic thermal parameters. An isotropic extinction coefficient was also taken into account.

2.1.0. *25,26,27,28-Tetrakis(2-ethoxyethoxy)-28-hydroxy-2, 4-dinitropentacyclo [19,3,1,1^{3,7}, 1^{9,13}, 1^{15,19}]octacosa-1(25),3,6,9,11,13(27),15,17,19(26),21,23-undecaene-5-one*

*(**1**)*

The reaction was carried out following the procedure described in Ref. [15]. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2\EtOAc 98 : 2) to give **1** in 5% yield as a dark red solid. m.p. 147–149°C (MeOH). Mass spectrum (FAB, NBA, negative mode): m/z 833.0 (M–H$^+$, *calc.* 833.4). ^{1}H-NMR ($CDCl_3$): δ 7.09 (*d*, 2H, J = 7.3 Hz, ArH), 6.95 (*t*, 1H, J = 7.3 Hz, ArH), 6.52 and 5.98 (*d*, 4H, J = 7.1 Hz, ArH), 6.37 (*t*, 2H, J = 7.7 Hz, ArH), 4.30, 4.02 and 3.23, 3.10 (*ABq*, 8H, J = 13.8 and 13.9 Hz, ArCH$_2$Ar), 4.3–4.2 (*m*, 2H, ArOCH_2CH$_2$OCH$_2$CH$_3$), 4.0–3.3 (*m*, 22H, ArOCH_2CH_2OCH_2CH$_3$), 1.24, 1.13 and 1.10 (*t*, 12H, J = 7.0 Hz, ArOCH$_2$CH$_2$OCH$_2$CH_3). ^{13}C-NMR ($CDCl_3$): δ 168.5 (*s*, C = 0), 159.0, 158.1 (*s*, ArCOR), 153.5 [*s*, *C* = C(NO$_2$)], 146.0 [*s*, C = *C*(NO$_2$)], 136.6, 134.4 (*s*, Ar*C*CH$_2$), 130.0, 129.2 (*d*, ArCH), 126.7 (*s*, Ar*C*CH$_2$), 125.8, 123.8, 122.8 (*d*, ArCH), 94.7 [*s*, C(OH)(OR)], 77.7–64.4, 53.6

TABLE II. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms, with e.s.d.s in parentheses. $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Atom	x	y	z	B_{eq}
O(111)	0.6638(2)	0.2296(2)	0.3453(1)	2.19(7)
O(114)	0.5511(2)	0.2436(3)	0.4237(1)	3.11(8)
O(211)	0.8680(2)	0.3735(3)	0.3954(1)	2.39(8)
O(214)	0.8129(2)	0.3442(3)	0.5071(1)	3.31(9)
O(217)	0.9760(2)	0.3492(3)	0.4893(1)	3.14(8)
O(219)	0.9853(3)	−0.0155(3)	0.4012(2)	4.1(1)
O(220)	1.0896(3)	0.0121(3)	0.4861(2)	4.4(1)
O(221)	1.1905(2)	0.1604(3)	0.4425(2)	3.62(9)
O(223)	1.2456(3)	0.4162(4)	0.4519(2)	7.2(1)
O(224)	1.2186(2)	0.3438(4)	0.3659(2)	4.7(1)
O(311)	0.8584(2)	0.6089(3)	0.3344(2)	3.8(1)
O(314)	0.7472(3)	0.7547(4)	0.3703(2)	7.5(1)
O(411)	0.6747(2)	0.4602(3)	0.2691(1)	2.80(8)
O(414)	0.4785(2)	0.4761(3)	0.2776(2)	3.38(9)
N(218)	1.0344(3)	0.0429(4)	0.4394(2)	3.4(1)
N(222)	1.1977(3)	0.3651(4)	0.4115(2)	3.4(1)
C(1)	0.5906(3)	0.2721(4)	0.2194(2)	2.5(1)
C(2)	0.8510(3)	0.1599(4)	0.4021(2)	2.4(1)
C(3)	1.0231(3)	0.4907(4)	0.3867(2)	3.1(1)
C(4)	0.7577(4)	0.6080(4)	0.2076(3)	4.3(2)
C(11)	0.6837(3)	0.2191(4)	0.2476(2)	2.1(1)
C(12)	0.7189(3)	0.2038(4)	0.3089(2)	2.1(1)
C(13)	0.8102(3)	0.1673(4)	0.3345(2)	2.1(1)
C(14)	0.8621(3)	0.1381(4)	0.2965(2)	2.5(1)
C(15)	0.8267(3)	0.1463(4)	0.2354(2)	2.7(1)
C(16)	0.7385(3)	0.1886(4)	0.2113(2)	2.6(1)
C(21)	0.9467(3)	0.2096(4)	0.4187(2)	2.2(1)
C(22)	0.9525(3)	0.3296(4)	0.4268(2)	2.5(1)
C(23)	1.0340(3)	0.3791(4)	0.4098(2)	2.3(1)
C(24)	1.1100(3)	0.3217(4)	0.4187(2)	2.6(1)

