



HAL
open science

Visual light photoswitches derived from bindone: Toward stabilization of colored photo-isomers

Vladimir Lokshin, Laura Bekere, Vladimir Khodorkovsky

► **To cite this version:**

Vladimir Lokshin, Laura Bekere, Vladimir Khodorkovsky. Visual light photoswitches derived from bindone: Toward stabilization of colored photo-isomers. *Dyes and Pigments*, 2017, 145, pp.570-575. 10.1016/j.dyepig.2017.06.052 . hal-03500754

HAL Id: hal-03500754

<https://hal.science/hal-03500754v1>

Submitted on 6 Jan 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1 Visual light photoswitches derived from bindone: toward
2 stabilization of colored photo-isomers.

3

4 Vladimir Lokshin, Laura Bekere, Vladimir Khodorkovsky*

5

6 Aix Marseille Université, CNRS, CINaM UMR 7325, 13288, Marseille, France

7

E-mail: khodor@cinam.univ-mrs.fr

8 Abstract: Condensation of bindone and cinnamaldehydes afforded five cyclic
9 products instead of the expected merocyanines. The structures of all products
10 were confirmed by the X-ray data. In solution, the weakly colored cyclic isomers
11 form deeply colored (orange to red shades) open isomers upon irradiation in the
12 UV and visible range (up to 530 nm). The colored isomers are very stable and
13 undergo thermal discoloration with the half-life times between 13 h and 128 h,
14 depending on the substituent and solvent at room temperature. Heating their
15 solutions above 130°C gives rise to rapid discoloration. High fatigue resistance
16 was demonstrated by repeating the irradiation/heating cycles.

17 Keywords: Photochromism, Merocyanine, Photochemical switching, bindone.

18 **1. Introduction**

19 During the past decades, photochromic derivatives have been the focus of
20 numerous research studies owing to the importance of this class of organic
21 compounds in different fields of materials science [1-3].

22 According to the definition, photochromism is a reversible transformation

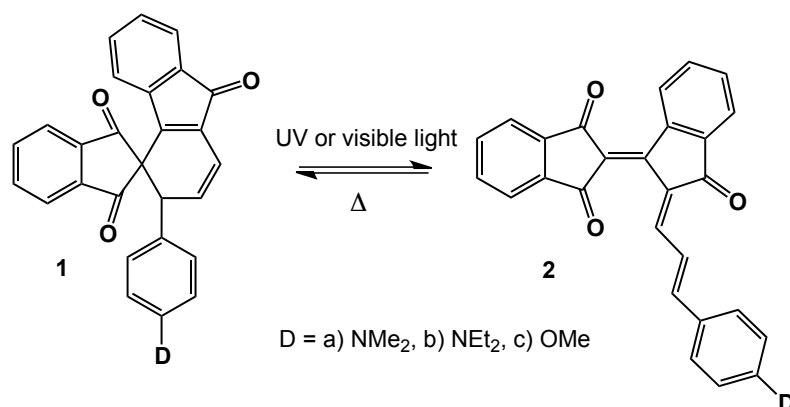
1 of a chemical species induced in one or both directions by absorption of
2 electromagnetic radiation between two forms, A and B, having different
3 absorption spectra and, correspondingly, a difference of other physical
4 properties [4]. Many classes of organic photochromic molecules are therefore
5 considered as molecular switches, namely, photoswitches [5].

6 Most of the known photochromic molecules undergo photochemical
7 conversions upon action of light of the UV range. However, UV light may damage
8 the polymeric substrates involving photochromic molecules or moieties and its
9 use as a photo-activator for biological and medical applications is very limited.
10 Therefore, the search for molecular photoswitches that can be activated by
11 visible or near infrared light became the focus of numerous researches during
12 the past years [6].

13 Among the most studied new classes of visible light photoswitches are *o*-
14 fluoroazabenzene [7, 8] and Donor–Acceptor Stenhouse Adducts (DASA) [9]
15 that exhibit *negative* photochromism: irradiation of their deeply colored
16 solutions by visible light gives rise to the formation of the colorless cyclic forms.
17 Discoloration is reversible and the color is restored in dark thermally [10-13].

18 Recently, we described a new photochromic system that exhibits
19 unprecedented behavior: the condensation products of bindone and *p*-
20 aminophenyl substituted cinnamaldehydes or *p*-methoxy cinnamaldehyde
21 produced not the expected colored merocyanines, but weakly colored cyclic
22 derivatives **1a-c** [14]. The amino-substituted derivatives **1a,b** exhibit two very
23 broad overlapping weak absorption bands between 300 and 650 nm ($\epsilon < 800 \text{ M}^{-1}$

1 cm⁻¹), whereas the spectra of methoxy substituted **1c** shows only one broad band
2 about 480 nm. The yellowish solutions of **1** undergo intense coloration upon
3 irradiation by visible light at any wavelength up to 640 nm (Scheme 1) owing to
4 the formation of the conjugated merocyanines **2**. The process is reversible and
5 the dark discoloration occurs, depending on the temperature and solvent
6 polarity, within seconds and a few hours. Quantum mechanical calculations
7 showed that the presence of a strong electron donating substituent is
8 substantial, as the longest wavelength absorption band of **1** is the intramolecular
9 charge transfer band from the *p*-aminophenyl electron donating moiety toward
10 the 1,3-indandione accepting moiety.



