Synthesis and properties of photoacylotropic (2*Z*)-2-(*N*-acyl-*N*-arylaminomethylidene)benzo[*b*]thiophen-3(2*H*)-ones with a chiral migrating group

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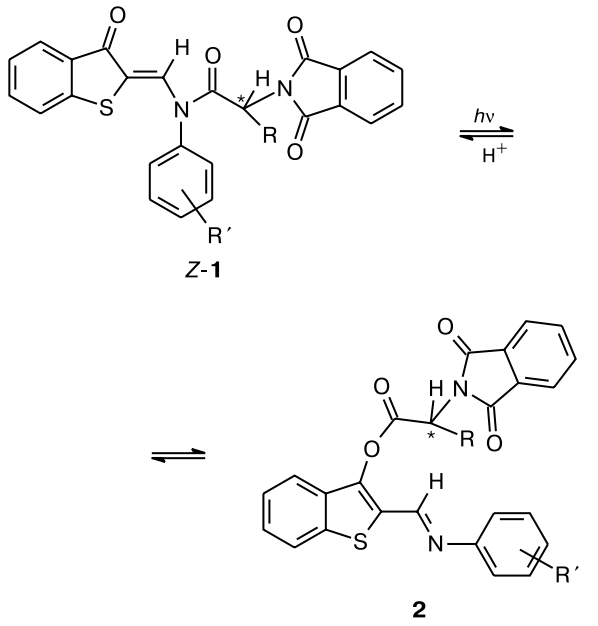
New photochromic (2*Z*)-2-(*N*-acyl-*N*-arylaminomethylidene)benzo[*b*]thiophen-3(2*H*)-ones containing L-amino acid derivatives as migrating groups were synthesized. Light irradiation of their solutions at 436 nm leads to the photoinduced acylotropic rearrangement N → O accompanied by migration of the chiral fragment. The bulky *N*-acyl group causes steric strain thus destabilizing the amide form of compounds and facilitating the photorearrangement.

Key words: benzo[*b*]thiophene, ketoenamine, photochromic compounds, chirality.

The photoinduced acylotropic rearrangement of (2*Z*)-2-(*N*-acyl-*N*-arylaminomethylidene)benzo[*b*]thiophen-3(2*H*)-ones (Scheme 1)[1] makes it possible to perform migration of large fragments within the molecules under light, resulting in changes in their physical and chemical properties. Such molecular systems can exhibit properties of molecular switches, as we have demonstrated earlier for photoacylotropic systems containing a fluorophoric migrating group[2] and photoacylotropic chemosensors.[3,4]

Scheme 1



The aim of the present study was to synthesize photoacylotropic systems containing a chiral migrating acyl group and investigate their structures and photochromic properties for the purpose of designing chiroptical switches.[5,6]

Results and Discussion

We chose natural amino acids, such as L-alanine, L-leucine, L-isoleucine, and L-methionine, as the starting compounds containing a chiral center, *viz.*, the asymmetric carbon atom, because the chiral center in these compounds is at the carbon atom nearest to the carboxy group. In addition, optically pure enantiomers of these compounds are commercially available. The target compounds with chiral acyl migrating groups were synthesized as follows. Amino acid chlorides with the phthalimide protection of the amino group were prepared. The reactions of the latter with ketoenamines **3** in acetonitrile in the pres-

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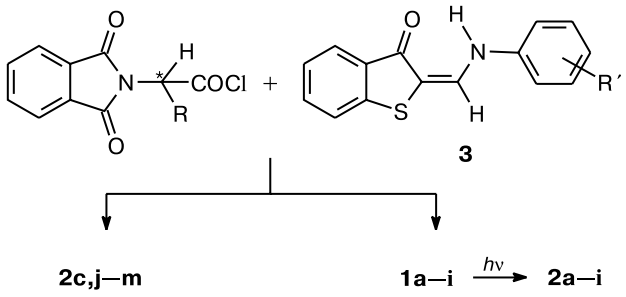
ence of triethylamine gave *N*- and *O*-acyl derivatives **1a—i** and **2c,j—m**. Photoirradiation of solutions of **1a—i** afforded solutions of compounds **2a—i**, which were not isolated preparatively (Scheme 2).

Scheme 2



R = Me, R′ = 2-OMe (**a**); R = Me, R′ = 2-Br (**b**);
R = Me, R′ = 4-I (**c**); R = CH(Me)CH_2Me, R′ = 2-OMe (**d**);
R = CH(Me)CH_2Me, R′ = Mes (**e**); R = $CH_2CH(Me)_2$,
R′ = 2-OMe (**f**); R = $(CH_2)_2$SMe, R′ = 2-OMe (**g**);
R = $(CH_2)_2$SMe, R′ = 4-I (**h**); R = $(CH_2)_2$SMe, R′ = Mes (**i**);
R = Me, R′ = 2-Me (**j**); R = Me, R′ = 2-NO_2 (**k**);
R = Me, R′ = 2,3-$(CH)_4$ (**l**); R = $(CH_2)_2$SMe, R′ = 2,3-$(CH)_4$ (**m**)

Only compounds **1a—i** were prepared in the *N*-acyl *Z* form necessary for the photoinduced acylotropic rearrangement N → O. Attempts to synthesize isomeric compounds **2j—m** in the *N*-acyl form failed. In these cases, acylation occurs only at the oxygen atom (see Scheme 2). Fractional crystallization of the reaction product of 2-[*N*-(4-iodophenyl)aminomethylidene]benzo[*b*]thiophen-3(2*H*)-one with (2*S*)-(1-phthal)iminopropionyl chloride afforded both isomers, *viz.*, *N*-acylated (*Z*-**1c**) and *O*-acylated (**2c**). The structures of the reaction products were established by electronic and vibrational spectroscopy and ^{1}H NMR spectroscopy.

