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Synthesis and Some Transformations of 2-(2-Thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole

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Abstract—Three-component reaction of acenaphthenequinone, 9,10-thiophene-2-carbaldehyde and ammonium acetate in glacial acetic acid afforded 2-(2-thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole. Its *N*-methylated product undergoes electrophilic substitution reactions (nitration, bromination, sulfonation, formylation, acylation) in KOH–1-methyl-2-pyrrolidone mixture. Depending on the reaction conditions electrophilic attack occurred at both thiophene ring and acenaphthene fragment.

Keywords: 9,10-acenaphthenequinone, thiophene-2-carbaldehyde, 2-(2-thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole, *N*-methylation, electrophilic substitution reactions

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Published data on the synthesis and reactions of acenaphtho[1,2-*d*]imidazole containing thiophene moiety are scarce. At the same time, biheterocyclic compounds of this type are of interest as potential biologically active substances [1–3] and organic luminophores [4].

The aim of this work was to develop a convenient method of the synthesis of 2-(2-thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole **I** and to study its behavior under the action of electrophilic reagents.

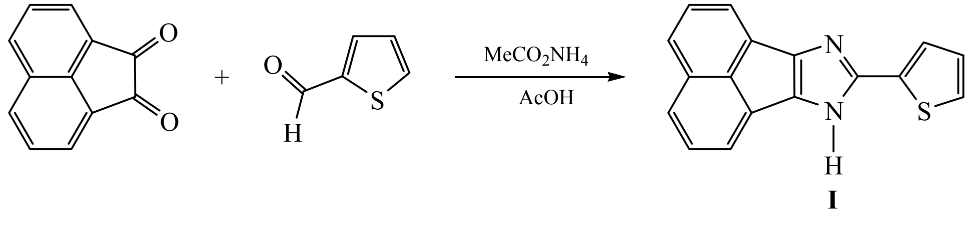
Reactions of acenaphthenequinone with aromatic aldehydes in the ammonia medium have been previously studied [5]. The reactions with various aromatic aldehydes at low temperature afforded only oxazoles. However, when reactions were performed at high temperature, imidazoles or their mixture with oxazoles were formed. The reactions with 4-nitro-, 4-hydroxy-, and 4-methoxybenzaldehydes in ammonia medium resulted only in imidazoles both at low and high temperature. However, we failed to obtain 2-thienyl-substituted acenaphtho[1,2-*d*]imidazole **I** in this manner. Therefore, we applied the approach [6] based on the condensation of 9,10-acenaphthene-quinone, thiophene-2-carbaldehyde, and ammonium acetate in acetic acid. The yield of the desired imidazole **I** was 76% (Scheme 1).

Methylation of **I** with an equivalent amount of methyl iodide was carried out in a KOH–1-methyl-2-pyrrolidone mixture; no appreciable formation of the quaternization product was observed.

1-Methyl-2-(2-thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole **Ia** was subjected to electrophilic reactions with acetyl nitrate, bromine in dichloroethane, sulfuric acid and polyphosphoric acid (PPA), hexamine and carboxylic acids in polyphosphoric acid.

