

Synthesis of some carboxamid derivatives from substituted Quinoline-4-carbonyl chloride compounds

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Abstract:

In this paper some of carboxamide derivatives (A7 - A9) were prepared from the reaction of substitution quinoline-4-carbonyl isothiocyanate (A4-A6) with o-phenylenediamine in acetone and refluxed. On another hand, Compounds of quinoline-4-carbonyl chloride derivatives (A1-A3) were synthesis from the reaction of substituted quinolone -4-carboxylic acid compounds with thionyl chloride SOCl_2 . The prepared compounds were characterized on the basis of their microanalysis Fourier-transform infrared spectroscopy FT-IR.

Keywords: Carboxamide, Qunoline-4-carbonyl thiocyanate, Thionyl chloride, o- phenylenediamine, heterocyclic compounds.

تخليق بعض مشتقات الكربوكساميد من مركبات الكينولين 4- كلوريد الكربونيل البديلة

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الخلاصة:

في هذا البحث تم تحضير بعض مشتقات الكربوكساميد (A7 - A9) من تفاعل الاستعاضة عن الكينولين 4-كاربونيل ايزوثيوسيانات (A4-A6) مع o-phenylenediamine في الاسيتون. من ناحية أخرى ، تم تخليق مركبات مشتقات كلوريد الكينولين -4-كاربونيل (A1-A3) من تفاعل مركبات حمض الكينولون -4- الكربوكسيلية المستبدلة مع كلوريد الثيونيل SOCl_2 .

تم تمييز المركبات المحضرة على أساس التحليل الطيفي للأشعة تحت الحمراء Fourier-transform FT-IR.

المفاتيح: كاربوكساميد، كونولين -4-كاربونيل ثيوسيانات، كلوريد الثيونيل، أورثو- فينيلين ديامين، مركبات حلقة غير متجانسة.

Introduction:

In recent decades, quinolone consists of a benzene ring fused to the Alpha and beta positions of a pyridine ring ⁽¹⁾. It derives its name from the fact that it was first

obtained by heating the famous antimalarial alkaloid "quinine". Quinoline occurs in coal-tar, bone oil, and in angostura bark ^(2, 3). Quinoline is a slightly weaker base quinoline also undergoes nucleophilic substitution reactions ⁽⁴⁾. The quinolines are a class of anti-malarials that are distinct from the quinolones, which are a class of antibiotics. Certain quinolines are also used to treat disorders of the immune system ^(5, 6). On other hand, Quinoline is used in the manufacture of dyes, the preparation of hydroxyquinoline sulfate and niacin. It is also used as a solvent for resins and terpenes. ⁽⁷⁻⁹⁾.

Experimental section:

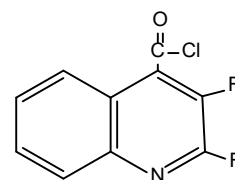
1. All chemicals used were supplied from Merck, Fluka and BDH-chemical Company.

2. Melting points were determined on Gallen Kamp melting points apparatus MFB-600-Olof, and Stuart Scientific Co. LTD melting point SMP1, in Baghdad University, College of Science and are uncorrected.

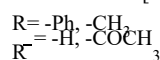
3. Fourier transform infrared spectra FT-IR were recorded using solid KBr discs by using Shimadzu FT-IR 8000 series Fourier transform infrared spectrophotometer, Ministry of Industry and Materials, Ibn Sina State Company.

Preparations .2.1

2.1.1 Synthesis of substituted quinoline-4-carbonyl chloride compounds (A1-A3):

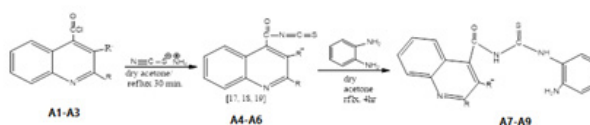


[14, 15, 16]



Thionyl chloride (2mL) was added drop wise to a mixture of quinoline-4-carboxylic acid derivatives about (0.0016 mol) (1, 2, 3 and 4) in (15 mL) of trichloromethane (CHCl₃). The mixture was refluxed until the evolution of all of hydrogen chloride gas. The acid chloride was used in the next reactions without further purification. The physical properties of prepared compounds in succession are M.P. (192-194, 141-143, 145-147), color (pale -brown), yields % (75, 78 and 60).

