

**Data collection**

Marresearch Image Plate 2211 reflections with  
 95 frames at 2° intervals,  $I > 2\sigma(I)$   
 counting time 2 min  $\theta_{\max} = 25.92^\circ$   
 Absorption correction: none  $h = 0 \rightarrow 9$   
 2544 measured reflections  $k = -12 \rightarrow 13$   
 2544 independent reflections  $l = -11 \rightarrow 13$

**Refinement**

Refinement on  $F^2$   $(\Delta/\sigma)_{\max} < 0.001$   
 $R[F^2 > 2\sigma(F^2)] = 0.050$   $\Delta\rho_{\max} = 0.20 \text{ e } \text{Å}^{-3}$   
 $wR(F^2) = 0.159$   $\Delta\rho_{\min} = -0.20 \text{ e } \text{Å}^{-3}$   
 $S = 1.092$  Extinction correction:  
 2544 reflections *SHELXL93*  
 218 parameters Extinction coefficient:  
 H atoms: see below 0.23 (2)  
 $w = 1/[\sigma^2(F_o^2) + (0.0795P)^2$  Scattering factors from  
 $+ 0.3806P]$  *International Tables for*  
 where  $P = (F_o^2 + 2F_c^2)/3$  *Crystallography* (Vol. C)

H atoms were fixed at ideal positions with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the C atom to which they were bonded. Data analysis used the *XDS* program (Kabsch, 1988). The N atoms in each pyridine ring were unequivocally identified by having the lowest displacement parameters and not having an attached H atom in the difference Fourier map. Uncertainties on C—C bonds do not exceed 0.004 Å.

Data collection: *XDS*. Cell refinement: *XDS*. Data reduction: *XDS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1994).

We thank EPSRC and the University of Reading for funds for the Image Plate System and the EC for support (Contract F141-CT-96-0010). The University of Reading is also thanked for the provision of the Supercomputer for the *GAUSSIAN94* calculations.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1223). Services for accessing these data are described at the back of the journal.

**References**

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## Tetraundecylpentacyclooctacosadodecaen- octol Tetraethanol Solvate, (I), and Tetra- undecylpentacyclooctacosadodecaenedo- decol Hydrate 2.5-Ethanol Solvate, (II)†

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**Abstract**

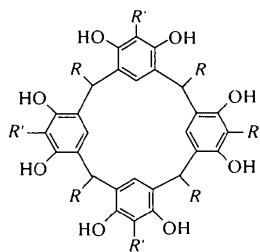
The X-ray crystal structures for the title compounds, (I) (C<sub>72</sub>H<sub>112</sub>O<sub>8</sub>.4C<sub>2</sub>H<sub>6</sub>O) and (II) (C<sub>72</sub>H<sub>112</sub>O<sub>12</sub>.2.5C<sub>2</sub>H<sub>6</sub>O.H<sub>2</sub>O) (also called alkyl calix[4]resorcinarene and calix-[4]pyrogallene, respectively), have been determined. The 'legs' of the long alkyl chains on both compounds are deeply interdigitated and this observation accounts for the spontaneous formation of multilayers of such molecules. Both compounds are in a cone conformation in the crystal with very similar geometry parameters. The arrangement of the molecules in the crystal is also similar, with the long alkyl chains lying nearly parallel to the *c* axis and with 'bowl'-to-'bowl' interactions being effected through van der Waals forces and hydrogen bonds involving solvate molecules [ethanol in the case of (I), and ethanol and water in the case of (II)].

**Comment**

The structures and behaviour of calix[4]resorcinarenes, (I), have attracted widespread attention in recent years

† Systematic names: 2,8,14,20-tetraundecylpentacyclo[19.3.1.1<sup>3,7</sup>.-1<sup>9,13</sup>.1<sup>15,19</sup>]octacosal(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octol tetraethanol solvate and 2,8,14,20-tetraundecylpentacyclo[19.3.1.1<sup>3,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]octacosal(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,5,6,10,11,12,16,17,18,22,23,24-dodecol hydrate 2.5-ethanol solvate.

