

## New thienoyl-substituted pyrrolo[1,2-*c*]quinazoline derivatives

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### Abstract

By the reaction of quinazoline with  $\omega$ -bromo-2-acetylthiophene in methanol followed by treatment of the intermediate mixture of quaternary salts with unsymmetrical activated alkynes in propenoxide, 3-(2-thienoyl)pyrrolo[1,2-*c*]quinazoline derivatives were obtained. 3-(2-Thienoyl)-pyrrolo[1,2-*c*]quinazolines were also obtained by an alternative one-pot procedure directly from quinazoline,  $\omega$ -bromo-2-acetylthiophene and unsymmetrical activated alkynes in propenoxide, by one-pot, multi-step sequences of reactions. Heating the same mixture of quinazolinium salts in the presence of the strong base 1-(2-thienoyl)-2-(2-thienoyl)pyrrolo[1,2-*c*]quinazoline, an interesting inactivation product of the intermediate quinazolinium-3-thienoylmethylide was obtained.

**Keywords:** 1,3-Dipolar cycloadditions, pyrrolo[1,2-*c*]quinazoline, 3-(2-thienoylmethyl)-quinazolinium bromide, 3-(2-thienoylmethyl)-4-methoxy-3,4-dihydroquinazolinium bromide

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### Introduction

Pyrrolo[1,2-*c*]quinazoline derivatives have been the subject of considerable interest from the physical, chemical and biological points of view and an important topic for our laboratory.<sup>1-3</sup> In our previous works<sup>4-6</sup> we have presented new N-bridgehead heterocyclic compounds obtained from 1,3-dipolar cycloaddition reactions of the corresponding N-heterocyclic ylides with activated alkynes. It is well known that 1,3-dipolar cycloaddition reactions, conducted in a sequential manner, are efficient approaches for the synthesis of new interesting heterocyclic compounds, otherwise difficult to obtain.<sup>7-10</sup>

Herein we describe new thienoyl-substituted pyrrolo[1,2-*c*]quinazolines obtained from 1,3-dipolar cycloaddition reactions of the quinazolinium-thienoylmethylide, generated *in situ* from

the corresponding quaternary salt, with unsymmetrical activated alkynes. A theoretical study at a semiempirical AM1 level offers mechanistic insights into the stereochemical outcome.

## Results and Discussion

### Synthetic procedure

1,3-Dipolar cycloaddition reaction of quinazolinium-ylide with activated alkynes was considered for the synthesis of thienoyl-substituted pyrrolo[1,2-*c*]quinazolines. This method involves quaternary salts of quinazoline as intermediates.

