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Lower rim modification of calix[4]arenes to incorporate a single group functionality. Single crystal X-ray structures of 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene and 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene

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The compound 5-(3-Bromopropyl)-25,26,27,28-tetrahydroxycalix-[4]arene has been prepared by the anti-Markownikov addition of hydrogen bromide to 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene. The structure of the compound was established by a combination of ^1H, ^{13}C NMR and IR spectroscopy, and finally confirmed by single crystal X-ray crystallography. 5-(3-Bromopropyl)-25,26,27,28-tetra-hydroxycalix[4]arene crystallizes in a monoclinic $P2_1/n$ space group with $a = 12.4127(9)$ Å, $b = 20.754(4)$ Å, $c = 19.751(3)$ Å, $\beta = 97.524(8)°$ and $Z = 8$. The structure refined to R = 0.103 and $R_w = 0.121$. A precursor compound used in the synthesis of 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene is the compound 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene. This compound is prepared by treating 25-hydroxy-26,27,28-tribenzoyloxycalix[4]arene with sodium hydride and then allyl bromide, followed by a Claisen rearrangement and hydrolysis of the benzoyl groups. By a modification of the first step of the reaction sequence, which involves the removal of the excess sodium hydride before the addition of methanol, the compound 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene has been prepared. The compound 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]-arene crystallizes in a monoclinic Pn space group with $a = 10.840(2)$ Å, $b = 13.958(2)$ Å, $c = 12.928(2)$ Å, $\beta = 98.23(1)°$ and Z = 2. The structure refined to R = 0.071 and $R_w = 0.091$.

INTRODUCTION

The calixarenes are phenolic metacyclophanes that can be used to selectively occlude organic molecules or metal ions as guests into their host cavities. The selectivity of this binding depends on both the size and shape of the guest and the calixarene host.[1] The growing interest in calixarene chemistry comes from the ease with which chemical modifications can be made to both their upper and lower rims, as well as to the conformational and structural properties of these three-dimensional hosts. The phenolic groups at the calixarene upper rim are particularly amenable to synthetic modification, and functional groups such as ketones,[2] esters,[2,3] ethers,[4] amides,[5] and carboxylates[6] can be assembled onto this rim. The resulting molecular assemblies have been used for the selective binding of inorganic ions such as Na^+,[7] Ca^{2+},[8] and UO_2^{2+}.[9]

The applications of this chemistry makes it attractive to bind these chemically modified calixarenes to a polymeric support. For certain applications it is advantageous for this support to be available in a solid form, whereas in other circumstances it is preferable to have the polymer available in solution form.[10] For the purpose of this research it was necessary to obtain a chemically-modified calixarene that could be readily attached to a polymer support *via* its lower rim. At the same time it is necessary to retain the integrity of the phenolic groups on the lower rim unchanged in order that they can be used as binding sites for metal ions. An additional requirement is that the modified-polymers that result are soluble in fluid medium. This latter requirement is particularly im-

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portant because the attachment to a soluble biopolymer will allow the calixarenes to be used as carriers for targeted delivery in an *in vivo* environment. In this work we describe our approach to synthesizing 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]-arene that can be used for the single linkage attachment to a wide range of soluble polymers.

EXPERIMENTAL SECTION

All compounds used were of reagent purity and used as supplied. Hydrogen bromide was purchased from Aldrich. The compounds 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene, 25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene, and 5,11,17,23-tetrachloromethyl-25,26,27,28-tetrahydroxycalix[4]arene were prepared according to the literature procedures.[11,12] Infrared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a GE Omega 400 NMR spectrometer. Fast atom bombardment (FAB) mass spectra were obtained using a Kratos Concept 1H spectrometer with the samples introduced in a *m*-nitrobenzyl alcohol matrix. Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Photolyses were carried out using a 200 watt mercury lamp contained in an Ealing housing. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

25,27-Diallyloxy-26,28-dibenzoyloxycalix[4]arene

A mixture containing 25,26,27-tribenzoyloxycalix[4]-arene (7.91 g, 10.73 mmol), sodium hydride (1.28 g of an 80% suspension in mineral oil, 42.67 mol) and allyl bromide (5.65 mL, 33.41 mmol) in a solvent mixture of tetrahydrofuran (235 mL) and dimethylformamide (24 mL) was refluxed for 6 h. The solvents were then removed under reduced pressure. Methanol (50 mL) was added slowly to the mixture while the excess sodium hydride was reacting. The resulting solution was evaporated to dryness and dissolved in a 1:1 mixture of chloroform and water (60 mL). The chloroform layer was separated, and the aqueous layer extracted with an additional aliquot of chloroform (30 mL). The combined chloroform fractions were dried over anhydrous magnesium sulfate and the filtrate evaporated to dryness. The residue was dissolved in the minimum volume of chloroform, and the solution treated with methanol to give the product as a colorless solid. Yield 3.29 g (43%). The compound was purified by recrystallization from a mixture of chloroform and methanol, mp 252–4°C. Anal. Calcd for $C_{48}H_{40}O_6$: C, 80.9; H, 5.65. Found: C, 81.1; H, 5.35%. FAB mass spectrum: *m/z* 713, 712, 671, 607 calcd M = 712.834. IR (KBr pellet): 1724 cm^{-1} (ν(C=O)), 1602 cm^{-1} (ν(C=C)). ^1H NMR: 3.40–3.73 m (8H, ArCH_2Ar and OCH_2), δ 4.28 s (4H, ArCH_2Ar), δ 5.08–5.27 m (4H, =CH_2), δ 5.87–5.96 m (2H, =CH), δ 6.40–7.91 m (22H, aromatic). ^{13}C (DEPT): δ 37.0 (ArCH_2Ar), δ 71.4 (OCH_2), δ 116.3 (=CH_2), δ 122.0–134.1 (aromatic and =CH), δ 147.6 ($COCH_2$), δ 156.4 (COC=O), δ 164.3 (C=O).

