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Methyl (±)-(1α,2β,8α,9α,10β)-2-chloro-4-aza-3-oxatetracyclo[8.4.0.0^{2,9}.0^{4,8}]-tetradecane-9-carboxylate oxalic acid monohydrate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.085
Data-to-parameter ratio = 14.4

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

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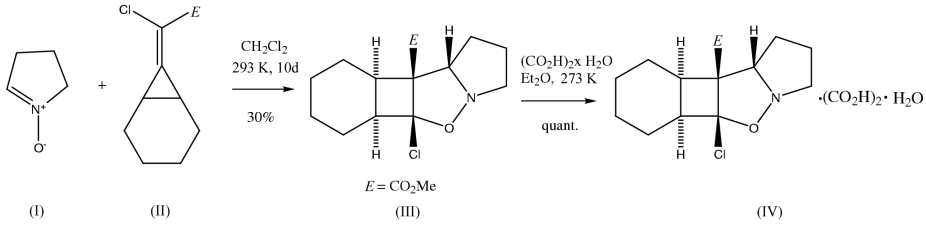
In the crystal structure of the title compound, $C_{14}H_{20}ClNO_3 \cdot C_2H_2O_4 \cdot H_2O$, there are infinitive flat ribbons, parallel to the [0$\bar{1}$1] direction. Molecules in the ribbons are linked together by an extensive network of hydrogen bonds.

Comment

The tetracyclic title compound, (III), was obtained upon an attempted 1,3-dipolar cycloaddition of 3,4-dihydro-2*H*-pyrrole 1-oxide, (I), to methyl 2-chloro-2-(bicyclo[4.1.0]hept-7-ylidene)acetate, (II) (Brandi *et al.*, 2003), during systematic studies of 1,3-dipolar cycloadditions to substituted methylenecyclopropanes (Goti *et al.*, 1996; de Meijere, Kozhushkov & Khlebnikov, 2000; de Meijere & Kozhushkov, 2000). The relative configuration of (III) was established by an X-ray crystal structure analysis of its solvate with oxalic acid and water (1:1:1) (IV).



Chlorine and methoxycarbonyl substituents at the two bridgehead atoms of the tetracyclic system are *cis*-oriented with respect to each other (Fig. 1).

All four rings are substantially non-planar. The four-membered ring is folded around the C6···C12 line by 24.7 (1)°. The cyclohexane ring has a slightly flattened chair conformation, while the five-membered heterocycles adopt conformations of O1-envelope and twisted half-chair. The solvent molecule of oxalic acid is also not entirely planar, with a torsion angle O5—C15—C16—O6 of −7.5 (2)°.

The most remarkable feature is the packing of the molecules in the crystal. The molecules of oxalic acid and water form flat ribbons; the tetracyclic molecules are attached to both edges of the ribbons by very strong hydrogen bonds between oxalic acid and the tetradecane N atom (Fig. 2). The molecules of oxalic acid and water are linked together by a network of O—H···O hydrogen bonds. Tetracyclic molecules in the same ribbon are also connected by C6—H6···O3 [C···O = 3.290 (1) Å] interactions. In the crystal structure, these ribbons are parallel to the [0$\bar{1}$1] direction and show a number of weak C—H···O interactions.

Experimental

Crystals of (IV) were obtained by slow evaporation from a solution in Et_2O at 277 K.

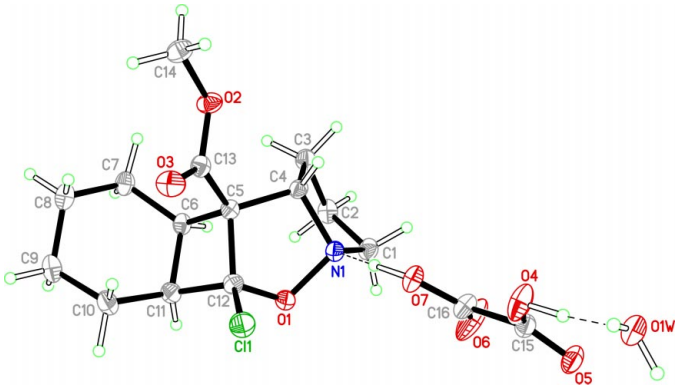


Figure 1
View of the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level.

