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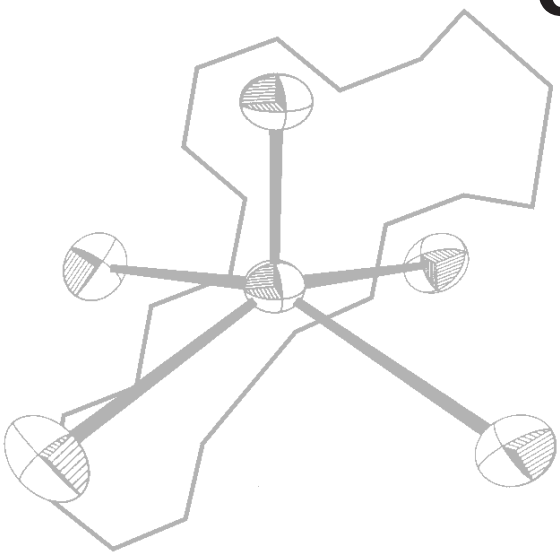

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Synthesis and Characterization of *p*-t-Butyl Calix[4]crown-4 and its Double Calix[4]arene Dimer

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The preparation, separation, characterization and crystal structure determinations of the 1+1 and 2+2 condensation products, *p*-t-butyl calix[4]crown-4 (1) and its dimer double calix[4]arene double crown-4 (2), resulting from the reaction of *p*-t-butylcalix[4]arene with triethylene glycol ditosylate in the presence of a base are reported.

Introduction

The present wide development of macrocyclic and supramolecular chemistry has originated from the study of molecular families such as crown ethers, cryptands and spherands.[1] Intense research efforts have recently been devoted to the chemistry of *calixarenes*.[2–4] These molecules presently occupy a prominent place due to their ready access, easy functionalization and strong complexing properties towards cations, anions, and neutral substrates; such properties make them important supramolecular hosts.[3,4]

Early in the development of calixarene chemistry, the possibility was considered of obtaining superior hosts by fusion of the calixarene structure with that of other macrocycles.[5] Calix[4]arene is particularly well suited for such a purpose since it forms a rather rigid platform (with four extreme conformations: *cone, partial cone, 1,2-alternate, 1,3-alternate*) suitable for building large assemblies by functionalization of the lower (phenolic hydroxy functions) or upper rims.[2–4] The ability of crown ethers to complex and transport cations has been widely demonstrated, and synergistic effects in metal ion extraction by *p*-t-butylcalix[4]arene/crown ether mixtures have been attributed to the formation of complex ion pairs including both ligands.[6,7] Selectivities were shown to depend on the crown size, which shows a complementarity effect between the cavity and the cation sizes.[6] The association of calixarenes and polyether chains to form a single molecular species therefore appeared as a promising research direction.[8–10]

'Calixcrowns' constitute a family of macropolycyclic or cage molecules containing the calixarene and crown ether elements in the same framework. Following the synthesis of polypodands with open ethylene glycol chains as substituents on the phenolic oxygen atoms, the first calix[4]arene crown compound, *p*-t-butyl calix[4]crown-6, was synthesized by Alfieri *et al.*[11] from *p*-t-butylcalix[4]arene and pentaethylene glycol ditosylate under basic conditions. Subsequent to this publication, several studies have been devoted to the preparation and complexation properties of calixcrowns resulting from condensations of calixarenes with various glycol ditosylates.[8–10] It was shown that, depending on the reaction conditions (nature of the base, structure of the ditosylates, and stoichiometry of the reactants), one can drive the reacting processes to the desired calixcrown structures.[8–10] In spite of the usefulness of f.a.b. mass spectrometry, the characterization of those calixcrowns is doubtful because n.m.r. techniques are unable to differentiate between products corresponding to 1+1, 2+2, etc., condensations.

In the present paper, we present the preparation, separation, characterization and crystal structure determinations of the 1+1 and 2+2 condensation products, *p*-t-butyl calix[4]crown-4 (1)[12*] and double calix[4]arene double crown-4 (2), resulting from the reaction of *p*-t-butylcalix[4]arene with triethylene glycol ditosylate in the presence of a base.

Experimental

Instrumentation and Analysis

Melting points were measured in sealed capillaries under nitrogen with a Büchi 500 apparatus. Chromatography columns were prepared from Merck Kieselgel No. 11567. ^{1}H n.m.r. spectra were recorded on a Bruker SY200 spectrometer, and f.a.b. mass spectra on a VG-Analytical ZAB HF instrument. Elemental analyses were provided by the Service de Microanalyse of the Institut de Chimie de Strasbourg.

* *p*-t-Butyl calix[4]crown-4 (1) has been reported three times.[12] However, up to now no *analytical data* have been given.

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Table 1. Atomic parameters and equivalent isotropic displacement parameters (Å^2) for (1).2CHCl$_3$

Here, and in Table 2, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Here, the two independent molecules are denoted A and B, and the two positions of disordered atoms are denoted i and j