2.1.2. Synthesis of substituted quinoline-4-carbonyl isothiocyanate (A4-A6) and N-[(2-aminophenyl) carbamothioyl] substituted quinoline-4-carboxamide compounds derivatives (A7-A9) :⁽¹⁰⁾

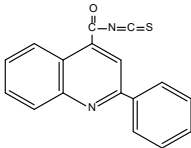
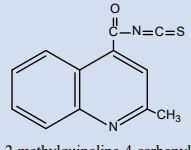
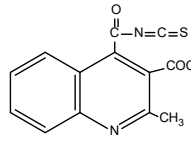
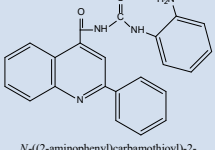
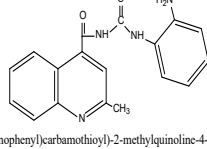
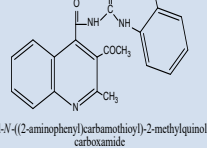


Scheme 1

(0.2gm, 0.0016 mol) from solution of substituted quinoline-4-carbonyl chloride compounds (A1-A3) (15 mL) acetone, was added dropwise to (0.13gm, 0.0016 mol) of suspension from ammonium thiocyanate in (5 mL) acetone and the reaction mixture was refluxed for 30 minutes. After cool-

ing at room temperature, a solution of o-phenylenediamine (0.1gm, 0.0016 mol) in acetone (5 mL) was added and the resulting mixture refluxed for (3 hours). The physical properties of the prepared compounds are shown in Table (1).

Table(1): The physical properties of compounds [A4-A9]

Comp. No.	Molecular formula	Melting Point	Color	Yield (%)
A4	 2-phenylquinoline-4-carbonyl isothiocyanate	128-130	white	-
A5	 2-methylquinoline-4-carbonyl isothiocyanate	116-118	Pale-yellow	-
A6	 3-acetyl-2-methylquinoline-4-carbonyl isothiocyanate	122-124	White	-
A7	 N-(2-aminophenyl)carbamothioyl-2-phenylquinoline-4-carboxamide	200 deco.	black	94
A8	 N-(2-aminophenyl)carbamothioyl-2-methylquinoline-4-carboxamide	240 deco.	Dark-brown	92
A9	 3-acetyl-N-(2-aminophenyl)carbamothioyl-2-methylquinoline-4-carboxamide	198 deco.	brown	88

3- Results and Discussion:

Refluxing of substituted quinoline-4-carbonyl chloride (A1-A3) fig. 1 and 2 respectively with ammonium thiocyanate in presence of acetone as a solvent for 30 minutes, gave substituted quinoline-4-carbonyl isothiocyanate (A4-A6) (fig.3, 4 and 5). The reaction was complete by adding solution of o-phenylenediamine in acetone produced substituted quinoline-4-carbonylthio urea compounds (A7-A9). The FT-IR for compounds A1 and A2 are shown in table 2.

The FT-IR spectra of respective compounds (A7, 8 and 9) (fig.6), (fig.7) and (fig.8) respectively exhibited bands at the rang (3321-3286) cm^{-1} (3275-3213) cm^{-1} , bands at (3406-3213) cm^{-1} due to ν NH and NH_2 str., (2067-2056) cm^{-1} due to ν (C=S str.) isothiocyanats group ⁽¹¹⁾. The spectra of compounds (A7-A9) show weak absorption at rang (2500-2490) cm^{-1} due to ν (SH str.); excess absorption at (1269) due to ν C=S str. stretching. The absorption of ν SH and C=S indicates thiol-thion tautomerism.

