

## Cone and 1,3-alternate conformers of 1,3-bis(ethoxycarbonylmethoxy)-2,4-dihydroxycalix[4]arene and 1,2,3,4-tetrakis(ethoxycarbonylmethoxy)calix[4]arene

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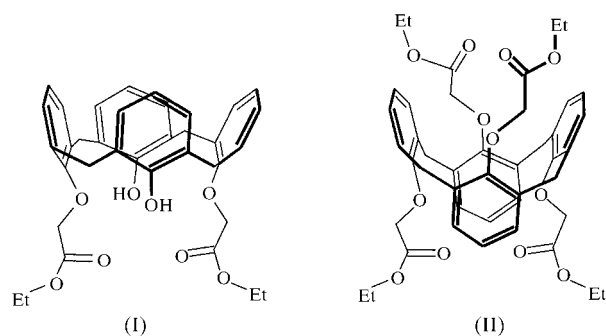
The two title ethoxycarbonylmethoxy derivatives of calix[4]arene, namely diethyl 2,4-dihydroxycalix[4]arene-1,3-diyl-di(oxyacetate), C<sub>36</sub>H<sub>36</sub>O<sub>8</sub>, (I), and tetraethyl calix[4]arene-1,2,3,4-tetrayltetra(oxyacetate), C<sub>44</sub>H<sub>48</sub>O<sub>12</sub>, (II), form two different conformations, *viz.* a cone in (I), where intramolecular hydrogen bonds are formed through OH groups in a partially substituted calix[4]arene, and a 1,3-alternate form of a completely substituted calix[4]arene in (II). A unique three-dimensional array of molecules exists in (II), with the channels extended along the entire crystal.

### Comment

Substituted calix[4]arenes are synthetic macrocycles that have attracted much interest in recent years owing to their increased conformational flexibility compared with cyclodextrins, their ability to complex cations and small molecules, and their usefulness in the design of supramolecular structures [for a survey, see Gutsche (1998)].

Moreover, self-assembled nanotubes have recently been constructed using sodium cations to trigger the one-dimensional polymerization of four guanosine moieties attached to a calix[4]arene 1,3-alternate scaffold (Sidorov *et al.*, 2000); secondary amides have also been used to form self-assembled channels in an anion-dependent process (Sidorov *et al.*, 2002). The conformation of bis-OH-calix[4]arene possesses unique structural peculiarities, such as two hard phenolic OH groups and two soft  $\pi$ -basic benzene rings that form two binding sets, at the edges of the calix[4]arene cavity, which are linked together by a  $\pi$ -basic benzene tunnel. Since unequivocal evidence exists that metal cations can easily pass through

$\pi$ -basic holes with the aid of  $\pi$  interactions, and thus play a crucial role in metal transport through ion channels, a nanotube with a well defined inner diameter for the metal passage may be synthesized. The 1,3-alternate core thus orients two orthogonal pairs of self-complementary guanosine molecules to form an artificial ion channel (Ikeda & Shinkai, 1994). When we searched for structural parameters to show that appropriate introduced substituents immobilize the calix[4]arene conformation, we found that the crystal structures of the title compounds, (I) and (II), have not yet been reported, although Brunink *et al.* (1992) reported the synthesis and preliminary structure of the 1,2-alternate isomer of (I) and a CHCl<sub>3</sub> solvate of (I) has recently been reported (Coles *et al.*, 2002). Coles *et al.* (2002) found that the parent precursor, *viz.* 2,4-dihydroxy-1,3-bis(methoxycarbonylmethoxy)calix[4]arene, exhibited a honeycomb supramolecular structure of columnar hexagonal tubes. These results prompted us to determine the crystal structures of the well established building blocks and scaffolds. A much simplified procedure to obtain the crystals of (I) and (II) was also used.



