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SYNTHESIS OF 4-HETARYL-5,6-(2,5-DIMETHYL-3-THIENYL)-2-PHENYL-4H-THIAZINES AND INVESTIGATION OF THEIR PHOTOCHROMISM

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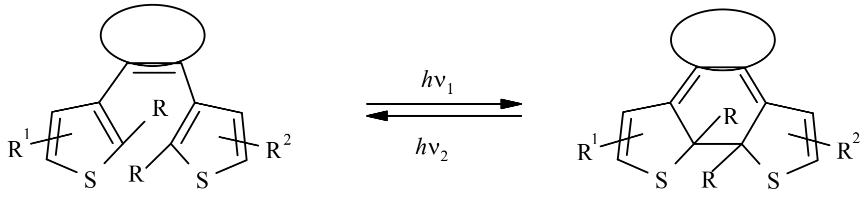
The polar [4+2] cycloaddition reaction of 1,2-bis(2,5-dimethyl-3-thienyl)acetylene with thiobenzamide and certain aldehydes of the thiophene and furan series catalyzed by boron trifluoride etherate gives the corresponding 4-hetaryl-5,6-di(2,5-dimethyl-3-thienyl)-2-phenyl-4H-1,3-thiazines. The photochromic properties of the products have been studied.

Keywords: 1,2-bis(2,5-dimethyl-3-thienyl)acetylene, hetarenecarbaldehydes, 4-hetaryl-5,6-di(2,5-dimethyl-3-thienyl)-2-phenyl-4H-1,3-thiazines, thiobenzamide, photochromism.

A search is being conducted for new dithienylethenes capable of reversible photoinduced valence isomerization [2] in connection with solving the problem of building a three-dimensional optical memory with a superlarge information capacity [1].



A **B**

On irradiation with UV light $h\nu_1$ the colorless open form **A** is converted into the colored cyclic form **B**, which on absorption of visible radiation $h\nu_2$ reverts once again to the initial colorless state. A distinctive feature of such photochromic compounds is the thermal stability of the open and cyclic forms, which makes possible their use in optical memory devices [3].

The aim of the present investigation is the synthesis of new dihetarylethenes and the study primarily of their photochromic properties. We have recently proposed a new strategy for the synthesis of such systems. The key stage is a cycloaddition reaction involving a dihetarylacetylene, which provides a cyclic dihetarylethene with a fixed *cis* configuration [4-6].

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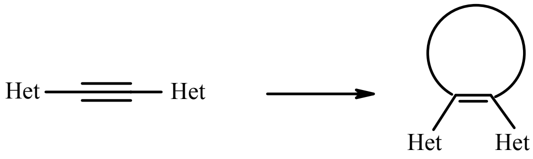
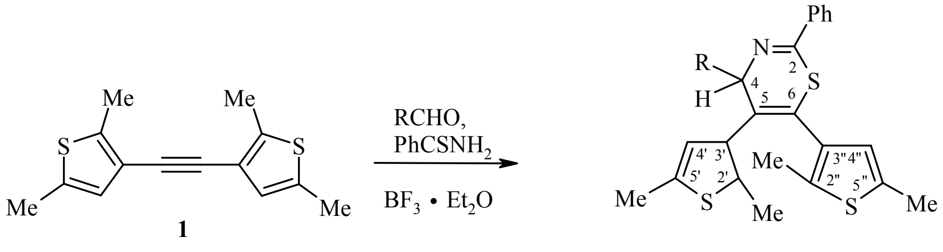
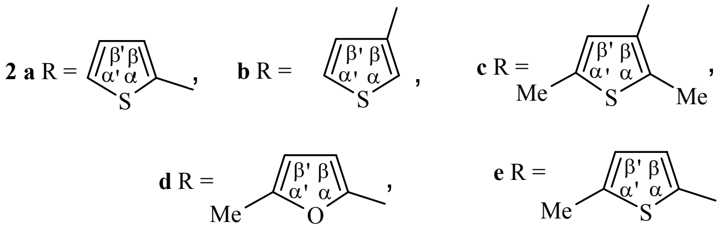


