

## Photochromic properties of 2-(*N*-acetyl-*N*-arylamino-methylene)benzo[*b*]furan-, thiophene-, selenophene- and tellurophene-3(2*H*)-ones

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**Dedicated to Professor V. Minkin on the occasion of his 70<sup>th</sup> birthday**

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### Abstract

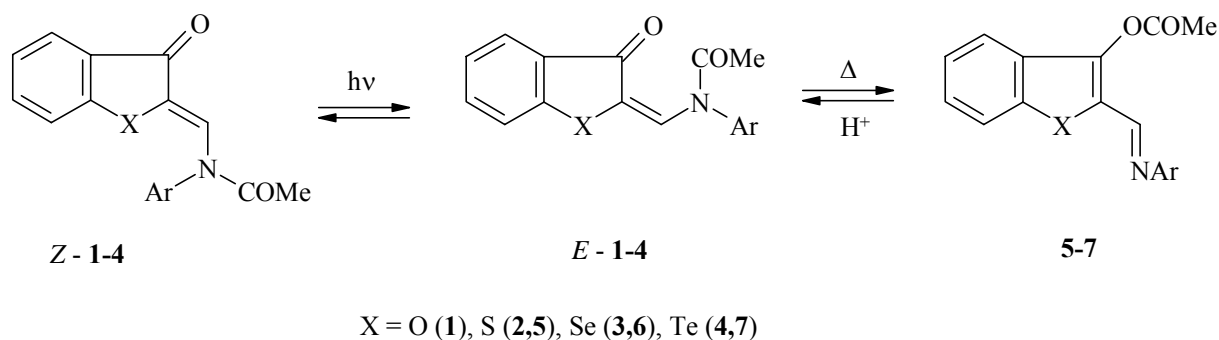
Novel photochromic systems – (2*Z*)-2-(*N*-acetyl-*N*-arylamino-methylene)benzo[*b*]tellurophene-3(2*H*)-ones have been synthesized. Their properties were studied in comparison with analogous benzo[*b*]furan, benzo[*b*]thiophene, and benzo[*b*]selenophene derivatives. The long-wave absorption band of these compounds shifts bathochromically in the following order of heteroatoms: O < S < Se < Te from 380 nm to 455 nm and the quantum yields of photoinitiated N→O acyl rearrangement (including *Z/E*-isomerization around the C=C bond and fast thermal migration of the acetyl group) increase from 0.60 (S) to 0.71 (Te). The acid catalyzed reverse O→N acyl rearrangement constant rates are  $1.1 \cdot 10^{-4} \text{ s}^{-1}$  (Te) <  $4.2 \cdot 10^{-4} \text{ s}^{-1}$  (Se) <  $1.0 \cdot 10^{-3} \text{ s}^{-1}$  (S).

**Keywords:** Benzo[*b*]tellurophene-3(2*H*)-ones, photochromism, *Z/E*-isomerization, acyl rearrangement

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### Introduction

Photochromism of five-membered benzo[*b*]annelated heterocyclic (2*Z*)-2-(*N*-acetyl-*N*-arylamino-methylene)derivatives is based on the original mechanism (Scheme 1): photoinitiated *Z/E*-isomerization around the exocyclic C=C bond of *N*-acylketoenamines **1-3** followed by fast thermal N→O migration of the acetyl group.<sup>1-3</sup>



