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Crystal and molecular structure of a chiral calixarene: (+)5,11,17,23-tetra-tert-butyl-25,27- di[(camphorsulfonyl)oxy]-26,28-dihydroxycalix[4]arene

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Treatment of p-tert-butylcalix[4]arene with (+) camphorsulfonyl chloride in pyridine allows the synthesis of the title compound. It crystallizes in the triclinic space group P1 with a = 14.671(4), b = 17.530(3), c = 13.085(9)Å, α = 103.69(3), β = 111.37(4), γ = 84.60(2)°; d_{calc} = 1.172 g/cm^3. Refinement on 17295 reflections; final R value of 0.084. The asymmetric unit contains two independent molecules, both in a cone conformation. The calixarene cavities have a pseudo C_{2v} symmetry with the two opposite phenolic rings bearing the camphorsulfonyl groups almost parallel to one another. The norborane skelton of the (+) camphorsulfonyl group is similar to the ones found in literature. The shortest intermolecular contacts concern oxygens of the camphorsulfonyl group.

INTRODUCTION

Chirality in calixarenes is obtained by three different approaches: the first of them consists of treating calixarenes with chiral compounds (Muthukrishnan and Gutsche[1], Shinkai[2]); the second one consists of making the calixarene from unsymmetrical building blocks (Böhmer[3]). In the third one, chirality is obtained by functionalization of achiral calixarenes leading to an inherently chiral conformation (Pappalardo[4,5]).

The synthesis of the title compound utilises the first method and consists of treating p-tert-butylcalix[4]arene with (+) camphorsulfonyl in pyridine. Synthesis and study of a chiral calixarene were undertaken with the intention of obtaining enantioselection in the complexation of small molecules.

EXPERIMENTAL

Synthesis

In a 250 mL round bottom flask equiped with a condenser, a dropping funnel and a gas supply, 150 mL of dry pyridine were added to 0.92 g (1.42 m mol) of p-tert-butylcalix[4]arene in a nitrogen atmosphere. The reacting medium was then refluxed. 1.7 g (6,8 m mol) of (+) camphorsulfonyl chloride were dissolved in 90 mL of pyridine and put in the dropping funnel with a syringe. The solution was added drop-wise to the reaction mixture which was then allowed to reflux for two hours. After the flask was cooled at room temperature, the solvent was evaporated. The residue was collected, dissolved in dichloromethane, washed and neutralized in a separating funnel with a 1N HCl solution, salted water, saturated $NaHCO_3$ solution and salted water. The organic phase was decanted and dried on sodium sulfate. The solvent was evaporated and after a fractional crystallization of the solid in a dichloromethane-methanol mixture, 0.52 g of the title compound was obtained. A second crystallization gave 0.46 g (30% yield) of the pure compound. Anal. Calcd for $C_{64}H_{84}S_2O_{10}$: C, 71.39; H, 7.86; O, 14.86; S, 5.94. Found: C, 71.41; H, 7.97; O, 14.82; S, 5.80. ^{1}H NMR ($CDCl_3$) δ 0.86 (18 H, s, $C(CH_3)_3$); 0.97 (6 H, s, CH_3); 1.21 (6 H, s, CH_3); 1.34 (18 H, s, $C(CH_3)_3$); 1.5 – 2.7 (14 H, m, CH and CH_2 camphor); 3.44 (2 H, d, CH_2SO_2, J = 14.7 Hz); 3.48 (4 H, d, CH_2Ar, J = 12.5 Hz); 4.00 (2 H, d, CH_2SO_2, J = 14.8 Hz); 4.33 (2 H, d, CH_2, Ar, J = 14.1 Hz); 4.35 (2 H, d, CH_2Ar, J = 14 Hz); 6.70 (4 H, s, Ar-H); 7.15 (4 H, s, Ar-H).