In the present work we have studied the boron trifluoride etherate catalyzed reaction of 1,2-bis(2,5-dimethyl-3-thienyl)acetylene (**1**) [6] with thiobenzamide and a series of heteroaromatic aldehydes. This leads to 4-hetaryl-5,6-di(2,5-dimethyl-3-thienyl)-2-phenyl-4H-1,3-thiazines **2a-e** (Tables 1 and 2). A similar reaction has been described for diphenylacetylene [7] and is represented as a process of polar [4+2] cycloaddition.The reaction is complicated by resinification and by the formation of 2,4,6-triphenyl-1,3,5-triazine, a condensation product of thiobenzamide.



2a–e



A spectral kinetic investigation was carried out on the potentially photochromic dihetarylethenes **2a-e**. According to the spectral characteristics (Figs. 1-3 and Table 3) both the open and the closed forms of compounds **2a-e** are characterized by shorter wave absorption bands in comparison with, in particular, 1,2-dithienyl-substituted hexafluorocyclopentenes [3]. In the spectra of diarylethenes **2c** and **2d** (Figs. 2 and 3) clearly expressed absorption bands for the cyclic form were absent, and the bands were distorted with increasing irradiation time.

TABLE 1. Conditions of Synthesis and Characteristics of Compounds **2a-e**

Compound	Reaction time, h (temp. °C)	Empirical formula	Found, % / Calculated, %				mp, °C (from MeCN)	Yield, %
			C	H	N	S		
2a	21 (~20)	$C_{26}H_{23}NS_4$	65.28 65.37	4.96 4.85	—	26.81 26.85	106-108	18
2b	19 (-5)	$C_{26}H_{23}NS_4$	65.50 65.37	4.72 4.85	2.85 2.93	26.93 26.85	104-106	23
2c	28 (~20)	$C_{28}H_{27}NS_4$	66.88 66.49	5.86 5.38	2.64 2.77	24.62 25.36	Oil	35
2d	20 (15)	$C_{27}H_{25}NOS_3$	67.87 68.17	5.73 5.30	3.05 2.94	19.48 20.22	154-155	19
2e	22 (18)	$C_{27}H_{25}NS_4$	65.70 65.95	4.95 5.12	3.22 2.85	25.08 26.08	130-131	24

TABLE 2. ^{1}H NMR Spectra of Compounds **2a-e**

<table>
<tr><th rowspan="3">Com-pound</th><th colspan="6">Chemical shifts, δ, ppm</th></tr>
<tr><th rowspan="2">H-4, s</th><th colspan="2">Thiophene ring, s</th><th rowspan="2">Het*</th><th rowspan="2">Ph*^{2}</th><th rowspan="2">Methyl group signals, s</th></tr>
<tr><th>H-4'</th><th>H-4"</th></tr>
<tr><td>2a</td><td>6.35</td><td>6.46</td><td>6.54</td><td>7.20 (d, H-α'),
7.13 (d, H-β),
6.95 (dd, H-β')</td><td>8.00 (dd, o-H$_{Ph}$);
7.44 (m, m-H$_{Ph}$ + p-H$_{Ph}$)</td><td>2.36, 2.33
(C-2")- and (C-5")-CH$_3$,
2.12, 1.85
C(2')- and C(5')-$\underline{CH}_3$</td></tr>
<tr><td>2b</td><td>6.14</td><td>6.38</td><td>6.51</td><td>7.30 (s, H-α),
7.25 (dd, H-α'),
7.20 (d, H-β')</td><td>8.00 (dd, o-H$_{Ph}$),
7.44 (m, m-H$_{Ph}$ + p-H$_{Ph}$)</td><td>2.36, 2.33
(C-2")- and (C-5")-$\underline{CH}_3$,
2.11, 1.84
(C-2')-$\underline{CH}_3$ and (C-5')-$\underline{CH}_3$</td></tr>
<tr><td>2c</td><td>5.94</td><td>6.30</td><td>6.57</td><td>6.95 (s, H-β')</td><td>8.02 (dd, o-H$_{Ph}$),
7.43 (ddd, m-H$_{Ph}$ + p-H$_{Ph}$)</td><td>2.36, 2.33
(C-2")- and (C-5")-$\underline{CH}_3$,
2.11, 1.84
(C-2')- and (C-5')-$\underline{CH}_3$</td></tr>
<tr><td>2d</td><td>6.11</td><td>6.48</td><td>6.56</td><td>6.24 (d, H-β),
5.88 (d, H-β')</td><td>8.01 (dd, o-H$_{Ph}$),
7.44 (m, m-H$_{Ph}$ + p-H$_{Ph}$)</td><td>2.36, 2.34
(C-2")- and (C-5")-$\underline{CH}_3$,
2.28, CH$_3$ $_{fur}$,
2.08, 1.85
(C-2')- and (C-5')-$\underline{CH}_3$</td></tr>
<tr><td>2e</td><td>6.29</td><td>6.49</td><td>6.56</td><td>6.91 (d, H-β),
6.58 (d, H-β')</td><td>8.00 (d, o-H$_{Ph}$),
7.46 (m, m-H$_{Ph}$ + p-H$_{Ph}$)</td><td>2.37, 2.34
(C-2")- and (C-5")-$\underline{CH}_3$,
2.44, CH$_3$ $_{thioph}$,
2.11, 1.86
(C-2')- and (C-5')-$\underline{CH}_3$</td></tr>
</table>

