Crystal structure of 3-chlorobenzo[b]thiophene-2-carbonyl chloride

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3-Chlorobenzo[b]thiophene-2-carbonyl chloride was synthesised from cinnamic acid and thionyl chloride. The single crystal X-ray structure determination confirmed the earlier proposed structure and the product was further characterised by ^{1}H NMR, ^{13}C NMR and mass spectrometry. The X-ray structure determination revealed two sets of symmetry related molecules along the *b*-axis that are loosely connected by relatively *weak CH...π (3.626, 3.628 Å) interactions, giving rise to two infinite chains*. The packing structure is dominated by Van der Waals forces between these chains. No significant π–π interactions are found in the crystal structure.

Keywords: benzothiophene, single crystal X-ray diffraction, C–H...π interaction

The reaction of cinnamic acid derivatives with thionyl chloride and pyridine is a general procedure for the synthesis of benzothiophene derivatives from readily available starting materials. These compounds can be easily converted to their corresponding acids, esters and amines.[1-4] Being a heterocyclic compound, benzothiophenes are useful compounds in research as a starting material for the synthesis of larger structures that have special properties such as switching units, excellent thermal stability and pesticidal activity.[5-9] They have also pharmacological properties as antibiotics, analgesics and enzyme inhibitors[10,11] and are found within the chemical structures of some drugs such as raloxifene,[12] zileuton, and sertaconazole.[10]

3-Chlorobenzo[b]thiophene-2-carbonyl chloride had been reported several times by different groups.[1-3] For the first time, in 1968, Krubsack and Higa synthesised the title compound with a very low yield.[1] After that, in 1970, Nakagawa and co-workers succeeded to improve a little the yield, from 31.4 to 46%.[2] In 1971 Wright and Brabander obtained a significantly better yield (69%) of this structure with a slightly different synthetic method.[3] McKenney and co-workers prepared the title compound as a starting material for several larger structures.[4] None of these groups obtained a crystal structure of the compound, and their reports were just based on NMR spectroscopy and elemental analysis. We have now synthesised 3-chlorobenzo[b]thiophene-2-carbonyl chloride, in part to confirm its structure by getting suitable crystals for crystallography.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-500 spectrometer.

Thionyl chloride (36.5 mL, 0.5 mol) was added to a stirring solution of cinnamic acid (14.8 g, 0.1 mol) in chlorobenzene (100 mL). The resulting suspension was stirred for 1 hour, and then pyridine (0.8 mL, 0.01 mol) was added dropwise followed by reflux for 3 days. The insoluble impurities were then filtered out from the hot solution. Two different procedures were applied for the crystallisation. Firstly, the excess solvent of filtration was evaporated under reduced pressure. The residual solid with 75% yield was dissolved in hexane for recrystallisation. Extremely fine needle crystals appeared after two days which were not suitable for crystallography. Secondly, leaving the resulting solution of chlorobenzene to remain undisturbed and slow evaporation of the mother liquor afforded suitable crystals for crystallography. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 7.958(d, 14 Hz, H_4), 7.893(d, 17 Hz, H_1), 7.536(t, 14 Hz, $H_{2,3}$). ^{13}C NMR (500 MHz, $CDCl_3$): δ_C (ppm) 58.31, 140.47, 137.20, 130.75, 126.28, 124.81, 122.85. MS, *m/z* (%): 309 (M^+, 53.5), 232 (M^{+2}, 35.7), 234 (M^{+4}, 7.1), 195 (100), 167 (82).

The X-ray data were collected at ambient temperature by means of a STOE IPDS II, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). No intensity variations due to decomposition of the crystals were observed. Selected crystallographic and experimental details are summarised in Table 1. X-Area program packages were used for indexing and integrating the single crystal reflections.[13]

The structure was solved by direct methods using SHELXS-97, and refined by full matrix least squares on F^2, SHELXL-97.[14] Minimum and maximum final electron density was 0.319 and 0.378 eA^{-3}. Absorption correction was performed with the programs X-RED and X-Shape.[15] Symmetry equivalent reflections were used to optimise crystal shape and size. All non-hydrogen atoms were refined anisotropically. Aromatic H atoms were placed in calculated positions (C–H = 0.93 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2\ U_{eq}(C)$. Plots were produced with the Diamond[16] and Mercury programs, and PLATON[17] software was used to prepare materials for publication. Crystallographic data have been deposited at the Cambridge Crystal Structure Database (CCDC), with CCDC-number 713482. Copies of available materials can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: (44)01223 336033); E-mail: deposit@ccdc.ac.uk).

