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### 5,17-Dinitro-11,23-diphtalimido-25,26,27,28-tetrapropoxycalix[4]arene

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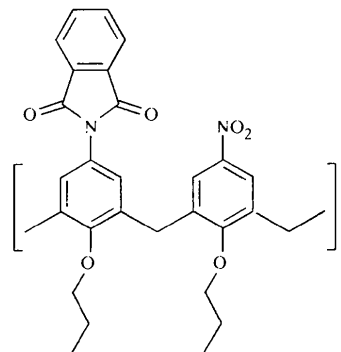
#### Abstract

The aromatic phthalimido moieties of the title compound, C<sub>56</sub>H<sub>52</sub>N<sub>4</sub>O<sub>12</sub>, do not (mutually) stack either intra- or intermolecularly, but rather intermolecularly

with the nitrobenzyl moieties. The molecules show twist-distorted C<sub>2v</sub> symmetry.

#### Comment

The calix[4]arene class of compounds is well known for the substantial number of functionalized derivatives having the ability to complex guest molecules (Böhmer, 1995). The title dinitrodiphtalimidocalix[4]arene, (I), has previously been used as an intermediate in the synthesis of a potential receptor molecule (Timmerman *et al.*, 1995). Interest in compound (I) was renewed by its possible application in large well organized molecular structures (Vreekamp *et al.*, 1996; Timmerman *et al.*, 1997). A crystal structure determination was carried out to elucidate whether the two large aromatic moieties (*i.e.* the phthalimido groups) prefer intermolecular stacking, giving equally directed molecules, or intramolecular stacking, resulting in a 'tweezer' conformation of the individual molecules.



(I)

Although, in the solid-state structure, the phthalimido groups exhibit intermolecular stacking to some extent, the molecules are alternating and not equally directed, which might prove to be a disadvantage for applications in larger molecular structures. The closest intermolecular ring–ring interaction is found between N2, C21, C22, C27, C28 and C1–C6, with a center-of-gravity distance of 4.081 (2) Å and a dihedral angle of 21.2 (1)°.

The molecule is positioned on a crystallographic twofold axis. The molecular non-crystallographic symmetry of the central core may be described as twist distorted by 4.3 (1)° about this axis from exact C<sub>2v</sub> symmetry (Fig. 1). One of the two crystallographically independent side chains is in the all-*trans* conformation, whereas the other one involves one *gauche* conformation in order to avoid the symmetry-related chain. The dihedral angle between the two rings connected through N2–C15 amounts to 63.9 (1)°.

The structure contains no guest molecules and no significant solvent-accessible voids (checked with *SOLV* in *PLATON*; Spek, 1994) larger than 11 Å<sup>3</sup>.

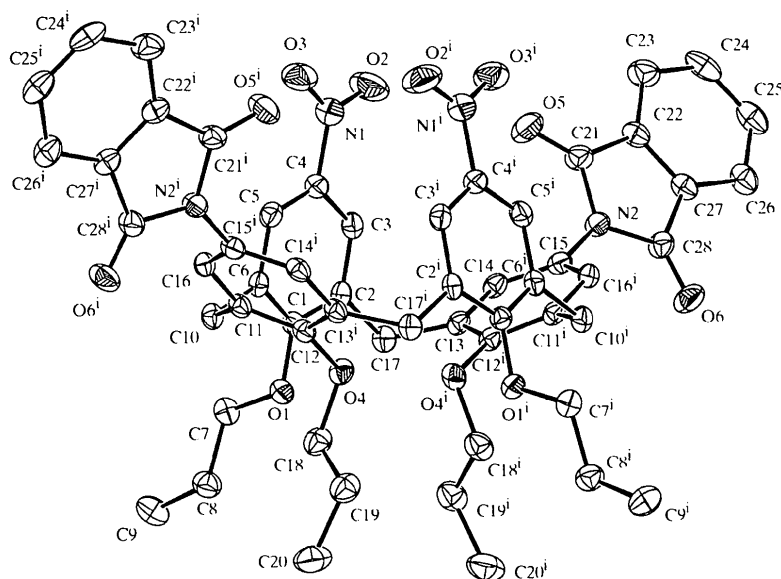


Fig. 1. PLATON (Spek, 1990) plot showing the structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ ]

## Experimental

The title compound was prepared by the reaction of 5,17-diiodo-11,23-dinitro-25,26,27,28-tetrapropoxycalix[4]arene with phthalimide, in the presence of Cu<sub>2</sub>O in collidine, at reflux temperature for 24 h, as described elsewhere (Timmerman *et al.*, 1995). Colorless crystals were obtained after recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (1:1 *v/v*).

### Crystal data

C<sub>56</sub>H<sub>52</sub>N<sub>4</sub>O<sub>12</sub>  
*M<sub>r</sub>* = 973.05  
 Monoclinic  
 C2/c  
*a* = 23.437 (3) Å  
*b* = 11.8595 (13) Å  
*c* = 17.898 (2) Å  
 $\beta$  = 97.418 (10)<sup>o</sup>  
*V* = 4933.1 (10) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.310 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

### Data collection

Enraf-Nonius CAD-4T diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 9931 measured reflections  
 5655 independent reflections  
 3602 reflections with  $I > 2\sigma(I)$

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.050  
*wR*(*F*<sup>2</sup>) = 0.117

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 7–14<sup>o</sup>  
 $\mu$  = 0.09 mm<sup>-1</sup>  
*T* = 150 K  
 Irregular block  
 0.55 × 0.50 × 0.22 mm  
 Colorless

