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7,15,23-Triphenyl-25,26,27-triethylester-2,3,10,11,18,19-hexahomo-3,9,11-trioxacalix[3]arene in a Partial-Cone Conformation

SAAD KHRIFI,* ABDELHALIM GUELZIM
AND FRANCOIS BAERT

Laboratoire de Dynamique et de Structure des Matériaux Moléculaires, URA CNRS 801, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, CEDEX, France

MAMOUN MUSSRABI, ZOUHAIR ASFARI
AND JACQUES VICENS

Laboratoire de Chimie Analytique et Minérale, URA CNRS 405, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 rue Blaise Pascal, F-67000 Strasbourg, France

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Abstract

Reaction of *p*-phenylhexahomocalix[3]arene (I-H) with bromomethyl acetate and potassium carbonate in acetone leads to the title triester derivative, (I-CH₂CO₂Et) {triethyl 7,15,23-triphenyl-3,11,19-trioxatetracyclo[19.3.1.1^{5,9}.1^{13,17}]heptacos-1(25),5,7,9(27),-13,15,17(26),21,23-nonaene-25,26,27-triyltris(oxyacetate), C₅₄H₅₄O₁₂}, in a partial-cone conformation, which crystallizes with two molecules in the asymmetric unit. In this conformation, (I-CH₂CO₂Et) is adapted for selective complexation of the K⁺ cation. We describe in this paper the synthesis and conformational behaviour of (I-CH₂CO₂Et) as determined by ¹H NMR spectroscopy and X-ray diffractometry.

Comment

The chemistry of calixarenes is a well developed field of research. Calixarenes have been shown to be easily prepared and transformed into functionalized derivatives with interesting properties with respect to the binding of metal cations (Gutsche, 1989; Vicens & Böhmer, 1991). In particular, alkyl ester derivatives of *p*-*tert*-butylcalixarenes have been shown to complex alkali cations and their binding properties have been evidenced by phase-transfer experiments, determination of stability constants, selectivities and transport properties (Gutsche, 1989; Vicens & Böhmer, 1991). In 1991 cation binding property studies were extended to the tetraethyl ester of tetrahomodioxacalix[4]arene (Arnaud-Neu, Cremin, Cunningham, Har-

ris, McArdle, McKervery, McManus, Schwing-Weill & Ziat, 1991). Subsequently, the synthesis and selectivity of conformers of the triethyl ester derivatives of *p*-*tert*-butylhexahomotrioxacalix[3]arene were reported (Araki, Hashimoto, Otsuka & Shinkai, 1993). The partial-cone conformer was obtained as the major product and was shown by two-phase extraction to be selective for the K⁺ cation (Araki, Hashimoto, Otsuka & Shinkai, 1993). The present study was carried out to obtain information on the molecular structure of the title compound (I-CH₂CO₂Et) related to triethyl ester derivatives of *p*-*tert*-butylhexahomotrioxacalix[3]arene.

The synthesis of the title compound was conducted as shown in Fig. 1. Fig. 2 shows the 400 MHz ¹H NMR spectrum of (I-CH₂CO₂Et) in deuterated chloroform at room temperature. A partial-cone conformation is indicated by the presence of two triplets at 0.78 ($J_{H-H} = 7.10$ Hz) and 1.10 p.p.m. ($J_{H-H} = 7.15$ Hz) with an integration ratio of 2:1, and of three AB systems at 4.34 and 4.80 p.p.m. with $J_{A1B1} = 11.78$ Hz, at 4.40 and 5.01 p.p.m. with $J_{A2B2} = 12.58$ Hz, and at 4.46 and 5.05 p.p.m. with $J_{A3B3} = 10.44$ Hz, with an integration ratio of 1:1:1.

A perspective view of the molecule with the atomic numbering is shown in Fig. 3; the molecule clearly displays the partial-cone conformation as deduced from ¹H NMR experiments, in which two ester groups are on one side of the macrocycle while the third is on the other side.

The molecular geometry can be referred to this mean molecular plane where the three atoms of each ether bridge (C17—O4—C18) show out-of-plane distances of 0.1547, -0.5523 and 0.3026 Å, 0.2177, -0.5198 and 0.3335 Å, and -0.0344, -0.3234 and 0.4206 Å

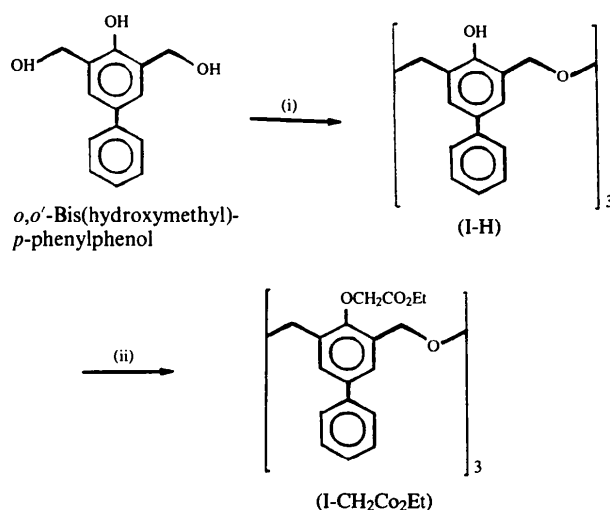


Fig. 1. Synthesis of the *p*-phenylhexahomotrioxacalix[3]arene triethyl ester (I-CH₂CO₂Et). (i) Xylene, reflux. (ii) Bromoethyl acetate, K₂CO₃, acetone, reflux 15 h.