X-Ray data, structure determination and refinement

A single crystal of the title compound was sealed in a

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*Corresponding author:

capillary tube. The X-ray measurements were performed at room temperature on an Enraf Nonius CAD4 diffractometer using graphite monochromatized CuK$_\alpha$ radiation. Accurate lattice parameters were obtained by least-squares fit of 25 reflections in the range ($13° \le \theta \le 50°$). Intensities were collected in the range $1° < \theta < 73°$ using the (ω - 2θ) scan mode. Three standard reflections were measured every hour to control intensity variations and a test was performed every 100 measurements to check the orientation of the crystal.

Intensities were corrected for Lorentz, polarisation and absorption effects using programs of the SDP[6] system. The structure was solved by Multan[7] and refined using SHELX[8,9]. The S and O atoms and the carbons of the eight phenolic units were obtained from the direct methods. The camphor groups were obtained progressively from Fourier maps. Hydrogen atoms have been localised at their theoretical positions. Non-hydrogen atoms were refined first with isotropic, then anisotropic structure factors. Hydrogens were refined isotropically, riding on the coordinates of the previous atom with the thermal parameter fixed at 1.3 times the equivalent thermal parameter of the attached atom. The configuration of the camphor group has been inferred by internal comparison with the known absolute stereochemistry of (+) camphor (Allen and Rogers[10]) and other derivatives of (+) camphor (Ziolo[11], Sakai[12]). The Flack[13] parameter calculated after the last refinement was $\chi = 0.06(2)$. This is a confirmation that the correct enantiomer has been selected and that the absolute structure of the title compound has been obtained. The final R value calculated on the 17295 observed reflections was 0.084 and the goodness of fit 1.096. A summary of data collection and refinement parameters is given in Table 1.

Table 1 Crystal data

Molecular formula:	$S_2C_{64}H_{84}O_{10}$	
Molecular weight:	1077.49	
Crystal system:	triclinic	
Space group:	P1	
Cell Constants:		
a = 14.671(4)Å		α = 103.69(3)°
b = 17.530(3)Å		β = 111.37(4)°
c = 13.085(9)Å		γ = 84.60(2)°
Volume: 3044(2)Å^3		
Formula units/unit cell:	2	
d_{calc}:	1.172 g/cm^3	
F(000):	1160	
CuK$_\alpha$ radiation:	λ = 1.54056 Å	
μ:	12.3 cm^{-1}	
Number of reflections measured:	23876	
observed:	17295	
Final R value:	0.084	
Goodness of fit:	1.096	

RESULTS AND DISCUSSION

The asymmetric unit contains two independant molecules, A and B. Figure 1 shows the numbering scheme of atoms and rings for both molecules. Final fractional coordinates and equivalent isotropic thermal parameters for non hydrogen atoms are reported in Table 2. Bond distances and angles are deposited as supplementary data.

Molecules are in a cone conformation. The four planes (1, 2, 3 and 4) correspond to the phenolic units; the angles made by these planes with the least-squares plane defined by the four bridging methylene groups (plane 5) are, respectively, 146.5(2), 94.2(1), 140.8(1) and 91.5(1)° for molecule A and 146.8(2), 90.5(1), 141.0(1) and 90.8(1)° for molecule B. Angles between plane 2 and plane 4 are 6 (1)° for molecule A and 1(4)° for molecule B: the two rings bearing the camphorsulfonyl groups are almost parallel to one another. A similar

