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Inverse photochromic systems based on ketoenamine derivatives

A. D. Dubonosov[a]* **and V. A. Bren'**[b]

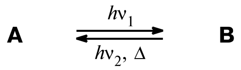
[a]Southern Scientific Center of the Russian Academy of Sciences,
41 ul. Chekhova, 344006 Rostov-on-Don, Russian Federation.
E-mail: dubon@ipoc.rsu.ru
[b]Institute of Physical and Organic Chemistry, Rostov State University,
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.
E-mail: bren@ipoc.rsu.ru

The results of studies into inverse photochromic systems (systems with negative photochromism) based on ketoenamines and ketoenehydrazines of benzo[*b*]annelated heterocycles and their acylated derivatives carried out at the Institute of Physical and Organic Chemistry at the Rostov State University in the last two decades are summarized.

Key words: photochromism, ketoenamines, ketoenehydrazines, *N*-acylated ketoenamines, *Z*/*E*- and *E*/*Z*-photoisomerization, acylotropic rearrangement.

Photochromism means a reversible, electromagnetic radiation-induced transformation of a bi-stable molecule between isomeric states **A** and **B** (Scheme 1), which are characterized by different spectral-luminescent and some other properties[1—8].

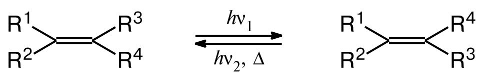
Scheme 1



The back transformation of form **B** into **A** can take place in different ways: photochemically (on irradiation with light with a different wavelength and the energy $E_2 = h\nu_2$), on exposure to magnetic or electric field, on changing the temperature, or on treatment with chemical agents. In most cases, colorless or pale-yellow form **A** is converted into colored form **B** (positive photochromism). Negative photochromism (λ_{max}(**A**) > λ_{max}(**B**)) is observed much more rarely and these systems are called inverse photochromic.[2,3]

The action of monomolecular inverse photochromic systems is based on simple chemical transformation mechanisms; most often, light-induced geometric *E*/*Z*-isomerization at the C=C bond (Scheme 2).[9—13]

Scheme 2



Studies of the transformations of inverse photochromic compounds shown in Scheme 2 are topical not only as regards the development of the fundamental views on the nature of photochromism,[1—4] but also owing to their useful properties, because these systems can be used to accumulate light energy,[1,6] as materials for information receiving and processing or molecular switching of optical signals,[14—18] and for the design of new photochromic chemosensors for metal cations.[19,20]

Geometric isomerization of heterocyclic ketoenamines

The photochemical *Z*/*E* and *E*/*Z* isomerization at the C=C bond has been an object of intensive studies during the last decades.[6,9,12,13,21—23] However, published data on the photoisomerization at the C=C bond conjugated with keto or amino groups are less abundant. Exceptions are indigo, thioindigo and its derivatives (see, for example, a review,[6] chapter 2).

Although some attempts have been made to relate the presence of an intramolecular hydrogen bond (IMHB) to the possible existence of various molecules including ketoenamines, as *E* or *Z* isomers and to possible *E*/*Z*-isomerization in the ground or electronically excited state,[24—27] the foundation for the study of ketoenamine isomerization was laid in Ref. 28, where the theoretical, spectroscopic, and X-ray diffraction data[29—34] concerning the structures of ketoenamines derived from benzo[*b*]annelated five-membered heterocycles were related to different contributions of the bipolar resonance structures **A** and **B** (Scheme 3). Whereas ketoenamines with X = O tend to exist as the *Z* isomers in the crystal phase,

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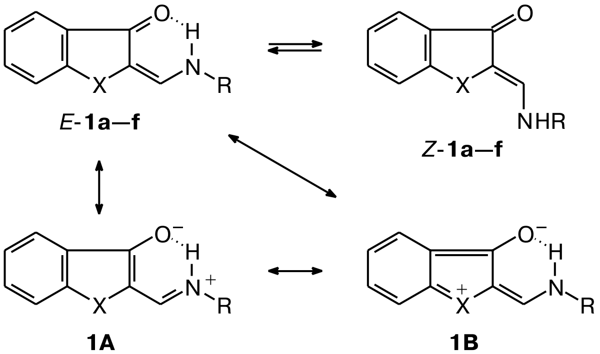
for compounds with X = S and NMe, *E*-structure is typical. The contribution of form **B** increases with a growth of the electron-releasing properties of the heteroatom in the series CO < CH_2 < O < S < Se < NMe, which promotes the formation of a strong intramolecular hydrogen bond and a quasiaromatic ring. The conclusion that, among physicochemical methods (certainly, except for X-ray diffraction), IR spectroscopy provides the most clear data on the fine structure of molecules **1** is especially important.

The decrease in the stretching frequency of the ketoenamine fragment clearly corresponds to the degree of polarization of the conjugated bonds. These theoretical statements were soon verified in practice.[35] Indeed, 2-(*N*-phenylaminomethylene)-1-methylindol-3(2*H*)-one (**1f**, X = NMe) exists only as the *E*-ketoenamine form with a strong IMHB and does not exhibit photochromic properties. Compounds **1a,c,d** exist in solutions as an equilibrium of *E*- and *Z*-forms (Scheme 3, upper line) the position of which depends on the nature of the heterocycle annelated to the ketoenamine fragment. The rate constant for the thermal *E*/*Z*-isomerization decreases in the sequence of heteroatoms X = O > CO > S > NMe, with an increase in the solvation capacity of the solvent, and in the presence of acid or base catalysts. For ketoenamines **1**, the photochemical *Z*/*E*-isomerization is observed for X = O, *E*/*Z*-isomerization takes place at X = S, and reversible $E \rightleftharpoons Z$-isomerization is typical of X = CO.

Scheme 3



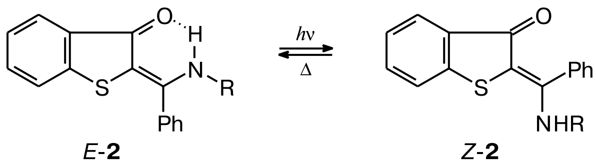
X = CO (**a**), CH_2 (**b**), O (**c**), S (**d**), Se (**e**), NMe (**f**); R = Ar, Alk

In the latter cases, irradiation induces a minor hypsochromic shift (3—4 nm), which allows one to consider systems **1a,d** to be the first examples of inverse photochromic ketoenamines.

In order to increase the difference between the absorption peaks of *E*- and *Z*-forms, we studied ketoenamines containing bulky groups at the exocyclic carbon atom.

2-Benzoyl-3-hydroxybenzo[*b*]thiophene imines **2** exist in the ketoenamine form[36] (Scheme 4).