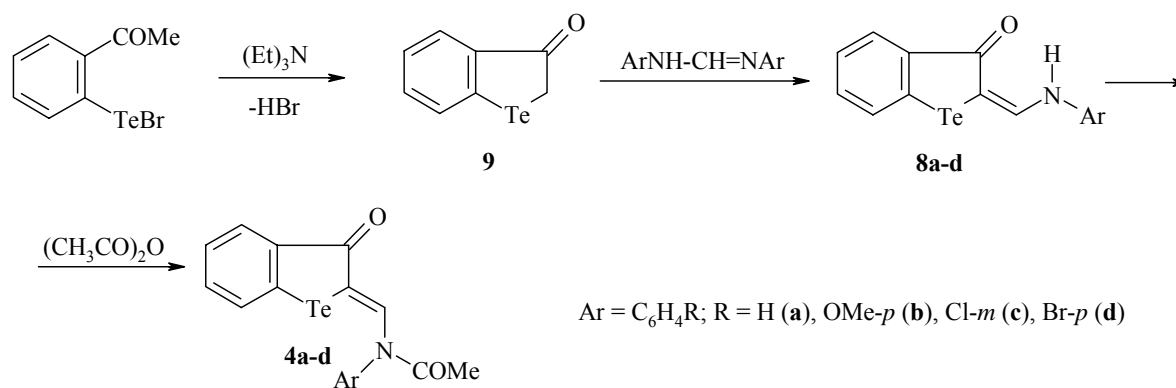
### Scheme 1

This reversible rearrangement was first used for abiotic solar energy storage.<sup>1</sup> Modification of the *N*-acylketoenamines **2** structure imparts to them the properties of molecular switches,<sup>2,4</sup> photochromic pH-sensors<sup>5</sup> and chemosensors for metal cations.<sup>2,6</sup> However the photochemical properties of *N*-arylketoenamines **1-3** significantly depend on the heteroatom X: the irradiation of benzo[*b*]furan derivatives **1** results only in *Z/E*-isomerization without the possible change to subsequent migration of the acetyl group. Benzo[*b*]thiophene and benzo[*b*]selenophene ketoenamines **2,3** under these conditions efficiently form stable *O*-acetyl isomers **5,6**. For the further investigation of the influence of the heteroatom X on the photochromic properties of the ketoenamines **1-3** we have synthesized a series of (*ZZ*)-2-(*N*-acetyl-*N*-arylamino)methylene)benzo[*b*]tellurophene-3(*2H*)-ones **4a-d**.

## Results and Discussion

### Synthesis

Compounds **4a-d** were obtained by acylation of ketoenamines **8a-d** with acetic anhydride according to the previously described procedure.<sup>4,6</sup> *N*-Acylketoenamines **1-3** were synthesized earlier.<sup>1,3-5</sup> Ketoenamines **8** have been synthesized by condensation of benzo[*b*]tellurophene-3(*2H*)-one **9** with corresponding diarylformamidines.