The electronic absorption spectra of the *N*-acyl isomers are virtually identical to each other and are characterized by a long-wavelength band at λ = 426—429 nm, which is independent of the nature of the substituent in the *N*-phenyl ring (Table 1).

The IR spectra of the *N*-acyl derivatives show, along with symmetric and asymmetric carbonyl stretching bands of the phthalimide protecting group at $\nu^s_{C=O}$ ~1780—1760 cm^{-1} and $\nu^{as}_{C=O}$ ~1730—1710 cm^{-1}, respectively, carbonyl stretching bands of the benzothiophene fragment at $\nu_{C=O}$ ~1675—1655 cm^{-1}. The stretching bands of the amide carbonyl group at 1720—1690 cm^{-1} overlap with the asymmetric stertching bands of the phthalimide fragment. In the ^{1}H NMR spectra, the singlet of the methine proton at δ 8.60—9.08 is evidence for the *Z* configuration of the *N*-acyl derivatives, which is confirmed by X-ray diffraction data for compound **1i**.

Table 1. Spectroscopic and photochromic characteristics of acylated ketoenamines

Compound	Solvent	Electronic absorption spectrum, λ_{max}/nm ($\varepsilon_{max} \cdot 10^{-4}$/L mol^{-1} cm^{-1})		Quantum yield, $\varphi_{1\to2}$
		N Isomer	*O* Isomer	
1a	Toluene	307 (2.20), 426 (1.24)	310 (1.96), 347 (1.44)	0.41
	MeCN	259 (2.14), 307 (2.20), 427 (1.16)	305 (2.07), 342 (1.41)	
1b	Toluene	306 (2.45), 424 (1.16)	312 (2.09), 345 (1.77)	0.48
	MeCN	258 (2.08), 306 (2.55), 424 (1.11)	254 (1.37), 308 (2.20), 339 (1.81)	
1c	Toluene	308 (2.18), 426 (1.19)	351 (2.70)	0.45
	MeCN	255 (2.42), 308 (2.25), 425 (1.19)	310 (2.16), 345 (2.70)	
1d	Toluene	308 (2.29), 425 (1.29)	309 (2.06), 346 (1.56)	0.41
	MeCN	259 (2.14), 308 (2.30), 427 (1.25)	305 (2.11), 342 (1.42)	
1e	Toluene	311 (2.70), 429 (1.40)	307 (2.60), 341 (0.96)	0.43
	MeCN	260 (2.50), 312 (2.71), 430 (1.31)	254 (1.76), 307 (2.81), 340 (0.80)	
1f	Toluene	308 (2.44), 427 (1.32)	310 (2.14), 347 (1.64)	0.50
	MeCN	260 (2.49), 309 (2.47), 425 (1.22)	307 (2.29), 341 (1.50)	
1g	Toluene	309 (2.41), 428 (1.30)	310 (2.08), 347 (1.56)	0.55
	MeCN	309 (2.31), 427 (1.15)	306 (2.12), 345 (1.40)	
1h	Toluene	310 (2.32), 428 (1.30)	315 (2.10), 351 (2.62)	0.61
	MeCN	310 (2.35), 424 (1.13)	313 (2.19), 349 (2.75)	
1i	Toluene	310 (2.77), 429 (1.36)	304 (2.62), 340 (0.96)	0.55
	MeCN	311 (2.59), 429 (1.17)	305 (2.26), 333 (0.86)	
2c	MeCN	—	310 (2.16), 345 (2.70)	—
2j	MeCN	—	307 (2.08), 342 (1.68)	—
2k	MeCN	—	310 (2.08), 343 (1.96)	—
2l	MeCN	—	308 (2.16), 350 (1.49)	—
2m	MeCN	—	310 (2.18), 352 (1.51)	—

The electronic spectra of solutions of the *O*-acyl isomers of **2a—m** show a characteristic long-wavelength absorption band at λ = 340—351 nm, whose intensity, shape, and position depends on the nature of the *N*-phenyl substituent R´ (see Table 1). For examples, this band in the spectra of compounds **2h**, **2g**, and **2i** in toluene is observed at λ (ε) of 351 (2.62), 347 (1.56), and 340 (0.96) nm, respectively. In this series, the intensity of the band decreases and is virtually independent of the structure of the substituent in the acyl group. In addition to the above-described two C=O bands of the phthalimide protecting group, the double-bond stretching vibration region in the IR spectra of these isomers contains a stretching band of the ester carbonyl group at ~1760—1750 cm^{-1}, which can overlap with the symmetric stretching band of the phthalimide group.

The ^{1}H NMR spectra of solutions of the *N* and *O* isomers show, along with signals of the ketoenamine fragment, a four-proton multiplet of the phthalimide protecting group at low field and characteristic signals for the protons of the amino acid residues at high field.

Light irradiation of solutions of all *N*-acyl isomers (*Z*-**1**) in toluene and acetonitrile at λ_{exc} = 436 nm leads to the photoinduced acylotropic rearrangement N → O (see Scheme 1) giving rise to *O*-acyl isomers **2** with high quantum yields (see Table 1). The structures of the photoacylotropic rearrangement products were established based on characteristic absorption in the UV spectra. The product obtained in a photoreactor (light irradiation at λ_{exc} = 436 nm) from compound **1c** is identical to the *O*-acyl isomer (**2c**).

