

## PHOTOSYNTHESIS OF HETEROPOLYCYCLIC QUINOLONES

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**Abstract-** Four new anilidoquinolones; 9-anilidobenzo[*b*]thieno[2,3-*c*]quinolin-6(5*H*)-one (**6**), 9-*N*'-methylanilidobenzo[*b*]thieno[2,3-*c*]-5-*N*-methylquinolin-6-one (**7**), 9-anilidothieno[4,5-*b*']thienyl[2,3-*c*]quinolin-6(5*H*)-one (**16**), and 9-*N*'-methylanilidothieno[4,5-*b*']thienyl[2,3-*c*]-5-*N*-methylquinolin-6-one (**17**) were prepared by photochemical dehydrohalogenation from the dianilides (**4**, **5**, **14** and **15**). Photochemical dehydrogenation of the anilides to produce multicondensed diquinolones did not occur.

In our previous papers we reported on the applicability of the photochemical cyclization reaction for preparing various quinolones condensed with heterocyclic nuclei: furoquinolones,<sup>1</sup> furo-bis-quinolones,<sup>2</sup> benzofuro-phenanthridones and benzothienophenanthridones,<sup>3</sup> and naphthothienothierylquinolones.<sup>4</sup> In order to continue our efforts to synthesize polycyclic heterocycles of the quinolone type, we prepared a series of new condensed heterocyclic dianilides (**4**, **5**, **14**, and **15**). Dianilides were irradiated with uv light to prepare the corresponding quinolones and diquinolones by photodehydrogenation and/or photodehydrohalogenation reaction (See Schemes 1 and 2).

Photochemical dehydrogenation of aromatic and heteroaromatic anilides is well known<sup>5-9</sup> and photodehydrohalogenation was observed for **4**, **5**, **14**, and **15**. A good correlation has been shown to exist between the effect of electron impact and the effect of uv irradiation on stilbene analogues.<sup>10</sup> The possibility that mass spectrometry might prove to be a useful tool<sup>11</sup> for distinguishing between compounds which photodehydrocyclize and those which do not, led us to investigate this technique. The cyclization was shown to occur in the mass spectrometer by a similar mechanism to that by which cyclization takes place in the photochemical reactor.<sup>12</sup> The mass spectral data for the aforementioned compounds were in agreement with the photochemical results described below. In the mass spectra of anilidoquinolones (**6**, **7**, **16**, and **17**) fragment ion [M-2] which could give rise from the dehydrocyclization reaction and prove the formation of diquinolones was not detected.

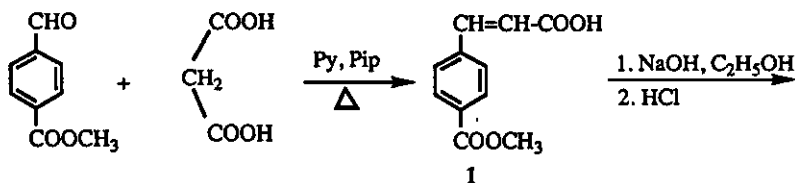
The well known photodehydrohalogenation reaction<sup>13-15</sup> occurred with the dianilides (**4**, **5**, **14**, and **15**)

so that anilidoquinolones (**6**, **7**, **16**, and **17**) were prepared in the yields from 7.5 to 69 %.

