

**PHOTOSYNTHESIS OF HETEROPOLYCYCLIC DIQUINOLONES  
TWOFOLD PHOTODEHYDROHALOGENATION REACTION OF  
BENZO[1,2-*b*:4,5-*b'*]DITHIOPHENE- AND DITHIENO[3,2-*b*:2',3'-*d*]THIOPHENEDICARBOXANILIDES**

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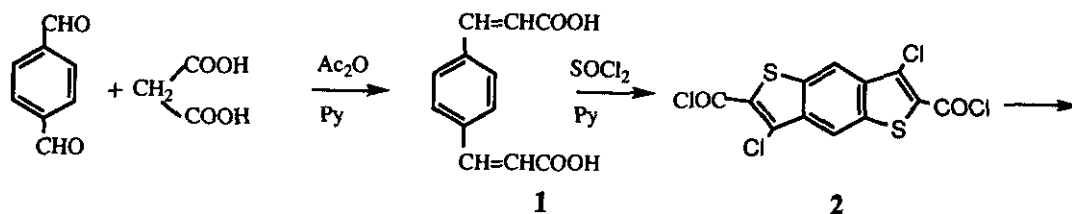
**Abstract-** Heteropolycyclic diquinolones; benzo[1,2-*b*:4,5-*b'*]dithieno[2',3'-*c*:2'',3''-*c*']-5,13-*N,N'*-dimethyldiquinoline-6,14-dione (9) and dithieno[3,2-*b*:2',3'-*d*]thienyl[2'',3''-*c*:2'',3''-*c*']-5,10-*N,N'*-dimethyldiquinoline-6,9-dione (17) are prepared by twofold photochemical dehydrohalogenation reaction of corresponding benzodithiophene- and dithienothiophenedicarboxanilides; 3,7-dichloro-*N,N'*-dimethylbenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxanilide (8) and 3,5-dichloro-*N,N'*-dimethyldithieno[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarboxanilide (16). The products of onefold photochemical dehydrohalogenation reaction, anilidoquinolones; 9-chloro-10-*N'*-methylanilidobenzo[1,2-*b*:4,5-*b'*]dithieno[2,3-*c*']-5-*N*-methylquinolin-6-one (10) and 10-chloro-9-*N'*-methylanilidodithieno[3,2-*b*:2',3'-*d*]thienyl[2'',3''-*c*']-5-*N*-methylquinolin-6-one (18) were also isolated to prove the mechanism of the reaction.

Recently we reported<sup>1</sup> on the applicability of photochemical dehydrohalogenation reactions of some heteropolycyclic dicarboxanilides in producing anilidoquinolones. Photochemical dehydrogenation reaction of anilidoquinolones to produce multicondensed diquinolones didn't occur. In our previous papers we reported on the usefulness of photochemical dehydrocyclisation reaction for preparing quinolones condensed with heterocyclic nuclei: furoquinolones,<sup>2</sup> furo-bis-quinolones,<sup>3</sup> benzofurophenanthridones and benzothienophenanthridones.<sup>4</sup> This reaction was examined and applied to aromatic and heteroaromatic anilides<sup>5-9</sup> but the yields of the corresponding heterocyclic quinolones were not high. It was shown that the more applicable reaction to produce heterocyclic quinolones, was photochemical dehydrohalogenation reaction which was first reported by Terashima and coworkers.<sup>10</sup> The authors examined photochemical dehydrohalogenation reaction on a few different heterocyclic amide systems where the halogen atom was situated in the position 2 of the amino part of heterocyclic nuclei or in the same position of the acidic part of the heterocyclic nuclei. The authors noticed that the reaction of photochemical dehydrohalogenation was facilitated when the halogen atom