(Gutsche, 1989). These resorcinol–aldehyde oligomers are very easily synthesized and because of their amphiphilic properties, have been widely studied in supramolecular constructions (Cram & Cram, 1994), host–guest interactions and complexation with metal ions and with sugars (Aoyama *et al.*, 1989), and most recently in thin film assemblies (Huisman *et al.*, 1995; Van-Velzen *et al.*, 1995; Adams *et al.*, 1994; Davis *et al.*, 1996). Calix[4]resorcinarenes as a class are conformationally mobile but the mobility is modified by substituents. Only very few crystal structures have been determined because the compounds are generally difficult to crystallize (Gutsche, 1989). The exceptions involve examples in which the hydroxyl groups on the bowl rims are modified, *e.g.* by acylation or when the compounds are reacted under Mannich conditions (Leigh *et al.*, 1994). The present investigation had its origin in our studies of the behaviour of calix[4]resorcinarenes in ultra-thin organic films assembled either by gold–thiol deposition (Adams *et al.*, 1994) or by spontaneous multilayering on a variety of substrates (Davis & Stirling, 1995; Davis *et al.*, 1996). A striking result of the study was that calix[4]resorcinarenes with C<sub>11</sub> chains at the 2,8,14,20-positions formed multilayers up to 40 layers thick as deduced by neutron reflectometry and IR spectroscopy (Davis *et al.*, 1996). Such ordered multilayering is characteristic only of calix[4]resorcinarenes with free hydroxyl groups and the extent of multilayering is determined by the length of the alkyl chains. The multilayering behaviour of the related compound calix[4]pyrogallene, (II) (Beer *et al.*, 1989; Holmes & Tasker, 1990), is considerably different from that in the calix[4]resorcinarene. IR measurements of carbon-etching intensities in the multilayers suggest that only some five layers build up spontaneously. This different multilayering behaviour of the two chemically and structurally related compounds seemed difficult to explain, and we undertook X-ray crystal structural studies to obtain information on the disposition of the alkyl chains and the nature of intermolecular (especially inter-bowl) interactions. It was assumed that bowl-to-bowl interactions through hydrogen bonding and/or van der Waals interactions would be mainly responsible for the multilayering behaviour of such compounds.



(I)  $R = C_{11}H_{23}$ ;  $R' = H$

(II)  $R = C_{11}H_{23}$ ;  $R' = OH$

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively, whilst the unit-cell contents are shown in Figs. 3 and 4, respectively. The structures of the pentacyclooctacosadodecaene–octol/dodecol moieties (bowls) in the two compounds are illustrated

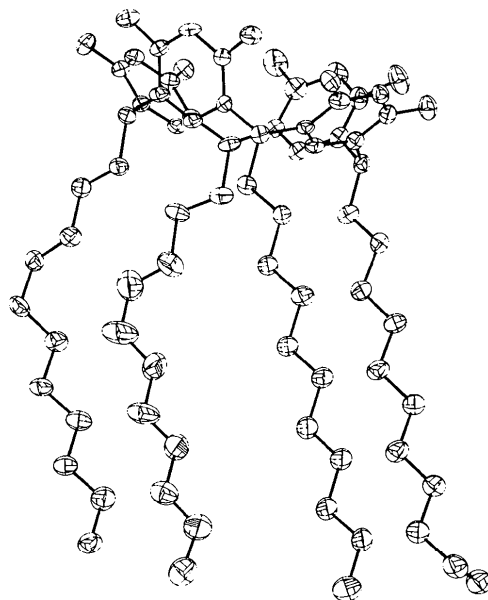


Fig. 1. A general view of the molecular structure of (I). The ellipsoids are drawn at the 50% probability level. The H atoms and solvate species have been omitted for clarity.

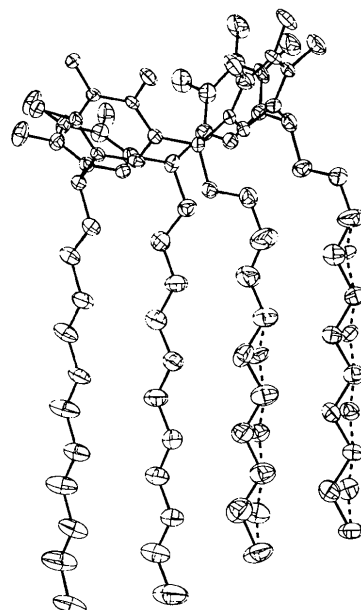


Fig. 2. A general view of the molecular structure of (II). The ellipsoids are drawn at the 50% probability level. Atoms joined by dashed lines represent the alternative sites for the disordered atoms in two of the alkyl chains. The H atoms and solvate species have been omitted for clarity.