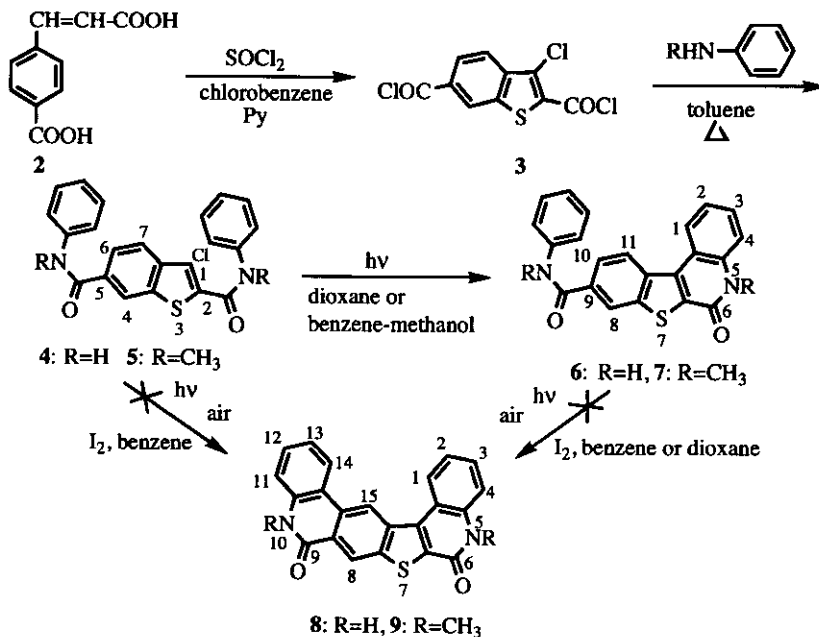
Dianilides (**4**, **5**, **14**, and **15**) and anilidoquinolones (**6**, **7**, **16**, and **17**) are particularly interesting multicondensed heteroaromatic compounds because they have a potential to serve as the planar aromatic core of DNA intercalators. Similar heterocyclic systems have been used to form the basis of DNA intercalators.<sup>16,17</sup>

Dianilides (**4**, and **5**) were prepared in the multistep synthesis starting from 4-carbomethoxybenzaldehyde and malonic acid. 4-Carbomethoxycinnamic acid (**1**) was prepared in the yield of 99.4%.<sup>18</sup> 4-Carboxycinnamic acid (**2**) was prepared in the yield of 83.3% by the hydrolysis of **1**. The reaction of **2** with SOCl<sub>2</sub> in the presence of a catalytic amount of pyridine gave 1-chlorobenzo[*b*]thiophene-2,5-dicarbonyl chloride (**3**) in the yield of 36% by the method described earlier.<sup>19</sup> 1-Chlorobenzo[*b*]thiophene-2,5-dicarboxanilide (**4**) and 1-chloro-*N,N'*-dimethylbenzo[*b*]thiophene-2,5-dicarboxanilide (**5**) were prepared in the yields of 82 and 92% in the reaction of **3** with aniline and *N*-methylaniline, respectively. Irradiation of a dioxane solution of **4** with a 400 W high pressure mercury arc lamp, fitted with a pyrex filter, at the room temperature gave the photodehydrohalogenation product 9-anilidobenzo[2,3-*c*]quinolin-6(*5H*)-one (**6**) in 36% yield. 9-*N'*-Methylanilidobenzo[*b*]thieno[2,3-*c*]-5-methylquinolin-6-one (**7**) was prepared in a 69% yield by irradiation of a methanol-benzene solution of **5** at room temperature with a 125 W high pressure mercury arc lamp using a quartz filter.

