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### Structure of Diethyl 5,11,17,23-Tetra-*tert*-butyl-26,28-bis(2-methoxyethoxy)-calix[4]arene-25,27-bis(oxyacetate)

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## Abstract

We present here the synthesis and X-ray crystal structure of a new 2 + 2' modified *p-tert*-butylcalix[4]arene, diethyl {5,11,17,23-tetra-*tert*-butyl-26,28-bis(2-methoxyethoxy)pentacyclo[19.3.1.1<sup>3,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]-octacosal(25),3,5,7(28),9,11,13(27),15,17,19(26),-21,23-dodecaene-25,27-diyldioxy}diacetate, bearing glycol methyl ether and ethyl ester functional groups. <sup>1</sup>H NMR spectra of this compound indicated that it has a cone conformation; this is confirmed by the crystallographic study.

## Comment

Calix[4]arenes are a new class of macrocyclic compounds, which are easily transformed into various derivatives at the 'lower rim' by complete alkylation of the phenolic functional groups (Gutsche, 1989; Vicens & Böhmer, 1991). As a result of selective 1,3-dialkylation of *p-tert*-butylcalix[4]arene (Gutsche, 1989; Vicens & Böhmer, 1991), conformationally stable modified-tetrameric structures with the 2 + 2' functional group disposition having distal 1,3-regiochemistry have been developed. They are synthesized by treatment of *p-tert*-butylcalix[4]arene with various electrophiles such as ethyl bromoacetate, chloroacetone, bromopinacolone and chloroacetonitrile in basic conditions (Collins, McKervey & Harris, 1989; Collins *et al.*, 1991).

Final atomic coordinates of non-H atoms and equivalent isotropic thermal parameters are listed in Table 1; bond lengths and angles are shown in Table 2. As depicted in Fig. 1, the molecule clearly shows a cone structure, although slightly distorted in two regions. Molecular geometry can be related to the mean molecular plane of the methylene groups where the CH<sub>2</sub> bridges show out-of-plane distances of –0.188, 0.189, –0.188 and 0.187 Å. With respect to this ideal plane, we can distinguish a hydrophilic region above it, created by the oxygens of the ether and ester groups, and a hydrophobic cavity below it, created by the aromatic and *tert*-butyl groups. The conformation of the macrocycle may be defined by the dihedral angles between the aromatic rings and this mean molecular plane, which are 44.3, 85.7, 132.9 and 93.7°. The relative dihedral angles between two adjacent rings are 79.1, 84.9, 86.4 and 80.9°, and between two opposite rings are 88.7 and 80.5°.

The conformation of the ester chains may be conveniently described by the C(1)–O(1)–C(7)–C(8) and C(35)–O(6)–C(36)–C(37) torsion angles which are 95.2 and 86.4°, respectively, whereas the corresponding values for the ether oxide chains, C(21)–O(4)–C(22)–C(23) and C(50)–O(9)–C(51)–C(52), are 173.7 and 165°, respectively. Therefore the ether oxide chains attached to the aromatic rings are almost parallel to each other and perpendicular to the mean molecular plane. Thus the methylene groups of the ether oxide chains point outwards, whereas the methylene groups of the ester chains point inwards and the COOEt moieties are inside the hydrophilic cavity (Fig. 2). Bond angles involving the bridging methylenes are 112.0 (11), 110.4 (11), 112.3 (10) and 106.1 (10)°, which deviate slightly from the theoretical value of 109.5°. This shows that the macrocycle conformation, in the absence of any intramolecular hydrogen bonding, is mainly determined by steric interaction between the different chains. This is also confirmed by the torsion angles involving the bridging methylene C atoms

which deviate significantly from the value of  $90^\circ$  observed in other cyclic oligomers, where the cone structure was essentially determined by strong intramolecular hydrogen bonds (Ungarro, Pochini, Andreotti & Domiano, 1985; Andreotti, Ungarro & Pochini, 1979; Coruzzi, Andreotti, Pochini & Ungarro, 1982).