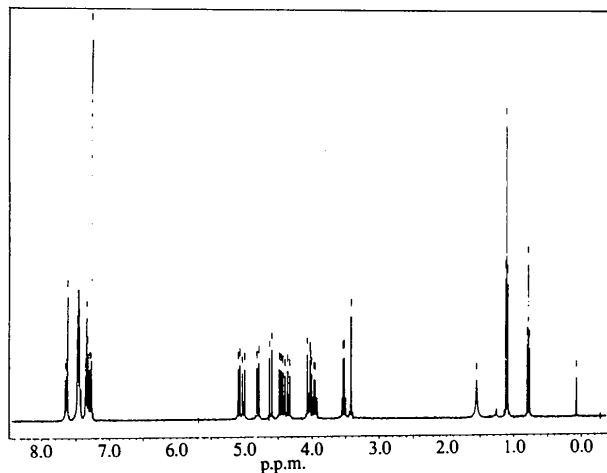


Fig. 2. ¹H NMR spectrum of the title compound.

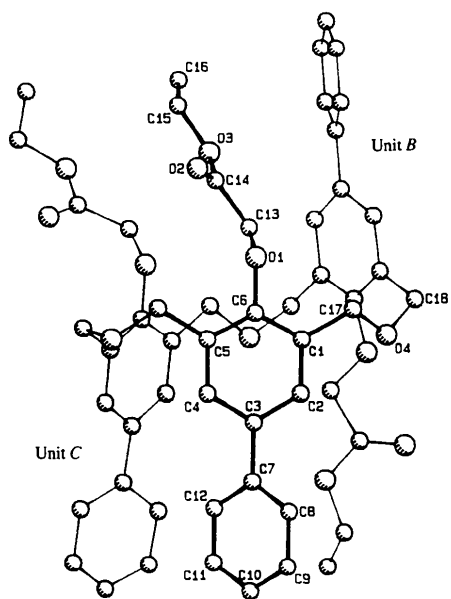


Fig. 3. View of the title compound with atomic numbering scheme. H atoms have been omitted for clarity.

for units *A* (C1–C18), *B* (C1'–C18') and *C* (C1''–C18''), respectively, of molecule 1, and -0.1891 , 0.5580 and -0.2343 Å, -0.2228 , 0.4862 and -0.3513 Å, and 0.1148 , 0.3061 and -0.4677 Å for units *A*, *B* and *C*, respectively, of molecule 2. So the conformation of the macrocycle may be defined by the dihedral angles that the aromatic rings of the three units *A*–*C* make with the mean molecular plane of the bridging ether groups which link them. For units *A* and *C*, the values of the dihedral angles are 91.48 and 77.55° , respectively, for molecule 1, and 84.92 and 84.30° , respectively, for

molecule 2, and for unit *B*, 95.24° for molecule 1 and 91.42° for molecule 2, but oriented in the opposite direction. The relative dihedral angles between two rings are: $A^{\wedge}B$ 56.94 and 59.96° , $B^{\wedge}C$ 80.48 and 79.77° , $C^{\wedge}A$ 44.99 and 42.10° , for molecules 1 and 2, respectively.

The conformation of the ester chains may be conveniently described by the values of the torsion angle C6–O1–C13–C14, which are, for the chains *A*, *B* and *C*, respectively, 141.17 , -155.07 and 105.32° for molecule 1, and -135.54 , 141.58 and 111.05° for molecule 2.

Bond angles involving the bridging ether groups deviate slightly from theoretical values. This shows that the conformation of the macrocycle, in the absence of any intramolecular hydrogen bonds, is determined mainly by steric interactions between the ester chains.

The chain structure of the atoms which define the central cavity of the receptor (I–CH₂CO₂Et) is shown in Fig. 4. In spite of the steric hindrance of the ethyl ester groups the cavity is approximately 4 Å in diameter. This lends support to possible complexation of large cations such as Cs, K, Rb and Co. The preference found for the K⁺ cation may be explained, as indicated by Araki, Hashimoto, Otsuka & Shinkai (1993), by a covering during the binding as depicted for lariat ethers (Gokel, 1992).

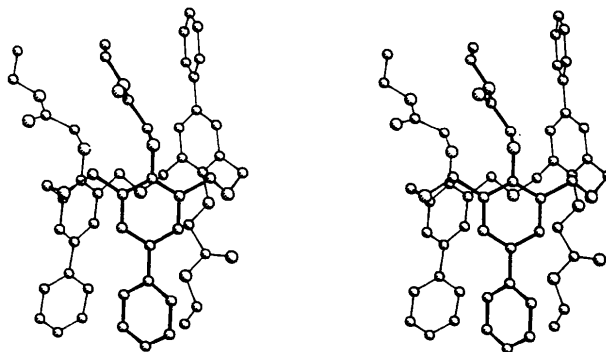


Fig. 4. Stereoview of the title compound.

