The synthesis and study of multilayer polymer structures based on 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene*

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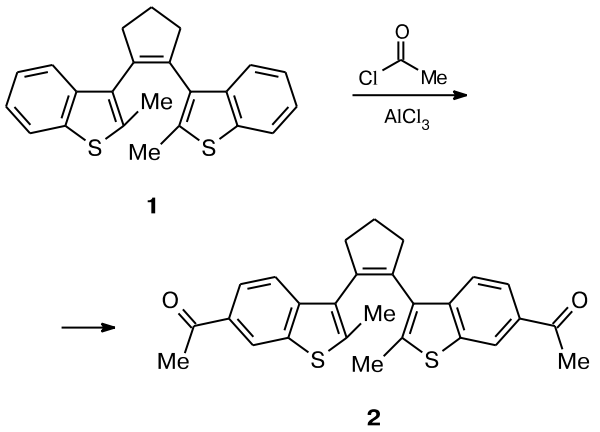
Acylation of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene gave symmetric and asymmetric 1,2-dihetarylethenes, which are of interest as photosensitive components of photochromic recording media for optical read/write storage. The formation of the photoinduced diffraction grating in a dihetarylethene-containing photochromic photorefractive layer of a waveguide multilayer system was studied.

Key words: 1,2-dihetarylethenes, acylation, benzothiophenes, 2D NMR spectra, diffraction gratings.

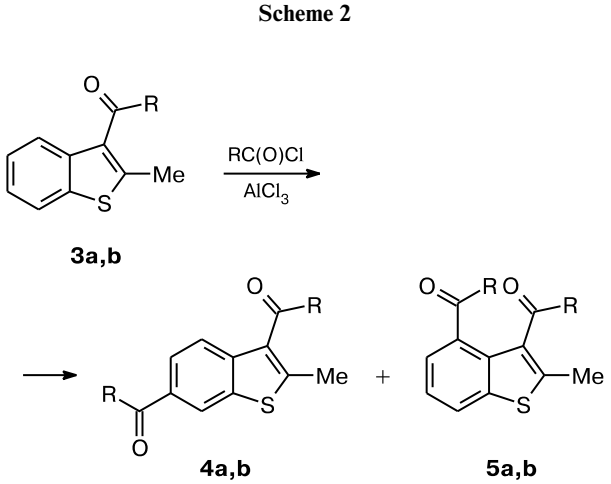
Earlier,[1] we have studied the acetylation of benzothienyl derivative **1** and obtained photochromic 1,2-bis(6-acetyl-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (**2**) (Scheme 1).

Scheme 1



According to X-ray diffraction data, the electrophilic substitution reactions occur at positions 6 and 6′ of the benzothienyl fragments. More recently,[2] we also studied the acylation of 3-acyl-2-methylbenzo[*b*]thiophenes (**3a**,**b**) as model compounds to compare the directing effects of the acyl group and the cyclopentene bridge. A NMR study revealed that these electrophilic substitution reactions occur at two positions 6 and 4 to give compounds **4** (major products) and **5**, respectively (Scheme 2).

Scheme 2



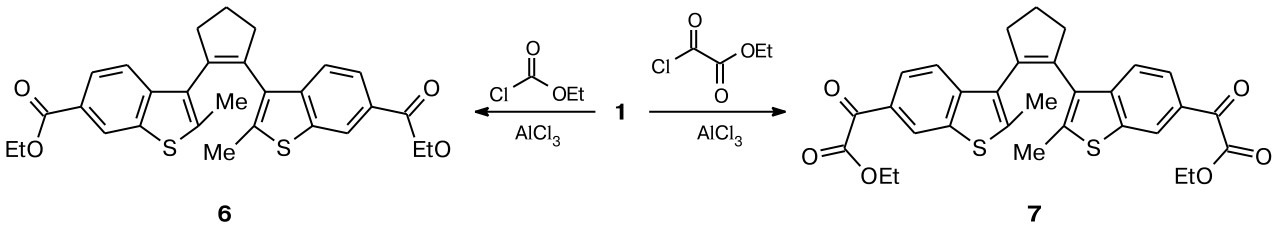
R = Me (**a**), CH_2Cl (**b**)

Our quantum chemical (MNDO, HF/3-21G, and B3LYP/3-21G) calculations of a model protonation reac-

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2487—2494, December, 2011.
1066-5285/11/6012-2536

Scheme 3



6 **7**

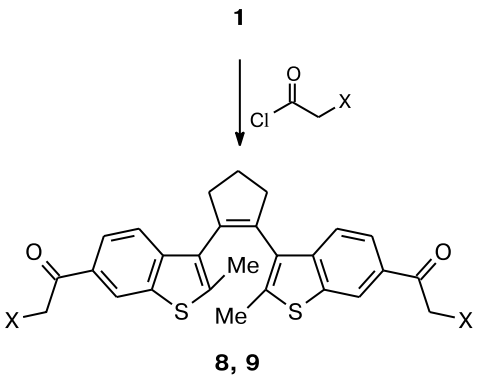
tion of 3-acetyl-2-methylbenzothiophene (**3a**) confirmed that positions 4 and 6 in 3-acetyl-2-methylbenzothiophene are most reactive in acylation reactions.[3]

In the present work, we describe acylation of dihetarylethene **1** with ethyl chloroformate and ethoxalyl chloride. The resulting mono- and disubstituted cyclopentenes are of interest as photochromes and starting materials for further transformations.