Scheme 4

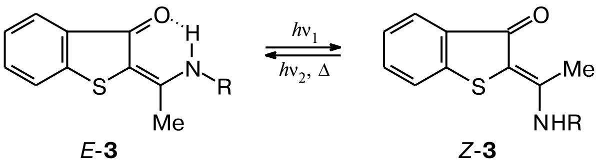


R = Ar, Alk

Attention is attracted by the fact that the stretching frequencies of the carbonyl group of ketoenamines **2** are much lower (Δν = 35—85 cm^{-1}) than the $\nu_{C=O}$ of imines **1d** (X = S). On the one hand, this attests to a more probable *E*-structure of compounds **2** with a strong IMHB, and on the other hand, this is indicative of a substantial contribution of bipolar structures of types **A** and **B** (see Scheme 3) to the molecular geometry. Indeed, only in the case of *p*-nitrophenylimine **2**, which has the smallest $\Delta\nu_{C=O}$ compared to *p*-nitrophenylimine **1** (X = S), can one observe slight, thermally reversible spectral changes (the hypsochromic shift of the absorption peak $\Delta\lambda_{max} \approx$ 1—2 nm and hypsochromic effect $\Delta\varepsilon_{max} \approx$ 3—5%) corresponding to *E*/*Z*-photoisomerization (heptane solution). Thus, the introduction of a phenyl group to the exocyclic carbon atom does not promote *E*/*Z*-isomerization; moreover, this appreciably stabilizes the *E*-**2** form due to the contribution of bipolar resonance structures. Therefore, in further search for inverse photochromic systems capable of photoinduced *E*/*Z*-processes, only alkyl substituents were introduced in ketoenamine molecules.

According to UV, IR, and ^1H NMR spectroscopy, 2-acetyl-3-hydroxybenzo[*b*]thiophene imines **3**, exist in the ketoenamine form *E*-**3**, irrespective of the type of substituent R or solvent polarity (Scheme 5).[37]

Scheme 5



R = Ar, Alk

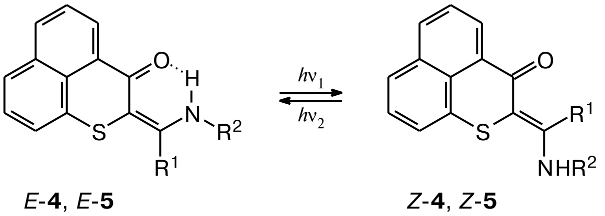
The IR spectra of ketoenamines **3** exhibit strong absorption bands at 1610—1620 cm^{-1} for the conjugated ring carbonyl group. The decrease in the $\nu_{C=O}$ frequencies for compounds **3** with respect to those of 3-hydroxybenzo[*b*]thiophene-2-carbaldimine **1d** (X = S) is only 15—40 cm^{-1}, which is much lower than that for ketoenamines **2**.

The irradiation of solutions of ketoenamines **3** at the long-wavelength absorption band (λ 436 nm) at 293 K results in fast *E*/*Z*-isomerization at the C=C bond until the photostationary state, *E*-**3** $\rightleftharpoons$ *Z*-**3**, is attained. The back *Z*/*E*-isomerization can be performed either thermally or photochemically to completely restore the initial spectrum of *E*-**3**. At 293 K, the rate constant $k_{Z\to E}$ has an order of ~$8 \cdot 10^{-2}$ s^{-1} and increases in the following sequence of substituents R: Ph < C_6H_4Me-2 ≈ C_6H_4Cl-2 < < $C_6H_2Me_3$-2,4,6. The irradiation of a photostationary mixture of *Z*- and *E*-isomers with light at λ 313 nm brings the system back to the initial state with the quantum yield $\varphi_{Z\to E} \approx 0.25$. The Δλ value between the *E* and *Z* forms of ketoenamines **3** amounts to 10—15 nm.

Thus, the presence of the alkyl substituent at the exocyclic carbon atom in the molecules of 2-acetyl-3-hydroxybenzo[*b*]thiophene imines **3** results in a higher efficiency of *E*/*Z*-photoisomerization and a greater difference between the absorption spectra of the *E* and *Z* isomers ($\Delta\lambda_{max}(E—Z)$).

The influence of the heterocycle size on *E*/*Z*-photoisomerization was studied by comparing 2-acetyl-3-hydroxynaphtho[1,8-*bc*]thiopyran imines **4** with 3-hydroxynaphtho[1,8-*bc*]thiopyran-2-carbaldehyde imines **5** devoid of the methyl group at the exocyclic carbon atom (Scheme 6).[38]

Scheme 6



E-**4**, *E*-**5** *Z*-**4**, *Z*-**5**

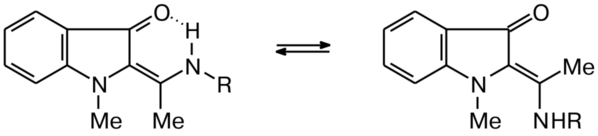
R^1 = Me (**4**), H (**5**); R^2 = Ar, Alk

The irradiation of solutions of ketoenamines **4**, **5** at the long-wavelength absorption peak at λ 436 nm induces the following changes. For 3-hydroxynaphtho[1,8-*bc*]thiopyran-2-carbaldehyde imines (**5**), the spectral pattern was typical of *Z*/*E*-isomerization, the 490—500 nm band being shifted bathocromically to the photostationary state between the *Z* and *E* forms.

The irradiation of an equilibrium mixture at λ 546 nm induces the back *E*/*Z*-photoisomerization and brings the system to a new equilibrium with a lower content of the *E* isomer. When irradiation is terminated, fast thermal *E*/*Z*-isomerization with the rate constant $k_{Z\to E} \approx 10^{-2}$ s^{-1} takes place until the initial spectral pattern is restored. 2-Acetyl-3-hydroxynaphtho[1,8-*bc*]thiopyran imines are non-photochromic; together with relatively great $\Delta\nu_{C=O}$ values, this suggests a *E* structure with a strong IMHB. Thus, ketoenamines **5** tend to exist as the *Z* form, the introduction of a methyl group to the exocyclic carbon atom in ketoenamines **4** stabilizes the *E* structure and the presence of the strong IMHB prevents *E*/*Z*-photoisomerization.

Further enhancement of the steric strain can be expected for 2-acetyl-3-hydroxy-1-methylindole imines (**6**) (Scheme 7).[39]

Scheme 7



E-**6** *Z*-**6**

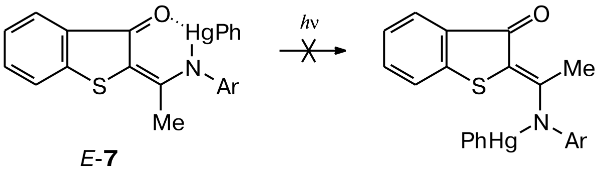
R = Ar, Alk

Interactions both between the bulky electron-releasing NMe group in the ring and the neighboring CMe substituent and between the Me group and the N-aryl fragment are possible in these structures. Relying on the similarity of the spectral data of ketoenamines **6** and 1-methylindole ketoenamines **1f** (X = NMe), which were shown by X-ray diffraction to have a planar *E* structure,[34] the compounds obtained can be assigned *E* ketoenamine structure *E*-**6**. Nevertheless, the excess negative charge on the carbonyl oxygen atom in 1-methylindole derivatives facilitates the formation of a very strong IMHB,[28] which prevents *E*/*Z*-photoisomerization.

