Photochromic 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophene-3(2*H*)-ones with fluorescent labels and/or crown-ether receptors

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Dedicated to Professor B. Trofimov on occasion of his 65th birthday

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Abstract

Novel *N*-acylaminovinyl ketones of the benzo[*b*]thiophene series (AAB) capable of molecular switching of fluorescence or complexation with metal ions have been synthesized and their photochromic behavior studied using UV-Vis absorption/emission and ^{1}H- / ^{7}Li- NMR spectroscopy. Under UV irradiation the AAB compounds **2a–c** containing fluorescent labels as their *N*-aryl substituents undergo *Z/E*- photo-isomerization and N→O acyl rearrangement resulting in the formation of *O*-acyl isomers **3a–c**. The photo-switching of fluorescence has been found in the 4-fluorenonyl derivative **2a**. The benzo-15-crown-5- containing AAB **2d,e** are also susceptible to the same type of photo-initiated rearrangement. The corresponding *O*-acyl isomers **3d–e** represent a group of chemosensors which readily form stable complexes with alkali- and alkali-earth- metal cations. The AAB **2d** exhibits specific selectivity for Li^+ ion in the presence of Na^+, K^+ and Cs^+.

Keywords: 2-(*N*-Acyl-*N*-arylaminomethylene)benzo[*b*]thiophene-3(2*H*)-ones, photochromism, molecular switches, chemosensors

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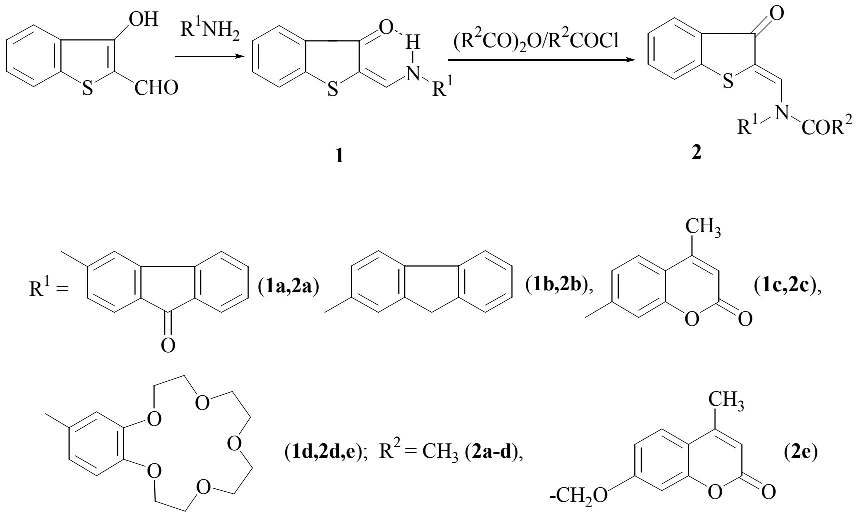
Introduction

The photo-initiated reversible N→O acyl rearrangement of 2-(*N*-acyl-*N*-arylamino-methylene)benzo[*b*]thiophene-3(2*H*)-ones (AAB) has been found to be an efficient mechanism for abiotic solar energy storage.[1] Due to the presence of fluorescent and ligating centers in their molecules the AAB compounds may have a potential for use as molecular switches and photochromic fluorescent sensors for metal cations.[2,3] In order to explore this possibility [4–6] we have prepared from aminovinyl ketones (AVK) **1** and investigated the properties of two groups of novel AAB derivatives: (i), compounds with fluorescent *N*-aryl substituents **2a–c**, and (ii), benzo-15-crown-5- containing compounds **2d,e**. The present paper reports on the synthesis, photochemical and fluorescent properties of these compounds, and their complexes with various metal cations.

Results and Discussion

Synthesis

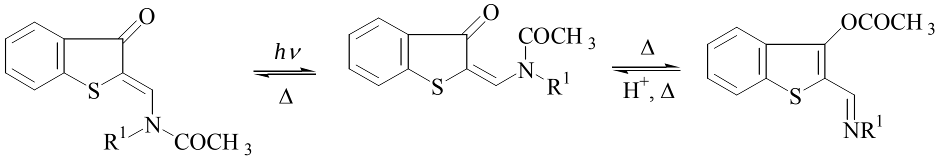
The AAB compounds, **2a–c** have been obtained by acylation of AVK **1** with acetic anhydride or 4-methyl-1,2-benzopyrone-7-yloxyacetyl chloride according to the previously described procedure.[2,3] The AVK **1** have been synthesized by condensation of 3-hydroxybenzo[*b*]thiophene-2-carboxaldehyde with the corresponding amines (Scheme 1).



