ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2011. Том 52, № 3 *Май – июнь* *С. 653 – 656*

КРАТКИЕ СООБЩЕНИЯ

UDC 541.6:547.12

STRUCTURAL STUDIES OF 3-CHLORO-*N*-(8′-QUINOLYL)BENZO[*b*]THIOPHENE-2-CARBOXAMIDE

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Received August, 30, 2009

3-Chloro-*N*-(8′-quinolyl)benzo[*b*]thiophene-2-carboxamide was synthesized from 3-chlorobenzo[*b*] thiophene -2-carboxyl chloride and 8-aminoquinoline in the presence of triethylamine. The single crystal X-ray structure determination confirmed the earlier proposed structure and also characterized by ^{1}HNMR, and Mass spectroscopy. Crystallographic study reveals that the structure crystallizes in monoclinic system, $a = 14.878(4)$, $b = 8.4292(15)$, $c = 25.461(7)$ Å, $\beta = 112.022(18)°$, $Z = 8$, $V = 2960.20(12)$ Å^3 with space group $C2/c$ (No. 15). In the structure packing, three kinds of interactions are responsible for the stability of the structure. Infinite two-dimensional stair-like layered chains are formed by relatively strong intermolecular hydrogen bonds [C14—H14…O1]. These parallel chains are connected by several π—π and CH—π interactions, alternatively. There are two such parallel chains with 70.53°, which are in contact by Van der Waals interactions.

K e y w o r d s: benzothiophene, carboxamide, crystal structure, hydrogen bonding, CH—π interaction, π—π interaction.

Synthesis of polycyclic heterocyclic ring systems have been followed by many groups of researchers [1, 2]. One of the best procedures in this field is photochemical reaction, in which a good leaving group will leave an aromatic ring under a radically mechanism, producing a radical that can facilitate the formation of fused neighbor ring systems [1, 2]. Our interest in these structures arises from easily converting to larger useful structures. Nowadays, many research groups reported this type of structures. Among them, Carminski—Zamola and coworkers have reported such compounds with a carboxyl group as substitution [3]. Following our previous work in the synthesis of 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride (**1**) [4], we were interested in preceding these reactions in order to get phenanthroline ring systems, which have widespread biological, pesticidal and pharmacological activities [5—9]. 3-Chloro-*N*-(8′-quinolyl)benzo[*b*]thiophene-2-carboxamide (**2**), with a chloride group is a suitable choice for photocyclization system that can serve as a basic substance for preparation of [1]benzothieno[2,3-c][1,10]phenanthroline (**3**) (see scheme 1). Compound **2** was previously reported in one step in 1996 by Halverson and Castle [10]. However their report was merely based on NMR and elemental analysis. In the current study, we synthesized compound **2** with some modifications (*i.e.* using different solvent and crystallization technique, resulting in better yield), in part to confirm its structure by getting suitable crystals for crystallography.

Experimental. The synthesis was performed starting from 3-chlorobenzo[*b*]thiophene-2-carboxyl chloride (**1**) that was reported in our previous work [3]. A solution of 8-aminoquinoline (0.95 g, 6.56 mmol) in 150 ml of benzene was added to (**1**) (1.52 g, 6.56 mmol). Triethylamine (6.8 mmol) was then added slowly, followed by four hours reflux. Insoluble impurities were filtered out from the hot solution. Allowing to remains undisturbed and slow evaporation of the mother liquor, instead of previously reported fast evaporating of the solvent under vacuum [10], afforded needle, colorless, suitable

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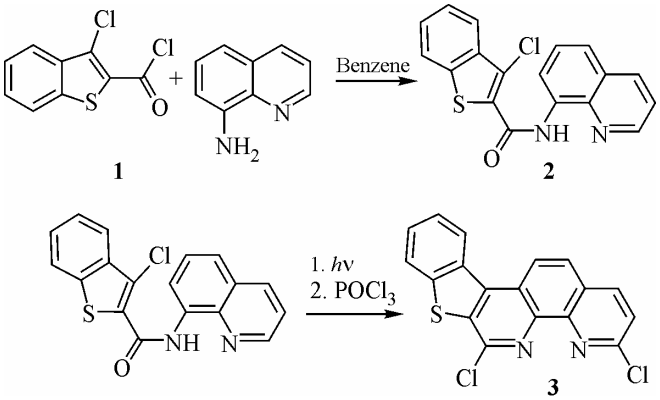

Scheme 1

crystals for crystallography. The crystallographic data have been deposited at the Cambridge Crystal Structure Database (CCDC), with CCDC-number 717714, and is freely available upon request from www.ccdc.cam.ac.uk/data_request/cif web site. 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).