In the case of compounds **2a,b,d—g,i**, the reverse acylotropic rearrangement O → N occurs upon the addition of trichloroacetic acid to solutions of the *O*-acyl isomers prepared photochemically. For compounds **2c,h**, the acylotropic rearrangement O → N ceased once the equilibrium is reached, whereas this rearrangement is not observed for compounds **2j—m**.

The ^{1}H NMR spectra of mesityl derivatives **1e**,**i** show diastereotopism of the *ortho*-methyl and aromatic protons of the mesityl ring (Fig. 1). In deuterionitrobenzene, this anisochronism of the signals is retained upon heating to 180 °C. This is evidence for hindered rotation of the mesityl ring about the C_{Ar}—N bond, which, in turn, confirms the atropoisomerism in (2*Z*)-2-(*N*-acyl-*N*-arylaminomethylidene)benzo[*b*]thiophen-3(2*H*)-ones containing the *ortho*-substituted *N*-phenyl ring, which we have found earlier.[6]

As expected, acylation of ketoenamines containing the *ortho*-substituted aryl ring with chiral acid chlorides afforded a mixture of atropoisomeric diastereomers. This is evidenced by the doubling of the signals for the methine proton of the ketoenamine fragment, the proton at the chiral center of the amino acid residue, and the protons of the substituents in the *ortho* position of the *N*-phenyl ring (Fig. 2).

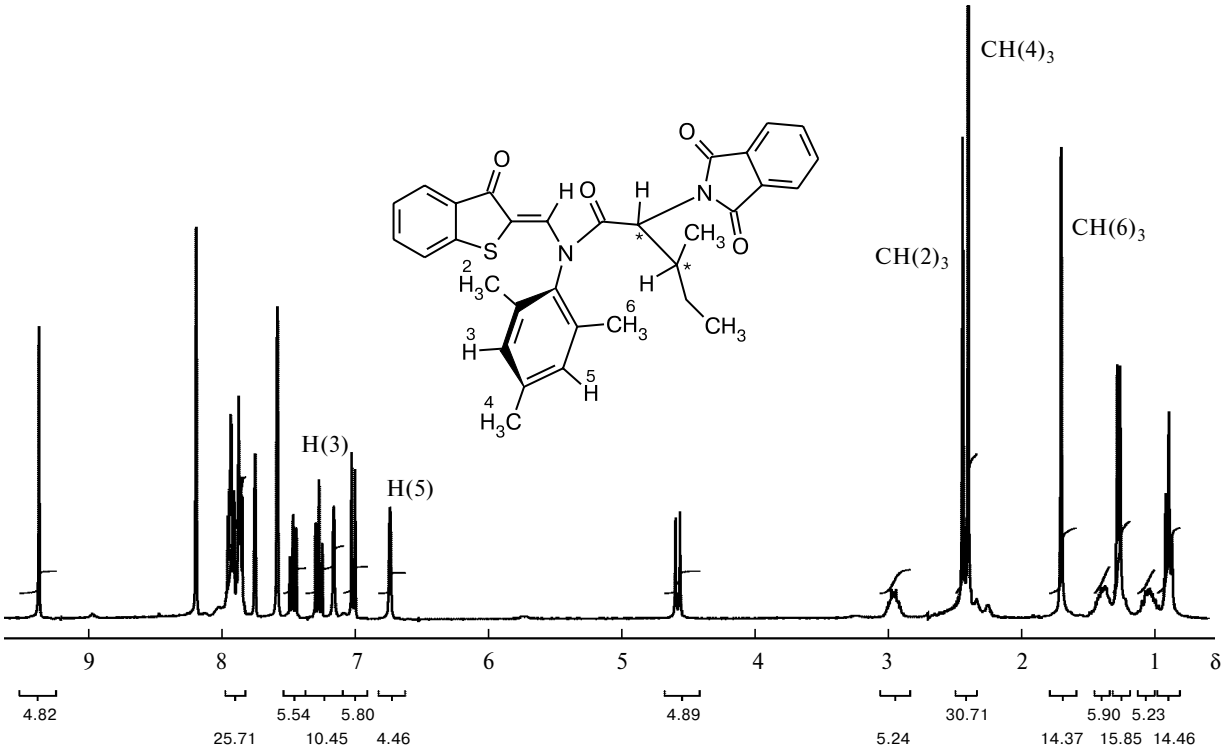


Fig. 1. ^{1}H NMR spectrum of compound **1e** at 20 °C in deuterobenzene.

