cis-(6RS,13RS)-3,3,10,10-Tetramethyl-6,13-diphenyl-1,8-dioxa-4,11-diazacyclotetradecane-2,5,9,12-tetraone and two of its precursors

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cis-(6RS,13RS)-3,3,10,10-Tetramethyl-6,13-diphenyl-1,8-dioxo-4,11-diaza-
cyclotetradecane-2,5,9,12-tetraone and two of its precursors

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Received 13 April 2006
Accepted 19 April 2006
Online 24 May 2006

The title macrocycle, C_{24}H_{30}N_{2}O_{6}, (VI), was obtained by ‘direct amide cyclization’ from the linear precursor 3-hydroxy-
N-[1-methyl-1-(N-methyl-N-phenylcarbamoyl)ethyl]-2-phenyl-
propanamide, the N-methylinamide of rac-2-methyl-2-[(3-
hydroxy-2-phenylpropanoyl)amino]propanoic acid, C_{16}H_{17}NO_{4}, (IV). The reaction proceeds via the intermediate rac-2-
(2-hydroxy-1-phenylethyl)-4,4-dimethyl-1,3-oxazol-5(4H)-one, C_{16}H_{15}NO_{3}, (V), which was synthesized independently and whose structure was also established. Unlike all previously

described analogues, the title macrocycle has the cis-diphenyl
configuration. The 14-membered ring has a distorted rect-
angular diamond-based [3434] configuration and inter-
molecular N—H···O hydrogen bonds link the molecules into a three-dimensional framework. The propanoic acid
precursor forms a complex series of intermolecular hydrogen
bonds, each of which involves pairwise association of molecules and which together result in the formation of extended two-dimensional sheets. The oxazole intermediate
forms centrosymmetric hydrogen-bonded dimers in the solid
state.

Comment

Cyclic depsipeptides are renowned for their biological activity, mainly as antibiotics, due to their ability to allow cations selectively to pass through the cell membrane (Ballard et al., 2002). A useful method for the synthesis of some analogues, which contain α,α-disubstituted α-amino acids, from linear precursors is the so-called ‘direct amide cyclization’ (Obrecht & Heimgartner, 1987, 1987). The starting materials for the cyclization are hydroxy oligoamides, such as compound (III)
(see scheme), which possess one or several α,α-disubstituted α-amino acids and which are conveniently accessible from the corresponding hydroxy acids [e.g. (I)] and 2H-azirin-3-amines [e.g. (II)] via the ‘azirine/oxazolone method’ (Wipf & Heimgartner, 1990; Heimgartner, 1991). Treatment of the hydroxy

oligoamides with HCl gas in toluene at 373 K yields nine-
to 24-membered cyclic depsipeptides in good yields via the formation of 1,3-oxazol-5(4H)-ones as intermediates (Obrecht & Heimgartner, 1987; Koch et al., 2000, 2001; Köttgen et al., 2006).

Our recent studies have shown that, when β-hydroxy acid
amides analogous to compound (III) are used, 14-membered
cyclodepsipeptides were formed instead of the expected
seven-membered monomers. Again, the corresponding 1,3-
oxazol-5(4H)-ones were shown to be intermediates (Iliev et al., 2003, 2006). Furthermore, in comparable experiments with racemic starting materials, the cyclodimers obtained were trans-configured and no cis isomers could be detected. Other
cyclization methods that started from hydroxy acids [e.g. (IV)], which were derived from α,α-disubstituted analogues of compound (III), gave the same result (Iliev et al., 2003, 2006). Further studies showed that, in order for the reactions to have a practical value, it is a requirement that the β-hydroxy acid is α,α-disubstituted. When that was not the case, water elimination occurred and no cyclic products could be isolated, although the intermediate oxazolone, like compound (V), could be detected by means of IR spectroscopy and its presence proven chemically (Iliev et al., 2006). Only in a single case, when the starting β-hydroxy acid amide, (III), contained the α-phenyl-β-hydroxy acid moiety, could crystals of a 14-
membered cyclodepsipeptide be isolated, namely the title