To summarize the results, one can conclude that, on the one hand, steric contacts in ketoenamine molecules promote isomerization, and, on the other hand, the strong IMHB present in the same molecules retards this process. Thus, the possibility of *E*/*Z*-photoisomerization in heterocyclic ketoenamines is determined by the balance of two key factors: steric contacts in the molecule and the strength of the IMHB. A weak IMHB can result in ketoenamines existing in the *Z* form (compounds **5**), while a strong one inhibits the *E*/*Z*-isomerization (compounds **6**). Evidently, by selecting appropriate substituents, one can either preclude *E*/*Z*-isomerization in systems where it has been observed (for example, in ketoenamines **3**), or, conversely, weaken the IMHB to enable photoisomerization at the C=C double bond in systems where it was totally missing (for example, in ketoenamines **6**).

Indeed, the incorporation of the organometallic HgR group instead of the amine hydrogen atom into the structure of ketoenamines **3** (compound **7**) gives rise to a strong quasi-aromatic ring and precludes *E*/*Z*-isomerization of 2-acetyl-3-hydroxybenzo[*b*]thiophene imines (Scheme 8)[40]. The difference $\Delta\nu_{C=O} = \nu_{C=O}(\mathbf{3}) - \nu_{C=O}(\mathbf{7})$ is 10—25 cm^{-1}, which attests to additional stabilization of isomer *E*-**7** due to the strong intramolecular PhHg...O=C< coordination.

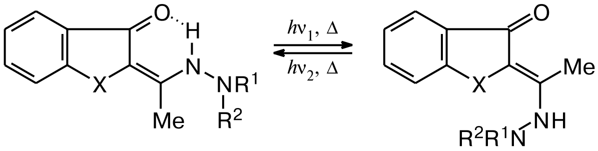
Scheme 8



E-**7** *Z*-**7**

Simultaneously, electronegative substituents present at the amine nitrogen atom in ketoenamines derived from benzo[*b*]annelated five-membered heterocycles contribute to weakening of the IMHB and decrease (in the case of NR^1R^2; R^1, R^2 = Alk, Ar) the stability of the keto form due to the unfavorable conditions for the *n*,π-conjugation.[41,42] The strength of the IMHB in compounds **8**, **9** (Scheme 9) can be controlled by selecting a heteroatom and electron-releasing or electron-withdrawing substituents R^1 and R^2.[43–45]

Scheme 9



E-**8**, *E*-**9** *Z*-**8**, *Z*-**9**

X = S (**8**), O (**9**); R^1, R^2 = Ar, Alk

The irradiation of hydrazones **8** and **9** at the long-wavelength absorption peaks (λ 365 nm for benzo[*b*]furan derivatives and λ 436 nm for benzo[*b*]thiophene derivatives) induces a considerable modification of the spectra, typical of the *E*/*Z*-photoisomerization, with appearance of the band for the *Z* isomer at 330—350 nm. The *E*/*Z*-photoisomerization is accompanied by thermal *Z*/*E*-isomerization, resulting in an equilibrium (see Scheme 9) in which the content of the *Z* isomer increases with a decrease in the solvent polarity and with an increase in the number of alkyl substituents in the hydrazone fragment (Table 1). The kinetics of the thermal *Z*/*E*-isomerization was studied in the 252—293 K temperature range. The results were used to calculate the activation parameters of this process (Table 2). Under the same conditions and for identical compounds, the photoinduced *Z*-isomer of the benzo[*b*]furan hydrazones proves to be more stable than that of the benzo[*b*]thiophene derivatives.

Table 1. Thermodynamic parameter of the equilibria *E*-**8** ⇌ *Z*-**8**, *E*-**9** ⇌ *Z*-**9**

Compound	X	R^1	R^2	Solvent	*Z*-Isomer[a] (%)	K^0 [b]	ΔG°_{293} [c]
8a	S	Me	Me	Heptane	24	0.32	2.8
				MeCN	2	0.02	9.5
8b	S	$(CH_2)_5$		Heptane	27	0.37	2.4
				MeCN	3	0.03	8.5
8c	S	Me	Ph	Heptane	51	1.04	–0.1
				MeCN	4	0.04	7.8
9a	O	Me	Ph	Heptane	59	1.44	–0.9
				MeCN	30	0.43	2.1

[a] The content of the *Z*-isomer.

[b] The equilibrium constant is $K^0 = [Z]/[E]$.

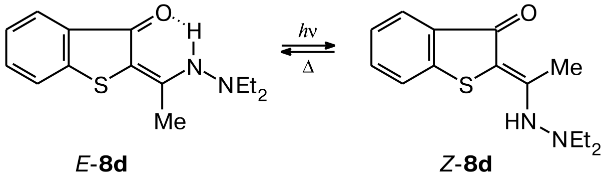
[c] In kJ mol^{-1}

Table 2. Activation parameters ($\Delta G^\#$, $\Delta H^\#$/kJ mol^{-1}, $\Delta S^\#$/J mol^{-1} K^{-1}) of the thermal *Z*/*E*-isomerization of hydrazones **8a**,**d** and **9a** (in the temperature range of 252—293 K)

Compound	X	R^1	R^2	*T*/K	$k_{Z\to E}$	$\Delta G^\#_{293}$	$\Delta H^\#_{293}$	$\Delta S^\#_{293}$
9a	O	Me	Ph	292	$6.1 \cdot 10^{-4}$	89.3	38.9	–172.6
8a	S	Me	Me	293	$1.2 \cdot 10^{-3}$	87.9	38.5	–168.6
8d	S	Et	Et	293	$6.2 \cdot 10^{-5}$	95.4	38.5	–194.2

Analysis of the spectral and X-ray diffraction data obtained[46,47] indicates that a system capable of *E*/*Z*-isomerization at room temperature with full formation of the *Z* isomer and non-overlapping absorption bands of the *E*- and *Z*-forms, should be sought (1) in the benzo[*b*]thiophene series in which the heteroatom X = S ensures a moderate contribution of the resonance bipolar structures to the overall molecular structure (O < S < NMe), (2) among the 2-acetoxy- rather than 2-benzoyl-substituted heterocycles, (3) in the ketoenehydrazine rather than ketoenamine series, (4) among hydrazones having *N*,*N*-dialkyl rather than *N*,*N*-diaryl groups. All these conditions are met for 2-[1-(*N*,*N*-diethylhydrazino)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**8d**), which undergoes photochemical *E*/*Z*-isomerization, resulting in full formation of *Z*-**8d** on exposure to light with λ 436 nm with the quantum yield $\varphi_{Z\to E}$ 0.06 (Scheme 10, Fig. 1).

Scheme 10



E-**8d** *Z*-**8d**

The product exhibits an absorption peak at λ_{max} 345 nm, the band separation in heptane being $\Delta\lambda = \lambda_{max}(E) - \lambda_{max}(Z)$ = 78 nm, which ensures complete lack

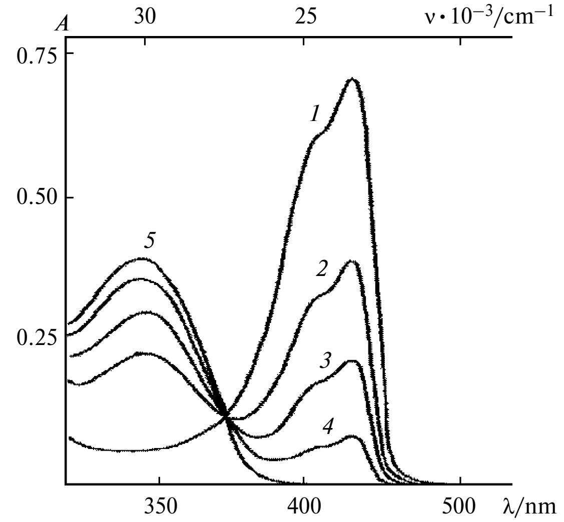


Fig. 1. Electronic absorption spectra of 2-[1-(*N*,*N*-diethylhydrazino)ethylidene]benzo[*b*]thiophen-3(2*H*)-one (**8d**) in heptane at 293 K before (*1*) and after irradiation for 0.5 (*2*), 2 (*3*), 6 (*4*), and 12 min (*5*), λ 436 nm, $C = 5 \cdot 10^{-5}$ mol L^{-1}.