5-(3-Bromopropyl)-25,26,27, 28-tetrahydroxycalix[4]arene

5-Allyl-25,26,27,28-tetrahydroxycalix[4]arene (1.015 g, 2.18 mmol) was dissolved in toluene (100 mL) in a quartz flask. The solution was irradiated with light from a mercury lamp for 5 h while a stream of hydrogen bromide was bubbled through the solution. The reaction mixture was then treated with sodium carbonate to remove excess hydrogen bromide, and then the mixture was evaporated to dryness. The residue was dissolved in the minimum volume of chloroform, and then treated with methanol to give the compound as light brown crystals. Yield 0.98 g (81.7%). The compound was purified by recrystallization from a mixture of chloroform and methanol, mp 238 – 240°C. Anal. Calcd for $C_{31}H_{29}BrO_4$: C, 68.3; H, 5.36; Br, 14.7. Found: C, 66.8; H, 5.12; Br, 12.4%. By ^1H NMR analysis the dried crystalline analytical sample contained a small quantity of chloroform. IR (Nujol mull): 3163 cm^{-1} (ν(OH)). ^1H NMR: 2.10 quintet (2H, ^3J(HH) = 7.0 Hz, CH_2CH_2C), δ 2.63 t (2H, ^3J(HH) = 7.35 Hz, ArCH_2CH_2), δ 3.39 t (2H, ^3J(HH) = 6.5 Hz, CH_2Br), δ 3.58 and δ 4.32 broad s (8H, ArCH_2Ar), δ 10.30 s (4H, OH). ^{13}C (HETERO-COSY): δ 31.80 and δ 31.82 (ArCH_2Ar), δ 33.1 (ArCH_2CH_2), δ 33.5 (CH_2Br), δ 34.1 ($CH_2CH_2CH_2$), δ 122.3 – 148.9 (aromatic).

Crystal data for 25,27-diallyloxy-26, 28-dibenzoyloxycalix[4]arene

A clear colorless crystal was obtained by slow cooling of a mixed solution of the compound in a mixed solvent system comprised of chloroform and methanol. The crystal was cut to give a piece of single crystal of dimensions 0.44 × 0.46 × 0.40 mm. This piece was mounted on a thin glass fiber. X-ray data were collected on an Enraf Nonius CAD-4 diffractometer. Crystallographic data are collected in Table 1. No significant intensity variations were observed during the data collection. Scattering factors were taken from reference 13. The general procedures for unit cell determination and data collection on the CAD-4 diffractometer have been published.[14] Intensity data were corrected for Lorentz and polarization factors, but no absorption correction was applied. The

Table 1 Crystallographic data for 25,27-diallyloxy-26,28-dibenzoyloxy calix[4]arene

formula	$C_{48}H_{40}O_6$
formula wt.	712.83
Cryst. syst.	Monoclinic
space group	Pn
a, Å	10.840(2)
b, Å	13.958(2)
c, Å	12.928(2)
β, *deg*	98.23(1)
V, Å^3	1935.9(5)
Z	2
Temperature (°C)	25
d_{calc}, g-cm^3	1.223
2Θ range (deg) for unit cell detn. (No. of refls)	20.00 – 31.92(25)
$\mu(Mo_1K\alpha)$, cm^{-1}	0.7
radiation Mo,Kα (graphite monochromated,	$\lambda = 0.71073$ Å)
2Θ range for data coll (deg)	1.00 – 42.00
scan type	$\omega - 2\Theta$
scan width (deg)	0.8 + 0.2 tan Θ
scan speed (deg min^{-1})	0.6 – 4.1
no. data measured	4002
no. of data used [$1 \geqslant 3\sigma(I)$]	2771
programs used	Enraf-Nonius MolEN[a]
no. variables	365
largest shift/esd in final cycle[a]	0.21
R[b]	0.071
R_w[c]	0.091
GOF[d]	3.20

[a] MolEN, An Interactive Structure Procedure, Enraf-Nonius, Delft, The Netherlands (1990).
[b] $R = \sum||F_o| - |F_c||/\sum F_o$.
[c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ with $w = 1/(\sigma_F)^2$ where $\sigma_F = \sigma(F^2)/2F$ and $\sigma(F^2) = [(\sigma_I)^2 + (0.04F^2)^2]^{1/2}$.
[d] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o and N_v are, respectively, the number of observations and variables.