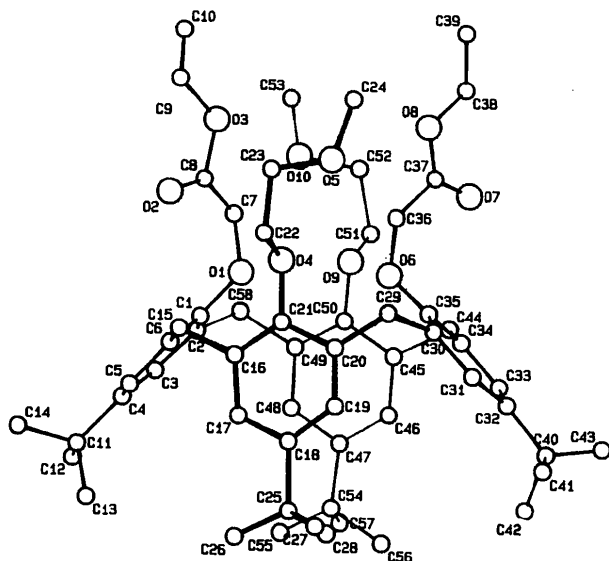


Fig. 1. PLUTO (Motherwell & Clegg, 1978) perspective view of (2).

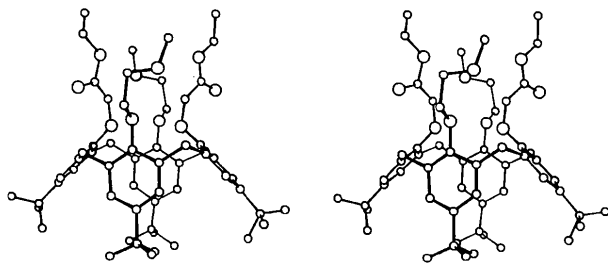


Fig. 2. Stereoscopic diagram of (2) viewed in the same orientation as Fig. 1.

## Experimental

### Crystal data

$C_{58}H_{80}O_{10}$

$M_r = 937.3$

Monoclinic

$Cc$

$a = 25.767(2) \text{ \AA}$

$b = 13.897(2) \text{ \AA}$

$c = 19.867(4) \text{ \AA}$

$\beta = 126.91(1)^\circ$

$V = 5688.3(4) \text{ \AA}^3$

$Z = 4$

$D_x = 1.095 \text{ Mg m}^{-3}$

Cu  $K\alpha$  radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 15\text{--}27^\circ$

$\mu = 0.55 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Parallelepiped

$0.75 \times 0.30 \times 0.30 \text{ mm}$

Colourless

### Data collection

Enraf-Nonius CAD-4

diffractometer

$\omega/2\theta$  scans

Absorption correction: none

8108 measured reflections

4225 independent reflections

3068 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.03$

$\theta_{\text{max}} = 60^\circ$

$h = -28 \rightarrow 28$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 27$

