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

Vladimir A. Bren,a,b Alexander D. Dubonosov,*b Lidiya L. Popova,a Vladimir P. Rybalkin,a Igor D. Sadekov,a Evgenii N. Shepelenko,a and Alexey V. Tsukanov a

a Institute of Physical and Organic Chemistry, Rostov State University, 194/2 Stachka av., Rostov on Don, 344090, Russia, and b Southern Scientific Center of Russian Academy of Sciences, 41 Chekhova st., Rostov on Don, 344006, Russia

E-mail: dubon@ipoc.rsu.ru

Dedicated to Professor V. Minkin on the occasion of his 70th birthday
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Abstract
Novel photochromic systems – (2Z)-2-(N-acetyl-N-arylamino)methylene)benzo[b]tellurophene-3(2H)-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 · 10⁻⁴ s⁻¹ (Te) < 4.2 10⁻⁴ s⁻¹ (Se) < 1.0 10⁻³ s⁻¹ (S).

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

Introduction
Photochromism of five-membered benzo[b]annelated heterocyclic (2Z)-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-acylketoamines 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. Modification of the \( N \)-acylketoenamines 2 structure imparts to them the properties of molecular switches, photochromic pH-sensors and chemosensors for metal cations. 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. 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 (2\( Z \))-2-(\( N \)-acetyl-\( N \)-arylaminomethylene)benzo[\( b \)]tellurophene-3(2\( H \))-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. \( N \)-Acylketoenamines 1-3 were synthesized earlier. Ketoenamines 8 have been synthesized by condensation of benzo[\( b \)]tellurophene-3(2\( H \))-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.\textsuperscript{1,3-5} IR spectra of 4 display characteristic amide (1680-1690 cm\textsuperscript{-1}) and exocyclic carbonyl group (1630-1640 cm\textsuperscript{-1}) vibration frequencies. Their Z-configuration is evidenced by the low-field resonance \( ^1\)H NMR signals of the methine protons at 9.3-9.4 ppm.\textsuperscript{1,3} The signals of the E-form methine protons were previously attributed to \( \sim 5.90 \) ppm.\textsuperscript{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 (\( \lambda_{irr} = 436 \) nm, \( C = 2.5 \times 10^{-5} \) M, \( l = 1 \) cm, \( V = 2 \) ml, \( \tau_{irr} = 1 \) 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→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)

<table>
<thead>
<tr>
<th>X</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
<th>( \varepsilon \times 10^4 ), dm(^3) mol(^{-1}) cm(^{-1})</th>
<th>( \phi^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>380</td>
<td>1.52</td>
</tr>
<tr>
<td>2</td>
<td>S</td>
<td>425</td>
<td>1.08</td>
</tr>
<tr>
<td>3</td>
<td>Se</td>
<td>435</td>
<td>1.02</td>
</tr>
<tr>
<td>4</td>
<td>Te</td>
<td>455</td>
<td>0.59</td>
</tr>
</tbody>
</table>

* N→O acyl photorearrangement quantum yield.
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 1775-1780 cm\(^{-1}\) (in CCl\(_4\)). The attempts to isolate compounds 7 were uneffective because, contrary to the benzo\([b]\)thiophene derivative \(5\) (\(Ar = C_6H_4NO_2-3\), 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 (\(\lambda_{\text{max}} = 470-480\) 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 O\(\rightarrow\)N acyl migration constant rates (\(C_5 = C_6 = C_7 = C_{\text{TCA}} = 2.5 \cdot 10^{-5}\) M; \(Ar = Ph\)) increase in the sequence: \(Te (1.1 \ 10^{-4} \ \text{s}^{-1}) < Se (4.2 \ 10^{-4} \ \text{s}^{-1}) < S (1.0 \ 10^{-3} \ \text{s}^{-1})\). 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**

\(2-(N\text{-Acetyl}-N\text{-arylaminomethylene})\)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. $^1$H 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 ($\lambda_{irr} = 436$ nm). Potassium ferrioxalate was used as an actinometer for the quantum yield calculations. $^8$ Fluorescence spectra in CH$_3$CN were measured on a Hitachi 650-60 spectrofluorimeter.

