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5,17-Diethoxycarbonyl-25,26,27,28-tetrahydroxycalix[4]arene

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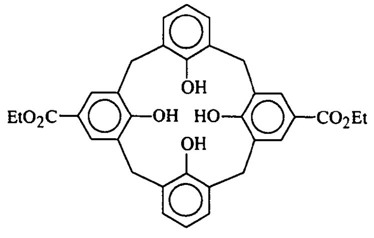
Abstract

The title compound, diethyl 25,26,27,28-tetrahydroxypentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7-(18),9,11,13(27),15,17,19(26),21,23-dodecaene-5,17-dicarboxylate, $C_{34}H_{32}O_8$, a tetrahydroxy calix[4]arene, adopts an open-cone conformation in the solid state; this conformation is dictated by the presence of intramolecular O—H···O hydrogen bonding of the phenolic OH groups [O···O 2.673 (2)–2.708 (2) Å]. The planes of the aromatic rings are inclined at 120.8 (1), 133.1 (1), 118.0 (1) and 128.5 (1)° to the plane of the methylene C atoms which link them. Self-inclusion occurs when the molecules assemble in pairs about inversion centres.

Comment

The use of calixarenes as building blocks for the construction of more sophisticated host molecules and larger molecular assemblies requires calixarene derivatives with various functional groups (Böhmer, 1995). For their synthesis, two principally different strategies are available: the more-or-less selective modification of the easily accessible *tert*-butylcalixarenes (van Loon, Verboom & Reinhoudt, 1992) or the direct synthesis of special calixarenes by fragment condensation (Böhmer, Marschollek & Zetta, 1987; Böhmer, Merkel & Kunz, 1987), and of course both strategies may be combined. The diester title compound (I) was synthesized as part of a series of such synthetic studies.



(I)

A view of (I) with our crystallographic numbering scheme is given in Fig. 1. Molecular dimensions are normal [*e.g.* mean aromatic C—C 1.388 (8) Å, mean C_{ar}—O_{phenol} 1.378 (7) Å]. The molecule has an 'open-cone' conformation dictated by the intramolecular O—H···O hydrogen bonding of the phenolic OH groups with O···O 2.673 (2)–2.708 (2) Å. The phenolic H atoms are disordered equally over two sites to give two sets of intramolecular eight-membered (O—H···)$_4$ rings. The open-cone conformation is quantitatively described by the interplanar angles between the planes of the aromatic rings (*A–D* as indicated by the atomic labelling) and the plane of the methylene C atoms (C7*A*,C7*B*,C7*C*,C7*D*) which link them; these values are 120.8 (1), 133.1 (1), 118.0 (1) and 128.5 (1)° for aromatic rings *A* to *D*, respectively. An alternative way of describing calixarene conformations involving the values of torsion angles about the methylene CH_2 atoms was introduced by Ugozzoli & Andreetti (1992); these values are shown in Table 2.

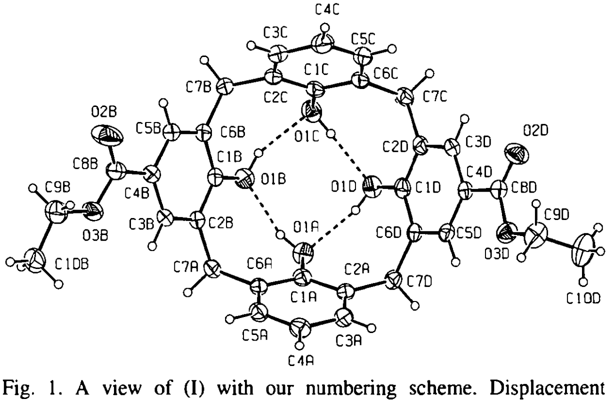


Fig. 1. A view of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one of the two orientations of the disordered phenolic H atoms is shown.

Pairs of molecules pack about inversion centres (Fig. 2) such that the ethyl C atoms C9*D* and C10*D* of one molecule lie in the cup of the inversion-related molecule to generate loosely held dimers. The shortest intermolecular contact (calix cup···ethyl-C atom) is 3.577 (3) Å between calix ring atom C5*D* and ethyl C atom C9*D* (at equivalent position 1 −*x*, 1 −*y*, −*z*).

We reported previously (Gallagher, Ferguson, Böhmer & Kraft, 1994) similar [3.55 (2), 3.57 (2) Å] intermolecular C···C (calix···alkyl-C atom) contacts in a pentahydroxycalix[5]arene which also had an open-cone conformation. In the calix[5]arene structure, a methyl carbon of a *tert*-butyl group was enclathrated in the cup of an adjacent molecule and the operation of a *c*-glide plane led to infinite polymeric chains. The molecules of (I) pack so that the other ethyl group (C9*B*, C10*B*) lies outside the calix cup of an adjacent inversion-related molecule.