The acylation of compound **1** was carried out under the conditions found in the synthesis of diketones from benzothiophene.[2] The amount of $AlCl_3$ proved to have a substantial effect on the yield of the target product. The highest yield was achieved with 4—6 equivalents of $AlCl_3$, while the use of greater amounts of the catalyst lowered the yield because of resinification of the reaction mixture. When the amount of $AlCl_3$ was lower than 4 equivalents, the reaction was not completed. In the synthesis of diacylated derivatives, the yield of the product did not depend on the order in which the reagents were added. The above reactions gave photochromes containing the carboxylate (**6**) or oxo ester group (**7**) (Scheme 3).

Reactions of dihetarylethene **1** with haloacetyl chlorides produced the corresponding α-chloro (**8**) or α-bromo ketones (**9**) (Scheme 4). It is advisable to obtain α-bromo ketones because their yields are higher and they are more reactive than the chlorides.

Scheme 4



8, 9

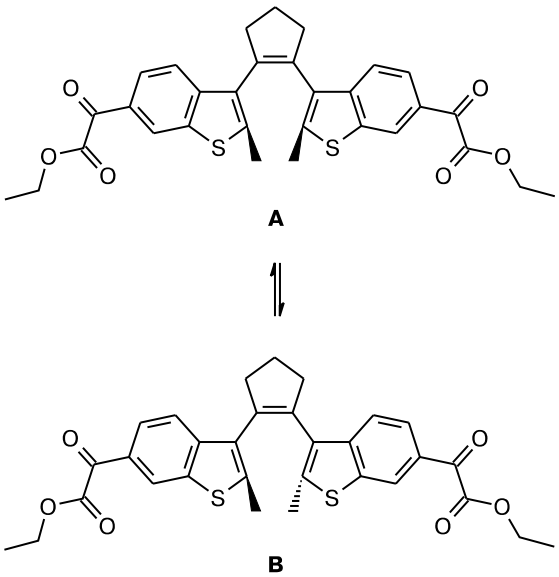
X = Cl (**8**), Br (**9**)

Unlike the acylation of 3-acyl-2-methylbenzothiophene, acylation of photochromic compound **1** gives product **2** only. Since the acylation of photochrome **1** may produce structural regioisomers with respect to the benzene ring, we analyzed 1D and 2D NMR spectra suggesting the presence of the oxo ester groups in position 6 of the photochromic system of product **7**.

The spectrum of compound **7** shows distinct correlation peaks for the atoms separated by three bonds (H(7)/CO and H(7′)/CO; H(5)/CO and H(5′)/CO), which is evidence for the location of the fragment —C(O)—C(O)—OEt at the C(6) atom (Fig. 1, Table 1).

At 273 K, one can distinguish between the subspectra of two conformations of compound **7**; the ratio of the parallel (major, **A**) and antiparallel conformers (minor, **B**) is 2 : 1 (Scheme 5, Fig. 2, *a*). With an increase in the recording temperature, the chemical shifts become averaged because of rapid (on the NMR time scale) interconversions of the conformers. At 353 K, the spectrum in DMSO-d_6 contains only one set of signals (Fig. 2, *b*).

Scheme 5



A **B**

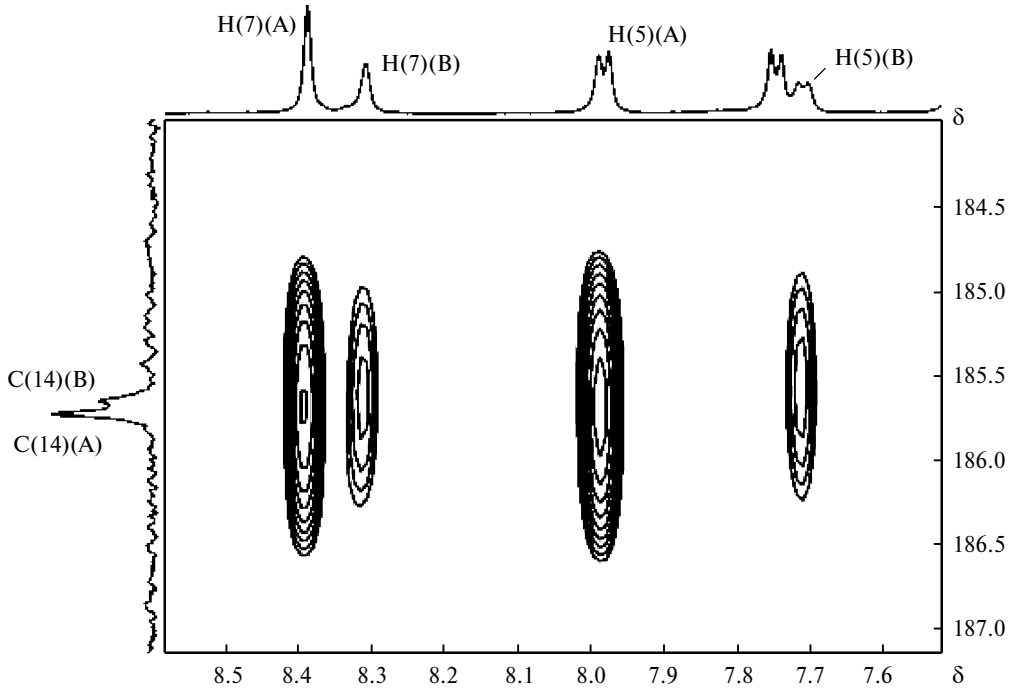
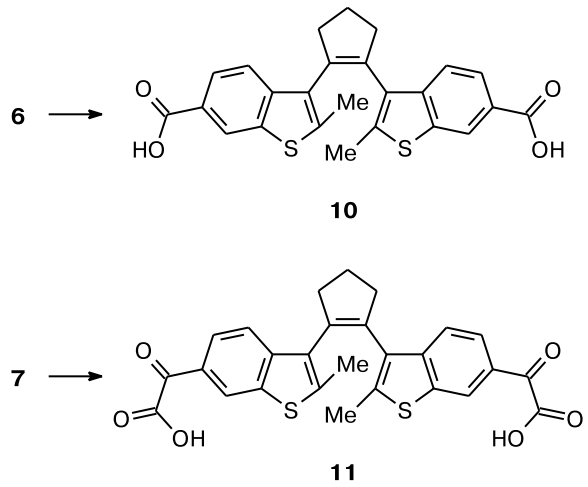