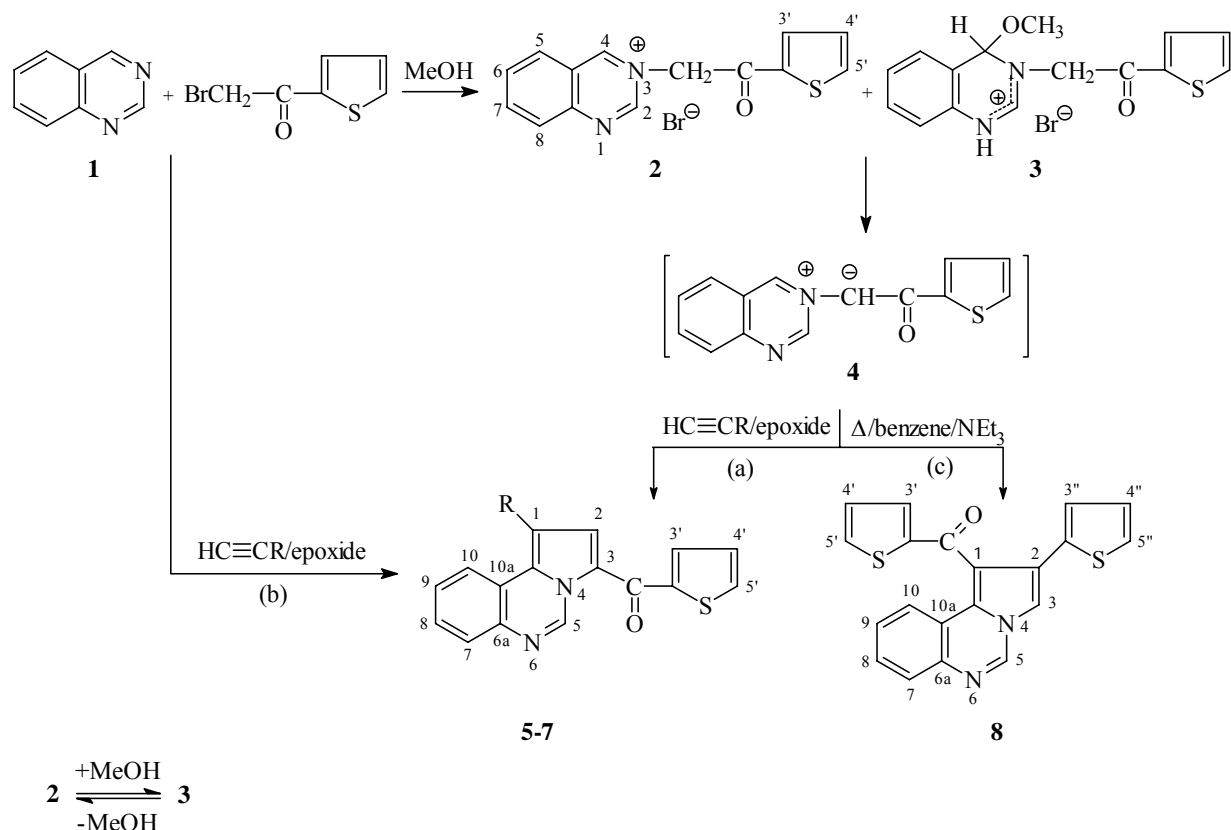
The quaternization reaction of the quinazoline **1** with  $\omega$ -bromo-2-acetylthiophene in methanol led to a mixture of 3-(2-thienoylmethyl)quinazolinium bromide **2** and 3-(2-thienoylmethyl)-4-methoxy-3,4-dihydroquinazolinium bromide **3** as the major reaction product, stabilized by a strong amidinique resonance (scheme 1). In chloroform no defined structure compound was obtained. The known high reactivity of 4-position of the quinazolinium salts towards nucleophilic reagents<sup>11,12</sup> is probably responsible for the formation of 3-(2-thienoylmethyl)-4-methoxy-3,4-dihydro-quinazolinium bromide **3** from the 3-(2-thienoylmethyl)quinazolinium bromide **2**. In solution of methanol there is equilibrium between the two quinazolinium salts **2** and **3**.<sup>13</sup>

The treatment of the mixture of quinazolinium salts **2** and **3** with unsymmetrical activated alkynes such as ethyl propiolate, 1-butyne-3-one and phenylethynyl ketone, in propenoxide as acid acceptor and reaction solvent, led to new 3-(2-thienoyl)pyrrolo[1,2-*c*]quinazolines **5-7** (scheme 1 - route a). Only one regioisomer was obtained in each reaction. They are the expected 1,3-dipolar cycloaddition compounds of the intermediate quinazolinium-3-thienoylmethylide **4**, generated *in situ* from the quinazolinium salt, with activated alkynes.

3-(2-Thienoyl)pyrrolo[1,2-*c*]quinazolines **5-7** were also synthesized by an alternative one-pot procedure directly from quinazoline,  $\omega$ -bromo-2-acetylthiophene and the corresponding activated alkynes in an epoxide (scheme 1 – route b). The reaction mechanism probably implies the intermediate formation of the quinazolinium salt **2** which, in a further step, reacts with the alkyne *via* quinazolinium-3-(2-thienoyl)methylide **4**. These are all one-pot, multi-step sequences of reactions.<sup>14</sup>

When the same mixture of quinazolinium salts **2** and **3** was heated in benzene, in the presence of an equimolecular amount of triethylamine, a new compound, 1-(2-thienoyl)-2-(2-thienyl)-pyrrolo[1,2-*c*]quinazoline **8**, was obtained (scheme 1 – route c).

