

# Thermally irreversible organic photochromic compounds for optical memory

V. A. Barachevsky,<sup>1\*</sup> Yu. P. Strokach,<sup>1</sup> Yu. A. Puankov<sup>2</sup> and M. M. Krayushkin<sup>3</sup>

<sup>1</sup>Photochemistry Center, Russian Academy of Sciences, Moscow, Russia

<sup>2</sup>Moscow Physicotechnical Institute, Dolgoprudnyi, Moscow Region, Russia

<sup>3</sup>Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

Received 16 March 2007; accepted 17 March 2007

**ABSTRACT:** For some photochromic compounds (58 diarylethenes and 9 fulgimides), the results of our spectral and kinetic studies are presented. Aiming at targeted synthesis of new photochromic compounds, the structure – photochromic behavior relationship (SPBR) for the synthesized compounds has been analyzed. The perspectives for application of these compounds in development of recording media for use in optical memory devices are outlined. Copyright © 2007 John Wiley & Sons, Ltd.

**KEYWORDS:** photochromism; diarylethenes; fulgimides; spectral and kinetic characteristics; optical memory

## INTRODUCTION

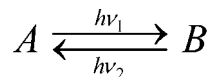
Interest in photochromic compounds and systems exhibiting a reversible change in their optical parameters (absorption, emission, refractive index, etc.) under the action of activating radiation is prompted by their potential practical implementation.<sup>1–4</sup>

Recent progress in the laser and information technologies makes photochromic materials promising for use as recording media in devices for recording, storage, and processing of optical information.

Development of information technologies (such as telecommunications and databases with super-high information capacity) requires a new organization of memory devices that would surpass the existing magnetic, magneto–optical information carriers, CD and DVD devices in their information capacity.<sup>4</sup> In this context, of especial interest are multilayer optical disks for three-dimensional (3D) bitwise working optical memory in which information recording is based on the principle of two-photon absorption.

A possible approach to resolution of the problem has been suggested by the discovery of thermally irreversible photochromic compounds<sup>5</sup> which, unlike the most of conventional ones, undergo the interconversion between their two forms A and B only under the action of activating radiation (Scheme 1). Such compounds (not so

numerous in their count) have been found among some diarylethenes,<sup>6–8</sup> fulgides, fulgimides,<sup>9,10</sup> phenoxy derivatives of quinine,<sup>11</sup> etc.



Scheme 1

This work was focused on outlining the perspectives for practical implementation of some recently synthesized thermally stable diarylethenes and fulgimides as photochromic recording media. Accordingly, we investigated the properties not of individual molecules but of the overall processes taking place under the action of exciting radiation in the systems formed by the above molecules: position of absorption maxima for two thermally stable forms of the above compounds, rate constants for photocoloration and photobleaching, photo-induced changes in the maximum optical density of the photoinduced form, and photodegradation (fatigue) of the photochromic system under the combined (simultaneous) action of UV and visible radiation.

Candidate photochromic compounds for use in recording media have to meet the following requirements:

- Absorption bands of both the forms must comply with emission wavelengths of existing pulsed lasers;
- High sensitivity to photoinduced changes in the optical density;
- Close rates for direct and reverse photoconversion at the same light intensity;

\*Correspondence to: V. A. Barachevsky, Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7a, Moscow, 119421 Russia.

E-mail: barva@photonics.ru

- Maximum tolerance for irreversible phototransformations (fatigue resistance).

## EXPERIMENTAL

The absorption spectra in the range 200–800 nm (toluene,  $C = 2.10^{-4}$  M) as well as position of absorption band maxima for the initial *A* ( $\lambda_{\max}^A$ , nm) and photoinduced *B* ( $\lambda_{\max}^B$ , nm) form were measured with a Varian Cary 50 spectrophotometer. The photoinduced (closed) form *B* was formed upon UV irradiation (Hg lamp DRSh-250 + UV-transmitting glass filter). Return to the initial form *A* was achieved upon irradiation within the absorption band of form *B* (the same lamp + glass filters transmitting in the visible). The kinetics of photocoloration and photobleaching under the action UV and visible radiation was measured at  $\lambda_{\max}^B$ . The kinetic curves were used to determine the photoinduced optical density  $D_{\max}^B$  and the rate constants for photocoloration ( $k_{AB}$ ,  $s^{-1}$ ) and photobleaching ( $k_{BA}$ ,  $s^{-1}$ ) at the comparable intensities of exciting irradiations. The values of  $D_{\max}^B$  were used as a measure of the light sensitivity of the compounds under study. The relative efficiency of photocoloration and photobleaching was characterized by the  $k_{AB}/k_{BA}$  ratio.

The photodegradation (fatigue) curves were obtained upon irradiation of solutions with unfiltered radiation from the above Hg lamp. As a measure of photodegradation (fatigue resistance), we used the half-decay time ( $\tau_{0.5}$ , s) for the photostationary value of  $D^B$ .

In between the experiments, the solutions were kept in the dark.

### Photochromic properties of diarylethenes

Photochromism of diarylethenes (DAEs) is based (Scheme 2) on reversible photocyclization of the open

(UV-absorbing) form *A* into the closed (cyclic) form *B* (absorbing in the visible).

In the experiments, we used the following recently synthesized<sup>12–15</sup> thienyl-containing DAEs containing five-membered cyclic bridging groups: perfluorocyclopentenes **I**, cyclopentenes **II**, maleic anhydrides **III**, lactones **IV**, 5-R-furan-2-ones **V**, 1-R-maleimides **VI**, 1,3-dioxalan-2-ones **VII**, 3-N-oxazol-2-ones **VIII**, 1-R-imidazoles **IX**, 2-R-thiazoles **X**, 6-R-pyridazin-3-ones **XI**, 2-phenyl-4-R-thiazines **XII**, pyrrolo[2,3-*d*]pyrimidines **XIII**, 2-R-cyclopentenediones **XIV**, and 2,2-R,R'-cyclopentenediones **XV** (Scheme 2).

