Synthesis and crystal structure of 1,2-dihydro-1-(4-chlorophenyl)naphtho [1,2-*e*][1,3]oxazin-3-one

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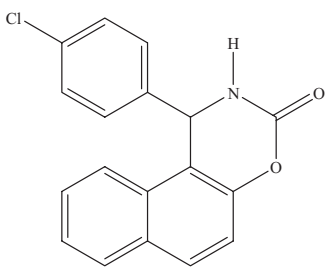
1,2-dihydro-1-(4-chlorophenyl)naphtho[1,2-*e*][1,3]oxazin-3-one, $C_{18}H_{12}ClNO_2$, was prepared from β-naphthol, 4-chlorobenzaldehyde, urea and acetic acid and its structure elucidated by X-ray diffraction method.

Keywords: naphtho[1,2-*e*][1,3]oxazin-3-one, X-ray crystal structure, hydrogen bonding

Naphthalene-condensed 1,3-oxazin-3-ones have been reported as anti-bacterial agents.[1] This class has also been used as precursors in the preparation of phosphinic ligands for asymmetric catalysis.[2] However, to the best of our knowledge, there was only very few reports of the synthesis of aphthalene-condensed oxazinone derivatives in the literature. All methods have used either expensive, toxic and hazardous reagents and solvents or starting material such as amino alkylnaphthol, which was prepared in a multi-step reaction using harsh reaction conditions.[3] Therefore, the discovery of new, simple, green and one-pot methods for synthesis of naphthoxazinone derivatives is of prime importance. Here, we report on the synthesis and crystal structure of the title compound (Scheme 1).



Scheme 1

Experimental

Melting points were measured on an Electrothermal 9200 apparatus. Mass spectra were recorded on a Finnigan-Mat 8430 mass spectrometer operating at an ionisation potential of 70 eV. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300.13 and 75.47 MHz in CD_3SOCD_3 using TMS as external standard. Infrared spectra (4000–250 cm^{-1}) of solid sample were taken as 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. All reagents were used as received.

Synthesis of 1,2-dihydro-1-(4-chlorophenyl)naphtho[1,2-e][1,3] oxazin-3-one: A mixture of β-naphthol (1 mmol), 4-chloro-benzaldehyde (1 mmol), urea (1.5 mmol) and acetic acid (0.5 mmol) were finely mixed together. The reaction mixture was placed in a screw-capped vial and heated at 130°C for 2 h. After cooling, the reaction mixture was washed with water and then recrystallised from EtOAc/hexane (1 : 3) to afford the pure product. White powder (74%), m.p. 208–210°C; IR (KBr) (ν_{max}/cm^{-1}): 3224, 3146, 1734. ^{1}H NMR (300 MHz, CD_3SOCD_3): δ_H (ppm) 6.1 (1H, s, CH), 7.0–8.11(10H, m, arom), 8.93 (1H, s, NH). ^{13}C NMR (75 MHz, CD_3SOCD_3): δ_C(ppm) 53.52, 114.02, 117.34, 123.52, 125.62, 127.92, 128.06, 129.15, 129.24, 129.37, 129.45, 130.89, 133.06, 142.23, 147.91, 149.63. MS, *m/z* (%): 309 (M^+, 5), 265(60), 231(100), 202(27), 115(15).

X-ray crystallography

The X-ray diffraction measurement was made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K_α radiation. A colourless needle crystal was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 5641 unique reflections. Data were collected in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA software package.[4] A numerical absorption correction was applied using X-RED[5] and X-SHAPE[6] softwares. The data were corrected for Lorentz and polarising effects. The structures were solved by direct methods and subsequent difference Fourier map and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters[7]. All of hydrogen atoms were located in a difference Fourier map and then after refined isotropically. All refinements were performed using the X-STEP32 crystallographic software package[8]. A summary of the crystal data, experimental details and refinement results is given in Table 1.

Table 1 Crystal data and structure refinement for $C_{18}H_{12}ClNO_2$

Formula	$C_{18}H_{12}ClNO_2$
Formula weight	309.74
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size/mm^3	0.40 × 0.06 × 0.03
Unit cell dimensions	a = 9.2549(14) Å
	b = 19.429(4) Å
	c = 17.124(3) Å
	α = 90°
	β = 101.781(12)°
	γ = 90°
Volume	3014.3(9) Å^3
Z	8
Density (calculated)	1.365 g/cm^3
Theta ranges for data collection	1.60–26.83°
F(000)	1280
Absorption coefficient	0.259 mm^{-1}
Index ranges	$-11 \le h \le 11$
	$-24 \le k \le 24$
	$-21 \le l \le 21$
Data collected	20267
Independent reflections	6396 [R(int) = 0.0627]
Data/restrains/parameters	6396/0/493
Final R indices [I>2σ(I)]	R^1 = 0.0740, wR^2 = 0.1300
R indices (all data)	R^1 = 0.1161, wR^2 = 0.1445
Final weighting scheme	calc w = 1/[σ^2(Fo^2) + (0.0364P)^2 + 1.8776P] where P = (Fo^2 + 2Fc^2)/3
Goodness of fit on F^2	1.162
Largest diff peak and hole	0.309, –0.417 e Å^{-3}
CCDC	638218