Fig. 1. Fragment of the $^{1}H—^{13}C$ HMBC NMR spectrum (600 MHz) of compound **7** at 273 K.

6,6′-Dicarboxy derivatives are of considerable interest for further modification of photochromes. Products **10** and **11** were obtained by basic hydrolysis of the ester groups in methanol (Scheme 6).

Scheme 6



Reagents and conditions: KOH, MeOH.

Of course, the synthesis of asymmetric dihetarylethenes seemed to hold promise as well: by varying substituents in them, one can substantially extend the range of derivatives and thus finely adjust their physicochemical parameters.[4—7] However, preparation of asymmetric derivatives containing different substituents in the benzothiophene fragments was a real challenge.

Although the Friedel—Crafts reaction is well known, the literature data on regioselective processes involving various aromatic structures are very scarce; as a rule, the acylation conditions are cited only, without generalization. The electrophilic regioselective reactions of cyclopentene and perfluorocyclopentene photochromes virtually have not been studied before.

We managed to solve the problem of regioselective introduction of substituents into one of two benzene rings of dihetarylethenes at low temperatures while using minimum concentrations of reagents. An optimum procedure for regioselective acylation of photochrome **1** is as follows: pyridine (0.5 equiv.) is added at −10 to −5 °C to a suspension of $AlCl_3$ (2.5 equiv.) in CH_2Cl_2; after 20 min, a solution of a dihetarylethene (1 equiv.) in CH_2Cl_2 is added; finally, an acylating reagent (1.3 equiv.) diluted with CH_2Cl_2 is added for 30 min.

Under the above conditions, reactions of compound **1** with haloacetyl chlorides and ethoxalyl chloride gave a number of monosubstituted derivatives containing the haloacetyl and oxo ester groups (Scheme 7).

Sequential acylation of photochrome **1** afforded compounds **15** and **16** with different functional groups in the benzothiophene fragments (Scheme 8).

To find out whether the photochromes obtained can be used to prepare films with controllable spectroscopic characteristics, here we experimentally studied the forma-

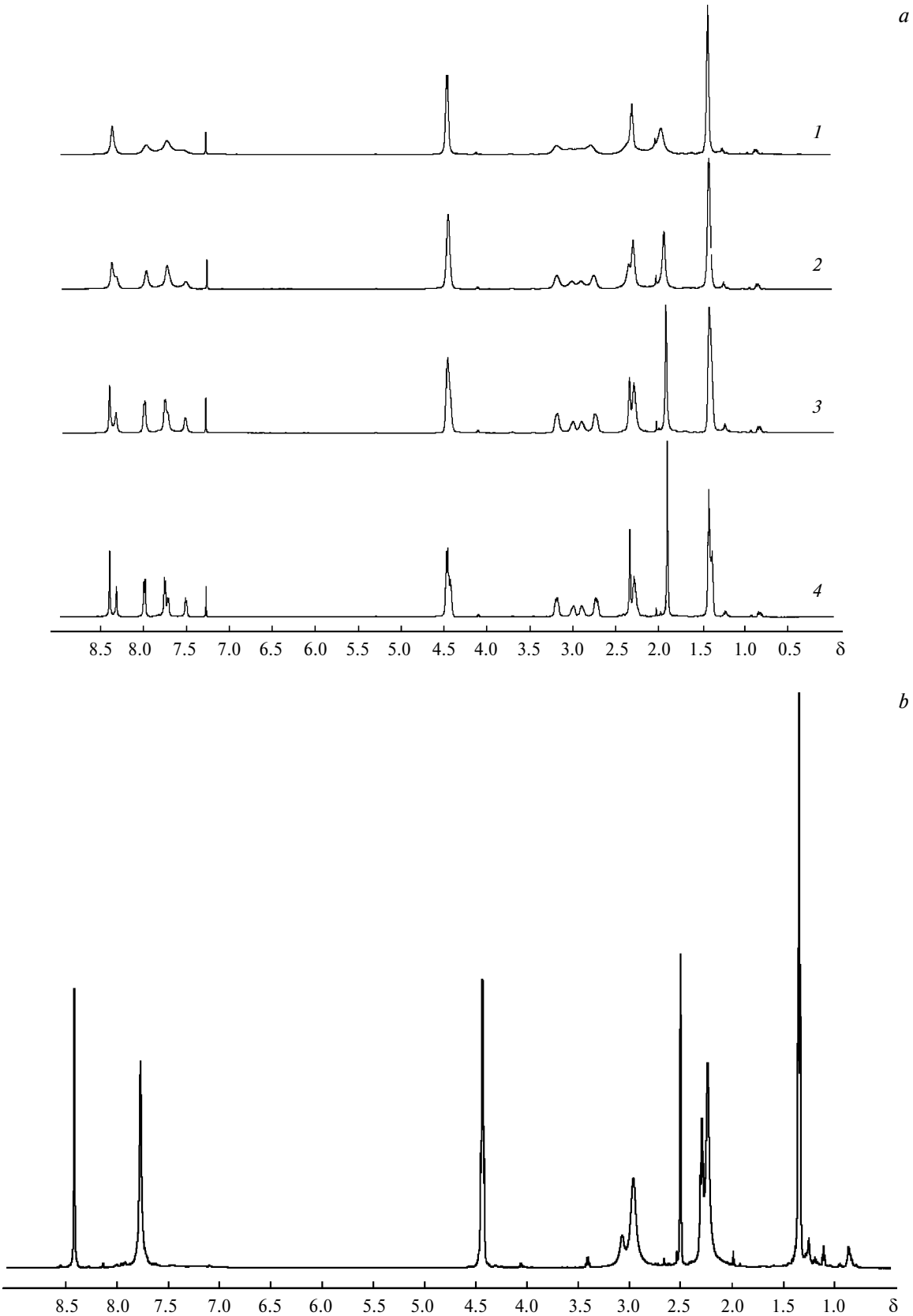
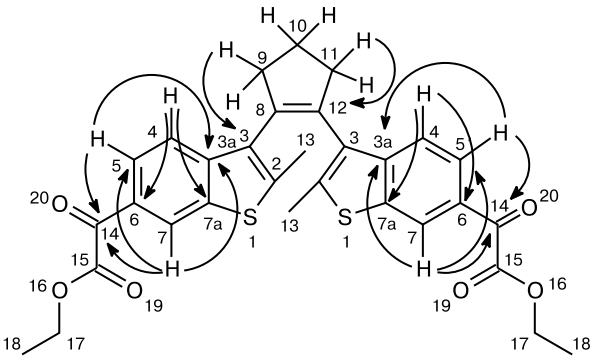


