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2-Fluoro-*N*-[7-fluoro-3,4-dihydro-2-methyl-3-oxo-4-(prop-2-ynyl)-2*H*-1,4-benzoxazin-6-yl]benzamide

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.054
wR factor = 0.137
Data-to-parameter ratio = 12.5

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

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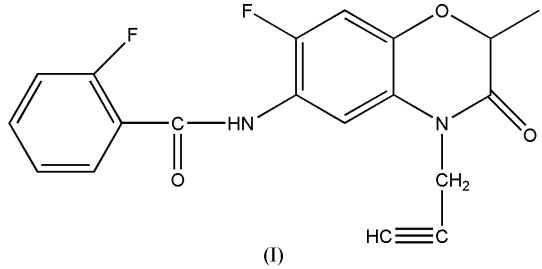
The title compound, $C_{19}H_{14}F_2N_2O_3$, known as a protox inhibitor, was synthesized from 7-fluoro-3,4-dihydro-2-methylbenzoxazinone. The bond lengths and angles are unexceptional and the heterocyclic ring adopts a screw-boat conformation. Molecules are linked into two-dimensional layers by intermolecular C—H···O hydrogen bonds, with an H···O distance of 2.22 Å.

Comment

The title compound, (I), is a potent inhibitor of the plant enzyme protoporphyrinogen oxidase (protox; Birchfield & Casida, 1997). It exhibits good control for broadleaf weeds (Chamilleri *et al.*, 1988). The molecular structure is illustrated in Fig. 1.



(I)

The conformation of the six-membered heterocyclic ring is close to screw-boat, with atoms C1 and C2 out of the plane of the remaining four atoms by 0.361 (5) and 0.820 (4) Å, respectively. The structure is very similar to that of a related benzoxazinone (Cao *et al.*, 2004). The bond lengths and angles also agree well with those in a related compound (Karolak-Wojciechowska *et al.*, 2001), although the latter adopts a twist-chair conformation. In the crystal structure, screw-related molecules are linked by intermolecular C—H···O hydrogen bonds, with an H···O distance of 2.22 Å, forming layers parallel to the *bc* plane (Fig. 2).

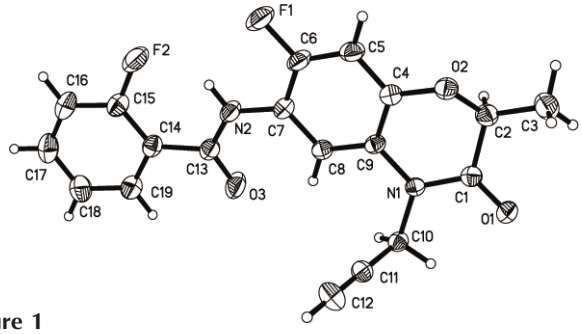


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level.

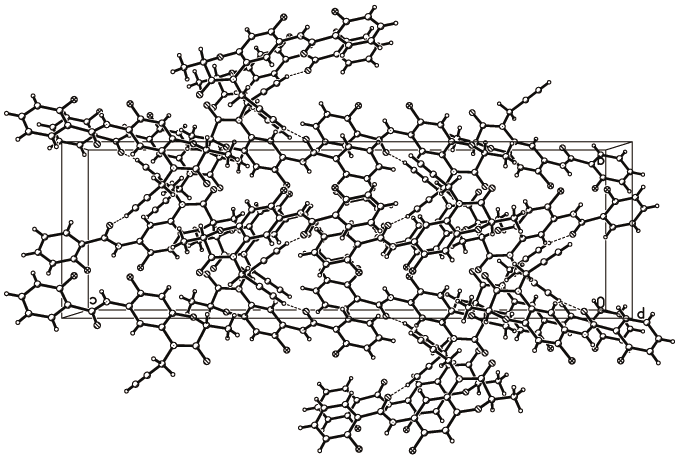


Figure 2
The crystal structure of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

Experimental

7-Fluoro-3,4-dihydro-2-methylbenzoxazinone, (II), was prepared according to a previously published method (Terni *et al.*, 1988). (II) (100 mmol) was then reacted with 3-bromoprop-1-yne (100 mmol) in dimethylformamide (50 ml) at room temperature for about 4 h to form 7-fluoro-3,4-dihydro-2-methyl-4-(prop-2-ynyl)benzoxazinone. After nitration with nitric acid (20 ml, 37%)/sulfuric acid (50 ml, 98%) at room temperature for about 2 h, it was reduced with hydrogen and 10% Pd–C (2 g). This yielded 6-amino-7-fluoro-3,4-dihydro-2-methyl-4-(prop-2-ynyl)benzoxazinone, which was then treated with 2-fluorobenzoyl chloride (100 mmol) in dimethylformamide (50 ml) at room temperature for about 2 h. The reaction mixture was poured into ice water, and the precipitated solid was filtered off, washed with water and then dried. The crude product was purified by column chromatography (silica gel, petroleum ether–acetone 2:1) to yield the title compound, (I) (m.p. 502–503 K). ^{1}H NMR ($CDCl_3$, p.p.m): 1.66 (3H, *d*), 2.39 (1H, *m*), 4.82 (2H, *s*), 4.98 (1H, *m*), 6.85 (1H, *s*), 7.24 (1H, *d*), 7.32 (1H, *m*), 7.42 (1H, *d*), 7.74 (1H, *m*), 7.81 (1H, *d*), 8.10 (1H, *s*). Compound (I) (20 mg) was dissolved in ethyl acetate (20 ml), and the solution was kept at room temperature for about 10 d. Natural evaporation afforded colorless single crystals of (I) suitable for X-ray analysis.

Crystal data

$C_{19}H_{14}F_2N_2O_3$
M_r = 356.32
Orthorhombic, *Pbca*
a = 10.904 (4) Å
b = 8.670 (3) Å
c = 35.271 (13) Å
V = 3334 (2) Å^3
Z = 8
D_x = 1.419 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 783 reflections
θ = 3.1–21.8°
μ = 0.11 mm^{-1}
T = 293 (2) K
Block, colorless
0.34 × 0.30 × 0.22 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.937, T_{max} = 0.976
14 457 measured reflections
2942 independent reflections
2003 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 25.0°
$h = -12 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = -41 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.137
S = 1.11
2942 reflections
236 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 2.5094P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O3^{i}	0.93	2.22	3.104 (4)	159

Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, z$.

H atoms were positioned geometrically, with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and refined in the riding model approximation, with U_{iso}(H) = 1.2U_{eq}(carrier atom).

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

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