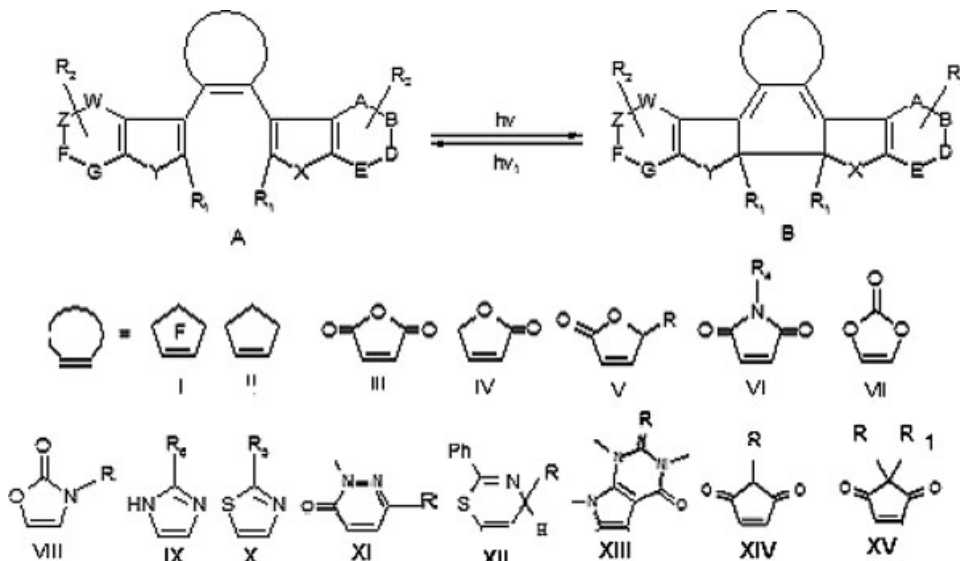
The open form *A* of all the thienyl derivatives **I** (Table 1, Fig. 1) exhibits absorption in the spectral range 285–320 nm. Position of  $\lambda_{\max}^A$  is virtually independent of the molecular structure of these compounds. For compound **D1**,  $\lambda_{\max}^B = 625$  nm (Table 1, Fig. 1).

The open form *A* of benzothienyl analogs absorbs at longer wavelengths while  $\lambda_{\max}^B$  is blue-shifted down to 555 nm (Table 1). Both compounds exhibit acceptable light-sensitivity. Unlike thienyl derivatives, benzothienyl analogs show a better photocoloration/photobleaching ratio. Benzothienyl analogs exhibit a higher fatigue resistance.

On going from perfluorocyclopentene to cyclopentene bridging groups (compounds **D3** and **D4** from group **II**), the values of  $\lambda_{\max}^B$  undergo a hypsochromic shift down to 495 nm, while the values of  $\lambda_{\max}^A$  become shifted toward longer wavelengths (Fig. 2).

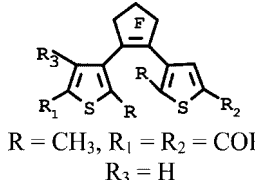
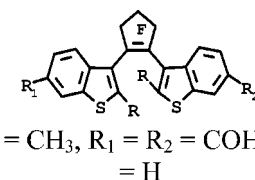
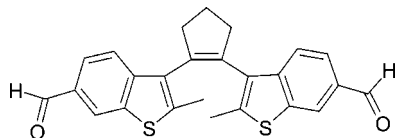
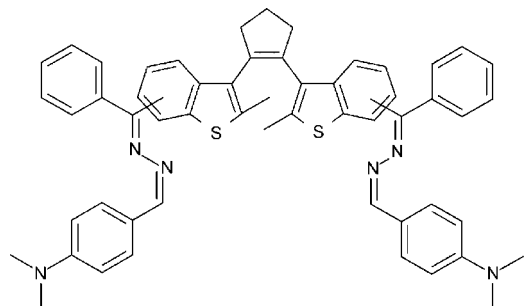
Like derivative **D2**, compound **D3** exhibits a higher light sensitivity (at the same  $k_{AB}/k_{BA}$  ratio) and lower fatigue resistance (although to an extent tolerable for potential applications).

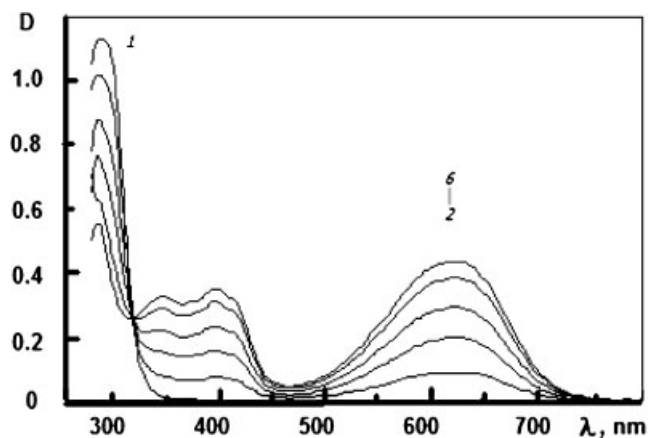
In contrast to the above compounds, derivative **D4** exhibits only a slightly pronounced photochromic behavior, which can be associated with the *cis-trans*-photoisomerization of the aza-containing moieties.