The formation of the 1-(2-thienoyl)-2-(2-thienyl)pyrrolo[1,2-*c*]quinazoline **8** seems to be the result of an inactivation process of the intermediate quinazolinium-3-(2-thienoyl)methylide **4**. A similar structure, identified as 1-benzoyl-2-phenylpyrrolo[1,2-*c*]quinazoline, was obtained by heating quinazolinium-3-benzoylmethylide in benzene in the presence of triethylamine.<sup>15</sup> The mechanism probably involves the nucleophilic attack of the ylide carbanion to the high reactive carbon atom from 4 position of the quaternary salt **2** with the elimination of one equivalent of quinazoline.<sup>15</sup>



**Scheme 1.** The reactions scheme.

**Table 1.** New thienoyl-substituted pyrrolo[1,2-*c*]quinazoline derivatives

Compound	R	Yield (%)		
		Route a	Route b	Route c
<b>5</b>	CO <sub>2</sub> Et	34	32	-
<b>6</b>	COMe	33	26	-
<b>7</b>	COPh	31	28	-
<b>8</b>	-	-	-	30

The structures of all thienoyl-substituted pyrrolo[1,2-*c*]quinazolines **5-8** were confirmed by microanalysis, IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectral data.

The IR spectra of compounds **5-7** exhibit the characteristic carbonyl absorption bands at about 1601-1609 cm<sup>-1</sup>. The IR spectrum of the compound **8** reveals the carbonyl absorption band at 1632 cm<sup>-1</sup> due to the nearby position of thienyl group.

All <sup>1</sup>H-NMR spectra of the compounds **5-8** show the signals of the qinazoline ring H-5, at δ 9.52-10.26, as characteristic singlets. The <sup>1</sup>H-NMR spectra of 3-(2-thienoyl)pyrrolo[1,2-*c*]quinazolines **5-7** exhibit the characteristic singlet signals of the pyrrolo ring H-2 at different chemical shifts according to the different

nearby substituents and the signals for the protons of different substituents from position 1 of the pyrrolo ring appear at normal chemical shifts.

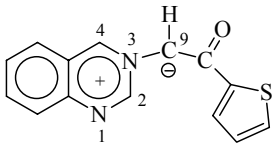
The  $^{13}\text{C}$ -NMR spectra of **5-8** show characteristic signals for the carbonyl carbon at  $\delta$  176.46-178.62 (CO from thienoyl group),  $\delta$  191.74 (CO from benzoyl group) and  $\delta$  163.7 (CO from carboxy group).

### Theoretical study

The cycloaddition reactions of intermediate quinazolinium-3-(2-thienoyl)methylide **4** with 1-butyne-3-one, phenylethyne ketone and ethyl propiolate have been studied theoretically by performing semiempirical calculations with full optimization of the molecules at the AM1 level using the HyperChem Program.<sup>16,17</sup>

Atomic charges, energies and molecular frontier orbitals for all the reactive centers involved in these reactions are presented in Table 2.

**Table 2.** Atomic charges, energies and frontier molecular orbitals for all reagents

Compounds	FMO	OE (eV)	Orbital coefficients / Total charges (C)				
			N-1	C-2	N-3	C-4	C-9
	HOMO	-7.8429	-0.0466	0.2005	0.0457	0.4559	-0.6602
	LUMO	-1.1781	0.3175	-0.1450	-0.3742	0.4149	0.3238
	Q		-0.076	-0.059	0.152	-0.206	-0.413
			C-1	C-2			
$\text{HC}\equiv\text{C}^2-\text{C}^1(\text{O})-\text{CH}_3$	HOMO	-1.3750	0.0498	0.0544			1)
	LUMO	0.1456	0.3876	-0.5657			
	Q		-0.183	-0.096			
$\text{HC}\equiv\text{C}^2-\text{C}^1(\text{O})-\text{COOC}_2\text{H}_5$	HOMO	-1.1792	$2.9 \cdot 10^{-7}$	$-1.3 \cdot 10^{-6}$			2)
	LUMO	0.0490	0.3208	-0.5106			
	Q		-0.230	-0.125			
$\text{HC}\equiv\text{C}^2-\text{C}^1(\text{O})-\text{C}_6\text{H}_5$	HOMO	-9.9880	-0.0030	-0.0019			3)
	LUMO	-0.6018	0.1397	-0.2891			
	Q		-0.217	-0.130			