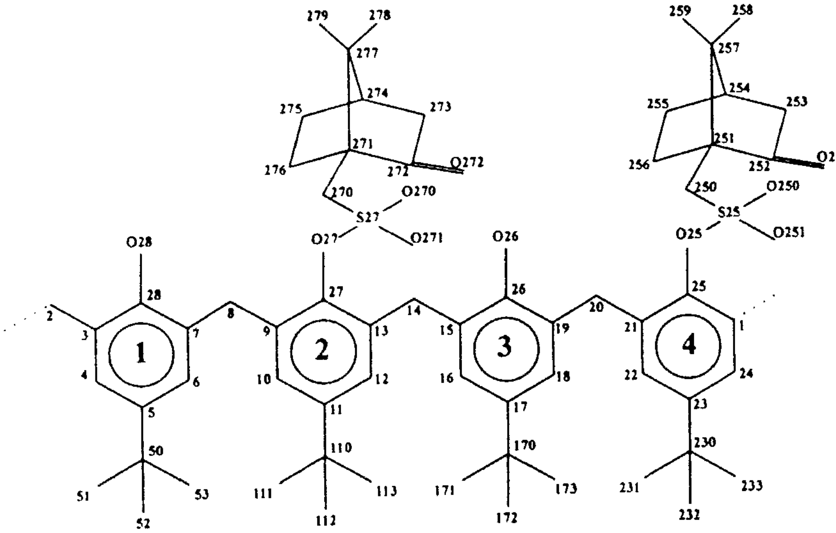

Figure 1 Numbering scheme

Table 2 Positional and thermal parameters.