structure was solved using direct methods (MULTAN 11/82).[15] All calculations were performed using the Enraf-Nonius MolEN system.[16] The remaining non-hydrogen atoms were located by successive cycles of full-matrix refinement followed by difference Fourier synthesis. Hydrogen atoms were included at the later stages of the refinement as fixed contributions in calculated positions and updated periodically. The carbon atoms constituting the four aromatic rings of the calix[4]arene core were refined with isotropic thermal parameters. All remaining non-hydrogen atoms were refined anisotropically. The final difference Fourier map does not show any residual peaks having significant intensity. Final positional parameters are shown in Table 2.

Crystal data for 5-(3-bromopropyl)-25,26-27, 28-tetrahydroxycalix[4]arene

A clear light brown crystal was obtained by the slow evaporation of a solution of the compound in a mixed solvent system comprised of chloroform and methanol. The crystal was cut to give a piece of single crystal of dimensions 0.26 × 0.26 × 0.53 mm. This piece was

Table 2 Positional parameters and their estimated standard deviations for the non-hydrogen atoms of 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene

Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
O1	0.6215(4)	0.2137(4)	0.5650(3)	5.6(1)
O2	1.0219(3)	0.2038(3)	0.5293(3)	3.60(8)
O3	0.9231(4)	0.5119(3)	0.5606(3)	5.2(1)
O4	0.863	0.3325(3)	0.845	4.11(8)
O5	1.0740(5)	0.1079(3)	0.4031(3)	5.9(1)
O6	0.8063(5)	0.3935(4)	0.9909(4)	7.6(1)
C1	0.8784(8)	0.0486(6)	0.7512(7)	6.6(2)*
C2	0.8018(7)	0.1069(5)	0.7961(6)	5.9(2)*
C3	0.7138(7)	0.1654(5)	0.7372(5)	5.0(1)*
C4	0.7068(6)	0.1588(5)	0.6276(5)	4.8(1)*
C5	0.7896(6)	0.1035(4)	0.5815(5)	4.4(1)*
C6	0.8750(7)	0.0475(5)	0.6435(6)	5.6(1)*
C7	0.6542(6)	0.3381(5)	0.7571(5)	5.2(1)*
C8	0.7677(6)	0.3862(4)	0.7839(5)	4.5(1)*
C9	0.7929(6)	0.4757(5)	0.7523(5)	4.8(1)*
C10	0.6950(8)	0.5247(5)	0.6934(6)	6.2(2)*
C11	0.5817(9)	0.4823(7)	0.6691(7)	7.5(2)*
C12	0.5589(8)	0.3946(6)	0.6975(7)	6.9(2)*
C13	1.0198(6)	0.4703(4)	0.7310(5)	4.0(1)*
C14	1.0178(5)	0.4644(4)	0.6231(5)	3.9(1)*
C15	1.1008(6)	0.4092(4)	0.5776(5)	4.1(1)*
C16	1.1987(6)	0.3658(5)	0.6427(5)	4.8(1)*
C17	1.2093(7)	0.3764(5)	0.7490(6)	5.1(1)*
C18	1.1186(7)	0.4260(6)	0.7927(5)	5.2(1)*
C19	0.9625(5)	0.3405(4)	0.4214(4)	3.5(1)*
C20	0.8742(6)	0.3836(4)	0.3481(5)	4.4(1)*
C21	0.7621(6)	0.3405(5)	0.3123(5)	4.9(1)*
C22	0.7361(6)	0.2519(5)	0.3492(5)	4.6(1)*
C23	0.9334(5)	0.2500(4)	0.4546(4)	3.41(9)*
C24	0.8203(5)	0.2039(4)	0.4230(5)	3.9(1)*
C25	0.9669(5)	0.2775(4)	1.0054(4)	3.9(1)
C26	0.9790(6)	0.2741(5)	1.1138(5)	4.8(1)
C27	1.0654(7)	0.2158(6)	1.1699(5)	6.0(2)
C28	1.1388(7)	0.1572(5)	1.1190(6)	6.3(2)
C29	1.1298(7)	0.1607(6)	1.0129(6)	6.3(2)
C30	1.0455(6)	0.2202(5)	0.9550(5)	4.9(1)
C31	1.1739(6)	0.0871(4)	0.5774(5)	4.6(1)
C32	1.1983(7)	0.1204(5)	0.6767(5)	5.5(2)
C33	1.2890(8)	0.0762(7)	0.7500(6)	7.9(2)
C34	1.3478(8)	−0.0048(6)	0.7180(6)	9.1(2)
C35	1.321(1)	−0.0389(6)	0.6209(8)	9.9(2)
C36	1.2352(9)	0.0054(6)	0.5513(7)	8.5(2)
C37	0.6336(7)	0.2392(7)	0.7850(5)	6.3(2)
C38	0.9201(8)	0.5201(5)	0.7769(5)	5.4(2)
C39	1.0838(6)	0.3882(4)	0.4613(5)	4.2(1)
C40	0.7889(6)	0.1074(5)	0.4650(5)	5.0(1)
C41	0.8712(6)	0.3412(5)	0.9490(5)	4.7(1)
C42	1.0882(5)	0.1318(4)	0.4933(5)	4.2(1)
C43	0.5031(7)	0.168(1)	0.5355(7)	9.3(3)
C44	0.4310(7)	0.239(1)	0.4548(7)	10.9(3)
C45	0.365(1)	0.221(1)	0.380(1)	11.6(4)
C46	0.966(1)	0.5949(5)	0.5064(7)	7.7(2)
C47	0.940(1)	0.6841(6)	0.5513(9)	10.0(3)
C48	1.009(2)	0.752(1)	0.580(1)	14.5(5)