Atom	X/a	Y/b	Z/c	U_{eq}	Atom	X/a	Y/b	Z/c	U_{eq}
O(1A)	0·6685(4)	0·6280(3)	0·3028(3)	0·0341(14)	C(3B)	−0·0656(8)	0·7313(5)	0·1313(4)	0·047(2)
O(2A)	0·5925(5)	0·7104(4)	0·3777(3)	0·056(2)	C(4B)	0·0451(9)	0·7039(6)	0·1427(5)	0·060(3)
O(3A)	0·3588(5)	0·7187(4)	0·3600(3)	0·048(2)	C(5B)	0·1862(7)	0·7818(5)	0·1483(4)	0·040(2)
O(4A)	0·3713(4)	0·5647(3)	0·3740(2)	0·0301(13)	C(6B)	0·2389(7)	0·8131(5)	0·1924(4)	0·035(2)
O(5A)	0·5949(4)	0·5246(3)	0·4141(2)	0·0326(13)	C(7B)	−0·1811(6)	1·0004(4)	0·1248(3)	0·026(2)
O(6A)	0·4482(4)	0·6592(3)	0·2644(2)	0·0352(14)	C(8B)	−0·2495(6)	0·9792(5)	0·1759(4)	0·032(2)
C(1A)	0·7294(7)	0·6898(4)	0·3055(4)	0·032(2)	C(9B)	−0·3056(6)	1·0345(5)	0·1882(4)	0·029(2)
C(2A)	0·7014(8)	0·7055(6)	0·3635(4)	0·049(2)	C(10B)	−0·2947(6)	1·1101(4)	0·1540(4)	0·027(2)
C(3A)	0·5422(9)	0·7716(6)	0·3321(5)	0·068(4)	C(11B)	−0·2223(6)	1·1296(5)	0·1055(3)	0·028(2)
C(4A)	0·4284(7)	0·7794(5)	0·3566(4)	0·045(2)	C(12B)	−0·1636(6)	1·0745(5)	0·0898(3)	0·028(2)
C(5A)	0·3622(8)	0·6610(5)	0·4171(4)	0·041(2)	C(13B)	−0·3609(7)	1·1698(5)	0·1699(4)	0·037(2)
C(6A)	0·3082(7)	0·5948(5)	0·4134(4)	0·035(2)	C(14B)	−0·3281(8)	1·2495(5)	0·1339(4)	0·047(3)
C(7A)	0·7140(6)	0·5906(4)	0·2653(4)	0·026(2)	C(15B)	−0·3551(7)	1·1575(5)	0·2377(4)	0·041(2)
C(8A)	0·7813(6)	0·5285(5)	0·2935(3)	0·027(2)	C(16B)	−0·4797(8)	1·1619(6)	0·1535(4)	0·053(3)
C(9A)	0·8276(6)	0·4926(4)	0·2567(4)	0·028(2)	C(17B)	−0·2557(6)	0·8986(4)	0·2193(4)	0·031(2)
C(10A)	0·8057(6)	0·5151(4)	0·1932(3)	0·028(2)	C(18B)	−0·1822(6)	0·8849(4)	0·2740(3)	0·027(2)
C(11A)	0·7345(6)	0·5744(4)	0·1682(4)	0·030(2)	C(19B)	−0·0812(6)	0·8526(5)	0·2774(4)	0·031(2)
C(12A)	0·6869(6)	0·6137(4)	0·2036(4)	0·028(2)	C(20B)	−0·0118(7)	0·8441(4)	0·3266(4)	0·031(2)
C(13A)	0·8631(6)	0·4735(5)	0·1552(4)	0·031(2)	C(21B)	−0·0493(7)	0·8668(4)	0·3744(4)	0·034(2)
C(14A)	0·8168(8)	0·4962(5)	0·0895(4)	0·045(2)	C(22B)	−0·1514(7)	0·8972(5)	0·3754(4)	0·033(2)
C(15A)	0·9815(7)	0·4937(5)	0·1498(4)	0·044(2)	C(23B)	−0·2173(6)	0·9057(4)	0·3240(4)	0·031(2)
C(16A)	0·8520(7)	0·3889(5)	0·1863(4)	0·039(2)	C(24B)	−0·1946(7)	0·9183(5)	0·4285(4)	0·036(2)
C(17A)	0·7980(7)	0·4970(5)	0·3623(3)	0·030(2)	C(25B)	−0·2328(8)	1·0004(5)	0·4043(4)	0·050(3)
C(18A)	0·7146(6)	0·4370(5)	0·3922(3)	0·028(2)	C(26B)	−0·2898(7)	0·8682(6)	0·4574(4)	0·048(2)
C(19A)	0·6160(6)	0·4538(4)	0·4142(3)	0·027(2)	C(27B)	−0·1106(7)	0·9109(6)	0·4778(4)	0·049(3)
C(20A)	0·5398(6)	0·3991(4)	0·4370(3)	0·024(2)	C(28B)	0·1025(6)	0·8156(4)	0·3296(3)	0·028(2)
C(21A)	0·5638(6)	0·3263(5)	0·4395(3)	0·030(2)	C(29B)	0·1783(6)	0·8807(4)	0·2996(3)	0·026(2)
C(22A)	0·6607(6)	0·3059(5)	0·4201(3)	0·028(2)	C(30B)	0·2015(6)	0·9052(4)	0·2382(4)	0·027(2)
C(23A)	0·7346(6)	0·3637(5)	0·3960(3)	0·028(2)	C(31B)	0·2609(6)	0·9692(4)	0·2095(4)	0·025(2)
C(24A)	0·6900(7)	0·2261(5)	0·4233(4)	0·038(2)	C(32B)	0·3027(6)	1·0054(5)	0·2482(4)	0·032(2)
C(25A)	0·7250(10)	0·2273(6)	0·3595(4)	0·065(3)	C(33B)	0·2864(6)	0·9821(5)	0·3102(3)	0·029(2)
C(26A)	0·5935(8)	0·1720(6)	0·4429(5)	0·053(3)	C(34B)	0·2216(6)	0·9202(4)	0·3353(4)	0·030(2)
C(27A)	0·7796(7)	0·1949(5)	0·4694(4)	0·044(2)	C(35B)	0·3446(7)	1·0197(5)	0·3503(4)	0·034(2)