Atom	*x*	*y*	*z*	$B(A^2)$	*Atom*	*x*	*y*	*z*	$B(A^2)$
Molecule A					Molecule B				
C(1)	0.5611(3)	0.1377(2)	0.1993(3)	3.3(1)	C(1)	0.4429(3)	0.8628(2)	0.8536(4)	3.5(1)
C(2)	0.5038(3)	0.1490(3)	0.0799(4)	3.8(1)	C(2)	0.4991(3)	0.8543(3)	0.9719(4)	3.8(1)
C(3)	0.5706(3)	0.1605(3)	0.0190(3)	3.5(1)	C(3)	0.4331(3)	0.8420(2)	1.0326(4)	3.5(1)
C(4)	0.5763(3)	0.1049(3)	-0.0740(4)	3.8(1)	C(4)	0.4286(3)	0.8984(3)	1.1248(4)	3.9(1)
C(5)	0.6343(3)	0.1139(3)	-0.1336(4)	3.7(1)	C(5)	0.3703(3)	0.8884(3)	1.1857(4)	3.8(1)
C(50)	0.6352(4)	0.0574(3)	-0.2396(5)	5.1(2)	C(50)	0.3657(4)	0.9506(3)	1.2892(5)	5.0(1)
C(51)	0.5936(8)	0.0958(5)	-0.3418(6)	9.2(3)	C(51)	0.2687(7)	0.9545(6)	1.2982(9)	10.7(4)
C(52)	0.5749(6)	-0.0163(4)	-0.2670(6)	7.2(2)	C(52)	0.399(1)	1.0283(5)	1.297(1)	12.1(5)
C(53)	0.7387(6)	0.0328(6)	-0.2295(9)	11.0(4)	C(53)	0.426(1)	0.9177(7)	1.3911(6)	13.4(4)
C(6)	0.6886(3)	0.1830(3)	-0.0937(4)	3.9(1)	C(6)	0.3148(3)	0.8211(3)	1.1480(4)	3.8(1)
C(7)	0.6897(3)	0.2388(3)	0.0002(3)	3.5(1)	C(7)	0.3162(3)	0.7637(2)	1.0541(4)	3.6(1)
C(8)	0.7558(3)	0.3093(3)	0.0462(4)	3.9(1)	C(8)	0.2512(3)	0.6928(3)	1.0105(4)	3.6(1)
C(9)	0.8375(3)	0.3013(2)	0.1559(4)	3.6(1)	C(9)	0.1705(3)	0.6998(2)	0.9007(3)	3.5(1)
C(10)	0.9011(3)	0.2385(3)	0.1578(5)	4.5(1)	C(10)	0.1091(3)	0.7643(3)	0.8939(4)	4.2(1)
C(11)	0.9686(4)	0.2237(3)	0.2551(5)	5.1(2)	C(11)	0.0399(3)	0.7775(3)	0.7920(4)	4.5(1)
C(110)	1.0409(5)	0.1536(4)	0.2554(7)	7.0(2)	C(110)	-0.0294(5)	0.8476(4)	0.7952(6)	6.4(2)
C(111)	0.986(1)	0.0816(7)	0.182(2)	20(1)	C(111)	0.025(1)	0.9232(5)	0.865(1)	12.0(5)
C(112)	1.102(1)	0.163(1)	0.188(1)	16.6(8)	C(112)	-0.0826(9)	0.8676(8)	0.6808(9)	13.1(5)
C(113)	1.107(2)	0.149(1)	0.365(1)	30(1)	C(113)	-0.105(1)	0.8314(7)	0.837(2)	18.8(9)
C(12)	0.9733(3)	0.2745(3)	0.3549(5)	4.4(1)	C(12)	0.0416(4)	0.7258(3)	0.6949(4)	4.5(1)
C(13)	0.9097(3)	0.3388(3)	0.3589(3)	3.6(1)	C(13)	0.0991(3)	0.6588(3)	0.6946(4)	3.8(1)
C(14)	0.9097(4)	0.3887(3)	0.4724(4)	4.5(1)	C(14)	0.1004(4)	0.6088(3)	0.5847(4)	4.2(1)
C(15)	0.8707(3)	0.3432(3)	0.5321(4)	3.8(1)	C(15)	0.1350(3)	0.6544(3)	0.5204(4)	3.9(1)
C(16)	0.9356(3)	0.3190(3)	0.6280(4)	3.9(1)	C(16)	0.0717(4)	0.6765(3)	0.4256(4)	4.4(1)
C(17)	0.9052(3)	0.2764(3)	0.6879(4)	3.7(1)	C(17)	0.1006(4)	0.7204(3)	0.3675(4)	4.1(1)
C(170)	0.9734(4)	0.2490(3)	0.7913(4)	4.9(1)	C(170)	0.0262(4)	0.7474(4)	0.2635(5)	5.2(2)
C(171)	0.9467(6)	0.2854(7)	0.8907(5)	9.7(3)	C(171)	0.0610(6)	0.7274(8)	0.1657(7)	11.5(4)
C(172)	0.9672(7)	0.1598(6)	0.771(1)	12.2(4)	C(172)	-0.0702(9)	0.718(1)	0.229(1)	18.0(7)
C(173)	1.0807(4)	0.2690(5)	0.8181(5)	6.5(2)	C(173)	0.0234(8)	0.8385(6)	0.2920(9)	10.7(4)
C(18)	0.8054(3)	0.2597(3)	0.6462(4)	3.8(1)	C(18)	0.1989(3)	0.7392(3)	0.4047(4)	4.2(1)
C(19)	0.7392(3)	0.2818(2)	0.5518(3)	3.3(1)	C(19)	0.2662(3)	0.7185(3)	0.5021(4)	3.9(1)
C(20)	0.6334(3)	0.2559(3)	0.5039(4)	3.6(1)	C(20)	0.3710(3)	0.7471(3)	0.5491(4)	4.1(1)
C(21)	0.6191(3)	0.1885(2)	0.4014(3)	3.2(1)	C(21)	0.3827(3)	0.8133(3)	0.6494(4)	3.7(1)
C(22)	0.6756(3)	0.1215(3)	0.4134(4)	3.6(1)	C(22)	0.3236(3)	0.8784(3)	0.6390(4)	3.8(1)
