2,2'-Oxybi(3-methyl-5-nitro-8-bromo-2H-chromene) (IIIj). This compound was similarly obtained from 0.20 g (0.70 mmole) of α-methyl-3-bromo-5-nitro-2-hydroxycinnamaldehyde. The product was purified with a column packed with silica gel by elution with carbon tetrachloride–ether (3:1). The yield of a yellowish crystalline powder (from chloroform–ethanol) was 0.18 g (Rf 0.78). IR spectrum: 1525, 1348 cm^{-1} (NO_2).

2-Ethoxy-3-methyl-6-nitro-8-bromo-2H-chromene (IVj). A 0.15-g (0.52 mmole) sample of aldehyde Ij was refluxed in 30 ml of ethanol for 6 h, after which the solvent was evaporated and 5 ml of hexane was added to the residue. The resulting yellowish crystals were removed by filtration and washed with hexane to give 0.14 g of product. IR spectrum: 1530, 1340 cm^{-1} (NO_2).

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BENZENOID-QUINOID TAUTOMERISM OF AZOMETHINES AND THEIR STRUCTURAL ANALOGS.

41.* PHOTO- AND THERMOCHROMIC TRANSFORMATIONS OF ACYLATED N-ALKYLIMINES OF 3-HYDROXYBENZO[b]THIOPHENE-2-CARBALDEHYDE AND 3-HYDROXY-1-METHYLINDOLE-2-CARBALDEHYDE

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O- and N-Acylated alkylimines of 3-hydroxybenzo[b]thiophene-2-carbaldehyde and 3-hydroxy-1-methylindole-2-carbaldehyde were synthesized. Their Z → E isomerizations and N → O-acyl photo- and thermotransformations were investigated by means of electronic and IR spectroscopy. On irradiation N-acyl-N-methyl(or benzyl)aminomethylene derivatives of benzo[b]thiophen-3-one and 1-methylindol-3-one undergo only Z → E isomerization. The introduction of bulkier alkyl substituents (isopropyl, cyclohexyl) relative to the amino nitrogen atom increases the stability of the O-acyl isomers and their conjugate acids and leads to irreversible photoinitiated or acid-catalyzed N → O-acyl rearrangements. Exclusively the O-acyl isomer is realized for compounds with the most bulky N-tert-butyl substituent.

We have previously observed and investigated photo- and thermochromic rearrangements of acylated N-arylimines of 3-hydroxybenzo[b]thiophene-2-carbaldehyde and 3-hydroxy-1-methylindole-2-carbaldehyde of the IZ ⇄ III and IIZ ⇄ IV type (R = Ar, R^1 = CH_3, OCH_3) [2-4]. The task of the present research was to investigate the effect of replacement of aryl groups R in the I-IV molecules by alkyl radicals on the character of photoinduced and thermal acid-catalyzed acylotropic rearrangements [see schemes (1) and (2)]. For this we synthesized a number of N- and O-acylated I-IV with variable structural fragments: the

*See [1] for Communication 40.