Experimental

o,o'-Dihydroxy-*p*-phenylphenol (No & Gutsche, 1982) was dehydrated thermally (Zerr, Mussrabi & Vicens, 1991) in refluxing xylene to afford *p*-phenylhexahomotrioxacalix[3]arene (I–H), which was further alkylated by treatment with excess bromoacetate in the presence of potassium carbonate in refluxing acetone for 15 h. Recrystallization of the crude mixture from methanol gave crystals of (I–CH₂CO₂Et) suitable for X-ray diffraction.

Crystal data

C₅₄H₅₄O₁₂
*M*_r = 859.03

Mo *K*α radiation
 λ = 0.7107 Å

Triclinic	Cell parameters from 25 reflections	C'6	0.4805 (4)	0.4295 (3)	0.4451 (3)	0.053 (8)
$P\bar{1}$	$\theta = 16\text{--}24^\circ$	C'7	0.3263 (3)	0.6913 (3)	0.3286 (3)	0.049 (8)
$a = 16.150 (6) \text{ \AA}$	$\mu = 0.83 \text{ mm}^{-1}$	C'8	0.3517 (3)	0.7646 (4)	0.3237 (3)	0.061 (9)
$b = 16.842 (9) \text{ \AA}$	$T = 293 \text{ K}$	C'9	0.3010 (4)	0.8498 (4)	0.2887 (4)	0.073 (11)
$c = 19.599 (7) \text{ \AA}$	Parallelepiped	C'10	0.2252 (4)	0.8640 (4)	0.2570 (4)	0.076 (10)
$\alpha = 69.02 (5)^\circ$	$0.5 \times 0.5 \times 0.3 \text{ mm}$	C'11	0.1993 (4)	0.7924 (4)	0.2612 (3)	0.066 (10)
$\beta = 80.85 (4)^\circ$	Colourless	C'12	0.2494 (3)	0.7067 (4)	0.2962 (3)	0.057 (08)
$\gamma = 70.91 (6)^\circ$		O'1	0.5266 (2)	0.3477 (2)	0.4920 (2)	0.066 (05)
$V = 4698 \text{ \AA}^3$		C'13	0.5800 (3)	0.2835 (4)	0.4600 (3)	0.064 (9)
$Z = 4$		C'14	0.5899 (5)	0.1935 (4)	0.5159 (4)	0.064 (11)
$D_x = 1.265 \text{ Mg m}^{-3}$		O'2	0.5470 (4)	0.1755 (5)	0.5700 (3)	0.115 (09)
		O'3	0.6571 (3)	0.1367 (3)	0.4938 (3)	0.108 (08)
		C'15	0.6781 (7)	0.0436 (5)	0.5388 (5)	0.115 (16)
		C'16	0.7657 (8)	0.0163 (6)	0.5574 (6)	0.102 (17)
		C'17	0.6197 (3)	0.4766 (4)	0.4114 (3)	0.057 (8)
		O'4	0.6690 (2)	0.4224 (2)	0.3678 (2)	0.052 (15)
		C'18	0.6532 (3)	0.4660 (3)	0.2927 (3)	0.048 (7)
		C''1	0.6929 (3)	0.3559 (3)	0.1465 (2)	0.042 (7)
		C''2	0.7609 (3)	0.2805 (3)	0.1755 (3)	0.045 (7)
		C''3	0.7975 (3)	0.2645 (3)	0.2401 (3)	0.044 (7)
		C''4	0.7618 (3)	0.3250 (3)	0.2780 (2)	0.041 (6)
		C''5	0.6944 (3)	0.4011 (3)	0.2506 (2)	0.039 (7)
		C''6	0.6639 (3)	0.4177 (3)	0.1831 (3)	0.042 (6)
		C''7	0.8733 (3)	0.1850 (3)	0.2671 (3)	0.048 (8)
		C''8	0.9259 (5)	0.1433 (5)	0.2235 (4)	0.121 (14)
		C''9	0.9946 (5)	0.0666 (6)	0.2493 (5)	0.143 (17)
		C''10	1.0171 (5)	0.0355 (5)	0.3156 (5)	0.094 (12)
		C''11	0.9662 (7)	0.0754 (6)	0.3614 (5)	0.105 (18)
		C''12	0.8925 (6)	0.1503 (5)	0.3372 (4)	0.128 (16)
		O''1	0.5967 (2)	0.4951 (2)	0.1535 (2)	0.048 (4)
		C''13	0.6183 (3)	0.5768 (3)	0.1357 (3)	0.051 (7)
		C''14	0.6321 (4)	0.6167 (4)	0.0560 (3)	0.062 (9)
		O''2	0.6381 (4)	0.5829 (3)	0.0108 (3)	0.114 (10)
		O''3	0.6411 (3)	0.6951 (3)	0.0406 (2)	0.095 (8)
		C''15	0.6545 (8)	0.7451 (7)	-0.0341 (5)	0.092 (18)
		C''16	0.5790 (12)	0.8075 (7)	-0.0608 (6)	0.15 (2)
		C''17	0.6516 (3)	0.3664 (3)	0.0787 (3)	0.050 (7)
		O'4	0.5899 (2)	0.3162 (2)	0.0947 (2)	0.050 (5)
		C''18	0.5095 (3)	0.3532 (3)	0.1301 (3)	0.053 (7)
		C1A	1.0653 (3)	0.7206 (4)	0.1639 (3)	0.051 (8)
		C2A	1.0093 (4)	0.8057 (3)	0.1343 (3)	0.058 (9)
		C3A	0.9470 (4)	0.8490 (3)	0.1772 (3)	0.054 (8)
		C4A	0.9411 (3)	0.8047 (3)	0.2517 (3)	0.052 (8)