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1, 1) + b2*B(2, 2) + c2*B(3, 3) + ab(cos gamma)*B(1, 2) + ac(cos beta)*B(1, 3) + bc(cos alpha)*B(2, 3)].

Table 3 Crystallographic data for 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene

formula	$C_{31}H_{29}O_4Br$
formula wt.	545.47
Cryst. syst.	Monoclinic
space group	$P2_1/n$
a, Å	12.4127(9)
b, Å	20.754(4)
c, Å	19.751(3)
β, *deg*	97.524(8)
V, Å^3	5044(1)
Z	8
Temperature (°C)	25
d_{calc}, g-cm^3	1.438
2Θ range (deg) for unit cell detn. (No. of refls)	13.34 – 27.78(25)
$\mu(Mo_1K\alpha)$, cm^{-1}	16.5
radiation Mo,Kα (graphite monochromated,	λ = 0.71073 Å)
2Θ range for data coll (deg)	1.00 – 50.00
scan type	$\omega - 2\Theta$
scan width (deg)	0.8 + 0.2 tan Θ
scan speed (deg min^{-1})	0.8 – 4.1
no. data measured	9288
no. of data used [$1 \geqslant 3\sigma(I)$]	3736
programs used Enraf-Nonius MolEN[a]	
no. variables	409
largest shift/esd in final cycle[a]	0.04
R[b]	0.103
R_w[c]	0.121
GOF[d]	3.29

[a] MolEN, An Interactive Structure Procedure, Enraf-Nonius, Delft, The Netherlands (1990).
[b] $R = \sum||F_o| - |F_c||/\sum F_o$.
[c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ with $w = 1/(\sigma_F)^2$ where $\sigma_F = \sigma(F^2)/2F$ and $\sigma(F^2) = [(\sigma_I)^2 + (0.04F^2)^2]^{1/2}$.
[d] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o and N_v are, respectively, the number of observations and variables.

mounted on a thin glass fiber. X-ray data were collected on an Enraf Nonius CAD-4 diffractometer. Crystallographic data are collected in Table 3. No significant intensity variations were observed during the data collection. Scattering factors were taken from reference 13. An empirical absorption correction was applied using the program DIFABS.[17] The general procedures for unit cell determination and data collection on the CAD-4 diffractometer have been published.[14] Intensity data were corrected for Lorentz and polarization factors. The structure was solved using direct methods (MULTAN 11/82).[15] All calculations were performed using the Enraf-Nonius MolEN system.[16] The remaining non-hydrogen atoms were located by successive cycles of full-matrix refinement followed by difference Fourier synthesis. Hydrogen atoms were included at the later stages of the refinement as fixed contributions in calculated positions and updated periodically. The carbon atoms constituting the aromatic rings were refined with isotropic thermal parameters. All remaining non-hydrogen atoms were refined anisotropically. The final difference Fourier map showed the presence of a peak with intensity about one third of that of a carbon atom in the vicinity of the bromine atom in one of the two refined molecules, thus indicating a possible alternate location of some of the atoms in the bromopropyl group. Our efforts, however, to resolve this alternate location were unsuccessful. Final positional parameters are shown in Table 4.

RESULTS AND DISCUSSION

In order to synthesize calixarenes that can be attached to a polymer by a single chemical linkage to give a

Table 4 Positional parameters and their estimated standard deviations for 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]-arene