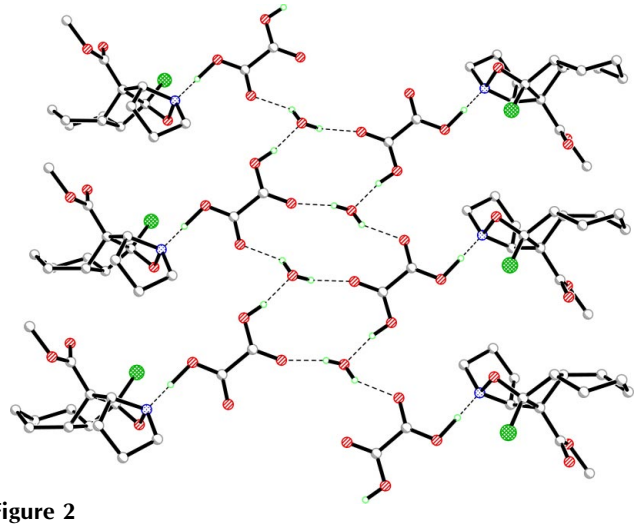


Figure 2
Arrangement of the molecules in hydrogen-bonded ribbons.

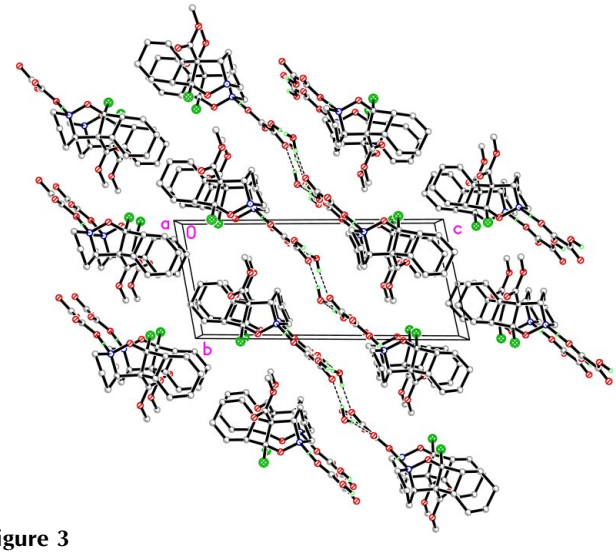


Figure 3
Packing diagram, viewed along the *a* axis.

Crystal data

$C_{14}H_{20}ClNO_3\cdot C_2H_2O_4\cdot H_2O$	$Z = 2$
$M_r = 393.81$	$D_x = 1.428$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 6.6133$ (2) Å	Cell parameters from 999 reflections
$b = 8.0737$ (2) Å	$\theta = 10.3$–$20.8°$
$c = 17.8848$ (5) Å	$\mu = 0.25$ mm^{-1}
$\alpha = 77.746$ (1)°	$T = 120$ (2) K
$\beta = 83.211$ (1)°	Block, colourless
$\gamma = 80.169$ (1)°	0.42 × 0.35 × 0.17 mm
$V = 916.14$ (4) Å^3	

Data collection

Bruker SMART-CCD 1K diffractometer	3835 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.026$
Absorption correction: none	$\theta_{max} = 29.0°$
11202 measured reflections	$h = -8 \rightarrow 9$
4763 independent reflections	$k = -10 \rightarrow 10$
	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.3P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.085$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.28$ e Å^{-3}
4763 reflections	
331 parameters	
All H-atom parameters refined	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7O···N1	1.22 (2)	1.34 (2)	2.5690 (14)	179 (2)
O4—H4O···O1W	0.94 (3)	1.63 (3)	2.5589 (14)	169 (2)
O1W—H1W···O5^{i}	0.86 (2)	1.94 (2)	2.7917 (14)	168 (2)
O1W—H2W···O6^{ii}	0.83 (2)	1.95 (2)	2.6886 (15)	147 (2)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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