Scheme 1

Photochemistry

The ground-state structure of AAB **2a–c** corresponds to the *N*-acyl form: their IR spectra are characterized by vibration frequencies related to the amide (1700–1720 cm^{-1}) and exocyclic thiophene carbonyl groups (1660–1680 cm^{-1}). Compounds **2a–c** possess the *Z*- configuration about the C=C bond, as indicated by the characteristic low-field resonance signals of the methine protons at 8.82–8.90 ppm. These values were previously attributed to this form of AAB compounds, based on the ^1H NMR data and X-ray structure determinations, whereas the signals of the methine protons of the *E*- isomers were found at 5.90 ppm.[1,7] Irradiation of acetonitrile solutions of AAB **2a–c** (Table 1) with 436 nm filtered light results in *Z/E*- isomerization about the C=C bond followed by the thermal N→O acyl migration that affords stable *O*-acyl isomers **3a–c** (Scheme 2).



Z-**2a-c** *E*-**2a-c** **3a-c**

Scheme 2

Table 1. Spectral and luminescent characteristics of AAB **2** in acetonitrile solutions

	Absorption, λ_{max} [nm], (ε x10^{-4}, dm^3 mol^{-1} cm^{-1})	Fluorescence, λ_{max} [nm]	φ, **2–3**
2a	260 (9.22), 310 (2.96), 428 (1.29)	-	0.08
2b	263 (3.66), 307 (2.42), 431 (1.16)	475	0.34
2c	264 (3.47), 310 (2.77), 424 (1.06)	468	0.41
2d	259 (2.38), 306 (1.88), 427 (1.23)	470	0.25
2e	258 (2.84), 311 (3.27), 430 (1.22)	473	0.48

Long-wave absorption bands of the *O*-acyl compounds **3a–c** are found in the spectral region 360–370 nm. Their IR spectra exhibit ester carbonyl group bands at 1780–1785 cm^{-1} (in CCl_4). Acidification of the solutions by adding small amounts of trifluoroacetic acid completely shifted the equilibrium to the initial form *Z*- **2a–c**. The cycle of **2** $\rightleftharpoons$ **3** transformations can be produced repeatedly. The *N*-acyl AAB compounds **2b,c** exhibit weak fluorescence with λ_{max} = 468–475 nm. Its intensity is decreases to zero during the photo-initiated N→O acyl migration, in parallel with reduction of the content of the *N*-acyl form in solution. The only exception from this mechanism is given by the fluorenonyl derivative AAB **2a** which did not show any fluorescence at room temperature. In contrast, the photo-induced *O*-acyl isomer **3a** shows a relatively low intensity, but distinct, fluorescence (λ_{max} = 545 nm, φ = 0.03) when excited with 350 nm light (Figure 1). To the best of our knowledge, this is the first example of a fluorescent benzenoid *O*-acyl form of type **3** compounds. As usual, these compounds do not exhibit luminescent properties, owing to the occurrence of fast intersystem crossing processes.[8]

In the solid state and in solution, crown-derivatized AAB compounds **2d,e** exist in the form of the *Z*-isomer. This conclusion is validated by the IR spectra displaying absorption bands of the amide ($\nu_{C=O}$ = 1660–1710 cm^{-1}) and exocyclic thiophene ($\nu_{C=O}$ = 1710 cm^{-1}) carbonyl groups, the ^{1}H NMR low-field shift of the methine proton signals (8.66–8.90 ppm), and the UV-Vis absorption spectra (Table 1). Irradiation of solutions of the AAB compounds **2d,e** (λ_{irr} = 436 nm) causes N→O acyl rearrangement to give the *O*-acyl isomers **3d,e** (Scheme 3).