5 standard reflections

frequency: 120 min

intensity variation: 4%

### Refinement

Refinement on  $F$

$R = 0.062$

$wR = 0.062$

$S = 2.31$

3068 reflections

613 parameters

H-atom parameters not refined

Unit weights applied

$(\Delta/\sigma)_{\text{max}} = 0.095$

$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV) and Stewart,

Davidson & Simpson

(1965)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

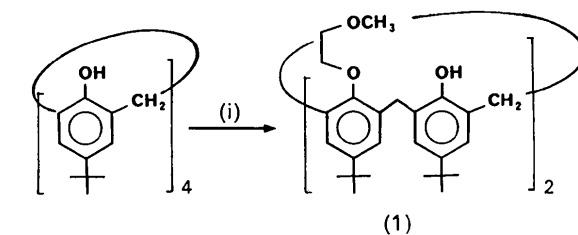
$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
C(1)	0.8479 (5)	0.1514 (9)	0.6798 (7)	0.097 (18)
C(2)	0.9062 (5)	0.1278 (9)	0.7561 (7)	0.060 (17)
C(3)	0.9430 (5)	0.0611 (10)	0.7507 (7)	0.067 (17)
C(4)	0.9224 (6)	0.0168 (10)	0.6783 (8)	0.096 (20)
C(5)	0.8615 (6)	0.0378 (9)	0.6042 (7)	0.083 (18)
C(6)	0.8219 (5)	0.1081 (8)	0.6038 (6)	0.050 (15)
O(1)	0.8079 (1)	0.2244 (3)	0.6792 (1)	0.094 (7)
C(7)	0.8336 (4)	0.3215 (6)	0.7036 (7)	0.109 (17)
C(8)	0.8147 (5)	0.3787 (9)	0.6370 (8)	0.112 (20)
O(2)	0.7928 (4)	0.3568 (5)	0.5604 (5)	0.123 (14)
O(3)	0.8155 (5)	0.4771 (5)	0.6540 (6)	0.139 (20)
C(9)	0.8065 (9)	0.5454 (8)	0.5911 (9)	0.129 (22)
C(10)	0.8241 (15)	0.6255 (12)	0.6199 (20)	0.149 (24)
C(11)	0.9643 (4)	-0.0609 (8)	0.6757 (5)	0.110 (15)
C(12)	1.0265 (5)	-0.0841 (11)	0.7558 (7)	0.107 (20)
C(13)	0.9280 (10)	-0.1483 (16)	0.6394 (18)	0.130 (24)
C(14)	0.9824 (8)	-0.0331 (12)	0.6209 (12)	0.141 (24)
C(15)	0.7554 (6)	0.1316 (9)	0.5244 (7)	0.075 (17)
C(16)	0.7013 (5)	0.0888 (9)	0.5254 (7)	0.058 (16)
C(17)	0.6939 (5)	-0.0121 (9)	0.5212 (7)	0.053 (16)
C(18)	0.6453 (6)	-0.0536 (9)	0.5226 (7)	0.065 (17)
C(19)	0.6071 (6)	0.0057 (9)	0.5322 (7)	0.075 (17)
C(20)	0.6129 (5)	0.1027 (8)	0.5390 (6)	0.050 (15)
C(21)	0.6617 (3)	0.1441 (5)	0.5336 (4)	0.056 (9)
O(4)	0.6668 (2)	0.2458 (3)	0.5393 (3)	0.063 (6)
C(22)	0.6264 (4)	0.2908 (5)	0.4597 (5)	0.094 (12)
C(23)	0.6292 (4)	0.3963 (6)	0.4722 (6)	0.118 (14)
O(5)	0.5917 (3)	0.4131 (4)	0.5018 (4)	0.109 (13)
C(24)	0.5886 (6)	0.5134 (7)	0.5261 (9)	0.127 (23)
C(25)	0.6358 (4)	-0.1675 (5)	0.5112 (5)	0.114 (14)
C(26)	0.6661 (8)	-0.2105 (7)	0.4801 (11)	0.122 (23)
C(27)	0.5685 (6)	-0.1922 (8)	0.4550 (15)	0.101 (22)
C(28)	0.6592 (13)	-0.2041 (9)	0.5954 (10)	0.133 (23)
C(29)	0.5757 (5)	0.1607 (9)	0.5589 (7)	0.061 (17)
C(30)	0.5928 (6)	0.1309 (9)	0.6447 (7)	0.063 (17)
C(31)	0.5557 (6)	0.0576 (10)	0.6469 (8)	0.070 (19)
C(32)	0.5762 (6)	0.0107 (10)	0.7229 (7)	0.066 (18)
C(33)	0.6379 (6)	0.0404 (10)	0.7968 (7)	0.069 (19)
C(34)	0.6733 (5)	0.1137 (10)	0.7931 (7)	0.060 (18)
C(35)	0.6518 (5)	0.1605 (8)	0.7183 (6)	0.053 (14)
O(6)	0.6920 (2)	0.2228 (4)	0.7195 (3)	0.064 (7)
C(36)	0.6726 (4)	0.3182 (7)	0.7014 (5)	0.092 (14)
C(37)	0.6895 (4)	0.3833 (7)	0.7766 (6)	0.086 (13)