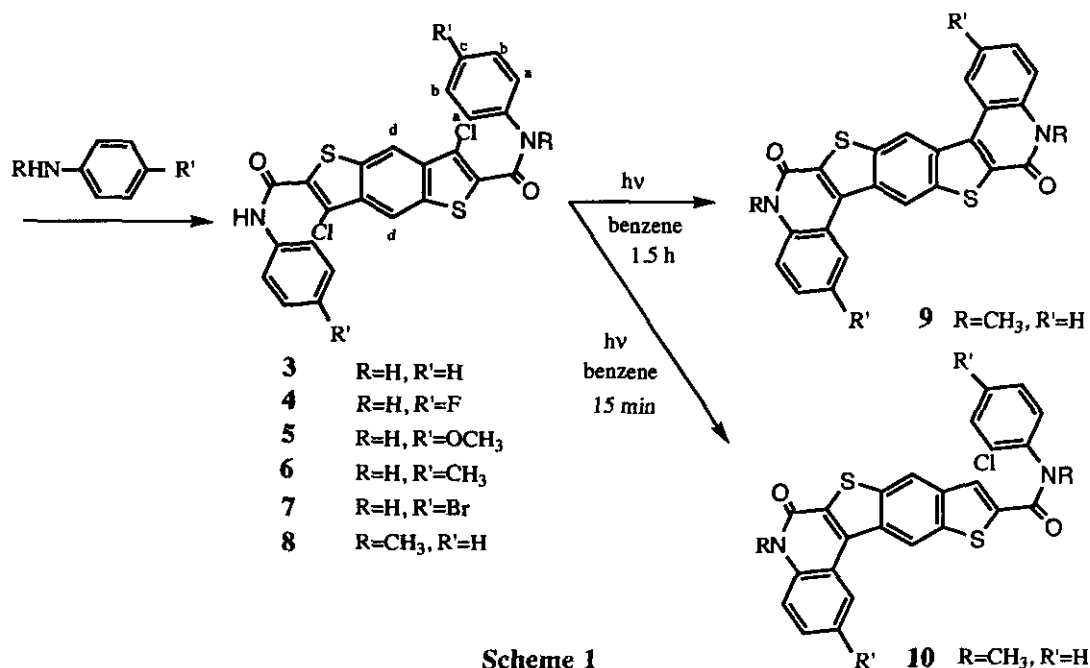
was situated in the position 2 of the acidic part of the heterocyclic nuclei. This comprehension was used later very widely in the synthesis of a new heteropolycyclic monoquinolones.<sup>11-14</sup>

The synthesis of 2,11-dichlorofuro[3,2-*b*:2',3'-*b'*]diquinoline-6(5*H*),7(8*H*)-dione was performed by twofold photochemical dehydrocyclization reaction starting from 3,4-furan-di(*p*-chloro)carboxanilide in our laboratory<sup>3</sup> and was the first example of the photochemically prepared heterocyclic diquinolone. In order to continue our efforts to synthesize heteropolycyclic diquinolones by the reaction of twofold photochemical dehydrohalogenation reaction and to compare the successfulness of this reaction with twofold photochemical dehydrocyclisation, as well as to study the mechanism of twofold photochemical dehydrohalogenation, we prepared a series of condensed heteropolycyclic dianilides (3-8) and (14-16).

