(1E,3S,4aR,12aR)-3-Isopropenyl-8-methoxy-3,4,4a,5,6,11,12,12a-octahydro-1(2H)-chrysenone oxime

Huub Kooijman and Anthony L. Spek
(1E,3S,4aR,12aR)-3-Isopropenyl-8-methoxy-3,4,4a,5,6,11,12,12a-octahydro-1(2H)-chrysenenone oxime

The title compound, C_{23}H_{29}NO_{2}, has two independent molecules in the asymmetric unit, differing in the conformation of the propylene side chain. Hydrogen bonding of the oxime moiety joins the independent molecules into a dimer, with graph-set $R_2^2[6]$.

Comment

The crystal structure of the title compound, (I), was determined to confirm, beyond any doubt, the stereochemistry around ring junction C4a—C12a of this (unnatural) $d$-homo-steroid skeleton (Drach et al., 2003). The configuration of atom C3 was known to be $R$. In both independent molecules (see below), the configurations of atoms C4a and C12a were found to be $S$ and $R$, respectively.

The title compound crystallizes with two independent molecules in the asymmetric unit. An atomic displacement ellipsoid plot is given in Fig. 1, together with the adopted labelling scheme for atoms and rings. The molecule labelled C1–C20 will be referred to as molecule 1. The labels of molecule 2 are obtained by adding 50 to the numerical part of the label of the corresponding atom in molecule 1. The independent molecules differ only slightly in conformation. Fig. 2 shows a plot of the superposition of the two molecules using the quaternion transformation method (Mackay, 1984). The independent molecules are related by a 172° rotation along the vector $[-0.02, 1.00, 0.00]$, see Fig. 3. The most obvious difference is the orientation of the isopropenyl moiety, as can be expressed by the torsion angles C2—C3—C15—C17 and C52—C53—C65—C67, which are $-22.7 (7)$ and $2.8 (7)^\circ$, respectively. There is also a small difference in the orientation of the oxime H atom, as is indicated by the torsion angles C1—N13—O14—H14 (160°) and C51—N63—O64—H64 (140°).

The conformation of the steroid skeleton in both independent molecules is the same. Ring $B$ adopts a screw-boat conformation, with the local twofold rotation axis running through the midpoint of the bond C10A—C10B [relevant asymmetry parameters (Duax & Norton, 1975) are...
\[ \Delta C_2[C10A\rightarrow C10B] = 5.1 (7) \text{°} \text{ for molecule 1 and}\]
\[ \Delta C_2[C60A\rightarrow C60B] = 1.7 (7) \text{°} \text{ for molecule 2; Cremer & Pople}\]
puckering parameters \( \theta \) and \( \varphi \) (Cremer & Pople, 1975) are 65.4 (7) and 94.6 (8) \( \text{°} \text{ for molecule 1, and 66.4 (7) and 91.6 (7) \text{°} for molecule 2; ideal values are 67.5 and 90 \text{°}, respectively.}\]

Ring \( C \) is in a half-chair conformation, with the local twofold axis running through the midpoint of the bond \( C4\rightarrow C10 \) [relevant asymmetry parameters are \( \Delta C_2[C4\rightarrow C10] = 4.9 (7) \text{°} \text{ for molecule 1 and} \Delta C_2[C60A\rightarrow C60B] = 4.5 (6) \text{°} \text{ for molecule 2; Cremer & Pople puckering parameters \( \theta \) and \( \varphi \) are} 51.8 (6) \text{ and} 276.9 (7) \text{° for molecule 1, and} 50.5 (6) \text{ and} 276.7 (7) \text{° for molecule 2; ideal values are 50.8 and} 270 \text{°, respectively.}\]

Ring \( D \) adopts a somewhat distorted chair conformation [all relevant asymmetry parameters are in the range 2.8 (5)\text{–}23.4 (6) \text{°} \text{ for molecule 1 and} 4.2 (4)\text{–}23.4 (5) \text{°} \text{ for molecule 2, respectively; the Cremer & Pople parameter \( \theta \) is} 157.1 (6) \text{°} \text{ for molecule 1 and} 160.5 (5) \text{°} \text{ for molecule 2, the ideal value is} 180 \text{°.}\]

The methoxy \( C\rightarrow O \) bond makes an angle of 3.5 (3) \text{°} \text{ with ring} A \text{ in molecule 1 and and an angle of} 6.2 (3) \text{°} \text{ in molecule 2.}\]

The oxime moieties of the independent molecules donate a hydrogen bond to each other, forming a hydrogen bonded dimer (see Fig. 3). The graph set (Bernstein et al., 1995) of the dimer is \( R_2^2[6] \).