11

12 Scheme 1. Bindone derived photochromes reactive to UV and visible ranges [14].

13 In this paper we report on the synthesis, structures and photochromic
14 properties of a series of analogs of **2** without the electron donating substituents.

15 2. Experimental

16 2.1. Equipment and reagents

17

1 Bindone, cinnamic aldehyde derivatives and solvents were obtained from
2 Sigma- Aldrich and Alfa-Aeser.

3 ^1H and ^{13}C NMR spectra were recorded in methylene chloride- d_2 on JEOL
4 ECS400 spectrometer at 399.78 and 100.53 MHz, respectively. Proton chemical
5 shifts are given in ppm downfield from tetramethylsilane and coupling constants
6 (J) in Hertz. ^{13}C NMR spectrum of solid **4b** was recorded on Bruker BioSpin
7 spectrometer at 10 kHz. IR spectra were recorded for solid samples on Perkin
8 Elmer Spectrum 100 spectrometer.

9 Melting points were determined on a Büchi-510 apparatus and were not
10 corrected.

11 The UV-Vis absorption spectra were recorded with Ocean Optics USB
12 4000 and JASCO V-660 in 2, 4, 10 and 100 mm quartz cells. Irradiation of
13 solutions was done using a UVP LLC 95000505 lamp (254 nm), LED sources
14 LUMOS 43 (Atlas Photonics) at 300, 315, 330, 350, 405, 450, 505 and 525 nm,
15 Luminus LED PT121 at 460 and 530 nm and lasers: Module Oxxius LBX-405-
16 500-HPE-PP 405 nm, LBX-642-130-CIR-PP 642 nm, CryLas FQSS 266-200 (266
17 and 532 nm) and FQSS 355-300 (355 nm).

18 2.2. Synthesis

19 A general procedure: a mixture of bindone **1** (1 mmol) and the
20 corresponding cinnamaldehyde (1.2 mmol) was refluxed in absolute ethanol for
21 2 - 3 hours. The precipitated in 70 - 80% yields products **5** (**4b** in the case of *p*-
22 fluorophenyl cinnamaldehyde) were washed with ethanol, dried on air and
23 crystallized.

1 2.2.1. 3-Phenylspiro[fluorene-4,2'-indene]-1',3',9(3 H)-trione (**5a**).

2 Yield: 78%. Bright scarlet plates from acetic acid, m.p. 230-232°C (dec).
3 IR: 1740, 1707 sh, 1699, 1600 sh, 1590 cm⁻¹. ¹H NMR: 7.92 (d, *J* = 7.6, 1H), 7.75
4 (td, *J* = 7.5, 1.2, 1H), 7.69 (td, *J* = 7.5, 1.1, 1H), 7.62 (d, *J* = 7.6, 1H), 7.38 (d, *J* = 7.6,
5 1H), 7.12 (t, *J* = 7.1, 1H), 7.06 – 6.95 (m, 6H), 6.56 (dd, *J* = 9.7, 3.4, 1H), 6.17 (d, *J* =
6 7.3, 1H), 6.07 (dd, *J* = 9.6, 2.8, 1H), 4.71 (t, *J* = 3.1, 1H). ¹³C NMR: 202.10 (CO),
7 196.36 (CO), 193.13 (CO), 149.09, 142.65, 141.63, 141.52, 137.29, 136.53 (CH),
8 136.02 (CH), 133.98, 133.48 (CH), 131.58, 131.38 (CH), 129.42 (2CH), 129.07
9 (CH), 128.36 (2CH), 127.69, 123.49, 122.87 (2CH), 120.61 (CH), 117.51 (CH),
10 62.11, 50.41 (CH). Anal. calcd. for C₂₇H₁₆O₃: C, 83.49%; H, 4.15%. Found: C,
11 83.38%, H, 4.12%.

12

13 2.2.2. 3-(4-Fluorophenyl)spiro[fluorene-4,2'-indene]-1',3',9(3 H)-trione (**5b**).

14 Derivative **4b** (20 mg, 49 μmol) was heated under reflux for one hour in
15 10 ml of octane. Insoluble **4b** slowly dissolves and the resulting orange solution
16 was evaporated and the residue crystallized from acetic acid affording **5b** in 80%
17 yield. Red prisms m.p. 236-238°C. IR: 1739, 1714, 1698, 1601, 1591 cm⁻¹. ¹H
18 NMR: 7.94 (d, *J* = 7.5, 1H), 7.79 (t, *J* = 7.4, 1H), 7.73 (t, *J* = 7.4, 1H), 7.66 (d, *J* = 7.5
19 Hz, 1H), 7.38 (d, *J* = 7.1, 1H), 7.10 (t, *J* = 7.4, 1H), 7.04-6.98 (m, 3H), 6.72 (t, *J* = 8.7,
20 2H), 6.56 (dd, *J* = 9.7, 3.4, 2H), 6.17 (d, *J* = 7.3, 2H), 6.03 (dd, *J* = 9.7, 2.9, 2H), 4.72
21 (t, *J* = 3.1, 2H). ¹³C NMR: 202.05 (CO), 196.35 (CO), 193.04 (CO), 162.08 (d, *J* =
22 246.4, CF), 149.04, 142.57, 141.53, 141.42, 136.76 (CH), 136.26 (CH), 133.87,
23 133.51 (CH), 133.24 (d, ⁴*J* = 3.2), 131.54, 131.11 (d, ²*J* = 12.2, 2CH), 131.09 (CH),
24 129.14 (CH), 123.59 (CH), 122.94 (d, ³*J* = 3.8, 2CH), 120.63 (CH), 117.67 (CH),

1 115.31 (CH), 115.10 (CH), 62.03, 49.51 (CH). Anal. calcd. for C₂₇H₁₅FO₃: C,
2 79.79%; H, 3.72%. Found: C, 79.92%, H, 3.91%.

