Chemistry of Heterocyclic Compounds, Vol. 42, No. 6, 2006

SYNTHESIS OF BIS- AND TETRAKIS-(ω-DIMETHYLAMINO)-SUBSTITUTED CROSS-CONJUGATED POLYENE α-DIKETONES OF THE THIOPHENE SERIES

Zh. A. Krasnaya, Yu. V. Smirnova, A. S. Tatikolov, and A. V. Kolotaev

Bis- and tetrakis(ω-dimethylamino)-substituted cross-conjugated polyene α-diketones, containing two thiophene rings, were synthesized from α-diketones of the thiophene series and β-dimethylamino-acrolein aminals and also 2-aza-3-dimethylaminoacrolein acetal.

Keywords: β-dimethylaminoacrolein aminals, dithienylethanediones, cross-conjugated (ω-dimethyl-amino)-substituted polyene diketones, absorption spectra, photolysis.

In recent years intensive investigations have been carried out on derivatives of the thiophene series in connection with new possible uses as photochromes (see the review [1]), components of materials for nonlinear optics [2, 3], absorption polarization [4], and others.

In 2003 a method was developed for the synthesis of α-diketones of the thiophene series [5], which are potential precursors of photochromic dithienylethenes (see the review [6]).

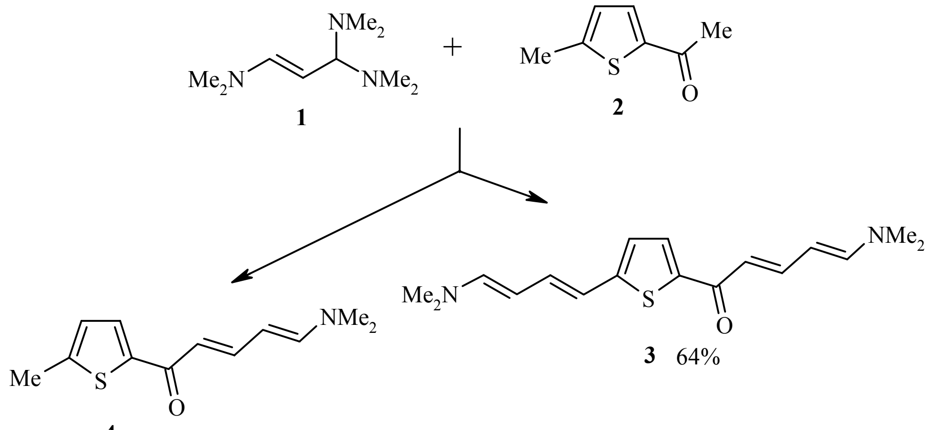
In the present work it was proposed to use the obtained α-diketones for the synthesis of cross-conjugated ω,ω'-dimethylaminopolyenediones containing two thiophene fragments. Photophysical investigation of the latter is of undoubted interest in view of the fact that the dithiophene fragment is present as bridging structure in the new polyene dyes proposed for use in nonlinear optical systems [2].

Earlier we showed that the aminals of β-dimethylaminoacrolein (**1**) and its homologs are suitable reagents for the introduction of an ω-dimethylaminopolyene fragment into various aliphatic, cyclic, and heterocyclic ketones, diketones, CH acids, and other compounds leading to aminopolyenes, many of which have unusual luminescence spectral characteristics (see the review [7]).

The reactivity of the aminals is so high that they can condense in the absence of a catalyst not only at the α-methyl or methylene group adjacent to the carbonyl group but also at the Me group separated from it by one or two double bonds or a heterocycle [8].

Thus, during the condensation of compound **1** with 2-acetyl-5-methylthiophene (**2**) as a result of reaction at both methyl groups the cross-conjugated ω,ω'-bisdimethylamino ketone **3**, containing a thiophene ring, is formed, while only the mono-ω-dimethylamino ketone **4** is formed if the reaction conditions are changed.

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow; e-mail: kra@ioc.ac.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 841-847, June, 2006. Original article submitted December 23, 2004.

