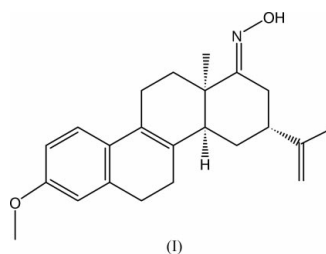


**(1*E*,3*S*,4*aR*,12*aR*)-3-Isopropenyl-8-methoxy-3,4,4*a*,5,6,11,12,12*a*-octahydro-1(2*H*)-chrysenone oxime****Huub Kooijman\* and Anthony L. Spek**Bijvoet Center for Biomolecular Research,  
Department of Crystal and Structural Chemistry,  
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Utrecht, The NetherlandsCorrespondence e-mail:  
h.kooijman@chem.uu.nl**Key indicators**Single-crystal X-ray study  
*T* = 150 K  
Mean  $\sigma(\text{C}-\text{C})$  = 0.007 Å  
*R* factor = 0.057  
*wR* factor = 0.156  
Data-to-parameter ratio = 8.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{23}\text{H}_{29}\text{NO}_2$ , 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  $R^2_2[6]$ .

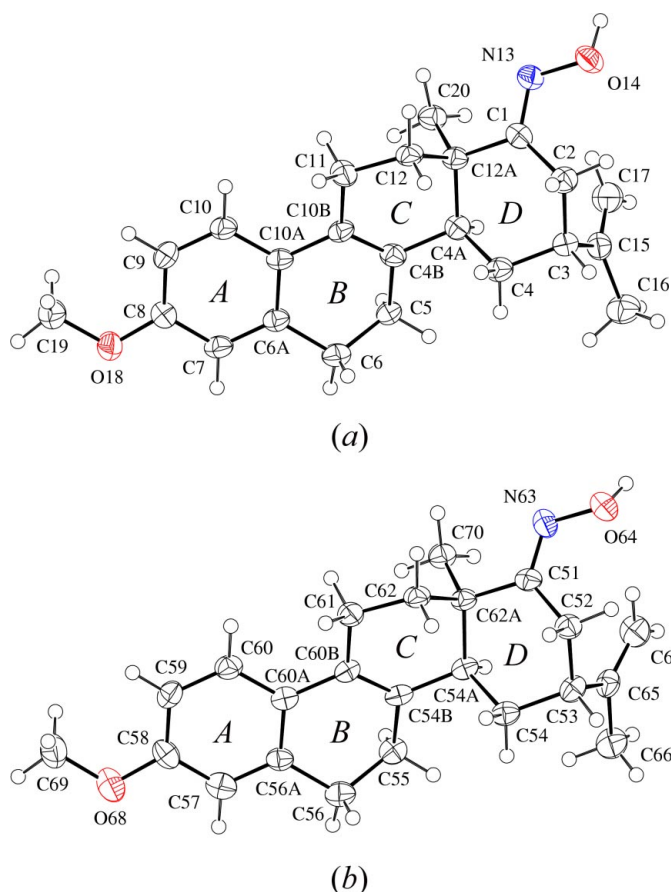
Received 20 December 2002  
Accepted 23 December 2002  
Online 10 January 2003**Comment**

The crystal structure of the title compound, (I), was determined to confirm, beyond any doubt, the stereochemistry around ring junction C4*a*–C12*a* of this (unnatural) D-homosteroid 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 C4*a* and C12*a* 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  $172^\circ$  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  $-22.7(7)^\circ$  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 ( $160^\circ$ ) and C51–N63–O64–H64 ( $140^\circ$ ).

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 C10*A*–C10*B* [relevant asymmetry parameters (Duax & Norton, 1975) are

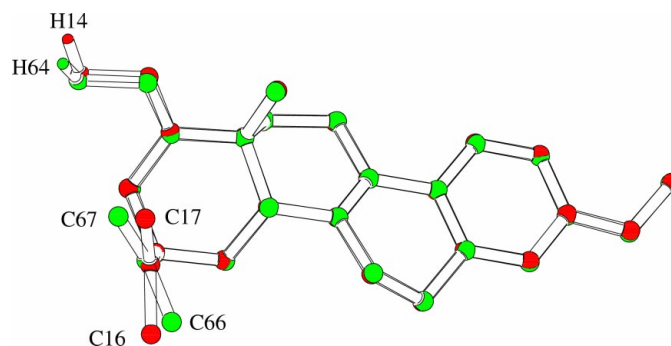

**Figure 1**

Displacement ellipsoid plots of the title compound drawn at the 50% probability level (Spek, 2002). H atoms are drawn with an arbitrary radius.