3

4 2.2.3. (2Z)-2-[(2E)-3-(4-Fluorophenyl)prop-2-en-1-ylidene]-1,2'-biindene-1',3,3'(2
5 H)-trione (**4b**).

6 Yield: 79%. Brown needles with metallic luster, m.p. 220-221°C. IR: 1696,
7 1672, 1607, 1587, 1565, 1530, 1509 cm⁻¹. ¹H NMR: 9.08(d, J = 7.8, 1H), 8.70 (dd, J
8 = 15.4, 11.8, 1H), 8.10 (d, J = 11.7, 1H). ¹³C NMR (solid): 190.18, 187.82, 167.13,
9 163.84, 155.42, 151.96, 147.17, 140.16, 137.71, 133.61, 130.93, 127.04, 124.50,
10 121.97, 119.54, 117.32. Anal. calcd. for C₂₇H₁₅FO₃: C, 79.79%; H, 3.72%. Found: C,
11 79.88%, H, 3.76%.

12

13 2.2.4. 3-(4-Chlorophenyl)spiro[fluorene-4,2'-indene]-1',3',9(3 H)-trione (**5c**).

14 Yield: 77%. Red prisms from ethanol, m.p. 184-185°C. IR: 1738, 1713,
15 1701, 1600 sh, 1588 cm⁻¹. ¹H NMR: 7.95 (d, J = 7.5, 1H), 7.81 (t, J = 7.4, 1H), 7.75
16 (t, J = 7.4, 1H), 7.67 (d, J = 7.9, 1H), 7.38 (d, J = 7.1, 1H), 7.10 (t, J = 7.2, 1H), 7.03 –
17 6.95 (m, 5H) 6.56 (dd, J = 9.6, 3.4, 1H), 6.16 (d, J = 7.3, 1H), 6.01 (dd, J = 9.7, 2.9,
18 1H), 4.71 (t, J = 3.1, 1H). ¹³C NMR: 201.85, 196.23, 192.99, 148.96, 142.51,
19 141.49, 141.36, 136.86 (CH), 136.38 (CH), 136.02, 133.82, 133.53 (CH), 133.50,
20 131.53, 130.86 (2CH), 130.74 (CH), 129.16 (CH), 128.51 (2CH), 123.65 (CH),
21 123.02 (CH), 122.94 (CH), 120.65 (CH), 117.78 (CH), 61.90, 49.51(CH). Anal.
22 calcd. for C₂₇H₁₅ClO₃: C, 76.69%; H, 3.58%, Cl, 8.38%. Found: C, 76.72%, H,
23 3.66%, Cl, 8.24%.

24

25 2.2.5. 3-(4-Bromophenyl)spiro[fluorene-4,2'-indene]-1',3',9(3 H)-trione (**5d**).

1 Yield: 72%. Red crystals from ethanol, m.p. 208-210°C, IR: 1742, 1713,
2 1702, 1600 sh, 1589 cm⁻¹. ¹H NMR: 7.95 (ddd, *J* = 7.6, 0.9, 1H), 7.81 (td, *J* = 7.4,
3 1.3, 1H), 7.76 (td, *J* = 7.4, 1.3, 1H), 7.68 (ddd, *J* = 7.5, 1.2, 0.8, 1H), 7.38 (ddd, *J* =
4 7.1, 1.2, 0.6, 1H), 7.17 (d, *J* = 8.5, 2H), 7.10 (td, *J* = 7.5, 0.9, 1H), 7.01 (td, *J* = 7.6,
5 1.2, 1H), 6.91 (d, *J* = 8.4, 2H), 6.56 (dd, *J* = 9.7, 3.4, 1H), 6.16 (d, *J* = 7.3, 1H), 6.00
6 (dd, *J* = 9.7, 2.9, 1H), 4.69 (t, *J* = 3.1, 1H). ¹³C NMR: 201.81, 196.22, 192.99, 148.94,
7 142.49, 141.48, 141.35, 136.88 (CH), 136.51, 136.41 (CH), 133.81, 133.53 (CH),
8 131.49 (2CH), 131.18 (2CH), 130.66 (CH), 129.17 (CH), 123.67 (CH), 123.03
9 (CH), 122.94 (CH), 121.67, 120.65 (CH), 117.79 (CH), 61.83, 49.55 (CH). Anal.
10 calcd. for C₂₇H₁₅BrO₃: C, 69.39%; H, 3.24%, Br, 17.10%. Found: C, 69.49%, H,
11 3.33%, Br, 16.93%.

12

13 2.2.6. 2-Methoxy-4-(1',3',9-trioxo-1',3,3',9-tetrahydrospiro[fluorene-4,2'-inden]-3-
14 yl)phenyl acetate (**5e**).