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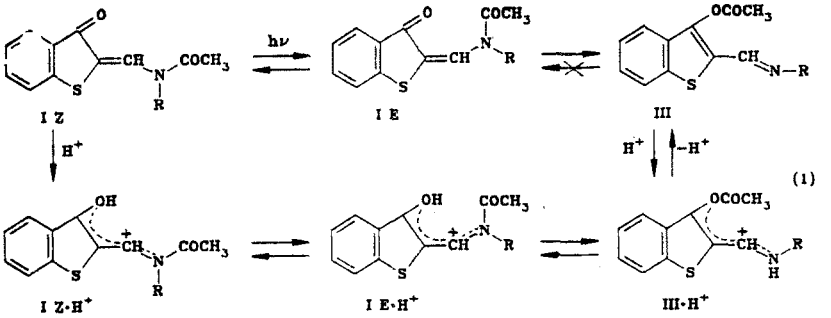
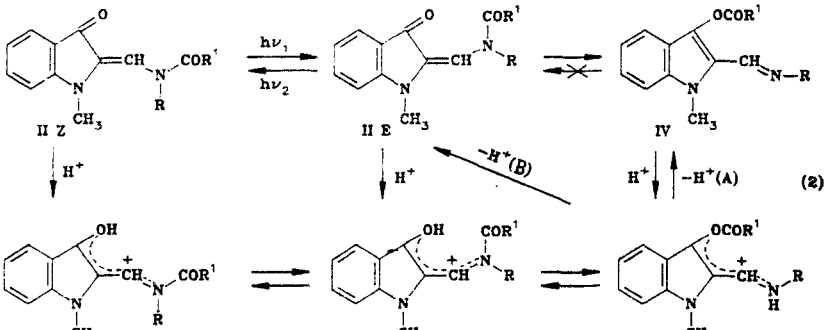
heteroatomic group of the ring and alkyl substituents attached to the nitrogen atom (R) and in the acyl group (R^1) (Table 1).

The acylation of alkylimines of 3-hydroxybenzo b thiophene-2-carbaldehyde and 3-hydroxy-1-methylindole-2-carbaldehyde leads to N-acyl derivatives (Ia-d, IIa-d), and an O-acyl isomer (IIIe) was isolated only in the case of the compound with R = tert-C_4H_9. Only intermolecular transacylation occurs in an attempt to obtain acylated alkylimines with R = C_6H_{11}, $CH(CH_3)_2$, and $C(CH_3)_3$ by condensation of 3-acetoxy-1-methylindole-2-carbaldehyde with the corresponding alkylamines, similar to 2-(N-acetyl-N-benzylaminomethylene)-1-methyl-3-indolone (IIa), which was previously obtained by this method [3].



I, III a R=CH_3; b R=$CH_2C_6H_5$; c R=C_6H_{11}; d R=i-C_3H_7; e R=t-C_4H_9

(1)



II, IVa,b R=$CH_2C_6H_5$; c,d R=C_6H_{11}; a,c R^1=CH_3; b,d R^1=H

(2)

The structures of I-IV were established by electronic and vibrational spectroscopy (Table 2), as well as by PMR spectroscopy and x-ray diffraction analysis [3]. Acyl derivatives Ia-d and IIa, c exist in the form of N-acylated Z isomers, while formyl derivatives IIb, d have an E configuration. Strong bands at 1660-1670 and 1690-1710 cm^{-1}, which correspond to aminoenone fragments —CO—C=C—N— and an amide acetyl or formyl group belonging to the N-acyl form, are observed in the IR spectra of I and II. This structure is confirmed by the absorption at 420-425 nm (I) and 435-480 nm (II) [2, 3] (Table 2). The presence in the vibrational spectrum of IIIe of a band at 1785 cm^{-1}, which is due to the enol acetate fragment CH_3COO—C=C— and absorption at 305 nm constitutes evidence for an O-acetyl structure.

TABLE 1. Acylated N-Alkylimines of 3-Hydroxybenzo[b]-thiophene-2-carbaldehyde (I, III) and 3-Hydroxy-1-methylindole-2-carbaldehyde (II)

Compound	mp, °C	Found, %			Empirical formula	Calculated, %		
		C	H	N		C	H	N
Ia	229	61,4	4,8	6,2	$C_{12}H_{11}NO_2S$	61,8	4,7	6,0
Ib	127	69,7	5,1	4,5	$C_{18}H_{15}NO_2S$	69,9	4,9	4,5
Ic	112	68,0	6,2	4,6	$C_{17}H_{19}NO_2S$	67,8	6,3	4,7
Id	96	64,5	5,5	5,5	$C_{14}H_{15}NO_2S$	64,4	5,7	5,4
IIc	136	72,0	7,5	8,9	$C_{18}H_{22}N_2O_2$	72,5	7,4	9,4
IId	Oil	72,0	7,2	10,0	$C_{17}H_{20}N_2O_2$	71,8	7,1	9,9
IIIe	110	65,2	6,0	5,0	$C_{15}H_{17}NO_2S$	65,5	6,2	5,1