C(28A)	0·4292(6)	0·4166(5)	0·4574(3)	0·030(2)	C(36B)	0·2897(8)	1·0060(6)	0·4111(4)	0·052(3)
C(29A)	0·3472(6)	0·4310(5)	0·4076(4)	0·029(2)	C(37B)	0·4601(7)	0·9863(6)	0·3612(5)	0·053(3)
C(30A)	0·3232(6)	0·5026(4)	0·3662(3)	0·025(2)	C(38B)	0·3527(8)	1·1039(5)	0·3171(4)	0·047(2)
C(31A)	0·2567(6)	0·5141(4)	0·3159(3)	0·023(2)	C(39B)	0·2764(6)	1·0021(4)	0·1410(3)	0·026(2)
C(32A)	0·2078(6)	0·4524(4)	0·3102(3)	0·027(2)	C(40B)	0·1994(6)	1·0668(4)	0·1104(3)	0·026(2)
C(33A)	0·2229(6)	0·3803(5)	0·3511(4)	0·030(2)	C(41B)	0·1010(6)	1·0530(4)	0·0891(3)	0·026(2)
C(34A)	0·2953(6)	0·3706(5)	0·3987(4)	0·031(2)	C(42B)	0·0275(6)	1·1117(4)	0·0636(3)	0·026(2)
C(35A)	0·1574(6)	0·3134(5)	0·3465(4)	0·042(2)	C(43B)	0·0542(6)	1·1830(5)	0·0604(3)	0·030(2)
C(36i)	0·0711(14)	0·2987(12)	0·3977(8)	0·050(5)	C(44B)	0·1519(6)	1·2000(4)	0·0809(4)	0·028(2)
C(36j)	0·0402(10)	0·3246(12)	0·3621(10)	0·056(6)	C(45B)	0·2229(6)	1·1397(5)	0·1058(3)	0·030(2)
C(37i)	0·1532(15)	0·3207(10)	0·2774(5)	0·030(4)	C(46B)	0·1836(7)	1·2790(5)	0·0757(4)	0·032(2)
C(37j)	0·1005(21)	0·3249(15)	0·2864(8)	0·073(7)	C(47B)	0·2213(8)	1·2802(5)	0·1388(4)	0·044(2)
C(38A)	0·2195(9)	0·2399(5)	0·3757(5)	0·053(3)	C(48B)	0·2790(7)	1·3050(5)	0·0306(5)	0·045(2)
C(39A)	0·2414(6)	0·5911(4)	0·2669(3)	0·029(2)	C(49B)	0·0899(7)	1·3358(5)	0·0528(4)	0·046(2)
C(40A)	0·3191(6)	0·6060(4)	0·2143(3)	0·028(2)	C(50B)	−0·0818(6)	1·0996(4)	0·0389(3)	0·027(2)
C(41A)	0·4208(6)	0·6367(4)	0·2170(3)	0·027(2)	C(1)	0·4714(7)	0·4169(6)	0·2222(4)	0·056(3)
C(42A)	0·4940(6)	0·6479(4)	0·1682(3)	0·027(2)	Cl(1)	0·5446(2)	0·4294(2)	0·15660(12)	0·0648(8)
C(43A)	0·4625(6)	0·6294(4)	0·1183(3)	0·026(2)	Cl(2i)	0·4532(5)	0·3074(3)	0·2675(3)	0·0629(15)
C(44A)	0·3637(6)	0·5998(4)	0·1139(3)	0·029(2)	Cl(2j)	0·4123(6)	0·3324(4)	0·2382(4)	0·084(2)
C(45A)	0·2951(6)	0·5881(4)	0·1631(4)	0·030(2)	Cl(3)	0·5399(2)	0·4371(2)	0·27727(12)	0·0664(8)
C(46A)	0·3273(7)	0·5841(5)	0·0554(4)	0·037(2)	C(2)	0·0248(9)	1·1143(4)	0·2488(4)	0·076(4)
C(47A)	0·2844(7)	0·5036(5)	0·0741(4)	0·043(2)	Cl(4)	−0·0482(2)	1·19678(14)	0·21199(15)	0·0676(8)
C(48A)	0·4166(7)	0·5940(5)	0·0106(4)	0·042(2)	Cl(5)	−0·0248(3)	1·0387(2)	0·23566(13)	0·0746(9)
C(49A)	0·2358(8)	0·6380(6)	0·0259(4)	0·049(2)	Cl(6)	0·0362(3)	1·0971(2)	0·32803(15)	0·0833(10)
C(50A)	0·6058(6)	0·6759(4)	0·1732(4)	0·030(2)	C(3)	0·4758(6)	0·8509(6)	0·0613(4)	0·067(3)
O(1B)	−0·1235(4)	0·9438(3)	0·1121(2)	0·0285(13)	Cl(7)	0·3598(2)	0·8948(2)	0·02415(14)	0·0789(10)
O(2B)	−0·0630(5)	0·8099(3)	0·0934(3)	0·0405(15)	Cl(8)	0·5236(2)	0·8936(2)	0·11099(14)	0·0751(9)
O(3B)	0·1031(5)	0·7348(3)	0·1799(3)	0·044(2)	Cl(9)	0·5754(2)	0·8491(2)	0·00837(14)	0·0857(11)
O(4B)	0·1610(4)	0·8644(3)	0·2034(2)	0·0290(13)	C(4)	0·0268(6)	0·3560(7)	0·5521(4)	0·081(4)
O(5B)	−0·0536(4)	0·8274(3)	0·2305(2)	0·0361(14)	Cl(10)	0·1216(3)	0·4160(3)	0·5039(2)	0·1050(14)
O(6B)	0·0818(4)	0·9817(3)	0·0900(2)	0·0298(13)	Cl(11)	−0·0889(2)	0·3558(2)	0·50993(12)	0·0670(9)
C(1B)	−0·1664(7)	0·9232(5)	0·0617(4)	0·043(2)	Cl(12)	−0·0007(2)	0·3783(2)	0·61615(12)	0·0613(8)
C(2B)	−0·1675(7)	0·8400(5)	0·0805(4)	0·038(2)					