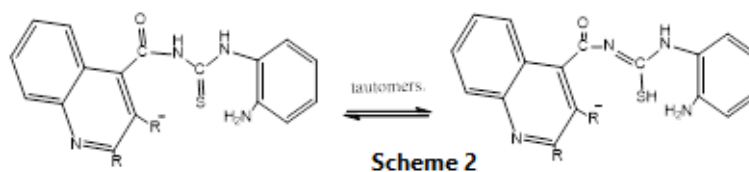


Table (2) FT-IR spectra of compounds (A1 and A2)

Comp. No.	Fig. No.	ν C=O acid chloride cm^{-1}	ν (C=N) cm^{-1}	ν C=C aromatic cm^{-1}	ν C-H aromatic cm^{-1}	ν C-H aliphatic cm^{-1}	ν C-Cl cm^{-1}
[A1]	(3-1)	1743	1616	1607	3016		752
[A2]	(3-2)	1762 (1720) carbonyl gr.	1635	1600	3070	(2924)asy. (2854) sym.	767

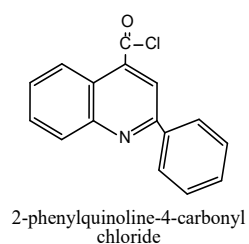
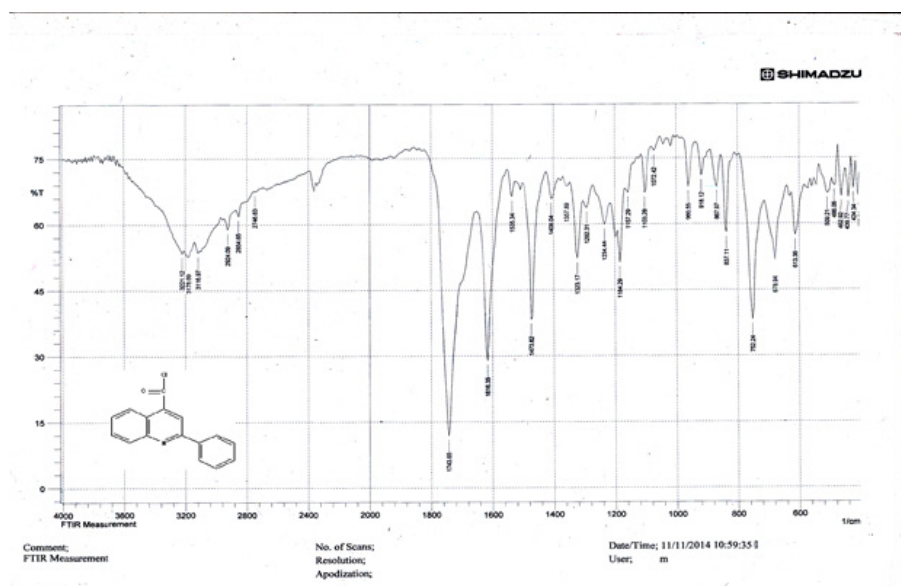


Figure (1)
Compound A1

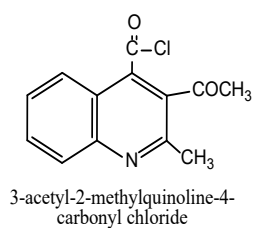
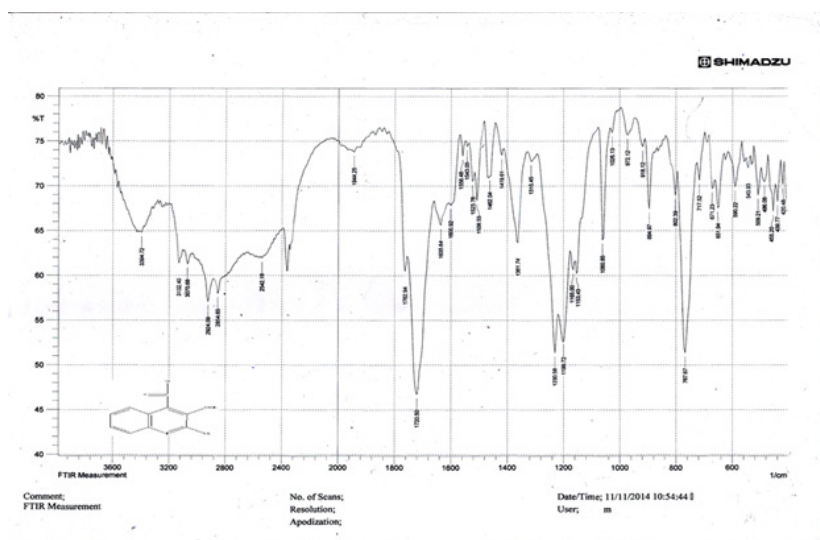