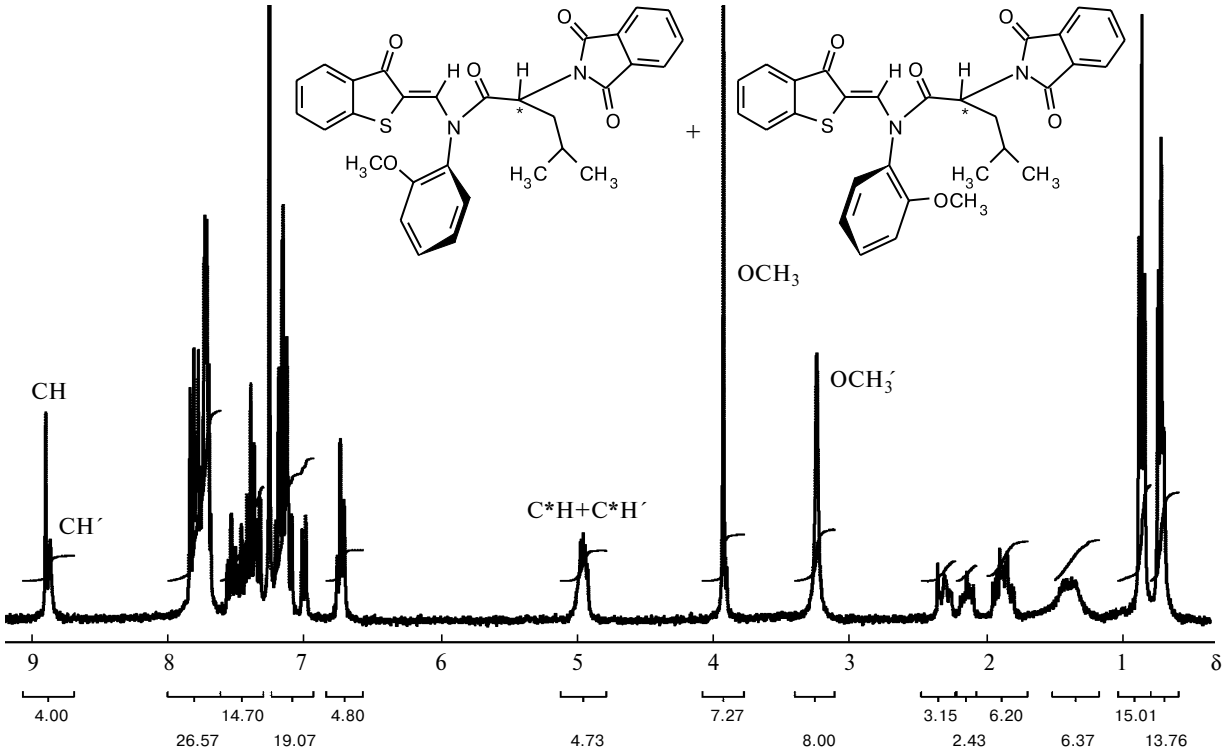


Fig. 2. ^{1}H NMR spectrum of compound **1f** at 20 °C in $CDCl_3$.

To reveal the structural factors, which hinder the synthesis of compounds *Z*-**1**, and with the aim of changing some photochromic properties, we studied compound **1i** by X-ray diffraction. The molecular structure of **1i** is shown in Fig. 3. The atoms of the benzothiophene fragment C(1)C(2)C(3)C(4)C(5)C(6)C(7)C(8)S(1) are in a single plane (I) (to within 0.01 Å). The N(1) atom is in a planar configuration (the sum of the angles at this atom is 360°).

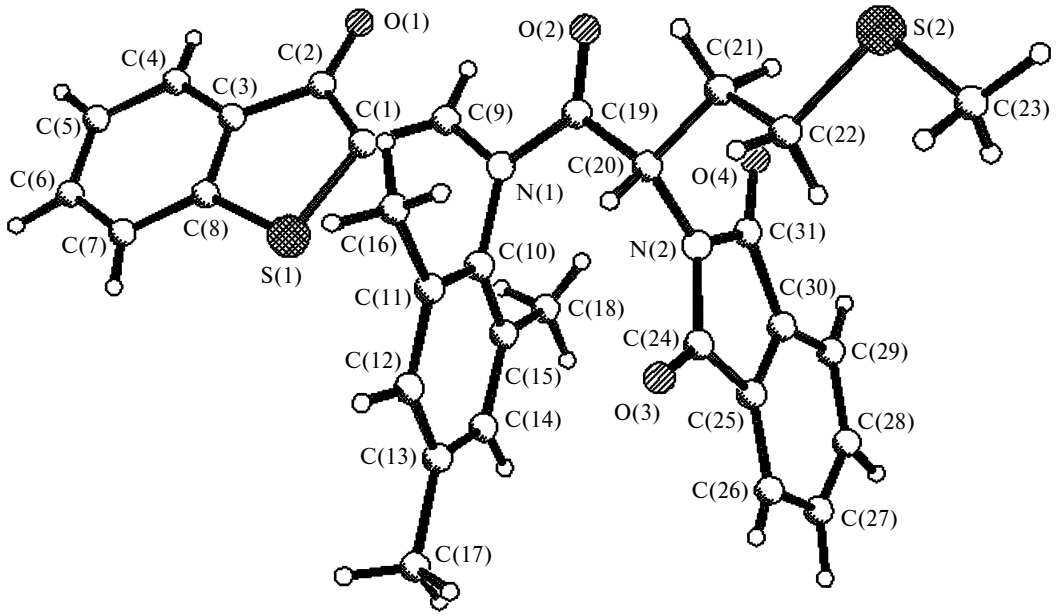


Fig. 3. Molecular structure of (2*Z*)-2-{*N*-[(*S*)-2-(1,3-dioxo-1,3-dihydroisoindol-2-yl)-4-methylthiobutyryl]-*N*-mesitylaminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (**1i**).