		C5A	0.9969 (3)	0.7203 (3)	0.2834 (2)	0.046 (7)
		C6A	1.0585 (3)	0.6793 (3)	0.2391 (3)	0.046 (8)
		C7A	0.8865 (4)	0.9391 (4)	0.1452 (3)	0.061 (9)
		C8A	0.9161 (5)	1.0074 (4)	0.0947 (3)	0.090 (11)
		C9A	0.8570 (7)	1.0933 (5)	0.0661 (4)	0.064 (14)
		C10A	0.7708 (7)	1.1070 (5)	0.0877 (4)	0.068 (15)
		C11A	0.7414 (5)	1.0417 (5)	0.1370 (4)	0.087 (12)
		C12A	0.7980 (5)	0.9582 (4)	0.1658 (3)	0.072 (10)
		O1A	1.1191 (2)	0.5976 (2)	0.2725 (2)	0.053 (5)
		C13A	1.1002 (3)	0.5214 (3)	0.2725 (3)	0.056 (8)
		C14A	1.1143 (3)	0.4506 (4)	0.3457 (3)	0.055 (8)
		O2A	1.1294 (5)	0.4590 (3)	0.4003 (2)	0.075 (7)
		O3A	1.1056 (2)	0.3777 (3)	0.3415 (2)	0.067 (6)
		C15A	1.1131 (4)	0.3024 (4)	0.4087 (3)	0.081 (10)
		C16A	1.1083 (6)	0.2285 (5)	0.3898 (4)	0.143 (15)
		C17A	1.1319 (3)	0.6764 (4)	0.1153 (3)	0.063 (9)
		O4A	1.0920 (2)	0.6912 (2)	0.0508 (2)	0.068 (6)
		C18A	1.1253 (3)	0.6196 (4)	0.0210 (3)	0.065 (8)
		C'1A	0.9714 (3)	0.4775 (4)	0.1130 (3)	0.048 (8)
		C'2A	1.0297 (3)	0.3983 (3)	0.1492 (3)	0.049 (7)
		C'3A	1.1195 (3)	0.3871 (3)	0.1432 (3)	0.047 (7)
		C'4A	1.1494 (3)	0.4600 (3)	0.1017 (3)	0.050 (7)
		C'5A	1.0919 (3)	0.5412 (3)	0.0654 (3)	0.052 (7)
		C'6A	1.0020 (3)	0.5484 (3)	0.0696 (3)	0.051 (7)
		C'7A	1.1803 (3)	0.2985 (3)	0.1803 (3)	0.050 (7)
		C'8A	1.1597 (3)	0.2205 (4)	0.1897 (3)	0.061 (9)
		C'9A	1.2157 (4)	0.1380 (4)	0.2242 (4)	0.071 (10)
		C'10A	1.2931 (4)	0.1304 (4)	0.2494 (3)	0.069 (9)
		C'11A	1.3144 (4)	0.2064 (4)	0.2405 (3)	0.063 (9)
		C'12A	1.2588 (3)	0.2892 (4)	0.2069 (3)	0.053 (8)
		O'1A	0.9483 (2)	0.6242 (2)	0.0239 (2)	0.066 (5)
		C'13A	0.9014 (4)	0.6941 (4)	0.0517 (3)	0.064 (8)
		C'14A	0.8998 (5)	0.7815 (5)	-0.0065 (4)	0.075 (13)
		O'2A	0.9419 (4)	0.7932 (4)	-0.0614 (3)	0.111 (10)
		O'3A	0.8388 (4)	0.8460 (3)	0.0140 (3)	0.110 (9)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	0.4243 (3)	0.2895 (4)	0.3289 (3)	0.046 (8)
C2	0.4801 (3)	0.2045 (4)	0.3577 (3)	0.052 (8)
C3	0.5486 (3)	0.1671 (3)	0.3154 (3)	0.047 (7)
C4	0.5592 (3)	0.2172 (3)	0.2419 (3)	0.047 (8)
C5	0.5031 (3)	0.3017 (3)	0.2110 (3)	0.044 (7)
C6	0.4362 (3)	0.3364 (3)	0.2558 (3)	0.043 (7)
C7	0.6090 (4)	0.0764 (3)	0.3469 (3)	0.055 (8)
C8	0.5783 (4)	0.0066 (4)	0.3934 (3)	0.076 (10)
C9	0.6374 (7)	-0.0774 (5)	0.4233 (4)	0.089 (14)
C10	0.7255 (6)	-0.0913 (5)	0.4071 (5)	0.089 (14)
C11	0.7562 (5)	-0.0235 (5)	0.3607 (4)	0.086 (12)
C12	0.6992 (4)	0.0597 (4)	0.3303 (3)	0.067 (9)
O1	0.3758 (2)	0.4188 (2)	0.2241 (2)	0.052 (5)
C13	0.3990 (3)	0.4933 (3)	0.2234 (3)	0.054 (8)
C14	0.3745 (3)	0.5671 (4)	0.1533 (3)	0.056 (9)
O2	0.3410 (3)	0.5652 (3)	0.1047 (3)	0.086 (8)
O3	0.3959 (2)	0.6367 (3)	0.1532 (2)	0.070 (6)
C15	0.3771 (4)	0.7151 (5)	0.0887 (4)	0.101 (12)
C16	0.4001 (6)	0.7846 (5)	0.1014 (5)	0.142 (16)
C17	0.3496 (3)	0.3286 (4)	0.3754 (3)	0.063 (9)
O4	0.3779 (2)	0.3029 (2)	0.4474 (2)	0.066 (5)
C18	0.3483 (3)	0.3732 (4)	0.4786 (3)	0.063 (8)
C'1	0.5216 (3)	0.4946 (4)	0.4097 (3)	0.049 (8)
C'2	0.4704 (3)	0.5793 (3)	0.3710 (3)	0.050 (8)
C'3	0.3795 (3)	0.5996 (3)	0.3673 (3)	0.046 (7)
C'4	0.3418 (3)	0.5309 (3)	0.4026 (3)	0.049 (7)
C'5	0.3912 (3)	0.4456 (3)	0.4413 (3)	0.052 (8)