A search of the Cambridge Structural Database (Version 5.2.1 of April 2001; Allen, 2002) gave no results for the

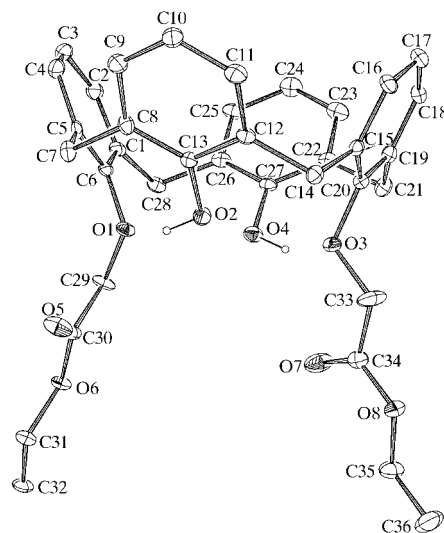


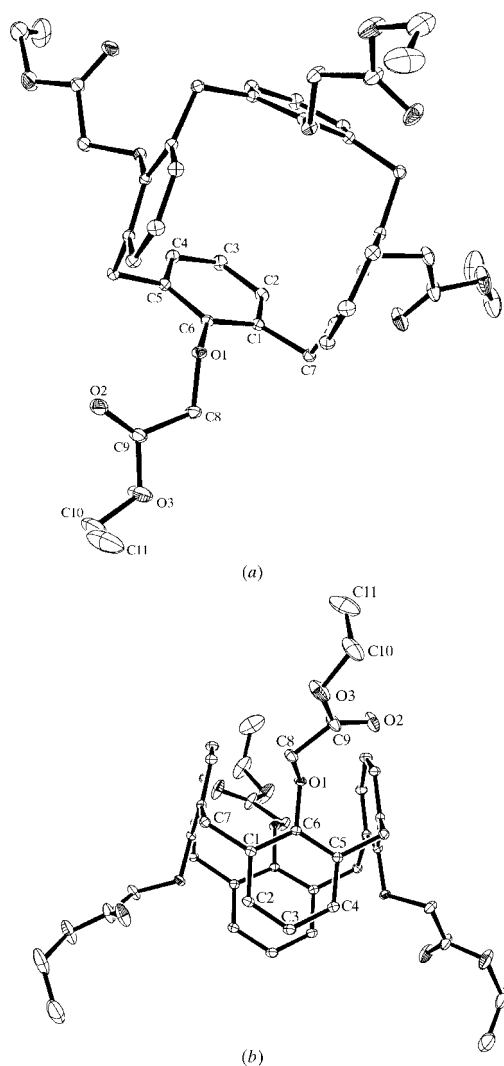
Figure 1

View of the molecule of (I), with displacement ellipsoids shown at the 30% probability level. H atoms (except for the phenol H atoms) have been omitted for clarity.

structure of (II). The search revealed frequent problems with the disorder of the side chains and the formation of solvates. In all these cases, the conventional *R* values of the known crystal structures were rather high.

The molecular structures of (I) and (II), together with the atomic numbering scheme, are shown in Figs. 1 and 2, while the packing of the molecules in (II) is depicted in Fig. 3. Details of the O—H···O and C—H···O hydrogen bonds in (I) and the C—H···O hydrogen bonds for (II) are presented in Tables 1 and 2.