These calculations showed a small positive charge of the ylide nitrogen atom N3. It means that the positive charge is rather delocalized on all the atoms of the quinazoline ring. The ylide carbon atom C9 is negatively charged meaning that the formal negative charge for the ylidic carbanion is less delocalized and this demonstrate a nucleophilic character of ylidic carbon atom. The total atomic charges of cyclic carbon atoms C2 and C4, adjacent to the ylide nitrogen atom, have small negative charges and could be explained by the resonance interaction between the heterocycle and carbanion.

The  $\Delta E$  of interaction  $\text{HOMO}_{\text{ylide}}\text{-LUMO}_{\text{dipolarophile}}$  and  $\text{HOMO}_{\text{dipolarophile}}\text{-LUMO}_{\text{ylide}}$  were calculated. The  $\text{HOMO}_{\text{ylide}}\text{-LUMO}_{\text{dipolarophile}}$  interactions show smaller energy gaps than the opposite  $\text{HOMO}_{\text{ethyl propiolate}}\text{-LUMO}_{\text{ylide}}$  interactions, which is consistent with ylide-HOMO controlled reactions.

In accordance with FMO postulates,<sup>18,19</sup> once the HOMO/LUMO pair closer in energy has been identified, the new bonds will be formed between centres with atomic orbital coefficients with the same sign, the relative sizes of the possible pairs of coefficients predicting the regioselectivity. In the presented reactions of the quinazolinium-thienoylmethylide with unsymmetrical substituted alkynes only one regioisomer was formed, the one in which the ylide carbanion makes the new bond with the most electrophilic carbon atom from alkyne. Thus, the regiochemistry predicted by the FMO analysis is in agreement with the experimental facts.

## Conclusions

The quaternization reaction of the quinazoline with  $\omega$ -bromo-2-acetylthiophene in methanol led to a mixture of 3-(2-thienoylmethyl)quinazolinium bromide and 3-(2-thienoylmethyl)-4-methoxy-3,4-dihydroquinazolinium bromide. The formation of 3-(2-thienoylmethyl)-4-methoxy-3,4-dihydroquinazolinium bromide could be explained by the high reactivity of 4-position of 3-(2-thienoylmethyl)quinazolinium bromide.

New 3-(2-thienoyl)pyrrolo[1,2-*c*]quinazoline derivatives were obtained by the reaction of the intermediate mixture of quaternary salts with unsymmetrical activated alkynes in propenoxide, probably by the means of 1,3-dipolar cycloaddition reaction of the corresponding quinazolinium-3-(2-thienoyl)methylide, generated *in situ* from the quinazolinium quaternary salt, in the presence of the propenoxide as acid acceptor.

3-Thienoyl-pyrrolo[1,2-*c*]quinazoline derivatives were also obtained by an alternative one-pot procedure directly from quinazoline,  $\omega$ -bromo-2-acetylthiophene and activated alkynes in propenoxide, by one-pot, multi-step sequences of reactions.

An interesting inactivation product of intermediate quinazolinium-3-(2-thienoyl)methylide, with the structure of 1-(2-thienoyl)-2-(2-thienyl)pyrrolo[1,2-*c*]quinazoline, was obtained.

## Experimental Section

**General Procedures.** Melting points were determined on a Boetius apparatus and are uncorrected. The IR spectra (in KBr) were recorded on a Nicolet Impact 410 spectrometer. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded at ambient temperature on a Varian Gemini 300BB instrument, operating at 300 MHz for  $^1\text{H}$ - and 75 MHz for  $^{13}\text{C}$ -NMR. Chemical shifts ( $\delta$ ) are given from TMS (0 ppm) as internal standard for  $^1\text{H}$ -NMR, and  $^{13}\text{CDCl}_3$  (77.0 ppm) for  $^{13}\text{C}$ -NMR. For unambiguous assignment  $^1\text{H}$ -decoupling, COSY ( $^1\text{H}$ - $^1\text{H}$ ) and COSY ( $^1\text{H}$ - $^{13}\text{C}$ ) were used. Elemental analyses were determined on COSTECH Instruments EAS32 (Center for