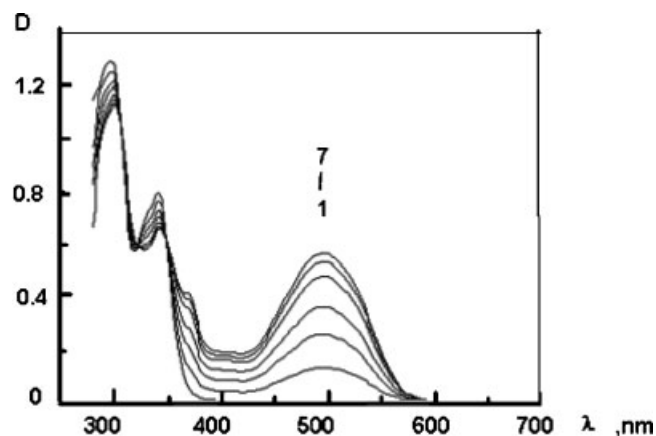
Scheme 2

**Table 1.** Spectral and kinetic characteristics of DAEs I and II

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
D1	 <p>R = CH<sub>3</sub>, R<sub>1</sub> = R<sub>2</sub> = COH, R<sub>3</sub> = H</p>	290	625	1.44	21.0	70
D2	 <p>R = CH<sub>3</sub>, R<sub>1</sub> = R<sub>2</sub> = COH, R<sub>3</sub> = H</p>	330	555	1.10	1.0	1040
D3		340	495	1.75	1.3	750
D4		385	500	Slightly pronounced photochromic behavior		

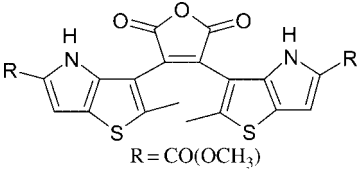
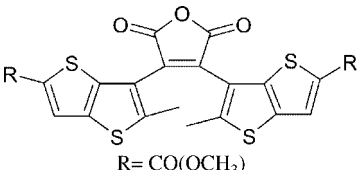
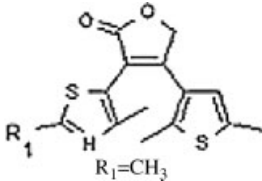
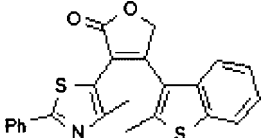
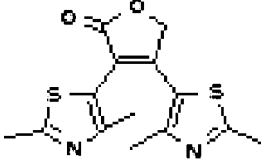


**Figure 1.** Absorption spectra of compound **D1** in toluene ( $C = 2 \cdot 10^{-4}$  M) before (1) and after successive UV irradiation ( $\lambda_{\text{ex}} 313$  nm) for 5 s (2), 15 s (3), 30 s (4), 1 min (5), and 2 min (6)



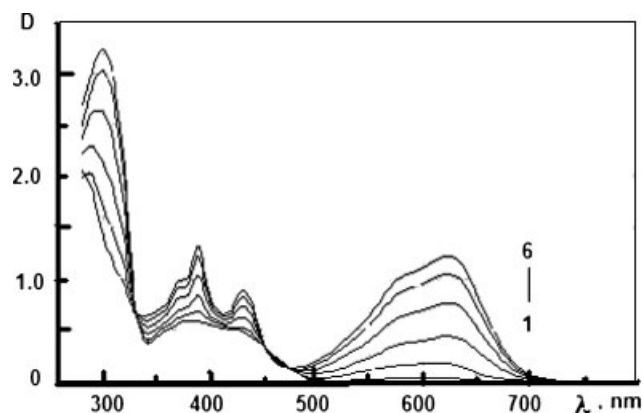
**Figure 2.** Absorption spectra of compound **D3** in toluene ( $C = 2 \cdot 10^{-4}$  M) before (1) and after successive UV irradiation (curves 2–7)

**Table 2.** Spectral and kinetic characteristics of DAEs **III** and **IV**

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D6</b>		295	510	0.48	24	1.0
<b>D7</b>		430	625	2.30	0.6	400
<b>D8</b>		315	455	0.4		130
<b>D9</b>	$R_1 = \text{Ph}$	340	470	0.8	3.1	120
<b>D10</b>		340	455	0.78	2.9	200
<b>D11</b>		310	405	1.0		>500

Among DAEs **III**, compounds **D6** and **D7** showed strongly different spectral characteristics of the closed form *B* (Table 2),  $\lambda_{\max}^B$  for compound **D7** being red-shifted (Fig. 3). Compared to **D6**, this compound exhibits a higher light sensitivity, acceptable photocoloration/photobleaching ratio, and poor fatigue resistance. In view of the very low  $\tau_{0.5}$  values, compound **D6** can hardly be recommended as a candidate for practical implementation.

Compared to DAEs **III**, compounds **D8–D11** from group **IV** exhibit absorption at shorter wavelengths (Table 2). On going from the methyl (compound **D8**) to phenyl substituent (compound **D9**),  $\lambda_{\max}^B$  undergoes a bathochromic shift accompanied by a twofold increase in the light sensitivity. Annellation of the benzene ring to the thienyl moiety (compound **D10**) gives rise to an insignificant hypsochromic shift of  $\lambda_{\max}^B$  accompanied



**Figure 3.** Absorption spectra of compound **D7** in toluene before (2) and after irradiation at  $\lambda_{\text{ex}}$  546 (1) and 436 nm (3–6)

by an increase in  $\tau_{0.5}$ . Still further hypsochromic shift of  $\lambda_{\max}^B$  and a decrease in  $\tau_{0.5}$  was observed for compound **D11**. All compounds of group **IV** exhibit acceptable  $k_{AB}/k_{BA}$  ratios.

The light sensitivity and fatigue resistance of compounds **V** are generally lower than those of compounds **IV** (Table 3).