Figure (2)
Compound A2

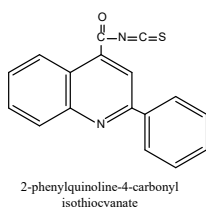
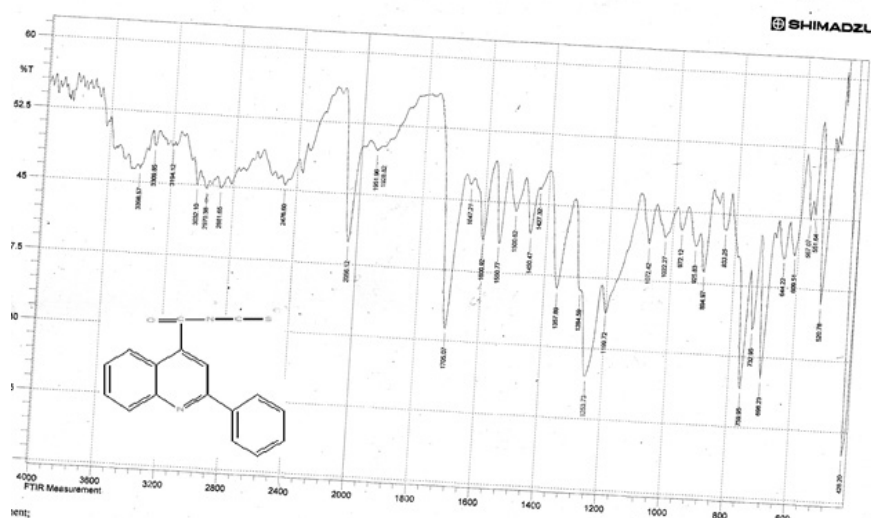