Organic Chemistry, Spl. Independentei 202B, Bucharest 060023, Romania). Satisfactory microanalyses for all new compounds were obtained. Quinazoline, 1-butyn-3-one, phenylethynyl ketone and ethyl propiolate were commercially available products. Propyleneoxide, technical grade (Oltchim), was used as epoxide.  $\omega$ -Bromo-2-acetylthiophene was obtained by the bromination of 2-acetylthiophene.<sup>20</sup>

**Quinazolinium salts.** A mixture of 1.3 g (10 mmol) quinazoline and (2.06 g, 10 mmol)  $\omega$ -bromo-2-acetylthiophene in 50 mL methanol was heated at reflux temperature for 10 hours. The mixture was cooled and left overnight at cool. The solid product was filtered and washed with a small quantity of methanol to give a mixture of quinazolinium salts **2** and **3** (1/2) as white-gray crystals (1.6 g, 43%), m.p. 195-198 °C (a small part) and 220-234°C (the major part). IR (KBr, cm<sup>-1</sup>): 1674 (v<sub>CO</sub>). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) for **2**: 2.98 (s, 3H, Me from the methanol, as a result of the equilibrium between **2** and **3**), 5.41 (d, 1H, *J* 18.0 Hz, 1H from CH<sub>2</sub>), 5.55 (d, 1H, *J* 18.0 Hz, 1H from CH<sub>2</sub>), 6.41 (s, 1H, 4-H), 7.35-7.60 (m, 5H, 5, 6, 7, 4', 5'-H), 8.22 (dd, 1H, *J* 2.9 Hz, *J* 1.1 Hz, 3'-H), 8.23 (dd, 1H, *J* 7.9 Hz, *J* 1.1 Hz, 8-H), 8.98 (s, 1H, 2-H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) for **2**:  $\delta$  185.31(C=O), 151.77 (CH-2), 139.86 (C<sub>q</sub>), 136.58 (CH), 134.77 (CH), 130.66 (C<sub>q</sub>), 129.33 (C<sub>q</sub>), 128.61 (CH), 128.18 (CH), 121.27 (C<sub>q</sub>), 117.20 (CH), 83.05 (CH), 56.50 (CH<sub>2</sub>), 50.90 (OMe). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) for **3**: 3.16 (s, 3H, OMe), 5.48 (s, 2H, CH<sub>2</sub>), 6.19 (s, 1H, 4-H), 7.35-7.60 (m, 5H, 5, 6, 7, 4', 5'-H), 8.21 (dd, 1H, *J* 2.9 Hz, *J* 1.1 Hz, 3'-H), 8.28 (dd, 1H, *J* 7.7 Hz, *J* 1.1 Hz, 8-H), 8.80 (s, 1H, 2-H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>,  $\delta$  ppm, *J* Hz) for **3**:  $\delta$  185.46 (C=O), 150.01 (CH-2), 139.93 (CH), 136.43 (CH), 134.61 (CH), 131.28 (CH), 130.43 (CH), 129.19 (CH), 128.38(CH), 127.65 (CH), 117.32 (C<sub>q</sub>), 116.86 (CH), 77.19 (CH), 55.78 (CH<sub>2</sub>), 48.54 (OMe).

### 3-(2-Thienoyl)pyrrolo[1,2-*c*]quinazolines (5-7)

**General procedure (a).** To the suspension of the obtained mixture of quinazolinium *N*-methylthienoyl salts **2** and **3** (1.835 g, about 5 mmol) in propenoxide (50 mL) an unsymmetrical activated alkyne (7.5 mmol) was added. The reaction mixture was stirred at room temperature for 10-12 days, and then the solution was concentrated under reduced pressure. The residue was treated with methanol (10 mL) and kept overnight at cool. The solid was filtered and washed with cold methanol and then with diethyl ether. All crude products were recrystallized from chloroform / methanol.