C(23)	0.6804(3)	0.0631(2)	0.3232(4)	3.5(1)	C(23)	0.3202(3)	0.9372(3)	0.7298(4)	4.2(1)
C(230)	0.7508(4)	-0.0064(3)	0.3440(5)	5.3(1)	C(230)	0.2515(4)	1.0082(3)	0.7106(5)	5.6(2)
C(231)	0.733(1)	-0.0492(7)	0.422(1)	14.2(6)	C(231)	0.2459(7)	1.0589(5)	0.8196(7)	10.7(3)
C(232)	0.7435(9)	-0.0671(5)	0.2388(7)	13.0(4)	C(232)	0.1519(5)	0.9811(7)	0.635(1)	12.4(4)
C(233)	0.8539(5)	0.0228(6)	0.414(1)	12.3(4)	C(233)	0.2921(9)	1.0592(6)	0.658(1)	12.1(5)
C(24)	0.6219(3)	0.0732(2)	0.2168(4)	3.5(1)	C(24)	0.3797(3)	0.9272(2)	0.8371(4)	3.9(1)
C(25)	0.5589(3)	0.1943(2)	0.2936(4)	3.4(1)	C(25)	0.4449(3)	0.8094(2)	0.7589(3)	3.4(1)
O(25)	0.5059(2)	0.2638(2)	0.2769(3)	3.73(8)	O(25)	0.5087(2)	0.7421(2)	0.7745(3)	4.31(8)
C(26)	0.7723(3)	0.3238(2)	0.4946(4)	3.6(1)	C(26)	0.2331(3)	0.6763(3)	0.5590(4)	3.9(1)
O(26)	0.7058(2)	0.3441(2)	0.4004(3)	4.51(9)	O(26)	0.2997(2)	0.6562(2)	0.6547(3)	4.46(9)
C(27)	0.8475(3)	0.3523(2)	0.2588(4)	3.3(1)	C(27)	0.1623(3)	0.6456(2)	0.8001(3)	3.4(1)
O(27)	0.7818(2)	0.4189(2)	0.2560(3)	4.46(9)	O(27)	0.2185(2)	0.5759(2)	0.8031(3)	4.02(8)
C(28)	0.6276(3)	0.2267(2)	0.0549(4)	3.5(1)	C(28)	0.3763(3)	0.7746(3)	0.9971(3)	3.4(1)
O(28)	0.6251(3)	0.2859(2)	0.1457(3)	4.46(9)	O(28)	0.3813(3)	0.7165(2)	0.9091(3)	4.35(9)
S(25)	0.396	0.275	0.276	4.43(3)	S(25)	0.6183(1)	0.75184(8)	0.7779(1)	4.96(4)
O(250)	0.3338(3)	0.2222(2)	0.1828(4)	6.6(1)	O(250)	0.6581(3)	0.8222(3)	0.8570(5)	8.3(2)
O(251)	0.3974(3)	0.2748(3)	0.3843(4)	7.6(2)	O(251)	0.6156(4)	0.7456(4)	0.6680(4)	7.9(2)
C(250)	0.3840(4)	0.3708(3)	0.2531(5)	4.7(1)	C(250)	0.6792(6)	0.6779(4)	0.8464(6)	7.2(2)
C(251)	0.2884(4)	0.4131(3)	0.2284(4)	5.4(1)	C(251)	0.6945(6)	0.5971(4)	0.7898(5)	8.3(2)
C(252)	0.2914(6)	0.4871(4)	0.1816(7)	7.5(3)	C(252)	0.6889(8)	0.5423(7)	0.8694(7)	9.9(4)
O(252)	0.3481(5)	0.4953(4)	0.1379(5)	9.3(2)	O(252)	0.6496(8)	0.5619(6)	0.9438(7)	14.0(4)
C(253)	0.2131(8)	0.5428(5)	0.2011(8)	10.2(4)	C(253)	0.7247(8)	0.4688(6)	0.8364(9)	9.4(3)
C(254)	0.1617(6)	0.4959(5)	0.2505(6)	8.7(3)	C(254)	0.7516(7)	0.4781(5)	0.7285(9)	9.6(3)
C(255)	0.1101(6)	0.4283(6)	0.1548(8)	10.3(3)	C(255)	0.6532(7)	0.4822(4)	0.6365(6)	7.9(3)
C(256)	0.1958(4)	0.3727(5)	0.1378(5)	7.2(2)	C(256)	0.6086(6)	0.5598(4)	0.6810(6)	7.0(2)
C(257)	0.2523(5)	0.4565(4)	0.3237(5)	6.5(2)	C(257)	0.7878(6)	0.5625(6)	0.7740(9)	14.4(4)
C(258)	0.2169(7)	0.3977(6)	0.3749(9)	9.4(3)	C(258)	0.8760(6)	0.5745(8)	0.881(1)	13.5(5)
C(259)	0.3286(7)	0.5105(5)	0.4181(7)	9.6(3)	C(259)	0.802(1)	0.598(1)	0.684(1)	16.8(7)
S(27)	0.8226(2)	0.49662(8)	0.2457(1)	6.89(5)	S(27)	0.16230(8)	0.50225(7)	0.8083(1)	4.39(3)
O(270)	0.8587(5)	0.4775(3)	0.1492(5)	9.1(2)	O(270)	0.0958(3)	0.4728(2)	0.7007(4)	6.9(1)
O(271)	0.8861(4)	0.5323(2)	0.3501(4)	7.3(1)	O(271)	0.1253(3)	0.5265(3)	0.9002(5)	7.0(2)
C(270)	0.7181(5)	0.5517(4)	0.2012(6)	6.8(2)	C(270)	0.2613(4)	0.4386(3)	0.8503(4)	4.8(1)
C(271)	0.6771(4)	0.6045(3)	0.2899(4)	5.6(2)	C(271)	0.3168(4)	0.3998(3)	0.7757(4)	4.6(1)
C(272)	0.6283(6)	0.5626(4)	0.3412(6)	7.9(3)	C(272)	0.2642(5)	0.3326(3)	0.6751(4)	5.4(2)