(t, ArO*C*H_2*C*H_2O*C*H_2CH_3), 30.7, 26.8 (t, ArCH_2Ar), 15.2 (q, CH_3). *Anal. calcd.* for $C_{44}H_{54}N_2O_{14}$: C, 63.30; H, 6.52; N, 3.36. *Found*: C, 63.21; H, 6.68; N, 3.27.

3. Results and Discussion

Recently, we reported the nitration of tetrakis(2-ethoxyethoxy)calix[4]arene [15] to give the mononitro **2** and the dinitro derivatives **3** and **4** in 20% and 30–40% yield, respectively. However, by repeatedly carrying out this reaction, we were also able

TABLE II. (continued)

C(25)	1.1175(3)	0.2087(4)	0.4336(2)	2.5(1)
C(26)	1.0277(3)	0.1582(4)	0.4306(2)	2.5(1)
C(31)	0.9757(3)	0.4921(4)	0.3197(2)	2.5(1)
C(32)	0.8958(3)	0.5535(4)	0.2958(3)	3.2(1)
C(33)	0.8502(3)	0.5533(4)	0.2343(2)	3.2(1)
C(34)	0.8896(3)	0.4953(5)	0.1982(2)	3.6(1)
C(35)	0.9686(4)	0.4365(5)	0.2205(2)	3.7(1)
C(36)	1.0103(3)	0.4332(4)	0.2814(2)	3.1(1)
C(41)	0.6876(3)	0.5274(4)	0.1757(2)	3.1(1)
C(42)	0.6532(3)	0.4516(4)	0.2076(2)	2.6(1)
C(43)	0.6063(3)	0.3622(4)	0.1812(2)	2.4(1)
C(44)	0.5835(3)	0.3552(5)	0.1191(2)	3.2(1)
C(45)	0.6100(3)	0.4325(5)	0.0845(2)	3.9(1)
C(46)	0.6632(3)	0.5163(5)	0.1137(3)	4.0(1)
C(112)	0.6206(3)	0.1392(4)	0.3625(2)	3.5(1)
C(113)	0.5355(3)	0.1672(4)	0.3779(2)	3.7(1)
C(115)	0.4742(3)	0.2612(5)	0.4455(2)	3.5(1)
C(116)	0.4902(4)	0.3578(5)	0.4833(2)	4.1(1)
C(212)	0.8227(3)	0.4483(4)	0.4239(2)	3.2(1)
C(213)	0.7591(3)	0.3990(5)	0.4548(2)	3.4(1)
C(215)	0.7593(3)	0.2838(5)	0.5377(2)	4.2(2)
C(216)	0.8253(4)	0.2204(5)	0.5848(2)	4.0(1)
C(312)	0.8825(4)	0.7177(5)	0.3430(4)	7.4(2)
C(313)	0.8399(5)	0.7613(6)	0.3912(4)	9.8(3)
C(315)	0.6841(7)	0.7717(7)	0.4152(3)	10.1(3)
C(316)	0.6698(6)	0.8724(7)	0.4197(4)	10.0(3)
C(412)	0.6303(3)	0.5458(4)	0.2910(2)	3.3(1)
C(413)	0.5617(3)	0.5066(5)	0.3210(2)	3.8(1)
C(415)	0.4093(4)	0.4410(5)	0.3039(2)	4.2(1)
C(416)	0.3255(4)	0.4077(5)	0.2555(3)	4.3(2)
H(217)	0.9186(37)	0.17555(46)	0.0065(26)	7.6(17)

to isolate an additional crystalline product in a yield of 5% (not optimized). The structure determined by X-ray analysis (Figure 2), reveals the compound to be calix[4]arene monohemiketal **1**. The torsion angles ϕ and χ around the Ar–CH_2 bonds (around C(1); C(2); C(3); C(4)), as defined in Ref. [16], are 102.7(6)°, -51.1(6)°; 47.8(6)°, -100.0(6)°; 97.1(6)°, -53.6(6)°; 55.5(7)°, -100.9(6)°, respectively, indicating that this calix[4]arene is in the cone conformation. The aromatic rings (with the exception of the quinoid ring) are almost flat, with a small but significant boat-like distortion. The inter-planar angles found between the best plane fitted to the 'connecting' methylene C-atoms and the different rings are: 77.9°, 41.5°, 83.4° and 43.7°, respectively. The interplanar angles between opposite aromatic