in Figs. 5 and 6, respectively. Selected bond lengths and angles are given in Tables 1 and 3 for (I) and (II), respectively, and the dimensions of possible hydrogen bonds are presented in Tables 2 and 4. Both molecules adopt very similar 'bowl' structures (Figs. 5 and 6), with the four long C<sub>11</sub> alkyl chains forming 'legs' to each bowl. The corresponding bond lengths

and angles in the two molecules are similar with only minor differences, and the values are as expected on the basis of the particular atom type (C or O) and the state of hybridization ( $sp^2$  or  $sp^3$ ) of the C atoms involved. Thus, the C<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>2</sup></sub> and C<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>3</sup></sub> distances are, respectively, 1.373 (6)–1.410 (7) (average 1.389) and 1.516 (6)–1.532 (6) Å (average 1.523 Å) in (I), and 1.368 (7)–1.407 (7) (average 1.388) and 1.507 (7)–1.547 (7) Å (average 1.528 Å) in (II). Similarly the C—OH distances are 1.373 (6)–1.400 (5) Å (average 1.385 Å) in (I) and 1.358 (6)–1.411 (6) Å (average

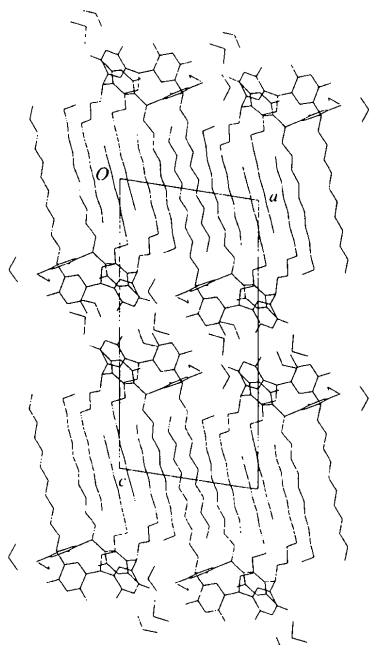


Fig. 3. Unit-cell contents for (I), viewed along *b*.

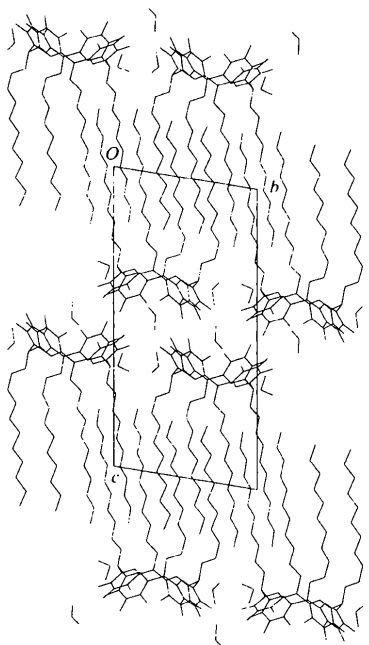


Fig. 4. Unit-cell contents for (II), viewed along *a*.

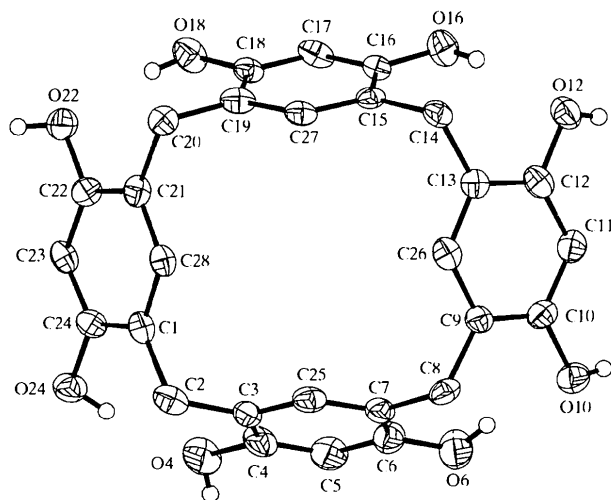


Fig. 5. The structure of the bowl in (I), showing the atom labelling. The ellipsoids are drawn at the 50% probability level. Only the hydroxy H atoms are shown (circles).