The bathochromic shift (compared to **D12**) of  $\lambda_{\max}^B$  is exhibited by compound **D13** (Table 3). In the presence of amine substituent (compound **D14**), no signs of photochromic behavior were found.

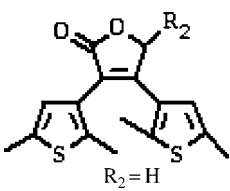
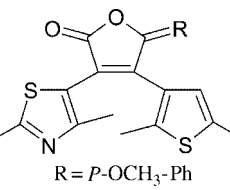
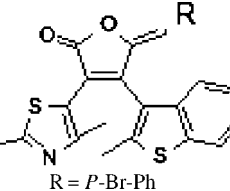
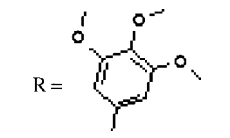
Replacement of one of thienyl groups in **D13** by the thiazole moiety (compounds **D15** and **D16**) leads to a marked hypsochromic shift of  $\lambda_{\max}^B$ . Annulation of the benzene ring (compound **D17**) causes still further shift of  $\lambda_{\max}^B$  to shorter wavelengths. Photochromic properties disappear upon introduction of the trimethoxy-substituted phenyl ring into the cyclopentene moiety (compound **D18**). This compound seems to be present only in its form *B*.

The symmetric maleimide derivatives **D19**, **D20** from group **VI** (Table 4) are characterized by the identical position of  $\lambda_{\max}^B$ , while the absorption bands of form *A* are shifted to longer wavelengths. Annulation of the benzene ring to the thienyl residue (compound **D20**) does not affect the spectral characteristics of *A* and *B* but markedly improves the fatigue resistance. Replacement of one of the thienyl moieties by the indoline fragment (compound **D21**) still further improves the fatigue resistance and strongly enhances the light sensitivity. As compared to **D19**, compounds **D20** and **D21** exhibit a better photobleaching/photocoloration ratio.

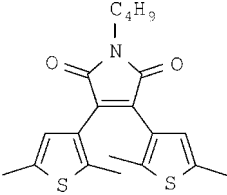
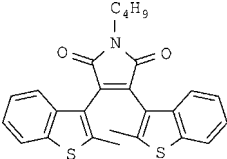
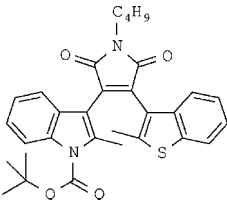
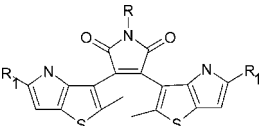
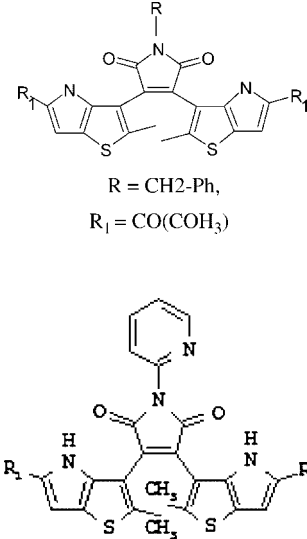
In contrast to other compounds of this group, the absorption bands of compounds **D22–D25** in their form *B* are red-shifted: form *B* of compound **D22** shows two absorption bands peaked at 420 and 595 nm (Fig. 4).

With increasing electron-donating ability of substituents in the bridging group (compounds **D23**, **D25**), the values of  $\lambda_{\max}^A$  and  $\lambda_{\max}^B$  undergo a slight shift to longer wavelengths (compared to **D22**). The presence of the

**Table 3.** Spectral and kinetic characteristics of DAEs **V**

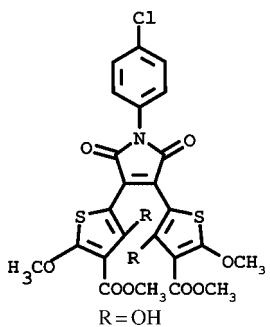
DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D12</b>	 R <sub>2</sub> =H	300	515	0.35	1.4	90
<b>D13</b>	R <sub>2</sub> = <i>p</i> -OCH <sub>3</sub> -Ph	375	550	0.51	8.3	70
<b>D14</b>	R <sub>2</sub> = <i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub> -Ph	445		no photochromic behavior		
<b>D15</b>	 R = <i>p</i> -OCH <sub>3</sub> -Ph	400	510	0.4	3.3	150
<b>D16</b>	R = <i>p</i> -Br-Ph	380	500	0.88	3.1	90
<b>D17</b>	 R = <i>p</i> -Br-Ph	385 (1.2)	470 (0.1)	0.45	9.6	200
<b>D18</b>	 R =	410		no photochromic behavior		

**Table 4.** Spectral and kinetic characteristics of DAEs VI

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D19</b>		400	505	0.26	5.2	20
<b>D20</b>		405	510	0.13	0.2	360
<b>D21</b>		410	510	2.0	0.2	560
<b>D22</b>	 R = CH <sub>3</sub> , R <sub>1</sub> CO(OCH <sub>3</sub> )	290	420, 595	0.65	12.0	32
<b>D23</b>	R = Ph, R <sub>1</sub> = CO(OCH <sub>3</sub> )	295	425, 605	0.86	2.7	70
<b>D24</b>		290	420/595	2.0	6.7	
<b>D25</b>	 R = CH <sub>2</sub> -Ph, R <sub>1</sub> = CO(COCH <sub>3</sub> )	295	425, 605	0.37	3.9	20

(Continues)

Table 4. (Continued)

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
D26	 R = OH	245, 290, 390, 470				no photochromic behavior
D27	R = O(CH <sub>2</sub> ) <sub>2</sub> COOEt	235, 280, 435				no photochromic behavior

separating —CH<sub>2</sub>— unit between the bridging and phenyl groups (compound **D24**) suppresses the effect of phenyl substituent on the spectral parameters and markedly improves the light sensitivity. All of the above compounds **VI** showed good  $k_{AB}/k_{BA}$  ratios. Compounds **D26** and **D27** did not exhibit photochromic transformation altogether.

