Journal of Molecular Structure 935 (2009) 47–52

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structural study on few co-crystals and a salt of quinoline derivatives having amide bond

Anirban Karmakar, Dipjyoti Kalita, Jubaraj B. Baruah *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781 039 Assam, India

ARTICLE INFO

Article history:
Received 22 May 2009
Received in revised form 18 June 2009
Accepted 18 June 2009
Available online 28 June 2009

Keywords:
Quinoline derivatives
Amides
Dihydroxyaromatics
Co-crystals
Perchlorate salt
Crystal structures

ABSTRACT

The *N*-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)-acetamide forms 1:1 co-crystals with aromatic diols namely 1,4-dihydroxybenzene, 1,5-dihydroxynaphthalene. In the later case co-crystal is formed in hydrated form. The hydrated form of co-crystal with 1,5-naphthalenediol has two symmetry independent host molecules in its unit cell, whereas such phenomenon in the co-crystal 1,4-dihydroxybenzene is not observed. The crystal structure of perchloric acid salt of (Quinolin-8-ylamino)-acetic acid is determined and this salt also shows two symmetry independent parent molecules in unit cell.

1. Introduction

The quinoline derivatives serve as template for guest binding and have interesting fluorescence properties [1]. The quinoline derivatives are acid sensitive and the understanding of the binding ability to guest molecule is of special interest [2]. It is also well known fact that the heterocyclic aromatic systems interact with hydroxy aromatics [3, 4] and can in turn effect the fluorescence emission [4]. Quinoline derivatives are also used as drugs for malaria, arthritis, and lupus [5–8]. Thus, the structural understanding on quinoline derivative having amide functionality is of importance. In this study we describe characterisation and structural aspects of two co-cystals (**2–3**) and a perchlorate salt of quinoline derivative (**4**) as shown in Fig. 1.

2. Experimental

The X-ray single crystal diffraction data were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H atoms, except those attached to nitrogen and oxygen atoms were placed at their calculated positions and refined in the isotropic approximation; some of the H atoms attached to nitrogen and oxygen were located in the difference Fourier maps, and refined with isotropic displacement coefficients, while rest of the H atoms attached to N and O were placed in their calculated position and refined (Table 1).

2.1. Synthesis of N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)-acetamide (*1*)

2-(4-Methoxyphenyl)ethylamine (1.51 g, 10 mmol) was dissolved in dry dichloromethane (20 ml) and triethylamine (1.01 g, 10 mmol) was added to it. The solution was stirred at 0 °C for 10 min after which bromoacetyl bromide (2.42 g, 12 mmol) was added dropwise to the stirred solution over a period of 30 min. The reaction mixture was then stirred overnight. Subsequently the reaction mixture was filtered to remove the hydrobromide salts, and the filtrate was collected. The filtrate was washed with water (10 ml), dried over sodium sulphate and then the solvent was removed under reduced pressure. The 2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide was obtained as a brown solid, the crude product was recrystallised from dichloromethane. The 2-Bromo-*N*-[2-(4-methoxy-phenyl)-ethyl] acetamide (2.72 g, 10 mmol), 8-hydroxyquinoline (1.45 g, 10 mmol) and K_2CO_3 (2.07 g, 15 mmol) was added to dry acetone (20 ml) in nitrogen atmosphere and the reaction mixture was stirred at 60 °C for 10 h. (The reaction

* Corresponding author. Tel.: +91 361 2582301; fax: +91 361 2690762.
E-mail address: juba@iitg.ernet.in (J.B. Baruah).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.06.029

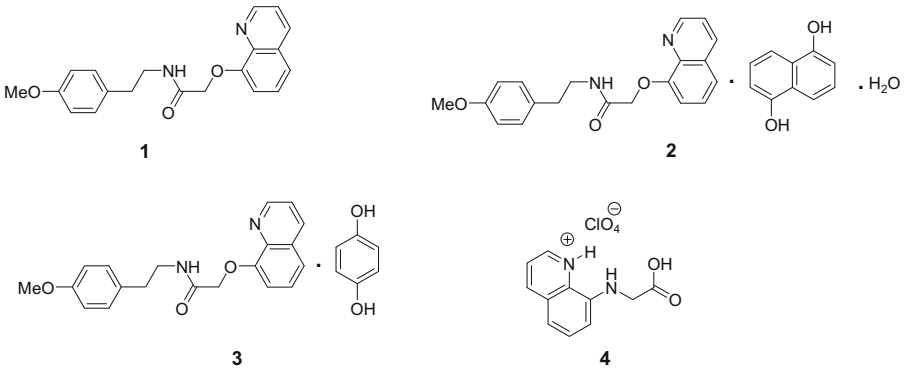

Fig. 1. Quinoline derivatives, co-crystals and a perchlorate salt.