TABLE 2. Spectral Characteristics of I-IV and Their Protonated Forms

Compound	IR spectrum, ν, cm^{-1}	UV spectrum,* λ_{max}, nm (log ε)	Compound	IR spectrum, ν, cm^{-1}	UV spectrum,* λ_{max}, nm (log ε)
Ia	1665, 1695	423 (3,98)	IIa	1660, 1700	435 (3,48)
Ia ·H$^+$	—	440	IIa ·H$^+$	—	440
Ib	1665, 1695	423 (3,95)	IVa ·H$^+$	1670, 1800	362 (4,15)
Ib ·H$^+$	—	440	IIb	1680, 1710	480 (3,85)
Ic	1665, 1690	420 (4,01)	IIb ·H$^+$	—	475
Ic ·H$^+$	—	444	IVb ·H$^+$	—	359 (4,78)
IIIc · H$^+$	1660, 1780	343 (4,38)	IIc	1665, 1700	435 (3,63)
IIIc	1780	308 (4,28)	IIc· H$^+$	—	445
Id	1670, 1690	423 (4,04)	IVc· H$^+$	—	359 (4,35)
Id ·H$^+$	—	440	IVc	—	308 (4,29)
IIId ·H$^+$	1660, 1780	342 (4,41)	IId	1670, 1700	470
IIId	1780	305 (4,31)	IId ·H$^+$	—	460
IIIe ·H$^+$	—	312 (4,27)	IVd ·H$^+$	—	363
IIIe	1785	305 (4,31)			

*In toluene (I, III) and heptane (II, IV).

For investigation of the photochromism solutions of N-acylated I and II were irradiated with the filtered light of a DRSh-250 mercury lamp in the region of the long-wave absorption band or with sunlight. 2-[N-Acetyl-N-methyl(or benzyl)aminomethylene]-3(2H)-benzo[b]thiophenones Ia, b proved to be inert with respect to irradiation and did not display solvato- and thermochromism. The reaction also was not subject to sensitization by triplet donors (eosin, anthracene). By means of pulse photolysis we were able to detect the formation of isomer IE with absorption at 440 nm (Fig. 1), which rapidly rearranged to the starting Z form after irradiation was discontinued. In contrast to N-acyl derivatives of benzothiophene, Z $\rightleftarrows$ E isomerization, which is manifested in the form of a 15-20 nm bathochromic (Z $\rightarrow$ E) or hypsochromic (E $\rightarrow$ Z) shift of the long-wave absorption maximum, is recorded in the electronic absorption spectra in the case of irradiation of 2-[N-acyl-N-benzyl(or cyclohexyl)aminomethylene]-1-methyl-3-indolones IIa, b, d [3]. In the irradiation of solutions of N-acetyl derivatives Ic, d and IIc with bulkier R substituents N $\rightarrow$ O transfer of the acetyl group with the formation of structures III and IV, which are characterized by an intense absorption maximum at 305-308 nm (Figs. 1 and 2), occurs after the formation of the E isomer. The absorption of the resulting forms III and IV is identical to the spectrum of 3-acetoxybenzo[b]thiophene-2-carbaldehyde N-tert-butylimine (IIIe), which has the structure of an O isomer. The N $\rightarrow$ O acyl conversion is irreversible in the case of benzothiophene derivatives Ic, d, while in the case of 2-(N-acetyl-N-cyclohexylaminomethylene)-1-methyl-3-indolone (IIc), depending on the solvent, irradiation leads to the formation of the O isomer (hexane) or an equilibrium mixture of the N and O forms (acetonitrile) (Fig. 3).