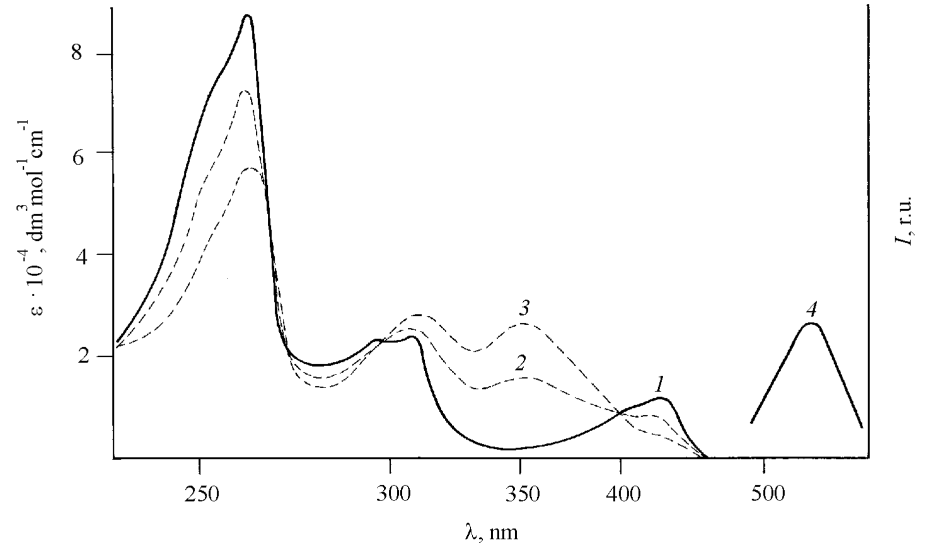
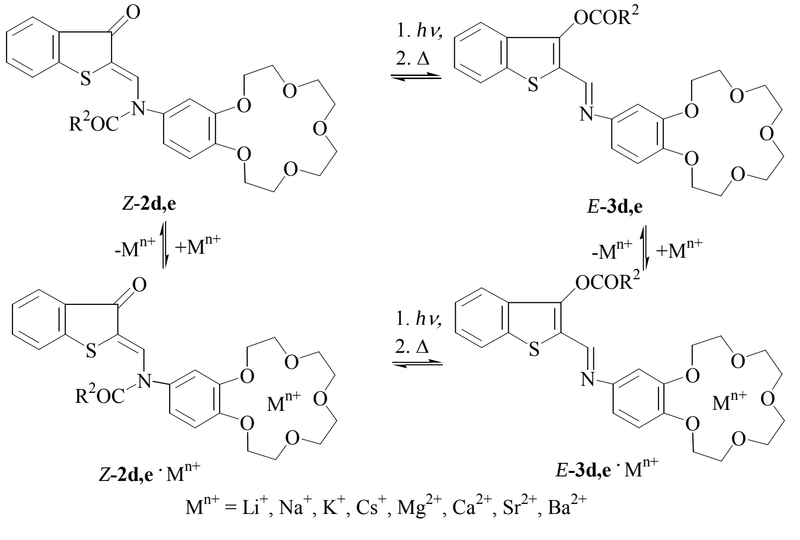


Figure 1. Absorption spectra of AAB **2a** in acetonitrile solution before irradiation (*1*), after 4 min (*2*), 8 min (*3*) of irradiation (λ_{irr} = 436 nm) and fluorescence spectrum (*4*) after 8 min of irradiation (λ_{exc} = 360 nm).

The structures of the initial form *Z*-**2d**, the photo-isomer **3d** and the corresponding lithium complexes **2d·Li$^+$, 3d·Li$^+$** were proved by the ^{1}H- and ^{7}Li- NMR spectral data (Table 2). The crown-ether methylene proton signals exhibit low-field shifts of 0.06–0.10 ppm in the complexes **2d·Li$^+$, 3d·Li$^+$** as compared with the isomers **2d,3d** respectively. The protons more distant from the crown moiety do not measurably respond to the presence of Li$^+$ in the crown-ether ring. In the ^{7}Li NMR spectrum of the compound **3d·Li$^+$** in acetonitrile the lithium signal is shifted by 0.78 ppm to low field with respect to LiI.



Scheme 3

Table 2. ^{1}H NMR data for AAB **2d,3d** before and after addition of Li$^+$ (CD$_3$CN, δ, ppm)

	CH$_3$	4-CH$_2$O	2-CH$_2$O	2-CH$_2$O	Ar	=CH
2d	2.06 s (3H)	3.64–3.71 m (8H)	3.77–3.88 m (4H)	4.05–4.21 m (4H)	6.96–7.80 m (7H)	8.79 s (1H)
2d·Li$^+$	2.07 s (3H)	3.70–3.78 m (8H)	3.87–3.97 m (4H)	4.12–4.31 m (4H)	7.07–7.81 m (7H)	8.79 s (1H)
3d	2.48 s (3H)	3.63–3.69 m (8H)	3.79–3.83 m (4H)	4.09–4.15 m (4H)	6.94 m (3H), 7.43–7.91 m (4H)	8.76 s (1H)
3d·Li$^+$	2.50 s (3H)	3.67–3.74 m (8H)	3.90–3.94 m (4H)	4.20–4.28 m (4H)	7.00–7.07m (3H), 7.44–7.93 m (4H)	8.79 s (1H)

