

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 70th birthday

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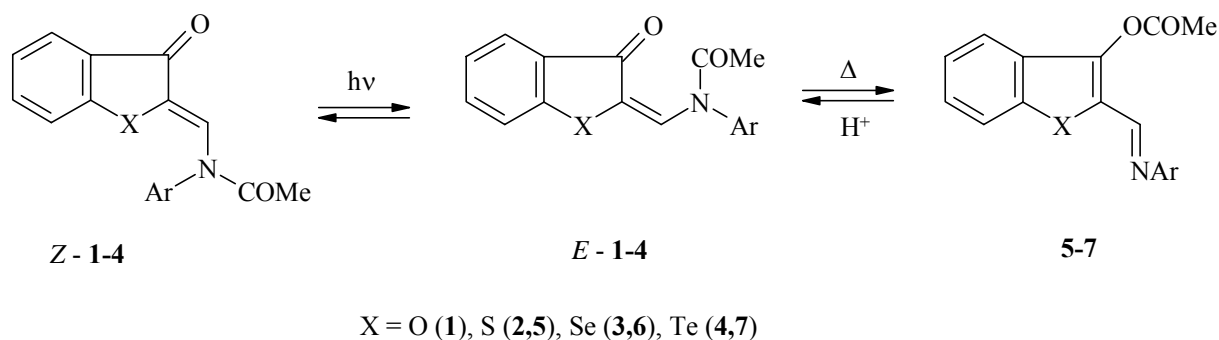
Abstract

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

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.¹⁻³



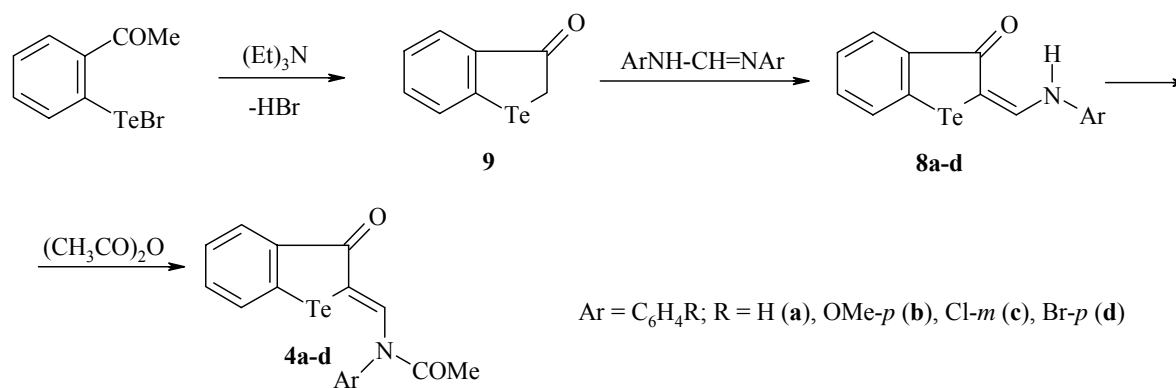
Scheme 1

This reversible rearrangement was first used for abiotic solar energy storage.¹ Modification of the *N*-acylketoenamines **2** structure imparts to them the properties of molecular switches,^{2,4} photochromic pH-sensors⁵ and chemosensors for metal cations.^{2,6} 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.^{4,6} *N*-Acylketoenamines **1-3** were synthesized earlier.^{1,3-5} 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**.^{1,3-5} IR spectra of **4** display characteristic amide (1680-1690 cm⁻¹) and exocyclic carbonyl group (1630-1640 cm⁻¹) vibration frequencies. Their *Z*-configuration is evidenced by the low-field resonance ¹H NMR signals of the methine protons at 9.3-9.4 ppm.^{1,3} The signals of the *E*-form methine protons were previously attributed to ~ 5.90 ppm.² 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,		ϕ^*
		λ_{max} [nm]	$\epsilon \cdot 10^{-4}$, dm ³ · mol ⁻¹ · cm ⁻¹	
1	O	380	1.52	-
2	S	425	1.08	0.60
3	Se	435	1.02	0.66
4	Te	455	0.59	0.70

* N \rightarrow O acyl photorearrangement quantum yield.

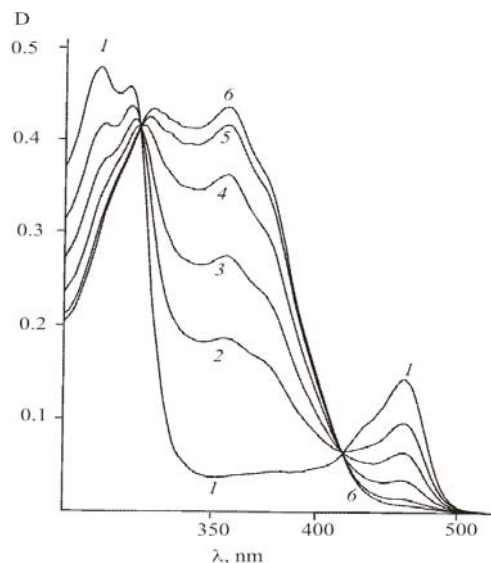


Figure 1. Absorption spectra of *Z*-4a in toluene: before irradiation (1); after 5s (2); 10s (3); 20s (4); 40s (5); 60s (6), of irradiation ($\lambda_{\text{irr}} = 436 \text{ nm}$, $C = 2.5 \cdot 10^{-5} \text{ M}$).

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 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.⁷ 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 $\text{O} \rightarrow \text{N}$ 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 $\text{N} \rightarrow \text{O}$ migration of acetyl group.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Varian Unity 300 (300 MHz) spectrometer with internal standard HMDS. IR spectra in Nujol and 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.⁸ Fluorescence spectra in CH_3CN were measured on a Hitachi 650-60 spectrofluorimeter.

Benzo[*b*]tellurophene-3(2*H*)-one (9). was obtained according to a modified procedure.⁹ 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 Na_2SO_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 (ν , cm^{-1}): 1630, 1540. ^1H NMR (CDCl_3 , δ , ppm): 4.26 (s, 2H, 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 diphenylformamidine¹⁰ (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 [λ , nm ($\epsilon \cdot 10^{-4}$, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 300 (0.88), 362 (1.12), 483 (0.93). IR (ν , cm^{-1}): 1640, 1580. ^1H NMR (CDCl_3 , δ , 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 [λ , nm ($\epsilon \cdot 10^{-4}$, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 304 (1.93), 316 (1.82), 455 (0.59). IR (ν , cm^{-1}): 1690, 1630, 1580. ^1H NMR (CDCl_3 , δ , ppm): 1.99-2.08 (s, 3H, 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)formamidine¹⁰ (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 [λ , nm ($\epsilon \cdot 10^{-4}$, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 305 (1.56), 316 (1.50), 455 (0.52). IR (ν , cm^{-1}): 1680, 1630, 1570. ^1H NMR (CDCl_3 , δ , ppm): 1.96-2.10 (s, 3H, CH_3), 3.96-3.98 (s, 3H, 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 [λ , nm ($\epsilon \cdot 10^{-4}$, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 303 (1.82), 454 (0.53). IR (ν , cm^{-1}): 1680, 1640, 1580. ^1H NMR (CDCl_3 , δ , ppm): 2.04-2.18 (s, 3H, 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 [λ , nm ($\epsilon \cdot 10^{-4}$, $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 303 (1.95), 455 (0.59). IR (ν , cm^{-1}): 1680, 1630, 1570. ^1H NMR (CDCl_3 , δ , ppm): 2.00-2.18 (br. s, 3H, 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%.

Acknowledgements

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