Table 2 Positional and thermal parameters. (continued)

Atom	*x*	*y*	*z*	*B(A²)*	*Atom*	*x*	*y*	*z*	*B(A²)*
Molecule A					Molecule B				
O(272)	0.6376(6)	0.4979(4)	0.3536(7)	11.7(3)	O(272)	0.1808(4)	0.3172(3)	0.6400(4)	7.7(2)
C(273)	0.5594(6)	0.6253(5)	0.3786(8)	8.9(3)	C(273)	0.3448(5)	0.2846(4)	0.6425(6)	6.6(2)
C(274)	0.5781(8)	0.6983(6)	0.3433(9)	9.8(4)	C(274)	0.4362(5)	0.3260(4)	0.7253(7)	7.0(2)
C(275)	0.6782(8)	0.7312(7)	0.4207(0)	11.6(4)	C(275)	0.4400(5)	0.4029(4)	0.6917(8)	7.9(3)
C(276)	0.7465(5)	0.6644(4)	0.3916(6)	6.7(2)	C(276)	0.3570(5)	0.4529(4)	0.7214(7)	6.8(2)
C(277)	0.5997(5)	0.6598(3)	0.2290(6)	6.2(2)	C(277)	0.4090(5)	0.3529(4)	0.8314(6)	6.4(2)
C(278)	0.5156(5)	0.6182(5)	0.1369(8)	8.8(3)	C(278)	0.4887(5)	0.4063(5)	0.9337(7)	8.2(2)
C(279)	0.6378(9)	0.7138(6)	0.1825(9)	11.4(4)	C(279)	0.3848(7)	0.2865(4)	0.8759(7)	8.0(3)

geometry has been found for tetraester or tetraketone derivatives of calix[4]arenes (Ferguson[14,15], Arnaud-Neu[16], Wolff[17]). Angles between plane 1 and 3 are 107.3(1)° for A and 107.9(1)° for B. This geometry leads to a pseudo C_{2v} symmetry for the macrocycle cavities.