TABLE III. Bond distances (Å) and angles (°) for the heavy atoms with e.s.d.s in parentheses.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O(111)	C(12)	1.380(6)	C(11)	C(12)	1.388(6)
O(111)	C(112)	1.427(6)	C(11)	C(16)	1.389(8)
O(114)	C(113)	1.410(6)	C(12)	C(13)	1.401(7)
O(114)	C(115)	1.401(7)	C(13)	C(14)	1.385(8)
O(211)	C(22)	1.382(5)	C(14)	C(15)	1.373(7)
O(211)	C(212)	1.435(7)	C(15)	C(16)	1.384(6)
O(214)	C(213)	1.433(6)	C(21)	C(22)	1.532(7)
O(214)	C(215)	1.436(7)	C(21)	C(26)	1.334(7)
O(217)	C(22)	1.419(6)	C(22)	C(23)	1.520(7)
O(219)	N(218)	1.227(5)	C(23)	C(24)	1.315(7)
O(220)	N(218)	1.225(5)	C(24)	C(25)	1.471(7)
O(221)	C(25)	1.217(6)	C(25)	C(26)	1.470(7)
O(223)	N(222)	1.198(6)	C(31)	C(32)	1.401(7)
O(224)	N(222)	1.220(6)	C(31)	C(36)	1.374(8)
O(311)	C(32)	1.379(7)	C(32)	C(33)	1.400(7)
O(311)	C(312)	1.426(7)	C(33)	C(34)	1.371(8)
O(314)	C(313)	1.335(9)	C(34)	C(35)	1.366(7)
O(314)	C(315)	1.62(1)	C(35)	C(36)	1.378(7)
O(411)	C(42)	1.380(6)	C(41)	C(42)	1.401(8)
O(411)	C(412)	1.439(7)	C(41)	C(46)	1.392(8)
O(414)	C(413)	1.414(5)	C(42)	C(43)	1.381(7)
O(414)	C(415)	1.416(7)	C(43)	C(44)	1.390(8)
N(218)	C(26)	1.477(7)	C(44)	C(45)	1.396(8)
N(222)	C(24)	1.475(7)	C(45)	C(46)	1.383(8)
C(1)	C(11)	1.516(6)	C(112)	C(113)	1.460(8)
C(1)	C(43)	1.508(7)	C(115)	C(116)	1.488(9)
C(2)	C(13)	1.521(6)	C(212)	C(213)	1.485(9)
C(2)	C(21)	1.507(6)	C(215)	C(216)	1.485(7)
C(3)	C(23)	1.506(7)	C(312)	C(313)	1.54(1)
C(3)	C(31)	1.517(7)	C(315)	C(316)	1.30(1)
C(4)	C(33)	1.513(7)	C(412)	C(413)	1.485(8)
C(4)	C(41)	1.499(8)	C(415)	C(416)	1.485(7)

rings are 18.9° and 95.8°, showing that the rings in the pair involving the partly saturated ring are almost perpendicular to each other, while the rings in the other pair are more parallel. The phenolic H(217) atom is involved in an intramolecular hydrogen bond to O(214) (distances: H(217)–O(217) 1.09(6)Å, H(217)...O(214) 1.60(6)Å, angle: O(217)–H(217)...O(214) 147(5)°).

The ^{1}H-NMR spectrum strongly suggests the structure in solution to be closely related to that in the solid state. The proton resonances of the ethoxyethyl chain

