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2-(3-Chlorophenyl)-3,4-dihydrobenzo[*f*][1,4]-oxazepin-5(2*H*)-one

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Keywords: crystal structure; mannich reaction; tankyrase inhibitor; nanomolar activity.

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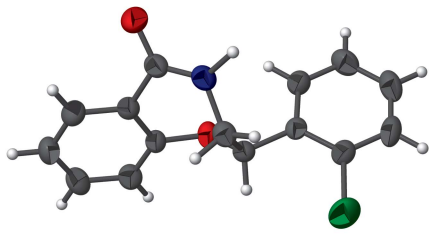
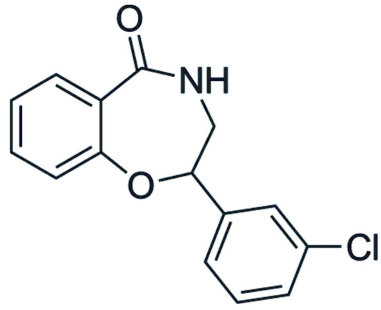
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{15}H_{12}ClNO_2$, the dihedral angle between the two benzene rings is 73.45 (11)°. The central seven-membered ring is in a psuedo-boat conformation. In the crystal, pairs of molecules are linked by N—H···O hydrogen bonds, forming inversion dimers.

3D view



Chemical scheme



Structure description

The development of benzo[*f*][1,4]oxazepinone derivatives for medical applications is a research topic of increasing interest because of their easy preparation, good stability and high nanomolar activity (Li *et al.*, 2016). It is believed that the derivatives can be modified structurally by using different aldehydes and ketones (Krapcho & Turk, 1966). We report here the synthesis and the structure of the title compoun whose molecular structure is shown in Fig. 1. The dihedral angle between the two benzene rings (C2–C7 and C10–C15) is 73.45 (11)°. The central seven-membered ring is in a psuedo-boat conformation with C9 forming the prow and C2/C7 forming the stern. In the crystal, pairs of molecules are linked by N—H···O hydrogen bonds, forming inversion dimers (Table 1, Fig. 2).

Synthesis and crystallization

A 25 ml round-bottom flask was charged with 3-chlorobenzaldehyde (0.5 mmol), phenylamine (0.75 mmol), I_2 (0.15 mmol) and 1-(2-hydroxyphenyl)ethan-1-one (0.6 mmol) and methanol (10 mL) and stirred at 318 K. After the reaction was complete (as determined by TLC), the solvent was evaporated and 10 mL of saturated $Na_2S_2O_3$ was added. The solution was extracted with CH_2Cl_2 (three × 10 mL). The organic layers

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	1.15 (2)	1.78 (2)	2.849 (2)	153.9 (16)

Symmetry code: (i) $-x+1, -y+2, -z$.

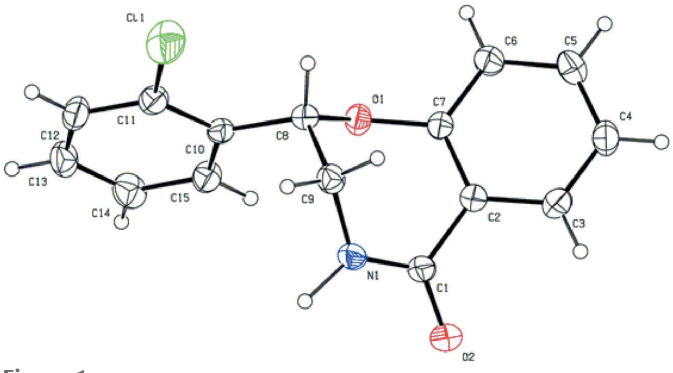


Figure 1
Molecular structure of the title compound with displacement ellipsoids drawn at 50% probability level.

were washed with saturated NaCl solution and then with ice–water. The solution was dried over Na_2SO_4 and concentrated under vacuum to a crude solid. The crude solid (6 mmol) and NaN_3 (500 mg) were added to a round-bottom flask with 9 mL of CH_3COOH and stirred at 273 K. 3 mL of concentrated H_2SO_4 was then added and stirred at 318 K. After the reaction was complete (as determined by TLC), the solvent was neutralized with $NaHCO_3$. The solution was extracted with ethyl acetate. This was chromatographed on flash silica gel, eluting with 75% cyclohexane and 25% ethyl acetate and concentrated to a solid, giving 1.0 g of product (69% yield), m.p. 352.2–354.3 K. Crystals for X-ray crystallography were grown by slow evaporation of a solution of the title compound in methanol and water.