15 Yield: 75%. Red prisms from ethanol, m.p. 190-192°C. IR: 1759, 1704,
16 1603, 1592, 1513 cm⁻¹. ¹H NMR: 7.94 (d, *J* = 7.6, 1H), 7.79 (t, *J* = 7.4, 1H), 7.74 (t,
17 *J* = 7.6, 1H), 7.66 (d, *J* = 7.5, 1H), 7.38 (d, *J* = 7.0, 1H), 7.11 (t, *J* = 7.5, 1H), 7.02 (t, *J*
18 = 7.5, 1H), 6.65 (d, *J* = 8.0, 1H), 6.61 – 6.55 (m, 3H) 6.19 (d, *J* = 7.3, 1H), 6.09 (dd, *J*
19 = 9.7, 2.8, 1H), 4.72 (t, *J* = 3.0, 1H), 3.64 (s, 3H), 2.12 (s, 3H).
20 ¹³C NMR: 202.22, 196.44, 193.05, 168.42, 150.87, 149.08, 142.67, 141.57, 141.50,
21 139.25, 136.81 (CH), 136.19 (CH), 136.14, 133.90, 133.51 (CH), 131.56, 130.95
22 (CH), 129.15 (CH), 123.57 (CH), 122.91 (CH), 122.77 (CH), 122.64 (CH), 121.75
23 (CH), 120.64 (CH), 117.73 (CH), 113.67 (CH), 62.14, 55.90 (CH), 50.37 (CH),
24 20.30 (CH). Anal. calcd. for C₃₀H₂₀O₆: C, 75.62%; H, 4.23%;. Found: C, 75.51%, H,
25 4.45%.

1

2 2.2.7. (2Z)-2-(3,3-Diphenylprop-2-en-1-ylidene)-1,2'-biindene-1',3,3'(2H)-trione
3 (6).

4 Yield 70%. Dark violet needles with green luster from octane/toluene,
5 m.p. 240-241°C. IR: 1687, 1670, 1595, 1583, 1559, 1509 cm⁻¹. ¹H NMR: 9.05 (d, *J*
6 = 7.9, 1H), 8.66 (d, *J* = 12.3, 1H), 7.92 – 7.70 (m, 7H), 7.69 (t, *J* = 6.9, 1H), 7.63 (t, *J*
7 = 6.9, 1H), 7.50 – 7.32 (m, 9H). ¹³C NMR: 191.35, 190.27, 188.14, 160.68, 158.63,
8 148.23 (CH), 143.38, 141.74, 141.44, 141.00, 138.93, 134.82 (CH), 134.63 (CH),
9 133.46 (CH), 131.71 (2CH), 130.39 (2CH), 130.10 (CH), 129.84, 129.50 (2CH),
10 129.16 (CH), 128.56 (2CH), 128.00 (2CH), 126.10, 123.55 (CH), 122.94 (CH),
11 122.80 (CH), 122.66 (CH). Anal. calcd. for C₃₃H₂₀O₃: C, 85.33%; H, 4.34%. Found:
12 C, 85.48%, H, 4.46%.

13

14 2.3. Crystallographic data

15

16 X-ray crystallography data were collected on a Bruker-Nonius KappaCCD
17 diffractometer with CCD detector using MoK α radiation, λ = 0.71073 Å. The CIF
18 files have been deposited at the Cambridge Crystallographic Data Centre: **5a**:
19 CCDC 1551457, **5b**: CCDC 1551461, **5c**: CCDC 1551459, **5d**: CCDC 1551462, **5e**:
20 CCDC 1551460, **6**: CCDC 1551458.

21

22 3. Results and discussion

23 3.1. Synthesis and structures.

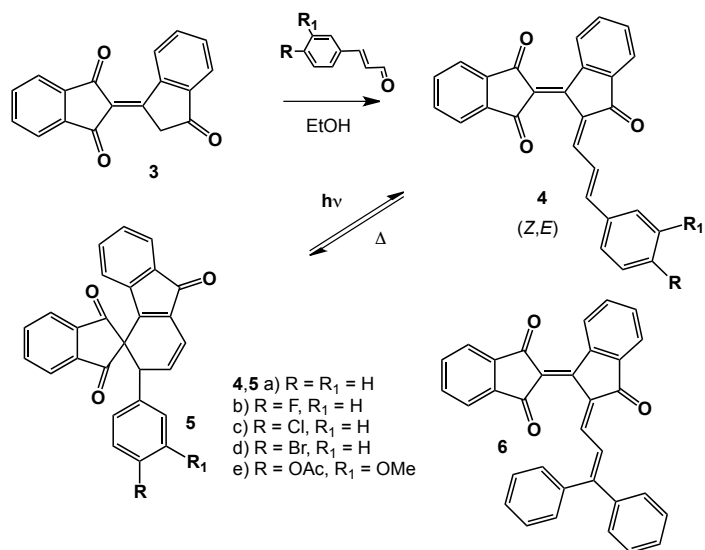
24 The new photochromes were prepared in one step from commercially

1 available bindone (1,2'-biindene-1',3,3'(2*H*)-trione, **3**) and the respective
2 cinnamic aldehydes (Scheme 2). All derivatives, except **4b**, precipitated from the
3 reaction mixture as cyclic isomers **5** according to their ¹H and ¹³C NMR spectra.
4 Derivative **5a** has been prepared at the beginning of 20th century, described as
5 merocyanine **4a** [15], and since then, to the best of our knowledge, no derivatives
6 of this type had been mentioned in the literature. In the case of *p*-fluorophenyl
7 cinnamaldehyde, the product of the reaction precipitates as poorly soluble thin
8 brownish shining needles. The IR ($\nu_{C=O}$ at 1696(s) 1672(as) cm^{-1} of the 1,3-
9 indandione moiety), and ¹³C NMR spectra ($\delta_{C=O}$ = 190.18, 187.82, 167.13 ppm) of
10 solid samples indicated the structure of **4b**. It is stable as the solid but attempts
11 to dissolve it resulted in the relatively slow at room temperature and rapid
12 above 100°C conversion into cyclic isomer **5b**. Irradiation of a concentrated
13 solution of **5b** in octane afforded precipitation of **4b** as the same thin brownish
14 needles. It is noteworthy that the isolation of both components of a thermo-
15 reversible photochromic system as pure substances is a very rare case.