C'15A	0.8279 (8)	0.9370 (6)	-0.0344 (6)	0.07 (2)	C''1—C''2	1.382 (7)	C''1A—C''2A	1.387 (7)
C'16A	0.7486 (9)	0.9773 (6)	-0.0573 (6)	0.14 (2)	C''1—C''6	1.389 (7)	C''1A—C''6A	1.380 (7)
C'17A	0.8734 (3)	0.4886 (3)	0.1223 (3)	0.054 (8)	C''1—C''17	1.510 (7)	C''1A—C''17A	1.512 (8)
O'4A	0.8278 (2)	0.5482 (2)	0.1632 (2)	0.050 (5)	C''2—C''3	1.384 (8)	C''2A—C''3A	1.383 (8)
C'18A	0.8568 (3)	0.5199 (3)	0.2347 (3)	0.047 (7)	C''3—C''4	1.395 (7)	C''3A—C''4A	1.400 (7)
C''1A	0.8163 (3)	0.6600 (3)	0.3579 (3)	0.049 (7)	C''3—C''7	1.482 (7)	C''3A—C''7A	1.481 (7)
C''2A	0.7504 (3)	0.7336 (3)	0.3216 (3)	0.050 (7)	C''4—C''5	1.376 (7)	C''4A—C''5A	1.390 (7)
C''3A	0.7149 (3)	0.7392 (3)	0.2597 (3)	0.050 (7)	C''5—C''6	1.386 (7)	C''5A—C''6A	1.388 (8)
C''4A	0.7514 (3)	0.6701 (3)	0.2303 (3)	0.046 (7)	C''6—O''1	1.395 (6)	C''6A—O''1A	1.396 (6)
C''5A	0.8168 (3)	0.5948 (3)	0.2657 (3)	0.045 (6)	C''7—C''8	1.325 (10)	C''7A—C''8A	1.359 (10)
C''6A	0.8455 (3)	0.5901 (3)	0.3305 (3)	0.045 (6)	C''7—C''12	1.330 (9)	C''7A—C''12A	1.371 (9)
C''7A	0.6399 (3)	0.8161 (3)	0.2260 (3)	0.058 (8)	C''8—C''9	1.389 (13)	C''8A—C''9A	1.361 (13)
C''8A	0.5795 (5)	0.8583 (5)	0.2680 (4)	0.103 (12)	C''9—C''10	1.278 (13)	C''9A—C''10A	1.330 (15)
C''9A	0.5110 (6)	0.9298 (6)	0.2378 (6)	0.116 (18)	C''10—C''11	1.329 (13)	C''10A—C''11A	1.380 (14)
C''10A	0.4964 (6)	0.9577 (6)	0.1669 (6)	0.111 (17)	C''11—C''12	1.415 (14)	C''11A—C''12A	1.407 (13)
C''11A	0.5570 (6)	0.9186 (6)	0.1214 (5)	0.093 (17)	O''1—C''13	1.437 (6)	O''1A—C''13A	1.485 (7)
C''12A	0.6300 (5)	0.8471 (4)	0.1520 (4)	0.092 (12)	C''13—C''14	1.475 (8)	C''13A—C''14A	1.447 (8)
O''1A	0.9090 (2)	0.5119 (2)	0.3654 (2)	0.055 (4)	C''14—O''2	1.191 (8)	C''14A—O''2A	1.228 (7)
C''13A	0.8811 (4)	0.4613 (4)	0.4397 (3)	0.069 (11)	C''14—O''3	1.298 (8)	C''14A—O''3A	1.300 (7)
C''14A	0.8710 (3)	0.3789 (3)	0.4402 (3)	0.053 (18)	O''3—C''15	1.427 (10)	O''3A—C''15A	1.427 (10)
O''2A	0.8889 (2)	0.3494 (3)	0.3890 (2)	0.074 (6)	C''15—C''16	1.35 (2)	C''15A—C''16A	1.429 (14)
O''3A	0.8418 (3)	0.3353 (3)	0.5035 (2)	0.095 (7)	C''17—O''4	1.438 (6)	C''17A—O''4A	1.416 (7)
C''15A	0.8312 (6)	0.2496 (5)	0.5193 (4)	0.082 (14)	O''4—C''18	1.432 (6)	O''4A—C''18A	1.427 (7)
C''16A	0.9128 (8)	0.1818 (5)	0.5381 (5)	0.106 (17)	C''18—C5	1.517 (8)	C''18A—C5A	1.521 (7)
C''17A	0.8566 (4)	0.6612 (3)	0.4220 (3)	0.058 (8)				
O''4A	0.9157 (2)	0.7130 (2)	0.4008 (2)	0.059 (5)	C2—C1—C6	118.6 (5)	C2—C3—C4	118.2 (5)
C''18A	0.9953 (3)	0.6745 (4)	0.3658 (3)	0.060 (8)	C2—C1—C17	120.7 (5)	C2—C3—C7	121.1 (5)
					C6—C1—C17	120.6 (5)	C4—C3—C7	120.7 (5)