**General procedure (b).** To a solution of 1.3 g (10 mmol) quinazoline in 50 mL propenoxide was added 2.05g (10 mmol)  $\omega$ -bromo-2-acetylthiophene and 15 mmol of alkyne. The mixture was stirred for 20 days at room temperature, then it was concentrated under reduced pressure and kept overnight at cool. The solid was filtered and washed with methanol and then diethyl ether. All crude products were recrystallised from chloroform-diethyl ether.

The yields are shown in Table 1. The melting points and spectral data are given below.

**1-Carboethoxy-3-(2-thienoyl)pyrrolo[1,2-*c*]quinazoline (5).** Yellow crystals, m.p. 130-131 °C; IR (KBr, cm<sup>-1</sup>): 1609, 1716 (v<sub>CO</sub>). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.45 (t, 3H, *J* 7.2 Hz, CH<sub>3</sub>), 4.43 (q, 2H, *J* 7.2 Hz, CH<sub>2</sub>), 7.24 (dd, 1H, *J* 5.0 Hz, *J* 3.8 Hz, 4'-H), 7.63 (ddd, 1H, *J* 1.4 Hz, *J* 7.1 Hz, *J* 7.3 Hz, 8/9-H), 7.73 (ddd, 1H, *J* 1.4 Hz, *J* 8.2 Hz, *J* 3 Hz, 9/8-H), 7.74 (dd, 1H, *J* 1.1 Hz, *J* 5.0 Hz, 5'-H), 7.88 (dd, 1H, *J* 3.8 Hz, *J* 1.1 Hz, *J* 3.8 Hz, 3'-H), 7.94 (dd, 1H, *J* 1.2 Hz, *J* 8.1 Hz, 7/10-H), 9.07 (s, 1H, 2-H), 9.66 (dd, 1H, *J* 1.4 Hz, *J* 8.3 Hz,

10/7-H), 10.13 (s, 1H, 5-H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 176.46 (C=O), 163.70 ( $\text{COOC}_2\text{H}_5$ ), 143.63 ( $\text{C}_q$ ), 141.02 ( $\text{C}_q$ ), 138.19 (CH), 136.59 ( $\text{C}_q$ ), 133.38 (CH), 133.02 (CH), 131.12 (CH), 128.36 (CH), 128.23 (CH), 128.06 (CH), 127.74 (CH), 123.19 ( $\text{C}_q$ ), 119.96 ( $\text{C}_q$ ), 110.74 ( $\text{C}_q$ ), 60.96 ( $\text{CH}_2\text{CH}_3$ ), 14.46 ( $\text{CH}_2\text{CH}_3$ ).  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$ : calcd. C 65.13, H 4.03, N 7.99, S 9.15%, found C 65.01, H 3.85, N 8.18, S 9.07%.

**1-Acetyl-3-(2-thienoyl)pyrrolo[1,2-c]quinazoline (6).** Yellow crystals, m.p. 192-194°C; IR (KBr,  $\text{cm}^{-1}$ ): 1601, 1667 ( $\nu_{\text{CO}}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 2.74 (s, 3H), 7.26 (dd, 1H,  $J$  3.7 Hz,  $J$  5.1 Hz, 4'-H), 7.68 (ddd, 1H,  $J$  1.5 Hz,  $J$  7.1 Hz,  $J$  7.3 Hz, 8/9-H), 7.78 (dd, 1H,  $J$  1.2 Hz,  $J$  5.1 Hz, 5'-H), 7.80 (td, 1H,  $J$  1.5 Hz,  $J$  7.1 Hz, 9/8-H), 7.90 (dd, 1H,  $J$  1.2 Hz,  $J$  3.7 Hz, 3'-H), 8.00 (dd, 1H,  $J$  1.4 Hz,  $J$  8.1 Hz, 7-H), 8.05 (s, 1H, 2-H), 9.72 (dd, 1H,  $J$  1.5 Hz,  $J$  8.4 Hz, 10-H), 10.20 (s, 1H, 5-H).  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ : calcd. C 67.48, H 3.77, N 8.74, S 10%, found C 67.21, H 3.85, N 8.55, S 9.83%.