The intramolecular O...O distances between two neighbouring oxygens are

	molecule A	molecule B
O(25)...O(26)	3.077(4)	3.226(5)
O(26)...O(27)	3.089(6)	3.239(6)
O(27)...O(28)	3.134(5)	3.288(5)
O(28)...O(25)	2.968(6)	3.124(6)

They are all greater than those usually found in calix[4]arenes. It may be due to the repulsion that exists between the two camphorsulfonyl groups. The norborane skelton of the (+) camphorsulfonyl group is similar to that in other camphorsulfonyl and camphorsulfonate (Lebioda[18], Sanka-Dobrowska[19], Soriano-Garcia[20]). Significant bond angles are listed in Table 3; the most typical of them are the bridgehead angles (C(251)-C(257)-C(254)) with values of 97.1(5) and 90.7(6)° in molecule A, 95.7(7) and 95.2(5)° in molecule B. With a mean value of $\chi 2 = 24$ for the planes defined by them, the four atoms C(251)-C(252)-C(253)-C(254) and C(251)-C(254)-C(255)-C(256) and the corresponding ones in the other camphor groups can be considered as coplanar.

The internal torsion angles in the six-membered ring in the norborane skelton are -4.3(8), -68.7(9), 71.0(9), 1.6(8), -75.1(7) and 73.1(9)° for the group on ring 4, -0.2(9), -72(1), 65(1), 6.2(9), -70.3(6) and 69.3(6)° for the group on ring 2 in molecule A. Values for molecule B are -1(1), -71.6(9), 66.2(8), 6.9(8), -75.1(7) and 73.1(9)° for the group on ring 4, 0.6(6), -72.7(7), 70.8(8), 2.8(8), -70.3(6) and 69.3(6)° for the group on ring 2. Distances between the S atom and the phenolic oxygen are between 1.593(4) and 1.624(4) Å. Other S-O lengths are between 1.381(4) and 1.499(8) Å.

In both calixarenes, the values of torsion angles C(1)-C(25)-O(25)-S(25) and C(21)-C(25)-O(25)-S(25) and torsion angles with corresponding atoms in the other groups are about 90° (between 90.9(4) and 96.4(4)°. The values for C(25)-O(25)-S(25)-C(250) are between 159.4(4) and 179.6(3)°. With this geometry the distances between the two groups of oxygens (O(250), O(251) and O(270), O(271) are maxima. This conformation is related with the repulsion between these oxygens.

The angles made by the phenolic rings which bear camphorsulfonyl groups and planes C(251)-C(257)-C(254) (or corresponding ones in other groups) are 20.1(7) and 24.4(6) for molecule A and 28.7(4) and 74.4(6) for molecule B. The values show that the conformations are rather similar for the two groups in molecule A and for the group connected on ring 2 in molecule B but the norborane skelton connected on ring 4 in molecule B is very twisted with regard to the orientation observed for the other groups; we can conclude that the two independant calixarenes don't exhibit the same geometry. Figure 2 is a stereoview, parallel to planes 2 or 4, of molecule B; the main features described above can be seen on it.

Figure 3 gives the arrangement of the molecules in the unit cell. The values of the positional parameters and this figure show that the two independant calixarene mole-

Table 3 Most significant bond angles for the camphor sulfonyl groups

	Molecule A		*Molecule B*	
Related phenolic ring	*2*	*4*	*2*	*4*
C(252)-C(251)-C(256)	104.6(5)	100.6(5)	103.7(5)	98.2(6)
C(251)-C(252)-C(253)	103.4(6)	108.0(8)	105.6(5)	108.9(9)
C(251)-C(252)-O(252)	130.6(9)	124.4(7)	126.9(6)	125(1)
O(252)-C(252)-C(253)	126(1)	127.6(8)	126.9(5)	126(1)
C(253)-C(254)-C(255)	109.1(9)	106.0(8)	107.1(6)	104.5(8)
C(251)-C(257)-C(254)	90.7(6)	97.1(5)	95.2(5)	95.7(7)
C(250)-C(251)-C(252)	116.0(5)	110.7(6)	116.8(4)	105.5(7)
C(250)-C(251)-C(257)	107.2(5)	121.0(4)	115.4(5)	126.9(7)