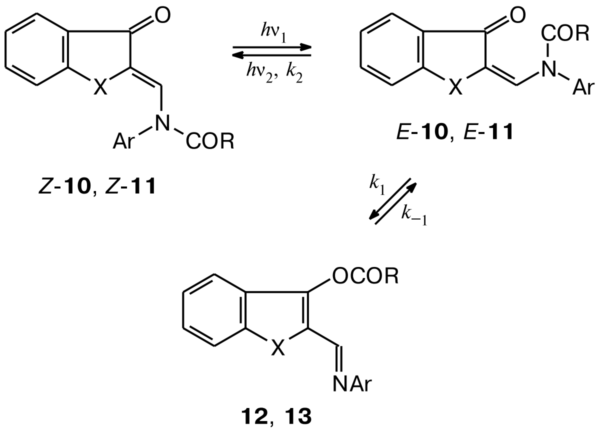
of overlap of the bands for *E*- and *Z*-isomers. The rate constant for the reverse thermal *Z*/*E*-isomerization at 293 K is given by $k_{Z\to E}$ $6.2 \cdot 10^{-5}$ s^{-1}. The rate of this process rapidly decreases with a decrease in temperature: $k_{Z\to E}$ $3.15 \cdot 10^{-5}$ (282 K), $1.8 \cdot 10^{-5}$ (264 K), $7.2 \cdot 10^{-6}$ (253 K); at 233 K, the reverse *Z*/*E*-isomerization is almost inhibited; no noticeable changes in the absorption spectrum of the irradiated ketoenehydrazine **8d** are observed for 3 h. Under these conditions, the quantum yield of photoisomerization $\varphi_{Z\to E}$ is 0.40. The activation parameters of the thermal *Z*-**8d** → *E*-**8d** process determined in the 252—293 K temperature range are as follows: $\Delta G^{\#}_{293}$ 95.4 kJ mol^{-1}, $\Delta H^{\#}_{293}$ 38.5 kJ mol^{-1}, $\Delta S^{\#}_{293}$ −194.2 J mol^{-1} K^{-1}.

The studies performed demonstrate that *E*/*Z*-photoisomerization of heterocyclic ketoenamines (ketoenehydrazines) can be deliberately influenced by steric and electronic factors. Consequently, the new inverse photochromic system **8d**, whose operation is based on *E*/*Z*-photoisomerization at the exocyclic C=C bond, is suitable for optical information recording (for example, in PMMA matrices or on application on a special Dacron support in the amorphous state).

Isomerization of acylated ketoenamines accompanied by acyl group migration

Acylated ketoenamines based on benzo[*b*]annelated heterocycles **10** possess a clear-cut negative photochromism (Scheme 11).[6,48—50] The long-wavelength edge of their absorption reaches 470—485 nm (ε ≈ 1.0 L mol^{-1} cm^{-1}), whereas isomers **12** formed by the photochemical route have no absorption maxima at $\lambda_{max} \geq$ 360—370 nm. Early studies have shown that, whereas benzo[*b*]furan derivatives **10** (X = O) undergo thermally reversible *Z*/*E*-isomerization at the C=C bond, for benzo[*b*]thiophene derivatives **10** (X = S) and benzo[*b*]selenophene derivatites **10** (X = Se), this process is accompanied by thermal acylotropic N→O rearrangement to give *O*-acyl derivatives **12**.

Scheme 11



R = H, Me, OMe; **10, 12:** X = O, S, Se; **11, 13:** X = NMe;

On the basis of pulse radiolysis data,[6,49] it was suggested that photoinitiated transformations of *N*-acylated ketoenamines **10** (X = S) (see Scheme 11) include two successive steps, namely, photochemical *Z*/*E*-isomerization at the exocyclic C=C bond and thermal N→O migration of the acyl group. In order to find a system that would allow one to observe separately the two steps under stationary irradiation at room temperature and to study the rearrangement mechanism in detail (see Scheme 11), we synthesized acylated 3-hydroxy-1-methylindole-2-carbaldehyde imines **11** (X = NMe) and compared them with the benzothiophene ketoenamines studied previously (Table 3).[51] This choice was due to the assumption[52] that steric interactions, especially those between the heteroatom X and the NAr fragment, are favorable for the occurrence of the first reaction step according to Scheme 11,

Table 3. Spectral characteristics of acylated ketoenamines **10**, **11**

Compound	X	R	Ar	λ_{max}/nm ($\varepsilon_{max} \cdot 10^{-4}$/L mol^{-1} cm^{-1})
10a	S	Me	Ph	310 (2.66), 428 (1.36)
11a	NMe	H	Ph	312 (1.04), 462 (0.58)
11b	NMe	Me	CH_2Ph	309 (1.11), 460 (0.33)
11c	NMe	H	CH_2Ph	305 (1.18), 490 (0.37)
11d	NMe	Me	C_6H_4Cl-4	354 (2.07)
11e	NMe	OMe	C_6H_4OMe-4	325 (0.82), 464 (0.62)

i.e., *Z*/*E*-isomerization, resulting in close arrangement of the nucleophilic N- and O-centers necessary for the N→O transfer of the acyl group.