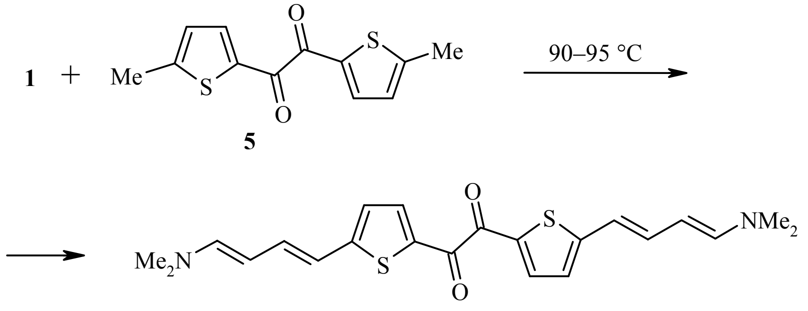


1 **2** **3** 64% **4** 85%

Reaction of the aminal **1** with α-diketones of the thiophene series **5**-**7**, containing two methyl groups, could lead in the case of successful reaction to new cross-conjugated systems with two thiophene rings and dimethylamino groups at the ends of the polyene chain, investigation of the optical characteristics of which was of undoubted interest.

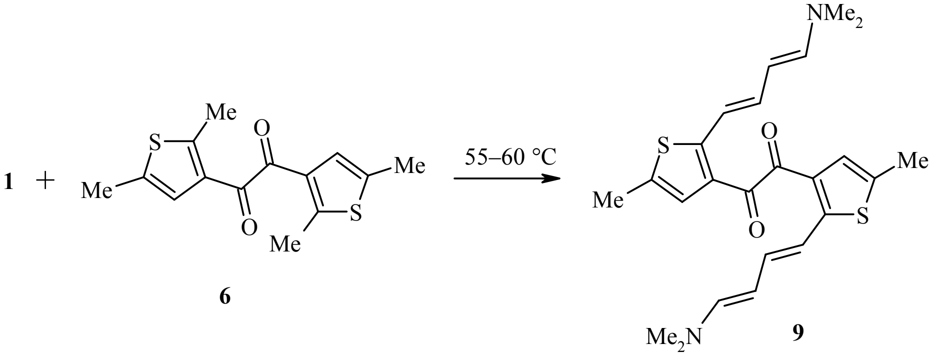
The reactions of the aminal **1** with the diketones **5**-**7** were carried out by briefly heating without a solvent.

In the reaction with the diketone **5** a 49% yield of the ω,ω'-bisdimethylamino diketone **8** was obtained.



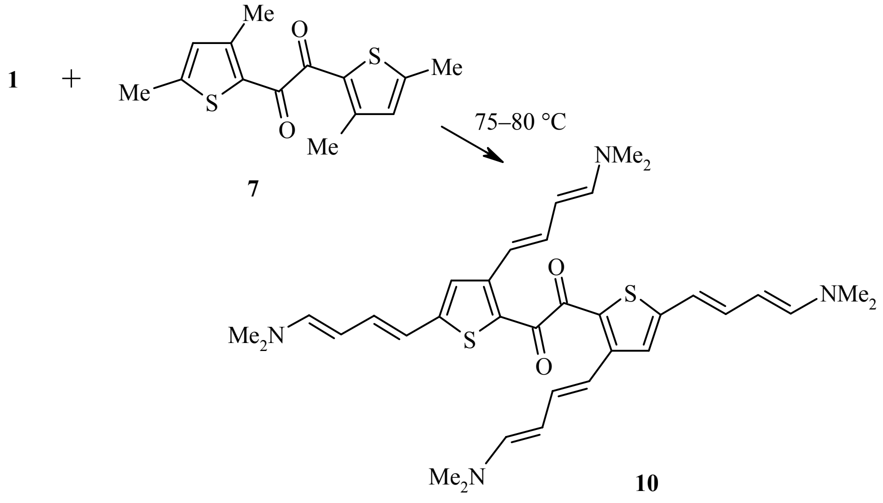
5 **8**

The reaction of the aminal **1** with the diketone **6** only took place at the methyl group at position 2, resulting in a 38% yield of the ω,ω'-bisdimethylamino diketone **9**.