**1-Benzoyl-3-(2-thienoyl)pyrrolo[1,2-c]quinazoline (7).** Yellow crystals, m.p. 210-212°C, IR (KBr,  $\text{cm}^{-1}$ ): 1607, 1647 ( $\nu_{\text{CO}}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 7.17 (dd, 1H,  $J$  4.9 Hz,  $J$  3.7 Hz, 4'-H), 7.54 (dd, 2H,  $J$  7.3 Hz,  $J$  7.0 Hz, phenyl 3''-, 5''-H), 7.59 (td, 1H,  $J$  8.4 Hz,  $J$  1.2 Hz, 9-H), 7.64 (tt, 1H,  $J$  1.2 Hz,  $J$  7.0 Hz,  $J$  7.3 Hz, phenyl 4''-H), 7.70 (dd, 1H,  $J$  4.9 Hz,  $J$  = 1.2 Hz, 5'-H), 7.75 (td, 1H,  $J$  8.4 Hz,  $J$  1.4 Hz, 8-H), 7.78 (s, 1H, 2-H), 7.79 (dd, 1H,  $J$  1.2 Hz,  $J$  3.7 Hz, 3'-H), 7.96 (dd, 2H,  $J$  7.0 Hz,  $J$  1.2 Hz, phenyl 2''-, 6''-H), 8.02 (dd, 1H,  $J$  8.4 Hz,  $J$  1.2 Hz, 7-H), 8.94 (dd, 1H,  $J$  8.4 Hz,  $J$  1.2 Hz, 10-H), 10.26 (s, 1H, 5-H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 191.74 (benzoyl C=O), 176.48 (thienoyl C=O), 143.38 (6a- $\text{C}_q$ ), 140.94 (4a- $\text{C}_q$ ), 138.97 (3- $\text{C}_q$ ), 138.16 (5-C), 136.34 (1'- $\text{C}_q$ ), 133.48 (4''-C), 133.01 (3'-C), 132.97 (5'-C), 131.36 (2-C), 129.96 (2''-, 6''-C), 128.62 (4'-C), 128.61 (3''-, 5''-C), 128.59 (9-C), 128.34 (8-C), 128.10 (7-C), 126.30 (10-C), 122.96 (1''- $\text{C}_q$ ), 119.93 (1- $\text{C}_q$ ), 117.83 (10a- $\text{C}_q$ ).  $\text{C}_{23}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ : calcd. C 72.23, H 3.69, N 7.32%, S 8.38%, found C 72.32, H 3.58, N 7.41, S 8.14%.

**1-(2-Thienoyl)-2-(2-thienyl)pyrrolo[1,2-c]quinazoline (8).** A suspension of 1.835 g (about 5 mmol) quinazolinium *N*-methylthienoyl quaternary salts **2** and **3** in 30 mL benzene was treated with 1 mL of triethylamine. The mixture was heated at reflux temperature for 30 minutes. The solid precipitated was filtered, washed with water and methanol. The crude product was recrystallized from chloroform-methanol. The yield for **8** is shown in Table 1; mustard crystals, m.p. 175-177°C, IR (KBr,  $\text{cm}^{-1}$ ): 1632 ( $\nu_{\text{CO}}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 6.75 (dd, 1H,  $J$  3.9 Hz,  $J$  5.0 Hz, 4''-H), 6.81 (dd, 1H,  $J$  3.9 Hz,  $J$  5.0 Hz, 4'-H), 6.85 (dd, 1H,  $J$  1.2 Hz,  $J$  = 3.9 Hz, 3''-H), 7.03 (d, 1H,  $J$  0.6 Hz, 3-H), 7.17 (dd, 1H,  $J$  1.2 Hz,  $J$  5.0 Hz, 5''-H), 7.26 (dd, 1H,  $J$  1.2 Hz,  $J$  3.9 Hz, 3'-H), 7.47 (dd, 1H,  $J$  1.2 Hz,  $J$  5.0 Hz, 5'-H), 7.51 (td, 1H,  $J$  1.8 Hz,  $J$  7.2 Hz,  $J$  8.1 Hz, 9/8-H), 7.56 (td, 1H,  $J$  1.8 Hz,  $J$  7.2 Hz,  $J$  8.1 Hz, 8/9-H), 7.83 (dd, 1H,  $J$  1.7 Hz,  $J$  8.1 Hz, 7-H), 8.00 (dd, 1H,  $J$  2.2 Hz,  $J$  = 7.2 Hz, 10-H), 9.52 (bs, 1H, 5-H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 178.62 (C=O), 144.10 ( $\text{C}_q$ ), 139.16 ( $\text{C}_q$ ), 138.02 ( $\text{C}_q$ ), 136.22 ( $\text{C}_q$ ), 134.21 (CH), 133.55 (CH), 133.42 (CH), 129.84 (CH), 129.50 (CH), 128.53 (CH), 128.22 (CH), 127.52 (CH), 126.82 (CH), 122.73 (CH), 121.20 ( $\text{C}_q$ ), 120.02 ( $\text{C}_q$ ), 103.44 ( $\text{C}_q$ ), 103.34 ( $\text{C}_q$ ).  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{OS}_2$ : calcd. C 66.64, H 3.35, N 7.77, S 17.79%, found C 66.71, H 3.29, N 7.65, S 17.33%.