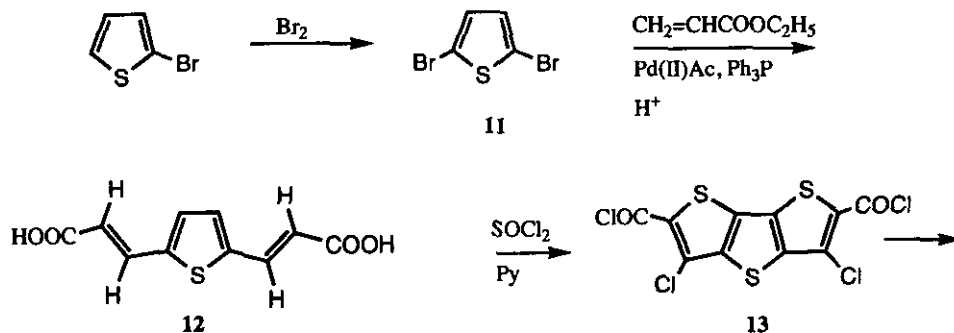
Dianilides (3-8) (see Scheme 1) were prepared in multistep synthesis starting from benzene-1,4-dicarboxaldehyde and malonic acid. 1,4-Phenylene-di-(2-ethenyl)carboxylic acid (1) was prepared in the yield of 93%. This compound was prepared earlier by the similar methods.<sup>15,16</sup> The reaction of 1 with SOCl<sub>2</sub> in the presence of catalytic amount of pyridine gave 3,7-dichlorobenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarbonyl chloride (2) in the yield of 47.4% by the method described earlier.<sup>17</sup> 3,7-Dichlorobenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxydianilides (3-7) were prepared by the reaction of 2 with corresponding substituted anilines in the yields of 45.4-57.0%. 3,7-Dichloro-*N,N'*-dimethylbenzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxanilide (8) was prepared from 2 and *N*-methylaniline in the yield of 47.6% by the method described earlier.<sup>1</sup> Unfortunately dianilides (3-7) were insoluble at room temperature in solvents ordinary used for photochemical reactions even in the concentrations of approximately 10<sup>-3</sup>. The solubility in dioxane was also insufficient to perform photochemical reaction. Other solvents like dimethylformamide couldn't be used because of its photoreactivity. Only soluble dianilide (8) was irradiated in benzene solution with 400 W high pressure mercury arc lamp, fitted with pyrex filter. After 1.5 h of irradiation, benzo[1,2-*b*:4,5-*b'*]dithieno[2',3'-*c*:2'',3''-*c'*]-5,13-*N,N'*-diquinoline-6,14-dione (9) was isolated as the product of twofold photodehydrohalogenation reaction in the yield of 76.8%. The structure of the compound (9) was determined by mass spectrometry.



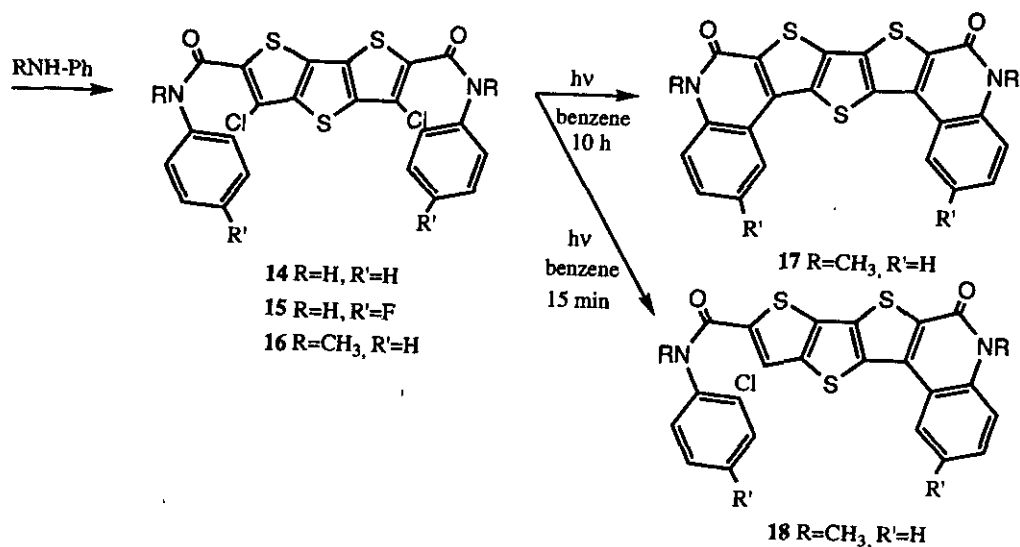
Scheme 1 (to be continued)