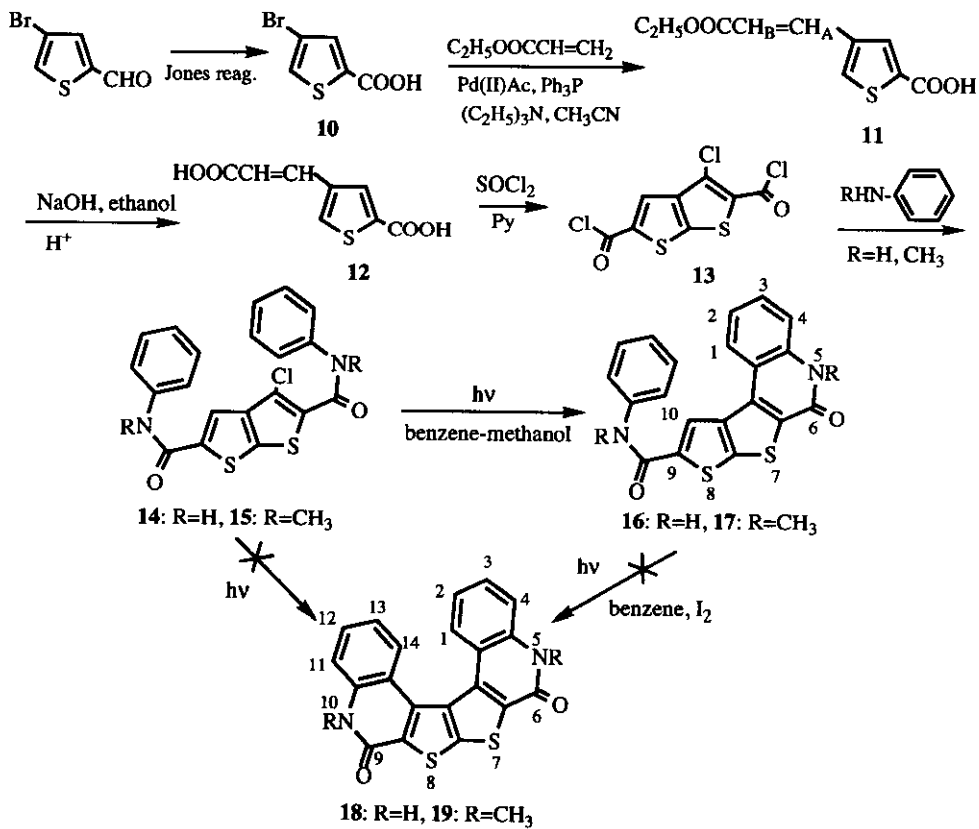
Dianilides (**14**, and **15**) were also prepared by a multistep synthesis starting from 4-bromo-2-thiophenecarbaldehyde which on oxidation by Jones reagent gave 4-bromo-2-thiophenecarboxylic acid (**10**) in the yield of 85%.<sup>20</sup> Ethyl 3-(5-carboxy-3-thienyl)acrylate (**11**) was prepared in the yield of 77% by catalytic vinylation of **10** using the described method;<sup>21</sup> similarly, 3-(5-carboxy-3-thienyl)acrylic acid (**12**) was obtained in the yield of 73%. 1-Chlorothieno[2,3-*b*]thiophene-2,5-dicarbonyl chloride (**13**) was prepared in the yield of 28% applying the previously described method.<sup>19</sup> Dianilides; 1-chlorothieno[2,3-*b*]thiophene-2,5-dicarboxanilide (**14**) and 1-chloro-*N,N'*-dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxanilide (**15**) were prepared from **13** and aniline or *N*-methylaniline in the yields of 33 and 55%, respectively. Dianilide (**14**) was photochemically dehydrohalogenated to 9-anilidothieno[4,5-*b'*]thienyl[2,3-*c*]quinolin-6(*5H*)-one (**16**) (7.5% yield) by irradiation of a methanol-benzene solution with a 400 W high pressure mercury arc lamp using a pyrex filter; whereas dianilide (**15**) was photochemically dehydrohalogenated to give 9-*N'*-methylanilidothieno[4,5-*b'*]thienyl[2,3-*c*]-5-*N*-methylquinolin-6-one (**17**) in the yield of 35% under similar reaction conditions.



Scheme 1 (to be continued)



Scheme 1



Scheme 2

## EXPERIMENTAL

Mps were determined on a Kofler hot stage microscope and are uncorrected. Ir spectra were recorded on a PERKIN-ELMER Model 257 spectrophotometer in KBr discs or as a liquid film between sodium chloride plates.  $^1\text{H}$  Nmr spectra were recorded on a VARIAN M 360 (60 MHz) or on VARIAN GEMINI 300 (300 MHz) with TMS as internal standard in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$ . Irradiation was performed by water cooled immersion well equipped with an "Original Hanau" 125 W or 400 W high pressure mercury arc lamp using quartz or pyrex filters at room temperature.

