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N,N'-Dibenzylethylenediamineterphthalate Dimer

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Abstract

The titled macrocyclic dimer, 3,6,13,16-tetrabenzyl-3,6,13,16-tetraazatricyclo[16.2.2.$2^{8,11}$]tetracosa-1(21),8,10,11,18(22),19-hexaene-2,7,12,17-tetraone, lies upon an inversion center; the N—C—C—N torsion angles of the ethylenediamine segment are ±145.7 (3)° and the *para*-phenylene subcyclic moieties are distorted from planarity toward the interior of the molecule.

Comment

The related 20-membered macrocyclic trimer of the title compound has been shown (Vögtle, Puff, Friedrichs & Müller, 1982) to form a stable 'neutral component complex' (Newkome, Taylor, Fronczek, Delord, Kohli & Vögtle, 1981), in which its crystal structure confirmed the presence of a single guest chloroform molecule within the macrocyclic cavity. During our repetition of the procedure for this trimer, the corresponding dimer and tetramer were isolated and spectrally characterized (Newkome & Rogers, 1988). Since this unusually stable host–guest relationship offers a novel entrance to microdetection using surface acoustic wave (SAW) devices (Overton, Yan, Zhang, Klinkhahorn & Newkome, 1990), the crystal structure of the dimer was undertaken to ascertain the conformational relationship(s) to that of the trimer and to provide coordinates for use in docking computations aimed at ascertaining if a neutral component complex may form between the title dimer and small solvent molecules, such as methylene chloride.

The title dimer, illustrated in Fig. 1, lies on an inversion center. The macrocyclic nature of this dimer imposes distortions upon it such that the phenylene moieties are nonplanar, with the two substituted (*para*) C atoms lying 0.011 (3) and 0.019 (3) Å to the same side of the best plane of the other four, toward the exterior of the molecule. The diminished bond angles for C5—C4—C9 and C6—C7—C8 further denote a slight elongation of the rings. The N—C—C—N torsion angles are ±145.7 (3)°. The lactam C atoms C3 and C10 bonded at the *para* positions lie 0.183 (3) and 0.247 (3) Å out of the plane, in the same direction as C4 and C7. The C(ring)—C(lactam) bonds form unequal angles with ring C—C bonds, averaging 116.4 (2) and 125.3 (2)°. The N atoms are slightly pyramidal, lying 0.099 (3) and 0.096 (3) Å out of the plane defined by the C atoms bonded to them. The

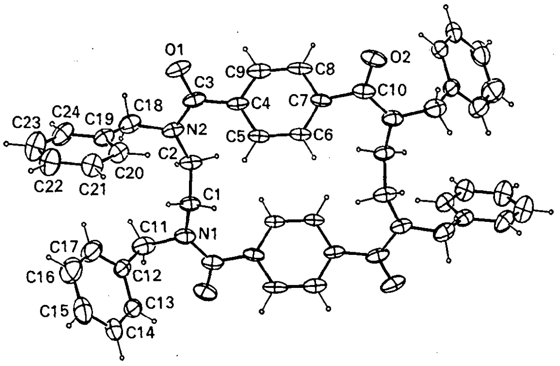

Fig. 1. The title molecule with thermal ellipsoids drawn at the 20% probability level and H atoms drawn as circles of arbitrary radii.

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center-to-center distance between these rings is 5.321 Å, and the perpendicular distance from the best plane of one to the center of the mass of the other is 3.727 Å.

Experimental

Crystal data

$C_{48}H_{44}N_4O_4$
$M_r = 740.9$
Monoclinic
$C2/c$
$a = 37.363$ (6) Å
$b = 10.7689$ (11) Å
$c = 9.8091$ (11) Å
$\beta = 95.929$ (11)°
$V = 3926$ (2) Å^3
$Z = 4$
$D_x = 1.254$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 20\text{–}25°$
$\mu = 0.60$ mm^{-1}
$T = 295$ K
Plate
0.30 × 0.30 × 0.05 mm
Colorless
Crystal source: recrystallized from ethanol

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.7994$, $T_{\max} = 0.9960$
3267 independent reflections
2048 observed reflections [$I > \sigma(I)$]

$R_{\text{int}} = 0.019$
$\theta_{\max} = 65°$
$h = 0 \rightarrow 43$
$k = 0 \rightarrow 12$
$l = -11 \rightarrow 11$
3 standard reflections frequency: 10 000 s intensity variation: random

Refinement

Refinement on F
Final $R = 0.072$
$wR = 0.060$
$S = 2.046$
2048 reflections
254 parameters
H-atom parameters not refined
$w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$
$(\Delta/\sigma)_{\max} = 0.07$