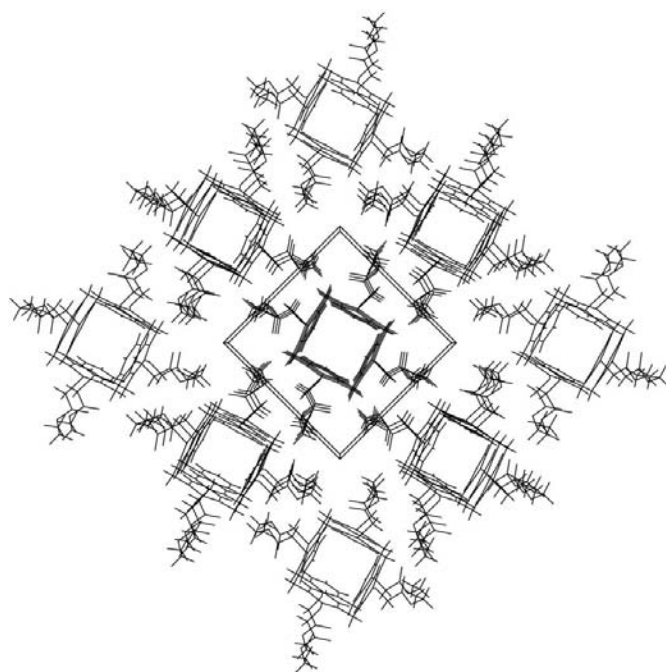
Using a simplified procedure, we were able to prepare solvent-free (I) and (II), which were stable in air. The bond lengths and angles are normal and in agreement with the values for related compounds, for example, 1,3-bis(ethoxycarbonylmethoxy)-2,4-dihydroxycalix[4]arene chloroform solvate (Coles *et al.*, 2002; *International Tables for X-ray Crystallography*, 1995, Vol. C, pp. 693–703).



**Figure 2**  
(a) Top and (b) side views of the molecule of (II), with displacement ellipsoids shown at the 30% probability level. H atoms have been omitted for clarity.

The conformation of (I), which exists as a cone, and the 1,3-alternate conformation of (II) are in agreement with the results of Grynszpan *et al.* (1991), who concluded that the presence of three phenolic OH groups is sufficient to stabilize the cone conformation, with a preference for OH-depleted or substituted calix[4]arenes to adopt the 1,3-alternate conformation. Furthermore, in our determination of (I), the two OH groups forced the molecule into the cone conformation. This result has also been found in cases where either two vicinal (Brunink *et al.*, 1992) or two opposite (Böhmer, 1995) phenolic groups replace the ester groups. Special attention was therefore devoted to the structure of (II). The most interesting feature of this structure is the packing of the molecules. 1,3-Alternate molecules are packed along the *c* axis, thus forming a kind of a nanotubular array (Fig. 3). The 1,3-bis-(ethoxycarbonylmethoxy) derivative, (I), does not exhibit this packing, although the similar 1,3-bis-(methoxycarbonylmethoxy) derivative (Coles *et al.*, 2002) produced a supra-molecular honeycomb structure.

The structures of (I) and (II) are described in a similar manner to those reported by Coles *et al.* (2002). The separations between *meso*-C atoms C7, C14, C21 and C28 in (I) are 5.073 (3), 5.106 (3), 5.103 (2) and 5.102 (3) Å, with cross-ring distances of 7.270 (3) and 7.130 (2) Å. Because of the symmetry, the corresponding distances in (II) are 5.041 (4) and 7.129 (5) Å. The dihedral angles between the planes of the aromatic rings and the mean plane of the macrocycle through the *meso*-C atoms are 64.58 (3), 48.61 (5), 67.54 (5) and 56.44 (5)° in (I), which differ from the angles in the chloroform solvate of (I). The corresponding angles in (II) are 80.43 (7) and 99.57 (7)°. The angle between the planes of the vicinal



**Figure 3**  
Packing of (II), perpendicular to [001], showing the pattern of channels along the *c* axis.

aromatic rings is  $88.41(9)^\circ$ , but the opposite aromatic rings are tilted with respect to each other by  $19.15(8)^\circ$  in (II).