TABLE III. (continued)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(12)	O(111)	C(112)	112.3(4)	C(23)	C(24)	C(25)	125.5(5)
C(113)	O(114)	C(115)	114.1(4)	O(221)	C(25)	C(24)	122.3(5)
C(22)	O(211)	C(212)	120.1(3)	O(221)	C(25)	C(26)	123.5(5)
C(213)	O(214)	C(215)	115.1(3)	C(24)	C(25)	C(26)	113.9(4)
C(32)	O(311)	C(312)	116.9(5)	N(218)	C(26)	C(21)	122.3(5)
C(313)	O(314)	C(315)	119.7(6)	N(218)	C(26)	C(25)	113.6(4)
C(42)	O(411)	C(412)	115.8(4)	C(21)	C(26)	C(25)	124.2(5)
C(413)	O(414)	C(415)	112.1(4)	C(3)	C(31)	C(32)	120.6(5)
O(219)	N(218)	O(220)	124.2(5)	C(3)	C(31)	C(36)	120.7(4)
O(219)	N(218)	C(26)	119.6(4)	C(32)	C(31)	C(36)	118.7(5)
O(220)	N(218)	C(26)	116.2(4)	O(311)	C(32)	C(31)	118.9(5)
O(223)	N(222)	O(224)	124.1(5)	O(311)	C(32)	C(33)	120.0(4)
O(223)	N(222)	C(24)	117.6(5)	C(31)	C(32)	C(33)	121.1(5)
O(224)	N(222)	C(24)	118.4(4)	C(4)	C(33)	C(32)	122.7(5)
C(11)	C(1)	C(43)	108.2(5)	C(4)	C(33)	C(34)	119.8(5)
C(13)	C(2)	C(21)	108.1(5)	C(32)	C(33)	C(34)	117.5(4)
C(23)	C(3)	C(31)	110.6(5)	C(33)	C(34)	C(35)	122.4(5)
C(33)	C(4)	C(41)	108.5(4)	C(34)	C(35)	C(36)	119.7(5)
C(1)	C(11)	C(12)	122.6(5)	C(31)	C(36)	C(35)	120.7(5)
C(1)	C(11)	C(16)	119.3(4)	C(4)	C(41)	C(42)	121.0(5)
C(12)	C(11)	C(16)	118.2(5)	C(4)	C(41)	C(46)	121.6(5)
O(111)	C(12)	C(11)	118.8(4)	C(42)	C(41)	C(46)	117.0(5)
O(111)	C(12)	C(13)	119.8(5)	O(411)	C(42)	C(41)	119.0(4)
C(11)	C(12)	C(13)	121.3(5)	O(411)	C(42)	C(43)	117.8(5)
C(2)	C(13)	C(12)	120.9(5)	C(41)	C(42)	C(43)	122.9(5)
C(2)	C(13)	C(14)	120.9(4)	C(1)	C(43)	C(42)	120.2(4)
C(12)	C(13)	C(14)	118.2(5)	C(1)	C(43)	C(44)	122.2(4)
C(13)	C(14)	C(15)	121.5(4)	C(42)	C(43)	C(44)	117.3(5)
C(14)	C(15)	C(16)	119.3(6)	C(43)	C(44)	C(45)	122.0(5)
C(11)	C(16)	C(15)	121.3(5)	C(44)	C(45)	C(46)	118.2(5)
C(2)	C(21)	C(22)	117.6(5)	C(41)	C(46)	C(45)	122.1(6)
C(2)	C(21)	C(26)	126.0(5)	O(111)	C(112)	C(113)	111.7(4)
C(22)	C(21)	C(26)	116.3(4)	O(114)	C(113)	C(112)	112.7(4)
O(211)	C(22)	O(217)	113.2(4)	O(114)	C(115)	C(116)	109.7(4)
O(211)	C(22)	C(21)	108.9(4)	O(211)	C(212)	C(213)	113.5(4)
O(211)	C(22)	C(23)	112.0(5)	O(214)	C(213)	C(212)	109.6(4)
O(217)	C(22)	C(21)	106.7(4)	O(214)	C(215)	C(216)	108.0(5)
O(217)	C(22)	C(23)	102.3(3)	O(311)	C(312)	C(313)	108.0(6)
C(21)	C(22)	C(23)	113.6(4)	O(314)	C(313)	C(312)	108.3(6)
C(3)	C(23)	C(22)	118.0(4)	O(314)	C(315)	C(316)	108.9(8)
C(3)	C(23)	C(24)	125.2(5)	O(411)	C(412)	C(413)	111.5(4)
C(22)	C(23)	C(24)	116.9(5)	O(414)	C(413)	C(412)	109.8(4)
N(222)	C(24)	C(23)	122.1(5)	O(414)	C(415)	C(416)	108.8(4)
N(222)	C(24)	C(25)	112.3(4)				

