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Crystal structure of 2-chloro-4-(prop-2-yn-1-yloxy)-6-(thiophen-2-yl)-1,3,5-triazine, $C_{10}H_6ClN_3OS$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.21 \times 0.20 \times 0.19$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	4.63 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω -scans
$\theta_{\max}$, completeness:	40.9° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3238, 1944, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1745
$N(\text{param})_{\text{refined}}$:	181
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], DIAMOND [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.67985(2)	0.72425(7)	0.73652(3)	0.04277(18)
S1A ^a	0.79385(17)	0.4418(4)	0.45055(11)	0.0255(6)
S1B ^a	0.88125(15)	0.4515(4)	0.60776(13)	0.0280(5)
O1	0.53199(5)	0.64669(16)	0.45533(6)	0.0253(3)
N1	0.73674(7)	0.59548(18)	0.63262(8)	0.0261(3)
N2	0.66076(7)	0.56407(17)	0.49395(8)	0.0221(3)
N3	0.60192(7)	0.67262(18)	0.58554(8)	0.0245(3)
C1A ^b	0.8725(8)	0.463(2)	0.6060(10)	0.057(5)
H1A ^b	0.884953	0.483479	0.661835	0.069*
C1B ^c	0.7936(8)	0.4493(16)	0.4553(7)	0.055(4)
H1B ^c	0.750551	0.462496	0.406637	0.067*
C2A ^a	0.9244(16)	0.402(3)	0.5641(11)	0.040(4)
H2A ^a	0.977739	0.373224	0.591689	0.048*
C2B ^a	0.8723(10)	0.388(4)	0.4651(12)	0.033(3)
H2B ^a	0.886922	0.351465	0.421070	0.040*
C3A ^a	0.8909(11)	0.389(3)	0.4841(11)	0.037(4)
H3A ^a	0.918244	0.354306	0.449785	0.044*
C3B ^a	0.9233(16)	0.388(3)	0.5423(10)	0.034(3)
H3B ^a	0.976745	0.356017	0.557177	0.041*
C4	0.79581(8)	0.4871(2)	0.54029(10)	0.0252(4)
C5	0.72775(8)	0.55127(19)	0.55677(10)	0.0215(3)
C6	0.60128(8)	0.6254(2)	0.51267(9)	0.0210(3)
C7	0.67156(8)	0.6550(2)	0.64087(10)	0.0255(3)
C8	0.52678(9)	0.6036(2)	0.37409(9)	0.0275(4)
H8A	0.527170	0.469546	0.366660	0.033*
H8B	0.571459	0.656985	0.362676	0.033*
C9	0.45378(9)	0.6813(3)	0.32072(10)	0.0314(4)
C10	0.39517(11)	0.7441(3)	0.27721(11)	0.0410(5)
H10	0.347786	0.794913	0.242032	0.049*

Occupancies: ^a = 0.5, ^b = 0.44, ^c = 0.56.

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Abstract

$C_{10}H_6ClN_3OS$, monoclinic, $C2/c$ (no. 15), $a = 18.3141(4)$ Å, $b = 7.31845(15)$ Å, $c = 17.7885(4)$ Å, $\beta = 110.495(3)^\circ$, $V = 2233.30(9)$ Å³, $Z = 8$, $T = 150(2)$, $R_{\text{gt}}(F) = 0.0331$, $wR_{\text{ref}}(F2) = 0.0904$.

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

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Source of materials

Under the protection of N₂, Mg (4.80 g, 0.2 mol) and I₂ (1.02 g, 0.004 mol) were added to the solution of tetrahydrofuran (150 mL). After 10 min 2-bromothiophene (32.60 g, 0.2 mol) was added dropwisely. When Mg dissolved, the reaction mixture was cooled to −15 °C. A solution of 2,4,6-trichloro-1,3,5-triazine (36.88 g, 0.2 mol) in tetrahydrofuran was added to the above solution of thiophen-2-yl magnesium bromide within 5 min. After 5 h, the mixture was filtered and the filtrate was evaporated to get a yellow solid, which was purified by chromatography on silica gel to get 2,4-dichloro-6-(thiophen-2-yl)-1,3,5-triazine (26.0 g, yield 56%) as a yellow solid. To a suspension of 2,4-dichloro-6-(thiophen-2-yl)-1,3,5-triazine (2.29 g, 0.01 mol) in 60 mL of tetrahydrofuran was added K₂CO₃ (2.76 g, 0.02 mol) and propiolic alcohol (0.67 g, 0.012 mol). The mixture was refluxed for 6 h and then filtered to get a yellow solution. The solvent was evaporated under reduced pressure to get a yellow solid, which was purified by chromatography on silica gel to afford 2-chloro-4-(prop-2-yn-1-yloxy)-6-(thiophen-2-yl)-1,3,5-triazine as a light yellow solid. (1.34 g, 54%). ¹H NMR (400 MHz, CDCl₃): δ: (dd, *J* = 1.2 Hz, *J* = 3.84 Hz, 1H), 7.70(d, *J* = 1.2 Hz, 1H), 7.22(dd, *J* = 3.88 Hz, *J* = 4.92 Hz, 1H), 5.14(d, *J* = 2.4 Hz, 2H), 2.58(t, *J* = 2.4 Hz, 1H). The crystals were obtained by recrystallization with ethyl acetate at room temperature.

Experimental details

The structure was solved with the ShelXT [2] structure solution program and refined with the SHELXL [3] refinement package. The positions of the hydrogen atoms were generated geometrically. The thiophene ring is disordered over two sites (S1A/S1B, C1A/C1B, C2A/C2B and C3A/C3B).

Comment

The s-triazine (1,3,5-triazine) ring is a remarkable building block to generate supramolecular interactions and an important unit to construct various nonlinear optical devices [5], organic light-emitting devices [6], luminescent sensors and photovoltaic cells [7], liquid-crystalline materials. The reason is that the electron deficient character of s-triazine ring can give rise to the formation of a variety of supramolecular interactions. There are a large number of tri-substituted s-triazine derivatives reported until now, but little attention has been paid to the disubstituted-triazine derivatives. In this paper, 2-chloro-4-(prop-2-yn-1-yloxy)-6-(thiophen-2-yl)-1,3,5-triazine was synthesized using cyanuric trichloride as starting material. This disubstituted-triazine derivative can be used as an intermediate to synthesize porous adsorbent materials which can be used to remove special metal ions [8] or to capture special gases [9]. There are some related structures [10–12] in the structural database.

In the title molecule, the typical bond length of C1A–C2A, S1–C4, N1–C5 and C9–C10 are 1.47(3) Å, 1.619(2) Å, 1.340(2) Å and 1.175(3) Å, respectively. The torsion angle of S1A–C4–C5–N2 is 3.0°, which demonstrated that the thiophene ring and the 1,3,5-triazine ring are almost coplanar (*cf.* the figure). Similar to the packing of other triazines non-classical hydrogen bonds [13] were observed as following: C2B–H3A···O1 (*d*(H3A···O1) = 2.55 Å, C2A–H3B···O1 (*d*(H3B···N3) = 2.55 Å, C10–H10···N1 (*d*(H10···N1) = 2.41 Å.

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