The presence of  $\text{CHCl}_3$  appears to have a significant influence on the conformation of the calix[4]arene skeleton in the solvate structure. The  $\text{C31}\cdots\text{C35}$  separation in (I) [ $7.528(3) \text{ \AA}$ ] is larger than that found in the solvate of (I) [ $7.141(3) \text{ \AA}$ ], probably because of the molecular packing of  $\text{CHCl}_3$ . One of the main differences between (I) and the solvate of (I) is seen in the conformation of the ester groups attached to the calix[4]arene rim. The methoxycarbonylethoxy groups exist in the fully extended form, with the corresponding torsion angles ranging from  $-168.4(2)$  to  $179.8(2)^\circ$ , but the torsion angles  $\text{C6}-\text{O1}-\text{C29}-\text{C30}$  and  $\text{C20}-\text{O3}-\text{C33}-\text{C34}$  are different [ $-124.9(2)$  and  $-157.9(2)^\circ$ ]. The dihedral angle between the extended, nearly planar, ester groups, using weighted least-squares planes through  $\text{O1}-\text{C29}-\text{C30}(\text{O5})-\text{O6}-\text{C31}-\text{C32}$  and  $\text{O3}-\text{C33}-\text{C34}(\text{O7})-\text{O8}-\text{C35}-\text{C36}$ , is  $63.03(5)^\circ$ . On the other hand, the overall conformation of the ester groups in (II) is completely different. The diversity of the torsion angles [ $\text{C6}-\text{O1}-\text{C8}-\text{C9} = 126.5(4)$ ,  $\text{O1}-\text{C8}-\text{C9}-\text{O3} = 167.7(4)$ ,  $\text{C8}-\text{C9}-\text{O3}-\text{C10} = -170.5(7)$  and  $\text{C9}-\text{O3}-\text{C10}-\text{C11} = 86.2(9)^\circ$ ] is a result of the molecular packing and  $\text{C}-\text{H}\cdots\text{O}$  interactions.

The cone conformation in (I) is caused by two intramolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds (see Table 1), which have a partial influence on the orientation of the ester groups. Two intramolecular hydrogen bonds ( $\text{O4}-\text{H4}\cdots\text{O3}$  and  $\text{O4}-\text{H4}\cdots\text{O7}$ ) seem to be bifurcated and lock the ester group in position, while the ester group attached to atom C6 forms only one stronger intramolecular bond ( $\text{O2}-\text{H2}\cdots\text{O1}$ ), with the consequence that the  $\text{O2}\cdots\text{O5}$  distance is considerably longer [ $3.780(2) \text{ \AA}$ ]. However, this ester group is also held in position by the  $\text{C7}-\text{H7B}\cdots\text{O5}$  interaction.

Taking into account the general discussion of  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonding by Leban *et al.* (2002), with reference to the work of Taylor & Kennard (1982, 1983), Steiner & Saenger (1992), Steiner (1997), Steiner & Desiraju (1998) and a review of Steiner (2002), all of which suggest that longer  $\text{H}\cdots\text{O}$  distances (of up to  $3.2 \text{ \AA}$ ) and an angular cut-off at angles greater than  $90^\circ$  could give evidence of the electrostatic interaction of  $\text{C}-\text{H}\cdots\text{O}$  bonds, we checked the values given for the  $\text{C}-\text{H}\cdots\text{O}$  interactions in Tables 1 and 2 for directionality at the acceptor site. Namely, in cases with  $\text{O}=\text{CR}_1\text{R}_2$  or  $\text{R}_1\text{C}-\text{O}-\text{CR}_2$  as acceptors, the  $\text{H}\cdots\text{O}-\text{C}$  angles at the acceptor site are expected to be dispersed around a value of  $120^\circ$ . Normalized  $\text{C}-\text{H}$  values were used in these calculations, which were performed with the program *PARST* (Nardelli, 1983, 1995). While only intermolecular, presumably electrostatic,  $\text{C}-\text{H}\cdots\text{O}$  interactions were found in (I), it appears that the  $\text{C7}-\text{H7A}\cdots\text{O2}^{\text{ii}}$  hydrogen bond (Table 2) is responsible for the arrangement of the ester groups in (II). There are also additional intermolecular  $\text{C}-\text{H}\cdots\text{O}$  interactions (Table 2).

No significant solvent-accessible areas were found in (I), showing that the cone molecules are relatively closely packed. However, the 1,3-alternate shape of (II) produces rather large calculated cavities of  $157 \text{ \AA}^3$  in the crystal, 14.1% of the volume of the crystal unit cell being void, hence the observed

difference in crystal density between (I) and (II) (*PLATON*; Spek, 2003). Channels extend along the entire crystal in the  $c$  direction in (II) (Fig. 3).

