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1,3-Diethoxy-2,4-didehydroxy-*p-tert*-butylcalix[4]arene

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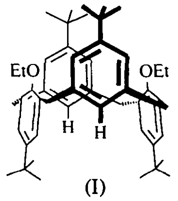
Abstract

The crystal structure of 5,11,17,23-tetrakis(*tert*-butyl)-25,27-diethoxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene, $C_{48}H_{64}O_2$, has been determined. The calix[4]arene is in the 1,3-alternate conformation. The OH-depleted phenyl rings are more coplanar with the plane of the methylene C atoms than the other two rings. Two phenyl rings show a small boat-like distortion from planarity.

Comment

Calixarenes have received considerable attention in the past decade in host–guest or supramolecular chemistry (Gutsche, 1989). The conformation of calixarenes has been studied in the solid state (Andreetti & Ugozzoli, 1991) and in solution (Groenen, van Loon, Verboom, Harkema, Casnati, Ungaro, Pochini, Ugozolli & Reinhoudt, 1991). Four basic conformations have been identified, which differ in the orientation of the phenyl rings with respect to the mean plane of the four 'connecting' methylene C atoms. The present structure determination was performed to establish the solid-state conformation of the title compound, (I), in which two phenolic hydroxy groups have been replaced by H atoms. Other examples of solid-state structures of these so-called OH-depleted calix[4]arenes have been given by Grynszpan, Goren & Biali (1991).



(I)

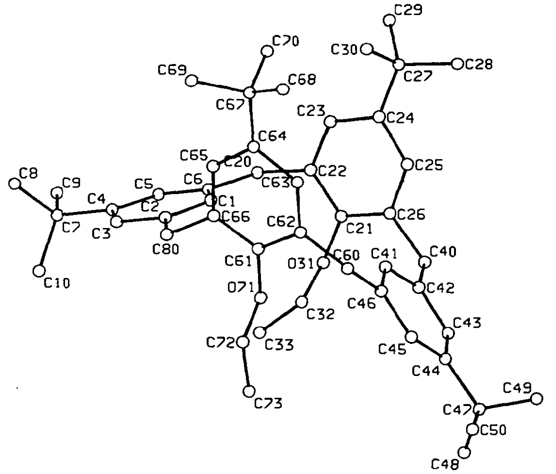


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the calix[4]-arene showing the atomic numbering.

The results of this study (Fig. 2) show the molecule to have the 1,3-alternate conformation. The OH-depleted phenyl rings are more coplanar with the best plane fitted to the 'connecting' methylene C atoms [interplanar angles 24.2 (2), 39.0 (2)°] than with the other two rings [angles 90.0 (2), 104.1 (2)°], as a result of the presence of the H atoms which allow a more coplanar arrangement than the larger ethoxy groups.

The phenyl rings in this compound are almost planar [maximum deviation 0.015 (4) Å, mean deviation 0.005 Å]. The two rings that on the basis of a χ^2 test deviate significantly from planarity (C1–C6; C61–C66), have a boat-like distortion, the symmetry plane of the distortion coinciding with C1–C4 and C61–C64, respectively. The same type of distortion has been reported previously (Timmerman, Harkema, van Hummel, Verboom & Reinhoudt, 1994) and is found to be the predominant deviation from planarity in calix[4]-arene structures (Harkema & Terpstra, 1995).

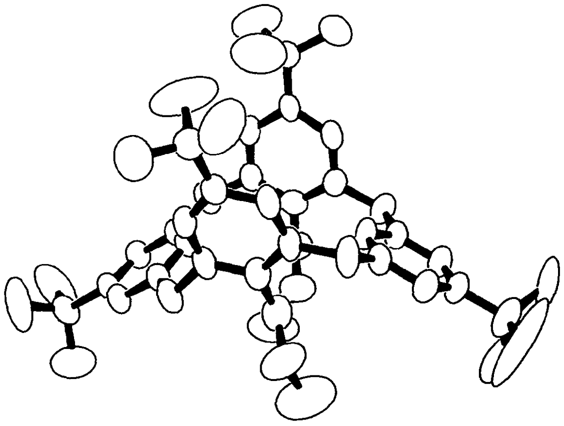


Fig. 2. *ORTEP*II (Johnson, 1976) view showing the 1,3-alternate conformation of the calix[4]arene molecule. Displacement ellipsoids are scaled to include 50% probability.

Experimental

The title compound was prepared from the corresponding 1,3-dihydroxycalix[4]arene (Ting, Verboom, Groenen, van Loon & Reinhoudt, 1990) by reaction with KO^{t}Bu/EtI in tetrahydrofuran. Colourless crystals (m.p. 521–522 K) were obtained by recrystallization from a 1:1 mixture of dichloromethane and ethanol.