Fig. 2. ^{1}H NMR spectrum (600 MHz) of compound **7** in $CDCl_3$ (*a*) and DMSO-d_6 (*b*) at 323 (*1*), 303 (*2*), 283 (3), 273 (*4*), and 353 K (*b*).

Table 1. Chemical shifts in the ^{1}H and ^{13}C NMR spectra of compound **7** and the correlation peaks in the HMBC spectrum that confirm the structures of the conformers

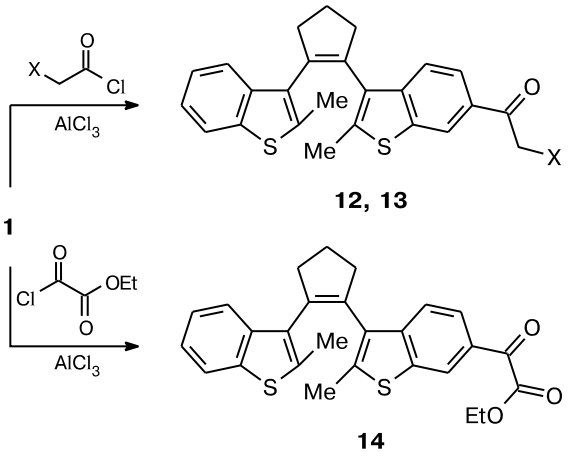


Atom	Conformer	^{13}C	^{1}H	Correlation peaks in the HMBC spectrum
C(2)	**A**	137.12		
	B	136.67		
C(3)	**A**	137.91		
	B	137.76		
C(3a)	**A**	143.63		
	B	143.27		
C(4)	**A**	125.54	7.98	C(6), C(7a)
	B	125.54	7.74	C(6), C(7a)
C(5)	**A**	124.74	7.70	C(7), C(3a), C(14)
	B	124.52	7.50	C(7), C(3a), C(14)
C(6)	**A**	130.54		
	B	130.16		
C(7)	**A**	122.22	8.31	C(5), C(3a), C(14)
	B	122.32	8.39	C(5), C(3a), C(14)
C(7a)	**A**	143.97		
	B	143.97		
C(8)	**A**, **B**	127.41		
C(9)	**A**, **B**	37.60		
C(10)	**A**, **B**	23.97		
C(11)	**A**, **B**	37.60		
C(12)	**A**, **B**	127.41		
C(13)	**A**, **B**	15.54	1.92	C(3)
C(14)	**A**	185.72		
	B	185.72		
C(15)	**A**	163.91		
	B	163.91		
C(17)	**A**	62.12	4.46—4.48	
	B	62.12	4.43—4.45	
C(18)	**A**	14.06	1.42	
	B	14.06	1.40	

tion of a photoinduced diffraction grating in a dihetarylethene-containing photochromic photorefractive layer of a waveguide multilayer system.

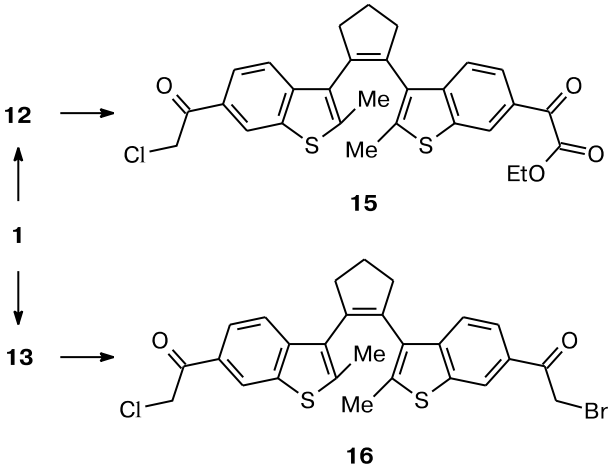
In particular, we studied various polymer blends for combination with photochromic dihetarylethene **7**. We found that polyurethane (PU) is best compatible with photochrome **7** for the moment, yielding smooth trans-