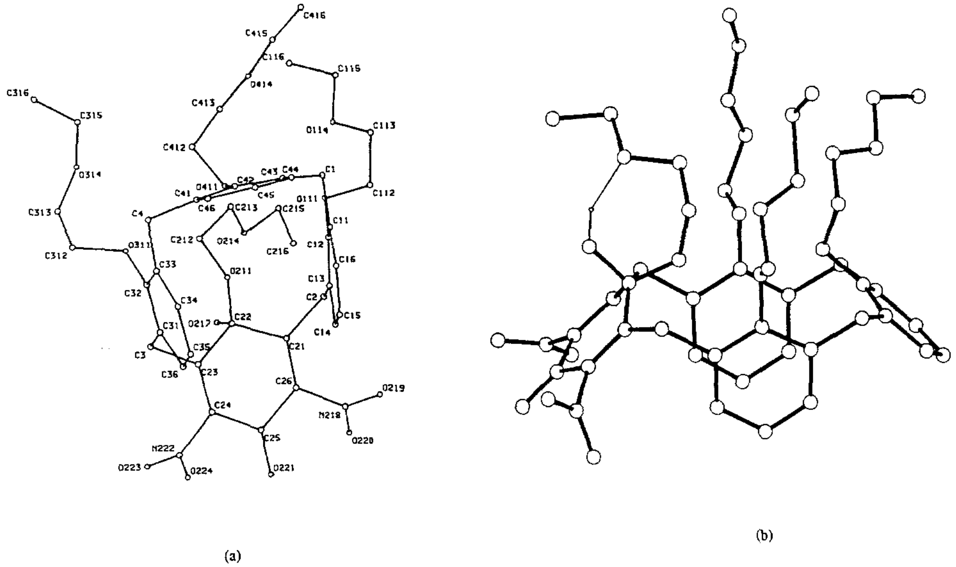
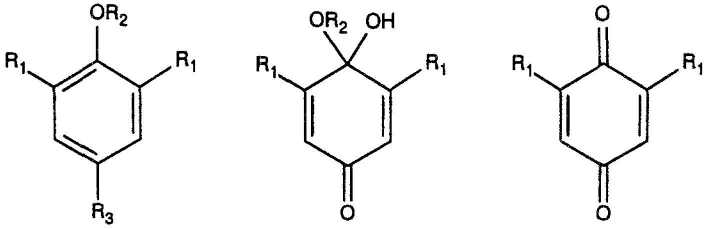


Fig. 2. View of the calix[4]arene monohemiketal **1** made by PLUTO [15]. (a) Atomic numbering; (b) molecular conformation.

of the partly saturated ring show a clear downfield shift, indicating that they are situated in a more shielded environment. Furthermore, the aromatic protons of the parallel rings are shifted upfield considerably, which is caused by the negative ring current effect of the perpendicular rings, which is in accordance with the structure in Figure 2.

An interesting aspect of the observed oxidation reaction is the possibility to yield two isomeric products. From the crystal structure it is evident that only one of the isomers is formed, i.e. the one with the hydroxyl group pointing out of the cavity and the 2-ethoxyethoxy chain pointing inwardly. No indication of the other diastereomer was found in the ^{1}H-NMR spectrum, not even in the mother liquor after crystallization. The oxidation reaction seems to be completely selective, probably because attack of the oxidizing species via the cavity of the calix[4]arene is far more hindered.

Apart from oxidation of one of the aromatic rings, a double nitration has occurred on this ring, as is evident from the crystal structure. Generally, the α-positions of a quinone are not activated for electrophilic attack, especially not under acidic conditions [17]. Therefore, it is likely that nitration has taken place in an intermediate stage of the oxidation process, i.e. when the aromatic ring is not yet fully oxidized. From the literature, it is known that oxidation of phenolic ethers (**5**) takes place via initial formation of a phenol (**6**). Because of the strong electron-releasing effect of the hydroxyl group, nitration seems to be most likely at this stage. The phenol is reoxidized to give monohemiketal **7**, which is normally rearranged to the corresponding quinone **8** [17]. However, in the case of **1**, the monohemiketal



5 R_3=H
6 R_3=OH

7

8

Fig. 3.

moiety seems to be stable under the strongly acidic reaction conditions. One of the reasons for this unusual stability certainly is the strong hydrogen bond (1.6 Å) between the free hydroxyl group and one of the etherial oxygens in the ethoxyethyl chain. In addition to this, the strong electron-withdrawing effect of the nitro groups can probably stabilize this intermediate to such an extent, that rearrangement to the corresponding quinone **8** is not observed here.

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