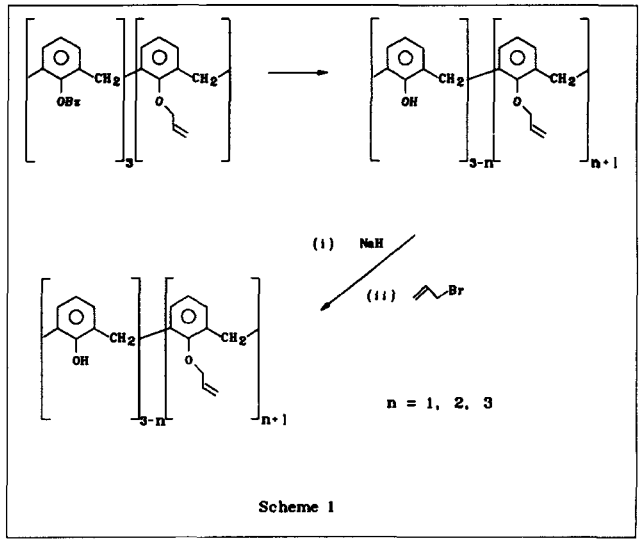
Atom	*x/a*	*y/b*	*z/c*	*B*(Å^2)
Br1	0.5080(2)	0.0924(1)	0.89112(9)	8.42(5)
Br2	0.4486(2)	0.24099(9)	0.4569(1)	7.96(5)
O1	0.8813(6)	−0.0811(4)	0.7407(4)	4.0(2)
O2	0.6956(6)	−0.1297(4)	0.6758(4)	3.8(2)
O3	0.6477(7)	−0.1632(4)	0.7978(4)	4.1(2)
O4	0.8372(7)	−0.1198(4)	0.8607(4)	4.1(2)
O5	0.9954(6)	0.2567(4)	0.5807(4)	3.5(2)
O6	0.9302(6)	0.3291(4)	0.6792(4)	3.9(2)
O7	1.1119(6)	0.2784(4)	0.7451(4)	3.8(2)
O8	1.1941(6)	0.2251(4)	0.6377(4)	4.1(2)
C1	0.8521(8)	0.0140(5)	0.6717(5)	2.6(2)*
C2	0.8921(9)	−0.0137(5)	0.7332(5)	3.0(2)*
C3	0.9409(9)	0.0199(6)	0.7890(6)	3.4(3)*
C4	0.9527(9)	0.0871(6)	0.7785(6)	3.8(3)*
C5	0.9190(9)	0.1158(6)	0.7185(6)	3.6(3)*
C6	0.8671(9)	0.0802(6)	0.6654(6)	3.8(3)*
C7	0.6247(9)	−0.0800(6)	0.6508(6)	3.3(3)*
C8	0.671(1)	−0.0309(6)	0.6198(6)	3.8(3)*
C9	0.600(1)	0.0227(6)	0.5924(6)	3.9(3)*
C10	0.491(1)	0.0220(6)	0.5994(6)	3.8(3)*
C11	0.456(1)	−0.0318(6)	0.6334(6)	3.8(3)*
C12	0.5170(9)	−0.0811(5)	0.6584(6)	2.9(2)*
C13	0.5557(9)	−0.1351(6)	0.8195(6)	3.7(3)*
C14	0.4671(9)	−0.1220(6)	0.7709(6)	3.7(3)*
C15	0.376(1)	−0.0952(6)	0.7927(6)	3.8(3)*
C16	0.371(1)	−0.0795(6)	0.8578(7)	4.8(3)*
C17	0.465(1)	−0.0901(7)	0.9061(7)	5.0(3)*
C18	0.558(1)	−0.1174(6)	0.8866(6)	3.7(3)*
C19	0.8201(9)	−0.0683(6)	0.9024(6)	3.2(2)*
C20	0.7382(9)	−0.0704(6)	0.9419(6)	3.6(3)*
C21	0.724(1)	−0.0198(7)	0.9851(7)	4.8(3)*
C22	0.788(1)	0.0338(7)	0.9860(7)	5.4(3)*
C23	0.872(1)	0.0355(7)	0.9472(7)	5.0(3)*
C24	0.8875(9)	−0.0161(6)	0.9046(6)	3.7(3)*
C25	0.7941(9)	−0.0243(6)	0.6125(6)	3.5(3)
C26	0.4709(9)	−0.1369(7)	0.6950(7)	4.5(3)
C27	0.657(1)	−0.1256(7)	0.9386(6)	4.7(3)
C28	0.978(1)	−0.0103(6)	0.8588(6)	4.1(3)
C29	0.417(1)	0.0746(7)	0.5720(7)	5.8(4)
C30	0.458(1)	0.1225(8)	0.5307(7)	6.0(4)