### 4-Carbomethoxycinnamic acid (1)

Compound (1) was prepared by the condensation of methyl 4-formylbenzoate (10.00 g, 0.06 mol) and malonic acid (6.76 g, 0.065 mol) in pyridine (75 ml) and in the presence of piperidine (1 ml). Reaction mixture was heated on 100-120°C during 19 h. After cooling reaction mixture was poured on ice (250 g) with strong stirring and acidified with conc. HCl. White crystals, 12.50 g (99.39%), mp 242-243°C, were used without further purification in the next step of the reaction.

### 4-Carboxycinnamic acid (2)

Compound (2) was prepared by hydrolysis of **1** (12.50 g, 0.061 mol) dissolved in ethanol (200 ml) which was added to the solution of sodium hydroxide (7.32 g, 0.18 mol) in water (150 ml) and the mixture was refluxed for 0.5 h, the solution was boiled with charcoal, filtered, and the filtrate was distilled off in vacuo, the residue was dissolved in water and acidified with conc. HCl. Precipitate was filtered off. Yellow crystals, recrystallized from diluted DMSO, 9.77 g (83.33%), mp > 300°C, were obtained ( lit.,<sup>18</sup> mp 250-260°C ).

### 1-Chlorobenzol[b]thiophene-2,5-dicarbonyl chloride (3)

Compound (3) was prepared from **2** (2.00 g, 0.01 mol) in chlorobenzene (10 ml) to which was added catalytic amount of pyridine (0.1 ml). Thionyl chloride (6.0 ml, 0.083 mol) was added dropwise in the mixture cooled on ice bath, then the mixture was heated by stirring under reflux for 4 h. Excess thionyl chloride was removed under reduced pressure and the remaining material was suspended in hot cyclohexane. The filtrate was allowed to cool. Yellow crystals, 1.06 g (36.01%), mp 155-157°C, were obtained ( lit.,<sup>19</sup> mp 162°C ).

### 1-Chlorobenzol[b]thiophene-2,5-dicarboxydianilide (4)

A solution of aniline (2.5 ml, 0.03 mol) in toluene (30 ml) was added dropwise to a stirred solution of **3** (2.66 g, 0.01 mol) in toluene (60 ml) at room temperature. After the addition was complete the mixture was refluxed for 1 h. After cooling, precipitated crystals were filtered off, washed with 10% HCl, then with water, then with hot methanol and recrystallized from  $\text{H}_2\text{O}$ -DMF (1:1). Light yellow crystals, 3.00 g (81.98%), mp 278°C, were obtained. Ir ( $\text{cm}^{-1}$ ): 3300 (NH), 1640 (CONH).  $^1\text{H}$  Nmr ( $\text{DMSO-d}_6$ ) ( $\delta$  ppm): 10.59 (s, 1H, NH), 10.44 (s, 1H, NH), 8.75 (d,  $J_{4,7}=1.55$  Hz, 1H, H<sub>4</sub>), 8.16 (dd,  $J_{6,7}=8.50$  Hz,  $J_{4,7}=1.55$  Hz, 1H, H<sub>7</sub>), 8.06 (d,  $J_{6,7}=8.53$  Hz, 1H, H<sub>6</sub>), 7.83-7.83 (m, 4H, H arom.), 7.43-7.36 (m, 4H,

H arom.), 7.20-7.11 (m, 2H, H arom.). Anal. Calcd for  $C_{22}H_{15}N_2O_2ClS$ : C, 64.94; H, 3.70; N, 68.88. Found: C, 65.06; H, 3.82; N, 6.91.