In the electronic absorption spectra of ketoenamines **11a,b**, the peaks in the 460—465 nm region are shifted bathochromically by 30—35 nm relative to analogous bands of benzothiophene compounds **10**. According to UV, IR, ^{1}H NMR, and X-ray diffraction data, molecules **11a,b** have a *Z*-configuration at the exocyclic C=C bond and their photoinitiated processes are limited to *Z*/*E*-isomerization. Conversely, ketoenamine **11c** is the *E* isomer being converted into the *Z* form upon irradiation. Finally, acylated ketoenamine **11d** is the *O*-isomer, which models the initial step of formation of the transition state to the back dark O→N transfer of the acyl group. Thus, isomers modeling all the three possible structures involved in the photoprocess according to Scheme 11, *Z*-*N*-acyl form, *E*-*N*-acyl form, and *O*-acyl isomer, can be implemented in the 1-methylindole series. Further variation of the structure of compounds **11** on the basis of these data gave[53] a model compound, 2-[*N*-methoxycarbonyl-*N*-(4-methoxyphenyl)aminomethylene]-1-methylindol-3(2*H*)-one (**11e**), for which the rearrangement steps can be detected (see Scheme 11). The irradiation of this compound at the long-wavelength absorption band (λ 436 nm) causes fast *Z*/*E*-isomerization relative to the exocyclic C=C bond; the formation of the *E* isomer is manifested in the spectra as the characteristic hypochromic effect and a bathochromic shift of the long-wavelength peak by 15—20 nm (Fig. 2, curve *2*). The formation of isomer *E*-**11e** is followed by thermal N→O transfer of the methoxycarbonyl group until the acyl *N*- and *O*-isomers are in equilibrium (see Fig. 2, curve *4*). The kinetics of the acyl N→O transfer was studied in the temperature range of 266—330 K, because at 266 K, the photoinitiated reaction according to Scheme 11 is limited to *Z*/*E*-isomerization without the subsequent formation of the *O*-acyl isomer **13e**. The results of kinetic measurements (Table 4) were used to calculate the activation parameters of the *E*-**11e** → **13e** transformation: $\Delta G^{\#}_{288}$ 87±8 kJ mol^{-1}, $\Delta H^{\#}_{288}$ 69±7 kJ mol^{-1}, $\Delta S^{\#}_{288}$ −62 J mol^{-1} K^{-1}. Thus, compound **11e** is the first example of inverse photochromic acylotropic system in which the two steps of the photoinitiated process, *Z*/*E*-isomerization at the C=C bond and the thermal N→O transfer of the acyl group, can be detected separately under stationary irradiation (Fig. 3).

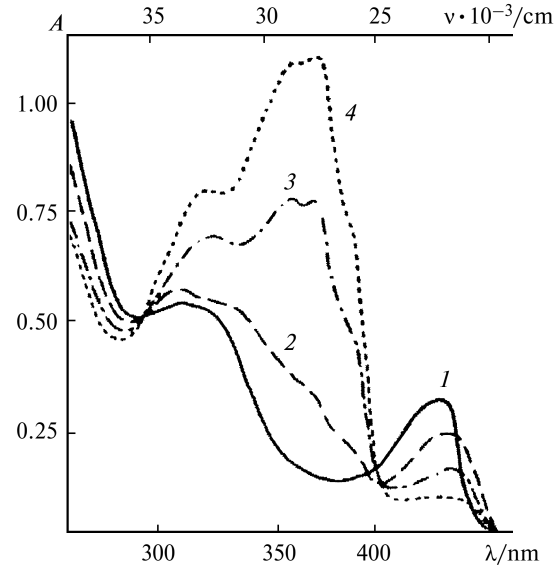


Fig. 2. Electronic absorption spectra of 2-[*N*-methoxycarbonyl-*N*-(4-methoxyphenyl)aminomethylene]-1-methylindol-3(2*H*)-one (**11e**) in hexane before (*1*) and after irradiation with λ 436 nm for 3 min (*2*); after 18 (*3*) and 100 min (*4*) at 288 K, $C = 5 \cdot 10^{-5}$ mol L^{-1}.

Table 4. Energetic parameters of the acylotropic reaction E-**11e** $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ **13** in toluene

T/K	$k_1 \cdot 10^3$/s^{-1}	$k_{-1} \cdot 10^3$/s^{-1}	K^0 = [**13e**]/[**11e**]
288	0.95	0.47	2.02
301	4.1	1.9	2.16
313	12	5.4	2.20
331	45	20.5	2.20

Note: k_1 and k_{-1} are the rate constant for the forward and reverse reaction, respectively.

Molecular switches based on inverse photochromic acylated ketoenamines

The *Z*/*E*-isomerization and the subsequent acylotropic N→O rearrangement described were used in original switches of optical and chemical sensor properties.[54—60]

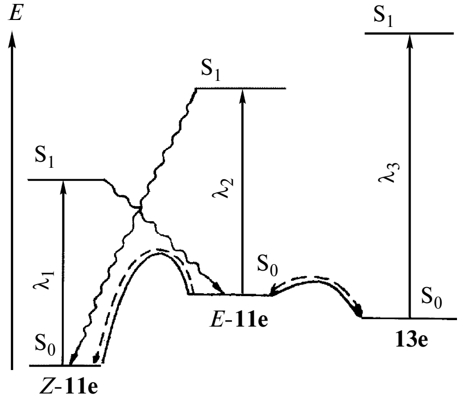
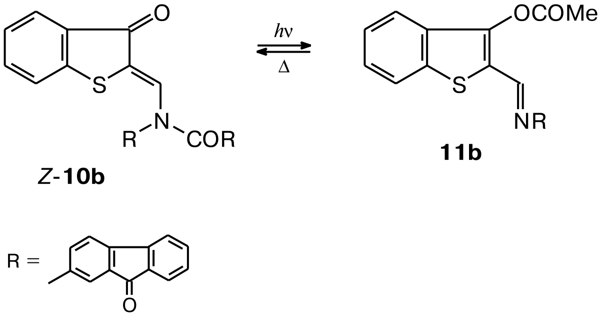


Fig. 3. Basic scheme of the photoinitiated reaction *Z*-**11e** ⇌ *E*-**11e** ⇌ **13e** according to the absorption spectra and thermodynamic parameters of the equilibrium: λ_1 = 450 nm, λ_2 = 460 nm, λ_3 = 365 nm.

N-Acylated ketoenamines **10** and **11** exhibit low-intensity fluorescence in the region of 456—475 nm, which is mirror symmetric to the absorption band. The intensity of this fluorescence decays to zero during the photoreaction (see Scheme 11) in parallel with the variation of the content of the acyl *N*-isomer in the solution (on/off process[61]). Since at 77 K the quantum yield of these phototransformations decreases almost to zero, a time-invariable strong fluorescence band is observed at low temperatures. The final products of the photoreaction (see Scheme 11) do not fluoresce due to the extremely high rate of the intersystem crossing.[62] One of the few known exceptions is fluorenone derivative **10b** in which the initial form has no fluorescence.[58] However, during the **10b** → **11b** photoreaction (Scheme 12), a new fluorescence with λ_{max} 545 nm and φ 0.03 appears (off/on process,[61] Fig. 4). This is the first example of 3-acetoxybenzo[*b*]thiophene derivative of type **10** that fluoresces at 293 K, while compound **10b** is a new type of the molecular switch of the fluorescence signal. The back conversion into the initial state takes place on thermal initiation or in the presence of catalytic quantities of trifluoroacetic acid.

Scheme 12



The luminescence of *N*-acylated ketoenamine **10c** is essentially inhibited due to the PET-effect (Photoinduced Electron Transfer).[54,61] The quantum yield of fluorescence with λ_{max} 470 nm in toluene is 0.0025. The irradiation of ketoenamine **10c** at the long-wavelength absorption peak causes thermally reversible *Z*/*E*-isomerization without the subsequent transfer of the acetyl group (Scheme 13).