Figure (3)
Compound A4

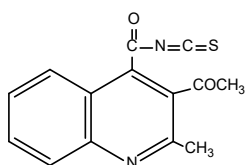
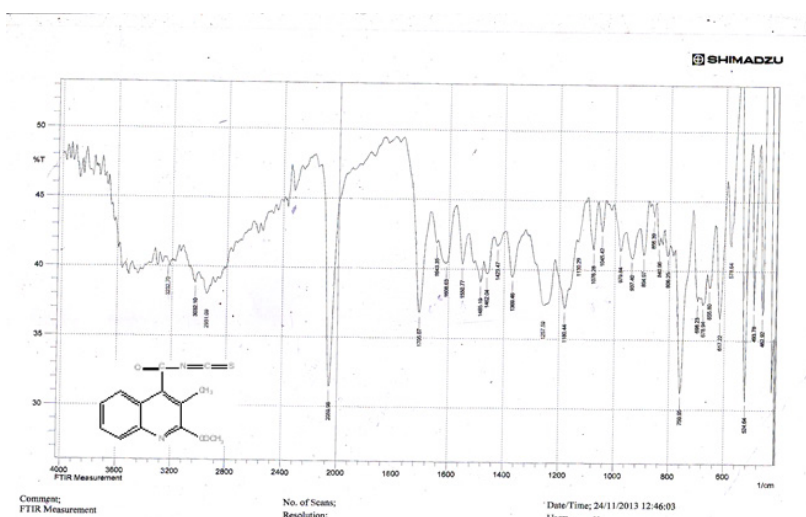
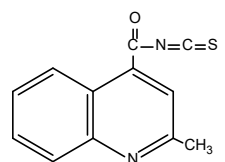
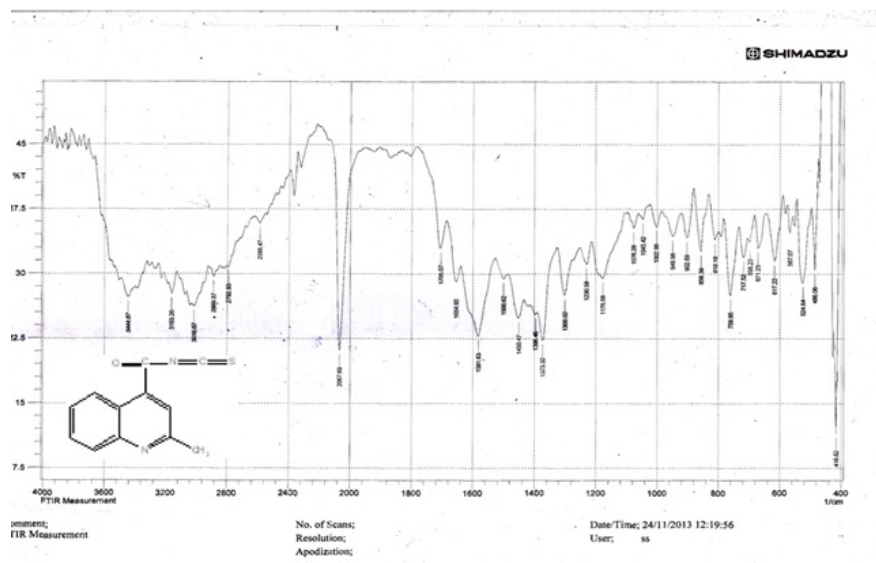
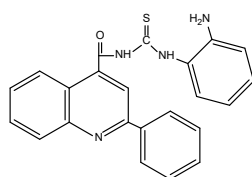
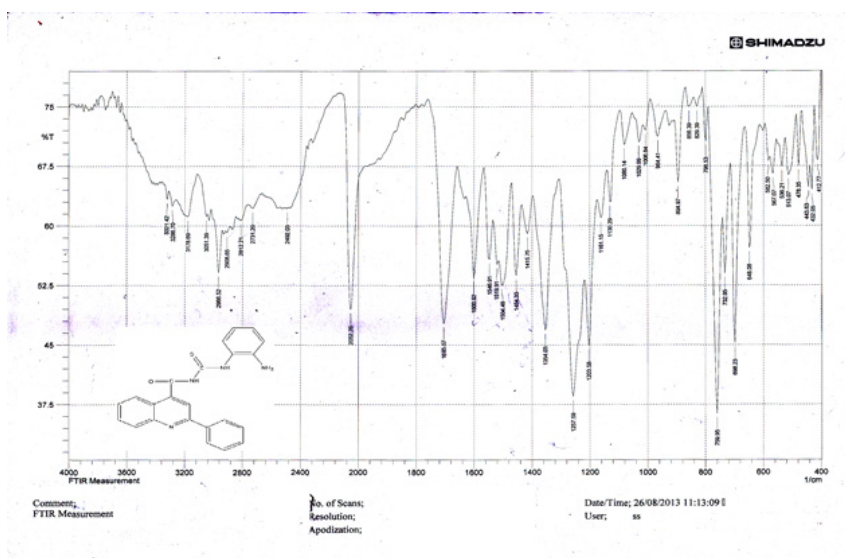