Dianilides (**14** and **15**) (see Scheme 2) were prepared in multistep synthesis starting from 2-bromothiophene over 2,5-dibromothiophene<sup>18</sup> (**11**), which was subjected to vinylation with ethyl acrylate in the presence of a catalytic amount of Pd(II) acetate, gave 2,5-thiophene-di-(2-ethenyl)carboxylic acid (**12**) in the yield of 82.6%.<sup>19</sup> This compound was prepared earlier by different method.<sup>20</sup> Compound (**12**) was cyclized into 3,5-dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarbonyl chloride (**13**) with SOCl<sub>2</sub> and a catalytic amount of pyridine, in the yield of 40% by the method described earlier.<sup>20</sup> Dianilides (**14-16**) were prepared from corresponding substituted anilines and compound (**13**) in the yields of 43.7-72.4% by the method described for dianilides (**3-8**). Only dianilide (**16**) was soluble in benzene and was irradiated with 400 W high pressure mercury arc lamp for 10 h. Dithieno[3,2-*b*:2',3'-*d*]thienyl[2'',3''-*c*:2''',3'''-*c'*:2''',3'''-*c'*]-5,10-*N,N'*-dimethylquinoline-6,9-dione (**17**) was obtained in the yield of 75.0%. The structure of the compound (**17**) was determined by mass spectrometry.

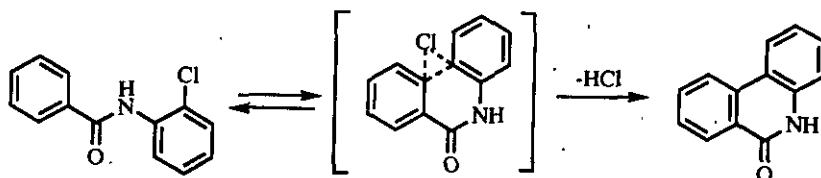


**Scheme 2**(to be continued)



Scheme 2

There is few literature data about the mechanism of the photochemical dehydrohalogenation. Grimshaw and Silva<sup>21</sup> suggested the mechanism of the monofold photochemical dehydrohalogenation reaction, which includes radical complexation assistance to carbon-halogen bond photolysis in the *cis* form of the compound in the Scheme 3



Scheme 3

It seems plausible also in the twofold photochemical dehydrohalogenation reaction. It was interesting also to establish whether the reaction of twofold photochemical dehydrohalogenation proceeds in one step or two-steps. As there is no literature evidence about photochemical synthesis of diquinolones by twofold photochemical dehydrohalogenation reaction, we tried to isolate the products of onefold photochemical dehydrohalogenation reaction from dianilides (**8**) and (**16**), namely the corresponding anidoquinolones. By changing the irradiation time and the strength of the uv arc, performing the reaction for 15 min with 125 W high pressure mercury arc lamp fitted with pyrex filter, we succeeded to isolate anidoquinolones; 9-chloro-10-*N'*-methylanilidobenzo[1,2-*b*:4,5-*b'*]dithieno[2,3-*c'*]-5-*N*-methylquinolin-6-one (**10**) and 10-chloro-9-*N'*-methylanilidodithieno[3,2-*b*:2',3'-*d'*]-thienyl[2'',3''-*c'*]-5-*N*-methylquinolin-6-one (**18**) in the mixture with diquinolones (**9**) and (**17**) in the low yields and unreacted starting dianilides in the yields of about 60%. It was the proof that the reaction proceeds in two step.

Photochemically prepared diquinolones (**9**) and (**17**) are particularly interesting multicondensed heteroaromatic compounds because they have a potential to serve as the planar aromatic core of DNA intercalators.

## 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 Gemini 300 (300 MHz) with TMS as internal standard in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$ . Mass spectra were recorded on Shimadzu QP-5000 GC/MS instrument at 70 eV using a direct inlet system and with an ion source temperature of  $300^\circ\text{C}$ . Irradiation was performed by water cooled immersion well equipped with an "Original Hanau" 125 W and 400 W high pressure mercury arc lamp using quartz or pyrex glass.