progress was monitored at regular intervals using TLC). After completion of the reaction the solvent was removed under reduced pressure that gave a brown solid. The solids were washed with dilute sodium hydroxide solution (5%), and water and then extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulphate. Subsequent removal of the solvent gave the crude product, which was purified by chromatography (silica gel; hexane/ethyl acetate 3:2). Isolated yield 46%. IR (KBr, cm^{-1}): 3328(m), 2935(m), 1655(s), 1545(s), 1514(s), 1377(s), 1298(s), 1250(s), 1182(s), 1109(s), 1031(s), 819(s), 785(s), 614(s). Elemental analysis for $C_{20}H_{20}N_2O_3$: calculated C, 71.35; H, 5.95; N, 8.32; found C, 71.51; H, 5.39; N, 8.73. ^{1}H NMR ($CDCl_3$): 8.79(dd, J = 4 Hz,1.2 Hz, 1H), 8.15(dd, J = 8.4,1.6 Hz, 1H), 7.99(bs, 1H), 7.45(m, 3H), 7.08(dd, J = 6.8,1.6 Hz, 1H), 6.95(d, J = 8.4 Hz, 2H), 6.61(d, J = 8.8 Hz, 2H), 4.76(s, 2H), 3.73(s, 3H), 3.53(q, J = 13.2 Hz, 2H), 2.72(q, J = 13.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 168.6, 158.2, 153.8, 149.3, 140.0, 136.6, 131.1, 129.7, 127.0, 122.1, 121.5, 113.9, 111.6, 69.60, 55.3, 40.7, 34.8.

2.2. Co-crystal 2

N-[2-(4-Methoxy-phenyl)-ethyl]-2-(quinolin-8-yloxy)-acetamide (**1**) (0.1 g, 0.3 mmol) and 1,5-Naphthalenediol (0.05 g, 0.3 mmol) were dissolved in 10 ml of methanol. The resultant solution was then kept for crystallization. After 9 days reddish block type crystals were appeared. Yield: 61%. IR (KBr, cm^{-1}): 3472(bs), 3297(w), 2983(w), 1629(s), 1590(w), 1509(s), 1381(s), 1262(s), 1244(s), 1181(m), 1119(s), 937(w), 823(w), 780(s), 751(m). Elemental analysis for $C_{60}H_{58}N_4O_{11}$: calculated C, 71.21; H, 5.74; N, 5.54; found C, 71.56; H, 5.31; N, 5.36.^{1}H NMR($CDCl_3$): 9.36(s, 2H), 8.84(d, J = 4.4 Hz, 1H), 8.36(bs, 1H), 8.24(d, J = 8.4 Hz, 1H), 7.71(d, J = 8.4 Hz, 2H) 7.54(m, 3H), 7.21(m, 3H), 6.98(d, J = 7.2 Hz, 2H), 6.88(d, J = 7.2 Hz, 2H), 6.67(d, J = 8.4 Hz, 2H), 4.78(s, 2H), 3.74(s, 3H), 3.53(q, J = 14 Hz, 2H), 2.76(t, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): 168.5, 158.1, 152.7, 148.9, 136.1, 134.2, 130.4, 129.2, 126.5, 126.1, 124.4, 121.6, 121.3, 113.4, 112.9, 111.8, 108.3, 69.6, 54.8, 40.2, 34.3.

Table 1
The crystallographic parameters of **2**, **3** and **4.**

Compound code	**2**	**3**	**4**
CCDC No.	727137	727136	727134
Empirical formula	$C_{60}H_{58}N_4O_{11}$	$C_{26}H_{26}N_2O_5$	$C_{11}H_{11}ClN_2O_6$
Formula weight	1011.10	446.49	302.67
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P-1$	$P2(1)2(1)2(1)$	$P2(1)/c$
Unit cell dimension	a = 10.8194(5) Å,	a = 5.6277(2) Å	
	b = 14.2801(7) Å,	b = 18.3147(6) Å,	a = 8.4382(2) Å,
	c = 17.6702(9) Å,	c = 22.0626(7) Å,	b = 32.4641(10) Å
	α = 79.482(4)°,	$\alpha = \beta = \gamma$ = 90.00°	c = 9.4498(3) Å,
	β = 88.028(3)°,		$\alpha = \gamma$ = 90.00°,
	γ = 74.127(3)°		β = 104.458(2)°
Volume (Å^3)	2581.5(2)	2273.98(13)	2506.68(13)
Z	2	4	8
Density (calculated)	1.301 mg/m^3	1.304 mg/m^3	1.604 mg/m^3
Absorption coefficient	0.090 mm^{-1}	0.091 mm^{-1}	0.334 mm^{-1}
F(000)	1068	944	1248
Crystal size	0.12 × 0.24 × 0.48 mm^3	0.16 × 0.21 × 0.28 mm^3	0.33 × 0.27 × 0.21 mm^3
Theta range for data collection (°)	1.73–25.00	1.45–28.33	1.25–24.99
Index ranges	$-12 \leqslant h \leqslant 12$	$-7 \leqslant h \leqslant 7$	$-9 \leqslant h \leqslant 10$
	$-16 \leqslant k \leqslant 15$	$-23 \leqslant k \leqslant 24$	$-35 \leqslant k \leqslant 38$
	$-21 \leqslant l \leqslant 21$	$-29 \leqslant l \leqslant 24$	$-10 \leqslant l \leqslant 11$
Reflections collected	23784	25648	19700
Independent reflections	8740	5630	4387
Completeness to theta	96.2%	99.3%	99.7%
Absorption correction	None	None	None
Data/restraints/parameters	8740/0/698	5630/0/305	4387/0/385
Goodness-of-fit on F^2	1.030	1.040	1.260
Final R indices [I > 2sigma(I)]	0.0471	0.0487	0.0541
R indices (all data)	0.0836	0.0713	0.0756