compound, (VI). The hydroxy acid, (IV), was obtained after selective hydrolysis of (III) by treatment with 3 N HCl in
tetrahydrofuran. The intermediate oxazolone, (V), could be
isolated after treatment of (IV) with N,N'-dicyclohexyl-
carbodiimide in ethyl acetate. As part of the full character-
ization of the reaction products shown in the scheme and in
order to confirm the stereochemistry of compound (VI),
the crystal structures of compounds (IV), (V) and (VI) were
determined and are described here.

Compound (IV) crystallizes in a centrosymmetric space

group and is therefore a racemate: the selected reference
molecule has the R configuration at C5 (Fig. 1). The geometric
parameters involving the non-H atoms are within normal
ranges. The molecule possesses three hydrogen-bond donors,
which are all involved in intermolecular interactions (Table 1).
These interactions combine to link the molecules into extended two-dimensional sheets which lie parallel to the
(001) plane (Fig. 2). Within the sheets, several hydrogen-
bonding motifs (Bernstein et al., 1995) can be discerned. The carboxylic acid H atom interacts with the carbonyl O atom of the carboxylic acid group of a neighbouring molecule, which,
in turn, acts as a donor for an identical interaction back to the original molecule. These interactions result in pairs of molecules being linked into dimers across crystallographic centres of inversion. This pattern can be described by a graph-set motif of \( R_2^2(8) \), which is one of the classic motifs found in the crystal structures of carboxylic acids. The H atom of the hydroxy group forms an intermolecular hydrogen bond with the amide O atom of a different neighbouring molecule. Again, this interaction links pairs of molecules into centrosymmetric dimers and the pattern can be described by a graph-set motif of \( R_2^2(12) \). In a similar fashion, the amide H atom forms an intermolecular hydrogen bond with the hydroxy O atom of a third neighbouring molecule. This interaction also links pairs of molecules into centrosymmetric dimers with the \( R_2^2(12) \) motif. The interactions involving the H atoms of the hydroxy and amide groups can also be combined in an alternating fashion to yield extended co-operative \( \cdots \cdot \cdot \cdot O \cdot H \cdot \cdot \cdot - N \cdot - H \cdots O \cdot - H \cdot \cdot \cdot \) chains, which run parallel to the \([100]\) direction and can be described by a binary graph-set motif of \( C_2^2(6) \).

Free refinement of the carboxylic acid H atom in (IV) resulted in a rather long O2–H2 distance, while the associated hydrogen-bonding H⋅⋅⋅O and O⋅⋅⋅O distances in the \( R_2^2(8) \) motif between the opposing carboxylic acid functions in two adjacent molecules are quite short (Table 2). This indicates that the pairwise intermolecular hydrogen-bonding interactions are quite strong. In such cases, some practitioners have described observations that suggest there may be a tendency for the hydrogen bonds to become more symmetrical, disordered across the O⋅⋅⋅O vector, or even perfectly symmetrical (Gilli et al., 1994; Alfonso et al., 2001). The refined position of atom H2, at first glance, seems to support the idea of partial symmetrization of the H-atom position, but other evidence suggests that the refined position may be misleading. Firstly, the refined isotropic atomic displacement parameter of atom H2 is somewhat larger than normal and larger than those of the hydroxy and amide H atoms, whose positions and atomic displacement parameters were also refined. Secondly, a contoured difference Fourier map produced by PLATON (Spek, 2003), in which the site-occupation factor of atom H2 had been set to 0.001, clearly shows that the electron density does indeed extend a low ridge towards the acceptor O atom, but that the maximum of the electron density is quite clearly defined and is located closer to atom O2 than the refined position of atom H2 (Fig. 3). The maximum is estimated to be

**Figure 1**
A view of the \( R \) enantiomer in racemic (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

**Figure 2**
A hydrogen-bonded sheet in (IV). The hydrogen bonds are shown by dashed lines and the \( R_2^2(8) \), two \( R_2^2(12) \) and \( C_2^2(6) \) motifs are clearly visible.