					C1—C2—C3	121.4 (5)	C3—C4—C5	121.7 (5)
					C4—C5—C6	117.9 (5)	C''6—O''1—C''13	115.3 (4)
					C4—C5—C''18	122.0 (5)	O''1—C''13—C''14	111.4 (4)
					C6—C5—C''18	120.0 (5)	C''13—C''14—O''2	126.8 (6)
					C1—C6—C5	122.1 (5)	C''13—C''14—O''3	110.3 (5)
					C1—C6—O1	119.4 (5)	O''2—C''14—O''3	122.9 (6)
					C5—C6—O1	118.4 (5)	C''14—O''3—C''15	118.8 (6)
					C3—C7—C8	121.6 (5)	O''3—C''15—C''16	110.7 (10)
					C3—C7—C12	120.1 (5)	C''1—C''17—O''4	112.3 (4)
					C8—C7—C12	118.3 (6)	C''17—O''4—C''18	113.6 (4)
					C7—C8—C9	119.9 (6)	O''4—C''18—C5	112.7 (4)
					C8—C9—C10	120.4 (8)	C2A—C1A—C6A	117.9 (5)
					C9—C10—C11	120.1 (9)	C2A—C1A—C17A	120.3 (5)
					C10—C11—C12	120.5 (8)	C6A—C1A—C17A	121.8 (5)
					C7—C12—C11	120.7 (6)	C1A—C2A—C3A	122.2 (5)
					C6—O1—C13	114.9 (4)	C2A—C3A—C4A	118.2 (5)
					O1—C13—C14	109.9 (4)	C2A—C3A—C7A	122.0 (5)
					C13—C14—O2	126.1 (6)	C4A—C3A—C7A	119.8 (5)
					C13—C14—O3	109.5 (5)	C3A—C4A—C5A	121.1 (5)
					O2—C14—O3	124.5 (6)	C4A—C5A—C6A	119.1 (5)
					C14—O3—C15	117.2 (5)	C4A—C5A—C''18A	121.3 (4)
					O3—C15—C16	108.5 (6)	C6A—C5A—C''18A	119.6 (4)
					C1—C17—O4	109.2 (5)	C1A—C6A—C5A	121.5 (5)
					C17—O4—C18	113.6 (4)	C1A—C6A—O1A	120.0 (5)
					O4—C18—C'5	112.4 (5)	C5A—C6A—O1A	118.3 (4)
					C'2—C'1—C'6	118.4 (5)	C3A—C7A—C8A	121.7 (6)
					C'2—C'1—C'17	119.4 (5)	C3A—C7A—C12A	120.6 (6)
					C'6—C'1—C'17	122.1 (5)	C8A—C7A—C12A	117.7 (6)
					C'1—C'2—C'3	121.9 (5)	C7A—C8A—C9A	120.4 (7)
					C'2—C'3—C'4	117.3 (5)	C8A—C9A—C10A	118.9 (8)
					C'2—C'3—C'7	120.7 (5)	C9A—C10A—C11A	121.3 (9)
					C'4—C'3—C'7	122.1 (5)	C10A—C11A—C12A	120.6 (8)
					C'3—C'4—C'5	122.1 (5)	C7A—C12A—C11A	121.1 (7)
					C'4—C'5—C'6	120.6 (5)	C6A—O1A—C13A	115.8 (4)
					C'4—C'5—C18	120.9 (5)	O1A—C13A—C14A	110.9 (4)
					C'6—C'5—C18	118.5 (5)	C13A—C14A—O2A	125.8 (5)
					C'1—C'6—C'5	121.8 (5)	C13A—C14A—O3A	109.2 (5)
					C'1—C'6—O'1	120.3 (5)	O2A—C14A—O3A	125.0 (6)
					C'5—C'6—O'1	117.6 (5)	C14A—O3A—C15A	117.1 (5)
					C'3—C'7—C'8	121.0 (5)	O3A—C15A—C16A	107.2 (6)
					C'3—C'7—C'12	121.1 (5)	C1A—C17A—O4A	109.2 (5)
					C'8—C'7—C'12	117.9 (5)	C17A—O4A—C18A	114.3 (4)
					C'7—C'8—C'9	120.6 (6)	O4A—C18—C'5A	111.5 (4)
					C'8—C'9—C'10	120.8 (6)	C'2A—C'1A—C'6A	119.7 (5)
					C'9—C'10—C'11	119.3 (6)	C'2A—C'1A—C'17A	120.3 (5)
					C'10—C'11—C'12	120.5 (6)	C'6A—C'1A—C'17A	120.0 (5)
					C'7—C'12—C'11	120.8 (5)	C'1A—C'2A—C'3A	121.5 (5)
					C'6—O'1—C'13	117.4 (4)	C'2A—C'3A—C'4A	118.3 (5)
					O'1—C'13—C'14	108.1 (5)	C'2A—C'3A—C'7A	119.4 (5)
					C'13—C'14—O'2	126.9 (7)	C'4A—C'3A—C'7A	122.2 (5)