#### 1-Chloro-*N,N'*-dimethylbenzo[*b*]thiophene-2,5-dicarboxanilide (5)

The suspension of *N*-methylaniline (1.3 ml, 0.012 mol) in 5% sodium hydroxide (4.5 ml, 5.5 mmol) was cooled to 2-3°C. The solution of oxalyl chloride (3) (1.50 g, 0.005 mol) in ether (700 ml) was added dropwise with stirring maintaining the temperature at 3-5°C. The stirring was continued for 0.5 h at 3-5°C and than 0.5 h at room temperature. The whole reaction mixture was transferred into the separatory funnel and washed with 10% HCl and then with water. Ethereal layer was separated and dried over  $MgSO_4$ . After evaporation of the solvent yellow crystals, 2.00 g (92.13%), mp 146-148°C, were obtained. Ir ( $cm^{-1}$ ) (KBr): 3000, 2900 (N-CH<sub>3</sub>), 1635 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (CDCl<sub>3</sub>) (δ ppm): 7.71 (s, 1H, H<sub>4</sub>), 7.45 (d, J<sub>6,7</sub>=8.55 Hz, 1H, H<sub>7</sub>), 7.23 (d, J<sub>6,7</sub>=8.50 Hz, H<sub>6</sub>), 7.21-7.12 (m, 9H, H arom), 7.00 (d, J=7.67 Hz, 1H, H arom.), 3.51 (s, 3H, N-CH<sub>3</sub>), 3.50 (s, 3H, N-CH<sub>3</sub>). Anal. Calcd for  $C_{24}H_{19}N_2O_2ClS$ : C, 66.28; H, 4.40; N, 6.44. Found: C, 66.40; H, 4.66; N, 6.33.

#### 9-Anilidobenzo[*b*]thieno[2.3-*c*]quinolin-6(5*H*)-one (6)

A solution of 4 (0.42 g, 0.001 mol) and triethylamine (0.15 ml, 1 mmol) in dioxane (1000 ml) was irradiated with 400 W high pressure mercury arc lamp through the pyrex filter at room temperature for 4 h. After removal the solvent in vacuo, the resulting yellow solid was collected by filtration, washed with water, and recrystallized from water - DMF (1:1). 0.12 g (31.62%) yellow crystals, mp>300°C, were obtained. Ir ( $cm^{-1}$ ): 3250 (NH), 1640 (CONH). <sup>1</sup>H Nmr (DMSO-*d*<sub>6</sub>) (δ ppm): 12.39 (s, 1H, NH-quinolono), 10.57 (s, 1H, NH-anilido), 9.09-9.07 (m, 1H, H<sub>1</sub>), 8.87 (s, H, H<sub>8</sub>), 8.85-8.82 (m, 1H, H<sub>4</sub>) 8.22 (d, J<sub>10,11</sub>=8.61 Hz, 1H, H<sub>11</sub>), 7.87-7.84 (m, 2H, H<sub>10</sub> and H arom.), 7.67-7.59 (m, 2H, H arom.), 7.48-7.39 (m, 3H, H arom.), 7.18-7.13 (m, 1H, H arom.). Anal. Calcd for  $C_{22}H_{14}N_2O_2S$ : C, 71.35; H, 3.78; N, 7.56. Found: C, 71.49; H, 4.04; N, 7.54.

#### 9-*N'*-Methylanilidobenzo[*b*]thieno[2.3-*c*]-5-*N*-methylquinolin-6-one (7)

A solution of 5 (1.00 g, 2.3 mmol) and triethylamine (300 mmol) in methanol-benzene (1:10) (550 ml) was irradiated for 3 h with 125 W high pressure mercury arc lamp in a quartz vessel. The air was bubbled through the solution. After reducing the solvent on 50 ml, the product crystallized. The resulting solid was collected by filtration, washed with water, dried and recrystallized from chloroform-cyclohexane. Yellow crystals 0.63g (68.78%) mp>300°C, were obtained. Ir ( $cm^{-1}$ ) (KBr): 3400 (N-CH<sub>3</sub>), 1620 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (CDCl<sub>3</sub>) (δ ppm): 8.56-8.54 (m, 1H, H<sub>1</sub>), 8.45-8.42 (m, 1H, H<sub>4</sub>), 8.04 (s, 1H, H<sub>8</sub>), 7.62-7.52 (m, 2H, H arom), 7.53 (d, J<sub>10,11</sub>=8.50 Hz, 1H, H<sub>11</sub>) 7.47-7.36 (m, 2H, H arom), 7.24-7.10 (m, 4H, H<sub>10</sub> and 3H arom.), 3.87 (s, 3H, N-CH<sub>3</sub> quinolono), 3.58 (s, 3H, N-CH<sub>3</sub> anilido). Anal. Calcd for  $C_{24}H_{18}N_2O_2S$ : C, 72.36; H, 4.55; N, 7.03. Found: C, 72.49; H, 4.8; N, 6.96.