Processes involving Z $\rightleftarrows$ E isomerization in the series of indole derivatives II can also occur in the absence of irradiation. An equilibrium between the Z and E isomers is established rapidly when organic acids of the acetic and trichloroacetic acid type are added to solutions of N-acylated N-alkylaminovinyl ketones [2, 5]. Strong acids (trifluoroacetic acid,

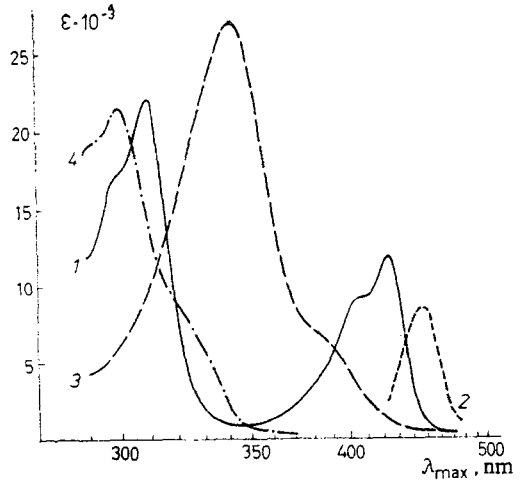


Fig. 1. Electronic absorption spectra of Id: 1) in toluene; 2) 10 sec after the addition of 5 μl of CF_3COOH; 3) 1 min after the addition of 5 μl of CF_3COOH; 4) after 2 min of irradiation of the starting solution or after the addition of triethylamine to the solution in (3) (c = $4\cdot10^{-4}$ M, V = 0.25 ml, λ_{irr} = 436 nm, l_{cuv} = 0.1 cm).

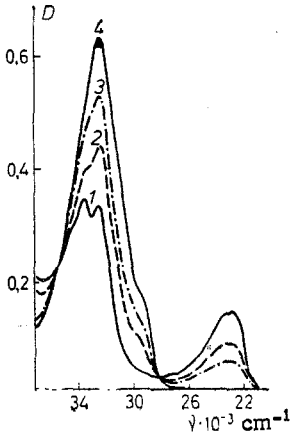


Fig. 2

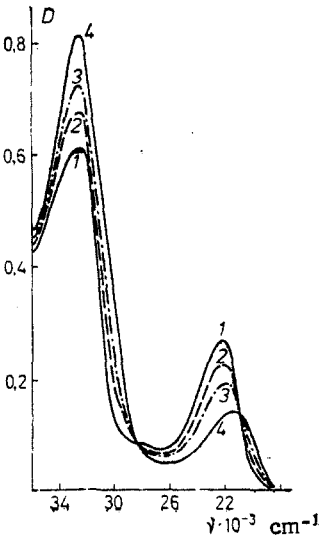


Fig. 3

Fig. 2. Electronic absorption spectra of IIc in heptane: 1) before irradiation; 2) after 10 sec of irradiation; 3) after 20 sec of irradiation; 4) after 110 sec of irradiation (c = $6.3 \cdot 10^{-5}$ M, λ_{irr} = 436 nm, l_{cuv} = 1 cm).

Fig. 3. Electronic absorption spectra of IIc in acetonitrile: 1) before irradiation; 2) after 10 sec of irradiation; 3) after 20 sec of irradiation; 4) after 140 sec of irradiation (c = $5 \cdot 10^{-5}$ M, λ_{irr} = 436 nm, l_{cuv} = 1 cm).

dry hydrogen chloride) react with N-acyl-N-aminovinyl ketones I and II to give protonated forms $I \cdot H^+$ and $II \cdot H^+$ (Table 2), which, in the case of compounds with bulky R^1 and R substituents, are rapidly [in 20-30 sec (IIIc, d) or 15-20 min (IVc)] converted to stable proton protonated forms of the most basic O-acylated compounds III and IV due to N → O transfer of the acetyl group (Fig. 4a). The $II \cdot H^+$ form can also be easily obtained by protonation of photoproduct IIc. A gradual decrease in the intensities of the long-wave absorption bands of the $I \cdot H^+$ and $II \cdot H^+$ forms with a simultaneous building up of a new maximum at 340-360 nm ($III \cdot H^+$ and $IV \cdot H^+$) is observed in the electronic absorption spectra (Fig. 5); distinct isobestic points are designated. The characteristic frequencies of vibrations of an O-acetyl carbonyl group at 1780-1800 cm^{-1} are present in the IR spectra of protonated forms $III \cdot H^+$ and $IV \cdot H^+$.