6 **9**

The condensation of the aminal **1** with the diketone **7** involved all the methyl groups and gave a 78% yield of the tetrakisdimethylamino diketone **10**.

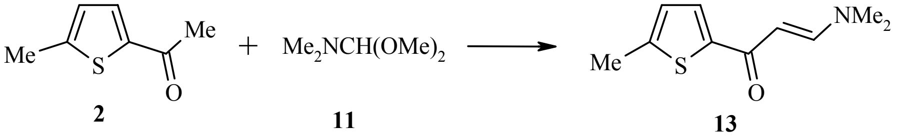


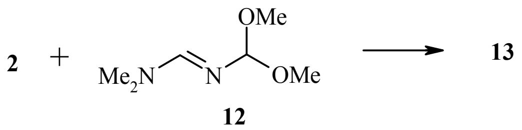
The diketones **8-10** are crystalline substances; their structure was confirmed by the results from elemental analysis and by the ^{1}H NMR, mass, and electronic absorption spectra.

It was established by means of the ^{1}H NMR data that the diketones **8-10** have the *trans* configuration of the methine protons and exist preferentially in the form of the *s-trans* conformers (J = 10.3-15.1 Hz).

Since it was found that the diketones **5-7** react fairly readily with the aminal **1**, it seemed of interest to study the reaction of these diketones and also of the ketone **2** with the acetals of DMF **11** and 2-aza-3-dimethylaminoacrolein (**12**). These acetals can be used for the introduction of the dimethylamino fragment at the α-position to the carbonyl group (see the review [9]). It was shown for a series of examples that the condensation of the ketones with the acetals **11** and **12** takes place with smaller yields and under more severe conditions than condensation involving the aminal **1**.

This observation was confirmed in the present work. It was found that unlike the aminal **1** the acetals **11** and **12** only react with the ketone **2** at the acetyl group, and only small yields (31 and 41% respectively) of the mono-β-dimethylamino ketone **13** are obtained.



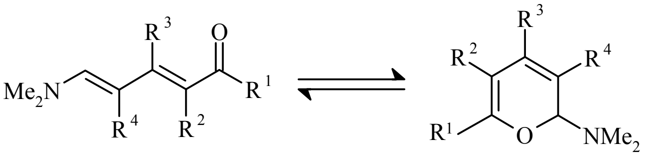


Nevertheless, we tried to condense the acetals **11** and **12** with the diketone **6** in order to obtain the diketone **14**, the structure of which contains two δ-dimethylaminodienone fragments.

The δ-aminodienones are interesting from the standpoint of their valence isomerization, δ-aminodienone – 2-amino-2H-pyran, which gives rise to solvato-, thermo-, and photochromism in such compounds (see the review [10]).

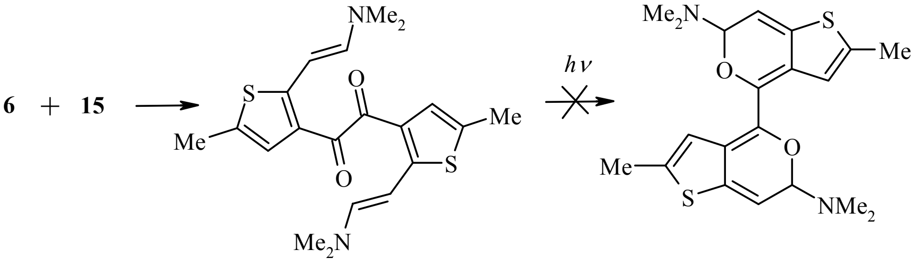
TABLE 1. The Maxima in the Absorption Spectra of the Diketones **8-10**

Compound	$\lambda_{\text{abs max}}$, nm	
	in *i*-PrOH	in toluene
8	540	523
9	518	501
10	510, 364	501, 364



It was only possible to obtain a very small yield (10%) of the diketone **14** by the reaction of the diketone **6** with the azaacetal **12**.