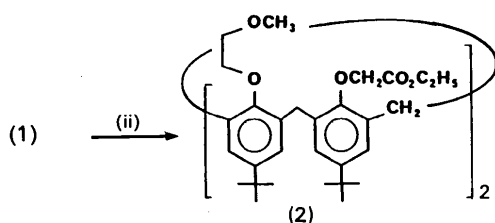
O(7)	0.6999 (4)	0.3552 (6)	0.8379 (5)	0.124 (16)	C(1)—C(6)—C(15)	123.6 (11)	C(20)—C(29)—C(30)	110.4 (11)
O(8)	0.6799 (4)	0.4686 (5)	0.7536 (5)	0.114 (15)	C(5)—C(6)—C(15)	121.2 (11)	C(29)—C(30)—C(31)	118.6 (12)
C(38)	0.6995 (8)	0.5309 (12)	0.8306 (13)	0.122 (24)	C(1)—O(1)—C(7)	118.1 (7)	C(29)—C(30)—C(35)	119.3 (12)
C(39)	0.6643 (8)	0.6244 (12)	0.7816 (13)	0.122 (24)	O(1)—C(7)—C(8)	113.1 (10)	C(31)—C(30)—C(35)	120.6 (13)
C(40)	0.5392 (3)	-0.0706 (6)	0.7263 (5)	0.086 (12)	C(7)—C(8)—O(2)	130.6 (12)	C(30)—C(31)—C(32)	122.3 (13)
C(41)	0.4810 (6)	-0.0977 (8)	0.6421 (5)	0.093 (20)	C(7)—C(8)—O(3)	113.0 (12)	C(31)—C(32)—C(33)	115.6 (13)
C(42)	0.5808 (5)	-0.1624 (7)	0.7558 (6)	0.122 (18)	O(2)—C(8)—O(3)	116.3 (12)	C(31)—C(32)—C(40)	123.3 (12)
C(43)	0.5331 (5)	-0.0596 (8)	0.7935 (5)	0.091 (17)	C(8)—O(3)—C(9)	116.7 (12)	C(33)—C(32)—C(40)	120.9 (12)
C(44)	0.7435 (5)	0.1355 (9)	0.8737 (6)	0.055 (16)	O(3)—C(9)—C(10)	111.7 (21)	C(32)—C(33)—C(34)	120.9 (13)
C(45)	0.7957 (5)	0.0898 (8)	0.8699 (6)	0.048 (14)	C(4)—C(11)—C(12)	116.6 (10)	C(33)—C(34)—C(35)	122.7 (12)
C(46)	0.8029 (6)	-0.0083 (9)	0.8746 (7)	0.080 (19)	C(4)—C(11)—C(13)	110.5 (14)	C(33)—C(34)—C(44)	118.5 (12)
C(47)	0.8503 (6)	-0.0561 (9)	0.8740 (7)	0.085 (19)	C(4)—C(11)—C(14)	112.3 (12)	C(35)—C(34)—C(44)	118.4 (11)
C(48)	0.8904 (5)	0.0017 (9)	0.8635 (7)	0.064 (17)	C(12)—C(11)—C(13)	108.5 (14)	C(30)—C(35)—C(34)	117.7 (12)
C(49)	0.8827 (5)	0.1029 (9)	0.8570 (6)	0.054 (17)	C(12)—C(11)—C(14)	103.6 (12)	C(30)—C(35)—O(6)	123.6 (11)
C(50)	0.8387 (3)	0.1469 (5)	0.8624 (4)	0.052 (9)	C(13)—C(11)—C(14)	104.5 (15)	C(34)—C(35)—O(6)	118.3 (11)
O(9)	0.8326 (2)	0.2448 (3)	0.8606 (3)	0.067 (6)	C(6)—C(15)—C(16)	112.0 (11)	C(35)—O(6)—C(36)	117.4 (8)
C(51)	0.8729 (3)	0.2913 (6)	0.9425 (4)	0.064 (11)	C(15)—C(16)—C(17)	118.7 (12)	O(6)—C(36)—C(37)	117.0 (8)