Table 2. Selected geometric parameters (Å, °)

C1—C2	1.385 (9)	C1A—C2A	1.390 (8)
C1—C6	1.384 (8)	C1A—C6A	1.389 (8)
C1—C17	1.510 (8)	C1A—C17A	1.510 (9)
C2—C3	1.391 (8)	C2A—C3A	1.393 (8)
C3—C4	1.400 (8)	C3A—C4A	1.387 (8)
C3—C7	1.486 (8)	C3A—C7A	1.481 (9)
C4—C5	1.388 (7)	C4A—C5A	1.388 (7)
C5—C6	1.390 (7)	C5A—C6A	1.389 (7)
C6—O1	1.397 (6)	C6A—O1A	1.399 (6)
C7—C8	1.389 (9)	C7A—C8A	1.392 (8)
C7—C12	1.397 (9)	C7A—C12A	1.385 (11)
C8—C9	1.399 (11)	C8A—C9A	1.415 (11)
C9—C10	1.368 (15)	C9A—C10A	1.358 (16)
C10—C11	1.365 (12)	C10A—C11A	1.342 (12)
C11—C12	1.377 (11)	C11A—C12A	1.375 (11)
O1—C13	1.417 (6)	O1A—C13A	1.414 (6)
C13—C14	1.489 (8)	C13A—C14A	1.495 (8)
C14—O2	1.198 (7)	C14A—O2A	1.198 (7)
C14—O3	1.314 (8)	C14A—O3A	1.314 (8)
O3—C15	1.449 (9)	O3A—C15A	1.453 (7)
C15—C16	1.447 (12)	C15A—C16A	1.447 (11)
C17—O4	1.423 (7)	C17A—O4A	1.414 (7)
O4—C18	1.435 (7)	O4A—C18A	1.438 (7)
C18—C'5	1.502 (8)	C18A—C'5A	1.512 (8)
C'1—C'2	1.396 (8)	C'1A—C'2A	1.371 (8)
C'1—C'6	1.381 (8)	C'1A—C'6A	1.384 (8)
C'1—C'17	1.517 (8)	C'1A—C'17A	1.521 (8)
C'2—C'3	1.403 (7)	C'2A—C'3A	1.392 (7)
C'3—C'4	1.394 (7)	C'3A—C'4A	1.396 (7)
C'3—C'7	1.482 (7)	C'3A—C'7A	1.487 (7)
C'4—C'5	1.392 (7)	C'4A—C'5A	1.387 (7)
C'5—C'6	1.387 (8)	C'5A—C'6A	1.408 (7)
C'6—O'1	1.392 (6)	C'6A—O'1A	1.376 (6)
C'7—C'8	1.392 (8)	C'7A—C'8A	1.402 (8)
C'7—C'12	1.390 (8)	C'7A—C'12A	1.388 (8)
C'8—C'9	1.380 (9)	C'8A—C'9A	1.381 (9)
C'9—C'10	1.374 (10)	C'9A—C'10A	1.368 (10)
C'10—C'11	1.371 (10)	C'10A—C'11A	1.377 (9)
C'11—C'12	1.383 (9)	C'11A—C'12A	1.377 (9)
O'1—C'13	1.417 (7)	O'1A—C'13A	1.414 (7)
C'13—C'14	1.494 (9)	C'13A—C'14A	1.501 (10)
C'14—O'2	1.170 (10)	C'14A—O'2A	1.167 (10)
C'14—O'3	1.321 (9)	C'14A—O'3A	1.342 (10)
O'3—C'15	1.452 (10)	O'3A—C'15A	1.453 (12)
C'15—C'16	1.400 (17)	C'15A—C'16A	1.302 (19)
C'17—O'4	1.436 (7)	C'17A—O'4A	1.448 (6)
O'4—C'18	1.412 (7)	O'4A—C'18A	1.414 (7)
C'18—C''5	1.523 (7)	C'18A—C''5A	1.507 (7)