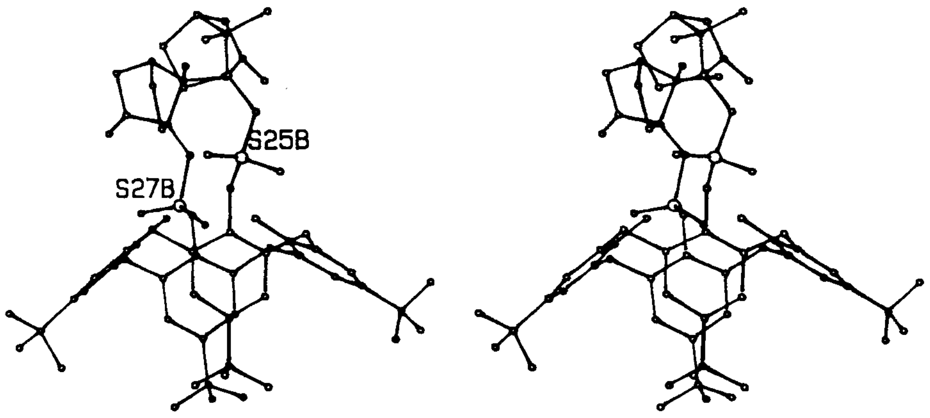

Figure 2 Stereoview of a molecule (B)

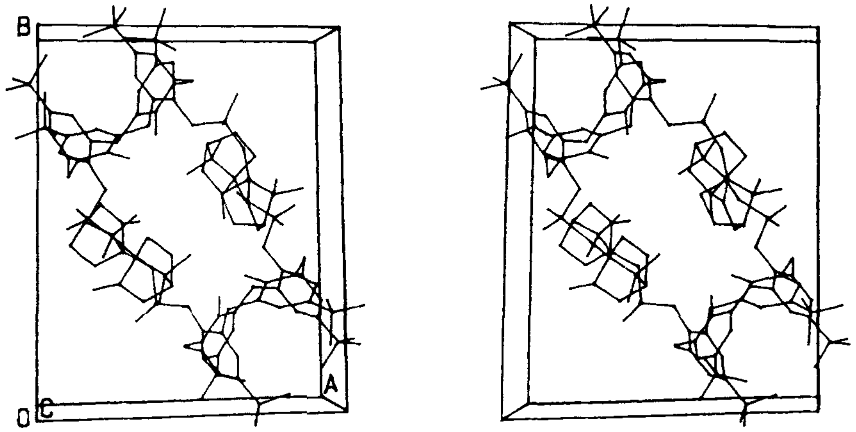

Figure 3 Stereoview of the unit cell

cules are in situation of pseudo symmetry around a center situated at $^1/_2$; $^1/_2$; $^1/_2$.

The shortest intermolecular contacts are deposited as supplementary data. They concern mostly oxygens of camphorsulfonyl groups and C-H belonging to neighbouring molecules deduced from the previous ones by a $\vec{a}$ or $\vec{c}$ translation. They are all van der Waals contacts with the shortest O. . .H distance of 2.478 Å. The only short intramolecular contact with these oxygens involves O(252) and H(278) in molecule A; the bond has the following geometry: O(252). . .H(278) = 2.618Å and O(252). . .H(278)-C(278) = 141.3°. This confirm the fact that O(250), O(251), O(252) and the corresponding ones in the other camphorsulfonyl groups are oriented *exo* to the calixarene. This result was expected because of the repulsion between polar oxygens in the molecule.

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