**Figure 3**
A contoured difference Fourier map slice in the plane of the carboxylic acid group of (IV), with the site-occupancy factor of atom H2 set to 0.001. The refined positions of the atoms are shown by + marks. The contour intervals are 0.1 e Å\(^{-3}\). [Symmetry code: (i) \(-x+1, -y+2, -z\).]
organic compounds

about 0.83 Å from atom O2, which is surprisingly close to the normally expected O—H distance of 0.84 Å at the temperature of the measurement (160 K). This result suggests that the refined position of atom H2 does not necessarily truly represent the majority of the electron-density distribution in this case and that there may be little, if any, symmetrization of the hydrogen bond. The result further shows the importance of examining contoured difference Fourier maps whenever potential unusual H-atom positions are being investigated.

Compound (V) also crystallized as a racemate and again the reference molecule was selected as having the R configuration (Fig. 4). The oxazole ring is planar, with this plane making an angle of 87.02 (6)° with the plane of the phenyl ring. The hydroxy H atom forms an intermolecular hydrogen bond with the N atom of the oxazole ring of a neighbouring molecule which, in turn, acts as a donor for an identical interaction back to the original molecule (Table 2). These interactions link centro symmetrically related pairs of molecules into dimers and can be described by a graph-set motif of R2(12).

Compound (VI) crystallized as a racemate, albeit in a non-centrosymmetric space group. The compound has the 6RS,13RS configuration, which means that the phenyl substituents have a cis relationship; the selected reference molecule has a 6R,13R configuration (Fig. 5). The cis orientation of the phenyl groups was unexpected, as all previous analogous reactions starting from racemic materials had yielded trans-configured cyclodimers (Liev et al., 2003, 2006). The 14-membered ring conformation, while corrugated, is not folded. When viewed perpendicular to the mean ring plane, the ring appears to have a distorted variant of the rectangular diamond-lattice [3434] conformation often observed for this size of organic macrocycle (Groth, 1979; Chan et al., 1985) and predicted to be slightly more stable than the [3344] and [3335] conformations (Dale, 1973). The lactone and lactam groups sit along the ‘3’ and ‘4’ sides of the rectangle, respectively, while the phenyl and methyl substituents occur at the corners. The torsion angles along the sides of the rectangle (Table 3) are close to the ideal value of 180°, with the greatest deviation of about 6° being observed within the lactam groups. The corners of an ideal [3434] rectangle are characterized by two consecutive torsion angles of the same sign and values of ±60°, and it is here that the ring in (VI) shows the greatest deviation from ideality. The dimethyl-substituted corners have a sharper turn, as demonstrated by both torsion angles being up to 17° less than 60°. The phenyl-substituted corners are completely outside the expected pattern, with one torsion angle having a magnitude of about 127° and the following torsion angle being opposite in sign and with a magnitude of about 64°. The five- and four-atom planes formed by the lactone and lactam sides of the rectangle, respectively, are reasonably planar, with the maximum deviations in each type of plane being 0.023 (2) and 0.042 (3) Å, respectively. The greater deviation from planarity of the sides containing the lactam groups is in keeping with the greater deviation of the lactam torsion angle from 180°. Most significantly, instead of the planes of opposing flanks being parallel, as in the ideal diamond-based conformation, the planes of the two lactam sides intersect at an angle of 24.4 (4)°, while those of the two lactone sides intersect at an angle of 80.6 (4)°, which means that the lactone carbonyl groups are turned well away from one another. The described distortions may all be a consequence of twists in the macrocyclic ring conformation, induced by the cis-positioned phenyl substituents preferring to occupy equatorial positions. The phenyl ring planes are approximately perpendicular to the mean plane of the macrocyclic ring. One of the phenyl rings is disordered with an approximately 2:1 ratio of orientations, and the two orientations differ by a twist of 22.0 (1)° about the C17···C20 axis.