C'13—C'14—O'3	107.6 (6)	C'3A—C'4A—C'5A	121.4 (5)
O'2—C'14—O'3	125.5 (7)	C'4A—C'5A—C'6A	120.7 (5)
C'14—O'3—C'15	117.7 (6)	C'4A—C'5A—C'18A	120.8 (5)
O'3—C'15—C'16	107.6 (8)	C'6A—C'5A—C'18A	118.4 (5)
C'1—C'17—O'4	112.4 (5)	C'1A—C'6A—C'5A	120.5 (5)
C'17—O'4—C'18	111.9 (4)	C'1A—C'6A—O'1A	121.8 (5)
O'4—C'18—C''5	109.9 (4)	C'5A—C'6A—O'1A	117.4 (5)
C''2—C''1—C''6	117.7 (5)	C'3A—C'7A—C'8A	120.4 (5)
C''2—C''1—C''17	119.4 (4)	C'3A—C'7A—C'12A	122.1 (5)
C''6—C''1—C''17	122.9 (4)	C'8A—C'7A—C'12A	117.4 (5)
C''1—C''2—C''3	122.0 (5)	C'7A—C'8A—C'9A	120.9 (6)
C''2—C''3—C''4	118.4 (5)	C'8A—C'9A—C'10A	120.7 (6)
C''2—C''3—C''7	120.0 (5)	C'9A—C'10A—C'11A	119.1 (6)
C''4—C''3—C''7	121.6 (5)	C'10A—C'11A—C'12A	120.9 (6)
C''3—C''4—C''5	121.2 (4)	C'7A—C'12A—C'11A	121.0 (5)
C''4—C''5—C''6	121.5 (4)	C'6A—O'1A—C'13A	118.4 (4)
C''4—C''5—C'18	120.0 (4)	O'1A—C'13A—C'14A	109.1 (5)
C''6—C''5—C'18	118.5 (4)	C'13A—C'14A—O'2A	127.3 (7)
C''1—C''6—C''5	121.8 (5)	C'13A—C'14A—O'3A	108.2 (6)
C''1—C''6—O''1	118.3 (4)	O'2A—C'14A—O'3A	124.5 (8)
C''5—C''6—O''1	119.7 (4)	C'14A—O'3A—C'15A	117.1 (7)
C''3—C''7—C''8	122.6 (6)	O'3A—C'15A—C'16A	113.0 (10)
C''3—C''7—C''12	122.0 (6)	C'1A—C'17A—O'4A	112.1 (4)
C''8—C''7—C''12	115.4 (6)	C'17A—O'4A—C'18A	114.0 (4)
C''7—C''8—C''9	122.5 (8)	O'4A—C'18A—C''5A	108.4 (4)
C''8—C''9—C''10	122.6 (9)	C'2A—C''1A—C''6A	117.3 (5)
C''9—C''10—C''11	116.7 (9)	C'2A—C''1A—C''17A	119.7 (5)
C''10—C''11—C''12	121.5 (9)	C''6A—C''1A—C''17A	122.9 (5)
C''7—C''12—C''11	121.0 (8)	C'1A—C''2A—C''3A	122.6 (5)
C''2A—C''3A—C''4A	118.1 (5)	C''8A—C''9A—C''10A	121.8 (10)
C''2A—C''3A—C''7A	120.7 (5)	C''9A—C''10A—C''11A	119.2 (10)
C''4A—C''3A—C''7A	121.2 (5)	C''10A—C''11A—C''12A	119.0 (9)
C''3A—C''4A—C''5A	120.6 (5)	C''7A—C''12A—C''11A	120.3 (7)
C''4A—C''5A—C''6A	121.3 (5)	C''6A—O'1A—C''13A	114.4 (4)
C''4A—C''5A—C'18A	120.2 (5)	O'1A—C''13A—C''14A	110.5 (5)
C''6A—C''5A—C'18A	118.5 (5)	C''13A—C''14A—O''2A	126.3 (5)
C''1A—C''6A—C''5A	122.4 (5)	C''13A—C''14A—O''3A	112.0 (5)
C''1A—C''6A—O''1A	121.2 (5)	O''2A—C''14A—O''3A	121.6 (5)
C''5A—C''6A—O''1A	116.4 (5)	C''14A—O''3A—C''15A	122.8 (5)
C''3A—C''7A—C''8A	120.5 (5)	O''3A—C''15A—C''16A	110.5 (7)
C''3A—C''7A—C''12A	121.3 (5)	C''1A—C''17A—O''4A	113.3 (5)
C''8A—C''7A—C''12A	118.2 (6)	C''17A—O''4A—C''18A	113.4 (4)
C''7A—C''8A—C''9A	121.2 (8)	O''4A—C''18A—C5A	112.0 (4)

Each H atom attached to the methyl groups was treated as part of a rigid unit with its original orientation taken from the strongest H-atom peak on a difference Fourier synthesis. Other H atoms were located from $\Delta\rho$ syntheses and constrained to be 1.08 Å from the corresponding C atoms, their positions being dictated by the geometry of the molecule; they were included as riding atoms in the structure-factor calculations. No H-atom parameters were refined.

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Program(s) used to solve structure: *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PA1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

RICHARD E. MARSH

*The Beckman Institute,†
California Institute of Technology, Pasadena,
California 91125, USA*

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Abstract

The crystal structure of diethyl {5,11,17,23-tetra-*tert*-butyl-26,28-bis(2-methoxyethoxy)pentacyclo-[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosane-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,27-diyl-dioxy}diacetate, C₅₈H₈₀O₁₀, is re-refined in space group *C2/c* rather than *Cc*, leading to improved values of bond lengths and angles. Revised coordinates are given.

Comment

The structure of this macrocyclic compound has been described (Guelzim, Khrifi, Baert, Asfari & Vicens, 1993) in space group *Cc* [monoclinic; *a* = 25.767 (2), *b* = 13.897 (2), *c* = 19.867 (4) Å, β = 126.91 (1)°, *Z* = 4]. It is better described in *C2/c*. Refinement in *C2/c* was based on the 3068 'observed'

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