Discussion

The molecular structure of 1,2-dihydro-1-(4-chlorophenyl) naphtho[1,2-*e*][1,3]oxazin-3-one is illustrated in Fig. 1. Asymmetric unit in the unit cell contains two independent molecules that they are similar in the bond distances and angles, and selected bond lengths and angles are summarised in Table 2 is only for one of them. The bond distances and angles are within normal ranges[9]. In this molecule. The rings A (C1–C6), B (C7/N1/C8/O2/C9/C18), C (C9–C12/C17–C18) and D (C12–C17) are, of course, planar and the dihedral angles between them are A/B = 85.6(3) °, B/C = 1.4(4) ° and C/D = 2.93 °. As shown in the packing of the title compound (Fig. 2), there exists

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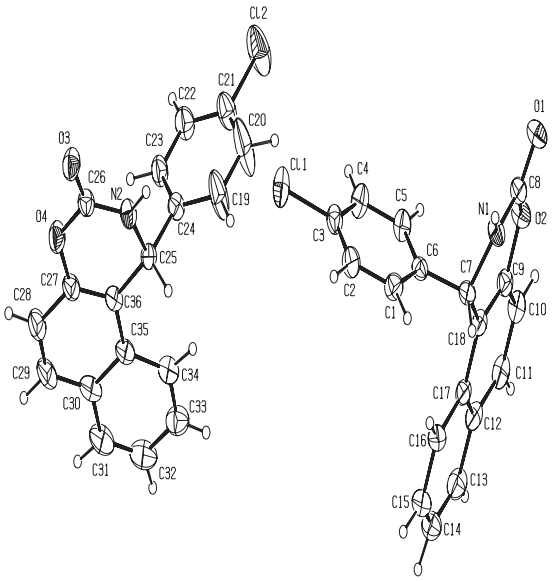

Fig. 1 The molecular structure with the atom-numbering scheme. Displacement ellipsoids are drawn at 30% probability level.

Table 2 Selected bond distances (Å), bond angles (/°)

C(1)—C(6)	1.384(4)
C(1)—C(2)	1.386(5)
C(3)—Cl(1)	1.747(3)
C(6)—C(7)	1.519(4)
C(7)—N(1)	1.467(4)
C(7)—C(18)	1.503(4)
C(8)—O(1)	1.214(3)
C(8)—N(1)	1.320(4)
C(8)—O(2)	1.374(3)
C(9)—C(18)	1.355(4)
C(9)—O(2)	1.399(3)
C(9)—C(10)	1.409(4)
C(2)—C(3)—Cl(1)	119.1(2)
C(4)—C(3)—Cl(1)	120.0(3)
C(1)—C(6)—C(7)	121.1(3)
C(5)—C(6)—C(7)	120.5(3)
N(1)—C(7)—C(18)	108.4(2)
N(1)—C(7)—C(6)	110.6(2)
C(18)—C(7)—C(6)	112.9(2)
O(1)—C(8)—N(1)	125.4(3)
O(1)—C(8)—O(2)	117.4(3)
N(1)—C(8)—O(2)	117.3(3)
C(18)—C(9)—O(2)	122.3(3)
C(18)—C(9)—C(10)	122.7(3)
O(2)—C(9)—C(10)	115.1(3)
C(8)—N(1)—C(7)	127.7(3)
C(8)—O(2)—C(9)	119.9(2)

two strong intermolecular N–H...O hydrogen bonds [H1B…O3^{i} = 1.976(3), N1…O3^{i} = 2.828(3)Å and N1–H1B…O3^{i} = 176.7(3)° and H2B…O1^{ii} = 2.144(3), N2…O1^{ii} = 2.993(3)Å and N1–H2B…O1^{ii} = 176.3(3)°, symmetry codes: (i) 1–*x*,–1/2 + *y*, 3/2–*z*; (ii) 1–*x*, 1/2 + *y*, 3/2–*z*] between adjacent molecules in the unit cell. There is also one C–H…O short contacts in the packing cell (H2…O3 = 2.450(4), C2…O3 = 3.268(4) Å and C2–H2…O3 = 144.0(3)°, symmetry codes; *x*, 3/2-*y*, 1/2 + *z*). In the packing, the oxazine, phenyl and naphthyl rings form π bonding stacks in which each oxazine ring have some interaction with phenyl ring of adjacent molecule and naphthyl ring from adjacent ring in the other site. The close contact distances between adjacent rings are 3.583–3.9993 Å. The N–H…O type of intermolecular interactions and also π–π stackings play major roles in stabilising the molecule in the unit cell.

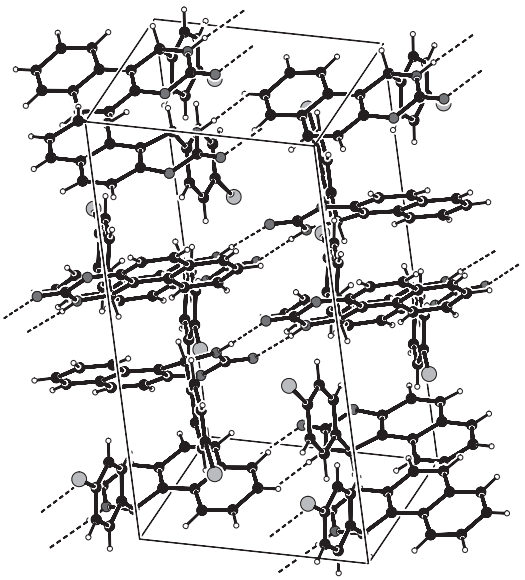

Fig. 2 Packing diagram. Hydrogen bonds are shown as dashed lines.

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