Scheme 7



X = Cl (**12**), Br (**13**)

Scheme 8



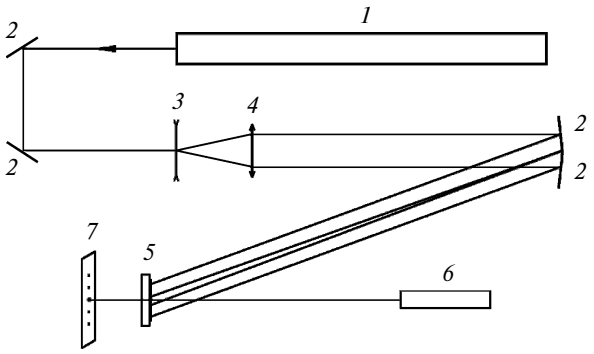


Fig. 3. Optical scheme for recording photoinduced diffraction gratings in polymer films with compound **3**: (*1*) He—Cd laser (λ = 320 nm), (*2*) mirrors, (*3*) negative lens, (*4*) positive lens, (*5*) photochromic film, (*6*) He—Ne laser, and (*7*) screen.

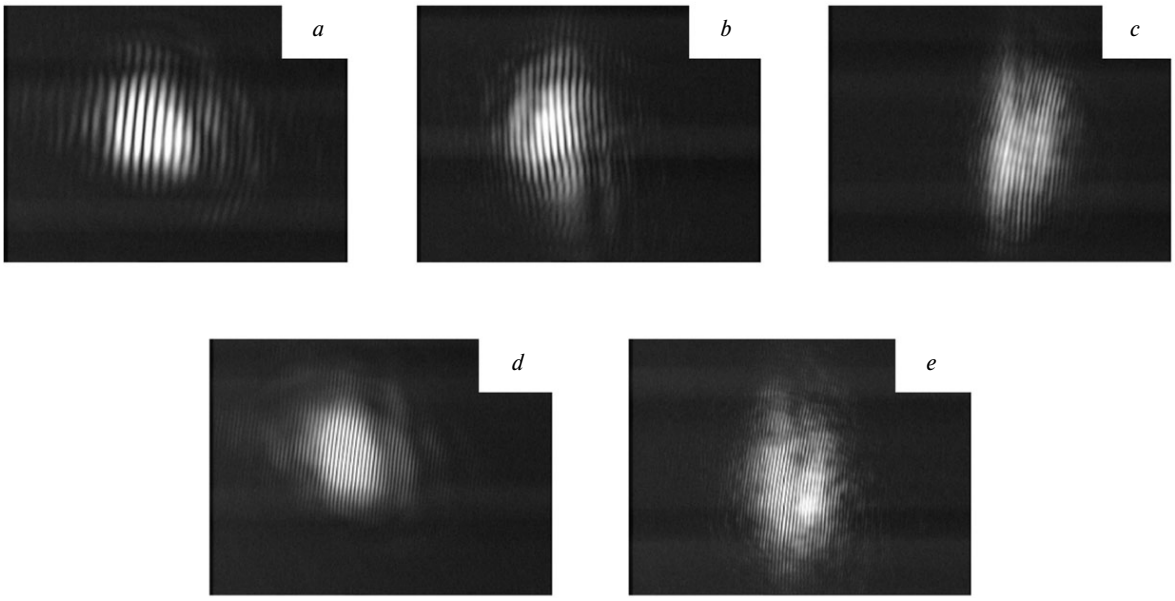


Fig. 4. Images of the photoinduced diffraction gratings with spacings of 360 (*a*), 210 (*b*), 70 (*c*), 35 (*d*), and 16 μm (*e*).

parent films over a wide range of the ratio of the components. Specifically, we examined polymer films with a **7** : PU ratio of 45 : 55.

The pronounced photorefractive properties of these films were confirmed by photoinduced changes in their refractive indices detected with an Abbe NAR-4T refractometer. For films with a **7** : PU ratio of 45 : 55, the refractive index change was $\Delta n_D = 0.0135$ ($n_D = 1.5755$ for the colorless form and $n_D = 1.589$ for the colored form). The photorefractive properties of polymer films containing compounds of this class make it possible to form photoinduced phase—amplitude diffraction gratings, which is a possible and promising way of data processing by optical methods.

For polymer films **7**—PU, we determined the parameters of formation of photoinduced diffraction gratings by observing the interference of coherent beams). The optical scheme used to obtain photoinduced diffraction gratings is shown in Fig. 3. A He—Cd laser with $\lambda = 320$ nm served as a radiation source.

To visualize the resulting diffraction gratings with a CCD matrix,* we employed small-angle (<2°) convergent beams. Figure 4 displays the images of the photoinduced diffraction gratings for the convergence angles of interfering beams from 0.05° to 1.15°. The spacing of the diffraction grating changed from 360 to 16 μm. The dependence of the grating spacing on the convergence angle is given in Table 2.

Diffraction gratings with spacings lower than 10 μm (the convergence angle >2°) are visually indiscernible because of the resolution limits of CCD-based cameras. The formation of such diffraction gratings was confirmed by the observed orders of a diffracted He—Ne laser beam ($\lambda = 630$ nm). The zero and first orders of the He—Ne laser beam diffracted by a photoinduced grating in the polymer film **7**—PU are shown in Fig. 5.