#### 4-Bromothiophene-2-carboxylic acid (10)

To a stirred solution of 4-bromo-2-thiophenecarboxaldehyde (18.90 g, 0.10 mol) in acetone (190 ml) under nitrogen at 5°C was added dropwise Jones reagent (60 ml, 2.67 mol). Stirring was continued at 5°C for 30

min followed by stirring at room temperature for 2 h. Methanol (300 ml) was added to the reaction mixture to destroy any excess oxidant, and the solid was filtered off. The filtrate was concentrated in vacuo, and the residue was partitioned between ether and water. The ethereal extract was washed with water (2x) and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure. Orange crystals, recrystallized from cyclohexane, 17.43 g, (85.04%), mp  $116^\circ\text{C}$  (lit.,<sup>20</sup> mp  $98-99^\circ\text{C}$ ), were obtained.

#### Ethyl 3-(5-carboxy-3-thienyl)acrylate (11)

Compound (11) was prepared by the method described earlier.<sup>21</sup> To the solution of palladium(II)acetate (0.08 g, 0.36 mmol) and triphenylphosphine (0.38 g, 1.45 mmol) in acetonitrile (60 ml) and triethylamine (35 ml) were added 10 (5.0 g, 0.024 mol) and ethyl acrylate (7.4 g, 0.074 mol). The reaction mixture was sealed in the glass tube and heated at  $100^\circ\text{C}$  for 20 h. The mixture was cooled, the content of the tube was evaporated in vacuo and the residue was dissolved in water, filtered. The filtrate was boiled with charcoal, acidified with 50% HCl. The precipitate was filtered off and recrystallized from ethanol; yield 4.18 g (77.05 %) yellow crystals, mp  $95-97^\circ\text{C}$ , were obtained. Ir ( $\text{cm}^{-1}$ ): 1710 (COOEt), 1670 (COOH), 1635 (C=C).  $^1\text{H}$  Nmr ( $\text{CDCl}_3$ ) ( $\delta$  ppm): 8.04 (d,  $J_{3,5}=1.41$  Hz, 1H,  $\text{H}_5$ ), 7.62 (d,  $J_{A,B}=16.06$  Hz, 1H,  $\text{H}_B$ ), 7.54 (d,  $J_{3,5}=1.55$  Hz, 1H,  $\text{H}_3$ ), 6.34 (d,  $J_{A,B}=16.00$  Hz, 1H,  $\text{H}_A$ ), 4.27 (q,  $J=7.13$  Hz, 2H,  $\text{CH}_2$ ), 1.34 (t,  $J=7.13$  Hz, 3H,  $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_4$ : C, 61.85; H, 5.15. Found: C, 61.52; H, 4.94.