## References

1. Paolini, J. A. *Special Topics in Heterocyclic Chemistry*, Weissberger, A., Taylor, E. C., Eds., John Wiley & Sons: New York, 1977, pp 1-115.
2. Georgescu, E.; Georgescu, F.; Gheorghiu, M.; Georgescu, E. G.; Petrovanu, M. *Rev. Roum. Chim.* **1985**, *30*, 611.
3. Georgescu, F.; Georgescu, E.; Draghici C.; Caproiu, M. T. *Rev. Roum. Chim.* **1997**, *42*, 17.
4. Georgescu, E.; Georgescu, F.; Roibu, C.; Draghici, C.; Caproiu, M. T. *Rev. Roum. Chim.* **2001**, *46*, 357.
5. Georgescu, E.; Georgescu, F.; Roibu, C.; Iuhas, P. C.; Draghici, C.; Caproiu, M. T. *Rev. Roum. Chim.* **2002**, *47*, 885.
6. Georgescu, E.; Draghici, C.; Iuhas, P. C.; Georgescu, F. *Arkivoc* **2005**, (x), 95.
7. Zugravescu, I.; Petrovanu, M. *N-Ylides Chemistry*, McGraw-Hill Internat., 1976.
8. Padwa, A. Ed., *1,3-Dipolar Cycloaddition Chemistry*, John Wiley & Sons: New York, 1984; Vols. 1 and 2.
9. Mangalagiu, I. I.; Mangalagiu, G.; Deleanu, C.; Drochioiu, G.; Petrovanu, M. *Tetrahedron* **2003**, *59*, 111.
10. Caprosu, M.; Zbancioc, Ghe.; Moldoveanu, C.; Mangalagiu, I. I. *Collect. Czech. Chem. Commun.* **2004**, *39*, 426.
11. Armarego, W. L. F. *J. Chem. Soc.* **1962**, 561.
12. Perrin, D. D. *J. Chem. Soc.* **1965**, 5590.
13. Georgescu, E.; Georgescu, F.; Chiraleu, F.; Petrovanu, M. *Rev. Roum. Chim.* **1983**, *28*, 841.
14. Tietze, L. F.; Beifuss, U. *Angew. Chem.* **1993**, *105*, 137.
15. Georgescu, E.; Georgescu, F.; Gheorghiu, M.; Filip, P. I.; Petrovanu, M. *Rev. Roum. Chim.* **1986**, *31*, 365.
16. Dewar, M. J. S.; Zoebish, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
17. (a) *Hyperchem User Manual*, Release 4.5., Ontario, Hypercube Inc., 1995. (b) Stewart, J. J. P. QCPE 689, MOPAC93 Fujitsu.
18. Pople, J.; Beveridge, B. L. In *Approximate Molecular Orbital Theory*, McGraw Hill, 1970.
19. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, John Wiley & Sons: New York, 1976.
20. Kipins, F.; Soloway, H; Ornfelt, J. *J. Am. Chem. Soc.* **1949**, *71*, 10.