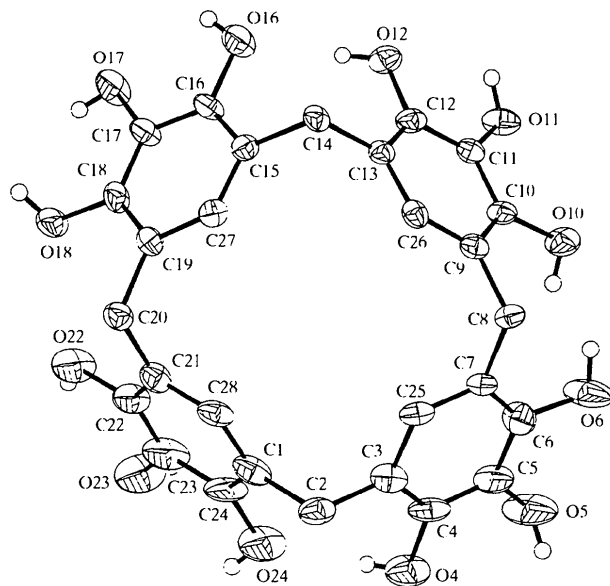


Fig. 6. The structure of the bowl in (II), showing the atom labelling. The ellipsoids are drawn at the 50% probability level. Only the hydroxy H atoms are shown (circles).

1.382 Å) in (II). It is also observed that all the six-membered rings in both compounds show nearly identical angular distortions which are most prominent at C3, C7 and C25, and at their corresponding counterparts in the other rings. The average values for the C—C—C angles at C4/C10/C16/C22, C5/C11/C17/C23 and C6/C12/C18/C24 are, respectively, 121.5, 120.1 and 121.3° for (I), and 120.7, 120.1 and 121.3° for (II), whilst those at C3/C9/C15/C21, C7/C13/C19/C1 and C25/C26/C27/C28 are 116.0, 116.2 and 125.0° for (I), and 117.3, 116.6 and 123.9° for (II). These angular distortions from an ideal value of 120.0° may be attributed to the strain suffered by the six-membered rings as a result of their being incorporated in the 16-membered macrocycle. The C<sub>11</sub> alkyl chains on both molecules are flexible and orientate themselves in a way to optimize inter-chain contacts (C···C non-bonded distances > 3.6 Å). One striking feature common to both the crystal structures is the interdigitation of the long alkyl chains which lie nearly parallel to the *c* axis of the unit cell. As seen from the packing diagrams, these chains are interdigitated to the extent of *ca* ten C atoms in (I) and *ca* eight C atoms in (II), but there are no intermolecular inter-chain contacts less than the appropriate van der Waals radii sum. This phenomenon of interdigitation is presumably a response to the favourable packing forces and it also imposes the bowl (cone) conformation as opposed to other possible arrangements (Gutsche, 1989). Two of the alkyl chains in (II) show some orientational disorder which, however, does not seem to affect the overall molecular geometry parameters or packing arrangement in the crystal. It may be mentioned further that the molecules are held together in the crystal by an extensive network of hydrogen bonding (Tables 2 and 4) involving the hydroxy groups on the bowl and solvate species [four ethanol molecules per resorcinarene in (I), and 2.5 ethanol and one water molecule per pyrogallene in (II)]. There is no direct bowl-to-bowl hydrogen bonding involving the hydroxy groups on neighbouring molecules; such interactions are effected *via* fairly strong van der Waals interactions [C17···O16(1 - *x*, -*y*, 1 - *z*) = 3.297 (8) Å and C23···O18(-*x*, -*y*, 1 - *z*) = 3.325 (8) Å for (I) (H···O contacts > 2.73 Å), and O23···O4(1 - *x*, 1 - *y*, 1 - *z*) = 3.086 Å, O6···O22(1 + *x*, *y*, *z*) = 3.169 Å and O23···O24(1 - *x*, 1 - *y*, 1 - *z*) = 3.393 Å for (II) (H···O contacts > 2.60 Å)]. Formation of intramolecular O—H···O hydrogen bonding involving the hydroxy groups in both molecules appears to favour the formation and stabilization of the observed 'cone' conformation.

## Experimental

Compound (I) was prepared from resorcinol and dodecanol under acid catalysis (Aoyama *et al.*, 1989); compound (II) was similarly prepared from pyrogallol and dodecanol. When crystallized from ethanol, both compounds contained ethanol

[and in the case of (II), also water] of crystallization as deduced from NMR spectroscopy and confirmed by X-ray crystallography. When the crystals were exposed to air, the solvate molecules were apparently lost, as seen by NMR, and the crystals degraded to a powder. Crystalline samples of both compounds were therefore stored in a saturated solution in ethanol. Crystals of both compounds were mounted using silicone oil which acted as both a coating and an adhesive.