The most blue-shifted absorption of form *B* ( $\lambda_{\max}^B < 520$  nm) was observed for the azole derivatives from group **VII** (Table 5).

The presence of methyl substituents in thienyl moieties (compounds **D28** and **D29**) gives rise to the bathochromic shift of  $\lambda_{\max}^B$  and improvement of the light sensitivity (at close  $k_{AB}/k_{BA}$  ratios). Replacement of one of thienyl fragments by the inverted one (compound **D31**) shifts  $\lambda_{\max}^B$  to shorter wavelengths and increases the light sensitivity. Upon replacement of the second thienyl fragment (compound **D32**), the photochromic behavior disappears. Similar to compounds **D19** and **D21** from group **VI**, the symmetric compound **D30** (containing two

benzothienyl fragments) and its thienyl analog **D29** show the identical values of  $\lambda_{\max}^B$ . For compounds **D28** and **D29**, photocoloration was found to prevail over photobleaching. The inverse situation is typical of compounds **D30** and **D31**. The fatigue resistance of compounds **VII** is lower than that of compounds **I–VI**.

The structure–photochromic behavior relationship (SPBR) for compounds **VIII** (Table 6) was found to be essentially the same as that for compounds **VII**. Unfortunately, the fatigue resistance of these compounds is rather low.

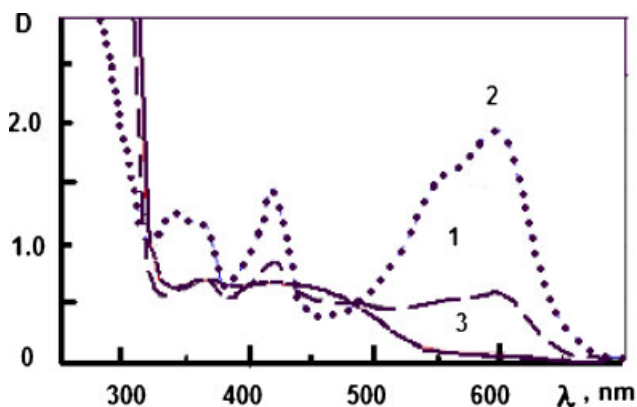
The spectral and kinetic data obtained for DAEs **IX** revealed their low fatigue resistance, which makes these compounds inapplicable for use as recording media in optical memory devices.

The characteristics of compounds **X–XII** are presented in Table 7. Compound **D37** from group **X** exhibits acceptable spectral and kinetic properties, although the efficiency of photobleaching prevails over that of photocoloration. Compound **D38** from group **XI** is characterized by the utmost red shift of  $\lambda_{\max}^B$  (585 nm), acceptable light sensitivity, and tolerable photocoloration/photobleaching ratio. With the increasing electron-accepting ability of substituent (compounds **D38** and **D39**),  $\lambda_{\max}^B$  becomes blue-shifted while the fatigue resistance grows.

Annulation of the benzene ring to one of the thienyl fragments and replacement of another thienyl fragment by the thiazolyl moiety (compound **D40**) gives rise to a large hypsochromic shift of  $\lambda_{\max}^B$  and to an increase in the light sensitivity and fatigue resistance.

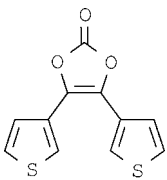
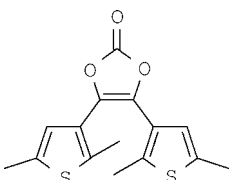
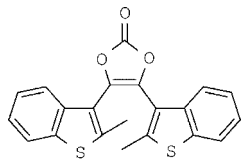
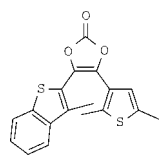
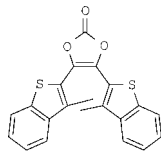
Compounds **D41** and **D42** from group **XII** undergo photochromic transformations, but the absence of well-pronounced absorption bands of the closed form *B* rules out the possibility of their practical implementation.

Compounds **D43–D46** from group **XIII** were found to exhibit good light sensitivity (Table 8). Spectral characteristics of these compounds depend on their



**Figure 4.** Absorption spectra of compound **D22** before (1) and after irradiation with the UV (2) and visible (3) light. This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

**Table 5.** Spectral and kinetic characteristics of DAEs VII

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D28</b>		295	425	0.18	1.3	90
<b>D29</b>		<300	450	0.41	1.1	25
<b>D30</b>		300	450	1.46	0.6	60
<b>D31</b>		310	410	0.8	0.8	80
<b>D32</b>		320	no photochromic behavior			

structure. Unfortunately, compounds of this group are low-sensitive to the action of visible light and show a low fatigue resistance, which makes them unsuitable for potential applications.

Photochromic behavior of compounds **D47–D52** from group **XIV** depends on the type of substituent in the bridging cyclopentene group and on the structure of the thienyl fragments (Table 9). Compound **D47** is characterized by a red shift of  $\lambda_{\max}^A$  and  $\lambda_{\max}^B$ , moderate light sensitivity, and low fatigue resistance. Its photocoloration rate prevails over that of photobleaching.