These ionic equilibria are specifically reflected in the UV-Vis absorption spectra of these compounds. No significant changes are observed in the spectra of the AAB compounds **2d,e** at 425–430 nm in the presence of alkali- and alkali-earth- metal (MI and M(ClO$_4$)$_2$) ions in acetonitrile, isopropanol or DMSO solutions. On the other hand, the photo-initiated *O*-acyl isomers **3d,e**, absorbing at 350–360 nm, readily form complexes **3d,e**·M^{n+} as evidenced by a substantial increase in the extinction of those bands (Δε) and their blue shifts (Δλ) (Table 3, Figure 2).

Table 3. Spectral changes in long-wave absorption band of complexes **3d,e**·M^{n+} as compared with **3d,e** and quantum yields of the **2d,e→3d,e** photo-rearrangements in acetonitrile in the presence of M^{n+}

	3d			**3e**		
	Δε, %	Δλ, nm	φ	Δε, %	Δλ, nm	φ
Li$^+$	13.1	10	0.43	12.9	9	0.62
Na$^+$	10.9	8	0.39	7.5	8	0.55
K$^+$	7.2	7	0.39	5.9	8	0.54
Cs$^+$	5.5	5	0.29	4.8	4	0.49
Mg^{2+}	29.4	19	0.32	76.3	57	0.62
Ca^{2+}	33.3	16	0.39	79.0	57	0.73
Sr^{2+}	23.5	16	0.37	69.9	55	0.49
Ba^{2+}	28.6	16	0.45	76.2	55	0.50

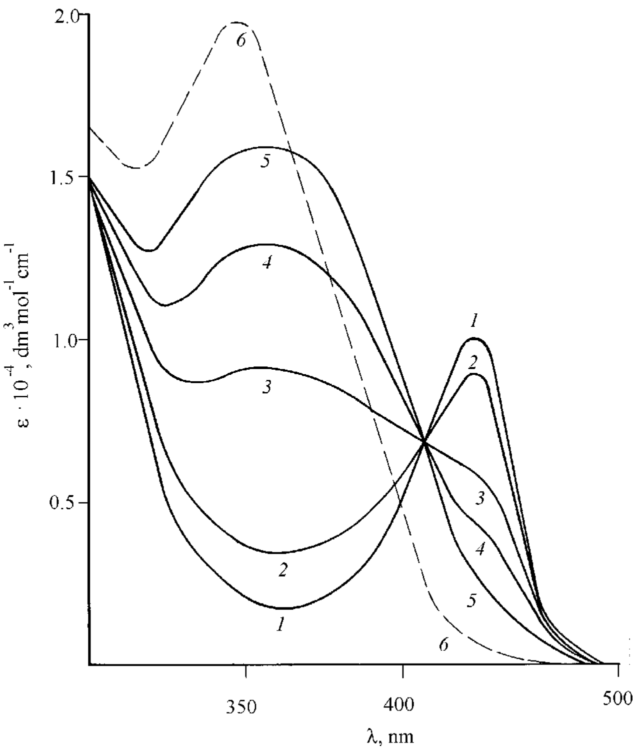


Figure 2. Absorption spectra of AAB **2d** in isopropanol solution before irradiation (*1*); after 2 s, (*2*); 10 s, (*3*); 20 s, (*4*); 60 s, (*5*), of irradiation (λ_{irr} = 436 nm, C = 2.5x10^{-5} *M*) and after addition of Ba(ClO$_4$)$_2$ (ten-fold molar excess) (*6*).

Under UV-Vis irradiation the compounds **2d,e**$\cdot$M^{n+} also undergo N→O acyl shift with formation of the same complexes **3d,e**$\cdot$M^{n+}. The quantum yields of this rearrangement correlate with the alkali metal ion radii (Table 3). The photo-isomer **3d** exhibits unique selectivity with respect to Li$^+$ cation in acetonitrile. For the lithium complex **3d**$\cdot$ Li$^+$, the characteristic spectral parameters (Δε, Δλ) are not affected by the presence in the solution of other alkali metal ions ($C_{Li^+} = C_{Na^+} = C_{K^+} = C_{Cs^+} = 5 \times 10^{-4}$ *M*).

