Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

Huub Kooijman and Anthony L. Spek

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Huub Kooijman* and Anthony L. Spek

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Correspondence e-mail: h.kooijman@chem.uu.nl

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
R factor = 0.057
wR factor = 0.156
Data-to-parameter ratio = 8.1

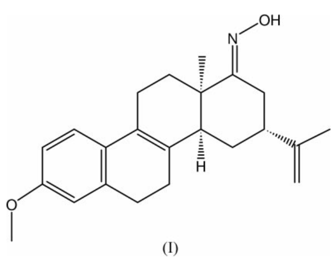
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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 $R^2_2[6]$.

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 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.



(I)

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

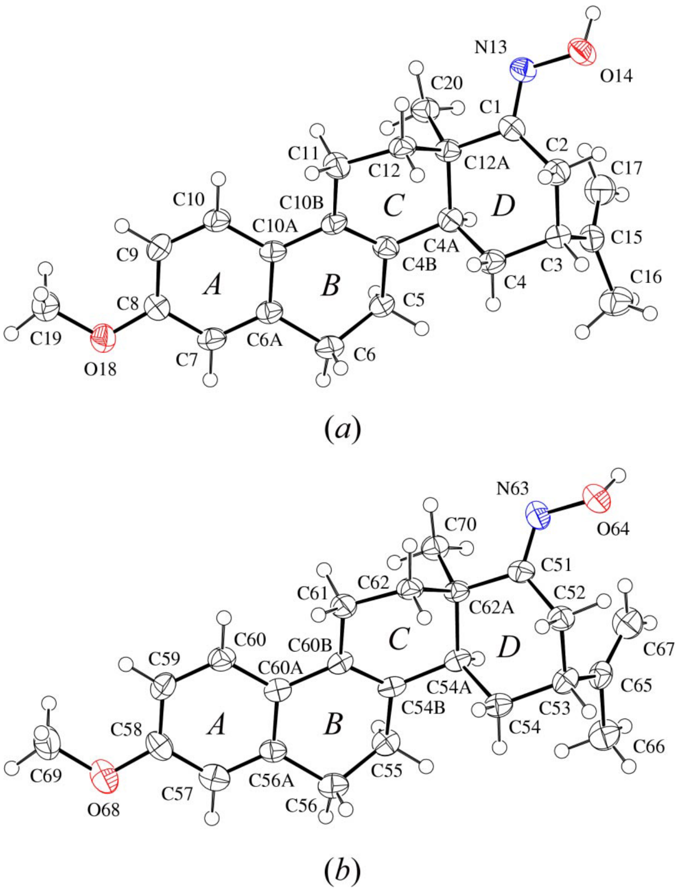


Figure 1

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

ΔC_2[C10*A*—C10*B*] = 5.1 (7)° for molecule 1 and ΔC_2[C60*A*—C60*B*] = 1.7 (7)° for molecule 2; Cremer & Pople puckering parameters θ and φ (Cremer & Pople, 1975) are 65.4 (7) and 94.6 (8)° for molecule 1, and 66.4 (7) and 91.6 (7)° for molecule 2; ideal values are 67.5 and 90°, respectively]. Ring *C* is in a half-chair conformation, with the local twofold axis running through the midpoint of the bond C4*B*—C10*B* [relevant asymmetry parameters are ΔC_2[C4*B*—C10*B*] = 4.9 (7)° for molecule 1 and ΔC_2[C60*A*—C60*B*] = 4.5 (6)° for molecule 2; Cremer & Pople puckering parameters θ and φ are 51.8 (6) and 276.9 (7)° for molecule 1, and 50.5 (6) and 276.7 (7)° for molecule 2; ideal values are 50.8 and 270°, respectively]. Ring *D* adopts a somewhat distorted chair conformation [all relevant asymmetry parameters are in the range 2.8 (5)–23.4 (6)° for molecule 1 and 4.2 (4)–23.4 (5)° for molecule 2, respectively; the Cremer & Pople parameter θ is 157.1 (6)° for molecule 1 and 160.5 (5)° for molecule 2, the ideal value is 180°.]

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

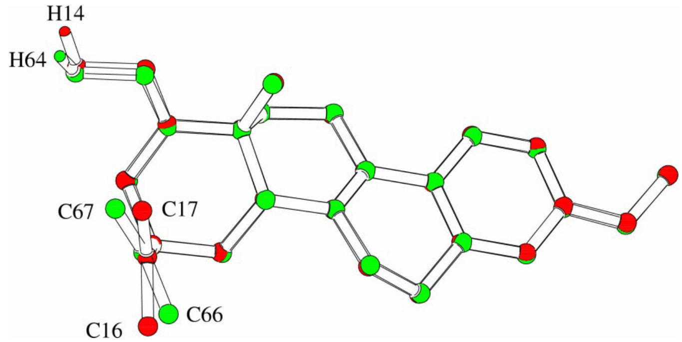


Figure 2

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

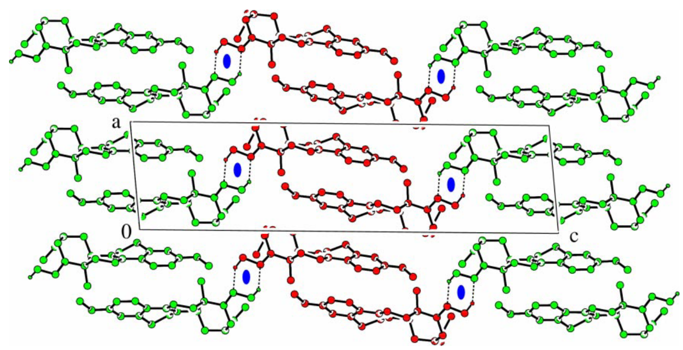


Figure 3

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

$C_{23}H_{29}NO_2$	D_x = 1.219 Mg m^{-3}
M_r = 351.47	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 212 reflections
a = 8.137 (2) Å	θ = 2.0–25.0°
b = 7.519 (2) Å	μ = 0.08 mm^{-1}
c = 31.439 (8) Å	T = 150 K
β = 95.535 (8)°	Plate, colourless
V = 1914.5 (8) Å^3	0.30 × 0.18 × 0.02 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	R_{int} = 0.096
φ scans and ω scans with κ offsets	θ_{max} = 25.4°
37857 measured reflections	$h = -9 \rightarrow 9$
3787 independent reflections	$k = -9 \rightarrow 9$
2770 reflections with $I > 2\sigma(I)$	$l = -37 \rightarrow 37$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 0.92P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.057	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.156	$(\Delta/\sigma)_{max} < 0.001$
S = 1.07	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
3787 reflections	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
469 parameters	
H-atom parameters constrained	

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)
C4*B*—C10*B*	1.344 (6)	C54*B*—C60*B*	1.346 (6)
O14—N13—C1	113.0 (4)	O64—N63—C51	114.3 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (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).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Drach, F., Charnikhova, T., Sarabèr, F. C. E., Jansen, B. J. M. & de Groot, Ae. (2003). *J. Org. Chem.* In preparation.
Duax, W. L. & Norton, D. A. (1975). In *Atlas of Steroid Structures*. New York: Plenum.
Mackay, A. L. (1984). *Acta Cryst.* A**40**, 165–166.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2002). *PLATON*. Utrecht University, The Netherlands. Internet: http://www.Cryst.Chem.uu.nl/PLATON/.