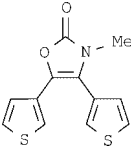
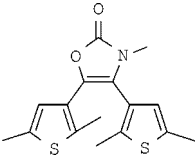
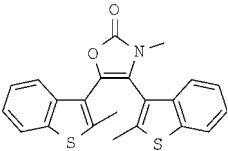
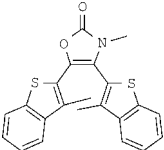
Introduction of methyl substituent to the *p*-position of the phenyl group (compound **D48**) leads to an insignificant bathochromic shift of  $\lambda_{\max}^B$  and to an increase in the

light sensitivity. Replacement of one of thienyl fragments by the thiazolyl moiety (compound **D49**) shifts  $\lambda_{\max}^B$  down to 520 nm and improves the fatigue resistance, without significant decrease in the light sensitivity. But replacement of the methyl-substituted group in the thiazolyl moiety by the phenyl group (compound **D50**) is accompanied by a growth of the fatigue resistance and a marked drop in the light sensitivity.

Annulation of the benzene cycle to the thienyl fragment (compounds **D51** and **D52**) increases the photostability but decreases the light sensitivity. Note that for compounds **D47** and **D48**, photocoloration was found to prevail over photobleaching, while for compounds **D49–D52** the situation was reverse.



**Table 6.** Spectral and kinetic characteristics of DAEs **VIII**

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D33</b>		300	430	0.19	1.6	32
<b>D34</b>		290	455	0.46	1.9	8
<b>D35</b>		300	455	0.38		24
<b>D36</b>		325		no photochromic behavior		

Photochromic properties of compounds **XV** depend on the presence/absence of second substituent in the bridging cyclopentene group (Table 10). The presence of electron-donating substituent (compounds **D53–D57**) leads to a bathochromic shift of  $\lambda_{\max}^B$ . Replacement of the thienyl fragment by the thiazolyl residue markedly improves the fatigue resistance. However, compound **D58** (containing two phenyl substituents in the cyclopentene fragment) does not show photochromic behavior altogether.

### Photochromic properties of fulgimides

Fulgimides are another type of light-sensitive compounds for potential use as photochromic recording media in optical memory devices.<sup>9,10</sup> These compounds are known to undergo thermally irreversible but photochemically reversible interconversion between the open form *A* (*Z*-isomer) and closed form *B* (*C*-isomer) (Scheme 3). For some fulgimides, these transformations may be complicated by occurrence (under UV irradiation) of the reversible

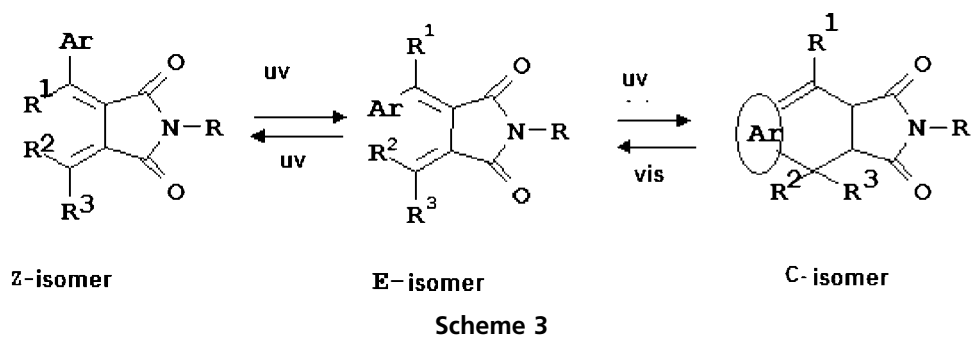
*E–Z*-photoisomerization which spectrally manifests itself in the UV spectral range.

The spectral and kinetic characteristics of some fulgimides (FULs) and *bis*-fulgimides (*b*-FULs)<sup>16</sup> are presented in Tables 11 and 12.

All investigated FULs exhibit intrinsic absorption in the spectral range 290–330 nm. As an example, Fig. 5 presents the absorption spectra of compound **F2** before and after successive exposure to UV radiation. The presence of the isosbestic point suggests that the *A* interconversion is not complicated by involvement of other reactive species; in other words, in our conditions the *E–Z* isomerization is insignificant.

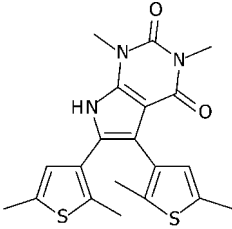
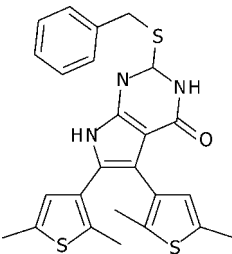
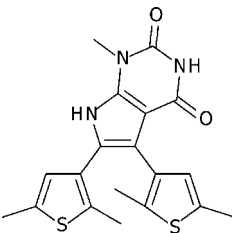
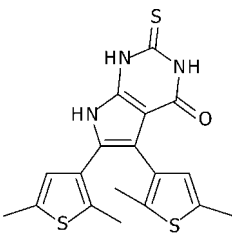
As follows from Table 11, the position of  $\lambda_{\max}^A$  is structure-dependent. With increasing electron-accepting ability of substituent *R*, the values of  $\lambda_{\max}^A$  undergo an insignificant hypsochromic shift.

For all compounds **F1–F5**, the values of  $\lambda_{\max}^B$  are within the range 520–540 nm (Fig. 5, Table 11). With increasing electron-accepting ability of substituent *R*, the absorption band of *B* shifts toward longer wavelengths. The larger  $\lambda_{\max}^B$  values are exhibited by compounds **F1** and **F2**. The

**Table 7.** Spectral and kinetic characteristics of DAEs X–XII

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D37</b>		300	515	0.30	0.7	105
<b>D38</b>		325	585	1.2	1.4	70
<b>D39</b> <b>D40</b>		335 345	530 485	1.2 2.0	1.1 1.3	130 250
<b>D41</b>		<300	470	0.28		>300
<b>D42</b>		<300	420,470	0.68	2.5	100

**Table 8.** Spectral and kinetic characteristics of DAEs **XIII**

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D43</b>		290	535	1.8	23.0	15
<b>D44</b>		310	560	0.96	28.0	120
<b>D45<sup>a</sup></b>		290	530	1.8	13.8	10
<b>D46<sup>a</sup></b>		315	550	0.96	6.2	10

<sup>a</sup> In acetonitrile.

spectral data for compound **F1** are consistent with the reported ones<sup>9</sup>. The compounds containing electron-accepting substituents (**F2–F5**) show low values of  $k_{AB}/k_{BA}$ .