16 Condensation of bindone with 3,3-diphenylacrylaldehyde in ethanol
17 afforded merocyanine-type derivative **6**. This compound is not photochromic
18 and does not convert into the cyclic form even upon prolonged heating.

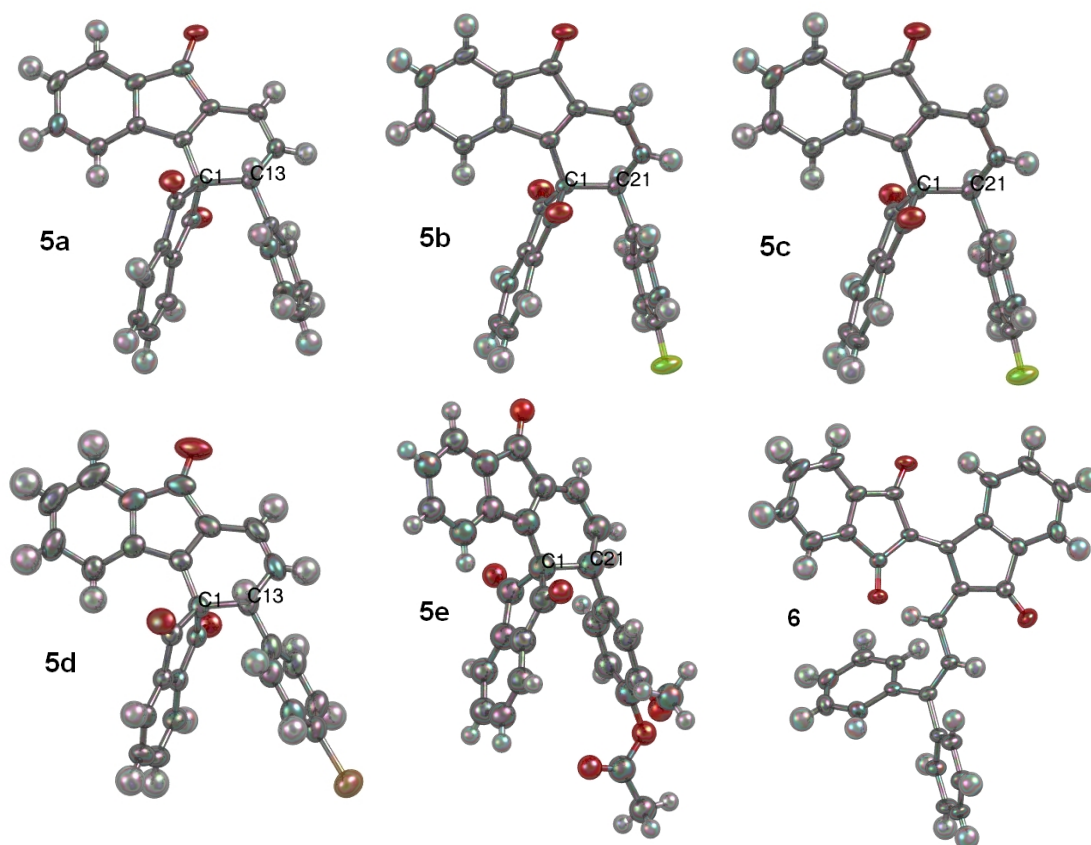
19 The X-ray structures were determined for derivatives **5a** – **e** and **6** (Fig.
20 1). All structures of **5a** – **e** involve long 3C – 4C bonds (1.58 – 1.59 Å) that are
21 somewhat longer than observed previously [14] in the structures of **1a** – **c** (1.57
22 – 1.58 Å). These bond length variations do not correlate with the substituents
23 nature within the series and can stem from the differences in the C-H...O
24 intermolecular H-bond patterns. At least four short intermolecular C-H...O

- 1 distances ranging from 3.91 to 3.62 Å can be found in the crystal lattice of each
 2 derivative.



- 4 Scheme 2. Synthesis and interconversion of derivatives **4** and **5**.

5



1

2 Fig. 1. ORTEP diagrams (50% probability ellipsoids) of **5a** – **e** and **6**. Selected3 bond length (Å). **5a**, C1-C13: 1.589(2); **5b**, C1-C21: 1.585(2); **5c**, C1-C21:4 1.575(4); **5d**, C1-C13: 1.581(3); **5e**, C1-C21: 1.577(2).