C(52)	0.8748 (4)	0.3987 (6)	0.9291 (5)	0.089 (13)	C(15)—C(16)—C(21)	122.5 (11)	C(36)—C(37)—O(7)	124.7 (10)
O(10)	0.9121 (2)	0.4181 (4)	0.8990 (4)	0.092 (9)	C(17)—C(16)—C(21)	118.8 (11)	C(36)—C(37)—O(8)	108.6 (9)
C(53)	0.9076 (6)	0.5139 (7)	0.8810 (7)	0.114 (20)	C(16)—C(17)—C(18)	120.1 (12)	O(7)—C(37)—O(8)	125.8 (11)
C(54)	0.8609 (4)	-0.1624 (6)	0.8788 (6)	0.120 (15)	C(17)—C(18)—C(19)	118.6 (13)	C(37)—O(8)—C(38)	107.1 (11)
C(55)	0.8727 (7)	-0.2031 (7)	0.8267 (9)	0.124 (24)	C(17)—C(18)—C(25)	118.0 (11)	O(8)—C(38)—C(39)	97.3 (15)
C(56)	0.8080 (6)	-0.2186 (7)	0.8743 (11)	0.108 (24)	C(19)—C(18)—C(25)	123.3 (12)	C(32)—C(40)—C(41)	112.4 (9)
C(57)	0.9172 (9)	-0.1860 (9)	0.9684 (8)	0.127 (23)	C(18)—C(19)—C(20)	124.3 (13)	C(32)—C(40)—C(42)	109.0 (9)
C(58)	0.9255 (5)	0.1605 (8)	0.8407 (7)	0.065 (17)	C(19)—C(20)—C(21)	115.9 (11)	C(32)—C(40)—C(43)	112.7 (9)
					C(19)—C(20)—C(29)	121.4 (12)	C(41)—C(40)—C(42)	102.8 (8)
					C(21)—C(20)—C(29)	122.4 (10)	C(41)—C(40)—C(43)	118.3 (9)
					C(16)—C(21)—C(20)	122.1 (9)	C(42)—C(40)—C(43)	99.9 (8)
					C(34)—C(44)—C(45)	112.3 (10)	C(45)—C(50)—O(9)	117.8 (7)
					C(44)—C(45)—C(46)	119.8 (11)	C(49)—C(50)—O(9)	122.6 (8)
					C(44)—C(45)—C(50)	122.0 (10)	C(50)—O(9)—C(51)	114.8 (6)
					C(46)—C(45)—C(50)	118.2 (11)	O(9)—C(51)—C(52)	108.5 (6)
					C(45)—C(46)—C(47)	123.8 (13)	C(51)—C(52)—O(10)	111.1 (7)
					C(46)—C(47)—C(48)	116.7 (12)	C(52)—O(10)—C(53)	108.8 (8)
					C(46)—C(47)—C(54)	126.7 (12)	C(47)—C(54)—C(55)	118.6 (11)
					C(48)—C(47)—C(54)	116.5 (11)	C(47)—C(54)—C(56)	112.2 (10)
					C(47)—C(48)—C(49)	120.1 (12)	C(47)—C(54)—C(57)	107.4 (11)
					C(48)—C(49)—C(50)	121.4 (11)	C(55)—C(54)—C(56)	110.0 (11)
					C(48)—C(49)—C(58)	117.1 (11)	C(55)—C(54)—C(57)	108.1 (12)
					C(50)—C(49)—C(58)	121.4 (10)	C(56)—C(54)—C(57)	98.6 (11)
					C(45)—C(50)—C(49)	119.6 (9)	C(2)—C(58)—C(49)	106.1 (10)