Table 2. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in molecule **1i**

Bond	*d*/Å	Angle	ω/deg	Bond angle	ω/deg
S(1)—C(1)	1.758(2)	C(1)—S(1)—C(8)	91.2(1)	C(22)—C(21)—(20)	113.2(2)
S(1)—C(8)	1.760(2)	C(9)—N(1)—C(19)	116.8(2)	C(21)—C(22)—S(2)	108.6(2)
S(2)—C(23)	1.781(3)	C(9)—N(1)—C(10)	120.1(2)	O(3)—C(24)—N(2)	124.4(2)
S(2)—C(22)	1.800(2)	C(19)—N(1)—C(10)	123.1(2)		
N(1)—C(9)	1.378(3)	C(9)—C(1)—C(2)	119.2(2)	Torsion angle	τ/deg
N(1)—C(10)	1.453(2)	C(9)—C(1)—S(1)	129.0(2)	C(8)—S(1)—C(1)—C(9)	174.5(2)
N(1)—C(19)	1.393(3)	C(2)—C(1)—S(1)	111.8(2)	C(9)—C(1)—C(2)—O(1)	5.5(3)
O(1)—C(2)	1.211(2)	O(1)—C(2)—C(3)	126.0(2)	S(1)—C(1)—C(2)—O(1)	−176.3(2)
C(2)—C(3)	1.459(3)	O(1)—C(2)—C(1)	124.7(2)	C(9)—N(1)—C(10)—C(11)	−101.1(2)
C(1)—C(9)	1.334(3)	C(3)—C(2)—C(1)	109.3(2)	C(19)—N(1)—C(10)—C(11)	76.8(3)
C(1)—C(2)	1.496(3)	C(8)—C(3)—C(2)	113.6(2)	N(1)—C(10)—C(11)—C(16)	1.3(3)
O(2)—C(19)	1.201(3)	C(3)—C(8)—S(1)	113.9(2)	C(9)—N(1)—C(19)—O(2)	4.7(4)
N(2)—C(20)	1.450(3)	C(1)—C(9)—N(1)	129.0(2)	C(10)—N(1)—C(19)—O(2)	−173.3(2)
N(2)—C(24)	1.408(3)	C(15)—C(10)—N(1)	118.3(2)	C(9)—N(1)—C(19)—C(20)	−177.9(2)
O(3)—C(24)	1.204(2)	O(2)—C(19)—N(1)	120.5(2)	C(24)—N(2)—C(20)—C(19)	−125.2(2)
O(4)—C(31)	1.208(3)	O(2)—C(19)—C(20)	121.6(2)	C(19)—C(20)—C(21)—C(22)	167.3(2)
C(11)—C(16)	1.499(3)	N(1)—C(19)—C(20)	117.8(2)	C(20)—C(21)—C(22)—S(2)	177.2(2)
C(19)—C(20)	1.529(3)	N(2)—C(20)—C(21)	112.7(2)	C(23)—S(2)—C(22)—C(21)	−171.3(2)
		N(2)—C(20)—C(19)	111.7(2)	C(31)—N(2)—C(24)—C(25)	−2.0(2)

The N(1)—C(9) and N(1)—C(19) distances are 1.378(3) and 1.393(3) Å, respectively, and the N(1)—C(10) distance is 1.453(2) Å.

The carbon atoms of the mesityl fragment from C(10) to C(18) are in a single plane (II) (to within 0.02 Å). This fragment is twisted about the N(1)—C(10) bond relative to the plane of the C(9)N(1)C(19) atoms. The C(9)N(1)C(10)C(11) torsion angle is 78.9(2)°. This mutual arrangement of the fragments is attributed to an increase in steric strain, as evidenced by the shortened intramolecular C(10)—S(1), C(11)—S(1), and C(15)—S(1) distances (3.037(5), 3.275(5), and 3.394(5) Å, respectively), resulting in the nearly perpendicular arrangement of the planes I and II.

The torsion angles in the C(9)N(1)C(19)C(20)C(21)S(2)C(23) chain are given in Table 2 and characterize the orientation of the chain fragment of the molecule relative to the planes I and II.

The plane of the phthalimide fragment involving the atoms from C(20) to C(31)O(3)O(4) (III) is nearly parallel to the plane II. The formal angle between these planes is 15°, the C(10)—N(1)—C(20)—N(2) pseudotorsion angle is 60.1(1)°, and the shortest distance between the atoms of the planes II and III in the molecule (C(15) and C(24)) is 3.249(5) Å.

A comparison of the O(1)—C(2), O(2)—C(19), O(3)—C(24), and O(4)—C(31) distances (1.211(2), 1.201(3), 1.204(2), and 1.208(3) Å, respectively) shows that there is conjugation between the π-orbitals of the O(1)—C(2) and C(1)—C(9) bonds and the amide conjugation in the N(1)C(19)O(2), N(2)C(24)O(3), and N(2)C(31)O(4) fragments. In the latter two fragments, the C=O bonds are equally elongated compared to the O(2)—C(19) bond, which is indicative of a uniform distribution of the amide conjugation over two oxygen atoms in the plane III. By contrast, the N(1) atom is involved not only in the amide conjugation with the O(2) atom but also in conjugation with the C(1)=C(9) π-bond. In single crystals, the molecules do not form intermolecular hydrogen bonds.

To summarize, irradiation of solutions of (2*Z*)-2-(*N*-acyl-*N*-arylaminomethylidene)benzo[*b*]thiophen-3(2*H*)-ones, which are L-amino acid derivatives, causes migration of the acyl group containing the asymmetric carbon atom due to the photoinduced acylotropic rearrangement N → O. An increase in the volume of the substituent in the acyl fragment compared to acetyl derivatives studied earlier[1] in going to amino acid derivatives containing the phthalimide protecting group leads to an increase in steric strain in *N*-acyl derivative *Z*-**1** and destabilization of this isomer, which can be responsible for irreversibility of the photorearrangement.