$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.10$ e Å^{-3}
Extinction correction: $(1+gI_c)^{-1}$ applied to F_c
Extinction coefficient: $g = 1.02(10) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

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

$$B_{\text{eq}} = \frac{8\pi^2}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.14983 (7)	−0.0865 (2)	0.5176 (2)	8.39 (7)
O2	0.29831 (7)	−0.1074 (2)	0.2154 (3)	8.63 (7)
N1	0.17489 (7)	0.4290 (2)	0.7127 (2)	6.26 (7)
N2	0.15604 (7)	0.0971 (2)	0.6273 (2)	6.19 (7)
C1	0.16981 (9)	0.3242 (3)	0.6166 (3)	5.72 (8)
C2	0.17890 (9)	0.1985 (3)	0.6852 (3)	6.38 (9)
C3	0.16800 (9)	0.0067 (3)	0.5463 (3)	6.39 (9)
C4	0.20314 (8)	0.0192 (3)	0.4902 (3)	5.49 (8)
C5	0.21291 (9)	0.1173 (3)	0.4092 (3)	5.55 (8)
C6	0.24438 (9)	0.1128 (3)	0.3488 (3)	5.57 (8)
C7	0.26702 (8)	0.0121 (3)	0.3642 (3)	5.67 (8)
C8	0.2572 (1)	−0.0854 (3)	0.4486 (3)	7.3 (1)
C9	0.2260 (1)	−0.0806 (3)	0.5093 (3)	7.1 (1)
C10	0.29798 (9)	−0.0114 (3)	0.2844 (3)	6.53 (9)
C11	0.1437 (1)	0.4573 (4)	0.7861 (4)	8.4 (1)
C12	0.11386 (9)	0.5182 (3)	0.6964 (3)	6.95 (9)
C13	0.11752 (8)	0.6362 (3)	0.6428 (4)	6.9 (1)
C14	0.09056 (9)	0.6903 (4)	0.5570 (4)	8.1 (1)
C15	0.0592 (1)	0.6265 (5)	0.5236 (5)	10.6 (1)
C16	0.0543 (1)	0.5098 (5)	0.5753 (6)	13.5 (2)
C17	0.0818 (1)	0.4587 (4)	0.6611 (5)	10.9 (1)
C18	0.1216 (1)	0.0760 (4)	0.6813 (3)	7.7 (1)
C19	0.08862 (9)	0.1136 (3)	0.5935 (3)	6.46 (9)
C20	0.08862 (9)	0.1592 (3)	0.4619 (3)	6.8 (1)
C21	0.05685 (9)	0.1928 (4)	0.3868 (3)	8.0 (1)
C22	0.0248 (1)	0.1806 (5)	0.4393 (4)	10.1 (1)
C23	0.0243 (1)	0.1348 (5)	0.5690 (5)	11.6 (2)
C24	0.0557 (1)	0.1013 (4)	0.6440 (4)	9.3 (1)

Table 2. *Geometric parameters* (Å, °)

O1—C3	1.228 (4)	C3—C4	1.481 (5)
O2—C10	1.236 (4)	C4—C5	1.393 (4)
N1—C1	1.470 (4)	C4—C9	1.372 (4)
N1—C10′	1.345 (4)	C5—C6	1.371 (5)
N1—C11	1.462 (5)	C6—C7	1.375 (4)
N2—C2	1.464 (4)	C7—C8	1.409 (4)
N2—C3	1.361 (4)	C7—C10	1.484 (5)
N2—C18	1.458 (5)	C8—C9	1.364 (5)
C1—C2	1.534 (4)		
C1—N1—C10′	124.5 (3)	C3—C4—C9	116.1 (3)
C1—N1—C11	114.7 (3)	C5—C4—C9	118.4 (3)
C10′—N1—C11	119.3 (3)	C4—C5—C6	120.5 (3)
C2—N2—C3	123.1 (3)	C5—C6—C7	121.7 (3)
C2—N2—C18	118.4 (3)	C6—C7—C8	117.3 (3)
C3—N2—C18	117.1 (3)	C6—C7—C10	125.5 (3)
N1—C1—C2	112.8 (2)	C8—C7—C10	116.6 (3)
N2—C2—C1	113.2 (2)	C7—C8—C9	121.0 (3)
O1—C3—N2	120.8 (3)	C4—C9—C8	121.2 (3)
O1—C3—C4	118.6 (3)	O2—C10—N1′	120.9 (3)
N2—C3—C4	120.6 (3)	O2—C10—C7	118.9 (3)
C3—C4—C5	125.1 (3)		
C1—C2—N2—C18	−86.1 (3)	C2—C1—N1—C11	−87.0 (3)
O1—C3—N2—C2	168.6 (3)	O2′—C10′—N1—C1	169.0 (3)
C10′—N1—C11—C12	93.5 (4)	C3—N2—C18—C19	−86.4 (4)
O1—C3—C4—C9	−50.8 (4)	O2—C10—C7—C8	50.2 (4)
C1—N1—C11—C12	−73.3 (4)	C10′—N1—C1—C2	106.9 (4)
N1—C1—C2—N2	145.7 (3)		

Symmetry code: (′) $0.5-x$, $0.5-y$, $1-z$.