## Scheme 2

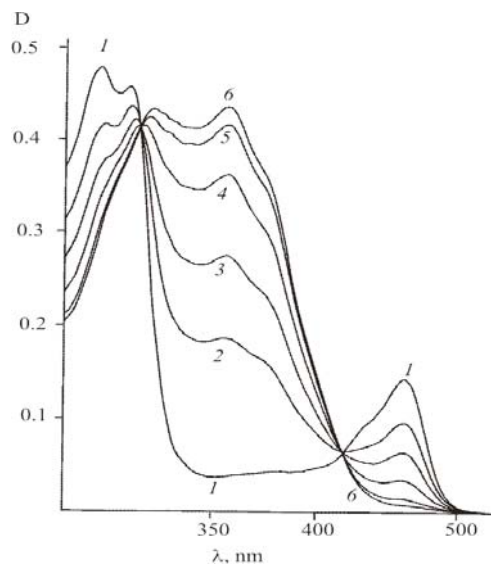
### Photochemistry

The structures of the novel compounds **4a-d** correspond to the *N*-acetyl isomers as well as **1-3**.<sup>1,3-5</sup> IR spectra of **4** display characteristic amide (1680-1690 cm<sup>-1</sup>) and exocyclic carbonyl group (1630-1640 cm<sup>-1</sup>) vibration frequencies. Their *Z*-configuration is evidenced by the low-field resonance <sup>1</sup>H NMR signals of the methine protons at 9.3-9.4 ppm.<sup>1,3</sup> The signals of the *E*-form methine protons were previously attributed to ~ 5.90 ppm.<sup>2</sup> The UV-Vis absorption spectra of *N*-acylketoenamines **4a-d** exhibit bathochromic shifts of the long-wave band due to increasing electron-donating properties of the heteroatom X (Table 1). Irradiation of toluene or acetonitrile solutions of *N*-acylated ketoenamines **4a-d** ( $\lambda_{\text{irr}} = 436 \text{ nm}$ ,  $C = 2.5 \cdot 10^{-5} \text{ M}$ ,  $l = 1 \text{ cm}$ ,  $V = 2 \text{ ml}$ ,  $\tau_{\text{irr}} = 1 \text{ min}$ , rate of conversion of **4a-d**  $\rightarrow$  **7a-d**  $\geq 97\%$ ) in the region of the low-wavelength absorption maxima results in *Z/E*-isomerization around the exocyclic C=C bond and fast thermal N $\rightarrow$ O migration of the acetyl group with formation of *O*-acetyl isomers **7a-d** (Scheme 1, Figure 1). This photorearrangement doesn't show any wavelength dependence.

**Table 1.** The characteristics of compounds **1-4** in toluene (Ar = Ph)

	X	Absorption,		$\phi^*$
		$\lambda_{\text{max}}$ [nm]	$\epsilon \cdot 10^{-4}$ , dm <sup>3</sup> · mol <sup>-1</sup> · cm <sup>-1</sup>	
<b>1</b>	O	380	1.52	-
<b>2</b>	S	425	1.08	0.60
<b>3</b>	Se	435	1.02	0.66
<b>4</b>	Te	455	0.59	0.70

\* N $\rightarrow$ O acyl photorearrangement quantum yield.



**Figure 1.** Absorption spectra of *Z*-4a in toluene: before irradiation (1); after 5s (2); 10s (3); 20s (4); 40s (5); 60s (6), of irradiation ( $\lambda_{\text{irr}} = 436 \text{ nm}$ ,  $C = 2.5 \cdot 10^{-5} \text{ M}$ ).

The quantum yields of the photoinitiated reactions  $2 \rightarrow 5$ ,  $3 \rightarrow 6$ , and  $4 \rightarrow 7$  increase in parallel with the dimension of the heteroatom  $X$ :  $S < Se < Te$  probably due to the decreasing distance between the acyl carbon and the ring carbonyl oxygen in *E*-**2-4**. Compounds **7a-d** absorb in the 330-360 nm region and the ester carbonyl group frequencies are found in their IR spectra at  $1775\text{-}1780 \text{ cm}^{-1}$  (in  $\text{CCl}_4$ ). The attempts to isolate compounds **7** were ineffective because, contrary to the benzo[*b*]thiophene derivative **5** ( $\text{Ar} = \text{C}_6\text{H}_4\text{NO}_2\text{-3}$ , see X-ray data in ref. 3), the reaction *Z*-**4**  $\rightarrow$  **7** conducted in a quartz photo-reactor with a non-filtered source of light lead to a hardly separable mixture of *Z*-**4**, **7**, and unknown by-products.

Benzo[*b*]thiophene and benzo[*b*]selenophene derivatives **2,3** exhibit weak fluorescence at room temperature ( $\lambda_{\text{max}} = 470\text{-}480 \text{ nm}$ ) and its intensity decreases to zero after the rearrangement to the *O*-acetyl isomers **5,6**. Benzo[*b*]tellurophene derivatives **4** do not possess distinguishable fluorescence probably due to the “heavy atom” effect.<sup>7</sup> Photo-produced *O*-acetyl isomers **7** are rather stable especially in non-polar solvents but under acid catalysis they rearrange back to **4**. The thermal *O*  $\rightarrow$  *N* acyl migration constant rates ( $C_5 = C_6 = C_7 = C_{\text{TCA}} = 2.5 \cdot 10^{-5} \text{ M}$ ;  $\text{Ar} = \text{Ph}$ ) increase in the sequence:  $\text{Te} (1.1 \cdot 10^{-4} \text{ s}^{-1}) < \text{Se} (4.2 \cdot 10^{-4} \text{ s}^{-1}) < \text{S} (1.0 \cdot 10^{-3} \text{ s}^{-1})$ . The cycle of  $4 \rightleftharpoons 7$  photoinitiated and catalysed transformations can be produced repeatedly with the use of cation exchange resin as a catalyst.