## Compound (I)

### Crystal data

C<sub>72</sub>H<sub>112</sub>O<sub>8</sub>.4C<sub>2</sub>H<sub>6</sub>O

*M<sub>r</sub>* = 1289.89

Triclinic

*P* $\bar{1}$

*a* = 12.533 (3) Å

*b* = 12.649 (3) Å

*c* = 25.319 (5) Å

$\alpha$  = 84.79 (3)°

$\beta$  = 80.74 (3)°

$\gamma$  = 83.84 (3)°

*V* = 3927.6 (15) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.091 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

$\lambda$  = 0.71069 Å

Cell parameters from 250 reflections

$\theta$  = 1.76–25.12°

$\mu$  = 0.071 mm<sup>-1</sup>

*T* = 150 (2) K

Prism

0.25 × 0.20 × 0.15 mm

Colourless

### Data collection

Delft Instruments FAST  
area-detector diffractometer

Method: Darr *et al.* (1993)

Absorption correction: none

14 448 measured reflections

9878 independent reflections

4060 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.052

$\theta_{\text{max}}$  = 25.12°

*h* = -13 → 13

*k* = -13 → 13

*l* = -20 → 27

### Refinement

Refinement on *F*<sup>2</sup>

$R[F^2 > 2\sigma(F^2)] = 0.074$

*wR*(*F*<sup>2</sup>) = 0.196

*S* = 0.783

9878 reflections

849 parameters

H atoms: riding model

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.1003*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = -0.010

Δρ<sub>max</sub> = 0.652 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.358 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

C1—C28	1.394 (6)	C12—C13	1.397 (6)
C1—C24	1.401 (6)	C13—C26	1.379 (6)
C1—C2	1.524 (6)	C13—C14	1.532 (6)
C2—C3	1.521 (7)	C14—C15	1.532 (6)
C2—C29	1.536 (6)	C14—C51	1.544 (6)
C3—C25	1.393 (6)	C15—C27	1.388 (6)
C3—C4	1.410 (7)	C15—C16	1.391 (5)
C4—C5	1.378 (7)	C16—O16	1.383 (5)
C4—O4	1.387 (6)	C16—C17	1.389 (6)
C5—C6	1.387 (7)	C17—C18	1.369 (6)
C6—O6	1.373 (6)	C18—C19	1.391 (6)
C6—C7	1.396 (7)	C18—O18	1.400 (5)
C7—C25	1.387 (7)	C19—C27	1.393 (6)
C7—C8	1.517 (6)	C19—C20	1.517 (6)
C8—C9	1.523 (6)	C20—C21	1.516 (6)
C8—C40	1.530 (6)	C20—C62	1.530 (6)
C9—C10	1.383 (6)	C21—C28	1.387 (6)