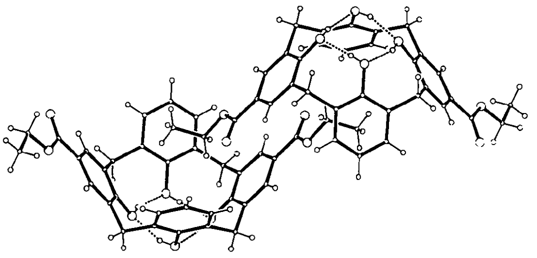


Fig. 2 A view of two inversion-related molecules of (I) showing the mutual packing; atoms are shown as small spheres of an arbitrary size.

Experimental

The title compound was prepared in four steps: (*a*) bisbromomethylation of ethyl *p*-hydroxybenzoate, (*b*) subsequent condensation with excess *tert*-butyl phenol, (*c*) cyclization to the calix[4]arene by condensation of the trimer with the bisbromomethylated ethyl *p*-hydroxybenzoate and (*d*) elimination of the *tert*-butyl groups by transbutylation (Gutsche, Levine & Sujeeth, 1985). Full experimental details and NMR-spectroscopic data are given in the Supplementary Material.

Crystal data

$C_{34}H_{32}O_8$
$M_r = 568.60$
Triclinic
$P\bar{1}$
$a = 8.5360\,(11)$ Å
$b = 11.805\,(2)$ Å
$c = 14.6716\,(15)$ Å
$\alpha = 91.429\,(13)°$
$\beta = 105.973\,(10)°$
$\gamma = 93.793\,(11)°$
$V = 1416.8\,(3)$ Å^3
$Z = 2$
$D_x = 1.333$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.70–19.65°$
$\mu = 0.095$ mm^{-1}
$T = 294\,(1)$ K
Block
0.35 × 0.30 × 0.29 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
6147 measured reflections
6147 independent reflections
3729 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 26.92°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0464$
$wR(F^2) = 0.1385$
$S = 1.068$
6147 reflections
383 parameters
H atoms riding (*SHELXL*93; Sheldrick, 1993) defaults, C—H 0.93-0.97, O—H 0.82 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.0993P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.375$ e Å^{-3}
$\Delta\rho_{\min} = -0.212$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1*A*	0.0725 (2)	0.12144 (12)	0.19497 (10)	0.0560 (4)
O1*B*	0.3009 (2)	0.08679 (11)	0.35576 (10)	0.0571 (4)
O1*C*	0.3369 (2)	0.30172 (12)	0.42435 (10)	0.0601 (4)
O1*D*	0.1318 (2)	0.34128 (12)	0.25322 (10)	0.0574 (4)
O2*B*	0.9872 (2)	−0.1127 (2)	0.3890 (2)	0.1227 (9)
O3*B*	0.8144 (2)	−0.23317 (12)	0.28625 (11)	0.0655 (4)
O2*D*	0.4788 (2)	0.72206 (14)	0.06443 (11)	0.0805 (5)
O3*D*	0.3484 (2)	0.61185 (12)	−0.06274 (9)	0.0594 (4)
C1*A*	0.1421 (2)	0.10293 (15)	0.12139 (13)	0.0417 (4)
C2*A*	0.1214 (2)	0.18022 (14)	0.04947 (13)	0.0419 (4)
C3*A*	0.1846 (2)	0.1568 (2)	−0.02537 (14)	0.0498 (5)
C4*A*	0.2679 (2)	0.0606 (2)	−0.02874 (14)	0.0548 (5)
C5*A*	0.2891 (2)	−0.0130 (2)	0.04422 (14)	0.0506 (5)
C6*A*	0.2282 (2)	0.00669 (14)	0.12070 (13)	0.0427 (4)
C7*A*	0.2570 (2)	−0.07511 (15)	0.20143 (14)	0.0488 (5)
C1*B*	0.4367 (2)	0.03581 (15)	0.34825 (13)	0.0454 (4)
C2*B*	0.4195 (2)	−0.04712 (14)	0.27597 (13)	0.0440 (4)
C3*B*	0.5562 (2)	−0.10326 (15)	0.27374 (13)	0.0484 (5)
C4*B*	0.7057 (2)	−0.0770 (2)	0.34087 (14)	0.0527 (5)
C5*B*	0.7189 (3)	0.0087 (2)	0.40985 (14)	0.0553 (5)
C6*B*	0.5860 (2)	0.06646 (15)	0.41500 (13)	0.0480 (4)
C7*B*	0.6037 (3)	0.1604 (2)	0.49077 (13)	0.0526 (5)
C8*B*	0.8507 (3)	−0.1397 (2)	0.3420 (2)	0.0644 (6)
C9*B*	0.9473 (3)	−0.3015 (2)	0.2826 (2)	0.0756 (7)
C10*B*	0.8773 (3)	−0.4015 (2)	0.2191 (2)	0.0764 (7)
C1*C*	0.4904 (2)	0.3446 (2)	0.42269 (12)	0.0467 (4)
C2*C*	0.6234 (3)	0.2784 (2)	0.45509 (12)	0.0485 (5)
C3*C*	0.7759 (3)	0.3240 (2)	0.45370 (14)	0.0583 (5)
C4*C*	0.7968 (3)	0.4321 (2)	0.4232 (2)	0.0657 (6)
C5*C*	0.6643 (3)	0.4958 (2)	0.39231 (14)	0.0605 (6)
C6*C*	0.5089 (3)	0.4531 (2)	0.38979 (12)	0.0490 (5)
C7*C*	0.3636 (3)	0.5224 (2)	0.34851 (13)	0.0540 (5)
C1*D*	0.1960 (2)	0.41221 (15)	0.19756 (13)	0.0439 (4)
C2*D*	0.3043 (2)	0.50408 (15)	0.24115 (13)	0.0455 (4)
C3*D*	0.3638 (2)	0.57645 (15)	0.18382 (13)	0.0463 (4)
C4*D*	0.3188 (2)	0.55915 (14)	0.08566 (13)	0.0433 (4)
C5*D*	0.2107 (2)	0.46686 (15)	0.04485 (13)	0.0433 (4)
C6*D*	0.1478 (2)	0.39116 (14)	0.09906 (13)	0.0414 (4)
C7*D*	0.0343 (2)	0.28862 (15)	0.05234 (14)	0.0473 (4)
C8*D*	0.3911 (2)	0.6395 (2)	0.03004 (14)	0.0483 (4)
C9*D*	0.4255 (3)	0.6795 (2)	−0.1235 (2)	0.0723 (6)
C10*D*	0.3217 (4)	0.7599 (3)	−0.1759 (2)	0.0994 (10)