*E,E*-1,4-Phenylene-di-(2-ethenyl)carboxylic acid (1)

Compound (1) was prepared by condensation of benzene-1,4-dicarboxaldehyde (10 g, 0.07 mol) with malonic acid (18 g, 0.17 mol) in pyridine (28 ml). A catalytic amount of piperidine (1 ml) was added. The reaction mixture was heated 2 h at  $45\text{--}50^\circ\text{C}$  and 3 h at  $100^\circ\text{C}$ . After cooling 300 ml water were added and the reaction mixture was acidified with 20% HCl. White crystals were filtered off and recrystallized from glacial acetic acid (250 ml). 14.5 g (93%), white crystals, mp  $>350^\circ\text{C}$  was obtained (lit.,<sup>16, 17</sup> mp  $>300^\circ\text{C}$ ).

3,7-Dichlorobenzol[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarbonyl chloride (2)

Thionyl chloride (31 ml, 0.43 mol) was added dropwise into the stirred mixture of 1 (11 g, 0.05 mol) and pyridine (1 ml) at room temperature. The reaction mixture was heated for 5 h at  $140^\circ\text{C}$ . Excess thionyl chloride was removed under reduced pressure and the remaining material was extracted with hot chloroform (100 ml) where soluble by-products were removed. The residue was crystallized from chlorobenzene. Yellow crystals were obtained in the yield of 9.05 g (47.4%), mp  $274^\circ\text{C}$  (lit.,<sup>18</sup> mp  $274^\circ\text{C}$ ).

3,7-Dichlorobenzol[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxanilides (3-7).

To the suspension of dichloride (2) (2 g, 5.00 mmol) in benzene (200 ml) was added equimolar amount of corresponding aniline (10 mmol) by stirring at room temperature. The reaction mixture was refluxed for 2 h. After cooling the obtained crystals were filtered off washed with 20% HCl, with water, then hot methanol and recrystallized from DMF. White crystals, in the yields of 30.6-51.7% mps  $>300^\circ\text{C}$  were obtained (see Table 1).

Table 1

Compd	R	R'	Yield (%)	mp ( $^\circ\text{C}$ )	Elemental Anal.		Ir ( $\text{cm}^{-1}$ )	$^1\text{H}$ Nmr ( $\delta$ ppm) ( $\text{DMSO-d}_6$ )	$\bar{M}^+$
					Calcd(%)	Found(%)			
3	H	H	51.31	> 300	C 57.96	57.77	3375 (NH)	7.21 (2H, t, J=7.56 Hz, arom. Hc)	496
					H 2.84	3.02	1650 (CONH)	7.42 (4H, t, J=7.65 Hz, arom. Hb)	
					N 5.63	5.29		7.76 (4H, d, J=7.76 Hz, arom. Ha)	
							8.15 (2H, s, arom. Hd)		
								10.50 (2H, s, N-H)	

4	H	F	57.00	>300	C 54.05 53.93 H 2.27 2.39 N 5.25 5.23	3390 (NH) 1660 (CONH)	7.22 (4H, t, J=8.90 Hz, arom. Hb) 7.75 (4H, q, J=9.10 Hz, arom. Ha) 8.12 (2H, s, arom. Hd) 9.94 (2H, s, N-H)	532
5	H	OCH <sub>3</sub>	51.56	> 300	C 56.03 55.83 H 3.26 3.89 N 5.03 5.16	3400 (NH) 1660 (CONH)	3.79 (6H, s, OCH <sub>3</sub> ) 6.98 (4H, d, J=8.90 Hz, arom. Hb) 7.66 (4H, d, J=8.60 Hz, arom. Ha) 8.12 (2H, s, arom. Hd) 10.38 (2H, s, N-H)	556
6	H	CH <sub>3</sub>	52.03	> 300	C 59.44 59.28 H 3.45 3.89 N 5.33 4.87	3390 (NH) 1650 (CONH)	7.22 (4H, d, J=8.20 Hz, arom. Hb) 7.63 (4H, d, J=8.03 Hz, arom. Ha) 8.12 (2H, s, arom. Hd) 10.43 (2H, s, N-H)	524
7	H	Br	45.38	> 300	C 44.00 44.43 H 1.85 1.39 N 4.28 4.17	3400 (NH) 1655 (CONH)	Insoluble	654