The lactam groups in the molecules of (VI) are oriented such that their donor H atoms point towards the same side of the macrocyclic ring and, in addition, the molecules pack such that all of the N—H bonds in the structure face in roughly the same direction. The crystallographic c-glide plane does not flip any molecules up the other way, as it lies approximately perpendicular to the mean plane of the macrocyclic ring. In the structures of the previously examined analogues (Liev et

Figure 4
A view of the R enantiomer in racemic (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

Figure 5
A view of the 6R,13R enantiomer in racemic (VI), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Only the major conformation of the disordered phenyl ring is shown.
The crystal packing in (VI), showing the intermolecular hydrogen bonds as dashed lines.

al., 2003, 2006), the centrosymmetric nature of the molecules meant that the amide H atoms pointed to opposite sides of the macrocyclic ring. This difference has consequences for the hydrogen-bonding pattern. In the previous structures, hydrogen bonds formed between the lactam N–H groups and the lactone O atoms of neighbouring molecules and assembled the centrosymmetric molecules into stacks of ladder-like columns, where the macrocycle acted as the ladder rung and the hydrogen bonds were the rung supports, with the directional sense of the support (the N–H → O direction) on opposing sides of a rung being opposite. In (VI), the lactam N–H groups also form intermolecular hydrogen bonds with the lactone O atoms of neighbouring molecules (Table 4), but instead of a ladder-like arrangement, the hydrogen bonds link to diagonally offset neighbouring molecules, having each of the two symmetry-independent interactions going off in different directions (Fig. 6). Taken individually, the interactions link the molecules into extended chains, each of which has a graph-set motif of C(5). The chains involving N4–H and N11–H run in the [010] and [001] directions, respectively. In essence, each molecule donates hydrogen bonds to two neighbouring molecules and accepts two hydrogen bonds from two other molecules, so that, taken together, these interactions serve to link the molecules into an extended three-dimensional framework.

Experimental

Compound (III) was prepared in 88% yield by the reaction of propionic acid, (I) (332 mg, 2 mmol), and 2,2’-trimethyl-N-phenyl-2H-azirin-3-amine, (II) (370 mg, 2.11 mmol), in tetrahydrofuran (20 ml) at room temperature, according to a known protocol (Obrecht & Heimgartner, 1987). Hydroxy acid (IV) was obtained by treatment of (III) (340 mg, 1 mmol) with a 3 N solution of HCl in tetrahydrofuran (3 ml) for 4 h at room temperature and subsequent extraction with ethyl acetate. Suitable crystals of (IV) were obtained by slow recrystallization from a mixture of dichloromethane–2-propanol–hexane (m.p. 498–501 K). The treatment of (IV) (126 mg, 0.5 mmol) with 1,2,4-dicyclohexylcarbodimide (104 mg, 0.5 mmol) in ethyl acetate (10 ml) overnight at room temperature, followed by filtration, washing with ethyl acetate and recrystallization of the residue from acetonitrile, yielded 93 mg (79%) of (V) (m.p. 392–395 K). The treatment of (IV) (126 mg, 0.5 mmol) with Bu4SnO (50 mg) in xylene (150 ml) under reflux for 2 d (Iliev et al., 2003), followed by evaporation of the solvent, washing with diethyl ether and recrystallization from acetone–hexane–2-propanol, yielded 9 mg (5%) of (VI) as colourless crystals. The same compound was isolated in small amounts by treatment of (III) (170 mg, 0.5 mmol) in toluene (100 ml) at 373 K with HCl (gas) for 8 min, followed by chromatographic purification (silica gel, dichloromethane–acetonitrile 20:1).