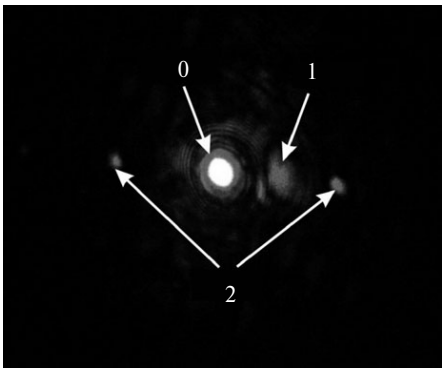


Fig. 5. Diffraction pattern for a photoinduced grating. The numbers refer to the orders of diffraction.

Table 2. Dependence of the spacing of the photoinduced diffraction grating on the convergence angle of interfering beams

α/deg	*d*/μm	α/deg	*d*/μm
0.05	360	3.2	5.7
0.17	108	11.5	1.6
0.7	26	27.2	0.7
1.15	16	39.7	0.5

* CCD is a charge-coupled device (the principal part in digital cameras).

To sum up, we discovered a pronounced photoinduced change in the refractive index of photochrome **7**. Using polymer films containing this compound, we obtained photoinduced diffraction gratings with spacings from 0.5 to 360 μm and determined the corresponding convergence angles of interfering beams. The efficiency of the photoinduced diffraction gratings was illustrated with a diffraction pattern showing first, second, and even, in some cases, third orders.

Experimental

^{1}H NMR spectra were recorded on Bruker Avance 600 (600 MHz) and Bruker Avance 300 instruments (300 MHz) in $CDCl_3$ with the signal for the residual protons of the solvent (δ 7.25) as the internal standard. Mass spectra were measured on a Kratos instrument (direct inlet probe, ionizing energy 70 eV, control voltage 1.75 kV). Melting points were determined on a Boetius microscope stage and are given uncorrected. Commercial reagents (Acros) were used.

The electronic absorption spectra of the open and cyclic forms of the photochromic compounds were recorded on a Shimadzu UV-VIS spectrophotometer in the 200—800 nm range. The cyclic form was generated by photoexcitation of a solution with a DRSh-250 mercury lamp through a UV light filter (λ = 313 nm).

Polymer films were prepared from TEXIN 3007 polyurethane (Bayer Material Science, Germany).

1,2-Bis(6-ethoxycarbonyl-2-methylbenzo[*b*]thiophen-3-yl)-cyclopent-1-ene (6). Anhydrous $AlCl_3$ (1.48 g, 11.08 mmol) was added at 0 °C to a well stirred mixture of compound **1** (1 g, 2.77 mmol) and ethyl chloroformate (0.66 g, 6.1 mmol) in nitrobenzene (20 mL). The mixture was stirred at 5—15 °C for 3 h and diluted with water (50 mL). The product was extracted with ethyl acetate (3×50 mL). The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography with light petroleum—ethyl acetate (4 : 1) as an eluent. Yield 39%, m.p. 149—150 °C. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.5—8.3 (m, 6 H, 6 CH_{arom}); 4.3—4.4 (m, 4 H, 2 CH_2); 2.6—3.0 (m, 4 H, 2 CH_2); 2.32 (s, 6 H, 2 Me); 2—2.15 (m, 2 H, CH_2); 1.30—1.35 (m, 6 H, 2 Me). MS, *m/z*: 504 ($[M]^+$). Found (%): C, 69.12; H, 5.51; S, 12.73. $C_{29}H_{28}O_4S_2$. Calculated (%): C 69.02, H 5.59, S 12.71.

1,2-Bis(6-ethoxalyl-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (7). Anhydrous $AlCl_3$ (5.76 g, 0.043 mol) was added at 0 °C to a well stirred mixture of compound **1** (6.6 g, 0.018 mol) and ethoxalyl chloride (5.4 g, 0.039 mol) in CH_2Cl_2 (100 mL). The mixture was stirred at 5—15 °C for 3 h and diluted with water (50 mL). The product was extracted with ethyl acetate (3×50 mL). The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography with light petroleum—ethyl acetate (4 : 1) as an eluent. Yield 46%, m.p. 158—162 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: first rotamer, 8.39 (s, H, CH_{arom}); 7.98 (d, H, CH_{arom}, J = 8.0 Hz); 7.74 (d, H, CH_{arom}, J = 8.0 Hz); 4.46—4.48 (m, 4 H, 2 CH_2); 3.20—3.22 (m, 4 H, 2 $CH_{2cyclopent}$); 2.31—2.35 (m, 2 H, $CH_{2cyclopent}$); 1.92 (s, 6 H, 2 Me); 1.42—1.45 (m, 6 H, 2 Me); second rotamer, 8.31 (s, H, CH_{arom}); 7.70 (d, H, CH_{arom}, J = 7.9 Hz); 7.50 (d, H, CH_{arom}, J = 8.1 Hz); 4.43—4.45 (m, 4 H, 2 CH_2); 2.73—2.75 (m, 4 H, 2 $CH_{2cyclopent}$); 2.25—2.29 (m, 2 H, $CH_{2cyclopent}$); 1.92 (s, 6 H, 2 Me); 1.39—1.41 (m, 6 H, 2 Me). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 185.72, 163.91, 143.97, 143.63, 143.27, 137.91, 137.76, 137.12, 136.67, 130.54, 130.16, 127.41, 125.54 (2 C), 124.74, 124.52, 122.22, 122.32, 62.12, 37.60, 23.97, 15.54, 14.06 MS, *m/z*: 560 ($[M]^+$). Found (%): C, 66.41; H, 5.03; S, 11.44. $C_{31}H_{28}O_6S_2$. Calculated (%): C, 66.34; H, 5.11; S, 11.53.