Table 2. Bond lengths (Å) and angles (°)

C(1)—C(2)	1.389 (17)	C(29)—C(30)	1.538 (17)
C(1)—C(6)	1.370 (15)	C(30)—C(31)	1.416 (22)
C(1)—O(1)	1.440 (14)	C(30)—C(35)	1.395 (17)
C(2)—C(3)	1.374 (20)	C(31)—C(32)	1.423 (18)
C(2)—C(58)	1.509 (17)	C(32)—C(33)	1.431 (19)
C(3)—C(4)	1.347 (18)	C(32)—C(40)	1.506 (18)
C(4)—C(5)	1.394 (19)	C(33)—C(34)	1.397 (21)
C(4)—C(11)	1.549 (20)	C(34)—C(35)	1.396 (16)
C(5)—C(6)	1.408 (20)	C(34)—C(44)	1.565 (17)
C(6)—C(15)	1.510 (17)	C(35)—O(6)	1.340 (15)
O(1)—C(7)	1.452 (10)	O(6)—C(36)	1.387 (11)
C(7)—C(8)	1.359 (17)	C(36)—C(37)	1.569 (13)
C(8)—O(2)	1.303 (15)	C(37)—O(7)	1.147 (13)
C(8)—O(3)	1.406 (15)	C(37)—O(8)	1.241 (12)
O(3)—C(9)	1.474 (18)	O(8)—C(38)	1.555 (21)
C(9)—C(10)	1.208 (23)	C(38)—C(39)	1.549 (26)
C(11)—C(12)	1.463 (15)	C(40)—C(41)	1.476 (13)
C(11)—C(13)	1.436 (27)	C(40)—C(42)	1.539 (14)
C(11)—C(14)	1.470 (25)	C(40)—C(43)	1.443 (14)
C(15)—C(16)	1.526 (23)	C(44)—C(45)	1.530 (20)
C(16)—C(17)	1.411 (18)	C(45)—C(46)	1.371 (17)
C(16)—C(21)	1.364 (17)	C(45)—C(50)	1.443 (16)
C(17)—C(18)	1.392 (22)	C(46)—C(47)	1.395 (23)
C(18)—C(19)	1.381 (22)	C(47)—C(48)	1.420 (22)
C(18)—C(25)	1.597 (14)	C(47)—C(54)	1.495 (15)
C(19)—C(20)	1.353 (17)	C(48)—C(49)	1.415 (18)
C(20)—C(21)	1.445 (17)	C(49)—C(50)	1.349 (17)
C(20)—C(29)	1.478 (20)	C(49)—C(58)	1.545 (20)
C(21)—O(4)	1.417 (8)	C(50)—O(9)	1.366 (8)
O(4)—C(22)	1.413 (9)	O(9)—C(51)	1.454 (8)
C(22)—C(23)	1.482 (11)	C(51)—C(52)	1.521 (12)
C(23)—O(5)	1.420 (15)	C(52)—O(10)	1.430 (13)
O(5)—C(24)	1.493 (12)	O(10)—C(53)	1.365 (11)
C(25)—C(26)	1.389 (24)	C(54)—C(55)	1.363 (20)
C(25)—C(27)	1.431 (25)	C(54)—C(56)	1.528 (22)
C(25)—C(28)	1.485 (20)	C(54)—C(57)	1.510 (17)
C(2)—C(1)—C(6)	126.3 (12)	C(16)—C(21)—O(4)	122.0 (8)
C(2)—C(1)—O(1)	118.4 (11)	C(20)—C(21)—O(4)	115.8 (7)
C(6)—C(1)—O(1)	115.2 (10)	C(21)—O(4)—C(22)	112.4 (6)
C(1)—C(2)—C(3)	114.8 (12)	O(4)—C(22)—C(23)	108.8 (7)
C(1)—C(2)—C(58)	124.2 (12)	C(22)—C(23)—O(5)	104.7 (8)
C(3)—C(2)—C(58)	120.5 (12)	C(23)—O(5)—C(24)	117.9 (9)
C(2)—C(3)—C(4)	122.9 (13)	C(18)—C(25)—C(26)	114.3 (11)
C(3)—C(4)—C(5)	120.2 (14)	C(18)—C(25)—C(27)	111.1 (11)
C(3)—C(4)—C(11)	121.3 (13)	C(18)—C(25)—C(28)	104.8 (12)
C(5)—C(4)—C(11)	118.4 (12)	C(26)—C(25)—C(27)	106.9 (13)
C(4)—C(5)—C(6)	120.3 (13)	C(26)—C(25)—C(28)	113.4 (13)
C(1)—C(6)—C(5)	115.1 (12)	C(27)—C(25)—C(28)	106.2 (14)