Table 2. Atomic parameters and equivalent isotropic displacement parameters ($Å^2$) for (2).2CH_3OH.4$CHCl_3$

The positions of disordered atoms are denoted a–c

Atom	*X/a*	*Y/b*	*Z/c*	U_{eq}	Atom	*X/a*	*Y/b*	*Z/c*	U_{eq}
O(1)	−0·5215(4)	0·4631(4)	0·6510(2)	0·0420(14)	C(57)	0·1095(7)	0·1065(5)	0·7652(3)	0·040(2)
O(2)	−0·3478(5)	0·2682(5)	0·6530(3)	0·078(2)	C(58)	0·0501(7)	0·0839(5)	0·8019(3)	0·041(2)
O(3)	−0·1241(4)	0·1985(4)	0·6647(2)	0·0420(14)	C(59)	0·1061(7)	0·0389(6)	0·8393(3)	0·045(2)
O(4)	0·0517(4)	0·1525(3)	0·7263(2)	0·0396(13)	C(60)	0·2214(6)	0·0130(5)	0·8435(3)	0·045(2)
O(5)	−0·0185(4)	0·4497(4)	0·7297(2)	0·0426(14)	C(61)	0·2735(7)	0·0390(5)	0·8054(3)	0·046(2)
O(6a)	0·0248(12)	0·4711(44)	0·6361(7)	0·073(18)	C(62)	0·2213(6)	0·0852(5)	0·7667(3)	0·038(2)
O(6b)	−0·0110(14)	0·4288(7)	0·6339(4)	0·067(5)	C(63)	0·2803(7)	−0·0392(6)	0·8837(3)	0·056(2)
O(7)	−0·1380(5)	0·5198(6)	0·5493(2)	0·083(2)	C(64a)	0·2002(19)	−0·0681(24)	0·9150(8)	0·114(13)
O(8)	−0·3663(5)	0·6224(7)	0·5439(2)	0·079(2)	C(64b)	0·2186(18)	0·0002(16)	0·9273(4)	0·109(9)
O(9)	−0·5594(5)	0·5521(5)	0·5619(2)	0·067(2)	C(65a)	0·3634(20)	−0·1278(12)	0·8667(8)	0·112(13)
O(10)	−0·3721(5)	0·5747(5)	0·6353(2)	0·056(2)	C(65b)	0·2593(21)	−0·1315(10)	0·8864(8)	0·111(10)
O(11)	0·1536(4)	0·2991(4)	0·7092(2)	0·0460(14)	C(66a)	0·3395(23)	0·0191(16)	0·9054(8)	0·094(11)
O(12)	−0·1179(5)	0·3005(4)	0·7573(2)	0·0472(15)	C(66b)	0·3970(10)	−0·0393(16)	0·8826(7)	0·095(9)
C(1)	−0·5325(8)	0·3782(7)	0·6631(4)	0·066(3)	C(67)	0·2846(7)	0·1184(5)	0·7278(3)	0·040(2)
C(2a)	−0·4364(10)	0·3075(11)	0·6846(5)	0·083(11)	C(68)	0·3141(7)	0·1995(5)	0·7429(3)	0·038(2)
C(2b)	−0·4583(9)	0·2959(10)	0·6374(6)	0·056(8)	C(69)	0·2434(6)	0·2879(6)	0·7347(2)	0·034(2)
C(3a)	−0·2764(14)	0·3311(11)	0·6633(7)	0·038(4)	C(70)	0·2663(6)	0·3628(5)	0·7518(3)	0·033(2)
C(3b)	−0·2920(15)	0·3236(12)	0·6423(7)	0·045(5)	C(71)	0·3603(6)	0·3463(6)	0·7771(3)	0·039(2)
C(4)	−0·1703(7)	0·2704(6)	0·6343(4)	0·065(3)	C(72)	0·4372(5)	0·2581(5)	0·7865(2)	0·041(2)
C(5)	−0·0153(7)	0·1475(6)	0·6522(3)	0·044(2)	C(73)	0·4079(6)	0·1865(6)	0·7676(3)	0·039(2)
C(6)	0·0408(7)	0·0899(6)	0·6925(3)	0·045(2)	C(74)	0·5356(6)	0·2393(5)	0·8132(3)	0·047(2)
C(7a)	−0·0759(20)	0·5271(12)	0·7007(4)	0·079(10)	C(75)	0·5564(8)	0·3262(6)	0·8260(4)	0·077(3)
C(7b)	−0·1163(11)	0·4855(26)	0·7034(5)	0·030(13)	C(76)	0·5279(9)	0·1837(9)	0·8564(3)	0·093(4)
C(8)	−0·0830(9)	0·5073(8)	0·6548(3)	0·092(4)	C(77)	0·6350(6)	0·1809(8)	0·7858(4)	0·090(4)
C(9)	0·0281(8)	0·4475(8)	0·5890(3)	0·076(3)	C(78)	0·1928(7)	0·4603(6)	0·7444(3)	0·042(2)
C(10)	−0·0479(9)	0·4419(9)	0·5541(4)	0·076(3)	C(79)	0·0992(7)	0·4880(5)	0·7796(3)	0·043(2)
C(11a)	−0·2162(19)	0·5448(18)	0·5146(8)	0·012(10)	C(80)	−0·0014(6)	0·4776(5)	0·7717(3)	0·037(2)
C(11b)	−0·2062(11)	0·4994(14)	0·5155(4)	0·061(5)	C(81)	−0·0814(7)	0·4911(5)	0·8068(3)	0·042(2)
C(12a)	−0·2917(20)	0·6440(19)	0·5094(9)	0·025(11)	C(82)	−0·0594(7)	0·5227(6)	0·8485(3)	0·047(2)
C(12b)	−0·2921(10)	0·5970(12)	0·5048(4)	0·060(5)	C(83)	0·0366(7)	0·5381(6)	0·8592(3)	0·055(2)
C(13)	−0·5927(7)	0·5367(6)	0·6750(3)	0·042(2)	C(84)	0·1164(8)	0·5180(6)	0·8225(3)	0·052(2)
C(14)	−0·6994(6)	0·5734(6)	0·6602(3)	0·039(2)	C(85)	0·0607(7)	0·5674(6)	0·9028(3)	0·079(4)
C(15)	−0·7687(6)	0·6510(6)	0·6820(3)	0·042(2)	C(86a)	−0·0011(34)	0·5408(33)	0·9422(5)	0·095(10)
C(16)	−0·7344(6)	0·6906(5)	0·7169(3)	0·038(2)	C(86b)	−0·0369(16)	0·5925(22)	0·9354(6)	0·071(8)
C(17)	−0·6274(7)	0·6515(5)	0·7301(3)	0·039(2)	C(86c)	−0·0289(29)	0·6847(23)	0·8986(12)	0·107(10)
C(18)	−0·5542(6)	0·5771(5)	0·7101(3)	0·037(2)	C(87a)	0·0996(23)	0·6487(14)	0·8979(6)	0·060(6)
C(19)	−0·8091(6)	0·7765(5)	0·7409(3)	0·049(2)	C(87b)	0·1542(15)	0·6056(16)	0·8982(6)	0·047(5)
C(20)	−0·8345(9)	0·7492(7)	0·7893(4)	0·075(3)	C(88a)	0·1476(18)	0·4866(12)	0·9276(6)	0·063(6)