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

O1*A*—C1*A*	1.387 (2)	O1*C*—C1*C*	1.380 (2)
O1*B*—C1*B*	1.369 (2)	O1*D*—C1*D*	1.374 (2)
C5*A*—C6*A*—C7*A*—C2*B*	86.0 (2)	C5*C*—C6*C*—C7*C*—C2*D*	84.4 (2)
C6*A*—C7*A*—C2*B*—C3*B*	−96.8 (2)	C6*C*—C7*C*—C2*D*—C3*D*	−92.5 (2)
C5*B*—C6*B*—C7*B*—C2*C*	98.2 (2)	C5*D*—C6*D*—C7*D*—C2*A*	94.4 (2)
C6*B*—C7*B*—C2*C*—C3*C*	−84.6 (2)	C3*A*—C2*A*—C7*D*—C6*D*	−87.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O1*B*	0.82	1.89	2.675 (2)	160
O1*B*—H1*B*···O1*C*	0.82	1.90	2.673 (2)	157
O1*C*—H1*C*···O1*D*	0.82	1.89	2.708 (2)	174
O1*D*—H1*D*···O1*A*	0.82	1.88	2.683 (2)	165
O1*A*—H2*A*···O1*D*	0.82	1.88	2.683 (2)	167
O1*B*—H2*B*···O1*A*	0.82	1.93	2.675 (2)	151
O1*C*—H2*C*···O1*B*	0.82	1.88	2.673 (2)	164
O1*D*—H2*D*···O1*C*	0.82	1.91	2.708 (2)	166

$\Delta\rho$ maps computed in the plane of the phenolic O atoms showed that the phenolic H atoms were disordered equally over two sites; this was allowed for in the *SHELXL*93 refinement (Sheldrick, 1993). Examination of the structure with *PLATON* (Spek, 1995*a*) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM CAD*-4/*PC*. Data reduction: *DATRD*2 (*NRCVAX*94; Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX*94, *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek, 1995*b*). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect* macro *PREPCIF*96.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1366). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(hydrazinium) *N*,*N'*-Dinitroethylenediaminate(2−)

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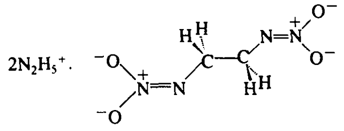
Abstract

The title compound, $2N_2H_5^+.C_2H_2N_4O_4^{2-}$, is an inherently insensitive high-energy material. The anion has C_i symmetry and is almost planar. The nitrate groups are asymmetric, with a mean nitrate N—O distance longer than that found in *N*,*N'*-dinitroethylenediamine and an N1—N2 distance close to a double-bond value.

Comment

Explosives are compounds or mixtures of compounds with a high potential energy. They release large amounts of hot gases in a fast exothermic reaction. One of the main tasks in the chemistry of high-energy materials is the synthesis of molecules with a high activation barrier to energy release (Schubert, 1993; Becuwe & Delclos, 1993; Atkins, Nielsen, Hollis & Willer, 1983). In this context, we have synthesized the title compound, (I), which is extremely insensitive to impact and fairly insensitive to friction.



(I)

The dinitroethylenediaminate dianion (Fig. 1) of (I) is located on an inversion center. The nitroaminate group is planar and the molecule as a whole is almost planar. Atom C1 deviates by 0.024 (2) Å from the best plane through atoms N1, N2, O1 and O2. The C1'—C1—N1—N2 torsion angle is −178.00 (7)°. This is in contrast to *N*,*N'*-dinitroethylenediamine (DNEDAM; Turley, 1967) which also has an almost planar CH_2NHNO_2 group, but whose C1'—C1—N1—N2 torsion angle is 83.8 (4)°. The N1—N2 distance of 1.273 (1) Å is close to a double-bond distance and shorter than that found in DNEDAM [1.301 (4) Å]. The mean nitrate N—O distance of 1.283 (1) Å is longer than that found

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