Compound **2** is a colorless crystalline solid (mp 170 °C, reported previously 168—169 °C [10]). The ^{1}H-NMR spectra were recorded on a Bruker FT-500 spectrometer in chloroform-d_1, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were registered on a Finnigan Mat TSQ-70 spectrometer. ^{1}H NMR (δ, ppm): 7.41—7.53 (m, 3H), 7.53—7.62 (m, 2H), 7.63—7.76 (m, 1H), 7.73—7.80 (m, 1H), 8.14 (dd. 1H), 8.88 (dd, 1H), 8.90—8.94 (m, 1H), 11.60 (s, H NH). MS, *m*/*z* (%): 338 (M+, 11.5), 340 (M++2, 5.3), 303 (38.4), 212 (88.4), 195 (100).

Results and discussion. Single crystal X-ray diffraction. The structure was solved by direct methods using SHELXS-97, and refined by full matrix least squares on F^2, SHELXL-97 [11]. Minimum and maximum final electron density was –0.319 and 0.378 e·Å^{-3}. Absorption corrections were performed with the programs X-RED and X-Shape [12]. 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 imide H atom was located in different density maps and treated as riding on the respective carrier atom, with U_{iso}(H) = 1.2 and 1.5 U_{eq} (for C and N, respectively). Plots were produced with the Diamond [13] and Mercury programs, and PLATON [14] software was used to prepare materials for publication.

The title compound was synthesized in a better yield, as compared to the previously proposed structure, by a facile one-step reaction of **1** and 8-aminoquinoline in the presence of triethylamine. We could get good crystals by slow evaporation in reaction vessel, using benzene as a solvent. The crystal data and structure refinement details are shown in Table 1. The title compound crystallizes in the monoclinic crystal system with the *C*2/*c* space group. The molecular structure and the atom numbering design are shown in Fig. 1. All bond lengths and angles are comparable with similar structures, such as the one reported by Carminski—Zamola, *et. al*. [3]. The C1—N2 bond distance [1.340(6) Å] is shorter than what expected for a single bond, indicating its resonance with C=O bond. There is one molecule in the asymmetric unit, which deviates very little from planarity with an r.m.s of only 0.0477 Å. Three rela-

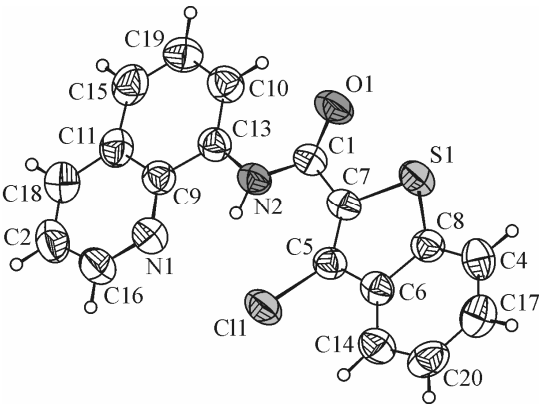

Fig. 1. ORTEP diagram of the title compound, with 50 % probability displacement ellipsoids. H atoms are shown as circled of arbitrary radii

Table 1

Crystal data and details of experiment for **2**

Molecular formula	$C_{18}H_{11}ClN_2OS$
M	338.80
T, K	290(2)
Crystal system	Monoclinic
a, *b*, *c*, Å	14.878(4), 8.4292(15), 25.461(7)
β, deg.	112.022(18)
V, Å^3	2960.20(12)
Space group	*C*2/*c*
Z	8
d_x, g/cm^3	1.520
Crystal size, mm	0.06×0.1×0.29
Color	Colorless
Crystal shape	Needle
Radiation, λ, Å	MoK_α, 0.71073
F(000)	1392
θ range, deg.	1.73—25.68
GOOF on F^2	1.035
h, *k*, *l* range	$-18 \le h \le 18$, $-10 \le k \le 10$, $-30 \le l \le 30$
Measured reflections	5452
Independent reflections	2717 (R_{int} = 0.0879)
Parameters refined	211
Final *R* for $I > 2\sigma(I)$	*R*1 = 0.0752, *wR*2 = 0.1517
R for all data	*R*1 = 0.1343, *wR*2 = 0.1764

Table 2

Hydrogen-bond geometry (Å, deg.)

D—H···*A*	D—H	*A*···H	D···*A*	D—H···*A*
N2—H1···Cl1	0.86(6)	2.47	3.13	134.3
N2—H1···N1	0.86(6)	2.11	2.65	120.2
O1···C10—H10	0.93	2.27	2.87	122.0
C14—H14···O1[1]	0.93	2.47	3.31	151.8

[1] Symmetry code (*i*) *x*–0.5, *y*+0.5, *z*.

tively strong non-classical intramolecular hydrogen bonds and a weaker intermolecular one are present in the structure (Table 2).