5

6

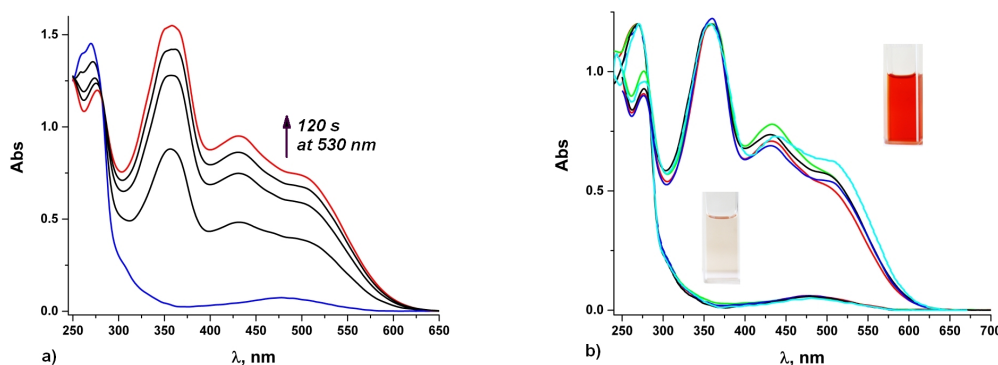
7

3.2. Photochromic behavior

8 Upon irradiation cyclic isomers **5** in solution undergo rapid conversion
 9 into conjugated open isomers **4**. The respective absorption spectra changes are
 10 shown in Fig. 2a on the example of **5a** to **4a** isomerization. Two isosbestic points
 11 at 252 and 280 nm are observed. The solutions of **5** are pinkish and on light
 12 change the color to deep orange - red (Fig. 2b). Variation of the substituents at

1 the phenyl group has very little effect on the absorption spectra of derivatives **5a**
2 - **e**, which are practically identical and resemble the spectrum of **1c**. Only one
3 broad weak absorption band with the maximum at about 480 nm ($600 - 800 \text{ M}^{-1}\text{cm}^{-1}$)
4 is observed for isomers **5**, in contrast to derivatives **2a,b**, which exhibit
5 two low intensity absorption bands centered at about 480 and 600 nm. The
6 absorption spectra the photo-induced open isomers **4** are also very similar (Fig.
7 2b). The spectra of these isomers exhibit four bands with the maxima at about
8 500 ($7\,200 \text{ M}^{-1}\text{cm}^{-1}$), 430 ($12\,000 \text{ M}^{-1}\text{cm}^{-1}$) and 360 ($16\,000 \text{ M}^{-1}\text{cm}^{-1}$). The
9 structures of **4** are corroborated also by the close similarity of their spectra with
10 the spectrum of derivative **6**.

11 The ^1H NMR spectra for solutions of pure derivatives **4** cannot be
12 recorded owing to thermal conversion into **5** during the spectra recording and
13 very low solubility of isolated **4b**. Nevertheless, the exceptional stability of
14 isomers **4** allowed to photochemically accumulate them in a sufficient for ^1H
15 NMR spectra concentrations (up to 50% conversion of **5** into **4**). Thus, the signals
16 at 9.08 (d, $J = 7.8$, 1H), 8.70 (dd, $J = 15.4$, 11.8, 1H) and 8.12 (d, $J = 11.8$, 1H), not
17 overlapping with the signals of cyclic isomers **5**, observed in the spectra of
18 irradiated samples clearly indicate the existence of **4** as *Z,E*-isomers [14]. The
19 similar features exhibit also ^1H NMR spectrum of **6**.



1

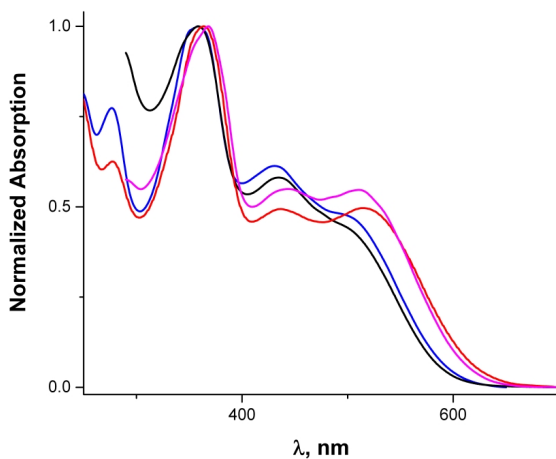
2 Fig. 2. a) Irradiation of **5a** in methylene chloride. b) Absorption spectra of **4**
 3 (generated at 530 nm) and **5** in methylene chloride: black – **a**, blue – **b**, green – **c**,
 4 red – **d**, cyan – **e**.

5 The absorption bands of photogenerated open isomers **4** and **6** are
 6 similar and exhibit slightly positive solvatochromic shifts (Fig. 3).

7 Thermal discoloration rates of **4** follow the first order kinetics, but are
 8 considerably slower than those observed previously for derivatives **2**. Thus,
 9 whereas the half-life time of **2a** in methylene chloride at 25°C is 9.3 s and of **2b** –
 10 1.44 s, the half-life times of the open isomers **4** vary between 11.3 h (**4a**) and
 11 17.5 h (**4c** and **d**) in this solvent. Discoloration in non-polar solvents occurs even
 12 slower: the half-life time of **4a** in *o*-xylene is 65.0 h and of **4c** in octane amounts
 13 128.4 h. The half-life time of **2c** in methylene chloride is 2.7 h. The kinetic data in
 14 methylene chloride are summarized in Fig. 4.