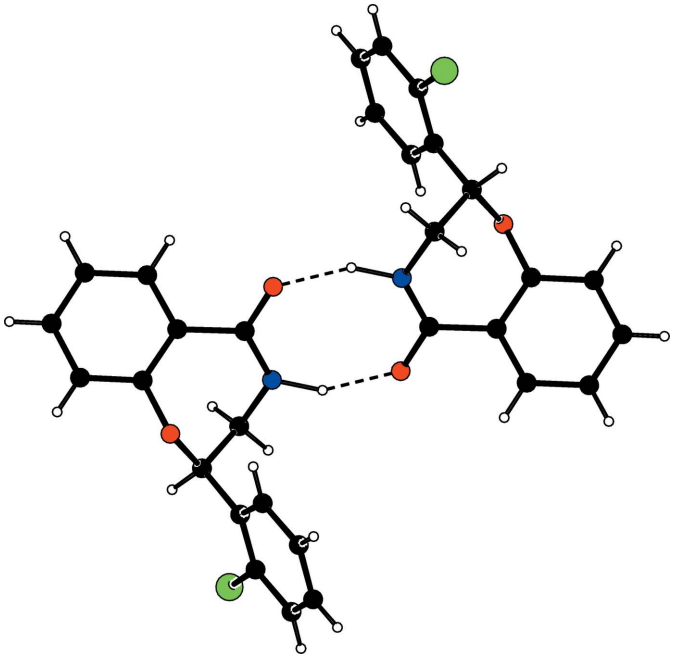


Figure 2
An inversion dimer of the title compound. Hydrogen bonds are shown as dashed lines

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{12}ClNO_2$
M_r	273.71
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, b, c (Å)	7.2162 (15), 8.0068 (14), 11.650 (3)
α, β, γ (°)	80.123 (17), 84.570 (18), 88.084 (15)
V (Å^3)	660.0 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.29
Crystal size (mm)	0.4 × 0.35 × 0.3
Data collection	
Diffractometer	Agilent Xcalibur, Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.896, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4864, 2678, 2002
R_{int}	0.016
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.118, 1.03
No. of reflections	2678
No. of parameters	176
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.32

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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References

Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Krapcho, J. & Turk, C. F. (1966). *J. Med. Chem.* **9**, 191–195.
Li, F., Mu, M., Yang, N., Zhong, L., Hu, R., Li, J., Bai, L., Shi, J. & Zhang, M. (2016). *Chin. J. Org. Chem.* **36**, 1419–1425.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2018). **3**, x180587 [https://doi.org/10.1107/S2414314618005874]

2-(3-Chlorophenyl)-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one

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Crystal data

$C_{15}H_{12}ClNO_2$
M_r = 273.71
Triclinic, $P\overline{1}$
a = 7.2162 (15) Å
b = 8.0068 (14) Å
c = 11.650 (3) Å
α = 80.123 (17)°
β = 84.570 (18)°
γ = 88.084 (15)°
V = 660.0 (2) Å^3
Z = 2
$F(000)$ = 284
D_x = 1.377 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1590 reflections
θ = 3.5–27.6°
μ = 0.29 mm^{-1}
T = 293 K
, colorless
0.4 × 0.35 × 0.3 mm