Table 4 *continued*

Atom	*x/a*	*y/b*	*z/c*	*B(Å²)*
C31	0.383(1)	0.1791(7)	0.5040(7)	5.5(4)
C32	0.8467(9)	0.2924(5)	0.6995(6)	3.0(2)*
C33	0.7673(9)	0.2661(6)	0.6518(6)	3.4(3)*
C34	0.687(1)	0.2286(6)	0.6738(6)	4.3(3)*
C35	0.683(1)	0.2156(6)	0.7402(6)	4.6(3)*
C36	0.763(1)	0.2424(6)	0.7879(6)	4.3(3)*
C37	0.8462(9)	0.2797(6)	0.7672(6)	3.7(3)*
C38	1.1081(9)	0.2435(6)	0.8052(6)	3.6(3)*
C39	1.0257(7)	0.2563(6)	0.8447(6)	3.4(3)*
C40	1.030(1)	0.2205(6)	0.9059(7)	4.6(3)*
C41	1.108(1)	0.1777(7)	0.9242(7)	4.8(3)*
C42	1.184(1)	0.1640(6)	0.8843(7)	4.6(3)*
C43	1.188(1)	0.1964(6)	0.8242(6)	3.8(3)*
C44	0.9284(9)	0.2108(6)	0.5482(6)	3.6(3)*
C45	0.817(1)	0.2212(6)	0.5400(6)	4.1(3)*
C46	0.752(1)	0.1749(7)	0.5007(7)	4.6(3)*
C47	0.797(1)	0.1239(7)	0.4744(7)	4.8(3)*
C48	0.905(1)	0.1139(7)	0.4833(7)	4.8(3)*
C49	0.975(1)	0.1553(6)	0.5202(6)	3.9(3)*
C50	1.1854(9)	0.1598(5)	0.6528(6)	3.0(2)*
C51	1.139(1)	0.1208(6)	0.6011(6)	3.7(3)*
C52	1.130(1)	0.0556(7)	0.6148(7)	5.2(3)*
C53	1.166(1)	0.0320(7)	0.6770(7)	5.0(3)*
C54	1.212(1)	0.0716(7)	0.7269(7)	4.9(3)*
C55	1.2237(9)	0.1382(6)	0.7156(6)	3.3(3)*
C56	0.768(1)	0.2766(7)	0.5742(7)	5.0(4)
C57	0.937(1)	0.3039(6)	0.8216(6)	4.6(3)
C58	1.268(1)	0.1792(6)	0.7746(7)	4.7(3)
C59	1.096(1)	0.1447(6)	0.5309(7)	5.0(3)
C60	0.596(1)	0.1732(8)	0.7651(8)	7.0(5)
C61	0.641(1)	0.1030(7)	0.7871(9)	7.7(4)
C62	0.560(1)	0.0614(8)	0.812(1)	9.1(5)

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1, 1) + b2*B(2, 2) + c2*B(3, 3) + ab(cos gamma)*B(1, 2) + ac(cos beta)*B(1, 3) + bc(cos alpha)*B(2, 3)].

functionalized-polymer that is soluble in fluid medium, it is necessary to introduce such a single functional group onto one of the rims of the calixarene that can be used to covalently bind to the polymer. Since all of the positions on the individual rims of the calixarenes have the same functional groups, many reactions of calixarenes lead to products that are multiply functionalized. Such compounds cannot be used as synthons because the attachment of a calixarene to the polymer by multiple chemical linkages will result in the formation of an insoluble cross-linked polymer. One of the few literature examples of a calixarene that has a unique substituent on one of the rims is 25-allyloxy-26,27,28-trihydroxycalix[4]arene, or its Claisen rearrangement product 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene. This former compound has been previously prepared by treating 26,27,28-tribenzoyloxycalix[4]arene with sodium hydride, then with allyl bromide, followed by hydrolytic cleavage of the benzoyl groups. During the attempted synthesis of 25-allyloxy-26,27,28-tribenzoyloxycalix[4]arene using this literature procedure we observe that a different product is obtained if we do not remove the excess sodium hydride from the reaction mixture by filtration before the addition of methanol to the reaction.[18] This new compound that is formed with sodium hydride and methanol present together in the reaction is 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene. This compound has been formed by partial hydrolysis of 25-allyloxy-26,27,28-tribenzoyloxycalix[4]arene, followed by reaction of the hydrolysis product with the excess of sodium hydride and allyl bromide (Scheme I). An ^1H NMR



Scheme 1

spectral analysis of the components present in the mother liquor of this reaction (separated *via* flash column chromatography on silica gel 200–400 mesh by using a mixture of CH_2Cl_2 and 1-hexane (3:1) as eluant) indicates one of them is 25,26,27,28-tetraallyloxycalix[4]arene.[18] The presence of this compound which is fully allyloxylated on the lower rim verifies that a portion of the starting compound 25-allyloxy-26,27,28-tribenzoyloxycalix[4]arene undergoes hydrolytic cleavage of all the benzoyloxy groups. This observation gives further support for our proposed sequence of reactions that lead to the formation of 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene. This diallyloxy product 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene has been characterized by a combination of FAB mass spectroscopy, IR and NMR spectroscopy, and its structure finally confirmed by single crystal X-ray crystallography. The infrared spectrum of the compound shows bands at 1724 cm^{-1} and 1602 cm^{-1} due to $\nu(C=O)$ and $\nu(C=C)$, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows resonances due to the allyloxy groups at δ 71.4 (OCH_2) and δ

Table 5 Selected bond distances (Å) and angles (°) for 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene

Bond distances (Å)			
O1–C43	1.44(1)	O3–C46	1.46(1)
C43–C44	1.56(2)	C46–C47	1.42(2)
C44–C45	1.14(2)	C47–C48	1.23(2)
C25–C41	1.48(1)	C31–C42	1.465(9)
C41–06	1.196(9)	C42–05	1.201(8)
C41–O4	1.341(8)	C42–O2	1.356(7)
O4–C8	1.417(8)	O2–C23	1.416(7)
O3?C14	1.481(8)	O1–C4	1.373(9)
Bond angles (°)			
O1–C43–C44	104(1)	O3–C46–C47	113.9(9)
C43–C44–C45	128(2)	C46–C47–C48	131(2)
C25–C41–O6	124.1(6)	C31–C42–O5	125.6(6)
O6–C41–O4	123.3(7)	O5–C42–O2	122.6(6)
C14–O3–C46	113.6(6)		