3-Chlorobenzo[b]thiophene-2-carbonyl chloride (I) was synthesised from cinnamic acid and thionyl chloride (Scheme 1). The molecular structure of (I) and the atom-numbering scheme are shown in Fig. 1. The structure contains a benzothiophene molecule that has chloride and acid chloride substitutions in the thiophenic ring. C1–C2 distance [1.706(4) Å] is significantly shorter than C2–C5 distance [1.417(6) Å], indicating its double nature. The bond length C2–Cl1 [1.706(4)Å], which is connected to the aromatic thiophene ring, is significantly shorter than C3–Cl2 [1.792(5)Å, see Table 2], due to the conjugation between the chloride substituent and the aromatic ring. Otherwise,

Table 1 Crystal data and structure refinement for the title compound

CCDC deposit no.	713482
Molecular formula	$C_9H_4Cl_2OS$
Molecular weight	231.09
Temperature (K)	295(2)
Radiation λ	0.71073
Crystal system	Monoclinic
Space group	P 21/*c*
a/Å	12.219(4)
b/Å	3.8909(7)
c/Å	20.345(6)
V/Å^3	913.2(4)
Z	4
D_{calc} (g cm^{-3})	1.681
Crystal size (mm)	0.12 × o.15 × 0.44
Crystal colour	Yellow
Absorption coefficient (cm^{-1})	0.888
Absorption correction T_{min} and T_{max}	0.6748 and 0.8963
F(000)	464
Reflections collected/unique	6028/1555 [R_{int} = 0.1351]
Range/indices (*h*, *k*, *l*)	–14,14; –4,4; –24,24
Θ limit (°)	1.77–24.99
No. of observed data, I > 2σ(I)	1070
No. of restraints	0
Goodness of fit on F^2	0.998
R^1, wR^2 [I≥2 σ(I)][a]	0.0576, 0.1216
R^1, wR^2 (all data)	0.0934, 0.1427

[a]*R* values are defined as: $R^1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$
$wR^2 = [\Sigma\ [w(F_o^2-F_c^2)^2]/\Sigma\ [w(F_o^2)^2]]^{1/2}$

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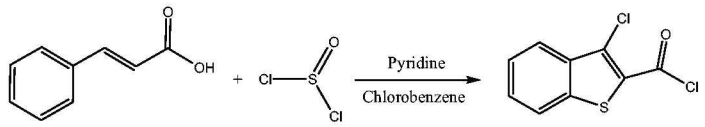

Scheme 1 Synthetic and chemical structure of the title compound (I).

all the bond lengths and angles are in their normal range (Table 2). There are two sets of symmetry related molecules along b-axis, which are loosely connected by relatively *weak CH...π interactions* (*e.g.* C9–H9 ···*Cg*1^{i} = 3.628 Å, C6-H6^{ii} ···*Cg*1^{iii} = 3.626 Å with *Cg*1 being the ring C4/C5/C6/C7/C8/C9 with i = *x*, *y*, 1, *z*, ii = 1, *x*, 0.5 + *y*, 0.5, *z* and iii = 1, *x*, 1.5 + *y*, 0.5, *z*, see Fig. 2). These independent infinite chains are connected by Van der Waals forces, stabilising the crystal structure (Fig. 3). No significant π–π interactions are found in the crystal structure. The packing structure has also an interesting view along the c axis. Every second molecule is coplanar while neighboring molecules in the same direction are twisted, making a sign multiplication with a dihedral angle of 49.42° (Figs 4 and 5).