C9—C26	1.393 (6)	C21—C22	1.398 (6)
C10—O10	1.373 (6)	C22—C23	1.386 (6)
C10—C11	1.385 (6)	C22—O22	1.390 (5)
C11—C12	1.385 (7)	C23—C24	1.385 (6)
C12—O12	1.394 (5)	C24—O24	1.379 (5)
C28—C1—C24	116.3 (4)	C12—C13—C14	121.6 (4)
C28—C1—C2	121.7 (4)	C15—C14—C13	109.8 (4)
C24—C1—C2	122.0 (5)	C15—C14—C51	113.2 (4)
C3—C2—C1	111.1 (3)	C13—C14—C51	111.8 (3)
C3—C2—C29	113.8 (4)	C27—C15—C16	116.3 (4)
C1—C2—C29	111.2 (4)	C27—C15—C14	122.6 (4)
C25—C3—C4	115.3 (5)	C16—C15—C14	121.1 (4)
C25—C3—C2	122.9 (5)	O16—C16—C17	115.8 (4)
C4—C3—C2	121.7 (5)	O16—C16—C15	123.4 (4)
C5—C4—O4	118.8 (5)	C17—C16—C15	120.8 (5)
C5—C4—C3	121.3 (5)	C18—C17—C16	120.3 (4)
O4—C4—C3	120.0 (5)	C17—C18—C19	121.9 (4)
C4—C5—C6	120.9 (5)	C17—C18—O18	116.6 (4)
O6—C6—C5	115.6 (5)	C19—C18—O18	121.5 (4)
O6—C6—C7	124.0 (5)	C18—C19—C27	115.6 (5)
C5—C6—C7	120.4 (5)	C18—C19—C20	122.6 (4)
C25—C7—C6	116.8 (5)	C27—C19—C20	121.8 (4)
C25—C7—C8	121.7 (5)	C21—C20—C19	110.5 (4)
C6—C7—C8	121.5 (5)	C21—C20—C62	113.2 (4)
C7—C8—C9	112.4 (3)	C19—C20—C62	113.4 (4)
C7—C8—C40	113.6 (4)	C28—C21—C22	115.4 (5)
C9—C8—C40	111.4 (4)	C28—C21—C20	122.3 (4)
C10—C9—C26	116.9 (4)	C22—C21—C20	122.3 (4)
C10—C9—C8	123.2 (5)	C23—C22—O22	120.4 (4)
C26—C9—C8	119.9 (4)	C23—C22—C21	122.5 (4)
O10—C10—C9	117.9 (4)	O22—C22—C21	117.0 (5)
O10—C10—C11	120.9 (5)	C24—C23—C22	119.3 (4)
C9—C10—C11	121.2 (5)	O24—C24—C23	120.2 (4)
C12—C11—C10	119.7 (5)	O24—C24—C1	118.5 (4)
C11—C12—O12	122.1 (4)	C23—C24—C1	121.3 (5)
C11—C12—C13	121.4 (4)	C7—C25—C3	125.3 (5)
O12—C12—C13	116.4 (5)	C13—C26—C9	124.4 (5)
C26—C13—C12	116.3 (5)	C15—C27—C19	125.0 (4)
C26—C13—C14	122.1 (4)	C21—C28—C1	125.2 (4)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4 $\cdots$ O15	0.82 (3)	1.93 (4)	2.676 (6)	152 (1)
O6—H6 $\cdots$ O10	0.82 (3)	1.97 (3)	2.779 (6)	170 (3)
O10—H10 $\cdots$ O35	0.82 (3)	1.89 (3)	2.696 (5)	167 (2)
O16—H16 $\cdots$ O12	0.82 (2)	2.00 (3)	2.777 (5)	157 (2)
O18—H18 $\cdots$ O22	0.82 (3)	1.92 (3)	2.702 (5)	159 (2)
O22—H22 $\cdots$ O25 $^i$	0.82 (2)	1.80 (3)	2.600 (6)	165 (1)
O15—H15 $\cdots$ O45 $^{ii}$	0.82 (3)	1.98 (2)	2.768 (6)	162 (2)
O25—H25 $\cdots$ O45 $^{ii}$	0.82 (3)	2.09 (4)	2.877 (6)	161 (2)
O12—H12 $\cdots$ O15 $^{iii}$	0.82 (3)	1.92 (3)	2.714 (5)	164 (2)
O45—H45 $\cdots$ O15 $^{iii}$	0.82 (4)	1.99 (4)	2.768 (6)	159 (4)
O24—H24 $\cdots$ O4	0.82 (3)	1.95 (4)	2.753 (5)	168 (3)

Symmetry codes: (i)  $x, 1+y, z$ ; (ii)  $x-1, y, z$ ; (iii)  $1+x, y, z$ .**Compound (II)***Crystal data* $C_{72}H_{112}O_{12} \cdot 2.5C_2H_6O \cdot H_2O$  $M_r = 1302.80$ 

Triclinic

 $P\bar{1}$  $a = 11.9971 (14) \text{\AA}$  $b = 12.700 (2) \text{\AA}$  $c = 25.742 (4) \text{\AA}$  $\alpha = 80.06 (2)^\circ$  $\beta = 84.22 (2)^\circ$  $\gamma = 82.372 (9)^\circ$  $V = 3817.0 (10) \text{\AA}^3$  $Z = 2$  $D_x = 1.134 \text{ Mg m}^{-3}$  $D_m$  not measuredMo  $K\alpha$  radiation $\lambda = 0.71069 \text{\AA}$ 

Cell parameters from 250 reflections

 $\theta = 1.84\text{--}25.04^\circ$  $\mu = 0.077 \text{ mm}^{-1}$  $T = 150 (2) \text{ K}$ 

Prism

 $0.36 \times 0.15 \times 0.10 \text{ mm}$ 

Colourless

*Data collection*

Delft Instruments FAST

area-detector diffractometer

Method: Darr *et al.* (1993)

Absorption correction: none

15 282 measured reflections

10 102 independent reflections

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.084$  $wR(F^2) = 0.241$  $S = 0.882$ 

10102 reflections

930 parameters

H atoms: riding model

 $w = 1/[\sigma^2(F_o^2) + (0.1184P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$ 