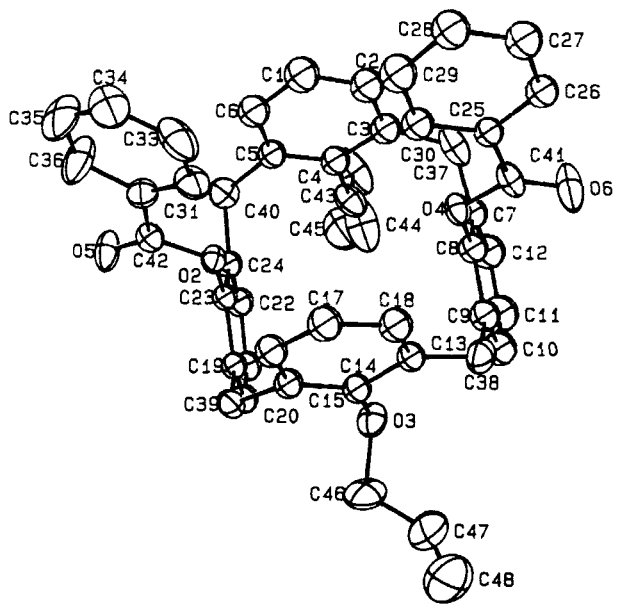


Figure 1 ORTEP drawing for 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene with 30% ellipsoids.

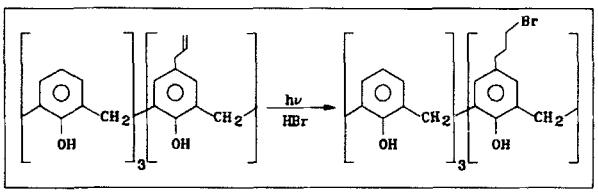
116.3 ($=CH_2$), and due to the benzoyloxy grouped at δ 156.4 ($COC=O$) and δ 164.3 ($C=O$).

Crystal structure of 25,27-diallyloxy-26, 28-dibenzoyloxycalix[4]arene

The crystal structure of 25,27-diallyloxy-26,28-dibenzoyloxycalix[4]arene shows that the molecule is present in the crystal in the partial cone conformation. Bond distances and angles are collected in Table 5, and an ORTEP representation of the structure is shown in Figure 1. One allyloxy group has the sequence of distances along the chain of O3–C14 = 1.381(8) Å, O3–C46 = 1.46(1) Å, C46–C47 = 1.42(2) Å and C47–C48 = 1.23(2) Å. The corresponding angles have the values of C14–O3–C46 = 113.6(6)°, O3–C46–C47 = 113.9(9)° and C46–C47–C48 = 131(2)°. The other allyloxy group has the sequence of distances along the chain of O1–C4 = 1.373(9) Å, O1–C43 = 1.44(1) Å, C43–C44 = 1.56(2) Å and C44–C45 = 1.14(2) Å. The corresponding angles have the values of C4–O1–C43 = 114.1(7)°, O1–C43–C44 = 104(1)° and C43–C44–C45 = 128(2)°. The apparent contraction of the bond lengths for the terminal carbon atoms of the allyloxy groups, C44–C45 and C47–C48 can be attributed to the high thermal motion of these fragments of the molecule. Careful inspection of the difference Fourier maps in the region of the two allyloxy groups does not indicate any resolvable disorder.

Synthesis of 5-(3-bromopropyl)-25,26,27, 28-tetrahydroxycalix[4]arene

If the sodium hydride that is used in the synthetic procedure is removed prior to the addition of methanol we can obtain the literature compound 25-allyloxy-26,27,28-tribenzoyloxycalix[4]arene in the described yield.[11] Following again a literature procedure, we have converted 25-allyloxy-26,27,28-tribenzoyloxycalix[4]arene into 5-allyl-25,26,27-28-tetrahydroxycalix[4]arene *via* the Claisen rearrangement, followed by the subsequent hydrolysis of the benzoyloxy groups on the lower rim. Since our attempts to obtain a copolymer of 5-allyl-25,26,27,28-tetrahydroxycalix[4]-arene with either methacrylic acid or maleic anhydride proved unsuccessful, we have therefore converted 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene into 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]-arene by the photochemically intiated reaction with hydrogen bromide (equation 2), since this compound



(2)

can be potentially used as an alkylating agent to a nucleophilic center on a polymer. Such an application is described in the following paper. This compound 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]-arene has been characterized by a combination of IR and NMR spectroscopy, as well as by single crystal X-ray crystallography. The anti-Markownikov direction of addition is confirmed by the presence of resonances due to the CH_2Br group at δ 3.39 in the ^1H NMR spectrum, and at δ 33.5 in the $^{13}C\{^1H\}$ NMR spectrum.