The structure of the diketone **14** was supported by the ^{1}H NMR, mass, and absorption spectra. However, the pyran form (PF) was not detected during photoexcitation of the diketone **14**.



14 **14** (PF)

During study of the photochemistry of the diketones **8-10** it was found that the long-wave absorption band of these diketones undergoes a bathochromic shift in the transition from the nonpolar solvent toluene or the polar isopropyl alcohol, demonstrating the charge-transfer nature of this band.

Comparison of the data from the absorption spectra of ω,ω'-bisdimethylamino diketone **8** and ω,ω'-bisdimethylamino ketone **3** shows that cross-conjugation of the polyene chains through the two thiophene rings linked at position 2 by two adjacent carbonyl groups (diketone **8**) leads to a significant bathochromic shift ($\Delta\lambda$ = 50 nm) compared with the ketone containing one thiophene ring and one carbonyl group.

Flash photolysis of compounds **8-10** and **14** (excitation in the long-wave absorption band) both in isopropyl alcohol and in toluene does not lead to the formation of any products. Stationary photolysis with visible light also does not give rise to photochemical transformations in the given diamino diketones. Photolysis with the full light of a DRSh-500 lamp (including the UV region) leads to a decrease in the strong absorption bands due to the irreversible photodecomposition of these compounds.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WM-250 (250 MHz). The mass spectra (EI, 70 eV, direct injection) were obtained on an MS-30 instrument. The absorption spectra were measured on a Specord UV-VIS spectrophotometer. Photolysis was conducted with excitation by a xenon lamp (energy 50 J, duration of flash at half-height τ = 7 μsec) [11].

The reactions were monitored by UV spectroscopy.

The reagent ratios, temperatures, and reaction times were optimum for the synthesis of compounds **8-10**, **13**, and **14**.

1,2-Bis[5-(dimethylamino-1,3-butadienyl)-2-thienyl]ethanedione (8). A mixture of the aminal **1** (130 mg, 0.8 mmol) and 1,2-bis(5-methyl-2-thienyl)ethanedione **5** (100 mg, 0.4 mmol) was heated at 90-95°C for 15 min. The crystalline reaction mass was cooled to 20°C, the crystals were suspended in absolute ether, the solvent was decanted, and the residue was washed with dry acetone and filtered. We obtained 80 mg (49%) of compound **8**; mp 177-180°C. UV spectrum, λ_{max}, nm (ε): in methylene chloride, 290 (19000), 420 plateau (12300), 532 (42900); in methanol, 287 (14500), 550 (26000). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 2.86 [12H, s, $2N(CH_3)_2$]; 5.17 (2H, t, *J* = 11.0, H-γ); 6.27 (2H, t, *J* = 14.7, H-α); 6.60 (2H, d, *J* = 12.5, H-δ); 6.78 (2H, d, *J* = 4.4); 6.93 (2H, dd, *J* = 14.7, *J* = 10.3, H-β); 7.78 (2H, d, *J* = 4.4, CH). Mass spectrum, *m/z* (*I*, %): 412 $[M]^+$ (22), 206 $[M/2]^+$ (100), 178 $[M/2\text{-}CO]^+$ (20), 163 $[M/2\text{-}CH_2NCH_3]^+$ (19), 134 $[M/2\text{-}CO\text{-}Me_2N]^+$ (22). Found %: C 63.82; H 5.87; S 15.54. $C_{22}H_{24}N_2O_2S_2$. Calculated %: C 64.05; H 5.86; S 15.54.