Crystal data

$C_{48}H_{64}O_2$
$M_r = 673.0$
Triclinic
$P\overline{1}$
$a = 10.412(3)$ Å
$b = 12.900(2)$ Å
$c = 16.892(5)$ Å
$\alpha = 81.48(3)°$
$\beta = 73.48(3)°$
$\gamma = 79.60(2)°$
$V = 2128(1)$ Å^3
$Z = 2$
$D_x = 1.05$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 7.0$–$14.1°$
$\mu = 0.058$ mm^{-1}
$T = 293(1)$ K
Parallelepiped
0.5 × 0.4 × 0.4 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7425 measured reflections
7425 independent reflections
3390 observed reflections $[I > 3\sigma(I)]$

$\theta_{max} = 25.0°$
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F
$R = 0.070$
$wR = 0.080$
$S = 2.38$
3390 reflections
451 parameters
All H-atoms treated as riding atoms
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.19$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O31	−0.2077 (3)	0.3305 (3)	0.3516 (2)	6.27 (9)
O71	0.1558 (3)	0.0545 (2)	0.2759 (2)	5.60 (9)
C1	0.1293 (4)	0.3509 (3)	0.2173 (3)	3.7 (1)
C2	0.2612 (4)	0.3155 (3)	0.2220 (3)	3.7 (1)
C3	0.3276 (4)	0.3820 (3)	0.2481 (3)	4.2 (1)
C4	0.2669 (4)	0.4821 (3)	0.2702 (3)	3.8 (1)
C5	0.1336 (4)	0.5125 (3)	0.2673 (3)	4.1 (1)
C6	0.0637 (4)	0.4487 (3)	0.2410 (3)	3.8 (1)
C7	0.3450 (4)	0.5522 (3)	0.2991 (3)	4.8 (1)
C8	0.4800 (6)	0.5613 (5)	0.2349 (5)	10.8 (2)
C9	0.2725 (6)	0.6627 (4)	0.3090 (4)	11.3 (2)
C10	0.3803 (7)	0.5011 (5)	0.3757 (4)	13.5 (2)
C20	−0.0815 (4)	0.4889 (3)	0.2395 (3)	5.3 (1)
C21	−0.2118 (4)	0.3349 (3)	0.2705 (3)	4.2 (1)
C22	−0.1542 (4)	0.4140 (3)	0.2143 (3)	4.0 (1)
C23	−0.1666 (4)	0.4246 (3)	0.1342 (3)	4.3 (1)
C24	−0.2335 (4)	0.3586 (3)	0.1069 (3)	4.0 (1)
C25	−0.2875 (4)	0.2802 (3)	0.1652 (3)	4.0 (1)
C26	−0.2791 (4)	0.2665 (3)	0.2462 (3)	4.1 (1)
C27	−0.2439 (4)	0.3722 (4)	0.0179 (3)	4.8 (1)
C28	−0.3510 (6)	0.3186 (6)	0.0063 (4)	14.5 (2)
C29	−0.2716 (8)	0.4890 (5)	−0.0138 (4)	11.8 (3)
C30	−0.1099 (7)	0.3312 (7)	−0.0378 (4)	12.7 (3)
C32	−0.1179 (5)	0.2458 (5)	0.3811 (3)	7.1 (2)
C33	−0.0670 (7)	0.2789 (6)	0.4425 (4)	13.3 (3)
C40	−0.3448 (4)	0.1803 (3)	0.3061 (3)	5.0 (1)
C41	−0.1361 (4)	0.0508 (3)	0.2463 (3)	4.3 (1)
C42	−0.2607 (4)	0.0701 (3)	0.3022 (3)	4.1 (1)
C43	−0.3116 (4)	−0.0124 (3)	0.3562 (3)	4.7 (1)
C44	−0.2433 (4)	−0.1151 (3)	0.3566 (3)	4.7 (1)
C45	−0.1182 (4)	−0.1314 (3)	0.2997 (3)	4.7 (1)
C46	−0.0625 (4)	−0.0508 (3)	0.2445 (3)	4.2 (1)
C47	−0.3047 (6)	−0.2038 (4)	0.4166 (3)	6.4 (2)
C48	−0.327 (1)	−0.1814 (6)	0.5047 (4)	13.9 (3)
C49	−0.4422 (8)	−0.2072 (6)	0.4125 (7)	23.7 (4)
C50	−0.223 (1)	−0.3053 (5)	0.4064 (6)	23.0 (4)
C60	0.0699 (4)	−0.0766 (3)	0.1807 (3)	5.7 (1)
C61	0.1983 (4)	0.0691 (3)	0.1898 (3)	4.1 (1)
C62	0.1543 (4)	0.0111 (3)	0.1425 (3)	4.1 (1)
C63	0.1950 (4)	0.0314 (3)	0.0575 (3)	4.3 (1)
C64	0.2801 (4)	0.1055 (3)	0.0167 (3)	4.2 (1)
C65	0.3181 (4)	0.1625 (3)	0.0679 (3)	4.0 (1)
C66	0.2808 (4)	0.1460 (3)	0.1527 (3)	4.1 (1)
C67	0.3296 (5)	0.1237 (4)	−0.0780 (3)	5.2 (1)
C68	0.3280 (9)	0.0275 (5)	−0.1194 (4)	13.9 (3)
C69	0.4771 (6)	0.1418 (6)	−0.1061 (4)	9.7 (2)
C70	0.2453 (7)	0.2178 (6)	−0.1106 (4)	14.3 (3)
C72	0.2318 (7)	−0.0302 (5)	0.3143 (3)	8.6 (2)
C73	0.173 (1)	−0.0404 (8)	0.4036 (4)	15.0 (4)
C80	0.3338 (4)	0.2062 (3)	0.2037 (3)	4.9 (1)