Neutralization of the protonated forms $III \cdot H^+$ and $IV \cdot H^+$ with triethylamine leads to 3-acetoxybenzo[b]thiophene-2-carbaldehyde alkylimines IIIc, d [scheme (1)] and 3-acetoxy-1-methylindole-2-carbaldehyde alkylimine IVc [scheme (2), pathway A]. O-Acylated N-arylimines III and IV are converted to starting forms I and II on heating or under the influence of acidic catalysts [2, 4]. On the other hand, N-alkyl O-acetyl tautomers IIIc, d, e and IVc proved to be thermodynamically stable and are not converted to N-acetyl forms I and II under the influence of the indicated factors.

Thus not only photoinduced acylotropic rearrangements [schemes (1) and (2), lower line] but also the thermal pathway of N → O-acyl transfer under the influence of acids [schemes (1) and (2), lower line; Fig. 4a], which is not realizable for aryl derivatives, occur in 2-(N-acetyl-N-alkylaminomethylene)-3(2H)-benzo[b]thiophenones and -1-methyl-3-indolones with the most bulky R^1 and R substituents (Ic, d; IIc) for which the S_0 levels of O-acyl tautomers III and IV are situated below the S_0 levels of N-acyl E isomers I and II.

The photochemically inactive N-acyl-N-alkyl derivatives of benzothiophene (Ia, b) also do not undergo thermal rearrangements under the influence of acids. In the irradiation of 2-(N-acyl-N-alkylaminomethylene)-1-methyl-3-indolones IIa, b, d the phototransformations are limited to only processes involving Z → E isomerization; however, N → O transfer of formyl and acetyl groups via a scheme that differs from that described above is observed in the presence of strong acids. Neutralization of protonated forms $IV \cdot H^+$ (a, b, d) with triethylamine leads not to O-acyl tautomers IV but rather to starting N-acyl derivatives II, which

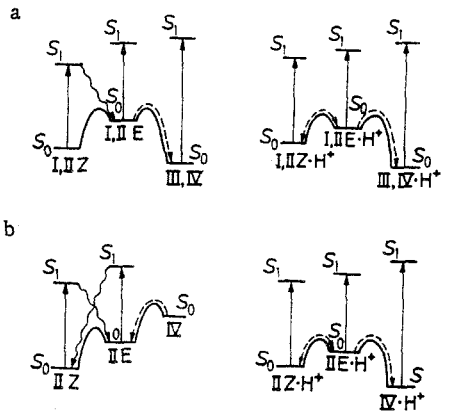


Fig. 4

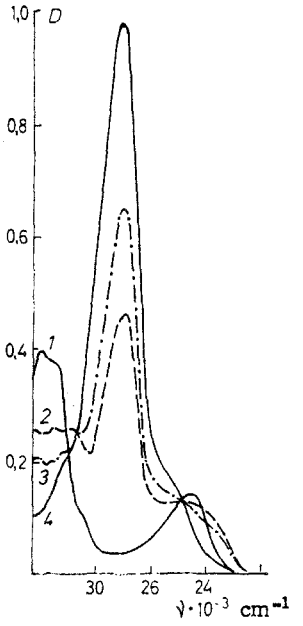


Fig. 5

Fig. 4. Schemes of photoinduced and thermal. Z ⇄ E isomerizations and N → O-acyl rearrangements a) Ic, d and IIc; b) IIa, b, d.