Table 2 Selected bond lengths (Å) and angles (°)

Cl1–C2	1.706(4)	C4–C5	1.395(6)
Cl2–C3	1.792(5)	C2–C5	1.417(6)
S1–C4	1.731(4)	C1–C3	1.447(6)
S1–C1	1.736(4)	C1–C2	1.376(6)
O1–C3	1.180(6)		
C4–S1–C1	91.3(2)	O1–C3–C1	128.1(4)
C2–C1–C3	126.1(4)	O1–C3–Cl2	119.0(4)
C2–C1–S1	112.0(3)	C1–C3–Cl2	112.9(3)
C3–C1–S1	121.9(3)	C9–C4–C5	121.2(4)
C1–C2–C5	112.7(4)	C9–C4–S1	127.1(4)
C1–C2–Cl1	125.0(3)	C5–C4–S1	111.6(3)
C5–C2–Cl1	122.2(3)	C4–C5–C6	119.5(4)
C4–C5–C2	112.3(4)	C6–C5–C2	128.2(4)
C7–C6–C5	118.1(4)	C7–C6–H6	121.0
C5–C6–H6	121.0	C6–C7–C8	121.6(4)
C6–C7–H7	119.2	C8–C7–H7	119.2
C9–C8–C7	121.0(4)	C9–C8–H8	119.5
C7–C8–H8	119.5	C8–C9–C4	118.6(4)
C8–C9–H9	120.7	C4–C9–H9	120.7

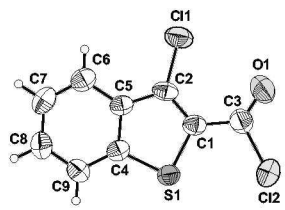

Fig. 1 ORTEP structure of the title compound, showing 50% probability ellipsoids. H atoms are shown as circles of arbitrary radii.

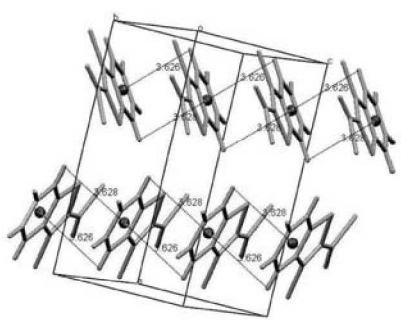

Fig. 2 Packing view of the title compound in the unit cell, showing C-H...π interactions.

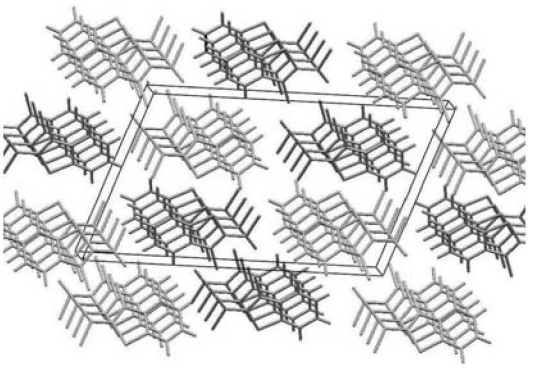

Fig. 3 Packing view of the title compound, showing infinite chains, which are in contact by Van der Waals forces.

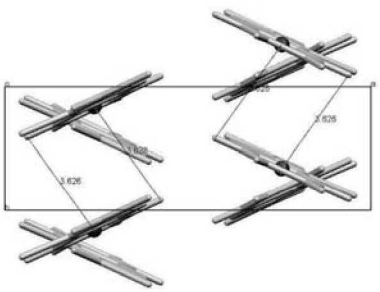

Fig. 4 Packing of the unit cell along the *c* axis.

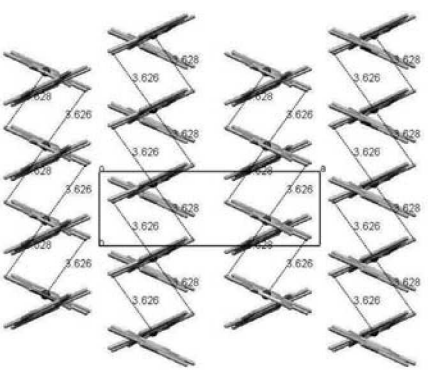

Fig. 5 Viewing the chains and their connections along the *c* axis.

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