Figure (4)
Compound A5



2-methylquinoline-4-carbonyl isothiocyanate

Figure (5)
Compound A6



N-((2-aminophenyl)carbamothioyl)-2-phenylquinoline-4-carboxamide

Figure (6)
Compound A7

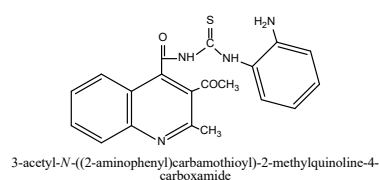
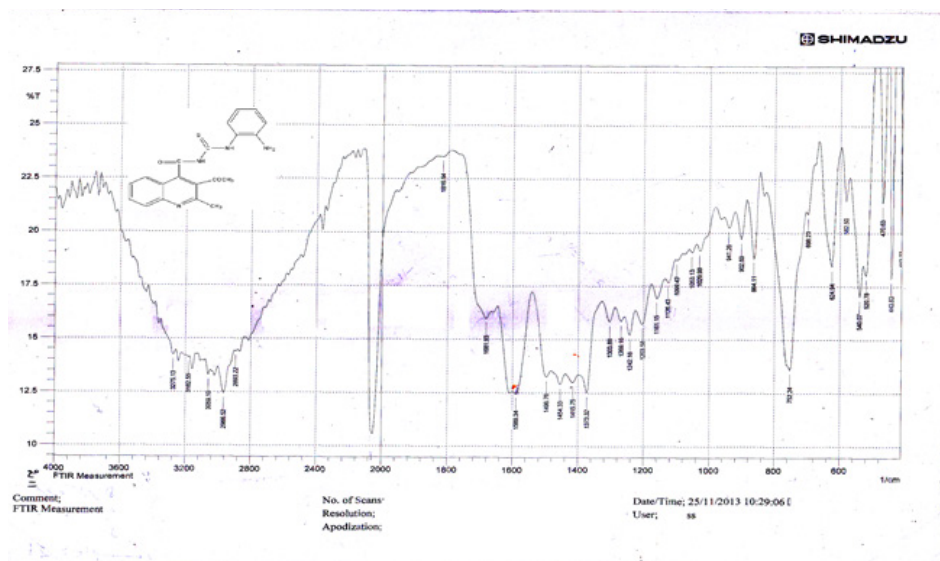


Figure (7)
Compound A8

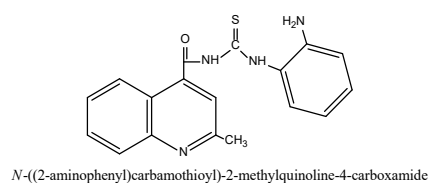
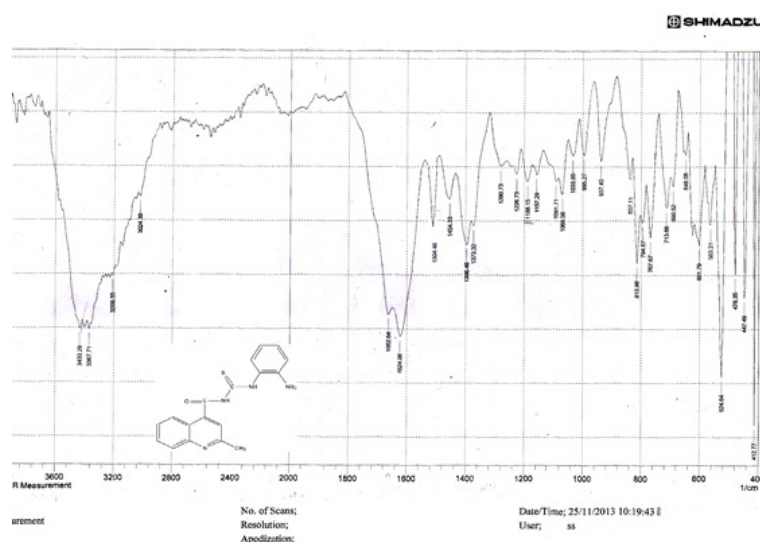


Figure (8)
Compound A9

Conclusions

New N-((2-aminophenyl)-N- 2 and 2, 3-substitutedquinoline-4-carbonylthio urea compounds were prepared by adding o-phenylenediamine in acetone to 2, 3-substitutedquinoline-4-carbonyl isothiocyanat.

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