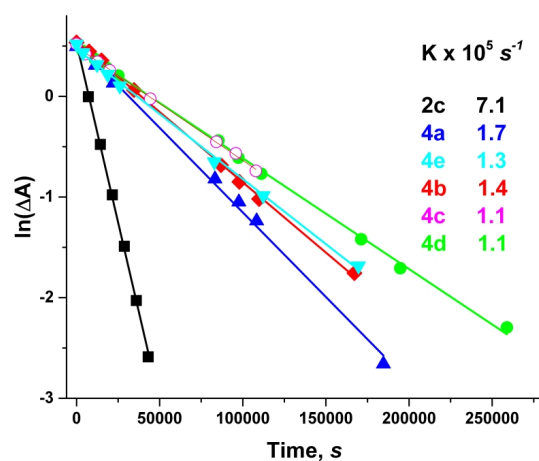
15 The effect of temperature on the rates of thermal discoloration was
 16 monitored at 25, 50 and 65°C and presented in Fig. 5. The activation energies
 17 ranging from 24.6 to 26 kcal/mol (102.9 – 109 kJ/mol) were estimated from the
 18 Arrhenius plot.

1 The observed first order discoloration kinetics is apparently related to
2 the rate-determining isomerization of the *Z,E*-isomers of **4** (incapable of
3 cyclization) into the *E,E* and *E,Z*-isomers. The half-life times, indeed, correlate
4 with the electron donating and accepting strength of the substituents at the
5 phenyl ring: the increase in the accepting strength and the decrease of the
6 solvent polarity give rise to the enhanced half-life times of **4**. The activation
7 energies for **2c**, **4a** and **4e** are noticeably higher than found for DASA [12] and
8 most of spiroheterocyclic compounds [16].

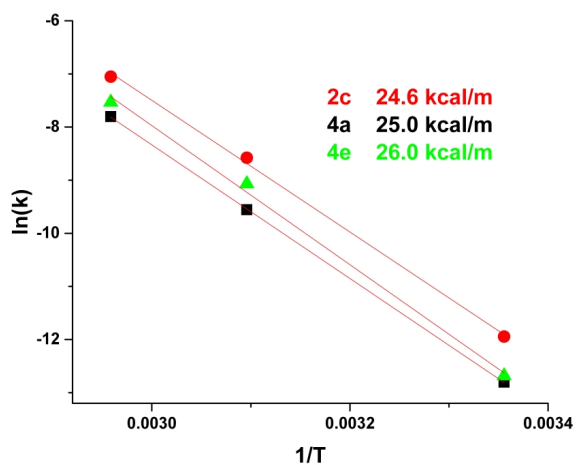


9

10 Fig. 3. Normalized absorption spectra in toluene **4a** – black, **6** – magenta; in
11 methylene chloride: **4a** – blue, **6** – red.



1

2 Fig. 4. Thermal discoloration kinetics of **2c**, **4a-d** in methylene chloride at 25°C.

3

4 Fig. 5. Temperature dependence of rate constants of thermal discoloration in
5 toluene at 25, 50 and 65°C.

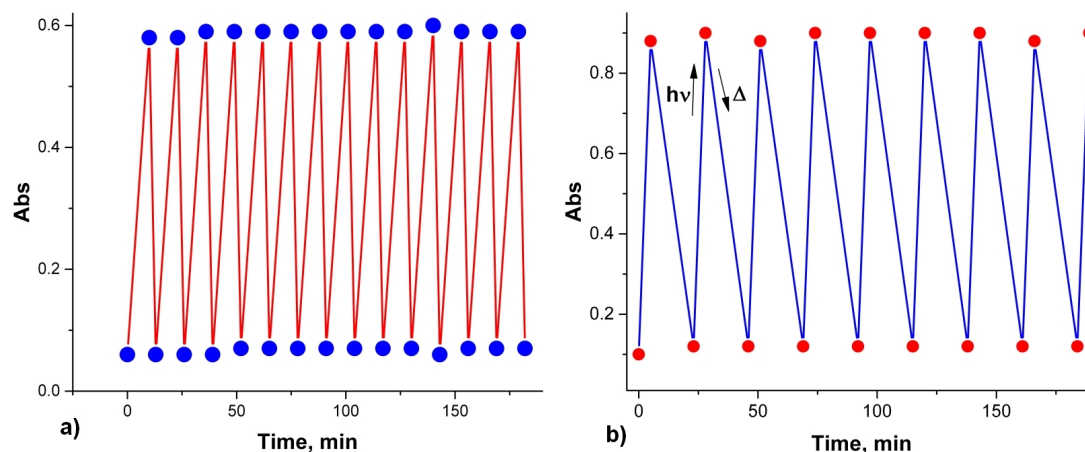
6

7

8 The fatigue resistance, as an important characteristic of switching
9 performance, was tested for derivative **5c** in xylene and butylacetate (Fig. 6a, b)
10 by repetition of irradiation at room temperature and heating.

11

12



1

2 Fig. 6. Irradiation of **5c** at 530 nm and heating cycles: a) in xylene, 10 min

3 irradiation, 3 min heating at 130°C; b) in butylacetate, 5 min irradiation, 18 min

4 heating at 100°C. Absorbance recorded at 500 nm.