The addition of trifluoroacetic acid to a toluene solution of the *E* isomer brings about the rearrangement to the protonated *O*-acylated species **12** according to the mechanism reported in the literature.[55] The substantial deterioration of the PET-effect in cation **12c** causes a 170-fold increase in the initial fluorescence intensity, which allows compound **10c** to be considered an efficient photoswitched molecular pH-sensor.[56]

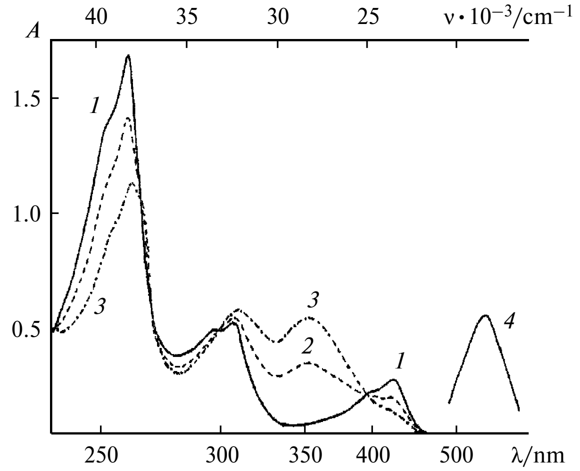
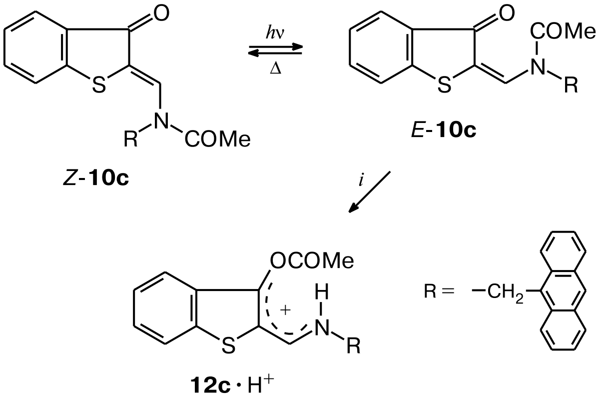


Fig. 4. Electronic absorption spectra of 2-[*N*-acetyl-*N*-(9-oxofluoren-2-yl)aminomethylene]benzo[*b*]thiophen-3-(2*H*)-one (**10b**) in acetonitrile before (*1*) and after irradiation at λ 436 nm for 4 (*2*) or 8 min (*3*); fluorescence after 8-min irradiation (*4*), $C = 2 \cdot 10^{-5}$ mol L^{-1}.

Scheme 13

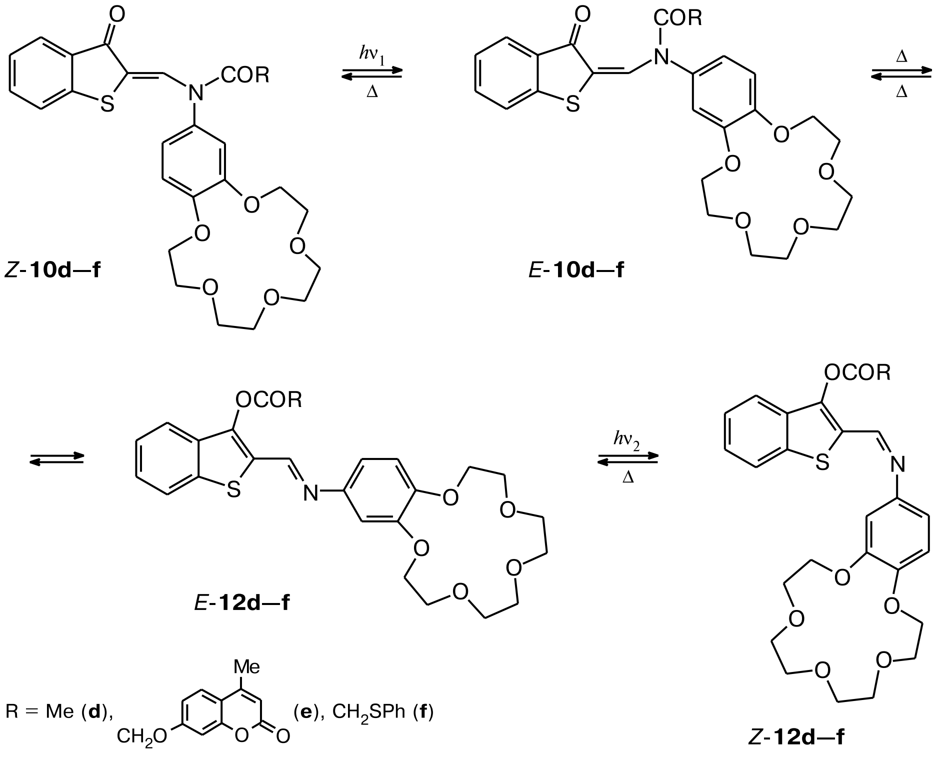


i. CF_3COOH.

The exposure of acylated 15-crown-5-containing ketoenamines to light with λ 436 nm at the long-wavelength absorption peak (Scheme 14) results in *Z*/*E*-isomerization at the double C=C bond followed by thermal N→O transfer of the acyl group to give *O*-acyl isomers **12d—f** with quantum yields of 0.25 (**d**), 0.48 (**e**), and 0.40 (**f**)[59,60].

The peak intensity at 435 nm decreases to zero and a new band appears at 360—370 nm (several clear isosbestic points are present). The resulting *O*-acyl photoisomers **12d—f** are stable in solutions for long periods. The back O→N migration of the acyl group can take place as a catalytic (in the presence of small amounts of trichloroacetic acid) or thermal reaction (heating of a toluene solution to 90 °C) but not a photochemical one. The irradiation of solutions of **12d—f** in solvents of different polarity (λ 365 nm) induces only thermally reversible *E*/*Z*-isomerization at the C=N bond until an equilibrium is established (see Scheme 14).

Scheme 14



A characteristic[6] decrease in the peak intensity at 360 nm and an increase in the peak intensity at 305 nm are observed in this case.

In 2-(*N*-acyl-*N*-aryl)aminomethylenebenzo[*b*]thiophen-3(2*H*)-ones **10** (X = S) studied previously,[6,49] no such processes have been detected at room temperature under stationary irradiation due to the exceptionally high rate of the thermal *Z*/*E*-isomerization at the C=N bond.

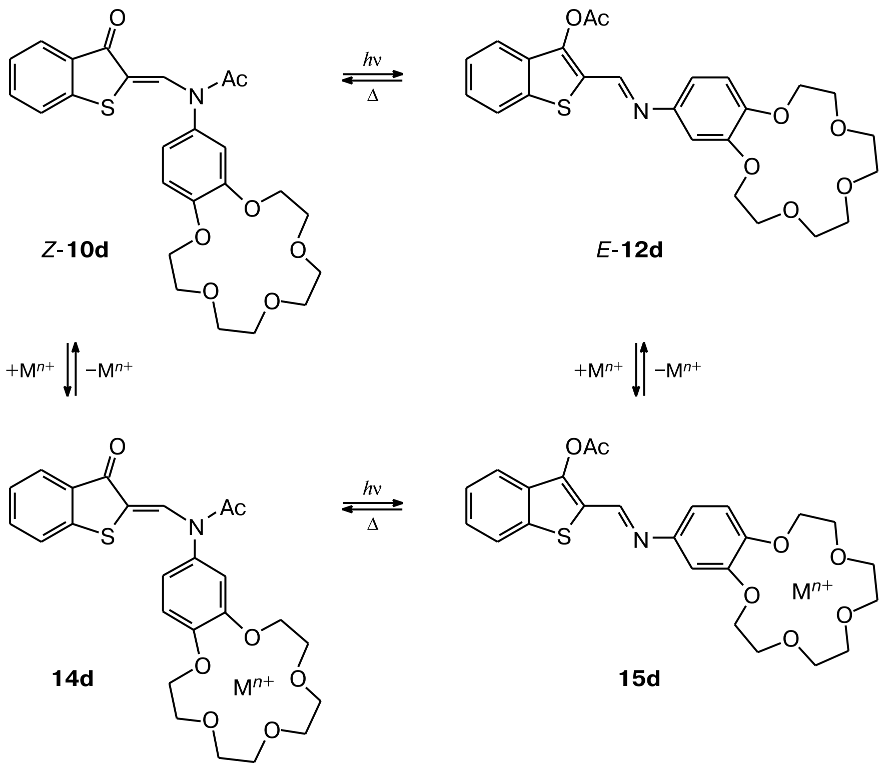
The addition of Group IA and IIA metal salts to solutions of acylated ketoenamine **10d** in acetonitrile, isopropyl alcohol, or dimethyl sulfoxide (Scheme 15) causes only minor changes in the absorption spectra.