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* Coupling constants, J, Hz: **2a** – J_{45} = 5.2, J_{34} = 3.9; **2b** – J_{45} = 4.6, J_{25} = 1.3; **2d** – J_{34} = 3.3; **2e** – J_{34} = 2.6.

*^{2} J_{om} = 7.9, J_{mp} = 7.2-7.4, J_{op} = 2.0.

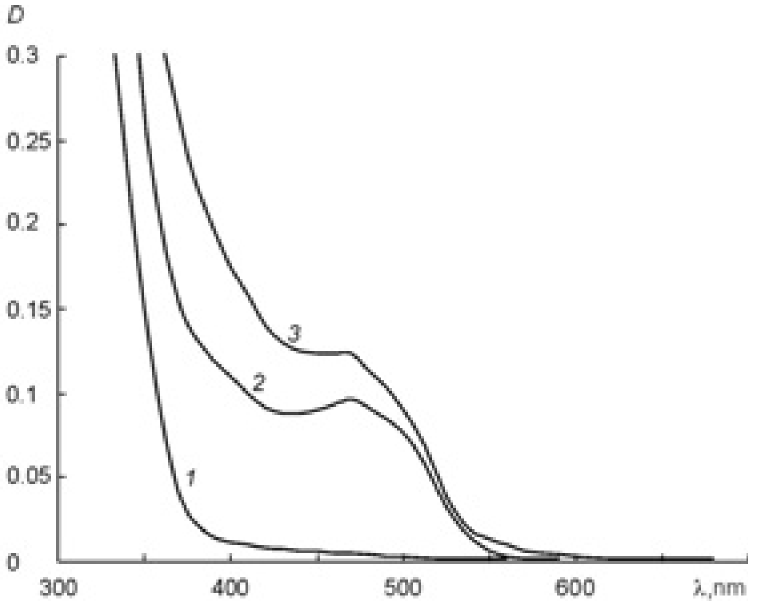


Fig. 1. Absorption spectra of thiazine **2a** in toluene 1) before and 2), 3) after successive UV irradiation.