Compound (IV)

Crystal data

\[ C_2H_4NO_2 \]  
M, ≈ 251.28  
Triclinic, \( P\bar{1} \)  
a = 6.6567 (2) Å  
b = 9.1317 (3) Å  
c = 10.8486 (3) Å  
\( \alpha = 98.278 (2)^\circ \)  
\( \gamma = 99.5405 (19)^\circ \)  

Data collection

Nonius KappaCCD area-detector diffractometer  
\( \psi \) and \( \omega \) scans with \( k \) offsets  
15315 measured reflections  
\( \theta_{\text{max}} = 27.5^\circ \)  

Refinement

Refinement on \( F^2 \)  
RI(F) > 2\( \sigma(F^2) \) = 0.052  
\( wR(F) = 0.139 \)  
S = 1.06  
2898 reflections  
178 parameters  
H atoms: see below  

Table 1 Hydrogen-bond geometry (Å, \( ^\circ \)) for (IV).

<table>
<thead>
<tr>
<th>( D-H \cdot \cdot \cdot A )</th>
<th>( D-H \cdot \cdot \cdot A )</th>
<th>( D-H \cdot \cdot \cdot A )</th>
<th>( D-H \cdot \cdot \cdot A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2–H2–O1'</td>
<td>1.08 (3)</td>
<td>1.55 (4)</td>
<td>2.6307 (16)</td>
</tr>
<tr>
<td>O7–H7–O4'</td>
<td>0.95 (3)</td>
<td>1.74 (3)</td>
<td>2.6780 (16)</td>
</tr>
<tr>
<td>N3–H3–O7''</td>
<td>0.89 (2)</td>
<td>1.98 (2)</td>
<td>2.8523 (18)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \( x+1, y+2, z \); (ii) \( x+1, y+1, z \); (iii) \( x, y+1, z \).

Compound (V)

Crystal data

\[ C_2H_4NO_2 \]  
M, ≈ 233.27  
Monoclinic, \( P2_1/c \)  
a = 10.1934 (2) Å  
b = 9.4646 (2) Å  
c = 11.9331 (3) Å  
\( \beta = 103.3915 (9)^\circ \)  
V = 1177.00 (4) Å³

Data collection

Nonius KappaCCD area-detector diffractometer  
\( \psi \) and \( \omega \) scans with \( k \) offsets  
28758 measured reflections  

Refinement

Refinement on \( F^2 \)  
RI(F) > 2\( \sigma(F^2) \) = 0.042  
\( wR(F) = 0.108 \)  
S = 1.04  
3421 reflections  
161 parameters  
H atoms: see below  

Table 1 Hydrogen-bond geometry (Å, \( ^\circ \)) for (V).

<table>
<thead>
<tr>
<th>( D-H \cdot \cdot \cdot A )</th>
<th>( D-H \cdot \cdot \cdot A )</th>
<th>( D-H \cdot \cdot \cdot A )</th>
<th>( D-H \cdot \cdot \cdot A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_1 = 1.316 )</td>
<td>( D_1 = 1.316 )</td>
<td>( D_1 = 1.316 )</td>
<td>( D_1 = 1.316 )</td>
</tr>
<tr>
<td>( Z = 4 )</td>
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</tr>
<tr>
<td>( D_1 = 1.316 )</td>
<td>( D_1 = 1.316 )</td>
<td>( D_1 = 1.316 )</td>
<td>( D_1 = 1.316 )</td>
</tr>
</tbody>
</table>
Table 2
Hydrogen-bond geometry (Å, °) for (V).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O15—H15···N1'&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0.915 (19)</td>
<td>1.92 (2)</td>
<td>2.8316 (12)</td>
<td>174.8 (16)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) −x + 2, −y + 1, −z + 1.