Conversely, the photoswitching **10d** → **12d** results in the sensor-active form **12d**, which exhibits significant specific changes in the electron absorption spectra. This is accompanied by a substantial increase in the molar extinction coefficient by 2—21% for alkali metals and by 5—33% for alkaline earth metals. The following features were found for alkali metals: in acetonitrile, the hypsochromic shift of the long-wavelength absorption peak (Δλ) regularly decreases from 10 to 5 nm with the increase in the cation diameter $Li^+ > Na^+ > K^+ > Cs^+$. The molar extinction coefficient of the band at 365 nm decreases from ~13 to 5.5% over the same series (Table 5). The

Table 5. Spectral characteristics of complexes **15** compared to ligands **12** and quantum yields of photoreactions in acetonitrile

M^{n+}	**15d**			**15e**			**15f**		
	Δε (%)	Δλ/nm	φ	Δε (%)	Δλ/nm	φ	Δε (%)	Δλ/nm	φ
Li^+	13.1	10	0.43	12.9	9	0.62	20.9	14	0.54
Na^+	10.9	8	0.39	7.5	8	0.55	14.1	12	0.49
K^+	7.2	7	0.39	5.9	8	0.54	13.0	10	0.48
Cs^+	5.5	5	0.29	4.8	4	0.49	7.65	2	0.41
Mg^{2+}	29.4	19	0.32	76.3	57	0.62	35.5	18	0.67
Ca^{2+}	33.3	16	0.39	79.0	57	0.73	38.0	20	0.64
Sr^{2+}	23.5	16	0.37	69.9	55	0.49	22.6	16	0.63
Ba^{2+}	28.6	16	0.45	76.2	55	0.50	24.3	18	0.61

Scheme 15



reaction of O-acylated compound **12d** with Group IIA metal cations is responsible for much more pronounced changes in the absorption spectra. In acetonitrile, the $\Delta\lambda$ value can be as great as 16—19 nm and the greatest $\Delta\varepsilon$ for Ca^{2+} is 33.3% (see Table 5).

The photoinduced sensor form of 15-crown-5-containing 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde phenylimine (**12d**) has a selective sensitivity toward lithium cations: the specific spectral characteristics of the complex of **15d** with Li$^+$ ($\Delta\varepsilon$, $\Delta\lambda$) are retained in the presence of other alkali metals in solution ($C_{\mathrm{Li}^+} = C_{\mathrm{Na}^+} = C_{\mathrm{K}^+} = C_{\mathrm{Cs}^+} = 5 \cdot 10^{-5}$ mol L^{-1}).

Compound **10e**, containing the bulky 4-methyl-2-oxobenzo[*b*]pyran-7-yloxyacetyl group as the migrant also undergoes *Z*/*E*-isomerization followed by the N→O acyl transfer. The interaction of the sensor active form **12e** thus formed with alkali metal cations is fairly similar to the properties of **12d** (for the changes in $\Delta\lambda$, $\Delta\varepsilon$, see Table 4), which contains a less bulky acetyl migrating group. However, the addition of the Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} cations to a solution of **12e** in acetonitrile brings about sharp changes in the absorption spectra (Fig. 5). The hypsochromic shift of the long-wavelength absorption band may reach 57 nm and the molar extinction coefficient increases almost twofold. It is clear that for structures **15d** and **15e**, which differ only by the migrating group, these pronounced spectral changes may be due to the simultaneous interaction of the cation with the crown ether ring and with the benzopyrone group. By analogy,[63]

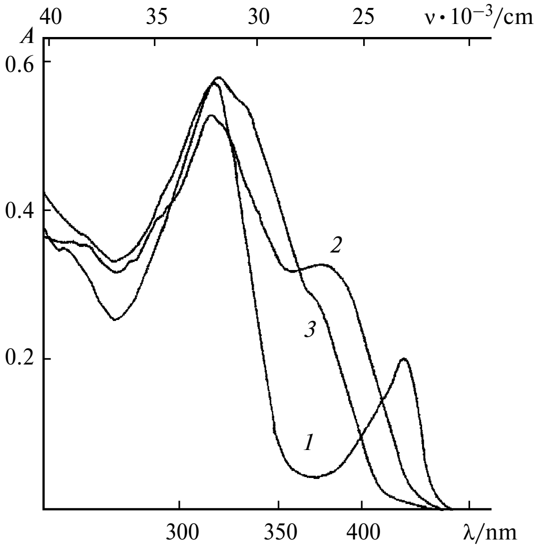
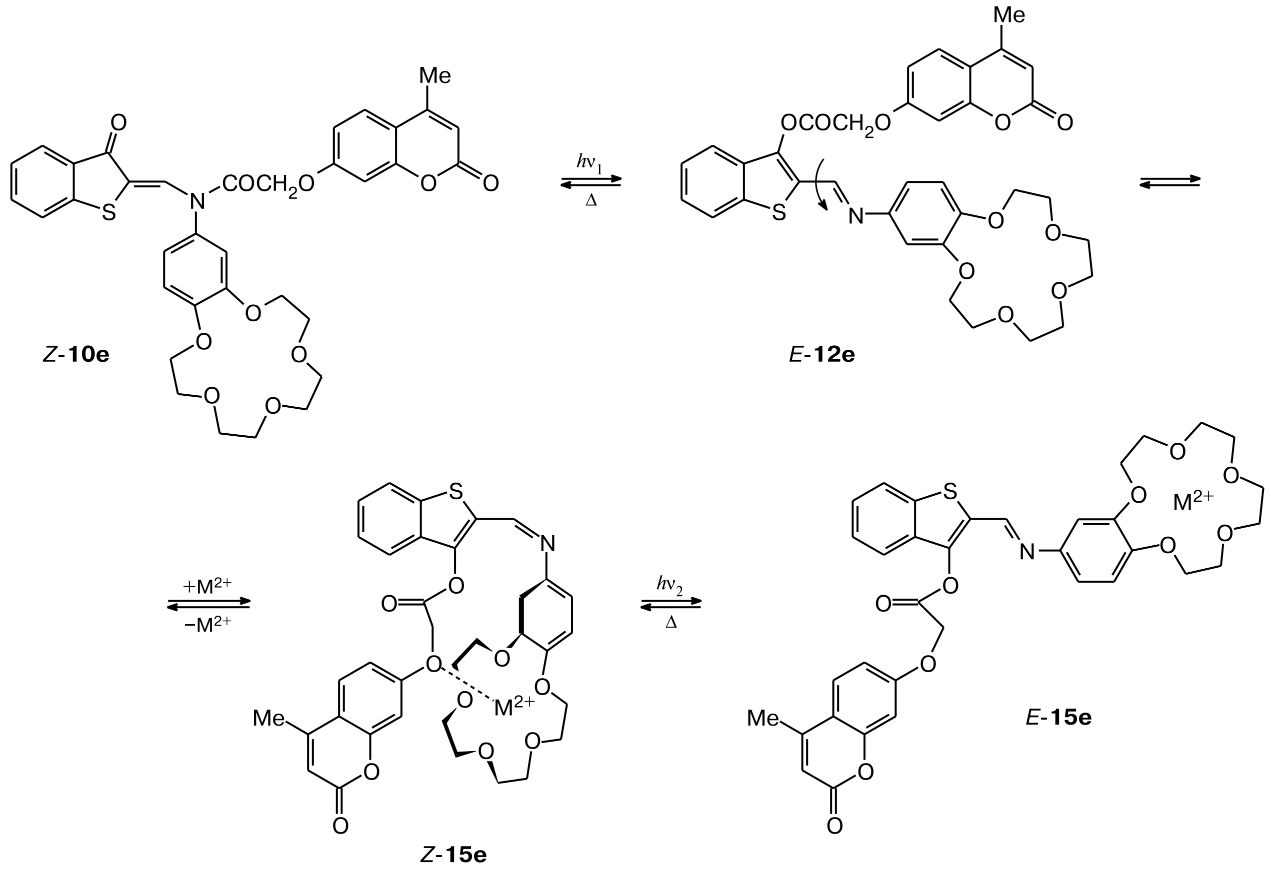