## Experimental

Derivatives (I) and (II) were synthesized by the reaction of calix[4]arene with ethyl bromoacetate according to modified procedures (Guillon *et al.*, 2000; Aoki *et al.*, 1992; Iwamoto & Shinkai, 1992). For the preparation of (I), calix[4]arene (1.00 g, 2.35 mmol),  $\text{Cs}_2\text{CO}_3$  (0.77 g, 2.35 mmol) and ethyl bromoacetate (5.23 ml, 47.2 mmol) were refluxed in acetone (70 ml) and stirred for 12 h under  $\text{N}_2$ . The reaction mixture was left to cool, and a solid residue was separated by filtration and washed with acetone. The solvent was removed, water (200 ml) was added, and the residue was extracted with two portions of  $\text{CHCl}_3$  (100 ml) and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation, a brown oil was obtained and dissolved in methanol (60 ml) on a steam bath. Water (25 ml) was added dropwise and the mixture was set aside at room temperature to form crystals (990 mg, 66%; m.p. 443–445 K), which were recrystallized from methanol/ $\text{CHCl}_3$  (7:1). For the preparation of (II), calix[4]arene (2.00 g, 4.70 mmol),  $\text{Cs}_2\text{CO}_3$  (30.12 g, 94 mmol) and ethyl bromoacetate (10.42 ml, 94 mmol) were suspended in acetone (150 ml) and refluxed for 13 h under  $\text{N}_2$ . The rest of the procedure followed that used for (I) and yielded crystals (620 mg, 17.1%; m.p. 381–383 K). Both sets of solvent-free crystals proved to be stable in air. The diffraction data for (I) and (II) were collected for several crystals, both at room temperature (Ljubljana) and at 150 K (Vienna). The best low-temperature data were used, because the  $R$  values of the room-temperature data were rather high [0.072 for (I) and 0.096 for (II)]. Neither the expected disorder in the ethoxycarbonylmethoxy moieties nor solvate formation was observed in either of the two determinations. The data were checked with SQUEEZE option of *PLATON* (Spek, 2003) and with the TWIN refinement.

## Compound (I)

### Crystal data

$\text{C}_{36}\text{H}_{36}\text{O}_8$   
 $M_r = 596.65$   
 Monoclinic,  $P2_1/c$   
 $a = 10.1364(5) \text{ \AA}$   
 $b = 10.9403(5) \text{ \AA}$   
 $c = 27.7309(10) \text{ \AA}$   
 $\beta = 97.917(3)^\circ$   
 $V = 3045.9(2) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.301 \text{ Mg m}^{-3}$   
 $D_m = 1.26(5) \text{ Mg m}^{-3}$

$D_m$  measured by flotation in chloroform/chlorobenzene  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5652 reflections  
 $\theta = 1.0\text{--}27.5^\circ$   
 $\mu = 0.09 \text{ mm}^{-1}$   
 $T = 150(2) \text{ K}$   
 Plate, colourless  
 $0.28 \times 0.24 \times 0.18 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  and  $\omega$  scans  
 13 551 measured reflections  
 6968 independent reflections  
 5280 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -14 \rightarrow 14$   
 $l = -36 \rightarrow 35$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.146$   
 $S = 1.05$   
 6968 reflections  
 407 parameters  
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 1.3240P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.91 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$

**Table 1**  
Hydrogen-bonding geometry (Å, °) for (I).

| D—H...A                    | D—H  | H...A | D...A     | D—H...A |
|----------------------------|------|-------|-----------|---------|
| O2—H2...O1                 | 0.94 | 1.78  | 2.679 (2) | 161     |
| O4—H4...O3                 | 0.94 | 1.93  | 2.823 (2) | 159     |
| O4—H4...O7                 | 0.94 | 2.65  | 3.271 (2) | 124     |
| C7—H7B...O5                | 1.08 | 2.54  | 3.593 (2) | 164     |
| C28—H28B...O7 <sup>i</sup> | 1.08 | 2.49  | 3.514 (2) | 158     |