## Conclusions

2-(*N*-Acetyl-*N*-arylamino)methylene)benzo[*b*]thiophene-, selenophene-, and tellurophene-3(2*H*)-ones represent the logical series of inverse photochromic systems with photoinitiated *Z/E*-isomerization followed by thermal *N*  $\rightarrow$  *O* migration of acetyl group.

## Experimental Section

**General Procedures.**  $^1\text{H}$  NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrometer with internal standard HMDS. IR spectra in Nujol and  $\text{CCl}_4$  were measured using a Specord 75IR spectrometer. UV-vis absorption spectra in toluene have been obtained with Specord M-40 spectrophotometer. Irradiation of solutions was carried out by filtered light from a high-pressure mercury lamp DRSh (250 W) fitted with a set of glass filters ( $\lambda_{\text{irr}} = 436 \text{ nm}$ ). Potassium ferrioxalate was used as an actinometer for the quantum yield calculations.<sup>8</sup> Fluorescence spectra in  $\text{CH}_3\text{CN}$  were measured on a Hitachi 650-60 spectrofluorimeter.

**Benzo[*b*]tellurophene-3(2*H*)-one (9).** was obtained according to a modified procedure.<sup>9</sup> A solution of 2-acetylphenyltellurenylbromide (1.64 g, 5 mmol) and triethylamine (50 mmol) in 20 ml of chloroform was heated under reflux for 5 h under an argon atmosphere. The reaction mixture was washed with water (3 x 20 ml) and the organic layer was dried with  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The precipitate was filtered and crystallized from cyclohexane. This yielded **9** as a white powder 1.05 g (85%), mp 107-108 °C. Lit. mp 107 °C. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1630, 1540.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 4.26 (s, 2H,  $\text{CH}_2$ ), 7.26-7.76 (m, 4H, Ar). Anal. Calc. for  $\text{C}_8\text{H}_6\text{OTe}$  (245.74): C, 39.10; H, 2.46. Found: C, 39.16; H, 2.43 %.

**2-(*N*-Phenylaminomethylene)benzo[*b*]tellurophene-3(2*H*)-one (8a).** A solution of benzo[*b*]tellurophene-3(2*H*)-one (4 mmol) and diphenylformamidine<sup>10</sup> (4 mmol) in 5 ml of 2-propanol was refluxed for 4 h and was then cooled to 10-15 °C. The precipitate was filtered and crystallized from toluene. This yielded **8a** as a red powder 55%, mp 162-163 °C. UV-Vis [ $\lambda$ , nm ( $\epsilon \cdot 10^{-4}$ ,  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ): 300 (0.88), 362 (1.12), 483 (0.93). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1640, 1580.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 6.84-7.81 (m, 9H, Ar), 8.59-8.64 (d, 1H, =CH,  $J = 14.0 \text{ Hz}$ ), 9.60-9.67 (d, 1H, NH,  $J = 14.0 \text{ Hz}$ ). Anal. Calc. for  $\text{C}_{15}\text{H}_{11}\text{NOTe}$  (348.87): C, 51.64; H, 3.18. Found: C, 51.68; H, 3.23%.