Table 2. *Selected geometric parameters* (Å, °)

O31—C21	1.375 (6)	C27—C30	1.498 (7)
O31—C32	1.433 (6)	C32—C33	1.44 (2)
O71—C61	1.388 (5)	C40—C42	1.529 (5)
O71—C72	1.418 (7)	C41—C42	1.376 (6)
C1—C2	1.388 (6)	C41—C46	1.394 (5)
C1—C6	1.378 (5)	C42—C43	1.374 (6)
C2—C3	1.381 (7)	C43—C44	1.387 (6)
C2—C80	1.506 (5)	C44—C45	1.384 (5)
C3—C4	1.386 (5)	C44—C47	1.515 (6)
C4—C5	1.385 (6)	C45—C46	1.382 (6)
C4—C7	1.530 (7)	C46—C60	1.506 (6)
C5—C6	1.383 (7)	C47—C48	1.50 (1)
C6—C20	1.513 (6)	C47—C49	1.46 (1)
C7—C8	1.523 (7)	C47—C50	1.433 (8)
C7—C9	1.497 (6)	C60—C62	1.513 (6)
C7—C10	1.475 (9)	C61—C62	1.386 (8)
C20—C22	1.504 (7)	C61—C66	1.390 (6)
C21—C26	1.391 (7)	C62—C63	1.375 (6)
C21—C22	1.382 (6)	C63—C64	1.392 (6)
C26—C25	1.379 (7)	C64—C65	1.390 (8)
C26—C40	1.508 (6)	C64—C67	1.530 (6)
C25—C24	1.380 (5)	C65—C66	1.369 (7)
C24—C23	1.392 (7)	C66—C80	1.507 (7)
C24—C27	1.520 (7)	C67—C68	1.517 (9)
C23—C22	1.379 (7)	C67—C69	1.524 (7)
C27—C28	1.485 (9)	C67—C70	1.496 (9)
C27—C29	1.526 (7)	C72—C73	1.455 (9)
C21—O31—C32	117.6 (3)	C26—C40—C42	115.1 (3)
C61—O71—C72	115.6 (3)	C42—C41—C46	120.6 (4)
C2—C1—C6	121.0 (4)	C40—C42—C41	122.2 (4)
C1—C2—C3	118.6 (3)	C40—C42—C43	118.9 (3)
C1—C2—C80	123.3 (4)	C41—C42—C43	119.0 (4)
C3—C2—C80	118.1 (4)	C42—C43—C44	122.9 (4)
C2—C3—C4	122.3 (4)	C43—C44—C45	116.5 (4)
C3—C4—C5	117.0 (4)	C43—C44—C47	120.9 (4)