C(21)	−0·9163(7)	0·8184(7)	0·7156(4)	0·070(3)	C(88b)	0·0734(56)	0·4907(24)	0·9394(7)	0·149(15)
C(22)	−0·7523(8)	0·8487(7)	0·7405(4)	0·071(3)	C(89)	−0·1844(7)	0·4657(5)	0·8022(3)	0·040(2)
C(23)	−0·7420(7)	0·5392(6)	0·6190(3)	0·047(2)	C(90)	−0·1722(6)	0·3761(6)	0·8277(3)	0·040(2)
C(24)	−0·7534(7)	0·6056(7)	0·5791(3)	0·052(2)	C(91)	−0·1336(6)	0·2933(5)	0·8032(3)	0·039(2)
C(25)	−0·6622(7)	0·6123(8)	0·5543(3)	0·060(3)	C(92)	−0·1188(7)	0·2093(5)	0·8279(3)	0·042(2)
C(26)	−0·6732(7)	0·6773(10)	0·5186(3)	0·079(4)	C(93)	−0·1395(7)	0·2084(6)	0·8744(3)	0·047(2)
C(27)	−0·7791(8)	0·7388(8)	0·5087(3)	0·075(3)	C(94)	−0·1774(6)	0·2902(6)	0·9009(2)	0·047(2)
C(28)	−0·8761(6)	0·7382(6)	0·5328(3)	0·058(3)	C(95)	−0·1910(6)	0·3709(6)	0·8741(3)	0·042(2)
C(29)	−0·8561(7)	0·6678(7)	0·5685(3)	0·056(3)	C(96)	−0·1954(6)	0·2828(5)	0·9504(3)	0·052(2)
C(30)	−0·9815(7)	0·8094(7)	0·5260(3)	0·066(3)	C(97a)	−0·0850(12)	0·2433(19)	0·9737(5)	0·084(9)
C(31a)	−1·0717(9)	0·7909(11)	0·5540(6)	0·063(6)	C(97b)	−0·0969(12)	0·2122(13)	0·9726(5)	0·051(6)
C(31b)	−1·0676(14)	0·7614(17)	0·5210(17)	0·139(17)	C(98)	−0·2873(10)	0·2444(10)	0·9607(4)	0·095(4)
C(32a)	−0·9768(13)	0·8967(7)	0·5491(6)	0·070(7)	C(99)	−0·2311(10)	0·3775(7)	0·9712(3)	0·082(3)
C(32b)	−1·0302(18)	0·8442(19)	0·5727(6)	0·105(14)	C(100)	−0·0737(6)	0·1201(5)	0·8032(3)	0·044(2)
C(33a)	−1·0030(12)	0·8313(12)	0·4751(4)	0·054(5)	Cl(1)	0·2719(3)	−0·0700(3)	0·41317(10)	0·1115(12)
C(33b)	−0·9826(21)	0·8625(21)	0·4812(8)	0·096(12)	Cl(2)	0·3855(3)	−0·0615(2)	0·32815(12)	0·0953(11)
C(34)	−0·5742(8)	0·6907(11)	0·4958(4)	0·097(5)	Cl(3)	0·1566(3)	0·0348(2)	0·33563(12)	0·0877(10)
C(35)	−0·5283(9)	0·7472(12)	0·5246(4)	0·087(4)	C(101)	0·2640(8)	−0·0642(7)	0·3528(3)	0·058(3)
C(36)	−0·4297(10)	0·7118(12)	0·5472(4)	0·082(4)	Cl(4)	0·5577(9)	0·8403(7)	0·0153(4)	0·183(4)
C(37)	−0·3986(9)	0·7657(12)	0·5779(4)	0·087(4)	Cl(5)	0·6207(12)	0·6607(9)	0·0334(4)	0·190(4)
C(38)	−0·4649(9)	0·8587(10)	0·5853(4)	0·081(4)	Cl(6)	0·7716(7)	0·7262(6)	−0·0067(3)	0·137(3)
C(39)	−0·5665(8)	0·8998(8)	0·5622(4)	0·105(5)	Cl(7)	0·7938(7)	0·7624(8)	0·0108(4)	0·170(4)
C(40)	−0·5917(9)	0·8394(13)	0·5316(4)	0·094(5)	Cl(8)	0·5686(15)	0·7179(17)	0·0217(7)	0·286(9)
C(41)	−0·6397(10)	0·9893(11)	0·5696(4)	0·108(5)	C(102)	0·6722(7)	0·7535(8)	0·0334(4)	0·122(5)
C(42a)	−0·7413(39)	0·9867(20)	0·5968(31)	0·219(58)	Cl(9)	0·5466(4)	0·5058(4)	0·0648(2)	0·086(2)
C(42b)	−0·7520(25)	0·9836(18)	0·5856(31)	0·182(42)	Cl(10)	0·5515(5)	0·4539(5)	0·0568(2)	0·102(2)
C(43)	−0·6685(11)	1·0468(9)	0·5254(4)	0·113(5)	Cl(11)	0·4042(4)	0·3889(3)	0·0959(2)	0·0728(12)
C(44a)	−0·5915(24)	1·0398(15)	0·6027(11)	0·122(10)	Cl(12)	0·5696(5)	0·4309(4)	0·1548(2)	0·082(2)
C(44b)	−0·6382(26)	1·0144(17)	0·6195(6)	0·117(10)	Cl(13)	0·5471(5)	0·4023(5)	0·1536(2)	0·096(2)
C(45)	−0·2959(7)	0·7301(9)	0·6059(3)	0·074(3)	C(103)	0·4812(6)	0·4608(6)	0·1078(2)	0·074(3)
C(46)	−0·3207(6)	0·7069(8)	0·6558(4)	0·060(3)	Cl(14)	0·0940(5)	0·0268(5)	1·0416(2)	0·110(2)
C(47)	−0·3587(6)	0·6328(7)	0·6675(3)	0·051(2)	Cl(15)	0·2807(10)	0·0032(8)	1·1019(5)	0·209(4)
C(48)	−0·3847(6)	0·6165(6)	0·7116(3)	0·041(2)	Cl(16)	0·3120(7)	0·0089(6)	1·0581(4)	0·162(3)
C(49)	−0·3649(6)	0·6686(5)	0·7466(3)	0·041(2)	Cl(17)	0·0798(9)	0·1137(7)	1·1183(3)	0·176(3)
C(50)	−0·3242(6)	0·7391(6)	0·7367(3)	0·047(2)	Cl(18)	0·1904(1)	0·0544(8)	1·1313(3)	0·196(4)
C(51)	−0·3034(7)	0·7567(6)	0·6912(4)	0·052(2)	C(104)	0·1738(8)	0·0734(7)	1·0727(3)	0·190(23)
C(52)	−0·3051(9)	0·7978(7)	0·7745(4)	0·069(3)	O(13)	0·2415(8)	0·2597(8)	0·8708(3)	0·113(3)
C(53)	−0·3791(14)	0·8934(8)	0·7706(6)	0·119(5)	C(105)	0·1354(8)	0·2704(8)	0·8602(4)	0·069(3)
C(54)	−0·1807(10)	0·7919(10)	0·7717(5)	0·099(4)	O(14)	0·1936(8)	0·2449(6)	0·6172(3)	0·107(3)
C(55)	−0·3210(10)	0·7596(8)	0·8226(4)	0·078(3)	C(106)	0·2937(13)	0·2641(10)	0·6117(6)	0·114(5)
C(56)	−0·4358(6)	0·5436(6)	0·7239(3)	0·039(2)					