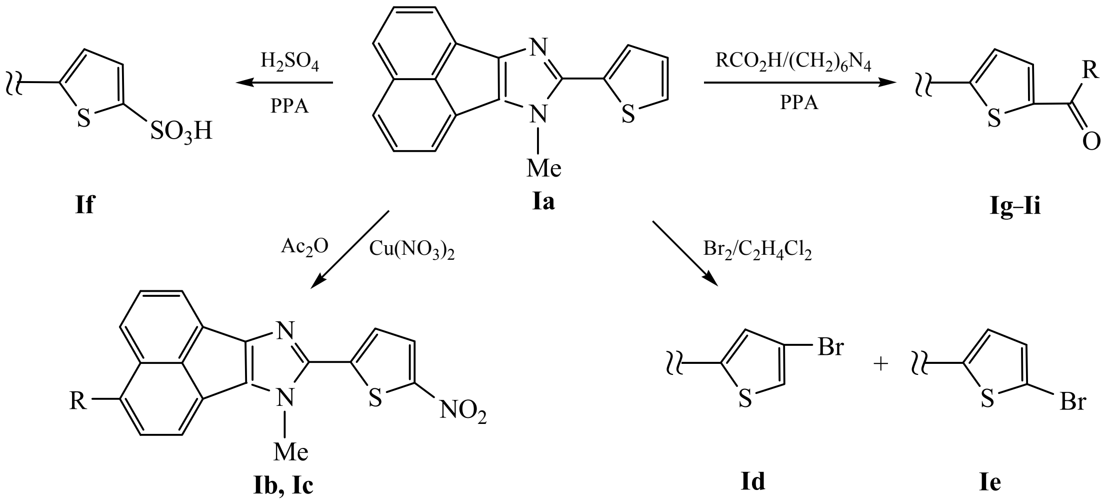
The nitration of **Ia** occurred readily at 20°C by the action of $Cu(NO_3)_2$ and acetic anhydride complex to

Scheme 1.



I

Scheme 2.



R = H (**b**), R = NO$_2$ (**c**), R = H (**g**), R = Me (**h**), R = Ph (**i**).

obtain 5-nitro derivative **Ib**. In contrast, dinitro derivative **Ic** was obtained when the reaction was carried out at 80°C (Scheme 2).

The bromination of **Ia** in dichloroethane proceeded ambiguously. According to ^{1}H NMR, a mixture of monobromo derivatives was obtained substituted in the positions *4* and *5* of the thiophene ring (isomers ratio 2 : 1). Isomers **Id** and **Ie** were separated by column chromatography with yields of 47 and 23%, respectively, and identified.

The sulfonation of **Ia** with two equivalents of sulfuric acid (d = 1.84 g cm^{-3}) in polyphosphoric acid at 110–120°C took place solely with the formation of 5-sulfo derivative **If**.

1-Methyl-2-(2-thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole **Ia** was not formylated by the Vilsmeier reagent even at high temperature (80–90°C), but its heating with hexamine in polyphosphoric acid at 90–100°C gave rise to the corresponding 5-formyl derivative **Ig** in 57% yield as the sole reaction product. Due to the deactivating effect of acenaphthoimidazole fragment on the reactivity of thiophene ring the acetylation of **Ia** was achieved only at the action of acetic anhydride in polyphosphoric acid at 110–120°C. The reaction proceeded unselectively to form a large number of by-products of unknown structure. Their content raised as the reaction temperature was increased. The desired methyl ketone **Ih** was obtained in a yield of less than 36%.

Benzoylation of **Ia** with benzoic acid occurred under the conditions described above, but at a higher temperature (150–160°C). In contrast to acetylation, benzoylation of imidazole **Ia** proceeded smoothly and without the formation of by-products due to a lack in the resulting product of an activated methyl group. Yield of phenyl ketone **Ii** was 73%.

EXPERIMENTAL

IR spectra of the samples as mulls in mineral oil were recorded on a Specord 75IR spectrometer. ^{1}H NMR spectra of the solutions in CDCl$_3$ or DMSO-d_6 were registered on a Varian Unity 300 (300 MHz) instrument, internal reference TMS. The reaction progress was monitored by TLC using plates covered with Al$_2$O$_3$ (Brockmann activity II), eluting with CH$_2$Cl$_2$ or CHCl$_3$ and detecting with iodine vapor. Elemental analysis was performed on a Perkin Elmer 2400 analyzer. Melting points were determined by capillary method on a PTP apparatus.

Physicochemical and spectroscopic characteristics of the obtained compounds are shown in Tables 1, 2.

2-(2-Thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole (I). A solution of 77 g (1 mol) of ammonium acetate and 7.84 g (70 mmol) of thiophene-2-carbaldehyde in 50 mL of acetic acid was rapidly added to a refluxing solution of 9.1 g (50 mmol) of acenaphthenequinone in 250 mL of acetic acid. The mixture was refluxed for 2–3 h and kept at room temperature for 4–6 h. The formed precipitate was filtered off and washed with 50 mL of acetic acid. The filtrate was diluted with 250 mL of cold water and neutralized with ammonia solution. The precipitated crystals were separated and dried. Yield 10.4 g.