### 3,7-Dichloro-*N,N'*-dimethylbenzof[1,2-*b*:4,5-*b'*]dithiophene-2,6-dicarboxanilide (8)

To the suspension of dicarbonyl dichloride (2) (2g, 5 mmol) in benzene (100 ml) was added *N*-methylaniline (2.14 g, 0.02 mol) by stirring at room temperature. The stirring was continued during 24 h. The solvent was distilled off. The crude product was washed with water and filtered. The obtained crystals were chromatographed on SiO<sub>2</sub> column with the mixture of benzene-acetone (3:1) as eluent. White crystals 1.3 g (47.6%), mp 270-272°C, were obtained. Ir (cm<sup>-1</sup>) (KBr): 2925 (CH<sub>3</sub>), 1650 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (DMSO-d<sub>6</sub>) (δ ppm): 7.74 (s, 2H, H<sub>d</sub> arom.), 7.37-7.19 (m, 10H, H arom.), 3.45 (s, 6H, N-CH<sub>3</sub>). M<sup>+</sup> 524. Anal. Calcd for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>S<sub>2</sub>: C, 59.44; H, 3.45; N, 5.33. Found: C, 59.40; H, 3.35, N, 5.34.

### Twofold photochemical dehydrohalogenation of compound (8)

A solution of compound 8 (500 mg, 0.9 mmol) and triethylamine (0.2 g, 1.8 mmol) in benzene (500 ml) was irradiated with 400 W high pressure mercury arc lamp through Pyrex filter for 1.5 h. During the irradiation the precipitate took rise. The precipitates were filtered off and washed with 20% HCl, water and hot chloroform. It was obtained 330 mg (76.8%) of white crystals of diquinolone (9) mp > 300°C. Ir (cm<sup>-1</sup>) (KBr): 1620 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (DMSO-d<sub>6</sub>) (δ ppm): 8.35-8.18 (m, 10H, H arom.), 2.35 (s, 6H, CH<sub>3</sub>-quinolono). M<sup>+</sup> 452. Anal. Calcd for C<sub>26</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 69.02; H, 3.56; N, 6.19. Found: C, 69.04; H, 3.35; N, 6.34.

### Onefold photochemical dehydrohalogenation of compound (8)

A solution of the compound **8** (500 mg, 0.9 mmol) and triethylamine (0.2 g, 1.8 mmol) in benzene (500 ml) was irradiated 15 min with 125 W high pressure mercury arc lamp through Pyrex filter. The precipitate was filtered off and washed as above. It was obtained 29 mg (6.75%) of the compound (**9**). The filtrate was evaporated and the residual oil was chromatographed on a SiO<sub>2</sub> column with toluene-ethyl acetate (7:3). First was isolated unreacted dianilide (**8**), 330 mg (66.0%), and then after recrystallization from DMF, white crystals of anilidoquinolone; 10-*N'*-methylanilidobenzo[1,2-*b*:4,5-*b'*]dithieno[2,3-*c*]-5-*N*-methylquinolin-6-one (**10**) in the yield of 40 mg (8.6%), mp >300°C. *Ir* (cm<sup>-1</sup>) (KBr): 1650 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (DMSO-*d*<sub>6</sub>) (δ ppm): 8.29-8.13 (m, 4H, H arom.), 7.36-7.12 (m, 5H, H arom.), 3.40 (s, 3H, CH<sub>3</sub>-anilido), 2.32 (s, 3H, CH<sub>3</sub>-quinolono). M<sup>+</sup> 488. Anal. Calcd for C<sub>26</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>ClS<sub>2</sub>: C, 63.87; H, 3.50; N, 5.73; S, 13.09; Cl, 7.25. Found: C, 63.70; H, 3.51; N, 5.84; S, 12.95, Cl, 7.25.