1,2-Bis(6-chloroacetyl-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (8). Aluminum trichloride (0.773 g, 5.8 mmol) was added at −5 to 0 °C to a solution of compound **1** (0.5 g, 1.38 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at −5 to 0 °C for 15—20 min, whereupon chloroacetyl chloride (0.343 g, 3.03 mmol) was added. The reaction mixture was stirred at 5—15 °C for 4 h and poured into 10% HCl. The product was extracted with CH_2Cl_2 (3×50 mL). The organic extracts were washed with water (3×150 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with light petroleum—ethyl acetate (4 : 1) as an eluent. Yield 57%, m.p. 109—110 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.61—8.30 (m, 6 H, 6 CH_{arom}); 4.71 (s, 4 H, 2 CH_2); 2.74—3.2 (m, 4 H, 2 $CH_{2cyclopent}$); 2.1—2.3 (m, 2 H, $CH_{2cyclopent}$); 1.25 (s, 3 H, Me). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 190.62, 143.39, 138.46, 130.45, 129.67, 125.91, 122.69, 122.61, 122.45, 122.38, 46.13, 38.21, 21.82, 15.40. MS (EI, 70 eV), *m/z* (I_{rel}): 514 (82), 512 (100), 480 (10), 477 (25), 465 (33), 463 (91), 437 (4), 435 (11). Found (%): C, 63.12; H, 4.29; Cl, 13.93; S, 12.51. $C_{27}H_{22}Cl_2O_2S_2$. Calculated (%): C, 63.15; H, 4.32; Cl, 13.81; S, 12.49.

1,2-Bis(6-bromoacetyl-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (9) was obtained from compound **1** and bromoacetyl chloride as described above for compound **8**. Yield 79%, m.p. 108—109 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.49—8.31 (m, 6 H, 6 CH_{arom}); 4.48 (s, 4 H, 2 CH_2); 2.87—3.14 (m, 4 H, 2 $CH_{2cyclopent}$); 2.32 (s, 3 H, Me); 2.30 (s, 3 H, Me); 2.06—2.15 (m, 2 H, $CH_{2cyclopent}$). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 190.86 (2 C=O), 138.31 (2 C), 137.23 (2 C), 130.43 (2 C), 130.14 (2 C), 129.36 (2 C), 124.27, 123.88 (2 C), 123.30, 123.48, 122.88, 122.34, 122.42, 37.89, 38.09, 30.95 (2 C), 24.18, 15.56, 15.39. MS, *m/z*: 602. Found (%): C, 53.78; H, 3.64; Br, 26.59; S, 10.70. $C_{27}H_{22}Br_2O_2S_2$. Calculated (%): C, 53.8; H, 3.68; Br, 26.53; S, 10.65.

1,2-Bis(6-carboxy-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (10). A solution of KOH (0.6 g, 10.7 mmol) was added to a solution of ester **6** (0.5 g, 0.89 mmol) in methanol. The reaction mixture was stirred at room temperature for 5—6 h and then acidified with HCl to pH 1. The precipitate that formed was filtered off and washed repeatedly with cold water. Yield 87%, m.p. 173—175 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.45—8.9 (m, 6 H, 6 CH_{arom}); 2.7—3.2 (m, 4 H, 2 $CH_{2cyclopent}$); 2.25—2.4 (m, 2 H, $CH_{2cyclopent}$); 2.06 (s, 3 H, Me). MS (EI, 70 eV), *m/z* (I_{rel}): 505 (10), 504 (56), 459 (35), 432 (100), 416 (32), 386 (59), 358 (24). Found (%): C, 66.92; H, 4.51; S, 14.33. $C_{25}H_{20}O_4S_2$. Calculated (%): C, 66.94; H, 4.49; S, 14.30.

1,2-Bis(2-methyl-6-oxalylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (11) was obtained by hydrolysis of oxo ester **7** as described above for compound **10**. Yield 87%, m.p. 167—169 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.51—8.4 (m, 6 H, 6 CH_{arom}); 2.6—3.2 (m, 4 H, 2 $CH_{2cyclopent}$); 2.15—2.4 (m, 2 H, $CH_{2cyclopent}$); 1.98 (s, 3 H, Me). MS (EI, 70 eV), *m/z* (I_{rel}): 449 (48), 404 (100), 359 (39). Found (%): C, 64.23; H, 4.05; S, 12.74. $C_{27}H_{20}O_6S_2$. Calculated (%): C, 64.27; H, 4.00; S, 12.71.

1-(6-Chloroacetyl-2-methylbenzo[*b*]thiophen-3-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (12). Pyridine (0.055 g, 0.695 mmol) was added at −5 to −10 °C to a suspension of $AlCl_3$ (0.463 g, 3.47 mmol) in CH_2Cl_2 (100 mL). After 20 min, a solution of compound **1** (0.5 g, 1.39 mmol) in CH_2Cl_2 was added. After an additional 30 min, chloroacetyl chloride (0.203 g, 1.8 mmol) diluted with CH_2Cl_2 was added. The reaction mixture was stirred at −5 to −10 °C for 4—5 h and poured into 10% HCl. The product was extracted with CH_2Cl_2 (3×50 mL). The organic extracts were washed with water (3×150 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with light petroleum—ethyl acetate (20 : 1) as an eluent. Yield 34%, m.p. 83—84 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.11—8.32 (m, 7 H, 7 CH_{arom}); 4.52 (s, 2 H, CH_2); 2.71—3.5 (br.m, 4 H, 2 $CH_{2cyclopent}$); 2.18 (s, 3 H, Me); 2.19 (s, 3 H, Me); 1.93—2.03 (br.m, 2 H, $CH_{2cyclopent}$). MS (EI, 70 eV), *m/z* (I_{rel}): 438 (67), 436 (100), 406 (10), 408 (7), 387 (23), 374 (9), 346 (14). Found (%): C, 68.69; H, 4.81; Cl, 8.14; S, 14.69. $C_{25}H_{21}ClOS_2$. Calculated (%): C, 68.71; H, 4.84; Cl, 8.11; S, 14.67.