4254 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.070$  $\theta_{\text{max}} = 25.04^\circ$  $h = -13 \rightarrow 9$  $k = -14 \rightarrow 14$  $l = -29 \rightarrow 28$  $(\Delta/\sigma)_{\text{max}} = -0.012$  $\Delta\rho_{\text{max}} = 0.864 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.277 \text{ e \AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)Table 3. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II)

C1—C28	1.396 (8)	C12—C13	1.408 (7)
C1—C24	1.405 (8)	C13—C26	1.381 (7)
C1—C2	1.525 (7)	C13—C14	1.520 (7)
C2—C29	1.530 (8)	C14—C51	1.507 (7)
C2—C3	1.544 (8)	C14—C15	1.548 (7)
C3—C4	1.380 (8)	C15—C27	1.377 (7)
C3—C25	1.409 (8)	C15—C16	1.381 (7)
C4—O4	1.375 (7)	C16—O16	1.382 (6)
C4—C5	1.388 (8)	C16—C17	1.383 (7)
C5—C6	1.368 (9)	C17—C18	1.369 (7)
C5—O5	1.376 (7)	C17—O17	1.372 (6)
C6—C7	1.378 (8)	C18—C19	1.400 (7)
C6—O6	1.405 (7)	C18—O18	1.412 (6)
C7—C25	1.381 (7)	C19—C27	1.382 (7)
C7—C8	1.534 (8)	C19—C20	1.524 (8)
C8—C40	1.513 (7)	C20—C21	1.516 (8)
C8—C9	1.539 (7)	C20—C62	1.539 (8)
C9—C26	1.390 (7)	C21—C28	1.387 (7)
C9—C10	1.393 (7)	C21—C22	1.391 (8)
C10—O10	1.382 (6)	C22—O22	1.383 (6)
C10—C11	1.386 (7)	C22—C23	1.392 (9)
C11—C12	1.385 (7)	C23—O23	1.370 (7)
C11—O11	1.390 (6)	C23—C24	1.386 (8)
C12—O12	1.357 (6)	C24—O24	1.383 (7)
C28—C1—C24	117.5 (5)	C12—C13—C14	119.9 (5)
C28—C1—C2	122.9 (5)	C51—C14—C13	113.3 (4)
C24—C1—C2	119.7 (6)	C51—C14—C15	112.3 (4)
C1—C2—C29	113.7 (5)	C13—C14—C15	110.3 (4)
C1—C2—C3	111.2 (5)	C27—C15—C16	117.3 (5)
C29—C2—C3	112.9 (5)	C27—C15—C14	122.9 (5)
C4—C3—C25	117.7 (6)	C16—C15—C14	119.8 (5)
C4—C3—C2	122.0 (6)	C15—C16—O16	119.3 (5)
C25—C3—C2	120.3 (5)	C15—C16—C17	121.2 (6)
O4—C4—C3	123.6 (6)	O16—C16—C17	119.5 (5)
O4—C4—C5	116.5 (6)	C18—C17—O17	123.8 (5)
C3—C4—C5	119.9 (6)	C18—C17—C16	118.8 (5)
C6—C5—O5	120.9 (6)	O17—C17—C16	117.3 (5)
C6—C5—C4	120.1 (6)	C17—C18—C19	122.6 (5)
O5—C5—C4	119.0 (6)	C17—C18—O18	118.0 (5)
C5—C6—C7	122.8 (6)	C19—C18—O18	119.4 (5)
C5—C6—O6	115.7 (6)	C27—C19—C18	115.5 (5)
C7—C6—O6	121.5 (6)	C27—C19—C20	122.7 (5)
C6—C7—C25	116.2 (6)	C18—C19—C20	121.7 (5)
C6—C7—C8	123.4 (5)	C21—C20—C19	111.3 (5)
C25—C7—C8	120.5 (5)	C21—C20—C62	111.7 (5)
C40—C8—C7	113.5 (5)	C19—C20—C62	113.2 (5)
C40—C8—C9	114.0 (5)	C28—C21—C22	117.1 (6)
C7—C8—C9	110.3 (4)	C28—C21—C20	122.5 (5)
C26—C9—C10	117.1 (5)	C22—C21—C20	120.4 (5)