*R*<sub>int</sub> = 0.047  
 $\theta_{\max}$  = 27.48<sup>o</sup>  
 $h$  = -30 → 30  
 $k$  = -15 → 9  
 $l$  = 0 → 23  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 1%

$(\Delta/\sigma)_{\max}$  = 0.001  
 $\Delta\rho_{\max}$  = 0.258 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.245 e Å<sup>-3</sup>

*S* = 1.004

5655 reflections

429 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$

+ 1.787*P*]

where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.376 (2)	O5—C21	1.201 (2)
O1—C7	1.437 (2)	O6—C28	1.204 (3)
O2—N1	1.221 (3)	N1—C4	1.464 (3)
O3—N1	1.228 (2)	N2—C15	1.433 (2)
O4—C12	1.379 (2)	N2—C21	1.400 (3)
O4—C18	1.446 (3)	N2—C28	1.402 (2)
O2—N1—O3	123.12 (18)	N2—C15—C14	120.34 (17)
O2—N1—C4	118.74 (17)	N2—C15—C16 <sup>i</sup>	118.92 (16)
O3—N1—C4	118.13 (17)	O5—C21—N2	125.03 (18)
C15—N2—C21	124.21 (15)	O5—C21—C22	129.45 (19)
C15—N2—C28	123.63 (16)	N2—C21—C22	105.52 (16)
C21—N2—C28	111.85 (16)	O6—C28—N2	125.20 (18)
N1—C4—C3	118.39 (17)	O6—C28—C27	129.08 (17)
N1—C4—C5	119.20 (17)	N2—C28—C27	105.72 (17)
C1—O1—C7—C8	-164.26 (16)	C12—O4—C18—C19	-83.3 (2)

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

H atoms were located from a difference Fourier map, and their positions and individual isotropic displacement parameters were refined.

Data collection: locally-modified *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *SET4* (Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1996*a*). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996*b*). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1536). Services for accessing these data are described at the back of the journal.

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## Methylphenylammonium Hydrogen 2,6-Pyridinedicarboxylate at 158 K

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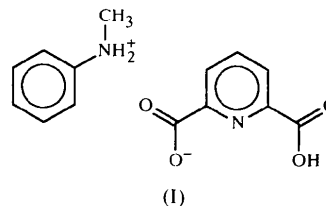
### Abstract

The hydrogen 2,6-pyridinedicarboxylate anions in methylphenylammonium hydrogen 2,6-pyridinedicarboxylate,  $C_7H_{10}N^+ \cdot C_7H_4NO_4^-$ , are linked by a hydrogen bond [ $O \cdots O = 2.472(2) \text{ \AA}$ ] into a zigzag chain; the methylphenylammonium cations are linked to the chain by four  $N \cdots O/N \cdots N$  hydrogen bonds.

### Comment

In the crystal structure of 2,6-pyridinedicarboxylic acid monohydrate, the 2,6-pyridinedicarboxylic acid molecules are linked into a linear chain through an

intermolecular hydrogen bond involving the carboxy COOH group of one molecule and the carboxy COO<sup>-</sup> group of an adjacent molecule [ $O \cdots O = 2.584(7) \text{ \AA}$ ]. The doubly-bonded carbonyl O atom of the first group and the hydroxyl O atom of the second group are linked to the water molecule, these hydrogen bonds giving rise to a sheet structure (Takusagawa *et al.*, 1973). In methylphenylammonium hydrogen 2,6-pyridinedicarboxylate, (I), the hydrogen 2,6-pyridinedicarboxylate anion is similarly linked into a chain running parallel to the *c* axis by a hydrogen bond involving the carboxy COOH group of one anion and the negatively charged carboxyl COO<sup>-</sup> group of a symmetry-related anion, but the hydrogen bond is much stronger [ $O \cdots O = 2.472(2) \text{ \AA}$ ]. The carbon–oxygen bonds in the carboxy [ $C—O = 1.310(3)$  and  $C=O = 1.216(3) \text{ \AA}$ ] and carboxyl [ $C—O = 1.283(3)$  and  $C=O = 1.242(3) \text{ \AA}$ ] groups can be differentiated into single and double bonds, with the difference in the pair of distances for the carboxy group being more marked. The ammonium cations surround the chain; one of the H atoms is linked to the pyridyl N atom and the singly-bonded O atom of the carboxyl group [ $N2 \cdots N1 = 3.074(3)$  and  $N2 \cdots O3 = 2.904(3) \text{ \AA}$ ]; the other H atom is linked to the carboxy O atom as well as to the doubly-bonded carboxyl O atom of the adjacent anion [ $N2 \cdots O1 = 2.809(3)$  and  $N2 \cdots O4 = 2.784(3) \text{ \AA}$ ].



The hydrogen-bonding distance that links the anions into a polyanionic zigzag chain is similar to that [2.484(3) Å] found in the (dimethyldithiocarbamyl)-acetate–(dimethyldithiocarbamyl)acetic acid monoanion (Ng, 1997b), as well as to that [2.448(3) Å] found in the

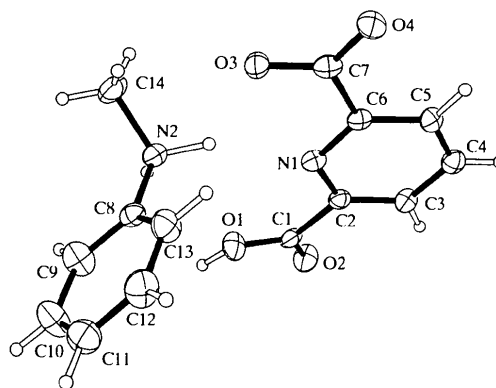


Fig. 1. ORTEP (Johnson, 1976) plot of (I) at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.