Table 1. Melting points, elemental analysis data, and yields of compounds **I–Ii**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
I	76	204–205	74.26	3.82	10.34	$C_{17}H_{10}N_2S$	74.43	3.67	10.21
Ia	91	107–109	75.32	3.92	10.02	$C_{18}H_{12}N_2S$	74.97	4.19	9.71
Ib	65	165–166	65.13	3.62	12.38	$C_{18}H_{11}N_3O_2S$	64.85	3.33	12.60
Ic	43	225–226	56.87	2.93	15.18	$C_{18}H_{10}N_4O_4S$	57.14	2.66	14.81
Id	47	157–158	59.16	2.88	–	$C_{18}H_{11}BrN_2S$	58.87	3.02	–
Ie	23	125–126	58.61	3.27	–	$C_{18}H_{11}BrN_2S$	58.87	3.02	–
If	66	>350	58.83	3.47	7.38	$C_{18}H_{12}N_2O_3S_2$	58.68	3.28	7.60
Ig	86	147–148	71.87	4.12	9.07	$C_{19}H_{12}N_2OS$	72.13	3.82	8.85
Ih	36	133–134	72.93	4.56	8.23	$C_{20}H_{14}N_2OS$	72.70	4.27	8.48
Ii	73	174–175	76.36	3.87	6.92	$C_{25}H_{16}N_2OS$	76.51	4.11	7.14