#### 3-(5-Carboxy-3-thienyl)acrylic acid (12)

Acid (12) was prepared by hydrolysis of 11 (3.50 g, 0.015 mol) dissolved in ethanol (60 ml), which was added to the solution of sodium hydroxide (1.96 g, 0.05 mol) in water (40 ml). The mixture was refluxed for 0.5 h. After that time, charcoal was added and the mixture refluxed a short time, filtered off. The filtrate was condensed in vacuo, the residue dissolved in water and acidified with conc. HCl. Precipitate was filtered off and recrystallized from ethanol. Yellow crystals 2.16 g (72.71%), mp  $264-266^\circ\text{C}$ , were obtained. Ir ( $\text{cm}^{-1}$ ): 1670 (COOH), 1620 (C=C).  $^1\text{H}$  Nmr ( $\text{DMSO}-d_6$ ) ( $\delta$  ppm): 8.23 (s, 1H,  $\text{H}_2$ ), 8.11 (s, 1H,  $\text{H}_4$ ), 7.58 (d,  $J_{A,B}=16.11$  Hz, 1H,  $\text{H}_B$ ), 6.48 (d,  $J_{A,B}=16.11$  Hz, 1H,  $\text{H}_A$ ). Anal. Calcd for  $\text{C}_8\text{H}_6\text{O}_4$ : C, 57.83; H, 3.61. Found: C, 57.62; H, 3.29.

#### 1-Chlorothienof[2,3-b]thiophene-2,5-dicarbonyl chloride (13)

Compound (13) was prepared by applying the described method<sup>16</sup> from 12 (5.00 g, 0.025 mol) dissolved in  $\text{SOCl}_2$  (20 ml, 0.27 mol) to which was added a catalytic amount of pyridine (0.5 ml). Reaction mixture was heated by stirring at  $120^\circ\text{C}$  for 5 h. Excess of  $\text{SOCl}_2$  was distilled off, and the residue was extracted with hot cyclohexane. After cooling the crystals were filtered off, yellow crystals 2.12 g (28.27%), mp  $156-161^\circ\text{C}$ , were obtained. Ir ( $\text{cm}^{-1}$ ): 1710 (COCl).  $^1\text{H}$  Nmr ( $\text{CCl}_4$ ) ( $\delta$  ppm): 8.23 (s, 1H,  $\text{H}_6$ ). Anal. Calcd for  $\text{C}_8\text{HO}_2\text{Cl}_3\text{S}_2$ : C, 32.05; H, 0.33. Found: C, 32.38; H, 0.29.

#### 1-Chlorothienof[2,3-b]thiophene-2,5-dicarboxanilide (14)

Compound (14) was prepared by the method described for 4. A solution of aniline (1.8 ml, 19.75 mmol) in toluene (15 ml) was added dropwise to a stirred solution of 13 (2.00 g, 6.68 mol) in toluene (55 ml). Light brown crystals 0.91 g (32.99%), mp  $236-238^\circ\text{C}$  were obtained. Ir ( $\text{cm}^{-1}$ ): 3400 (NH), 1640, 1620

(CO-NH).  $^1\text{H}$  Nmr (Acetone- $d_6$ ) ( $\delta$  ppm): 9.80 (s, 1H, NH), 9.33 (s, 1H, NH), 8.16 (s, 1H, H<sub>6</sub>), 7.84-7.77 (m, 4H, H arom.), 7.43-7.35 (m, 4H, H arom.), 7.21-7.12 (m, 2H, H arom.). Anal. Calcd for  $\text{C}_{20}\text{H}_{13}\text{N}_2\text{O}_2\text{ClS}_2$ : C, 58.20; H, 4.00; N, 6.80. Found: C, 58.28; H, 3.36; N, 6.82.

1-Chloro-*N,N'*-dimethylthienof[2,3-*b*]thiophene-2,5-dicarboxanilide (15)

Compound (15) was prepared, as earlier described for preparing 5, from the solution of *N*-methylaniline (0.8 ml, 7.38 mmol) in 5% sodium hydroxide (2.6 ml) and dicarbonyl chloride (13) (0.85 g, 2.85 mmol). After recrystallization from ether, brown crystals 0.81 g (55.06%), mp 211-213°C, were obtained. Ir ( $\text{cm}^{-1}$ ): 1635 (CO-N-CH<sub>3</sub>), 1615 (CO-N-CH<sub>3</sub>).  $^1\text{H}$  Nmr ( $\text{CDCl}_3$ ) ( $\delta$  ppm): 7.44-7.42 (m, 3H, H arom.), 7.26-7.20 (m, 5H, H arom.), 7.14-7.12 (m, 2H, H arom.), 6.56 (s, 1H, H<sub>6</sub>), 3.45 (s, 3H, CH<sub>3</sub>), 3.44 (s, 3H, CH<sub>3</sub>). Anal. Calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_2\text{ClS}$ : C, 59.92; H, 3.89; N, 6.35. Found: C, 60.03; H, 4.12; N, 6.37.