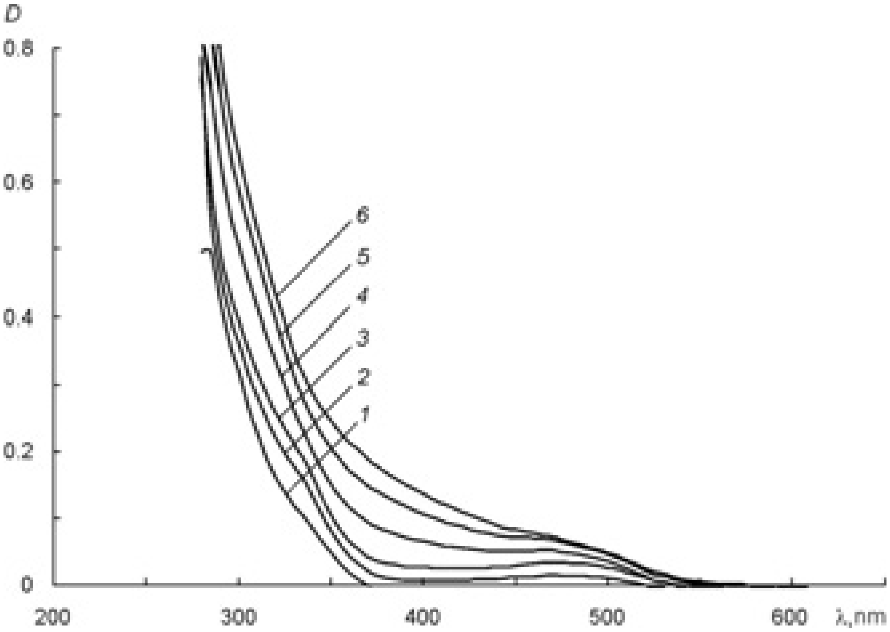


Fig. 2. Absorption spectra of diarylethene **2c** in toluene obtained
1) before and as a result of UV irradiation with 313 nm light for 2) 1, 3) 2, 4) 10, 5) 20, and 6) 30 min.

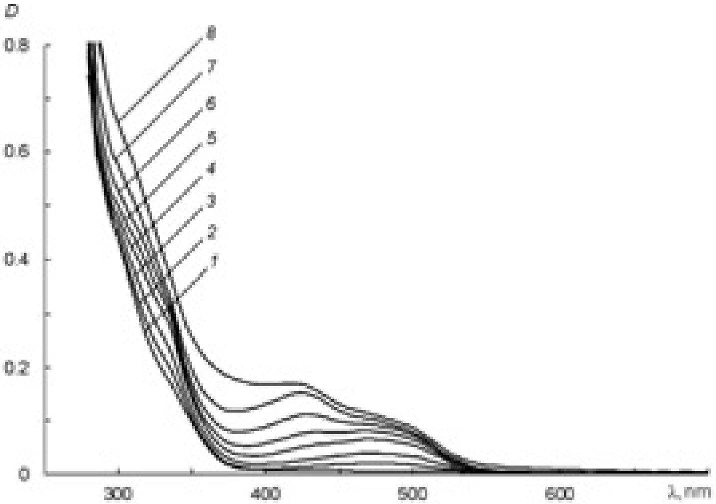
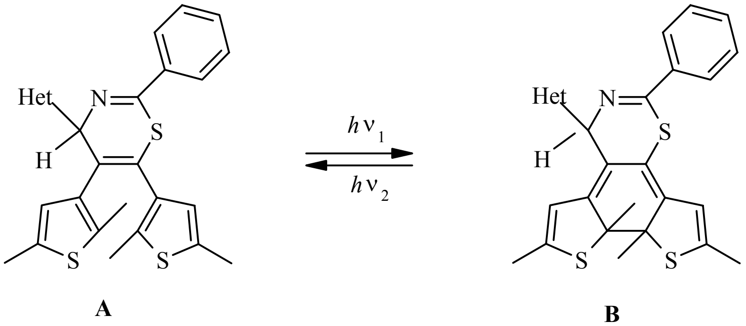


Fig. 3. Absorption spectrum of diarylethene **2d** in toluene obtained
1) before and as a result of UV irradiation with 313 nm light for
2) 0.25, 3) 0.5, 4) 2, 5) 4. 6) 8, 7) 16, and 8) 30 min.

It has has been shown, that in a study of the photoinduced change of the optical density of the cyclic form the corresponding curves for the processes of photocoloration and photodecoloration have no exponential character, but contain two components characterizing the complexity of the photochromic conversion. Judging by the photoinduced optical density at the maximum of the absorption band of the cyclic form (Table 2), the degree of conversion of the open form of compounds **2a-e** into the closed form on irradiation is small.