Three different types of interactions dominate in stabilizing the crystal structure packing (Figs. 2—4). One is intermolecular hydrogen bonding between hydrogen atoms from benzyl ring to wards an oxygen atom in the neighboring molecule with 2.47 Å distance between two molecular planes (C14—H14…O1^i, with i = *x*–0.5, *y*+0.5, *z*), thus giving rise to infinite stair-like layered chains (Fig. 2). Another is π-stacking, containing π—π and CH—π interactions (*e.g.* *Cg*1—*Cg*2^{ii} = = 3.762 Å, *Cg*2^{ii}—*Cg*3 = 3.795 Å, *Cg*3—*Cg*4^{ii} = = 3.846 Å, and C2—H2···*Cg*3iii = 3.875 Å, C18—H18···*Cg*1 = 3.921 Å, with *Cg*1 being the ring S1/C7/C5/C6/C8, *Cg*2 = N1/C9/C11/C18/C2/C16, *Cg*3 = C4/C8/C6/C14/C20/C17 and *Cg*4 = = C9/C11/C15/C19/C10/C13 with ii = 0.5–*x*, 0.5–*y*, –*z* and iii = –*x*, –*y*, –*z*, iv = 0.5–*x*, –0.5–*y*, –*z*, Fig. 4) between the inversion side by side symmetric molecules, which cause to hold these parallel neighboring layers together (Fig. 3). There are two different such parallel layers with an angle of 70.53°, that are in contact with each other by Van der Waals interactions, completing the entire structure packing (Fig. 4).

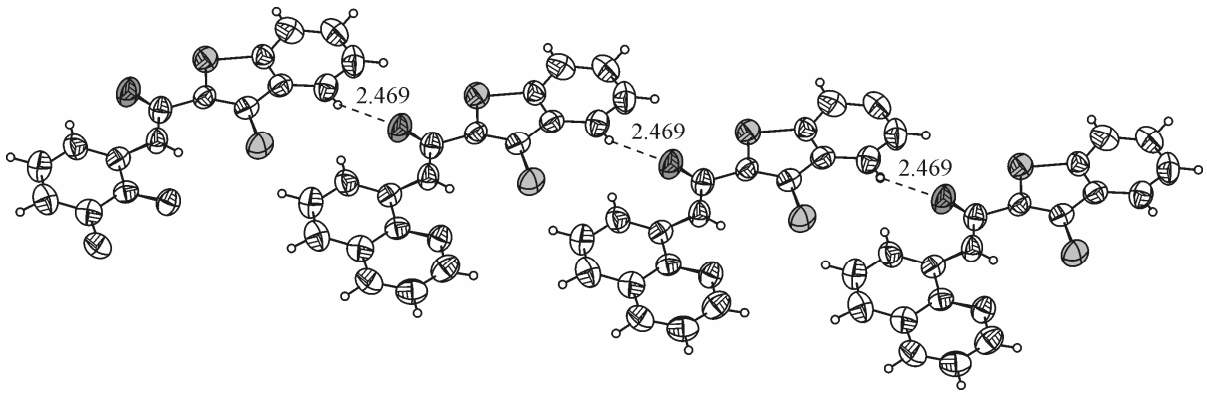

Fig. 2. Showing intermolecular hydrogen bonding and forming a chain

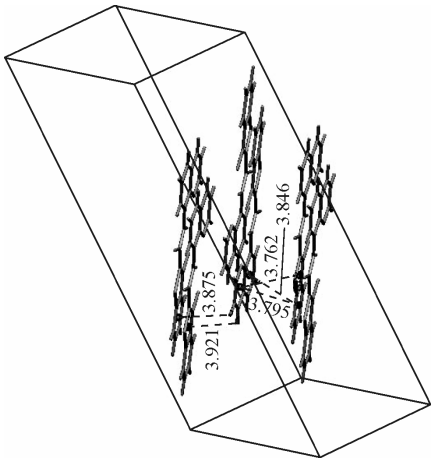

Fig. 3. π—π and CH—π interactions between infinite parallel layers

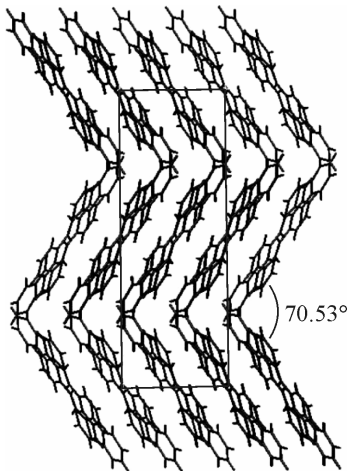

Fig. 4. Two different parallel layers with an angle of 70.53° between the least-squares planes defined by the two entire molecules

Single crystal X-ray structure determination confirmed the earlier proposed structure of 3-chloro-*N*-(8′-quinolyl)benzo[*b*]thiophene-2-carboxamide compound and also characterized by ^{1}HNMR, and Mass spectroscopy. Three kinds of interactions dominate in the three dimensional crystal structure. Relatively strong intermolecular hydrogen bonds stick the molecules to an infinite two-dimensional stair-like layered chains. These parallel chains are connected by π—π and CH—π interactions. There are two such parallel chains, which are in contact by Van der Waals interactions, stabilizing the crystal structure.

Acknowledgement. We gratefully acknowledge University of Tehran for financial support.

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