**(2*Z*)-2-(*N*-Acetyl-*N*-phenylaminomethylene)benzo[*b*]tellurophene-3(2*H*)-one (4a).** Keto-enamine **8a** (2 mmol) was dissolved in 5 ml of boiling acetic anhydride. The precipitate was filtered and crystallized from toluene. This yielded **4a** as a red-orange powder 49%, mp 210-211 °C. UV-Vis [ $\lambda$ , nm ( $\epsilon \cdot 10^{-4}$ ,  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ): 304 (1.93), 316 (1.82), 455 (0.59). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1690, 1630, 1580.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.99-2.08 (s, 3H,  $\text{CH}_3$ ), 7.10-7.85 (m, 9H, Ar), 9.38-9.41 (s, 1H, =CH). Anal. Calc. for  $\text{C}_{17}\text{H}_{13}\text{NO}_2\text{Te}$  (390.90): C, 52.24; H, 3.35. Found: C, 52.30; H, 3.36%.

**(2*Z*)-2-[*N*-Acetyl-*N*-(4-methoxyphenyl)aminomethylene]benzo[*b*]tellurophene-3(2*H*)-one (4b).** A solution of benzo[*b*]tellurophene-3(2*H*)-one (4 mmol) and di(4-methoxyphenyl)formamidine<sup>10</sup> (4 mmol) in 6 ml of 2-propanol was refluxed for 4 h. The precipitate was filtered and washed by hexane. Obtained 2-[*N*-(4-methoxyphenyl)aminomethylene]benzo[*b*]tellurophene-3(2*H*)-one **8b** was dissolved in 5 ml of acetic anhydride and boiled for 10 min. Hot reaction mixture was filtered and after cooling the precipitate **4b** was isolated and crystallized from toluene. This yielded **4b** as a red powder 46%,

mp 252-254 °C. UV-Vis [ $\lambda$ , nm ( $\epsilon \cdot 10^{-4}$ ,  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ): 305 (1.56), 316 (1.50), 455 (0.52). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1680, 1630, 1570.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.96-2.10 (s, 3H,  $\text{CH}_3$ ), 3.96-3.98 (s, 3H,  $\text{OCH}_3$ ), 7.20-7.86 (m, 8H, Ar), 9.38-9.43 (s, 1H, =CH). Anal. Calc. for  $\text{C}_{18}\text{H}_{15}\text{NO}_3\text{Te}$  (420.93): C, 51.36; H, 3.59. Found: C, 51.39; H, 3.57%.

**(2Z)-2-[N-Acetyl-N-(3-chlorophenyl)aminomethylene]benzo[*b*]tellurophene-3(2H)-one (4c).** was obtained in a similar way to **4b**. This yielded **4c** as a red powder 40%, mp 252-254 °C. UV-Vis [ $\lambda$ , nm ( $\epsilon \cdot 10^{-4}$ ,  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ): 303 (1.82), 454 (0.53). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1680, 1640, 1580.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.04-2.18 (s, 3H,  $\text{CH}_3$ ), 7.18-7.85 (m, 8H, Ar), 9.29-9.36 (s, 1H, =CH). Anal. Calc. for  $\text{C}_{17}\text{H}_{12}\text{NO}_2\text{ClTe}$  (425.35): C, 48.00; H, 2.84. Found: C, 48.01; H, 2.89%.

**(2Z)-2-[N-Acetyl-N-(4-bromophenyl)aminomethylene]benzo[*b*]tellurophene-3(2H)-one (4d).** was obtained in a similar way to **4b**. This yielded **4d** as a red powder 42%, mp 273-274 °C. UV-Vis [ $\lambda$ , nm ( $\epsilon \cdot 10^{-4}$ ,  $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ): 303 (1.95), 455 (0.59). IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1680, 1630, 1570.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.00-2.18 (br. s, 3H,  $\text{CH}_3$ ), 7.17-7.83 (m, 8H, Ar), 9.25-9.34 (s, 1H, =CH). Anal. Calc. for  $\text{C}_{17}\text{H}_{12}\text{NO}_2\text{BrTe}$  (469.80): C, 43.46; H, 2.57. Found: C, 43.49; H, 2.50%.

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