C3—C4—C7	120.1 (4)	C45—C44—C47	122.6 (4)
C5—C4—C7	122.9 (3)	C44—C45—C46	122.7 (4)
C4—C5—C6	122.5 (4)	C41—C46—C45	118.3 (3)
C1—C6—C5	118.6 (4)	C41—C46—C60	122.1 (3)
C1—C6—C20	122.7 (4)	C45—C46—C60	119.4 (3)
C5—C6—C20	118.7 (3)	C44—C47—C48	110.5 (6)
C4—C7—C8	109.4 (4)	C44—C47—C49	111.2 (5)
C4—C7—C9	113.2 (4)	C44—C47—C50	113.4 (5)
C4—C7—C10	110.1 (5)	C48—C47—C49	102.3 (7)
C8—C7—C9	106.7 (4)	C48—C47—C50	107.8 (7)
C8—C7—C10	105.3 (5)	C49—C47—C50	111.1 (7)
C9—C7—C10	111.8 (5)	C46—C60—C62	118.6 (4)
C6—C20—C22	116.2 (3)	O71—C61—C62	120.3 (4)
O31—C21—C26	121.3 (4)	O71—C61—C66	118.6 (4)
O31—C21—C22	118.1 (4)	C62—C61—C66	121.1 (4)
C26—C21—C22	120.4 (4)	C60—C62—C61	122.4 (5)
C21—C26—C25	118.3 (4)	C60—C62—C63	119.4 (5)
C21—C26—C40	121.9 (4)	C61—C62—C63	118.1 (4)
C25—C26—C40	119.9 (4)	C62—C63—C64	123.4 (5)
C26—C25—C24	123.7 (4)	C63—C64—C65	115.4 (4)
C25—C24—C23	115.7 (4)	C63—C64—C67	122.9 (5)
C25—C24—C27	122.8 (4)	C65—C64—C67	121.7 (4)
C23—C24—C27	121.5 (4)	C64—C65—C66	123.8 (4)
C24—C23—C22	123.0 (4)	C61—C66—C65	118.1 (4)
C20—C22—C21	121.1 (4)	C61—C66—C80	121.4 (4)
C20—C22—C23	120.0 (4)	C65—C66—C80	120.5 (4)
C21—C22—C23	118.8 (4)	C64—C67—C68	112.2 (5)
C24—C27—C28	113.6 (4)	C64—C67—C69	111.5 (5)
C24—C27—C29	111.6 (4)	C64—C67—C70	110.5 (4)
C24—C27—C30	109.2 (4)	C68—C67—C69	104.3 (5)
C28—C27—C29	107.6 (5)	C68—C67—C70	109.6 (6)
C28—C27—C30	109.5 (5)	C69—C67—C70	108.7 (5)
C29—C27—C30	105.0 (5)	O71—C72—C73	110.0 (5)
O31—C32—C33	110.8 (6)	C2—C80—C66	117.7 (4)

Data were collected with a scan width of (1.10 + 0.34tanθ)°. The intensity data were corrected for Lorentz and polarization effects, and for long-time scale variation.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least squares. All calculations were performed with *SDP* (B. A. Frenz & Associates Inc., 1983). An *ORTEP*II (Johnson, 1976) view (Fig. 2) shows rather large thermal motion for the terminal CH_3 and CH_2 groups which may affect the *R* value.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Andreetti, G. D. & Ugozzoli, F. (1991). *Solid State Studies on Calixarenes*. In *Calixarenes, a Versatile Class of Macrocyclic Compounds*, edited by J. Vicens & V. Böhmer. Dordrecht: Kluwer Academic Publishers.

B. A. Frenz & Associates Inc. (1983). *Structure Determination Package*. College Station, Texas, and Enraf–Nonius, Delft, The Netherlands.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

Groenen, L. C., van Loon, J.-D., Verboom, W., Harkema, S., Casnati, A., Ungaro, R., Pochini, A., Ugozolli, F. & Reinhoudt, D. N. (1991). *J. Am. Chem. Soc.* **113**, 2385–2392.

Grynszpan, F., Goren, Z. & Biali, S. E. (1991). *J. Org. Chem.* **56**, 532–536.

Gutsche, C. D. (1989). In *Calixarenes, Monographs in Supramolecular Chemistry*, Vol 1, edited by J. F. Stoddart. Cambridge: The Royal Society of Chemistry.

Harkema, S. & Terpstra, M. (1995). In preparation.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Timmerman, P., Harkema, S., van Hummel, G. J., Verboom, W. & Reinhoudt, D. N. (1994). *J. Incl. Phenom.* **16**, 189–197.

Ting, Y., Verboom, W., Groenen, L. C., van Loon, J.-D. & Reinhoudt, D. N. (1990). *J. Chem. Soc. Chem. Commun.* pp. 1432–1433.

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A Tautomeric Pair of 2,2-Dimethyl-6-carbamoyl-9-phenyldihydropurines

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Abstract

Two tautomeric dihydropurine derivatives, $C_{14}H_{15}N_5O$, namely 2,2-dimethyl-9-phenyl-1,2-dihydropurine-6-carboxamide, (*A*) (coloured orange–red), and 2,2-dimethyl-9-phenyl-2,3-dihydropurine-6-carboxamide, (*B*) (yellow), are confirmed to have hydrogen substituents at N1 and N3, respectively. A different pattern of observed bond lengths in the purine rings of (*A*) and (*B*) illustrates differences in conjugation in accordance with the different bond alternation. The tautomerism also gives rise to differences in the hydrogen bonding, although both tautomers have an internal hydrogen bond from an amide N—H to an N atom of the five-membered ring, with N···N distances 2.84 (2) Å in (*A*) and 2.836 (6) Å in (*B*).

Comment

The two structures were determined primarily to establish the relationship between the colour and the tautomeric form, and also to establish which is the major tautomer in solution. The compounds were synthesized