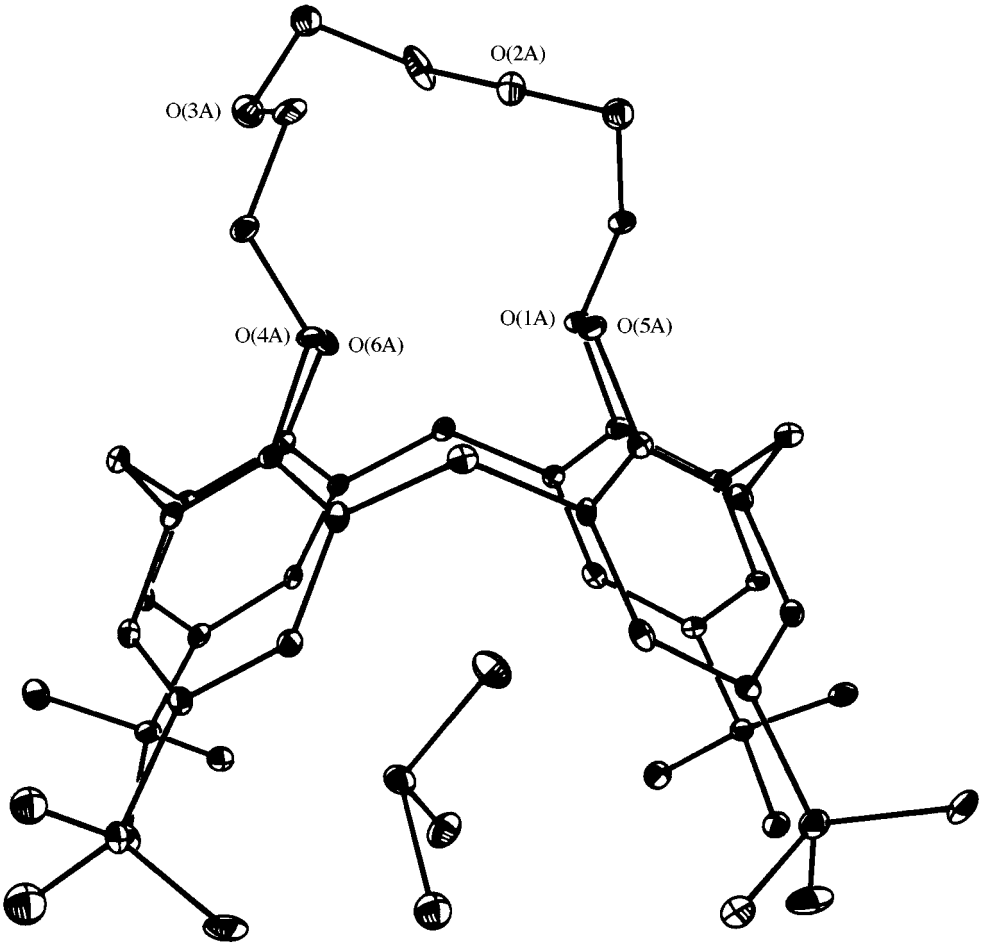


Fig. 1. Molecular unit of (1).2$CHCl_3$ (only one molecule is represented; hydrogen atoms and the non-included chloroform molecule have been omitted for clarity). Ellipsoids are drawn at the 15% probability level.

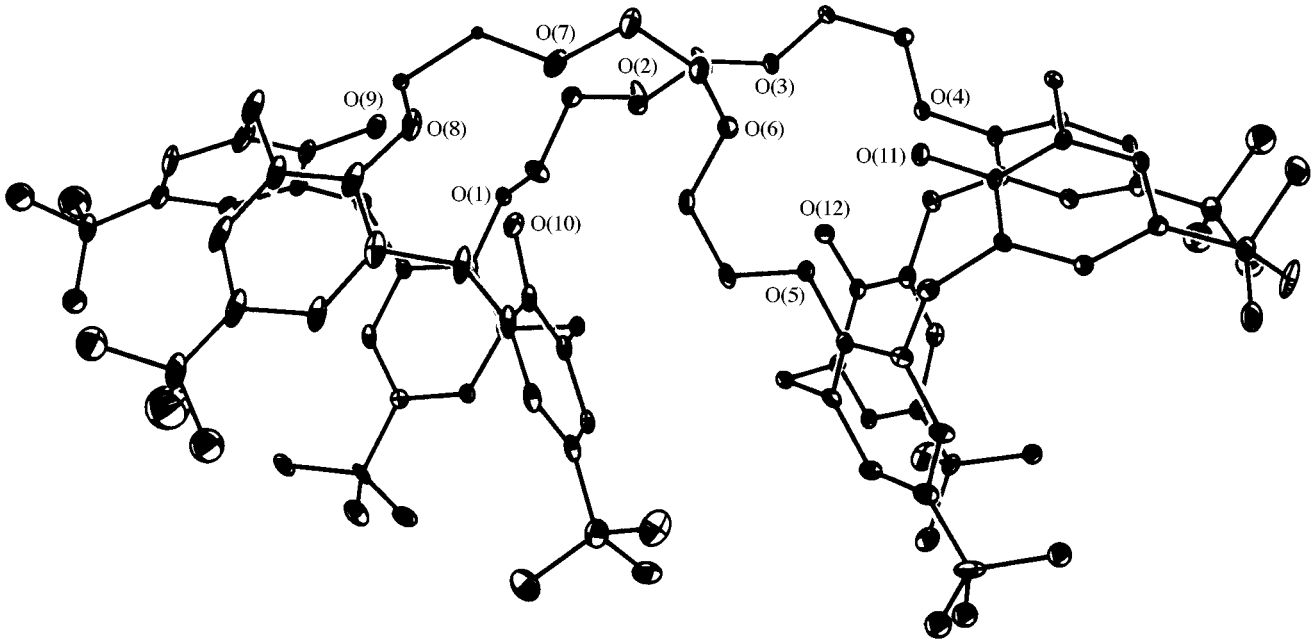


Fig. 2. Molecular unit of (2).2CH_3OH.4$CHCl_3$ (hydrogen atoms and solvent molecules have been omitted for clarity). Only one position of the disordered atoms is represented. Ellipsoids are drawn at the 15% probability level.

Chemicals

Triethylene glycol ditosylate (Aldrich) was used as received. All commercial solvents and basic reagents were also used without purification. *p*-t-Butylcalix[4]arene was prepared as described in ref. 13.

Preparation of (1) and (2)

p-t-Butylcalix[4]arene (19·47 g, 30·0 mmol) and potassium carbonate (4·15 g, 30·0 mmol) were stirred at room temperature in acetonitrile (1500 ml) for 3 h. Triethylene glycol ditosylate (15·13 g, 33·0 mmol) was added as a solid and the mixture was then heated to reflux. After 7 days the solvents were evaporated to dryness. The residue was acidified with 1 M HCl, and the aqueous phase was extracted with dichloromethane. The organic layer was dried over sodium sulfate, filtered and evaporated. After evaporation, the residue was chromatographed on a silica column with dichloromethane as eluent. Calixcrown-4 (1) (R_F 0·7; 11·87 g, 52%) was first eluted pure as a white solid (m.p. 195–196°C). Then, pure double calix[4]arene double crown-4 (2) (R_F 0·6; 3·46 g, 15%) was isolated as another white solid (m.p. 168–169°C).