9-Anilidothienof[4,5-*b'*]thienyl[2,3-*c*]quinolin-6(5*H*)-one (16)

A solution of 14 (0.50 g, 1.21 mmol) and triethylamine (0.17 ml) in methanol-benzene 1:10 (660 ml) was irradiated for 2.5 h at room temperature with 400 W high pressure mercury arc lamp in pyrex vessel. The air was bubbled through the solution. After evaporating of the solvent, the product crystallized. The resulting crystals were recrystallized from dioxane. 0.03 g (7.47%) white crystals mp > 300°C were obtained. Ir ( $\text{cm}^{-1}$ ): 3400 (N-H), 1630 (CO-NH).  $^1\text{H}$  Nmr ( $\text{DMSO-}d_6$ ) ( $\delta$  ppm): 12.20 (s, 1H, NH-quinolono), 10.50 (s, 1H, NH-anilido), 8.48-8.46 (m, 1H, H arom.), 7.80-7.76 (m, 2H, H arom.), 7.66-7.55 (m, 2H, H arom.), 7.53 (s, 1H, H<sub>10</sub>), 7.50-7.40 (m, 3H, H arom.), 7.19-7.14 (m, 1H, H arom.). Anal. Calcd for  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2$ : C, 63.81; H, 3.21; N, 7.44. Found: C, 63.70; H, 3.43; N, 7.48.

9-*N'*-Methylanilidothienof[4,5-*b'*]thienyl[2,3-*c*]-5-*N*-methylquinolin-6-one (17)

A solution of 15 (0.50 g, 1.13 mmol) and triethylamine (0.16 ml) in methanol-benzene 1:10 (660 ml) was irradiated for 3 h at room temperature with 400 W high pressure mercury arc lamp filtered with pyrex glass. The air was bubbled through the solution. After evaporation of the solvent, hot methanol was added to the residue. Undissolved light brown precipitate was filtered off and recrystallized from diluted DMSO and once again from dioxane; yield 0.16 g (35.45 %), mp 265-267°C. Ir ( $\text{cm}^{-1}$ ) (KBr): 1645, 1605 (CO-N-CH<sub>3</sub>).  $^1\text{H}$  Nmr ( $\text{DMSO-}d_6$ ) ( $\delta$  ppm): 8.27-8.24 (m, 1H, H<sub>1</sub>), 7.65-7.63 (m, 2H, H<sub>10</sub>, and H arom.), 7.54-7.48 (m, 2H, H arom.), 7.31-7.26 (m, 2H, H arom.), 7.20-7.15 (m, 1H, H arom.), 6.20-6.17 (m, 1H, H arom.), 5.32-5.30 (m, 1H, H arom.), 3.76 (s, 3H, CH<sub>3</sub>-quinolono), 3.36 (s, 3H, CH<sub>3</sub>-anilido). Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_2$ : C, 65.32; H, 3.99; N, 6.92. Found: C, 65.29; H, 4.12; N, 7.11.

Uv irradiation of 6, 7, 16 and 17

Compounds (6, 7, 16, and 17) (0.1 g) were irradiated in dioxane or in benzene solution (1000 ml) in the presence of I<sub>2</sub> (0.07 g) either with 125 W high pressure mercury arc lamp in quartz vessel or with 400 W high pressure arc lamp in pyrex at room temperature. The air was bubbled through the solution. After first few hours of irradiation there was not detected photochemical change (by checking the reaction solution with uv spectrometry) and after prolonged irradiations the compounds decomposed.

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