**Compound (VI)**

**Crystal data**

C<sub>2</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>

M<sub>r</sub> = 466.53

Monoclinic, Cc

α = 5.9437 (2) Å

b = 19.1979 (4) Å

c = 11.2587 (2) Å

β = 132.9182 (7)°

V = 2523.69 (8) Å<sup>3</sup>

**Data collection**

Nonius KappaCCD area-detector diffractometer

2217 independent reflections

1883 reflections with I > 2σ(I)

357 parameters

Extinction correction: SHELXL97

Extinction coefficient: 0.0056 (10)

**Refinement**

Refinement on F<sup>2</sup>

R<sub>f</sub> = 0.058

wR<sub>f</sub> = 0.107

S = 1.07

2215 reflections

Z = 4

D<sub>2</sub> = 1.228 Mg m<sup>−3</sup>

Mo Kα radiation

μ = 0.09 mm<sup>−1</sup>

T = 160 (1) K

Prism, colourless

0.15 × 0.15 × 0.10 mm

As the structure of compound (VI), one of the phenyl rings is disordered over two orientations which result from a pivot about the C17···C20 axis of the ring. Two positions were defined for each of the other four atoms of this ring and refinement of constrained site-occupation factors for the two orientations yielded a value of 0.67 (3) for the major conformation. All C···C bond lengths within both orientations of the disordered ring were restrained to be similar, while neighbouring atoms within and between each conformation of the disordered ring were restrained to have similar atomic displacement parameters. Compound (VI) crystallized in a non-centrosymmetric space group with a polar axis, but the presence of glide planes indicates that the compound in the crystal is racemic. In the absence of significant anomalous dispersion effects, Friedel opposites were merged prior to the final cycles of refinement and the absolute structure was assigned arbitrarily. The amide, hydroxy and carboxylic acid H atoms of (IV), the hydroxy H atom of (V) and the amide H atoms of (VI) were placed in the positions indicated by difference electron-density maps and their positions were allowed to refine together with individual isotropic displacement parameters. In each structure, the methyl H atoms were constrained to an ideal geometry [C–H = 0.98 Å and U<sub>H</sub>(H) = 1.5U<sub>eq</sub>(C)], but were allowed to rotate freely about the C–C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atom at distances of 0.95, 0.99 or 1.00 Å for phenyl, methylene or methine groups, respectively, and with U<sub>H</sub>(H) = 1.2U<sub>eq</sub>(C). For (IV), (V) and (VI), two, one and four low-angle reflections, respectively, were omitted from the final cycles of refinement because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop.

For all compounds, data collection: COLLECT (Nonius, 2000); cell refinement: DENZO-ŠMN (Otwinowski & Minor, 1997); data reduction: DENZO-ŠMN and SCALEPACK (Otwinowski & Minor, 1997); structure solution: SIR92 (Altomare et al., 1994); structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (Johnson, 1976); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3017). Services for accessing these data are described at the back of the journal.

**Table 3**

Selected torsion angles (°) for (VI).

| O1—C1—C2—C3 | 51.6 (3) |
| C2—C3—N1—C10 | 48.8 (3) |
| C3—N1—C10—C11 | 42.2 (3) |
| C4—N1—C10—C11 | 173.7 (2) |
| C5—C6—C7—C8 | -63.3 (3) |
| C6—C7—C8—C9 | -64.5 (3) |
| C7—O8—C9—C10 | -177.6 (2) |

**Table 4**

Hydrogen-bond geometry (Å, °) for (VI).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N4—H4···O2'</td>
<td>0.80 (3)</td>
<td>2.37 (3)</td>
<td>3.138 (3)</td>
<td>160 (3)</td>
</tr>
<tr>
<td>N11—H11···O9&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.85 (4)</td>
<td>2.16 (4)</td>
<td>2.983 (4)</td>
<td>161 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) −x + 1/2, −y + 1/2, −z + 1/2; (ii) x, −y + 2, z + 1/2.

**References**


Linden et al. • C<sub>1</sub>H<sub>2</sub>N<sub>2</sub>O<sub>4</sub>, C<sub>1</sub>H<sub>2</sub>N<sub>2</sub>O<sub>3</sub> and C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>