Fig. 5. Electronic absorption spectra of 2-{*N*-(4-methyl-2-oxobenzo[*b*]pyran-7-yloxyacetyl)-*N*-[(benzo-15-crown-5)-4´-yl]aminomethylene}benzo[*b*]thiophen-3(2*H*)-one (**10e**) in acetonitrile before (*1*) and after irradiation for 120 s (*2*), λ 436 nm; after the addition of Ca(ClO$_4$)$_2$ (*3*), $C = 1.7 \cdot 10^{-5}$ mol L^{-1}.

Scheme 16



$M^{2+} = Mg^{2+}, Ca^{2+}$

one can suggest a dual coordination of the M^{2+} ion with both the crown ether and the most basic oxygen atom of the acyl group, which is possible when the resulting complex has a *Z*-configuration (Scheme 16).

This mechanism of the reaction of crown compound **12e** with Mg^{2+} and Ca^{2+} is supported by our rough PM3 quantum-chemical calculations and the *Z*/*E*-isomerization of complex **15e** (λ 365 nm) detected by spectroscopy, which is thermally reversible. According to a publication,[63] the M^{2+} ions can function as a sort of intramolecular adhesive, which usually stabilizes the energetically less favorable *Z*-isomer.

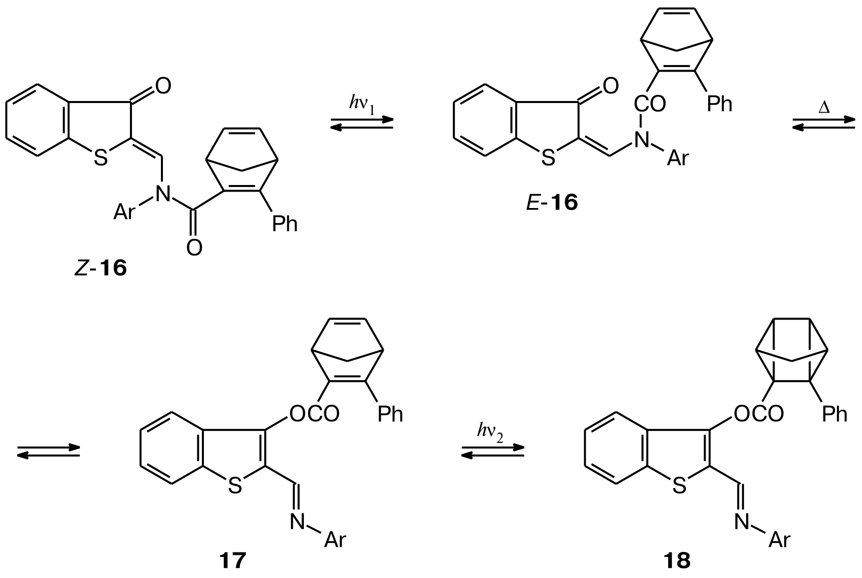
The properties of compound **10f** with the (phenylthio)acetyl migrating group are closely similar to the properties of the *N*-acetyl derivative **10d** as regards the alkali and alkaline earth metals. However, the photoinduced sensor-active form **12f**, unlike its analogs **12d,e**, has an enhanced sensitivity toward many transition metals: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. Although the hypsochromic shift Δλ is only 2—3 nm, Δε in acetonitrile reaches a value approximately equal for all the above-listed cations, Δε ≈ 30%. By analogy with structure *Z*-**15e**, additional coordination of the soft acids M^{n+} to the soft S center of the acyl group can be assumed in this case.

Thus, inverse photochromic crown-containing compounds **10d,e** exhibit a specific sensor activity with respect to the following types of metal cations: (1) *N*-acetyl derivatives to alkali metal ions (and selectively to Li^+); 2) *N*-(4-methyl-2-oxobenzo[*b*]pyran-7-yloxy)acetyl derivative to Group IIA metal ions; and 3) *N*-(phenylthio)acetyl derivative to some transition metal ions.

The possibility of relatively easy modification of the structures of acylated ketoenamines by selection of appropriate substituents and migrating groups can be illustrated in relation to the "hybrid" biphotochromic molecules, which combine the properties of two inverse photochromic systems: acylotropic systems capable of *Z*/*E*-isomerization at the C=C bond and the acyl N→O transfer and norbornadienes capable of valence isomerization according to the (2π+2π)-cycloaddition pattern.[64—66]

In polar solvents, irradiation of compounds **16** (Scheme 17) with λ 436 nm light causes *Z*/*E*-isomerization followed by N→O transfer of the acyl group.

Scheme 17



The formation of isomers **17** is manifested as absorption at 300—320 nm and was confirmed by IR and ^{1}H NMR data. The irradiation of these isomers with λ 365 nm light gives rise to a quadricyclane fragment. The back reaction, **18** → **16**, takes place without differentiation of steps upon the addition of catalytic amounts of CF_3COOH.

Thus, the first inverse photochromic system in which *Z*/*E*-photoisomerization at the ketoenamine C=C bond, N→O transfer of the norbornadiene-containing acyl group, and (2π+2π)-cycloaddition involving two C=C bonds of the norbornadiene fragment take place step-by-step.

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