TABLE 3. Spectral Kinetic Parameters of Thiazine Derivatives **2a-e** in Toluene*



A **B**

Compound	$\lambda^{\mathbf{A}}_{\max}$, nm	$\lambda^{\mathbf{B}}_{\max}$, nm	$D^{\mathrm{phot}}_{\max}$
2a	<350	470	0.30
2b*[2]	<350	—	—
2c	<300	410, 470	0.25
2d	<300	425	0.65
2e	<350	470	0.45

* $\lambda^{\mathbf{A}}_{\max}$ and $\lambda^{\mathbf{B}}_{\max}$ are the absorption band maxima of the open **A** and cyclic **B** forms respectively; $D^{\mathrm{phot}}_{\max}$ is the photoinduced optical density at the maximum of the absorption band of the cyclic form **B**.

*[2] The closed form of compound **2b** has a broad band in the visible region with $D^{\mathrm{phot}}_{\max} < 0.01$, which does not allow precise determination of a value for $\lambda^{\mathbf{B}}_{\max}$.

The synthesized compounds are characterized by the high thermal stability of the cyclic form, which does not change in photoinduced optical density after 30 days storage in the dark. The rate of photodegradation grows with the increase in solvent polarity on going from toluene to acetonitrile.

Analysis of the spectral kinetic characteristics given shows that the synthesized compounds display photochromic properties. They are characterized by moderate light sensitivity and thermal irreversibility of photochromic conversions.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM 250 (250 and 62 MHz respectively) in $CDCl_3$ relative to the solvent signal, internal standard was TMS. The EI mass spectra were registered on a Kratos instrument with direct insertion of the sample into the ion source, ionization energy was 70 eV. The 4H-1,3-thiazines were isolated by chromatography on a column of US INCORPORATED 40 μ FLASH silica gel (32-63 μ), eluent was petroleum ether (bp 40-70°C)–ethyl acetate, 9:1. Melting points were determined on a Kofler block and are not corrected.

The spectral kinetic investigations were carried out for solutions in toluene of A. C. S. spectrophotometric grade. The concentration of compounds in solution $c = 2.10^{-4}$ M. Cuvette thickness was 3 mm. The absorption spectra of the open and cyclic forms of the photochromic compounds were measured on a Shimadzu UV-VIS spectrophotometer in the range 200-800 nm. The cyclic form was obtained after photoexcitation of the solution with radiation from a DRSh 250 mercury lamp through a UV filter separating out radiation with λ = 313 nm.

The kinetics of photocoloration of solutions of dithienylthiazines were measured at the wavelength of the absorption band maximum on irradiation of previously decolorized solutions of these compounds by the same radiation. The kinetics of photodecolorization were measured on irradiation of previous colored solutions of these compounds by irradiation with the mercury lines of a DRSh 250 lamp in the visible region of the spectrum (436 nm), separated with an appropriate glass light filter.

With the aim of accelerating the testing of the photochromic compounds for the cyclic nature of the photochromic conversions, a comparative investigation was carried out of the photodegradation of solutions of dithienylthiazines under the action of high intensity irradiation. The photodecomposition of solutions was characterized by a reduction in the optical density of the photostationary state at the absorption maximum of the cyclic form on continuous irradiation with filtered (λ = 313 nm) or unfiltered light from a DRSh 250 mercury lamp.

Data on the kinetics of the thermal isomerization of the photoinduced form of dithienylthiazines were obtained by periodic (with an interval of several days) measurement of the absorption spectra of solutions. In the intervals between measurements solutions were stored protected from light.