In the second step, compound (1) reacted with ethyl bromoacetate (20 eq.) and potassium carbonate (30 eq.) in refluxing acetone under nitrogen for 8 d. The filtered solution was concentrated and the crude residue was precipitated with a mixture of dichloromethane and methanol to give compound (2) as a white solid (m.p. 411–412 K) in *ca* 69% yield. Crystals suitable for X-ray diffraction were obtained by slow evaporation at 298 K of an ethanol solution of (2).



The nature of the 2 + 2' functional group and the cone conformation were deduced initially from solution  $^1\text{H}$  NMR: two *tert*-butyl singlets at 1.04 and 1.13 p.p.m., and a single *AB* system for the bridging methylene groups at 3.16 and 4.69 p.p.m. ( $J_{AB} = 12.7$  Hz).

The structure was solved by direct methods using 499 reflections with  $E > 2.0$  in *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and anisotropic full-matrix refinement on *F* using *SHELX76* (Sheldrick, 1976). A Lorentz-polarization correction was applied. Phenyl H atoms were inserted at calculated positions; every methyl group was treated as a rigid  $\text{CH}_3$  unit with its original orientation taken from the strongest H-atom peak in a difference Fourier synthesis; other H atoms were found by difference synthesis and theoretically adjusted. No H atoms were refined. All calculations were performed on a MicroVAX II.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71234 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1034]

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## Structure of a Phenylsulfonyllallene

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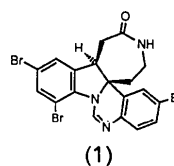
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## Abstract

The crystal structure of 2-phenyl-3-[2-(phenylsulfonyl)-2,3-butadien-1-yl]indole (2) shows that reaction of the Grignard derivative of 2-phenylindole with 2,3-diphenylsulfonylbuta-1,3-diene involves nucleophilic addition to the latter, with loss of phenylsulfinate, producing an allene.

## Comment

We are developing a synthetic route to the marine alkaloid hinckdentine (1) (Blackman, Hambley, Picker, Taylor & Thirasasana, 1987), and were seeking to establish a tricyclic nucleus containing both



the required 2,3-dihydroindole and a 2-aryl substituent, following the methodology recently described (Bäckvall, Plobeck, & Juntenen, 1989; Bäckvall & Plobeck, 1990), whereby the Grignard derivatives of indole, and 2-methylindole, undergo a cycloaddition with 2-phenylsulfonyl-1,3-butadiene. Unfortunately, we found that no reaction took place with 2-phenylindole and in seeking to encourage a comparable transformation we turned to the more electrophilic diene, 2,3-diphenylsulfonylbuta-1,3-diene (Jegathan & Okamura, 1982). Reaction of this with the Grignard derivative of 2-phenylindole led to an indolic, rather than a 2,3-dihydroindolic, product which was crystallized and for which the allenic