Fig. 5. Electronic absorption spectra of IIa: 1) in heptane; 2) 2 min after the addition of CF_3COOH; 3) 4 min after the addition of CF_3COOH; 4) 20 min after the addition of CF_3COOH [c(IIa) = $5\cdot10^{-4}$ M, c(CF_3COOH) = $5\cdot10^{-2}$ M, l_{cuv} = 0.1 cm].

exist in the E form, regardless of the starting Z or E configuration [scheme (2), pathway B]. This fact can be explained in the following way: O-acyl tautomer IV·H^+ (a, b, d) is the thermodynamically most stable species in the protonated form; neutralization with triethylamine restores the starting pattern of the energy levels (Fig. 4b) with location of the S_0 level of N-acyl E isomer II below the ground state of O-acyl tautomer IV [3]. It has been previously shown that $k_2 \ll k_1$ for the reverse O → N rearrangement of the $IV \xrightarrow{k_1} IIE \xrightarrow{k_2} IIZ$ type [4].

Thus photoinitiated acyltropic rearrangements are inhibited for 2-(N-acyl-N-alkylaminomethylene)-1-methyl-3-indolones with less bulky substituents attached to the amino nitrogen atom (IIa, b, d), but thermal N → O-acyl transfer is realized under the influence of acids. The rate constants and activation barriers ΔG^+ of the thermal acyl rearrangements are presented in Table 3.

EXPERIMENTAL

The electronic absorption spectra were recorded with a Specord M-40 spectrophotometer. The IR spectra of suspensions of the compounds in mineral oil were recorded with Specord IR-71 and Specord IR-75 spectrometers. The rate constants of the N → O-acyl transfer reactions were calculated by the usual method [6]. The measurements of the optical densities of the IV·H^+ isomers were made at 360 nm at a substance concentration of $5\cdot10^{-4}$ M and a trifluoroacetic acid concentration of $5\cdot10^{-2}$ M in cuvettes with l = 0.1 cm. The error in the determination of the rate constants did not exceed 10%.

2-(N-Alkylaminomethylene)-3(2H)-benzo[b]thiophenones and 2-(N-Alkylaminomethylene)-1-methyl-3-indolones. These compounds were synthesized by the methods in [7] and [8], respectively.

2-(N-Acetyl-N-aklylaminomethylene)-3(2H)-benzo[b]thiophenones Ia-d. A 0.1-mole (6.8 ml) sample of acetyl chloride was added to a solution of 0.01 mole of 2-(N-alkylaminomethylene)-3(2H)-benzo[b]thiophenone in 10 ml of benzene, and the mixture was refluxed for 2 h. The excess acetyl chloride and benzene were removed by distillation in vacuo, and the residue was crystallized from octane. The yellow crystalline products were obtained in 70-90% yields.

TABLE 3. Kinetic Parameters of N → O-Acyl Transfer of the $II \cdot H^+ \xrightarrow{k} IV \cdot H^+$ Type in Heptane–Trifluoroacetic Acid

Compound	$k \cdot 10^3$, sec^{-1}	$\Delta G^{\neq}$, kJ/mole
IIa	4,5	86
IIb	0,17	94
IIc	3,4	87

-formyl-

2-(N-Acetyl-N-benzylaminomethylene)- and 2-(N-formyl-N-benzylaminomethylene)-1-methyl-3-indolones IIa, b. These compounds were previously obtained in [3].

2-(N-Acetyl-N-cyclohexylaminomethylene)-1-methyl-3-indolone (IIc). This compound was synthesized by acylation of the alkylimine with acetyl chloride [4]. The preparation, isolation, and purification were carried out in the light of a red lamp. The light-yellow crystals were obtained in 34-40% yield.

2-(N-Formyl-N-cyclohexylaminomethylene)-1-methyl-3-indolone (IId). This compound was prepared by the method in [3]. The light-yellow oil was obtained in 23% yield.

2-(N-tert-Butylaminomethylene)-3-acetoxybenzo[b]thiophene (IIIe). This compound was obtained by the method in [9].

The results of elementary analysis and the melting points of the compounds are presented in Table 1.

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