Isopropylideneamino-12*H*-dibenzo[*d,g*]-[1,3]dioxocine-6-carboxylate

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Key indicators

Single-crystal X-ray study
$T = 298$ K
Mean σ(C–C) = 0.006 Å
R factor = 0.046
wR factor = 0.096
Data-to-parameter ratio = 8.3

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

The structure of the title compound, $C_{18}H_{17}NO_4$, an inhibitor of acetolactate synthase (ALS) and a promising candidate for an effective wheat herbicide, features a dioxaoctane ring fused with two benzene rings; the conformation of the eight-membered ring has approximate local mirror symmetry, but is not close to any of the canonical shapes of eight-membered rings. The dihedral angle formed by the planes of the benzene rings is 74.6 (1)°; only one of the endocyclic atoms, *viz.* the one carrying the azavinylidenecarboxylate substituent, shows substantial displacements [1.147 (6) and 1.234 (6) Å] from both of the benzene ring planes.

Comment

The title compound, (I), was synthesized in 2002, and showed excellent herbicidal activity at 100 g ha^{-1} (Li *et al.*, 2002). As an acetolactate synthase (ALS) inhibitor, it represents a promising candidate for use as a wheat herbicide (Li *et al.*, 2003). It is noteworthy that this compound is completely different from all commercially available ALS-inhibiting herbicides such as sulfonylureas, sulfonamides, imidazolinones and pyrimidinyloxybenzoic acids (Tomlin, 2003). A knowledge of the precise three-dimensional structure of (I) is important for quantitative structure–activity relationship (three-dimen-sional–QSAR) studies (Li, Song *et al.*, 2005; Li, Lan *et al.*, 2005) and may provide some clues for understanding its herbicidal properties.

(I)
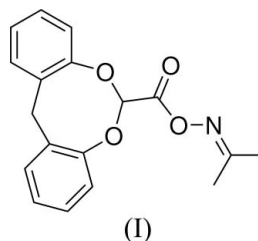
The structure of (I) (Fig. 1) features a dioxaoctane ring (O1/C13/C8/C7/C6/C1/ O2/C14) fused with benzene rings C1–C6 (*A*) and C8–C13 (*B*). The conformation of the eight-membered ring has an approximate mirror plane passing through atoms C7 and C14. Nevertheless, distribution of the endocyclic torsion angles (see Table 1) does not match any of the patterns typical for one of the canonical shapes known for eight-membered rings (Evans & Boeyens, 1988). Rings *A* and *B* form a dihedral angle of 74.6 (1)°; atoms O2 and O1 lie close to the planes of rings *A* and *B*, respectively [displacements 0.072 (5) and 0.006 (5) Å]; atom C7 is almost coplanar with both of the benzene rings [displacements from rings *A* and *B*
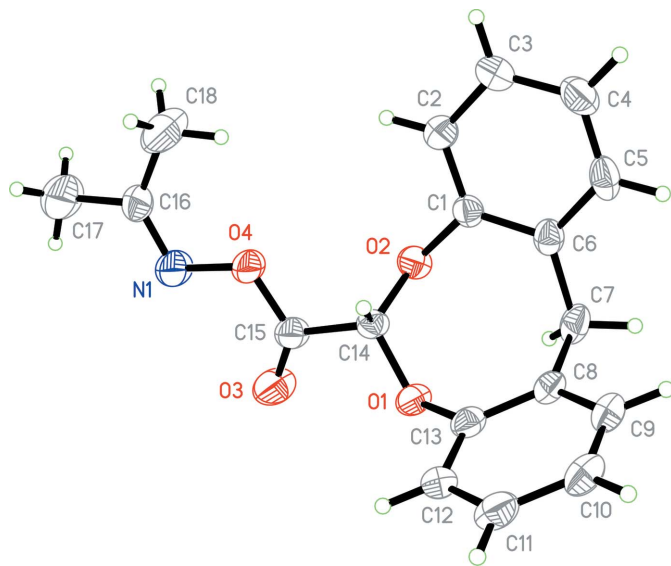
Figure 1
View of the molecular structure, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as circles of arbitrary size.

are 0.087 (6) and 0.049 (6) Å, respectively], whereas atom C14, carrying the azavinylidenecarboxylate substituent, is considerably displaced from the planes of both benzene rings [by 1.147 (6) and 1.234 (7) Å from *A* and *B*, respectively].

Experimental

According to the published procedure of Li *et al.* (2003), 2*H*-dibenzo-[*d*,*g*][1,3]dioxocin-6-carbonyl chloride (2.7 g, 10 mmol) was dissolved in dichloromethane (10 ml) and added dropwise with stirring at room temperature to a solution of acetoxime (0.8 g, 11 mmol) and triethylamine (1.1 g, 11 mmol) in 30 ml of dichloromethane. The mixture was stirred for an hour and then washed with water (50 ml). After evaporation of the solvent, 2.1 g of the target compound was obtained (yield 70%); 1.0 g of the product was then recrystallized from acetone and colorless prism-shaped crystals were collected (m.p. 416–418 K). Elemental analysis calculated for $C_{18}H_{17}NO_4$: C 69.44, H 5.50, N 4.50%; found: C 69.34, H 5.42, N 4.46%.

Crystal data

$C_{18}H_{17}NO_4$	$Z = 16$
$M_r = 311.33$	$D_x = 1.293$ Mg m^{-3}
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
$a = 14.542$ (4) Å	$\mu = 0.09$ mm^{-1}
$b = 40.468$ (11) Å	$T = 298$ (2) K
$c = 10.874$ (3) Å	Prism, colorless
$V = 6399$ (3) Å^3	$0.28 \times 0.24 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	9108 measured reflections
φ and ω scans	1743 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1046 reflections with $I > 2\sigma(I)$
$T_{min} = 0.977$, $T_{max} = 1.000$	$R_{int} = 0.070$
	$\theta_{max} = 26.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.454P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.11$ e Å^{-3}
1743 reflections	$\Delta\rho_{min} = -0.14$ e Å^{-3}
210 parameters	
H-atom parameters constrained	

Table 1
Selected torsion angles (°).

C14—O2—C1—C6	81.8 (4)	C7—C8—C13—O1	3.3 (5)
O2—C1—C6—C7	−6.6 (5)	C14—O1—C13—C8	−80.6 (4)
C1—C6—C7—C8	−81.0 (4)	C13—O1—C14—O2	95.9 (3)
C6—C7—C8—C13	84.3 (4)	C1—O2—C14—O1	−95.7 (3)

The H atoms were placed in calculated positions (C—H = 0.93–0.98 Å) and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}$(carrier atom) (1.5U_{eq} for methyl H atoms). In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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