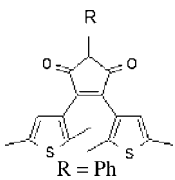
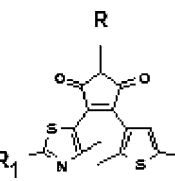
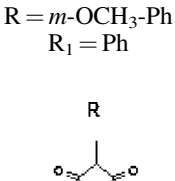
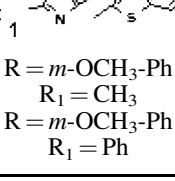

The efficiency of photocoloration was found to decrease on going from **F1** to compounds **F2–F5** containing the —N=N— link with substituent R. This can be explained by a partial loss of photoexcitation energy on the *cis–trans*-isomerization which does not manifest itself in spectral changes during photochromic transformations. The inverse behavior was observed for the photoinduced transformation  $B \rightarrow A$ . It is possible that

the geometry of the cyclic form *B* favors the process of photobleaching.

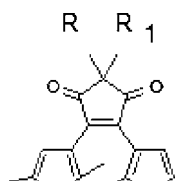
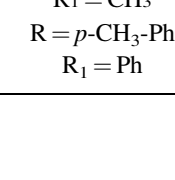
The spectral and kinetic characteristics of *b*-FULs (except for **BF4**) are close (Table 12) to those of their monomeric analog **F2**. The  $\lambda_{\max}^B$  values for these compounds are slightly shifted to longer wavelengths (as compared to **F2**). A decrease in the light sensitivity is accompanied by an increase in the fatigue resistance.

Analysis shows that the photochromic properties of fulgimides seem suitable for their use as photochromic recording media in optical memory devices, although on aggregate fulgimides are somewhat inferior to diarylethenes.

**Table 9.** Spectral and kinetic characteristics of DAEs **XIV**

DAE	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D47</b>	 R = Ph	375	580	0.5	4.5	32
<b>D48</b> <b>D49</b>	 R = <i>p</i> -CH <sub>3</sub> -Ph	375 370	585 520	0.77 0.65	7.2 0.4	45 210
<b>D50</b>	 R = <i>m</i> -OCH <sub>3</sub> -Ph R = CH <sub>3</sub> R <sub>1</sub> = Ph	390	520	0.14	0.2	420
<b>D51</b>	 R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = CH <sub>3</sub> R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = Ph	370	510	0.08		
<b>D52</b>	 R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = CH <sub>3</sub> R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = Ph	395	525	0.09	0.3	>600

**Table 10.** Spectral and kinetic characteristics of DAEs **XV**

DNA	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>D53</b>	 R = <i>p</i> -CH <sub>3</sub> -Ph R <sub>1</sub> = CH <sub>3</sub>	375	595	0.7	5.6	55
<b>D54</b>	 R = <i>p</i> -CH <sub>3</sub> -Ph R <sub>1</sub> = Ph	380	600	0.66	6.0	45

*(Continues)*

Table 10. (Continued)

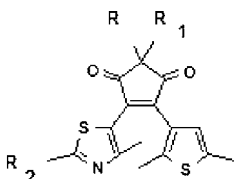
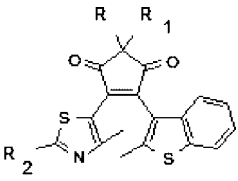
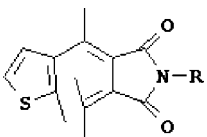
DNA	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
D55	 <p>R = <i>m</i>-OCH<sub>3</sub>-Ph R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub></p>	370	510	0.63	0.6	300
D56	R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = Ph	390	515	0.11	0.3	480
D57	 <p>R = <i>m</i>-OCH<sub>3</sub>-Ph R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub></p>	370	510	0.35	1.9	110
D58	R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = R <sub>2</sub> = CH <sub>3</sub> R = <i>m</i> -OCH <sub>3</sub> -Ph R <sub>1</sub> = R <sub>2</sub> = Ph	395		no photochromic behavior		

Table 11. Spectral and kinetic characteristics of some fulgimides (FULs)

FUL	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
F1	 <p>R = Ph</p>	250, 325	522	0.75	1.2	25
F2	R = NH <sub>2</sub>	325	520	0.9	1.0	70
F3	R = NHCO <sub>2</sub> Bu	230, 280, 330	530	0.70	0.9	40
F4	R = NPhCl	290	540	0.61	0.3	95
F5	R = NPhNO <sub>2</sub>	305	540	0.65	0.4	100

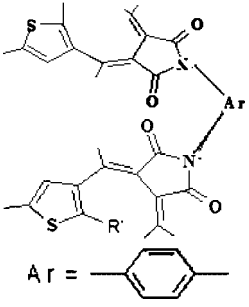
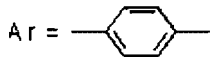
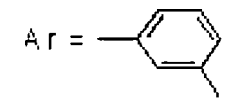
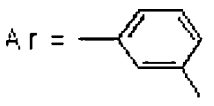
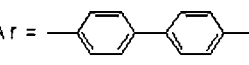
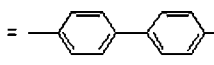
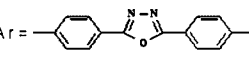
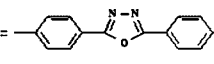
## CONCLUDING REMARKS