C26—C9—C8	123.1 (5)	O22—C22—C21	122.7 (6)
C10—C9—C8	119.8 (5)	O22—C22—C23	115.9 (5)
O10—C10—C11	119.3 (5)	C21—C22—C23	121.3 (5)
O10—C10—C9	120.2 (5)	O23—C23—C24	120.1 (6)
C11—C10—C9	120.4 (5)	O23—C23—C22	119.6 (5)
C12—C11—C10	121.2 (5)	C24—C23—C22	120.2 (6)
C12—C11—O11	122.3 (5)	O24—C24—C23	120.8 (5)
C10—C11—O11	116.6 (5)	O24—C24—C1	119.0 (5)
O12—C12—C11	115.0 (5)	C23—C24—C1	120.2 (6)
O12—C12—C13	125.1 (5)	C7—C25—C3	123.3 (5)
C11—C12—C13	119.8 (5)	C13—C26—C9	124.3 (5)
C26—C13—C12	117.2 (5)	C15—C27—C19	124.5 (5)
C26—C13—C14	122.9 (5)	C21—C28—C1	123.7 (5)

Table 4. Hydrogen-bonding geometry (Å, °) for (II)

D—H...A	D—H	H...A	D...A	D—H...A
O4—H4...O24	0.82 (4)	2.00 (4)	2.763 (6)	155 (4)
O6—H6...O10	0.82 (3)	2.04 (2)	2.812 (6)	157 (2)
O10—H10...O6	0.82 (5)	2.28 (4)	2.812 (6)	123 (4)
O11—H11...O4W	0.82 (4)	1.99 (4)	2.710 (6)	145 (2)
O12—H12...O16	0.82 (2)	1.93 (2)	2.750 (5)	176 (2)
O16—H16...O17	0.82 (4)	2.26 (3)	2.701 (6)	114 (2)
O16—H16...O1S	0.82 (4)	1.94 (3)	2.708 (5)	156 (3)
O17—H17...O18	0.82 (5)	2.38 (3)	2.797 (6)	113 (3)
O18—H18...O2S	0.82 (3)	1.90 (4)	2.711 (7)	169 (3)
O22—H22...O23	0.82 (4)	2.21 (5)	2.674 (7)	116 (3)
O1S—H1S...O16	0.82 (3)	1.98 (3)	2.708 (6)	146 (3)
O1S—H1S...O17	0.82 (4)	2.31 (4)	2.955 (6)	135 (3)
O5—H5...O4W'	0.82 (3)	2.18 (3)	2.980 (7)	167 (2)
O24—H24...O1S'	0.82 (5)	1.81 (5)	2.612 (7)	166 (2)
O4W—H4W2...O5''	0.94 (4)	2.28 (5)	2.980 (7)	130 (3)
O4W—H4W1...O4''	0.97 (4)	2.12 (4)	3.077 (6)	166 (3)

Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $x, 1 + y, z$ .

The unit-cell parameters and intensity data were recorded at 150 K on a FAST area-detector diffractometer using the routines ENDEX, REFIN and MADONL in the MADNES software (Pflugrath & Messerschmidt, 1989); detailed procedures are described by Darr *et al.* (1993). Seven CH<sub>2</sub> groups (C32, C34, C36, C38, C45, C47 and C49) on two of the alkyl chains in (II) were orientationally disordered; these were refined with partial site occupancies. For both compounds, all non-H atoms were anisotropic; the displacement coefficients of several atoms belonging to the solvate species [C1S, C2S and C8S for (I), and O3S, C5S and C6S for (II)] were kept approximately isotropic using the restraint parameter ISOR = 0.01 in SHELXL93 (Sheldrick, 1993). For (II), the H atoms on C39 and C50 were ignored and those on the water molecule included in positions obtained from a difference map. Other H atoms in the two compounds were included in calculated positions (riding model) with  $U_{iso}$  set at 1.2 (CH and CH<sub>2</sub>) and 1.5 (OH and CH<sub>3</sub>) times the  $U_{eq}$  of the parent atoms. The bond-length restraints C—C = 1.50 (1) and C—O = 1.40 (1) Å were used for the solvate ethanol molecules in (II).

For both compounds, data collection: MADNES; cell refinement: REFIN in MADNES; data reduction: ABSMAD (Karaulov, 1991); program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL93; molecular graphics: SNOOPI (Davies, 1983); software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1222). Services for accessing these data are described at the back of the journal.

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## 4,6-Dimethyl-2-(4-phenylpiperazin-1-yl-methyl)isothiazolo[5,4-b]pyridin-3(2H)-one

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## Abstract

The crystal structure of the title compound, C<sub>19</sub>H<sub>22</sub>-N<sub>4</sub>OS, is described. The isothiazolopyridine part of the molecule is planar, while the piperazine ring adopts a slightly deformed chair conformation. The structure is