Table 2. IR and ^{1}H NMR spectral data of compounds **I–Ii**

Comp. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz, $CDCl_3$)
I	–	7.18 t (1H, H^{4}_{Ht}, *J* 4.5), 7.42 d (1H, H^{3}_{Ht}, *J* 3.4), 7.44 d (1H, H^{7}_{Ar}, *J* 3.5), 7.48 d (1H, H^{6}_{Ar}, *J* 3.7), 7.60 d (1H, H^{5}_{Ht}, *J* 4.0), 7.63 d (1H, H^{9}_{Ar}, *J* 6.8), 7.70 t (2H, $H^{5,8}_{Ar}$, *J* 7.8), 7.84 d (1H, H^{4}_{Ar}, *J* 7.8)
Ia	–	4.18 s (3H, NCH_3), 7.20 d (1H, H^{4}_{Ht}, *J* 4.2), 7.43 d (1H, H^{3}_{Ht}, *J* 3.8), 7.46 d (1H, H^{7}_{Ar}, *J* 3.5), 7.51 d (1H, H^{6}_{Ar}, *J* 3.6), 7.58 d (1H, H^{5}_{Ht}, *J* 4.2), 7.64 d (1H, H^{9}_{Ar}, *J* 6.8), 7.72 t (2H, $H^{5,8}_{Ar}$, *J* 7.7), 7.88 d (1H, H^{4}_{Ar}, *J* 7.8)
Ib	1370 sym (NO_2) 1530 asym (NO_2)	4.18 s (3H, NCH_3), 7.48 d (1H, H^{7}_{Ar}, *J* 3.6), 7.52 d (1H, H^{6}_{Ar}, *J* 3.6), 7.60 d (1H, H^{3}_{Ht}, *J* 4.2), 7.65 d (1H, H^{9}_{Ar}, *J* 6.8), 7.73 t (2H, $H^{5,8}_{Ar}$, *J* 7.6), 7.86 d (1H, H^{4}_{Ar}, *J* 6.8), 7.98 d (1H, H^{4}_{Ht}, *J* 7.8)
Ic	1350 sym (NO_2) 1550 asym (NO_2)	4.25 s (3H, NCH_3), 7.52 d (1H, H^{6}_{Ar}, *J* 3.5), 7.60 d (1H, H^{3}_{Ht}, *J* 4.5), 7.68 d (1H, H^{9}_{Ar}, *J* 7.0), 7.72 t (1H, H^{5}_{Ar}, *J* 8.0), 7.86 d (1H, H^{4}_{Ar}, *J* 4.6), 7.96 d (1H, H^{4}_{Ht}, *J* 4.5), 8.46 d (1H, H^{8}_{Ar}, *J* 7.8)
Id	–	4.15 s (3H, NCH_3), 7.36 s (1H, H^{3}_{Ht}), 7.45 d (1H, H^{7}_{Ar}, *J* 7.6), 7.52 d (1H, H^{6}_{Ar}, *J* 7.6), 7.56 s (1H, H^{5}_{Ht}), 7.62 d (1H, H^{9}_{Ar}, *J* 6.8), 7.70 t (2H, $H^{5,8}_{Ar}$, *J* 7.6), 7.86 d (1H, H^{4}_{Ar}, *J* 6.5)
Ie	–	4.16 s (3H, NCH_3), 7.16 d (1H, H^{4}_{Ht}, *J* 4.0), 7.40 d (1H, H^{3}_{Ht}, *J* 4.0), 7.48 d (1H, H^{7}_{Ar}, *J* 7.6), 7.53 d (1H, H^{6}_{Ar}, *J* 7.6), 7.61 d (1H, H^{9}_{Ar}, *J* 6.8), 7.74 t (2H, $H^{5,8}_{Ar}$, *J* 7.5), 7.90 d (1H, H^{4}_{Ar}, *J* 6.8)
If	1260 (SO_2)	4.28 s (3H, NCH_3), 7.36 d (1H, H^{3}_{Ht}, *J* 4.4), 7.42 d (1H, H^{4}_{Ht}, *J* 4.4), 7.46 d (1H, H^{7}_{Ar}, *J* 3.8), 7.51 d (1H, H^{6}_{Ar}, *J* 3.7), 7.66 d (1H, H^{9}_{Ar}, *J* 6.6), 7.75 t (2H, $H^{5,8}_{Ar}$, *J* 7.7), 7.86 d (1H, H^{4}_{Ar}, *J* 7.8), 12.18 br.s (1H, SO_3H)
Ig	1680 (C=O)	4.30 s (3H, NCH_3), 7.44 d (1H, H^{7}_{Ar}, *J* 3.6), 7.53 d (1H, H^{6}_{Ar}, *J* 3.6), 7.60 d (1H, H^{3}_{Ht}, *J* 4.1), 7.64 d (1H, H^{9}_{Ar}, *J* 6.8), 7.73 d (2H, $H^{5,8}_{Ar}$, *J* 7.6), 7.90 d (1H, H^{4}_{Ar}, *J* 7.8), 7.96 d (1H, H^{4}_{Ht}, *J* 4.1)
Ih	1670 (C=O)	4.28 s (3H, NCH_3), 7.42 d (1H, H^{7}_{Ar}, *J* 3.6), 7.51 d (1H, H^{6}_{Ar}, *J* 3.6), 7.56 d (1H, H^{3}_{Ht}, *J* 3.9), 7.64 d (1H, H^{9}_{Ar}, *J* 6.8), 7.70 d (2H, $H^{5,8}_{Ar}$, *J* 7.6), 7.88 d (1H, H^{4}_{Ar}, *J* 7.8), 7.94 d (1H, H^{4}_{Ht}, *J* 3.9)
Ii	1640 (C=O)	4.30 s (3H, NCH_3), 7.43 d (1H, H^{7}_{Ar}, *J* 3.6), 7.48 d (1H, H^{6}_{Ar}, *J* 3.6), 7.52 d (1H, H^{3}_{Ht}, *J* 4.1), 7.55 m (3H, $H^{3',4',5'}_{Ar}$), 7.62 d (1H, H^{9}_{Ar}, *J* 6.8), 7.68 d (2H, $H^{5,8}_{Ar}$, *J* 7.6), 7.90 d (1H, H^{4}_{Ar}, *J* 7.8), 7.96 d (1H, H^{4}_{Ht}, *J* 4.1), 8.12 d (2H, $H^{2',6'}_{Ar}$, *J* 7.8)

1-Methyl-2-(2-thienyl)-1*H*-acenaphtho[1,2-*d*]imidazole (Ia). To a solution of 8.64 g (30 mmol) of **I** in 30 mL of 1-methyl-2-pyrrolidone was added in succession 1.86 g (33 mmol) of powdered KOH and 4.26 g (30 mmol) of methyl iodide. The reaction mixture was stirred at room temperature for 2 h and then diluted with 150 mL of water. The precipitate was separated and dried. Yield 7.86 g.