Conclusions

Novel 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophene-3(2H)-ones with fluorescent labels and/or crown-ether receptors susceptible to photo-initiated reversible *Z*/*E*- photo-isomerization followed by thermal N→O acyl migration represent a new type of molecular switches of fluorescence and chemosensors for metal ions.

Experimental Section

General Procedures. ^{1}H- and ^{7}Li- NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrometer with internal standard HMDS. IR spectra in Nujol were measured using a Specord 75IR spectrometer. UV-Vis absorption spectra in CH_3CN were obtained with a Specord M-40 spectrophotometer. Irradiation of solutions was carried out by filtered light of a high-pressure mercury lamp DRSh (250 W) supplied with a set of glass filters. Potassium ferrioxalate was used as an actinometer for the quantum yield calculations.[9] Fluorescence spectra in CH_3CN were measured on a Hitachi 650-60 spectrofluorimeter. The fluorescence quantum yield of AAB **3a** was determined using fluorenone as the standard.[10]

2-[*N*-(Fluorenone-2-yl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (1a). A solution of 2-aminofluorenone (0.46 g, 2.6 mmol) in 3 ml of toluene was added to a solution of 3-hydroxybenzo[*b*]thiophene-2-carboxaldehyde (0.50 g, 2.6 mmol) and refluxed for 3–5 min. The precipitate was filtered and crystallized from toluene. Yield of a red powder, 61%, mp 300–301 °C. IR (ν, cm^{-1}): 1720, 1640. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.27–7.36 (m, 2H, Ar), 7.51–7.65 (m, 4H, Ar), 7.70–7.82 (m, 5H, Ar), 8.32–8.39 (d, 1H, =CH, J = 12.0 Hz), 10.30–10.38 (d, 1H, NH, J = 12.0 Hz). Anal. Calc. for $C_{22}H_{13}NO_2S$ (355.42): C, 74.35; H, 3.69; N, 3.94. Found: C, 74.21; H, 3.72; N 4.13%.

2-[*N*-(Fluorene-3-yl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (**1b**) was obtained in a similar way to AVK **1a** using 3-aminofluorene, and crystallized from toluene with a few drops of DMFA. Yield of red crystals 84%, mp 259–260 °C. IR (ν, cm^{-1}): 1660, 1550. ^{1}H NMR (DMSO-d_6, δ, ppm): 3.91–3.97 (s, 2H, CH_2), 7.20–7.42 (m, 4H, Ar), 7.45–7.70 (m, 4H, Ar), 8.31–8.38 (d, 1H, =CH, J = 12.0 Hz), 10.15–10.21 (d, 1H, NH, J = 12.0 Hz). Anal. Calc. for $C_{22}H_{15}NOS$ (341.44): C, 77.39; H, 4.43; N, 4.10. Found: C, 77.26; H, 4.45; N 4.01%.

2-[*N*-(4-Methyl-1,2-benzopyrone-7-yl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (**1c**) was obtained in a similar way to AVK **1a** using 7-amino-4-methyl-1,2-benzopyrone. Yield of a red powder 77%, mp 336–337 °C. IR (ν, cm^{-1}): 1725, 1675, 1640. ^{1}H NMR (DMSO-d_6, δ, ppm): 2.35–2.50 (d, 3H, CH_3), 6.10–6.21 (bs, 1H, H-3), 7.20–7.40 (m, 3H, Ar), 7.50–7.90 (m, 4H, Ar), 8.31 (d, 1H, =CH, J = 11.5 Hz), 10.20–10.30 (d, 1H, NH, J = 11.5 Hz). Anal. Calc. for $C_{19}H_{13}NO_3S$ (335.38): C, 68.05; H, 3.91; N, 4.18. Found: C, 67.93; H, 3.78; N, 4.27%.

2-{[*N*-(Benzo-15-crown-5)-4-yl]aminomethylene}benzo[*b*]thiophene-3(2*H*)-one (**1d**) was obtained in a similar way to AVK **1a** using 4-aminobenzo-15-crown-5 and crystallized from ethanol. Yield of a red powder 70%, mp 187–188 °C. IR (ν, cm^{-1}): 1640, 1560. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.64 (s, 8H, $4CH_2O$), 3.82 (m, 4H, $4CH_2O$), 4.20 (m, 4H, $4CH_2O$), 6.71–7.89 (m, 8H, Ar), 8.00 (d, 1H, =CH, J = 11.6 Hz), 12.4 (d, 1H, NH, J = 11.6 Hz). Anal. Calc. for $C_{23}H_{25}NO_6S$ (443.53): C, 62.29; H, 5.68; N, 3.16. Found: C, 62.41; H, 5.65; N, 3.22%.