5

6 Derivatives **5** exhibit photochromic behavior also in solid polymer7 matrices. Thus, thin films prepared by spin-coating solutions of **5**, PMMA or

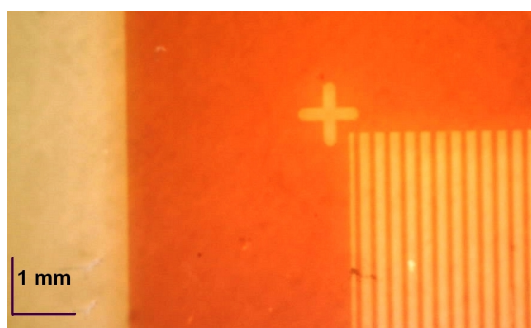
8 polystyrene in methylene chloride produced well resolved images upon

9 irradiation at 530 nm (Fig. 7). The images are visible during several days at room

10 temperature and their stability increases at lower temperatures or when the

11 residual solvent is removed in vacuum after irradiation.

12



13

14

15 Fig. 7. Thin film of **5a** in PMMA irradiated at 530 nm by a DLP projector.

1 **4. Conclusions**

2

3 Aiming the structural variations of bindone-derived photoswitches **1**
4 reacting with green and red light we prepared derivatives **5** not involving
5 electron donating groups. The new photochromes can easily be prepared from
6 commercially available precursors in one step. In spite of the changes in the
7 electronic structure, evidenced by the respective change in the absorption
8 spectra (the absence of the longest wavelength intramolecular charge transfer
9 band), these derivatives also exhibit photochromic properties. Both UV and
10 visible light up to 530 nm can activate the reversible color change. The photo-
11 generated merocyanines **4** are considerably more thermally stable than their
12 analogs **2** and their thermal discoloration occurs during several hours or days.
13 The merocyanine isomer **4b** can be isolated and is stable at least for several
14 months in solid state. The photoswitches retain the photochromic properties
15 also in a polymer matrix. However, not all structure variations lead to the
16 photochromic behavior as demonstrated on the example of a stable merocyanine
17 **6**.

18

19 This research did not receive any specific grant from funding agencies in the
20 public, commercial, or not-for-profit sectors.

21

22

23

24

25

1 **References**

2

3 [1] Crano JC, Guglielmetti RJ. Organic Photochromic and Thermochromic
4 Compounds: Main Photochromic Families (Topics in Applied Chemistry). New
5 York: Plenum Press; 1999.

6 [2] Dürr H, Bouas-Laurent H. Photochromism: Molecules and Systems.
7 Amsterdam: Elsevier Science; 2003.

8 [3] Tian H, Zhang J. Photochromic Materials: Preparation, Properties and
9 Applications. Weinheim: Wiley-VCH; 2016.

10 [4] Bouas-Laurent H, Dürr H. Organic photochromism (IUPAC Technical Report).
11 Pure and Applied Chemistry 2001;73:639-35.

12 [5] Feringa BL. Molecular Switches. Weinheim: Wiley-VCH; 2001.

13 [6] Bléger D, Hecht S. Visible-Light-Activated Molecular Switches. Angew Chem Int
14 Ed 2015;54:11338-49.

15 [7] Knie C, Utecht M, Zhao F, Kulla H, Kovalenko S, Brouwer AM, Saalfrank P,
16 Hecht S, Bléger D. Fluoroazobenzenes: Visible Light Switches with Very Long-Lived
17 Isomers. Chem Eur J 2014;20:16492-501.

18 [8] Bléger D, Schwarz J, Brouwer AM, Hecht S. Fluoroazobenzenes as Readily
19 Synthesized Photoswitches Offering Nearly Quantitative Two-Way Isomerization
20 with Visible Light. J Am Chem Soc 2012;134:20597-600.

21 [9] Lewis KG, Mulquiney CE. Aspects of the formation and use of stenhouse salts
22 and related compounds. Tetrahedron 1977;33:463-75.

23 [10] Helmy S, Oh S, Leibfarth FA, Hawker CJ, Read de Alaniz J. Design and
24 Synthesis of Donor–Acceptor Stenhouse Adducts: A Visible Light Photoswitch
25 Derived from Furfural. J Org Chem 2014;79:11316-29.

- 1 [11] Helmy S, Leibfarth FA, Oh S, Poelma JE, Hawker CJ, Read de Alaniz J.
2 Photoswitching Using Visible Light: A New Class of Organic Photochromic
3 Molecules. *J Am Chem Soc* 2014;136:8169-72.
- 4 [12] Hemmer JR, Poelma SO, Treat N, Page ZA, Dolinski N, Diaz YJ, Tomlinson W,
5 Clark KD, Hooper JP, Hawker CJ, Read de Alaniz J. Tunable Visible and Near
6 Infrared Photoswitches. *J Am Chem Soc* 2016;138:13960-66.
- 7 [13] Lerch MM, Wezenberg SJ, Szymanski W, Feringa BL. Unraveling the
8 Photoswitching Mechanism in Donor–Acceptor Stenhouse Adducts. *J Am Chem Soc*
9 2016;138:6344-47.
- 10 [14] Bekere L, Larina N, Lokshin V, Ellern A, Sigalov M, Khodorkovsky V. A new
11 class of spirocyclic photochromes reacting with light of both UV and visible ranges.
12 *New J Chem* 2016;40:6554-58.
- 13 [15] Hoyer E. Ueber einige Abkömmlinge des Anhydrobisdiketohydrindens. *Ber*
14 *Dtsch Chem Ges* 1901;34:3269-74.
- 15 [16] Minkin VI. Photo-, thermo-, solvato-, and electrochromic spiroheterocyclic
16 compounds. *Chem Rev* 2004; 104: 2751-76.
- 17