1-Methyl-2-(5-nitro-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (Ib). To a solution of 2.88 g (10 mmol) of **Ia** in 20 mL of the freshly distilled acetic anhydride was added by portions 2.85 mL of the nitrating mixture [7] with vigorous stirring at room temperature. After 1–1.5 h the resulting mixture was diluted with 50 mL of cold water and neutralized with ammonia solution. The product was extracted with methylene chloride and chromatographed on Al_2O_3 eluting with methylene chloride. Yield 2.16 g.

1-Methyl-2-(5-nitro-2-thienyl)-1*H*-7-nitroacenaphtho-[1,2-*d*]imidazole (Ic). To a solution of 2.88 g (10 mmol) of **Ia** in 20 mL of freshly distilled acetic anhydride was added by portions 2.85 mL of the nitrating mixture [7] with vigorous stirring at room temperature. The mixture was then heated in a water bath at 80°C for 10 min. The precipitated crystals were filtered off after cooling, washed with a small amount of acetic acid and water, neutralized with ammonia solution, and recrystallized from ethanol. Yield 1.63 g.

1-Methyl-2-(4-bromo-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (Id). A solution of 3.2 g (20 mmol) of bromine in 20 mL of dichloroethane was gradually added to a solution of 2.88 g (10 mmol) of **Ia** in 40 mL of dichloroethane at room temperature. Then the mixture was refluxed for 4 h, diluted with water and neutralized with ammonia solution. The lower layer was separated and chromatographed on Al_2O_3 eluting with methylene chloride. Yield 1.72 g.

1-Methyl-2-(5-bromo-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (Ie) was obtained by chromatography of the mixture of isomers from the previous experiment. Yield 0.84 g.

1-Methyl-2-(5-sulfo-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (If). A mixture of 2.88 g (10 mmol) of **Ia**, 1.95 g (20 mmol) of sulfuric acid ($d = 1.84$ g cm^{-3}), and 40 g of polyphosphoric acid was heated at 100–110°C for 2 h. After cooling the reaction mixture was diluted with 100 mL of water. The precipitated sulfonate was separated, dissolved in 5% alkaline solution, heated with activated carbon, and neutralized with hydrochloric acid until slightly acidic reaction. Yield 2.43 g.

1-Methyl-2-(5-formyl-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (Ig). A mixture of 2.88 g (10 mmol) of **Ia** and 4.2 g (30 mmol) of hexamine in 40 g of polyphosphoric acid was stirred at 90–100°C for 4 h, whereupon the reaction mixture was diluted with 100 mL of water and neutralized with ammonia solution. The separated reaction product was extracted with methylene chloride. The extract was dried over Na_2SO_4 and chromatographed on Al_2O_3 eluting with methylene chloride. Yield 2.71 g.

1-Methyl-2-(5-acetyl-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (Ih). A mixture of 2.88 g (10 mmol) of **Ia** and 3.06 g (30 mmol) of acetic anhydride in 40 g of polyphosphoric acid was stirred at 110–120°C for 18 h. The reaction product was isolated similarly to **Ig**. Yield 1.19 g.

1-Methyl-2-(5-benzoyl-2-thienyl)-1*H*-acenaphtho-[1,2-*d*]imidazole (Ii). A mixture of 2.88 g (10 mmol) of **Ia** and 6.1 g (50 mmol) of benzoic acid in 40 g of polyphosphoric acid was stirred at 150–160°C for 8 h. The reaction product was isolated similarly to **Ig**. Yield 2.86 g.

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