4-Hetaryl-5,6-bis(2,5-dimethyl-3-thienyl)-2-phenyl-4H-1,3-thiazines 2a-e (General Procedure). Boron trifluoride etherate (0.21 ml, 1.62 mmol) in chloroform (1 ml) was added with stirring during 15 min to a solution of 1,2-bis(2,5-dimethyl-3-thienyl)acetylene (0.200 g, 0.81 mmol), thiobenzamide (0.111 g, 0.81 mmol), and the appropriate aldehyde (0.81 mmol) in dry chloroform (3 ml) at the temperature indicated in Table 1. The dark solution obtained was stirred at the same temperature for 1 h. The solution was then stored as indicated in Table 1, and treated with 5% aqueous ammonia solution. The aqueous phase was separated and extracted with chloroform. The combined extracts and organic phase were washed with water to a neutral reaction, and dried with calcium chloride. After evaporating the solvent the solid residue obtained was chromatographed on a column of SiO_2, eluting with petroleum ether (40-70°C)–diethyl ether, 95:5.

5,6-Bis(2,5-dimethyl-3-thienyl)-2-phenyl-4-(2-thienyl)-4H-1,3-thiazine (2a). Mass spectrum, *m/z* (I_{rel}, %): 477 (28) $[M]^+$, 445 (84) $[M\text{-}S]^+$. 375 (76) $[M\text{-}PhCN]^+$, 246 (32) $[HetC{\equiv}CHet]^+$, 103 (100) $[PhCN]^+$.

5,6-Bis(2,5-dimethyl-3-thienyl)-2-phenyl-4-(3-thienyl)-4H-1,3-thiazine (2b). Mass spectrum, *m/z* (I_{rel}, %): 477 (85) $[M]^+$, 445 (100) $[M\text{-}S]^+$, 374 (91) $[M\text{-}PhCN\text{-}H]^+$, 246 (30) $[HetC{\equiv}CHet]^+$, 103 (81) $[PhCN]^+$.

4,5,6-Tris(2,5-dimethyl-3-thienyl)-2-phenyl-4H-1,3-thiazine (2c). Mass spectrum, *m/z* (I_{rel}, %): 505 (41) $[M]^+$, 473 (16) $[M\text{-}S]^+$, 402 (76) $[M\text{-}PhCN]^+$, 387 (100) $[M\text{-}PhCN\text{-}Me]^+$, 246 (46) $[HetC{\equiv}CHet]^+$, 103 (53) $[PhCN]^+$.

5,6-Bis(2,5-dimethyl-3-thienyl)-4-(5-methyl-2-furyl)-2-phenyl-4H-1,3-thiazine (2d). Mass spectrum, *m/z* (I_{rel}, %): 475 (36) $[M]^+$, 460 (6) $[M\text{-}Me]^+$, 443 (11) $[M\text{-}S]^+$, 372 (100) $[M\text{-}PhCN]^+$, 357 (45) $[M\text{-}PhCN\text{-}Me]^+$, 246 (16) $[HetC{\equiv}CHet]^+$, 103 (77) $[PhCN]^+$. ^{13}C NMR spectrum, δ, ppm: 161.03 (C-2), 152.03 (C-α), 149.55 (C-α'), 137.17 (C_{thioph}-5'), 135.78 (C-5''), 135.44 (*ipso*-C_{Ph}), 133.89 (C-2'), 135.23 (C-2''), 131.20 (C_{Ph}-4), 128.56 (C-3 and C_{Ph}-5), 127.81 (C-2 and C_{Ph}-6), 126.58 (C-4'), 126.04 (C-4''), 123.83 (C-5), 108.64 (C-β'), 106.04 (C-β), 64.17 (C-4), 15.33 and 15.27 (Me at C-5' and C-5''), 14.33 (Me at C-α'), 14.24 and 13.87 (Me at C-2' and C-2'').

5,6-Bis(2,5-dimethyl-3-thienyl)-4-(5-methyl-2-thienyl)-2-phenyl-4H-1,3-thiazine (2e). Mass spectrum, *m/z* (I_{rel}, %): 491 (61) $[M]^+$, 476 (5) $[M\text{-}Me]^+$, 459 (100) $[M\text{-}S]^+$, 388 (72) $[M\text{-}PhCN]^+$, 374 (22) $[M\text{-}PhCN\text{-}Me]^+$, 246 (14) $[HetC{\equiv}CHet]^+$, 103 (86) $[PhCN]^+$.

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