Data collection

Agilent Xcalibur, Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0874 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.896, T_{max} = 1.000
4864 measured reflections
2678 independent reflections
2002 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 26.4°, θ_{min} = 3.2°
h = −9→8
k = −7→9
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.118
S = 1.03
2678 reflections
176 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.2184P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.11743 (9)	0.53184 (10)	0.26327 (7)	0.0761 (3)
O1	0.52072 (19)	0.63356 (16)	0.32657 (12)	0.0408 (4)
O2	0.3115 (2)	1.0113 (2)	0.10901 (13)	0.0595 (5)
N1	0.5962 (3)	0.8897 (2)	0.13595 (14)	0.0419 (4)
H1	0.668 (3)	0.905 (2)	0.0428 (18)	0.045 (6)*
C1	0.4288 (3)	0.9404 (3)	0.17520 (17)	0.0425 (5)
C2	0.3808 (3)	0.9133 (3)	0.30392 (17)	0.0390 (5)
C3	0.2785 (3)	1.0356 (3)	0.3555 (2)	0.0492 (5)
H3	0.2416	1.1353	0.3091	0.059*
C4	0.2312 (3)	1.0108 (3)	0.4745 (2)	0.0507 (6)
H4	0.1646	1.0942	0.5083	0.061*
C5	0.2823 (3)	0.8631 (3)	0.54278 (19)	0.0509 (6)
H5	0.2488	0.8460	0.6229	0.061*
C6	0.3830 (3)	0.7394 (3)	0.49404 (18)	0.0450 (5)
H6	0.4171	0.6392	0.5410	0.054*
C7	0.4330 (3)	0.7651 (2)	0.37516 (17)	0.0354 (4)
C8	0.7130 (3)	0.6560 (2)	0.28206 (16)	0.0362 (4)
H8	0.7901	0.6389	0.3481	0.043*
C9	0.7429 (3)	0.8348 (2)	0.21354 (17)	0.0406 (5)
H9A	0.7467	0.9132	0.2681	0.049*
H9B	0.8622	0.8383	0.1673	0.049*
C10	0.7614 (3)	0.5194 (2)	0.20902 (16)	0.0342 (4)
C11	0.9417 (3)	0.4563 (3)	0.19450 (18)	0.0426 (5)
C12	0.9891 (3)	0.3338 (3)	0.1260 (2)	0.0522 (6)
H12	1.1112	0.2935	0.1179	0.063*
C13	0.8542 (4)	0.2723 (3)	0.0700 (2)	0.0554 (6)
H13	0.8845	0.1900	0.0236	0.066*
C14	0.6739 (4)	0.3327 (3)	0.0825 (2)	0.0551 (6)
H14	0.5826	0.2910	0.0443	0.066*
C15	0.6279 (3)	0.4545 (3)	0.15140 (19)	0.0445 (5)
H15	0.5054	0.4939	0.1593	0.053*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0405 (4)	0.0984 (6)	0.0982 (6)	0.0052 (3)	−0.0205 (3)	−0.0348 (4)
O1	0.0441 (8)	0.0336 (7)	0.0422 (8)	0.0024 (6)	0.0056 (6)	−0.0054 (6)
O2	0.0676 (11)	0.0680 (11)	0.0408 (9)	0.0247 (9)	−0.0110 (8)	−0.0048 (8)
N1	0.0568 (11)	0.0367 (9)	0.0304 (9)	0.0036 (8)	−0.0024 (8)	−0.0020 (7)
C1	0.0573 (14)	0.0360 (11)	0.0341 (10)	0.0076 (10)	−0.0080 (10)	−0.0054 (9)
C2	0.0426 (11)	0.0397 (11)	0.0352 (10)	0.0050 (9)	−0.0057 (9)	−0.0074 (8)
C3	0.0537 (14)	0.0438 (12)	0.0508 (13)	0.0123 (10)	−0.0111 (11)	−0.0091 (10)
C4	0.0486 (13)	0.0533 (14)	0.0530 (13)	0.0093 (11)	−0.0001 (11)	−0.0210 (11)
C5	0.0540 (14)	0.0579 (14)	0.0405 (12)	−0.0033 (11)	0.0080 (11)	−0.0133 (11)
C6	0.0493 (13)	0.0441 (12)	0.0389 (11)	0.0008 (10)	0.0018 (10)	−0.0032 (9)

C7	0.0359 (10)	0.0341 (10)	0.0361 (10)	0.0024 (8)	−0.0018 (8)	−0.0073 (8)
C8	0.0395 (11)	0.0366 (11)	0.0325 (10)	0.0033 (8)	−0.0059 (8)	−0.0053 (8)
C9	0.0456 (12)	0.0367 (11)	0.0392 (11)	−0.0014 (9)	−0.0009 (9)	−0.0074 (9)
C10	0.0373 (10)	0.0315 (10)	0.0314 (9)	0.0024 (8)	−0.0015 (8)	0.0001 (8)
C11	0.0398 (11)	0.0429 (12)	0.0432 (11)	0.0030 (9)	−0.0029 (9)	−0.0034 (9)
C12	0.0510 (14)	0.0461 (13)	0.0550 (14)	0.0153 (11)	0.0076 (11)	−0.0053 (11)
C13	0.0765 (18)	0.0374 (12)	0.0513 (13)	0.0048 (12)	0.0069 (13)	−0.0130 (10)
C14	0.0655 (16)	0.0495 (14)	0.0549 (14)	−0.0079 (12)	−0.0089 (12)	−0.0188 (11)
C15	0.0414 (12)	0.0434 (12)	0.0506 (12)	0.0031 (9)	−0.0073 (10)	−0.0118 (10)

Geometric parameters (Å, º)