Programs used were *MolEN* (Enraf-Nonius, 1990), *RANTAN* (Yao, 1981) and *ORTEP* (Johnson, 1965). Systematic absences *hkl* with $h + k$ odd and *h0l* with l odd are consistent with space groups *Cc* and *C2/c*. The latter was shown to be the appropriate choice by successful refinement of a centrosymmetric model.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data, and complete lists of bond distances, bond angles and torsion angles, as well as a stereoview of the molecule, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55911 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1021]

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4-Methyl-2,6-bis(phosphonomethyl)phenol Dihydrate

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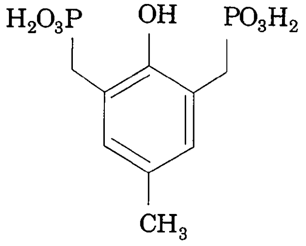
Abstract

The 4-methyl-2,6-bis(phosphomethyl)phenol molecule, which crystallizes with two water molecules per asymmetric unit, has approximate twofold symmetry and is involved in extensive three-dimensional hydrogen bonding in which every available OH group participates. The principal dimensions include P=O 1.4981 (13) and 1.5015 (14) Å, four P—OH distances in the range 1.5395 (14) to 1.5688 (13) Å, P—C 1.7857 (17) and 1.7893 (17) Å, and O· · ·O intramolecular and intermolecular hydrogen-bond distances in the range 2.458 (2) to 2.866 (2) Å.

Comment

Substituted 2,6-bis(methanephosphonic acid)phenols are obtained by reaction of the appropriate hydroxymethyl- or bromomethyl-substituted phenols with phosphorous acid trialkyl esters and subsequent hydrolysis; the pK_a values of the resulting compounds are strongly dependent on the nature and electronegativity of the ring substituents (Ageeva & Ivanov, 1967, 1968; Vogt, 1978; Kaiser, Schied, Trautmann & Vogt, 1993). The structure determination of the dihydrate of (1) was undertaken to establish the nature of the O—H· · ·O hydrogen-bond interactions of the bis(phosphonic acid) derivative in the solid state.



(1)

Fig. 1 shows that, if the H atoms are neglected, the diacid has approximate twofold symmetry with the twofold axis through atoms O(7), C(1), C(4) and C(8) [C(2)—C(7)—P(1)—O(1) −62.1 (1), C(6)—C(9)—P(2)—O(4) −65.1 (1)°]. The P(1)=O(1) and P(2)=O(6) bond lengths are 1.5015 (14) and 1.4981 (13) Å, respectively, while the four P—O distances are in the range 1.5395 (14) [P(2)—O(5)] to 1.5688 (13) Å [P(2)—O(4)] with an average value of 1.5507 (14) Å. A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for structures containing the C—P=O(—OH)$_2$ fragment revealed only two aliphatic diphosphonic acids and none with aromatic rings. Bond lengths in (1) are similar within experimental error to those measured in 1,2-ethanediphosphonic acid (Peterson *et al.*, 1977) and 1,3-propanediphosphonic acid (Gebert *et al.*, 1977). The P(1)—C(7) and P(2)—C(9) distances are 1.7857 (17) and 1.7893 (17) Å, while the C—C aromatic ring bond lengths are in the range 1.387 (2)-1.397 (2) Å with an average value of 1.393 (2) Å. The phosphonate groups are essentially fully staggered [C(2)—C(7)—P(1)—O(3) 174.4 (2), C(6)—C(9)—P(2)—O(5) −178.7 (2)°], with the orientation of the P=O and two P—OH groups (determined by the hydrogen-bonding process) different at each P atom. There are two intramolecular O—H· · ·O hydrogen bonds [O(7)· · ·O(1) 2.753 (2), HO(7)· · ·O(1) 1.92 (3) Å, O(7)—HO(7)· · ·O(1) 173 (3)°; O(4)· · ·O(7) 2.640 (2), HO(4)· · ·O(7) 1.88 (3) Å, O(4)—HO(4)· · · O(7) 164 (3)°] (Fig. 1) which control the molecular conformation.

Molecule (1) crystallizes with two molecules of water which are involved in extensive three-dimensional hy-