Analytical Data for (1)

^{1}H n.m.r. (200 MHz, $CDCl_3$, δ in ppm from $SiMe_4$, J in Hz) 8·68, s, 2H, ArO**H**; 7·05, s, 4H, ArH *meta*; 6·97, s, 4H, ArH *meta*; 4·36, d, J_{AB} 13·0 Hz, 4H, ArC**H**$_2$Ar; 4·17, s large, 8H, ArOC**H**$_2$C**H**$_2$O; 3·97, s, 4H, OCH_2CH_2O; 3·33, d, J_{AB} 13·0 Hz, 4H, ArC**H**$_2$Ar; 1·20, s, 18H, $C(CH_3)_3$; 1·18, s, 18H, $C(CH_3)_3$. F.a.b. mass spectrum (+) *m/z* 762·7. Found: C, 75·3; H, 8·4. $C_{50}H_{66}O_6.0{\cdot}5CH_2Cl_2$ requires C, 75·3; H, 8·4%.

Analytical Data for (2)

^{1}H n.m.r. (200 MHz, $CDCl_3$, δ in ppm from $SiMe_4$, J in Hz) 7·32, s, 4H, ArO**H**; 7·01, s, 8H, ArH *meta*; 6·74, s, 8H, ArH *meta*; 4·33, d, J_{AB} 13·0 Hz, 8H, ArC**H**$_2$Ar; 4·03, s large, 16H, OCH_2CH_2O; 3·24, d, J_{AB} 13·0 Hz, 8H, ArC**H**$_2$Ar; 1·24, s, 36H, $C(CH_3)_3$; 0·91, s, 36H, $C(CH_3)_3$. F.a.b. mass spectrum (+) *m/z* 1526·3. Found: C, 78·5; H, 8·5. $C_{108}H_{132}O_{12}$ requires C, 78·7; H, 8·7%.

Crystal Structure Determinations

Crystals of solvates of (1) and (2), of rather low quality but suitable for X-ray crystallography, were obtained from slow evaporation of $CHCl_3/CH_3OH$ (1:1) solutions, and sealed in Lindemann capillaries [recrystallization of (1) from a CH_3OH/CH_3CN (1:1) solution led to another form, for which the structure refinement was less satisfying]. Crystals of (2) were particularly unstable, readily losing their crystallization solvent, a problem which was overcome by using low temperatures for data recording (123 K for both compounds). Data were recorded on a Nonius Kappa-CCD area-detector diffractometer; graphite monochromatized Mo Kα radiation was used. The crystal-to-detector distance was set to 29 mm for both compounds, and the unit cells were determined from all the reflections measured on 10 plates (ϕ rotation with 1° steps). A 180° ϕ range was scanned during data recording (90 plates, ϕ rotation with 2° steps). The data were processed with the HKL package;[14] the structures were solved by direct methods with SHELXS86[15] and refined on F^2 with SHELXTL.[16] No absorption correction was made. Special details are given below.

Crystal data for (1).2$CHCl_3$: $C_{104}H_{136}Cl_{12}O_{12}$ (Z = 2, two molecules in the asymmetric unit), M_r 2003·53, triclinic, space group $P\bar{1}$, a 12·4725(8), b 19·0396(12), c 23·2382(9) Å, α 69·683(2), β 89·870(2), γ 89·127(2)°, V 5174(3) Å^3, Z 2, D_c 1·286 g cm^{-3}, μ 0·379 mm^{-1}, $F(000)$ 2120, crystal size 0·24 by 0·24 by 0·18 mm, 18940 unique reflections used, 1162 parameters refined, R 0·123, S = 1·06. Some atoms in the t-butyl groups and the solvent molecules were found disordered and were modelled with two positions and occupation factors set to 0·5. Some constraints on bond lengths and angles were applied on the disordered fragments. All non-hydrogen atoms were refined anisotropically except those of the disordered fragments. Hydrogen atoms were introduced at calculated positions (except for OH groups, disordered atoms and solvent molecules) and constrained to ride their parent carbon atom with isotropic thermal parameters equal to 1·2 (CH, CH_2) or 1·5 (CH_3) times that of the parent atom.

Crystal data for (1).$CH_3OH.CH_3CN$: $C_{53}H_{73}N_1O_7$ (formula for a complete molecular unit, but only half a molecule in the asymmetric unit), M_r 836·12, trigonal, space group $P3_221$, a 12·5654(3), c 28·1217(3) Å, V 3845(2) Å^3, Z 3, D_c 1·083 g cm^{-3}, μ 0·070 mm^{-1}, $F(000)$ 1362. The results of the structure refinement, not quite satisfying due to low crystal quality, are not given here.