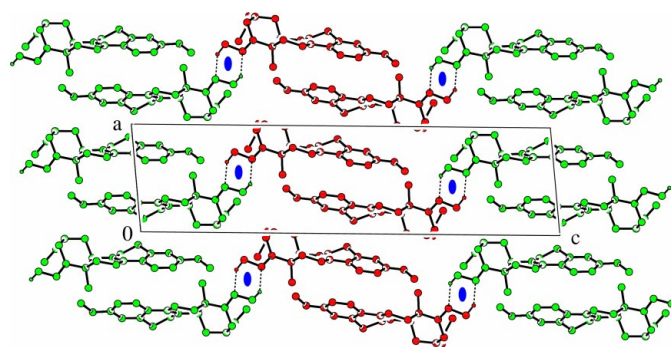
$\Delta C_2[C10A-C10B] = 5.1(7)^\circ$  for molecule 1 and  $\Delta C_2[C60A-C60B] = 1.7(7)^\circ$  for molecule 2; Cremer & Pople puckering parameters  $\theta$  and  $\varphi$  (Cremer & Pople, 1975) are  $65.4(7)$  and  $94.6(8)^\circ$  for molecule 1, and  $66.4(7)$  and  $91.6(7)^\circ$  for molecule 2; ideal values are  $67.5$  and  $90^\circ$ , respectively]. Ring C is in a half-chair conformation, with the local twofold axis running through the midpoint of the bond C4B–C10B [relevant asymmetry parameters are  $\Delta C_2[C4B-C10B] = 4.9(7)^\circ$  for molecule 1 and  $\Delta C_2[C60A-C60B] = 4.5(6)^\circ$  for molecule 2; Cremer & Pople puckering parameters  $\theta$  and  $\varphi$  are  $51.8(6)$  and  $276.9(7)^\circ$  for molecule 1, and  $50.5(6)$  and  $276.7(7)^\circ$  for molecule 2; ideal values are  $50.8$  and  $270^\circ$ , respectively]. Ring D adopts a somewhat distorted chair conformation [all relevant asymmetry parameters are in the range  $2.8(5)$ – $23.4(6)^\circ$  for molecule 1 and  $4.2(4)$ – $23.4(5)^\circ$  for molecule 2, respectively; the Cremer & Pople parameter  $\theta$  is  $157.1(6)^\circ$  for molecule 1 and  $160.5(5)^\circ$  for molecule 2, the ideal value is  $180^\circ$ .]

The methoxy C–O bond makes an angle of  $3.5(3)^\circ$  with ring A in molecule 1 and an angle of  $6.2(3)^\circ$  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  $R_2^2[6]$ .


**Figure 2**

Fit of molecule 1 (red) on molecule 2 (green). H atoms, except the oxime H atom, have been omitted for clarity.


**Figure 3**

Crystal packing, projected down  $b$ , showing the hydrogen-bonded dimer (molecule 1 is indicated in red and molecule 2 in green). The positions of local twofold axes are indicated with blue ellipses. H atoms not involved in hydrogen bonding have been omitted for clarity.

## 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,  $P2_1$   
 $a = 8.137(2) \text{ \AA}$   
 $b = 7.519(2) \text{ \AA}$   
 $c = 31.439(8) \text{ \AA}$   
 $\beta = 95.535(8)^\circ$   
 $V = 1914.5(8) \text{ \AA}^3$   
 $Z = 4$

$D_x = 1.219 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 212 reflections  
 $\theta = 2.0$ – $25.0^\circ$   
 $\mu = 0.08 \text{ mm}^{-1}$   
 $T = 150 \text{ K}$   
 Plate, colourless  
 $0.30 \times 0.18 \times 0.02 \text{ mm}$

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  scans and  $\omega$  scans with  $\kappa$  offsets  
 37857 measured reflections  
 3787 independent reflections  
 2770 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.096$   
 $\theta_{\text{max}} = 25.4^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -9 \rightarrow 9$   
 $l = -37 \rightarrow 37$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.156$   
 $S = 1.07$   
 3787 reflections  
 469 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.92P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

O14—N13	1.419 (5)	O64—N63	1.428 (5)
N13—C1	1.288 (6)	N63—C51	1.265 (6)
O18—C8	1.373 (5)	O68—C58	1.372 (6)
O18—C19	1.420 (7)	O68—C69	1.423 (7)
C4B—C10B	1.344 (6)	C54B—C60B	1.346 (6)
O14—N13—C1	113.0 (4)	O64—N63—C51	114.3 (4)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O14—H14...N63	0.96	1.92	2.772 (5)	147
O64—H64...N13	0.84	2.06	2.773 (5)	142

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* (Otwinowski & 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*.

We thank Professor Dr Aede de Groot and Ir Floor Sarabèr of the Laboratory of Organic Chemistry, Wageningen University, for the provision of the crystals. This work was supported in part (ALS) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO).

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