1,2-Bis[2-(4-dimethylamino-1,3-butadienyl)-5-methyl-3-thienyl]ethanedione (9). A mixture of 1,2-bis(2,5-dimethyl-3-thienyl)ethanedione **6** (100 mg, 0.36 mmol) and 190 mg (1.2 mmol) of the aminal **1** was heated at 55-60°C for 30 min. After cooling to 20°C, absolute ether was added to the reaction mass, and the precipitate was separated and washed with dry acetone. We obtained 60 mg (38%) of the product **9** in the form of dark-red crystals, melting at 185-188°C. UV spectrum, λ_{max}, nm (ε): in methylene chloride, 290 (28300), plateau 315 (16000), 520 (42400); in ethanol, 285 (14500), plateau 315 (18200), 523 (22900). ^{1}H NMR spectrum (deuterochloroform), δ, ppm (*J*, Hz): 2.31 (6H, s, CH_3); 2.84 [12H, s, $2N(CH_3)_2$]; 5.25 (2H, t, *J* = 11.0, H-γ); 6.52 (2H, d, *J* = 13.2, H-α); 6.73 (2H, s, CH); 6.83 (2H, dd, *J* = 13.2, *J* = 10.3, H-β); 7.45 (2H, d, *J* = 14.7, H-δ). Mass spectrum, *m/z* (*I*, %): 440 $[M]^+$ (47), 395 $[M - Me_2NH]^+$ (15), 379 $[M - Me_2NH - Me - H]^+$ (73), 361 $[M - Me_2NH - Me - H_2O - H]^+$ (54), 351 $[M - Me_2NH - Me_2N]^+$ (45), 348 $[M - 2Me - Me_2N - H_2O - CO]^+$ (100), 334 $[M - Me_2NH - Me - H_2O - CO]^+$ (55), 320 $[M - 2M - Me_2N - H_2O - CO]^+$ (95). Found %: C 65.01; H 6.49; S 13.99. $C_{24}H_{28}N_2O_2S_2$. Calculated %: C 65.42; H 6.41; S 14.55.

1,2-Tetrakis[3,5-(4-dimethylamino-1,3-butadienyl)-2-thienyl]ethanedione (10). A mixture of compound **1** (340 mg, 2.16 mmol) and 1,2-bis(3,5-dimethyl-2-thienyl)ethanedione **7** (100 mg, 0.36 mmol) was heated at 75-80°C for 40 min. Absolute ether was added to the reaction mass, cooled to 35-40°C, and the precipitate was rubbed. The crystals were filtered off and washed several times with hot methanol and then with absolute ether. We obtained 170 mg (78%) of the crystalline product; mp >250°C. UV spectrum, λ_{max}, nm (ε): in methylene chloride, 375 (44220), 525 (44220); in ethanol, 375 (16698), 520 (19481). ^{1}H NMR spectrum (deuterochloroform), δ, ppm (*J*, Hz): 2.81 [24H, s, $4N(CH_3)_2$]; 5.10 (2H, t, *J* = 11.8, H-γ'); 5.30 (2H, t, *J* = 12.5, H-γ); 6.20 (2H, d, *J* = 15.1, H-α); 6.40-6.51 (4H, m, H-α and H-β'); 6.76-7.02 (6H, m, CH, H-δ' and H-β); 7.45 (2H, br. d, *J* = 15.1, H-δ). Found %: C 67.35; H 6.82; N 8.95. $C_{34}H_{42}N_4O_2S_2$. Calculated %: C 67.77; H 6.97; N 9.30.

2-(3'-Dimethylamino-1'-oxo-2'-propen-1'-yl)-5-methylthiophene (13). A. A mixture of the ketone **2** (400 mg, 2.85 mmol) and the acetal **11** (340 mg) was heated at 90-92°C for 3 h 30 min. After cooling to 20°C the precipitate was removed and washed with dry ether. We obtained 170 mg (31%) of the product **13** in the form of yellow crystals; mp 121-122°C. UV spectrum (ethanol), λ_{max}, nm (ε): 255 sh (6600), 300 (7200), 360 (25200). ^{1}H NMR spectrum (deuterochloroform), δ, ppm (*J*, Hz): 2.50 (3H, s, CH_3); 3.0 (6H, br. s, $N(CH_3)_2$); 5.58 (1H, d, *J* = 12.5, H-α); 6.72 (1H, d, *J* = 4.4, CH); 7.46 (1H, d, *J* = 4.4, H); 7.72 (1H, d, *J* = 12.5, H-β). Found, %: C 61.42; H 6.46; N 7.10. $C_{10}H_{13}NOS$. Calculated, %: C 61.53; H 6.66; N 7.18.