2-[*N*-Acetyl-*N*-(fluorenon-2-yl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (2a). AVK **1a** (0.2 g, 0.56 mmol) was dissolved in acetic anhydride (5.0 ml, 51.9 mmol) in the presence of triethylamine (0.32 ml) and refluxed for 10 min. The precipitate was filtered and crystallized from toluene. Yield of yellow crystals 67%, mp 279–280 °C. IR (ν, cm^{-1}): 1720, 1690, 1670. ^{1}H

NMR ($CDCl_3$, δ, ppm): 2.03–2.30 (s, 3H, CH_3), 7.10–7.30 (m, 2H, Ar), 7.36–7.45 (m, 3H, Ar), 7.57–7.88 (m, 6H, Ar), 8.82 (s, 1H, =CH). Anal. Calc. for $C_{24}H_{15}NO_3S$ (397.46): C, 72.53; H, 3.80; N, 3.52. Found: C, 72.32; H, 3.73; N, 3.46%.

2-[*N*-Acetyl-*N*-(fluoren-3-yl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (**2b**) was obtained in a similar way to AAB **2a**. Yield of yellow crystals 87%, mp 247–248 °C. IR (ν, cm^{-1}): 1700, 1660, 1570. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.06–2.20 (s, 3H, CH_3), 4.01 (s, 2H, CH_2), 7.08–7.20 (m, 2H, Ar), 7.30–7.89 (m, 9H, Ar), 8.95 (s, 1H, =CH). Anal. Calc. for $C_{24}H_{17}NO_2S$ (383.47): C, 75.17; H, 4.47; N, 3.65. Found: C, 75.02; H, 4.56; N, 3.69%.

2-[*N*-Acetyl-*N*-(4-methyl-1,2-benzopyrone-7-yl)aminomethylene]benzo[*b*]thiophene-3(2*H*)-one (**2c**) was obtained in a similar way to AAB **2a**. Yield of a yellow powder 45%, mp 290–291 °C. IR (ν, cm^{-1}): 1720, 1700, 1680. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.10–2.25 (s, 3H, CH_3CO), 2.40–2.55 (m, 3H, CH_3), 6.41 (s, 1H, H-3), 7.12–7.60 (m, 5H, Ar), 7.73–7.92 (m, 2H, Ar), 8.8 (s, 1H, =CH). Anal. Calc. for $C_{21}H_{15}NO_4S$ (377.42): C, 66.83; H, 4.01; N, 3.71. Found: C, 66.70; H, 3.91; N, 3.75%.

2-{*N*-Acetyl-*N*-[(benzo-15-crown-5)-4-yl]aminomethylene}benzo[*b*]thiophene-3(2*H*)-one (**2d**) was synthesized in a similar way to AAB **2a** and crystallized from ethanol. Yield of a yellow powder 82%, mp 176–177 °C. IR (ν, cm^{-1}): 1710, 1660, 1600. Anal. Calc. for $C_{25}H_{27}NO_7S$ (485.56): C, 61.84; H, 5.60; N, 2.89. Found: C, 62.04; H, 5.65; N, 2.79%.

2-{*N*-(4-Methyl-1,2-benzopyrone-7-yloxyacetyl)-N-[(benzo-15-crown-5)-4-yl]aminomethylene}-benzo[*b*]thiophene-3(2*H*)-one (**2e**). AVK **1d** was partly dissolved in 15 ml of CH_3CN and a solution of 4-methyl-1,2-benzopyrone-7-yloxyacetyl chloride [3] (0.59 g, 2.25 mmol) in 15 ml of CH_3CN was added to this mixture. The precipitate of AAB **2e** was filtered and crystallized from DMFA. Yield of a yellow powder 0.84 g (56%), mp 272–273 °C. IR (ν, cm^{-1}): 1710, 1670, 1610. ^{1}H NMR ($CDCl_3$, δ, ppm): 2.39–2.60 (d, 3H, CH_3), 3.79–4.22 (m, 16H, 8- CH_2O), 4.80 (s, 2H, CH_2), 6.11 (s, 1H, H-3), 6.84–7.90 (m, 10H, Ar), 8.66 (s, 1H, =CH). Anal. Calc. for $C_{35}H_{33}NO_{10}S$ (659.71): C, 63.72; H, 5.04; N, 2.12. Found: C, 63.55; H, 5.11; N, 2.19%.

Acknowledgments

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