Benzo[b]tellurophene-3(2H)-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$_2$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 (v, cm$^{-1}$): 1630, 1540. $^1$H NMR (CDCl$_3$, $\delta$, ppm): 4.26 (s, 2H, CH$_2$), 7.26-7.76 (m, 4H, Ar). Anal. Calc. for C$_8$H$_6$OTe (245.74): C, 39.10; H, 2.46. Found: C, 39.16; H, 2.43 %.

2-(N-Phenylaminomethylene)benzo[b]tellurophene-3(2H)-one (8a). A solution of benzo[b]tellurophene-3(2H)-one (4 mmol) and diphenylformamidine $^{10}$ (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 ($\varepsilon \cdot 10^4$, dm$^3$mol$^{-1}$cm$^{-1}$)]; 300 (0.88), 362 (1.12), 483 (0.93). IR (v, cm$^{-1}$): 1640, 1580. $^1$H NMR (CDCl$_3$, $\delta$, ppm): 6.84-7.81 (m, 9H, Ar), 8.59-8.64 (d, 1H, =CH, J = 14.0 Hz), 9.60-9.67 (d, 1H, NH, J = 14.0 Hz). Anal. Calc. for C$_{15}$H$_{11}$NOTe (348.87): C, 51.64; H, 3.18. Found: C, 51.68; H, 3.23%.

(2Z)-2-(N-Acetyl-N-phenylaminomethylene)benzo[b]tellurophene-3(2H)-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 ($\varepsilon \cdot 10^4$, dm$^3$mol$^{-1}$cm$^{-1}$)]; 304 (1.93), 316 (1.82), 455 (0.59). IR (v, cm$^{-1}$): 1690, 1630, 1580. $^1$H NMR (CDCl$_3$, $\delta$, 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 C$_{17}$H$_{13}$NO$_2$Te (390.90): C, 52.24; H, 3.35. Found: C, 52.30; H, 3.36%.

(2Z)-2-[N-Acetyl-N-(4-methoxyphenyl)aminomethylene]benzo[b]tellurophene-3(2H)-one (4b). A solution of benzo[b]tellurophene-3(2H)-one (4 mmol) and di(4-methoxyphenyl)formamidine $^{10}$ (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(2H)-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 (\[\lambda \text{, nm (}\epsilon \text{ } \cdot \text{ } 10^{-4}, \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1})\]): 305 (1.56), 316 (1.50), 455 (0.52). IR (\nu, \text{ cm}^{-1}): 1680, 1630, 1570. \text{ }^1\text{H NMR (CDCl}_3, \delta, \text{ ppm}): 1.96-2.10 (s, 3H, CH\text{\text{3}}), 3.96-3.98 (s, 3H, OCH\text{\text{3}}), 7.20-7.86 (m, 8H, Ar), 9.38-9.43 (s, 1H, =CH). Anal. Calc. for C\text{\text{18}}H\text{\text{15}}NO\text{\text{3}}Te (420.93): C, 51.36; H, 3.59. Found: C, 51.39; H, 3.57%.

(2Z)-2-[\text{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 (\[\lambda \text{, nm (}\epsilon \text{ } \cdot \text{ } 10^{-4}, \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1})\]): 303 (1.82), 454 (0.53). IR (\nu, \text{ cm}^{-1}): 1680, 1640, 1580. \text{ }^1\text{H NMR (CDCl}_3, \delta, \text{ ppm}): 2.04-2.18 (s, 3H, CH\text{\text{3}}), 7.18-7.85 (m, 8H, Ar), 9.29-9.36 (s, 1H, =CH). Anal. Calc. for C\text{\text{17}}H\text{\text{12}}NO\text{\text{2}}ClTe (425.35): C, 48.00; H, 2.84. Found: C, 48.01; H, 2.89%.

(2Z)-2-[\text{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 (\[\lambda \text{, nm (}\epsilon \text{ } \cdot \text{ } 10^{-4}, \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1})\]): 303 (1.95), 455 (0.59). IR (\nu, \text{ cm}^{-1}): 1680, 1630, 1570. \text{ }^1\text{H NMR (CDCl}_3, \delta, \text{ ppm}): 2.00-2.18 (br. s, 3H, CH\text{\text{3}}), 7.17-7.83 (m, 8H, Ar), 9.25-9.34 (s, 1H, =CH). Anal. Calc. for C\text{\text{17}}H\text{\text{12}}NO\text{\text{2}}BrTe (469.80): C, 43.46; H, 2.57. Found: C, 43.49; H, 2.50%.

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