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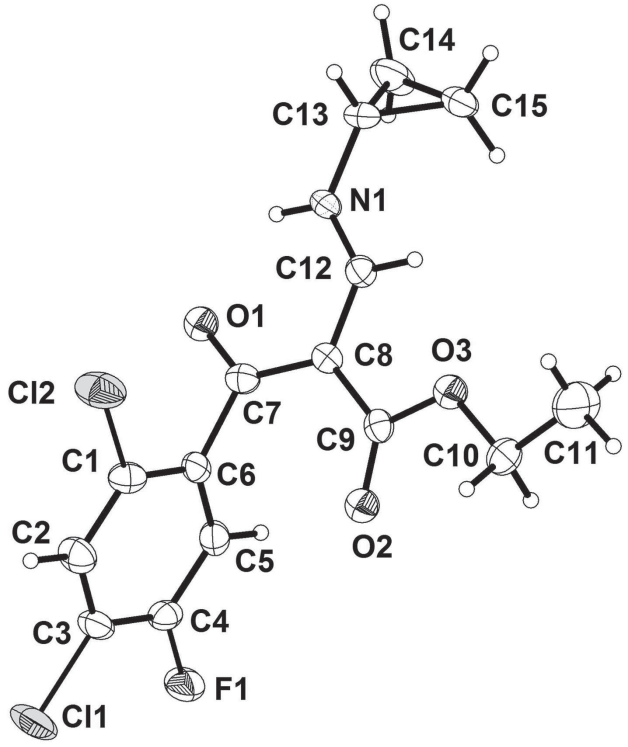
Crystal structure of ethyl (E)-3-(cyclopropyl-amino)-2-(2,4-dichloro-5-fluorobenzoyl) acrylate, $C_{15}H_{14}Cl_2FNO_3$



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Abstract

$C_{15}H_{14}Cl_2FNO_3$, triclinic, $P\bar{1}$ (no. 2), $a = 8.5995(8)$ Å, $b = 9.9579(9)$ Å, $c = 10.1418(10)$ Å, $\alpha = 113.4900(10)°$, $\beta = 95.8730(10)°$, $\gamma = 96.1610(10)°$, $V = 781.81(13)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0282$, $wR_{ref}(F^2) = 0.0788$, T = 100(2)K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	4.4 cm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5448, 2737, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2379
$N(param)_{refined}$:	200
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], OLEX2 [4]

Source of material

A mixture of 60 mL 1,2-dichlorobenzene and cyclopropylamine hydrochloride (5.61 g, 0.06 mol) was stirred at 180 °C. Formoxyl ethyl acetate sodium salt (8.28 g, 0.06 mol) was added in batches. The reaction was completely finished by circumfluence to repel water for 3 h. After cooling to room temperature, the reaction mixture was slowly added to a mixture of 2,4-dichloro-5-fluorobenzoyl chloride (13.65 g, 0.06 mol), trimethylamine (6.06, 0.06 mol) and 40 mL 1,2-dichlorobenzene at 25–35 °C. The temperature was at 50°C kept for three hours. When the reaction was complete, the mixture was filtered, and solid impurity was removed. The organic layer was washed with water (50 mL) and dried with

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.2093(2)	0.60661(19)	0.13129(18)	0.0180(4)
C2	0.1788(2)	0.45305(19)	0.06736(18)	0.0209(4)
H2	0.2003	0.3996	−0.0282	0.025*
C3	0.1167(2)	0.37837(19)	0.14470(19)	0.0189(4)
C4	0.0846(2)	0.45945(19)	0.28283(18)	0.0167(4)
C5	0.11564(19)	0.61196(19)	0.34668(18)	0.0167(4)
H5	0.0943	0.6649	0.4424	0.020*
C6	0.17852(19)	0.68844(18)	0.27023(18)	0.0152(4)
C7	0.2307(2)	0.85472(19)	0.34519(18)	0.0163(4)
C8	0.12550(19)	0.95872(18)	0.35028(17)	0.0145(3)
C9	−0.04483(19)	0.90967(18)	0.29682(17)	0.0146(4)
C10	−0.2913(2)	0.9771(2)	0.2391(2)	0.0209(4)
H10A	−0.3452	0.9442	0.3053	0.025*
H10B	−0.3117	0.8947	0.1407	0.025*
C11	−0.3511(2)	1.1115(2)	0.2343(3)	0.0382(5)
H11A	−0.2956	1.1439	0.1697	0.057*
H11B	−0.3317	1.1916	0.3326	0.057*
H11C	−0.4651	1.0869	0.1976	0.057*
C12	0.1859(2)	1.11044(18)	0.40642(17)	0.0155(4)
H12	0.1134	1.1744	0.4012	0.019*
C13	0.3889(2)	1.32970(19)	0.5171(2)	0.0213(4)
H13	0.4429	1.3605	0.4485	0.026*
C14	0.4532(2)	1.4164(2)	0.6748(2)	0.0285(5)
H14A	0.5455	1.4958	0.7012	0.034*
H14B	0.4511	1.3633	0.7391	0.034*
C15	0.2981(2)	1.43934(19)	0.6123(2)	0.0241(4)
H15A	0.2004	1.4004	0.6380	0.029*
H15B	0.2948	1.5329	0.6001	0.029*
Cl1	0.08210(6)	0.18670(5)	0.07389(5)	0.03043(15)
Cl2	0.29229(6)	0.69761(5)	0.03361(5)	0.02949(14)
F1	0.02051(12)	0.38588(11)	0.35657(11)	0.0240(2)
N1	0.33303(17)	1.17296(15)	0.46554(15)	0.0172(3)
H1	0.4013	1.1160	0.4741	0.021*
O2	−0.11463(13)	0.78444(13)	0.26150(13)	0.0190(3)
O3	−0.12146(13)	1.01987(13)	0.29207(13)	0.0189(3)
O1	0.37304(14)	0.89535(13)	0.39948(14)	0.0248(3)

$MgSO_4$. The title compound was obtained after the solvent was removed under reduced pressure.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C—H in the 0.95–1.00 Å range and with $U_{iso}(H) = 1.2U_{eq}(C, N)$ and $1.5U_{eq}(C_{methyl})$.

Discussion

Quinolones are one of the most widespread types of antibacterials in human daily lives [5]. Since the introduction of the first quinolone as a therapeutic agent of urinary tract infections [6], quinolones have become one of the main drugs to treat bacterial infections, widely used in the treatment of diseases including sexually transmitted diseases, urinary tract infections, chronic bronchitis, community acquired pneumonia, respiratory infections and so on [7]. Among these, the most notable ones are 4-quinolones [8–12], which form the core backbone of several quinolone-based and commercially-available antibiotics. For these reasons, it is necessary to develop simple and efficient approaches for the synthesis of 4-quinolones. So quinolone intermediates are a kind of important organic intermediate and play a vital role in the synthesis of quinolone main ring. In continuation of our previous work on the total synthesis of 4-quinolones, the structure of title compound was determined.

The compound crystallizes in the centrosymmetric triclinic space group with one molecule in the asymmetric unit. The amino group is involved in the donation of an intramolecular hydrogen bond to the benzoyl oxygen atom [D···A 2.643(2) Å and D–H···A 129°]. Bond lengths and angles are in the expected ranges.

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