**Experimental**

Crystals were obtained from hexane/ether. Details of the synthesis and crystallization are described by Drach et al. (2003).

**Crystal data**

\[ C_{23}H_{29}NO_2 \]

\( M_r = 351.47 \)

Monoclinic, \( P2_1 \)

\( a = 8.137 \) (2) \( \text{Å} \)

\( b = 7.519 \) (2) \( \text{Å} \)

\( c = 31.439 \) (8) \( \text{Å} \)

\( \beta = 95.535 \) (8) \( \text{°} \)

\( V = 1914.5 \) (8) \( \text{Å}^3 \)

\( Z = 4 \)

Data collection

Nonius KappaCCD area-detector diffractometer

\( \theta_{\text{max}} = 25.4 \) \text{°} \text{ for} \( \psi \) scans and \( \omega \) scans with \( \kappa \) offsets

37857 measured reflections

3787 independent reflections

2770 reflections with \( I > 2\sigma(I) \)

Refinement

Refinement on \( F^2 \)

\( R(F^2) = 0.057 \)

\( wR(F^2) = 0.158 \)

\( S = 1.07 \)

3787 reflections

469 parameters

H-atom parameters constrained

\( w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.92P] \)

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

\( \Delta(\sigma)_{\text{max}} < 0.001 \)

\( \Delta \rho_{\text{max}} = 0.24 \) e \( \text{Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.24 \) e \( \text{Å}^{-3} \)
Table 1

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Distance (Å)</th>
<th>Error</th>
<th>Bond/Angle</th>
<th>Distance (Å)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>O14—N13</td>
<td>1.419 (5)</td>
<td></td>
<td>O64—N63</td>
<td>1.428 (5)</td>
<td></td>
</tr>
<tr>
<td>N13—C1</td>
<td>1.288 (6)</td>
<td></td>
<td>N63—C51</td>
<td>1.265 (6)</td>
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<tr>
<td>O18—C8</td>
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<td>O68—C58</td>
<td>1.372 (6)</td>
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<tr>
<td>O18—C19</td>
<td>1.420 (7)</td>
<td></td>
<td>O68—C69</td>
<td>1.423 (7)</td>
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<tr>
<td>C4B—C10B</td>
<td>1.344 (6)</td>
<td></td>
<td>C54B—C60B</td>
<td>1.346 (6)</td>
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<tr>
<td>O14—N13—C1</td>
<td>113.0 (4)</td>
<td></td>
<td>O64—N63—C51</td>
<td>114.3 (4)</td>
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</tr>
</tbody>
</table>

Table 2

Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>Bond/Geometry</th>
<th>Distance (Å)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>O14—H14—N63</td>
<td>0.96</td>
<td>1.92</td>
</tr>
<tr>
<td>O64—H64—N13</td>
<td>0.84</td>
<td>2.06</td>
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</table>

Due to the absence of significant anomalous scatterers, the absolute configuration could not be determined *ab initio*. The chirality was chosen in agreement with the well known stereochemistry of atom C3. For 3152 of the 3787 unique reflections reported above, the intensities of the Friedel-related reflections were measured. Friedel opposites were merged before refinement. H atoms bonded to C atoms were introduced in calculated positions, and were riding on their carrier atoms during refinement. The oxime H atom could be located in a difference Fourier map. To improve the data/parameter ratio, the oxime H was not refined, but was included in the model in riding mode on the oxime O atom.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO (Otwinski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2002); software used to prepare material for publication: PLATON.

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References