### 2,5-Dibromothiophene (11)

The solution of bromine (15 ml, 0.29 mol) in CCl<sub>4</sub> (125 ml) was added dropwise to the solution of 2-bromothiophene (44 g, 0.27 mol) in CCl<sub>4</sub> (125 ml) at room temperature during 3 h. The mixture was stirred over night at the same temp. The solvent was distilled off. To the mixture was added NaOH (7 g), heated for 4 h at 100°C and the mixture was distilled at 200-210°C. The yield was 29.0 g (44.3%) (lit.,<sup>19</sup> bp 210°C).

### *E,E*-2,5-Thiophene-di-(2-ethenyl)carboxylic acid (12)

Compound (**12**) was prepared from **11** (4.5 g, 0.018 mol) and ethyl acrylate (9.3 g, 0.093 mol) on the way described earlier.<sup>20</sup> To the solution of palladium(II) acetate (0.12 g, 0.52 mmol) and triphenylphosphine (0.58 g, 0.46 mmol) in acetonitrile (60 ml) and triethylamine (40 ml) was added **11** (4.5 g, 0.018 mol) and ethyl acrylate (9.3 g, 0.093 mol). The reaction mixture was sealed in the glass tube and heated at 100°C for 20 h. The mixture was cooled, the content of the tube was evaporated in vacuum and the residue dissolved in methanol (50 ml), the solution was filtered. To the filtrate was added the solution of NaOH (7 g in 200 ml of water) and the mixture was boiled for 1 h. After that time, charcoal was added, the reaction mixture filtered and after cooling, the filtrate was acidified with 20% HCl and the precipitates were filtered off. Yellow crystals, 3.3 g (82.6 %) mp >310°C were obtained (lit.,<sup>21</sup> mp > 310°C).

### 3,5-Dichlorodithienof[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarbonyl chloride (13)

Compound (**13**) was prepared from **12** (2 g, 0.009 mol) and pyridine (0.2 ml) to which thionyl chloride (30 ml, 0.39 mol) was added dropwise at the room temperature and the mixture heated by stirring at reflux for 80 h. The excess of SOCl<sub>2</sub> was distilled off, to the residue was added chloroform, and the precipitated crystals were filtered and recrystallized from chlorobenzene. It was obtained 1.4 g (40.0%) of yellow crystals, mp 247-251°C (lit.,<sup>20</sup>).

### 3,5-Dichlorodithienof[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarboxdianilide (14 and 15)

To the suspension of dicarbonyl chloride (**13**) (1.00 g, 2.57 mmol) in benzene (150 ml) was added dropwise aniline (0.6 ml, 10.3 mmol). The mixture was refluxed for 2h. The obtained crystals were filtered off, washed with 20% HCl, water and hot methanol and recrystallized from DMF (See Table 2).

Table 2

Compd	R	R'	Yield (%)	mp (°C)	Elemental. Anal.		Ir (cm <sup>-1</sup> )	<sup>1</sup> H Nmr (δ ppm) (DMSO-d <sub>6</sub> )	M <sup>+</sup>	
					Calcd(%)	Found(%)				
14	H	H	43.74	> 300	C	52.50	52.34	3300 (NH)	Insoluble	502
					H	2.40	2.97	1640 (CONH)		
					N	5.57	5.83			
15	H	F	72.36	>300	C	49.00	49.20	3300 (NH)	7.26 (4H, t, J=9.00 Hz, arom. Hb)	538
					H	1.87	2.10	1640 (CONH)	7.75 (4H, q, J=9.00 Hz, arom. Ha)	
					N	5.20	4.96		10.39 (2H, s, N-H)	