B. A mixture of the ketone **2** (300 mg, 2.14 mmol), the azaacetal **12** (340 mg, 2.14 mmol) [12], and absolute 2-propanol (1.5 ml) was heated at boiling point for 4 h 30 min and cooled. Absolute ether was added, and the precipitate was separated and washed with dry ether. We obtained 170 mg (41%) of the product **13**; mp 121-122°C.

1,3-Bis[2-(2-dimethylaminoethenyl)-5-methyl-3-thienyl]ethanedione (14). A mixture of the diketone **6** (100 mg, 0.36 mmol), the azaacetal **12** (130 mg, 0.9 mmol), and absolute isopropyl alcohol (0.8 ml) was heated at boiling point for 10 h and evaporated. The remaining thick red oil was rubbed several times with dry ether. From the ether solutions we obtained 13 mg (10%) of the product **14** in the form of a brick-red precipitate; mp 150°C (decomp.). UV spectrum (ethanol), λ_{max}, nm (ε): 275 (17500), 310 (sh) (12500), 470 (13500). Mass spectrum, *m*/*z* (*I*, %): 388 $[M]^+$ (90), 298 $[M - 2Me_2NH]^+$ (70), 194 [M/2] (90), 179 $[M/2 - Me]^+$ (100). ^{1}H NMR spectrum (deuterochloroform), δ, ppm (*J*, Hz): 2.25 (6H, s, CH_3); 2.95 [12H, s, $N(CH_3)_2$]; 6.60 (2H, d, *J* = 12.5, H-α); 6.68 (2H, s, CH); 7.02 (2H, d, *J* = 12.5, H-β).

The work was carried out with support from the Program of the Department of Chemical Sciences and Materials "Theoretical and experimental study of the nature of the chemical bond and the mechanism of the most important chemical reactions and processes" and the Russian Fundamental Research Fund (project No. 02-03-32934).

REFERENCES

1. M. Irie, *Chem. Rev.*, **100**, 1685 (2000).
2. Cheng Zhang, H. R. Fetterman, W. Steier, and J. Michael, US Patent 6348992; *Chem. Abs.*, B 1, Feb. 19, 2002, G 02 F 1/00.
3. G. Koeckelberghs, S. Sioncke, T. Verbiest, A. Persoons, and C. Samyn, *Polymer*, **44**, 3785 (2003).
4. N. Tireli, S. Amabile, C. Cellai, A. Pucci, L. Regoli, G. Ruggeri, and F. Ciardelli, *Macromolecules*, **34**, 2129 (2001).
5. L. I. Belen'kii, V. Z. Shirinyan, G. P. Gromova, A. V. Kolotaev, Yu. A. Strelenko, S. N. Tandura, A. N. Shumskii, and M. M. Krayushkin, *Khim. Geterotsikl. Soedin.*, 1783 (2003).
6. M. M. Krayushkin, *Khim. Geterotsikl. Soedin.*, 19 (2001).
7. Zh. A. Krasnaya and A. S. Tatikolov, *Izv. Akad. Nauk. Ser. Khim.*, 1555 (2003).
8. Zh. A. Krasnaya, T. S. Stytsenko, E. P. Prokof'ev, and V. F. Kucherov, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1362 (1980).
9. Yu. V. Smirnova and Zh. A. Krasnaya, *Usp. Khim.*, **69**, 1111 (2000).
10. Zh. A. Krasnaya, *Khim. Geterotsikl. Soedin.*, 1443 (1999).
11. Yu. E. Borisevich, A. S. Tatikolov, and V. A. Kuz'min, *Khim. Vysok. Energ.*, **5**, 474 (1978).
12. W. Kantlehner, E. Hang, and P. Speh, *Chem. Ztg.*, **108**, 368 (1984).