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

## Compound (II)

### Crystal data

|                                     |   |
|-------------------------------------|---|
| $C_{44}H_{48}O_{12}$                | $D_m$ measured by flotation in chloroform/chlorobenzene |
| $M_r = 768.82$                      | Mo $K\alpha$ radiation                                  |
| Tetragonal, $P\bar{4}$              | Cell parameters from 5413 reflections                   |
| $a = 12.0173$ (8) Å                 | $\theta = 1.0$ – $29.1^\circ$                           |
| $c = 7.6972$ (5) Å                  | $\mu = 0.08$ mm <sup>-1</sup>                           |
| $V = 1111.60$ (13) Å <sup>3</sup>   | $T = 150$ (2) K   |
| $Z = 1$                             | Prism, colourless                                       |
| $D_x = 1.148$ Mg m <sup>-3</sup>    | $0.36 \times 0.24 \times 0.22$ mm                       |
| $D_m = 1.10$ (5) Mg m <sup>-3</sup> |   |

### Data collection

|  |                             |
|--|-----------------------------|
| Nonius KappaCCD diffractometer         | $R_{int} = 0.015$           |
| $\omega$ scans                         | $\theta_{max} = 29.2^\circ$ |
| 2991 measured reflections              | $h = 0 \rightarrow 16$      |
| 1604 independent reflections           | $k = -11 \rightarrow 11$    |
| 1453 reflections with $I > 2\sigma(I)$ | $l = -10 \rightarrow 10$    |

### Refinement

|                                 |   |
|---------------------------------|---|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.1240P)^2 + 0.2336P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | where $P = (F_o^2 + 2F_c^2)/3$                    |
| $wR(F^2) = 0.192$               | $(\Delta/\sigma)_{max} < 0.001$                   |
| $S = 1.09$                      | $\Delta\rho_{max} = 0.46$ e Å <sup>-3</sup>       |
| 1604 reflections                | $\Delta\rho_{min} = -0.23$ e Å <sup>-3</sup>      |
| 128 parameters                  |   |
| H atoms: see below              |   |

**Table 2**  
Hydrogen-bonding geometry (Å, °) for (II).

| D—H...A                     | D—H  | H...A | D...A     | D—H...A |
|-----------------------------|------|-------|-----------|---------|
| C7—H7A...O2 <sup>ii</sup>   | 1.08 | 2.49  | 3.481 (6) | 152     |
| C2—H2...O2 <sup>iii</sup>   | 1.08 | 2.55  | 3.525 (5) | 150     |
| C8—H8B...O3 <sup>iii</sup>  | 1.08 | 2.58  | 3.544 (6) | 149     |
| C10—H10B...O2 <sup>iv</sup> | 1.08 | 2.34  | 3.199 (8) | 135     |

Symmetry codes: (ii)  $1 - y, x, 1 - z$ ; (iii)  $-x, 1 - y, z$ ; (iv)  $y - 1, 1 - x, -z$ .

All H atoms were found in difference electron-density maps and were placed at calculated positions with isotropic displacement parameters taken from those of the parent atom multiplied by 1.2 (1.5 for methyl). The two phenol H atoms of (I) were left to refine freely. There were no suitable anomalous scatterers for Mo  $K\alpha$  radiation; therefore, determination of the absolute configuration was not possible from the X-ray data for (II), and the Friedel diffraction data were merged accordingly. There were only two peaks of residual electron density (1.08 Å from O8 and 1.43 Å from H35B) in (I). However, we were not able to resolve these effects, either as disorder or as an additional solvent molecule in (I). The refinement with the TWIN instruction did not affect these values.

For both compounds, data collection: COLLECT (Nonius, 1999); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor,

1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1971), PLUTON (Spek, 1991), PLATON (Spek, 2003; Farrugia, 2000), ORTEP-3 (Farrugia, 1997) and MERCURY (Bruno *et al.*, 2002); software used to prepare material for publication: SHELXL97, PARST (Nardelli, 1983, 1995) and WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1598). Services for accessing these data are described at the back of the journal.

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