Experimental

Electronic absorption spectra of compounds **1a—i** and **2c,j—m** were measured on a Specord M-40 spectrophotometer. The solutions were irradiated using a DRSh-250 mercury lamp equipped with a kit of glass light filters. The quantum yields in toluene were determined using potassium ferrioxalate.[7] The IR spectra were recorded on a Specord IR-75 instrument in Nujol mulls. The ^{1}H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in $CDCl_3$ with Me_4Si as the internal standard.

Phthaloylamino acids were synthesized according to a procedure described earlier[8] from phthalic anhydride and the cor-

responding amino acid in the presence of triethylamine and then recrystallized from aqueous ethanol.

Phthaloylamino acid chlorides were synthesized according to a known procedure[9] from the corresponding acids and thionyl chloride in anhydrous benzene.

Synthesis of aminovinyl ketones 3 (general procedure). Equimolar amounts of 2-hydroxybenzo[*b*]thiophene-2-carbaldehyde and the corresponding substituted aniline were condensed in acetonitrile followed by crystallization.[10]

Synthesis of compounds 1a—i and 2c,j—m (general procedure). Triethylamine (1.72 g, 0.017 mol) was added to a solution of aminovinyl ketone **3** (0.015 mol) in a minimum amount of anhydrous acetonitrile at 60 °C. *N*-Phthaloylamino acid chloride (0.017 mol) was added to this mixture. The reaction product was filtered off, washed with methanol, and recrystallized.

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)propanoyloxy]-*N*-(2-methoxyphenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1a). The yield was 38%, m.p. 265 °C (from acetonitrile). Found (%): C, 66.90; H, 4.15; N, 5.75. $C_{27}H_{20}N_2O_5S$. Calculated (%): C, 66.93; H, 4.16; N, 5.78. IR, ν/cm^{-1}: 1775, 1725, 1670. ^{1}H NMR, δ, diastereomer A: 8.93 (s, 1 H, CH); 7.84—6.53 (m, 12 H, Ar); 4.91 (q, 1 H, CH, *J* = 7.1 Hz); 3.93 (s, 3 H, OMe); 1.58 (d, 3 H, Me, *J* = 7.1 Hz); diastereomer B: 8.87 (br.s, 1 H, CH); 7.84—6.53 (m, 12 H, Ar); 5.02 (br.q, 1 H, *J* = 6.9 Hz); 3.02 (br.s, 3 H, OMe); 1.59 (d, 3 H, Me, *J* = 6.9 Hz). The isomer ratio A : B = 8 : 7.

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)propanoyloxy]-*N*-(2-bromophenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1b). The yield was 20%, m.p. 202—203 °C (from acetonitrile). Found (%): C, 58.56; H, 3.15; N, 5.29. $C_{26}H_{17}BrN_2O_4S$. Calculated (%): C, 58.55; H, 3.21; N, 5.25. IR, ν/cm^{-1}: 1775, 1750, 1730, 1680. ^{1}H NMR, δ, diastereomer A: 8.96 (br.s, 1 H, CH); 7.86—6.96 (m, 12 H, Ar); 5.15—4.90 (br.s, 1 H, CH); 1.8—1.6 (br.s, 3 H, Me); diastereomer B: 8.90 (br.s, 1 H, CH); 7.86—6.96 (m, 12 H, Ar); 4.93 (br.q, 1 H, CH, *J* = 6.9 Hz); 1.62 (d, 3 H, Me, *J* = 6.9 Hz). The isomer ratio A : B = 1 : 3.

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)propanoyloxy]-*N*-(4-iodophenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1c). The yield was 7.6%, m.p. 293 °C (from an acetonitrile—toluene mixture). Found (%): C, 53.93; H, 2.90; N, 4.82. $C_{26}H_{17}IN_2O_4S$. Calculated (%): C, 53.81; H, 2.95; N, 4.83. IR, ν/cm^{-1}: 1710, 1675, 1590. ^{1}H NMR, δ: 8.74 (br.s, 1 H, CH); 7.84—6.96 (m, 10 H, Ar); 7.05—6.88 (br.s, 2 H, Ar); 5.06 (br.q, 1 H, CH, *J* = 7.0 Hz); 1.63 (d, 3 H, Me, *J* = 7.0 Hz).

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-3-methylpentanoyl]-*N*-(2-methoxyphenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1d). The yield was 36%, m.p. 195 °C (from acetonitrile). Found (%): C, 68.38; H, 5.02; N, 5.28. $C_{30}H_{26}N_2O_5S$. Calculated (%): C, 68.42; H, 4.98; N, 5.32. IR, ν/cm^{-1}: 1760, 1720, 1675. ^{1}H NMR, δ, diastereomer A: 8.95 (s, 1 H, CH); 7.85—6.38 (m, 12 H, Ar); 4.63—4.40 (m, 1 H, CH); 3.94 (s, 3 H, OMe); 2.76—2.45 (m, 1 H, CH); 1.8—0.60 (m, 2 H, 6 H, CH_2, 2 Me); diastereomer B: 8.93 (br.s, 1 H, CH); 7.85—6.38 (m, 12 H, Ar); 4.63—4.40 (m, 1 H, CH); 2.85 (br.s, 3 H, OMe); 2.76—2.45 (m, 1 H, CH); 1.8—0.60 (m, 2 H, 6 H, CH_2, 2 Me). The isomer ratio A : B = 5 : 6.