1-(6-Bromoacetyl-2-methylbenzo[*b*]thiophen-3-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (13) was obtained from compound **1** and bromoacetyl chloride as described above for compound **12**. Yield 57%, m.p. 85—86 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.09—8.32 (m, 7 H, 7 CH_{arom}); 4.49 (s, 2 H, CH_2); 3.0—3.22 (m, 4 H, 2 $CH_{2cyclopent}$); 2.16 (s, 3 H, Me); 2.18 (s, 3 H, Me); 1.8—2.1 (br.m, 2 H, $CH_{2cyclopent}$). MS (EI, 70 eV), *m/z* (I_{rel}): 484 (17), 482 (62), 480 (60), 401 (80), 402 (42), 388 (53), 372 (100). Found (%): C, 62.34; H, 4.39; Br, 16.65; S, 13.37. $C_{25}H_{21}BrOS_2$. Calculated (%): C, 62.37; H, 4.40; Br, 16.60; S, 13.32.

1-(6-Ethoxalyl-2-methylbenzo[*b*]thiophen-3-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (14) was obtained from dihetarylethene **1** and ethoxalyl chloride as described for compound **12**. Yield 32%, m.p. 95—97 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.35—8.4 (m, 7 H, 7 CH_{arom}); 4.25—4.3 (m, 2 H, CH_2); 3.0—3.5 (m, 4 H, 2 $CH_{2cyclopent}$); 2.2—2.45 (m, 2 H, $CH_{2cyclopent}$); 1.98 (s, 3 H, Me); 1.99 (s, 3 H, Me); 1.3—1.45 (m, 3 H, Me). MS (EI, 70 eV), *m/z* (I_{rel}): 461 (10), 460 (32), 445 (31), 387 (100). Found (%): C, 70.38; H, 5.28; S, 13.97. $C_{27}H_{24}O_3S_2$. Calculated (%): C, 70.41; H, 5.25; S, 13.92.

1-(6-Chloroacetyl-2-methylbenzo[*b*]thiophen-3-yl)-2-(6-ethoxalyl-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (15). Aluminum trichloride (0.073 g, 0.549 mmol) was added at −5 to 0 °C to a solution of compound **12** (0.1 g, 0.229 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at −5 to 0 °C for 15—20 min, whereupon ethoxalyl chloride (0.037 g, 0.274 mmol) was added. The reaction mixture was stirred at 5—15 °C for 5 h and poured into 10% HCl. The product was extracted with CH_2Cl_2 (3×50 mL). The organic extracts were washed with water (3×150 mL), dried with $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography with light petroleum—ethyl acetate (4 : 1) as an eluent. Yield 48%, m.p. 158—159 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.3—8.45 (m, 6 H, 6 CH_{arom}); 4.58 (s, 2 H, CH_2); 4.3—4.45 (m, 2 H, CH_2); 3.1—3.4 (m, 4 H, 2 $CH_{2cyclopent}$); 2.3—2.45 (m, 2 H, $CH_{2cyclopent}$); 1.93 (s, 3 H, Me); 1.95 (s, 3 H, Me); 1.3—1.45 (m, 3 H, Me). MS (EI, 70 eV), *m/z* (I_{rel}): 539 (70), 537 (63), 501 (28), 493 (23), 495 (29), 493 (23), 460 (100), 437 (39). Found (%): C, 64.82; H, 4.66; Cl, 6.62; S, 11.96. $C_{29}H_{25}ClO_4S_2$. Calculated (%): C, 64.85; H, 4.69; Cl, 6.60; S, 11.94.

1-(6-Bromoacetyl-2-methylbenzo[*b*]thiophen-3-yl)-2-(6-chloroacetyl-2-methylbenzo[*b*]thiophen-3-yl)cyclopent-1-ene (16) was obtained from bromide **13** and chloroacetyl chloride as described above for compound **15**. Yield 43%, m.p. 168—169 °C (EtOH). ^{1}H NMR ($CDCl_3$), δ: 7.43—8.55 (m, 6 H, 6 CH_{arom}); 4.58 (s, 2 H, CH_2); 4.67 (s, 2 H, CH_2); 3.2—3.4 (m, 4 H, 2 $CH_{2cyclopent}$); 2.34—2.45 (m, 2 H, $CH_{2cyclopent}$); 1.97 (s, 3 H, Me); 1.98 (s, 3 H, Me). MS (EI, 70 eV), *m/z* (I_{rel}): 560 (28), 558 (32), 556 (41), 554 (38), 523 (67), 481 (43), 478 (45), 437 (100). Found (%): C, 58.08; H, 3.93; Br, 14.36; Cl, 6.37; S 11.51. $C_{27}H_{22}BrClO_2S_2$. Calculated (%): C, 58.12; H, 3.97; Br, 14.32; Cl, 6.35; S, 11.49.

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Received November 11, 2011