### 3,5-Dichloro-*N,N'*-dimethyldithieno[3,2-*b*:2',3'-*d*]thiophene-2,6-dicarboxanilide (**16**)

To the suspension of dicarbonyl chloride (**13**) (1.00 g, 2.57 mmol) in benzene (100ml) was added *N*-methylaniline (1.1 ml, 10.30 mmol) by stirring at room temperature. The stirring was continued for 24 h. The benzene solution was washed in the separatory funnel with 5% HCl (3x30 ml), water and dried over MgSO<sub>4</sub>. The solvent was distilled off in vacuum and the crude residue chromatographed on the SiO<sub>2</sub> column with benzene-acetone (3:1) as eluent. The desired product was the first fraction. Yellow crystals 650 mg (47.7%), mp 215-219°C, were obtained. Ir (cm<sup>-1</sup>) (KBr): 3400 (N-CH<sub>3</sub>), 1630 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (DMSO-d<sub>6</sub>) (δ ppm): 7.35-7.22 (m, 10H arom.), 3.41 (s, 6H, N-CH<sub>3</sub>). M<sup>+</sup> 530. Anal. Calcd for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>S<sub>3</sub>: C, 54.25; H, 3.04; N, 5.27. Found: C, 54.21; H, 3.25; N, 5.13.

### Twofold photochemical dehydrohalogenation of **16**

A solution of **16** (650 mg, 1.22 mmol) and triethylamine (0.2 g, 1.8 mmol) in benzene (400 ml) was irradiated as described for **8**. After 10 h the precipitate was filtered off and washed with 20% HCl, water, hot chloroform and recrystallized from DMSO (250 ml). It was obtained 420 mg (75.0%) of white crystals of diquinolone (**17**) mp > 300°C. Ir (cm<sup>-1</sup>) (KBr): 1630 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (DMSO-d<sub>6</sub>) (δ ppm): 8.15-7.92 (m, 8H, H arom.), 2.37 (s, 6H, CH<sub>3</sub>-quinolono). M<sup>+</sup> 458. Anal. Calcd for C<sub>24</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>: C, 62.88; H, 3.08; N, 6.11. Found C, 62.61; H, 3.25; N, 5.96.

### Onefold photochemical dehydrohalogenation of compound **16**

A solution of the compound **16** (500 mg, 0.9 mmol) and triethylamine (0.2 g, 1.8 mmol) in benzene (500 ml) was irradiated as described for **8**. The precipitate was filtered off and treated as above. It was obtained 20 mg (4.6%) of the compound (**17**). The filtrate was evaporated in vacuum and the residual oil was chromatographed on SiO<sub>2</sub> column with toluene-ethyl acetate (7:3). First was isolated unreacted dianilide (**16**), 420 mg (84%) and then after recrystallization from DMF, white crystals of anilidoquinolone; 10-chloro-9-*N'*-methylanilidodithieno[3,2-*b*:2',3'-*d*]thienyl[2'',3''-*c'*]-5-*N*-methylquinoline-6-one (**18**) in the yield of 30 mg



(6.5%) mp >300°C. Ir (cm<sup>-1</sup>) (KBr): 1640 (CO-N-CH<sub>3</sub>), 1650 (CO-N-CH<sub>3</sub>). <sup>1</sup>H Nmr (DMSO-d<sub>6</sub>) (δ ppm): 8.12-7.99 (m, 4H, H arom.), 7.32-7.19 (m, 5H, H arom.), 3.39 (s, 3H, CH<sub>3</sub>-anilido), 2.39 (s, 3H, CH<sub>3</sub>-quinolono). M<sup>+</sup> 494. Anal. Calcd for C<sub>24</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>ClS<sub>3</sub>: C, 58.15; H 3.06; N, 5.66; S 19.40; Cl 7.22. Found: C, 58.25; H, 3.33; N, 5.66; S, 19.70; Cl, 7.22.

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