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-3-methylpentanoyl]-*N*-mesitylaminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1e). The yield was 40%, m.p. 275—276 °C (from toluene). Found (%): C, 71.55; H, 5.58; N, 5.13. $C_{32}H_{30}N_2O_4S$. Calculated (%): C, 71.35; H, 5.61; N, 5.20. IR, ν/cm^{-1}: 1750, 1720, 1675. ^{1}H NMR, δ: 9.08 (s, 1 H, CH); 7.88—7.14 (m, 8 H, Ar); 7.12 and 6.57 (both br.s, 1 H, CH, Mes); 4.25 (d, 1 H, CH, *J* = 10.5 Hz); 2.80—2.60 (m, 1 H, CH); 2.36, 2.24, and 1.50 (all s, 3 H each, Me); 1.20—0.75 (m, 8 H, CH_2, 2 Me).

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-4-methylpentanoyl]-*N*-(2-methoxyphenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1f). The yield was 24%, m.p. 245 °C (from toluene). Found (%): C, 68.36; H, 5.02; N, 5.30. $C_{30}H_{26}N_2O_5S$. Calculated (%): C, 68.42; H, 4.98; N, 5.32. IR, ν/cm^{-1}: 1760, 1705, 1685, 1650. ^{1}H NMR, δ, diastereomer A: 8.90 (s, 1 H, CH); 7.86—6.68 (m, 12 H, Ar); 5.05—4.90 (m, 1 H, CH); 3.90 (s, 3 H, OMe); 2.40—1.80 (m, 2 H, CH_2); 1.50—1.25 (m, 1 H, CH); 0.90—0.80 and 0.75—0.65 (both m, 3 H each, Me); diastereomer B: 8.87 (br.s, 1 H, CH); 7.86—6.70 (m, 12 H, Ar); 5.05—4.90 (m, 1 H, CH); 3.24 (br.s, 3 H, OMe); 2.40—1.80 (m, 2 H, CH_2); 1.50—1.25 (m, 1 H, CH); 0.90—0.80 and 0.75—0.65 (both m, 3 H each, Me). The isomer ratio A : B = 7 : 8.

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-4-methylthiobutyryl]-*N*-(2-methoxyphenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1g). The yield was 35%, m.p. 228—229 °C (from a butanol—DMF mixture). Found (%): C, 63.87; H, 4.5; N, 5.16. $C_{29}H_{24}N_2O_5S_2$. Calculated (%): C, 63.95; H, 4.44; N, 5.14. IR, ν/cm^{-1}: 1750, 1720, 1600. ^{1}H NMR, δ, diastereomer A: 8.62 (s, 1 H, CH); 7.84—6.60 (m, 12 H, Ar); 5.00—4.90 (m, 1 H, CH); 3.95 and 1.98 (both s, 3 H each, Me); 2.50—2.00 (m, 4 H, 2 CH_2); diastereomer B: 8.58 (br.s, 1 H, CH); 7.84—6.60 (m, 12 H, Ar); 5.07—5.00 (m, 1 H, CH); 2.91 (br.s, 3 H, OMe); 2.50—2.00 (m, 4 H, 2 CH_2); 1.97 (s, 3 H, Me). The isomer ratio A : B = 1 : 2.

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-4-methylthiobutyryl]-*N*-(4-iodophenyl)aminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1h). The yield was 21%, m.p. 216—217 °C (from an acetonitrile—toluene mixture). Found (%): C, 52.49; H, 3.32; N, 4.35. $C_{28}H_{21}IN_2O_4S_2$. Calculated (%): C, 52.51; H, 3.30; N, 4.37. IR, ν/cm^{-1}: 1775, 1710, 1655. ^{1}H NMR, δ: 8.70 (br.s, 1 H, CH); 7.84—6.80 (m, 12 H, Ar); 5.25 (br.t, 1 H, CH); 2.60—2.34 (m, 4 H, 2 CH_2); 1.98 (s, 3 H, Me).

(2*Z*)-2-{*N*-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-4-methylthiobutyryl]-*N*-mesitylaminomethylidene}benzo[*b*]thiophen-3(2*H*)-one (1i). The yield was 22%, m.p. 183—184 °C (from acetonitrile). Found (%): C, 66.79; H, 4.97; N, 5.01. $C_{31}H_{28}N_2O_4S_2$. Calculated (%): C, 66.88; H, 5.07; N, 5.03. IR, ν/cm^{-1}: 1775, 1720, 1670. ^{1}H NMR, δ: 8.98 (s, 1 H, CH); 7.85—7.13 (m, 8 H, Ar); 7.08 and 6.76 (both br.s, 1 H each, Mes); 5.03—4.95 (m, 1 H, CH); 2.55—2.20 (m, 4 H, 2 CH_2); 2.38, 1.88, and 1.87 (all s, 3 H each, Me); 2.22 (br.s, 3 H, Me).