Cl1—C11	1.739 (2)	C6—C7	1.380 (3)
O1—C7	1.386 (2)	C8—H8	0.9800
O1—C8	1.441 (2)	C8—C9	1.527 (3)
O2—C1	1.255 (3)	C8—C10	1.510 (3)
N1—H1	1.14 (2)	C9—H9A	0.9700
N1—C1	1.326 (3)	C9—H9B	0.9700
N1—C9	1.464 (3)	C10—C11	1.386 (3)
C1—C2	1.487 (3)	C10—C15	1.387 (3)
C2—C3	1.391 (3)	C11—C12	1.383 (3)
C2—C7	1.389 (3)	C12—H12	0.9300
C3—H3	0.9300	C12—C13	1.370 (3)
C3—C4	1.378 (3)	C13—H13	0.9300
C4—H4	0.9300	C13—C14	1.376 (3)
C4—C5	1.368 (3)	C14—H14	0.9300
C5—H5	0.9300	C14—C15	1.380 (3)
C5—C6	1.378 (3)	C15—H15	0.9300
C6—H6	0.9300		
C7—O1—C8	117.07 (14)	C9—C8—H8	108.8
C1—N1—H1	130.6 (11)	C10—C8—H8	108.8
C1—N1—C9	122.40 (17)	C10—C8—C9	113.14 (15)
C9—N1—H1	105.8 (11)	N1—C9—C8	112.49 (16)
O2—C1—N1	123.09 (19)	N1—C9—H9A	109.1
O2—C1—C2	119.0 (2)	N1—C9—H9B	109.1
N1—C1—C2	117.87 (19)	C8—C9—H9A	109.1
C3—C2—C1	120.30 (19)	C8—C9—H9B	109.1
C7—C2—C1	121.27 (18)	H9A—C9—H9B	107.8
C7—C2—C3	118.42 (19)	C11—C10—C8	121.44 (18)
C2—C3—H3	119.6	C11—C10—C15	117.21 (18)
C4—C3—C2	120.8 (2)	C15—C10—C8	121.34 (18)
C4—C3—H3	119.6	C10—C11—Cl1	120.02 (16)
C3—C4—H4	120.1	C12—C11—Cl1	117.79 (18)
C5—C4—C3	119.8 (2)	C12—C11—C10	122.2 (2)
C5—C4—H4	120.1	C11—C12—H12	120.4
C4—C5—H5	119.7	C13—C12—C11	119.3 (2)
C4—C5—C6	120.7 (2)	C13—C12—H12	120.4

C6—C5—H5	119.7	C12—C13—H13	120.0
C5—C6—H6	120.2	C12—C13—C14	119.9 (2)
C5—C6—C7	119.6 (2)	C14—C13—H13	120.0
C7—C6—H6	120.2	C13—C14—H14	119.8
O1—C7—C2	120.41 (17)	C13—C14—C15	120.4 (2)
C6—C7—O1	118.60 (18)	C15—C14—H14	119.8
C6—C7—C2	120.71 (19)	C10—C15—H15	119.5
O1—C8—H8	108.8	C14—C15—C10	121.0 (2)
O1—C8—C9	110.50 (16)	C14—C15—H15	119.5
O1—C8—C10	106.64 (15)		

Cl1—C11—C12—C13	−179.61 (17)	C7—O1—C8—C10	−166.47 (15)
O1—C8—C9—N1	−43.5 (2)	C7—C2—C3—C4	0.4 (3)
O1—C8—C10—C11	−152.15 (17)	C8—O1—C7—C2	74.4 (2)
O1—C8—C10—C15	29.4 (2)	C8—O1—C7—C6	−111.7 (2)
O2—C1—C2—C3	−38.0 (3)	C8—C10—C11—Cl1	1.2 (3)
O2—C1—C2—C7	140.7 (2)	C8—C10—C11—C12	−178.64 (19)
N1—C1—C2—C3	141.2 (2)	C8—C10—C15—C14	178.42 (19)
N1—C1—C2—C7	−40.1 (3)	C9—N1—C1—O2	168.99 (19)
C1—N1—C9—C8	76.9 (2)	C9—N1—C1—C2	−10.1 (3)
C1—C2—C3—C4	179.2 (2)	C9—C8—C10—C11	86.2 (2)
C1—C2—C7—O1	−4.4 (3)	C9—C8—C10—C15	−92.3 (2)
C1—C2—C7—C6	−178.2 (2)	C10—C8—C9—N1	76.0 (2)
C2—C3—C4—C5	−1.1 (4)	C10—C11—C12—C13	0.2 (3)
C3—C2—C7—O1	174.33 (18)	C11—C10—C15—C14	−0.1 (3)
C3—C2—C7—C6	0.6 (3)	C11—C12—C13—C14	−0.1 (3)
C3—C4—C5—C6	0.8 (4)	C12—C13—C14—C15	−0.2 (4)
C4—C5—C6—C7	0.1 (3)	C13—C14—C15—C10	0.2 (3)
C5—C6—C7—O1	−174.72 (19)	C15—C10—C11—Cl1	179.69 (15)
C5—C6—C7—C2	−0.8 (3)	C15—C10—C11—C12	−0.1 (3)
C7—O1—C8—C9	−43.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	1.15 (2)	1.78 (2)	2.849 (2)	153.9 (16)

Symmetry code: (i) −*x*+1, −*y*+2, −*z*.