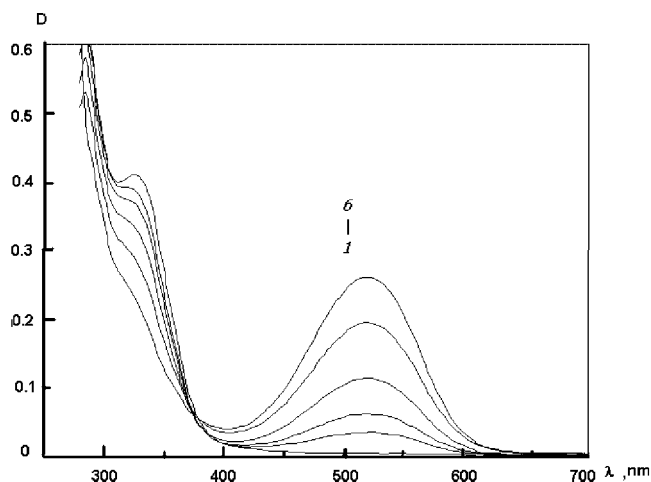
(1) The spectral and kinetic characteristics of the investigated compounds (58 diarylethenes and 9 fulgimides) suggest that some of these photochromic compounds satisfy the requirements to candidate materials for use in optical memory devices. The above data imply that diarylethenes **I–VI**, **X**, **XI**, **XIV**, and **XV** as well as fulgimides seem promising for use as photochromic recording media in optical memory devices. Variation in the structure of cyclopentene and the thienyl moieties may be used for

adjusting their spectral and kinetic characteristics within a wide range.

- (2) A wide range of variation in the spectral parameters of the open and cyclic forms of synthesized compounds opens up new horizons for development of the four-dimensional (4D) optical memory ensuring the recording and retrieval of optical information not only in the medium bulk but also at different wavelengths of laser radiation.
- (3) The established structure–photochromic behavior relationships provide a basis for targeted synthesis of new photochromic compounds.

**Table 12.** Spectral and kinetic characteristics of some *bis*-fulgimides (*b*-FULs)

<i>b</i> -FUL	Structure	$\lambda_{\max}^A$ , nm	$\lambda_{\max}^B$ , nm	$D_{\max}^B$	$k_{AB}/k_{BA}$	$\tau_{0.5}$ , s
<b>BF1</b>	 Ar = 	250, 330	528	1.2	0.8	30
<b>BF2</b>	 Ar = 	285, 335sh	530	1.48	0.4	50
<b>BF3</b>	 Ar = 	310	530	1.05	0.4	50
<b>BF4</b>	 Ar = 	335	495	0.75	0.1	220

**Figure 5.** Absorption spectra of compound **F2** in toluene ( $C=2 \cdot 10^{-4}M$ ) before (1) and after UV irradiation ( $\lambda_{\text{ex}}=313$  nm) for 0.5 (2), 1 (3), 2 (4), 4 (5), and 8 min (6)

## REFERENCES

- Brown GH (ed.). *Photochromism*. Wiley-Interscience: New York, 1971.
- Barachevsky VA, Lashkov GI, Tsekhomsky VA. *Fotokhromizm i ego primeneniye*, (Photochromism and its Application). Khimiya: Moscow, 1977.
- Crano JC, Guglielmetti RJ (eds). *Organic Photochromic and Thermochromic Compounds*. Plenum Press: New York/London, 1999.
- Barachevsky VA. *High Energy Chem.* 2003; **17**: 6–16.
- Irie M, Mohri M. *J. Org. Chem.* 1988; **53**: 803–808.
- Irie M. In *Organic Photochromic and Thermochromic Compounds*, vol. **1**, Crano JC, Guglielmetti RJ (eds). Plenum Press: New York/London, 1999; 207–222.
- Irie M. *Chem. Rev.* 2000; **100**: 1685–1713.
- Krayushkin MM. *Chem. Heterocycl. Comp. (Riga)* 2001; **1**: 19–40.
- Fan MG, Yu L, Zhao W. In *Organic Photochromic and Thermochromic Compounds*, vol. **1**, Crano JC, Guglielmetti RJ (eds). Plenum Press: New York/London, 1999; 141–206.
- Yokoyama Y. *Chem. Rev.* 2000; **100**: 1717–1739.
- Barachevsky VA. In *Organic Photochromic and Thermochromic Compounds*, vol. **1**, Crano JC, Guglielmetti RJ (eds). Plenum Press: New York/London, 1999; 267–311.
- Barachevsky VA, Strokach YuP, Krayushkin MM. *Mol. Cryst. Liq. Cryst.* 2005; **430**: 181–186.
- Strokach YuP, Valova TM, Golotyuk ZO, Barachevsky VA, Yarovenko VN, Kalik MA, Krayushkin MM. *Opt. Spectrosc.* 2005; **99**: 714–718.
- Strokach YP, Valova TM, Golotyuk ZO, Barachevsky VA, Kuznetsova OYu, Yarovenko VN, Semenov SL, Zavarzin IV, Shirinyan VZ, Krayushkin MM. *Opt. Spectrosc.* 2005; **99**: 573–578.
- Krayushkin MM, Kalik MA, Kozhinov DV, Martynkin AY, Strokach YP, Barachevsky VA. *Chem. Heterocycl. Comp. (Riga)* 2005; **41**: 312–316.
- Krayushkin MM, Shorunov SV, Luyksaar SI, Strokach YP, Valova NV, Golotyuk ZO, Barachevsky VA. *Chem. Heterocycl. Comp. (Riga)* 2006; **42**: 1012–1017.