3-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-propanoyloxy]-2-(4-iodophenyl)iminomethylbenzo[*b*]thiophene (2c). The yield was 57%, m.p. 189—191 °C (from a acetonitrile—butanol mixture). Found (%): C, 53.83; H, 2.90; N, 4.82. $C_{26}H_{17}IN_2O_4S$. Calculated (%): C, 53.81; H, 2.95; N, 4.83. IR, ν/cm^{-1}: 1780, 1770, 1710. ^{1}H NMR, δ: 8.66 (s, 1 H, CH); 7.94—7.16 (m, 12 H, Ar); 5.40 (q, 1 H, CH, *J* = 7.2 Hz); 1.87 (d, 3 H, Me, *J* = 7.2 Hz).

3-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-propanoyloxy]-2-(2-methylphenyl)iminomethylbenzo[*b*]thiophene (2j). The yield was 37%, m.p. 165 °C (from toluene). Found (%): C, 69.20;

H, 4.28; N, 5.99. $C_{27}H_{20}N_2O_4S$. Calculated (%): C, 69.22; H, 4.30; N, 5.98. IR, ν/cm^{-1}: 1780, 1760, 1710. ^{1}H NMR, δ: 8.55 (s, 1 H, CH); 7.94—7.14 (m, 12 H, Ar); 5.39 (q, 1 H, CH, J = 7.25 Hz); 2.27 (s, 3 H, Me).

3-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)propanoyloxy]-2-(2-nitrophenyl)iminomethylbenzo[*b*]thiophene (2k). The yield was 69%, m.p. 203 °C (from toluene). Found (%): C, 62.50; H, 3.40; N, 8.39. $C_{26}H_{17}N_3O_6S$. Calculated (%): C, 62.52; H, 3.43; N, 8.41. IR, ν/cm^{-1}: 1780, 1710, 1620. ^{1}H NMR, δ: 8.62 (s, 1 H, CH); 8.00—7.18 (m, 12 H, Ar); 5.40 (q, 1 H, CH, J = 7.25 Hz); 1.87 (d, 3 H, Me, J = 7.25 Hz).

3-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)propanoyloxy]-2-(naphth-1-yl)iminomethylbenzo[*b*]thiophene (2l). The yield was 35%, m.p. 211 °C (from a butanol—DMF mixture). Found (%): C, 71.39; H, 4.01; N, 5.54. $C_{30}H_{20}N_2O_4S$. Calculated (%): C, 71.41; H, 4.00; N, 5.55. IR, ν/cm^{-1}: 1778, 1705. ^{1}H NMR, δ: 8.73 (s, 1 H, CH); 8.42—7.18 (m, 15 H, Ar); 5.38 (q, 1 H, CH); 1.85 (d, 3 H, Me, J = 7.25 Hz).

3-[(*S*)-2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-4-methylthiobutyryloxy]-2-(naphth-1-yl)iminomethylbenzo[*b*]thiophene (2m). The yield was 20%, m.p. 199—200 °C (from a butanol—DMF). Found (%): C, 68.10; H, 4.26; N, 4.92. $C_{32}H_{24}N_2O_4S_2$. Calculated (%): C, 68.07; H, 4.28; N, 4.96. IR, ν/cm^{-1}: 1775, 1750, 1705. ^{1}H NMR, δ: 8.72 (s, 1 H, CH); 8.42—7.19 (m, 15 H, Ar); 5.60—5.50 (m, 1 H, CH); 2.80—2.50 (m, 4 H, 2 CH_2); 2.10 (s, 3 H, Me).

Compounds **2a—i** were prepared by light irradiation of solutions of compounds **1a—i** at λ_{exc} = 436 nm in a 10-mm spectrophotometric cell. The structures of compounds **2a,b,d,i** were proposed based on similarity of their electronic absorption spectra with the spectra of compounds **2c,j—m**.

X-ray diffraction study of compound 1i. The unit cell parameters and a three-dimensional X-ray diffraction data set were obtained on an automated four-circle KUMA diffractometer (Mo-Kα radiation, graphite monochromator). Pale-yellow transparent crystals **1i** are monoclinic, space group $P2_1/c$. The molecular formula is $C_{31}H_{28}N_2O_4S_2$, M 556.67, a = 11.469(4) Å, b = 18.686(6) Å, c = 14.289(5) Å, β = 112.71(4)°, V = 2824.9(17) Å^3, Z = 4, ρ_{calc} = 1.678 g cm^{-3}, μ(Mo-Kα) = 0.228 mm^{-1}.

The intensities of 5397 reflections were measured in the angle range $2\theta \leq 50.1°$ using the ω/2θ-scanning technique from a single crystal of dimensions 0.32×0.27×0.31 mm. After exclusion of systematic absences and merging of the intensities of equivalent reflections, the data set of measured $F^2(hkl)$ and $\sigma(F^2)$ contained 5218 independent reflections, of which 5003 reflections with $F^2 > 4\sigma(F^2)$ were used in subsequent calculations. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 using the SHELXL-97 program package[11] with anisotropic displacement parameters for nonhydrogen atoms. Most H atoms were located from difference Fourier maps (the positions of the H atoms at the C(17) and C(23) atoms were calculated geometrically) and were refined isotropically. In the final steps, the intensities of reflections were corrected for absorption by a semiempirical method and then refined by the least-squares method with the fixed atomic coordinates and thermal parameters of the H atoms. The final data obtained in the refinement of 352 parameters were as follows: R_1 = 0.041 for 5003 observed reflections with $I \geq 2\sigma(i)$; R_1 = 0.074 based on all 5218 measured reflections, Goof 1.08.[11,12]

The results of X-ray diffraction study, including the atomic coordinates and displacement parameters, were deposited with the Cambridge Structural Database.

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