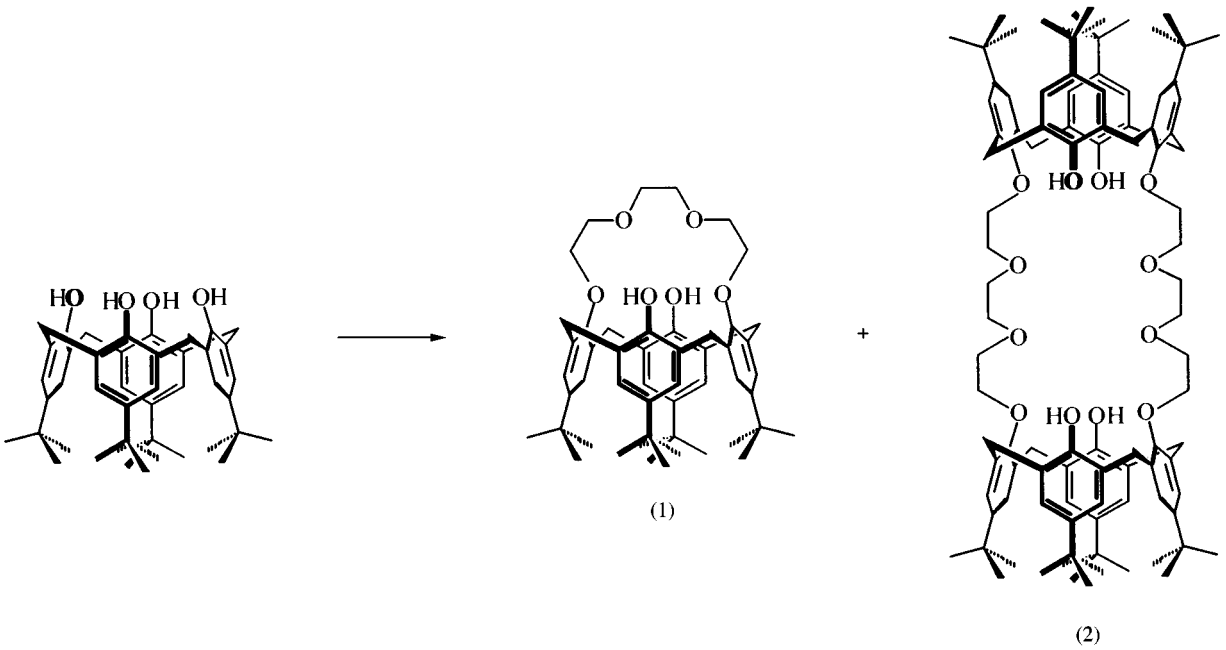
Crystal data for (2).2CH_3OH.4$CHCl_3$: $C_{106}H_{144}Cl_{12}O_{14}$, M_r 2067·58, triclinic, space group $P\bar{1}$, a 12·9861(12), b 15·4868(15), c 29·144(3) Å, α 87·494(2), β 88·122(3), γ 70·781(2)°, V 5528(3) Å^3, Z 2, D_c 1·240 g cm^{-3}, μ 0·358 mm^{-1}, $F(000)$ 2184, crystal size 0·30 by 0·25 by 0·25 mm, 19137 unique reflections used, 1210 parameters refined, R 0·141, S 1·13. Some t-butyl groups and some parts of the ether chains were disordered over two or three positions and were refined with occupation factors constrained to sum to unity. Three out of four chloroform molecules were also highly disordered and modelled with up to five chlorine atoms. Some constraints on bond lengths and angles were applied on the disordered fragments. All non-hydrogen atoms were refined anisotropically except those of the disordered solvent molecules. Hydrogen atoms were introduced at calculated positions (except for OH groups, disordered atoms and solvent molecules) and constrained to ride their parent carbon atom with isotropic thermal parameters equal to 1·2 (CH, CH_2) or 1·5 (CH_3) times that of the parent atom. The highest residual density peak (1·2 e Å^{-3}) is located near a badly resolved chloroform molecule.

Final atomic parameters and equivalent thermal parameters are given in Tables 1 and 2, and molecular drawings, done with SHELXTL,[16] in Figs 1 and 2. Bond lengths and angles lie in the usual range. Material deposited includes Tables of structure factor amplitudes, interatomic distances and angles, anisotropic thermal parameters and hydrogen atom coordinates in CIF format (copies are available, until 31 December 2004, from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066).

Results and Discussion

The reaction leading to (1) and (2) is presented in Scheme 1.

The condensation reaction was conducted according to a similar procedure prescription described elsewhere for related compounds.[17] After workup, the residue was chromatographed on silica to afford (1) and (2) as white solids in 67% total yield. The ^{1}H n.m.r. spectra of calixcrowns (1) and (2) were very similar, and presented the same integration ratio of calixarene unit to glycol chain. The only difference was the presence of a singlet at 4·17 ppm for the central OCH_2CH_2O protons in the spectrum of (1), a feature which cannot be distinguished in the spectrum of (2). This could probably be due to a more constrained bridging in (1) if corresponding to the 1+1 condensation product. F.a.b. mass spectrometry showed that (1) corresponded to a 1+1 condensation product and (2) to its dimer.



Scheme 1. Preparation of (1) and (2). Reaction conditions: K_2CO_3, $TsO(CH_2CH_2O)_3Ts$, acetonitrile, reflux.

The ^{1}H n.m.r. spectra of calixcrowns (1) and (2) also presented AB systems for the $ArC\mathbf{H}_2Ar$ protons in the calix macrocyclic structure at 4·36 and 3·33 ppm with J_{AB} 13·0 Hz for (1), and at 4·33 and 3·24 ppm with J_{AB} 13·0 Hz for (2). These AB systems could be attributed to *diastereotopic* CH_2 protons of a calix[4]arene either in a cone conformation or in a 1,3-alternate conformation. Hence X-ray diffraction techniques were used to determine the crystal structures of (1) and (2). The crystal structures unambiguously established the nature of the compounds and the *cone conformation* of the calix units.

In (1).2$CHCl_3$, two independent molecules are present in the asymmetric unit, each with a chloroform molecule in its cavity, positioned in such a way that the C–Cl bond is directed towards the calixarene inner cavity (two other chloroform molecules are present in the packing). These two molecules differ in the ether chain conformation. If, as is usually done, we characterize this conformation by the sequence of the signs of the *gauche* O–C–C–O angles, one of the molecules corresponds to $g^-g^-g^+$ (with two *anti* C–O–C–C angles becoming *gauche* ones), shown in Fig. 1, and the other one to the more regular conformation $g^-g^+g^-$ (with only a slightly distorted *anti* angle).

The structure of (2).2CH_3OH.4$CHCl_3$ is highly disordered. As shown in Fig. 2, the two calixarene units are not parallel to each other due to the length of the ether bridges which assume a curved shape, in contrast to what has been described in the case of two *p*-t-butylcalix[4]arene units bridged by four ethylene linkages.[18] This bridge shape and the disorder observed were consistent with the previous assumption about the low geometrical constraints present in compound (2) when in solution. Two methanol molecules are present in the structure. One of them forms a hydrogen bond with a phenolic oxygen atom [O(14)···O(11) 2·826 Å]. The other one is included in one of the cavities of the bis(calixarene), with the oxygen atom directed outwards, and possibly forms a hydrogen bond with C–H group of a chloroform molecule [O(13)···C(102i) 3·016 Å, with i = $1-x$, $1-y$, $1-z$].

The present data show that one can differentiate by ^{1}H n.m.r. a calix[4]crown from its dimer by taking into account the constraint imposed on the polyether chain by 1,3-bridging. Similar findings have already been made for related calixcrowns deriving from calix[4]mesitylene.[9]

Compounds (1) and (2) are useful synthons for further functionalizations: the presence of OH functionalities in diametrical positions make these substances attractive for the synthesis of highly symmetrical architectures to provide more complex and rigid receptors.[19–21]

References

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