Crystal structure of 5-(3-bromopropyl)-25,26,27, 28-tetrahydroxycalix[4]arene

The crystal structure of 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene shows that the compound crystallizes with two independent molecules in the unit cell, and that each is present in the crystal in the cone conformation. Bond distances and angles are collected in Table 6, and an ORTEP representation of the structure is shown in Figure 2. The 3-bromopropyl chain in molecule 1 has the sequence of distances along the chain of C10–C29 = 1.48(2)Å, C29–C30 = 1.41(2)Å, C30–C31 = 1.55(2)Å and C31–Br2 = 1.84(2)Å. The corresponding angles have the values of C10–C29–C30 = 118(1)°, C29–C30–C31 = 119(1)° and C30–C31–Br2 = 115(1)°. The 3-bromopropyl chain in molecule 2 has the sequence of distances along the chain of C35–C60 = 1.53(2)Å, C60–C61 = 1.60(2)Å, C61–C62 = 1.46(2)Å and C62–Br1 = 1.88(2)Å. The corresponding angles have the values of C35–C60–C61 = 112(1)°, C60–C61–C62 = 114(1)° and C61–C62–Br1 = 114(1)°.

Table 6 Selected bond distances (Å) and angles (°) for 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene

Bond distances (Å)			
Molecule 1			
Br2/C31	1.84(2)	O1–C2	1.41(1)
C30–C31	1.55(2)	O2–C7	1.40(1)
C29–C30	1.41(2)	O3–C13	1.40(1)
C10–C29	1.48(2)	O4–C19	1.38(1)
Molecule 2			
Br1–C62	1.88(2)	O5–C44	1.37(1)
C61–C62	1.46(2)	O6–C32	1.39(1)
C60–C61	1.60(2)	O7–C38	1.40(1)
C35–C60	1.53(2)	O8–C50	1.40(1)
Bond angles(°)			
Molecule 1			
Br2–C31–C30	115(1)	C8–C7–O2	115(1)
C29–C30–C31	119(1)	C12–C7–O2	122(1)
C10–C29–C30	118(1)	C14–C13–O3	118(1)
C1–C2–O1	119(1)	C18–C13–O3	119(1)
C3–C2–O1	117(1)	C20–C19–O4	120(4)
C24–C19–O4	119(1)		
Molecule 2			
Br1–C62–C61	114(1)	C33–C32–O6	121(1)
C62–C61–C60	114(1)	C37–C32–O6	119(1)
C61–C60–C35	112(1)	C39–C38–O7	119(1)
C45–C44–O5	119(1)	C43–C38–O7	119(1)
C49–C44–O5	120(1)	C51–C50–O8	117(1)
	C55–C50–O8	119(1)	

CONCLUSIONS

In this work we have developed a synthetic procedure for the attachment of a single 3-bromopropyl chain onto the upper rim of a calixarene. The linearity of the chain has been confirmed by a combination of spectroscopic and single crystal X-ray crystallographic techniques. The attachment of this compound to polyethyleneimine to give a soluble calixarene-modified polymer is the subject of the following paper.

ACKNOWLEDGEMENT

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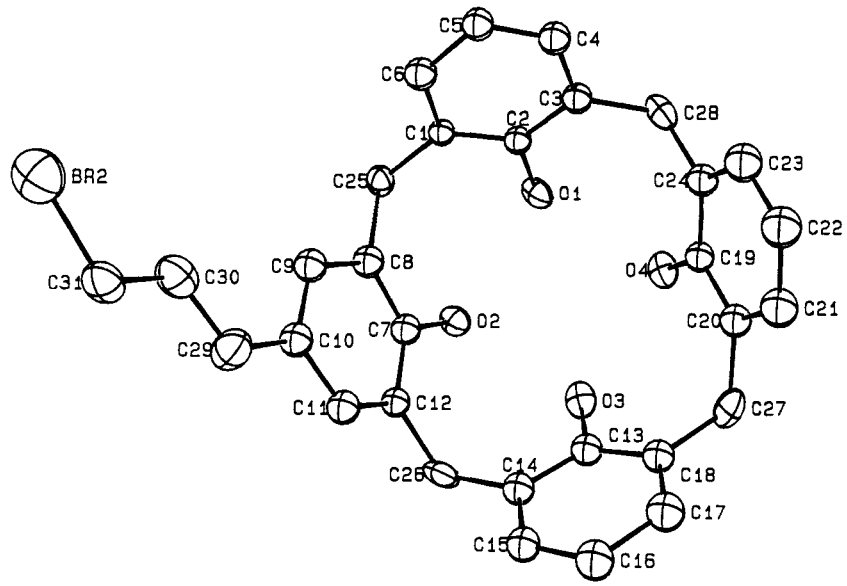

Figure 2 ORTEP drawing for 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene with 30% ellipsoids.

Louisiana Board of Reagents, for funds to purchase the 400 MHz NMR spectrometer.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of positional parameters, bond angles, bond distances, general displacement parameter expressions and values of 10* Fobs and 10* Fcalc (66 pages).

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